

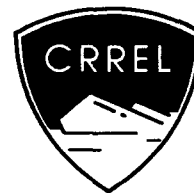
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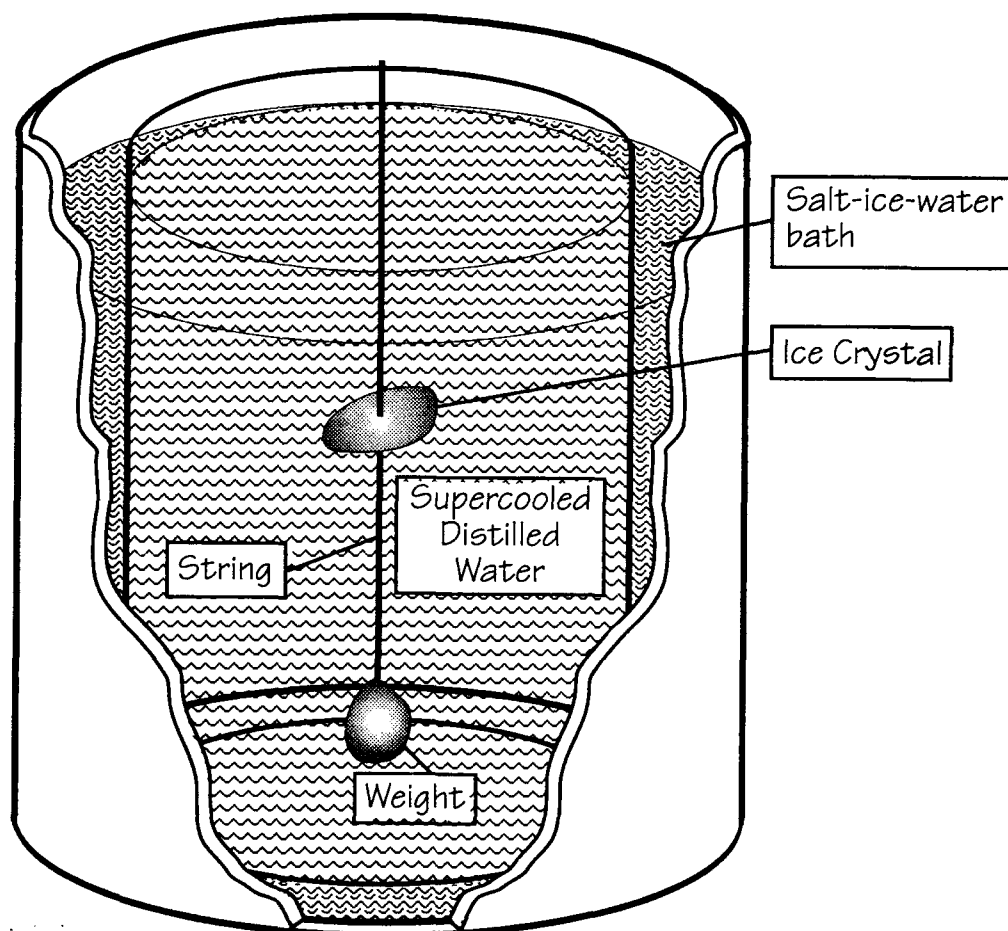


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The Slow Growth of Ice Crystals in Water

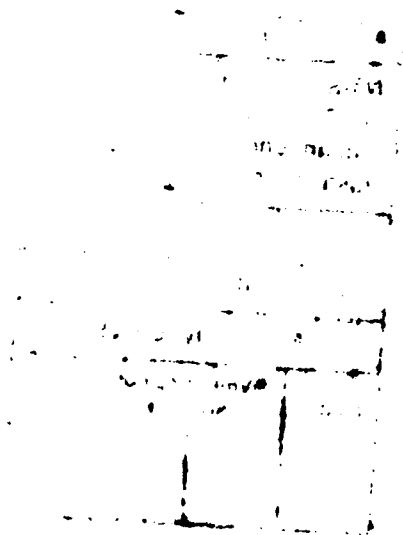
Samuel C. Colbeck

March 1992



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**U.S. Army Corps
of Engineers**
Cold Regions Research &
Engineering Laboratory

The Slow Growth of Ice Crystals in Water

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PREFACE

This report was prepared by Dr. Samuel C. Colbeck, Research Geophysicist, Snow and Ice Branch, Research Division, U.S.A. Cold Regions Research and Engineering Laboratory. Funding was provided under In-House Laboratory Independent Research Project 4A161101A91D/576, *Growth of Ice Crystals from Melt*. The report was technically reviewed by Steven Daly of CRREL and Dr. H.T. Shen of Clarkson University.

