Observations of an Impurity-driven Hysteresis Behavior in Ice Crystal Growth at Low Pressure

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Abstract. We describe observations of a novel hysteresis behavior in the growth of ice crystals under near-vacuum conditions. Above a threshold supersaturation, we find that the ice growth rate often exhibits a sudden increase that we attribute to an impurity-driven growth instability. We examine possible mechanisms for this instability, which can be used to produce clean, faceted ice surfaces.

1 Introduction

The formation of complex structures during solidification often results from a subtle interplay of nonequilibrium, nonlinear processes, for which seemingly small changes in molecular dynamics at the nanoscale can produce large morphological changes at all scales. One popular example of this phenomenon is the formation of snow crystals, which are ice crystals that grow from water vapor in an inert background gas. Although this is a relatively simple physical system, snow crystals display a remarkable variety of columnar and plate-like forms, and much of the phenomenology of their growth remains poorly understood, even at a qualitative level [1].

As we described in two earlier papers [2, 3], we have been investigating the growth behavior of ice under near-vacuum conditions in order to better understand the surface attachment kinetics that governs the crystal formation process. Toward this end, we have constructed an experimental apparatus that allows us to place single, faceted ice crystals, typically 10-50 μm in size, on a temperature-controlled substrate surrounded by an ice reservoir in a small vacuum chamber, as shown in Figure 1 [3].

We write the growth velocity v_n normal to the surface of a crystal facet in terms of the Hertz-Knudsen formula

$$v_n = \alpha v_{kin} \sigma$$

where v_{kin} is a temperature-dependent kinetic velocity derived from statistical mechanics, σ is the water vapor supersaturation just above the growing surface, and α is known as the condensation coefficient, which contains the attachment kinetics that governs how water molecules are incorporated into the ice lattice [1].

The supersaturation in these experiments is given by

$$\sigma = \frac{c_{sat}(T_{reservoir}) - c_{sat}(T_{substrate})}{c_{sat}(T_{substrate})}$$

where $c_{sat}(T)$ is the saturated vapor pressure of ice at temperature T, while $T_{reservoir}$ and $T_{substrate}$ are the temperatures of the ice reservoir and crystal sample, respectively (see Figure 1).

We use laser interferometry to measure the growth rate v_n, from which we can then extract α as a function of σ, $T_{substrate}$, and other experimental parameters. The measurements shown here were of the basal surfaces of thin, plate-like crystals growing near $T_{substrate} = -15$ C with a background air pressure near 5 mbar. At this pressure and with the small ice crystals observed, the crystal growth is not limited by molecular diffusion through the surrounding air, but is rather limited by attachment kinetics on the ice surface. Additional details describing our apparatus and important systematic errors can be found in [3].

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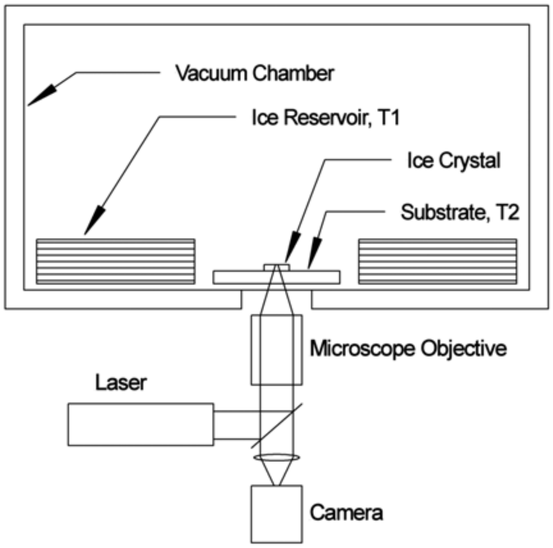

Figure 1. The basic layout of our experimental apparatus. An ice crystal is placed with known orientation on a substrate inside an evacuated growth chamber. An ice reservoir inside the chamber provides a source of water vapor to grow the sample crystal. The supersaturation is determined by the temperature difference between the ice reservoir (equal to the temperature of the rest of the growth chamber) and the substrate. The sample crystal is imaged using a microscope objective and a video camera. A low-power laser is focused onto the crystal by the same microscope objective. The laser spot is reflected by the top and bottom surfaces of the ice crystal, and the brightness of the two interfering beams oscillates as a function of crystal thickness [3].

2 Observations

In the course of our experiments we observed an unexpected hysteresis behavior, of which we show two examples in Figure 2. In both cases shown, an ice crystal was first placed on the substrate while the chamber pressure was near one bar, as described in [3]. The chamber pressure was then slowly reduced while keeping $\Delta T = T_{reservoir} - T_{substrate} \approx 0$ to prevent significant growth or evaporation of the crystal. This process typically took 3-5 minutes, ending with the chamber pressure near 5 mbar and the crystal at the "start" location shown in Figure 2.

Once the pressure and temperatures were stable, we then slowly reduced $T_{substrate}$ to increase σ while observing the crystal growth velocity. Once we obtained measurable growth, we adjusted $T_{substrate}$ (and thus σ) as a function of time and observed the growth behaviors shown in Figure 2. The data-taking process took several minutes and usually ended when the crystal was deemed to large to continue [3].

We observed considerable crystal-to-crystal variability in our data, but the following features shown in Figure 2 were often seen:

1) Crystal growth did not commence at a measurable rate until σ was fairly high, above roughly 0.5% for the examples shown.

2) The measured $\alpha(\sigma)$ remained relatively low for the early stages of growth. This is best seen in the second example in Figure 2, where σ was varied up and down while observing the crystal growth.

3) When σ was raised sufficiently, the growth exhibited a sudden "surge", as labeled in the Figure. The surge occurred in just a few seconds and increased the growth rate to nearly 1 μm/sec in some cases, implying $\alpha \approx 1$ at the peak growth. Calculations show that such rapid growth produced local heating at the crystal surface [1] that also limited the growth. Upon seeing the growth surge, σ was typically reduced to keep the crystal from growing too large.

4) After the spike in growth, the growth profile $\alpha(\sigma)$ remained substantially higher than the pre-surge profile.

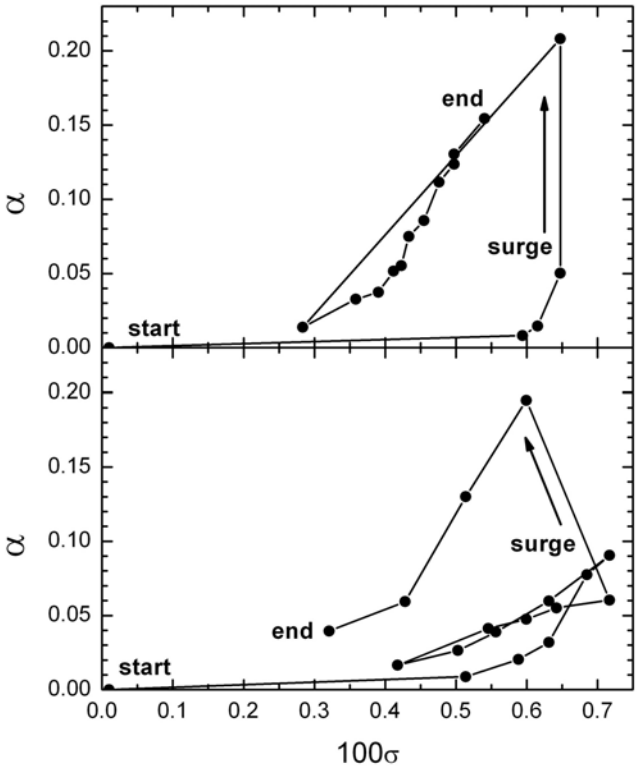

Figure 2. Two examples of the impurity-driven growth instability described in the text. Both panels show a time series of measurements of the condensation coefficient α for the basal facet a single plate-like ice crystal as a function of supersaturation σ. The background pressure in the experiments was approximately 5 mbar and the crystal temperature was near -15 C. In both cases the growth was relatively slow until the occurrence of a sudden "surge" of growth, after which $\alpha\left(\sigma\right)$ remained substantially higher than it was before the surge.