The Slow Growth of Ice Crystals in Water

SAMUEL C. COLBECK

INTRODUCTION

The growth of ice crystals is an important natural phenomenon and has led to many investigations of crystal growth. Most of the interest has been in the rapid growth of crystals from the vapor, such as in the atmosphere (e.g. Lamb and Scott 1974), but slow growth from the vapor has also received attention because of the importance of metamorphism in the seasonal snow cover (Colbeck 1983). Ice crystal growth from the melt is important in nature but has received considerably less attention, especially over the range of growth rates that are important in wet snow or even in frazil ice in rivers. The slowest growth rates occur in wet snow when the snow cover is freely drained and most of the pore volume is occupied by air. Then the ice crystals bond together in clusters (Colbeck 1979), as shown in Figure 1.

There are two common situations where ice crystals grow while immersed in the melt. First, slush is water-saturated snow consisting of poorly bonded ice particles that grow to a size of about 1 mm in 24 hr. As shown in Figure 2, these particles are very well rounded, and they develop in a population with a log-normal distribution (Colbeck 1986). This arises from the dynamics of growth in a population of particles competing among themselves due to slight curvature differences. The second common situation is frazil ice particles, which are rapidly growing disks (Fig. 3). These crystals grow only in turbulent, supercooled water, which is common in streams and rivers in winter. They grow at supercoolings of about 0.01°C with a concentration of about 10^6 per m^3 (Daly and Colbeck 1986). The mechanism of their growth is very different from that in slush because the crystals are well separated, so each one has a large reservoir of supercooled water into which it loses heat. Furthermore, the turbulence should enhance

the rate at which the growing crystals lose heat. Accordingly the growth rate is high and the crystals always develop as disks with sharp edges.

The growth of ice disks in water has been both observed and modeled (Hillig and Turnbull 1956, Hillig 1958, Bukina 1967, Pruppacher 1967, Daly and Colbeck 1986), with some interest in the stability of rapidly growing disks. Through thousands of observations of frazil disks, Daly and Colbeck (1986) never observed morphological instability except when the larger disks float to the air/water interface, probably because the growth rate of frazil is limited by the high concentration of crystals, which limits the supercooling. With supercoolings above 0.2°C , ice crystals grow as dendrites (Hillig 1958), but the supercoolings during frazil growth are only about 0.01°C .

The purpose here is to investigate the shape of ice crystals growing from the melt at the growth rates of interest in nature. This spans the range from slush, about 1×10^{-6} g/hr (Colbeck 1986), to that of frazil, about 3×10^{-3} g/hr (Daly and Colbeck 1986), and is accompanied by a dramatic change in morphology from disks at high growth rates to spheroids at low growth rates (Colbeck 1986).

Disks develop by growth along the a-axis of the ice crystal, with growth along the c-axis being slow due to a strong anisotropy in the interfacial growth kinetics. At a few degrees of supercooling, growth along the c-axis is about 100 times less than along the a-axis (Hallet 1968), and Hillig (1958) suggested that at supercoolings below 0.02°C , growth along the c-axis essentially disappears. While this may be true for ice crystals grown in capillaries, it is not true for the growth of frazil ice, and slowly growing crystals in slush are not even disks. Accordingly we should be cautious about applying the results of crystals growth experiments to environments different from those of the experiment.