5) If the supersaturation was reduced to $\sigma = 0$ for several minutes, or if a small quantity of gas was let into the chamber and pumped out, then $\alpha(\sigma)$ returned to lower values.

Not all crystals exhibited a growth surge, while some did so clearly. Figure 3 shows a set of all measurements taken during a single experimental run measuring basal growth at -15 C. The data show a rough lower bound, in that all crystals started growing once the supersaturation approached one percent. The data also show a rather distinct upper bound profile $\alpha(\sigma)$ that was not exceeded by any post-surge data.

3 Interpretation

We interpret these observations with a simple qualitative model involving impurities on the ice surface. After being nucleated in air at one bar [3], a typical sample crystal grows for 1-2 minutes before being placed in the vacuum chamber, and then it sits on the substrate for 3-5 minutes during the pump-out period. We believe that impurities build up on the ice surface during this time, which reduces $\alpha(\sigma)$. Because of this, σ must be raised quite high to produce the first measurable growth.

The impurity surface density is then apparently reduced as ice is deposited during growth (we discuss possible mechanisms for this below). For low growth rates, this surface cleaning is not very efficient, so $\alpha(\sigma)$ remains low, and the surface impurities mostly remain on the surface as they are rejected from being incorporated into the ice lattice. At a sufficiently high σ, however, the impurity cleaning process leads to a runaway growth instability. As impurities are removed from the surface, the growth rate increases on the now cleaner surface, which thus accelerates

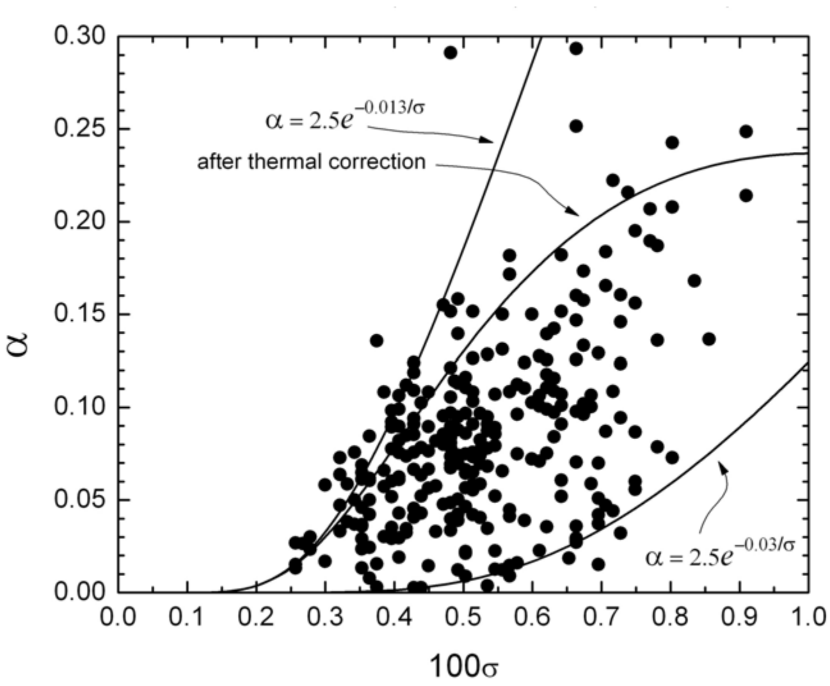

Figure 3. Combined measurements of eleven crystals, which includes all the crystals from a single set of observations. The higher points in this figure were all from "post-surge" measurements like those shown in Figure 2. The lower curve shows an approximate lower bound for the measurements, while the upper curve gives an approximate upper bound for post-surge measurements. The middle curve gives the upper bound after correcting for surface heating as described in [1]. The data show a fairly distinct upper bound in the growth, which we interpret as the intrinsic growth rate of an impurity-free basal surface at -15 C.

the removal of impurities. The resulting positive feedback causes the growth rate to suddenly increase, producing a growth surge. Once the surface has been cleaned by a period of rapid crystal growth, it remains relatively clean in the low-pressure environment, so $\alpha(\sigma)$ remains high. If the growth is halted for some period of time, however, then gaseous impurities will deposit and build up on the surface, decreasing $\alpha(\sigma)$ once again.

4 Impurity Removal Mechanisms

Assuming this overall picture is correct, there are several mechanisms for which crystal growth can remove surface impurities:

1) Incorporation. As ice is deposited during growth, adsorbed impurity molecules may become buried in the bulk. This would remove impurities from the surface, and we expect this process would increase with increasing growth rate. It is well known, however, that impurities are not readily incorporated into the lattice when ice forms from liquid water, so we expect that foreign molecules are not easily buried during ice growth from water vapor either. Unfortunately, our understanding of this process is not sufficient to allow us to make quantitative estimates for impurity incorporation rates.

2) Desorption. It is also possible that faster growth can cause impurities to become desorbed from the surface. In one sense this seems unlikely; ice has a high vapor pressure, which means that water molecules are continually condensing onto and evaporating off of the ice surface. During our measurements, these two processes are out of equilibrium by less than one percent (equal to σ), and it seems unlikely that such a small imbalance in growth and evaporation would lead to impurity desorption. On the other hand, growth will tend to push foreign molecules up to keep them from being incorporated into the lattice. This process could weaken the surface binding, and at sufficiently high growth rates it could cause desorption. Thus we cannot rule out this mechanism for impurity removal.

3) Flow. If impurity molecules are sufficiently mobile on the surface, they may also be swept laterally by expanding molecular terraces as the crystal grows. This process would push foreign molecules to the edges of small facets, and for the observed basal growth it would deposit impurities on the prism surfaces. In several cases we have seen small plate-like crystals grow upward into fairly tall columns (aspect ratios >5) as the rapid basal growth was accompanied by little growth of the prism surfaces. This odd behavior was unexpected at -15 C, where thin plates normally grow in air, but it would be explained by the impurity flow mechanism.

4) Combinations. The above mechanisms could also work in combination. For example, foreign molecules could flow to regions of high impurity density, where they could desorb or become buried. We have commonly seen crystals with slow-growing regions (for example, see Figure 2 in [3]) that appear to have a high concentration of surface impurities. It may be that surface flow is depositing impurities in these regions.

Whatever the mechanism, we see from Figure 2 that growth velocities of order $v_n \approx 0.1$ μm/sec are sufficient to engage this instability, at least under the conditions of our measurements.

5 Discussion

Our growth data showed considerable crystal-to-crystal variability, and the growth “surge” with its accompanying hysteresis was not always present. However, in many cases the surge was clear and unmistakable when seen in real time. We believe that the impurity-driven instability described above explains the data satisfactorily, and differences in impurity levels could easily explain the crystal-to-crystal variability as well.

These observations also suggest that our previous data were contaminated by impurities to some degree. In [2], our experiment was new and our impurity problems probably the most substantial. We rebuilt our apparatus for [3] and put additional effort into producing a cleaner growth chamber. The current experiment uses the same hardware as [3], but additional time has allowed some further outgassing of impurities. A comparison of these experiments indicates that α has steadily increased as the hardware has become cleaner.

Throughout these measurements we typically parameterized our data with $\alpha \rightarrow A\exp(-\sigma_0/\sigma)$, and in doing so we found that most of the variability was in A. The critical supersaturation σ_0 does not seem to change greatly with the addition of surface impurities. This implies that surface impurities do not substantially change the edge free energy β for a molecular terrace or the 2D nucleation process in general [2]. Instead, it appears that surface impurities reduce the growth of 2D islands, which then reduces A. We will discuss mechanisms for this in a subsequent paper.

It remains something of a puzzle why the data in [3] were so self-consistent, since subsequent data (for example Figure 3) have shown considerably higher crystal-to-crystal variability. The measurements in [3] were taken soon after our new chamber was constructed, so we speculate that the walls were still outgassing sufficiently to reduce α for the crystals we measured. We also suspect that the higher impurity levels suppressed growth surges. We are planning additional experiments in which impurities are systematically added to our growth chamber in order to investigate these effects further.

The overarching conclusions we draw from these observations are that even relatively low levels of surface impurities may have a substantial impact on ice crystal growth, and that the presence of surface impurities generally seems to reduce ice growth rates.

6 References

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