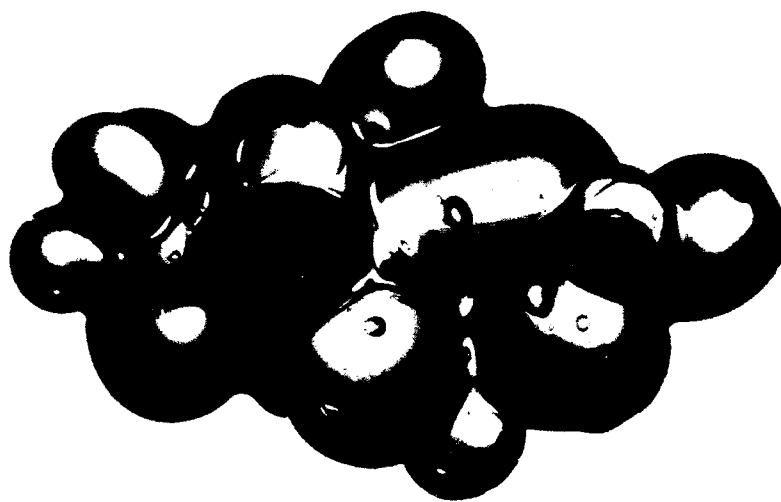


Figure 1. Cluster of ice crystals growing in snow with a low liquid content.

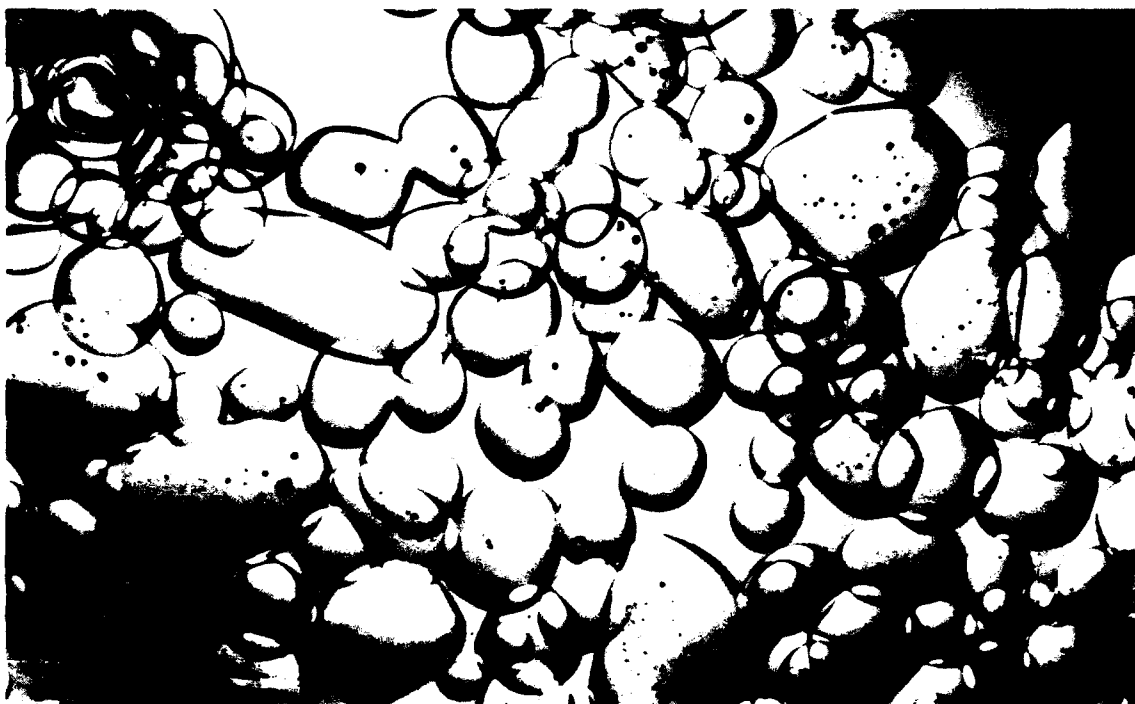


Figure 2. Ice crystals growing in water-saturated snow, or slush. These are typically poorly bonded, well rounded and about 1 mm in size.



Figure 3. Frazil disks growing in turbulent water. These are typically sharp disks with no sign of interaction with other crystals. Some are blurred due to motion or obscured due to ice on the surface of the water.

During rapid growth for short periods of time, usually tens to hundreds of seconds for frazil crystals, the growth along the a-axis controls the morphology but with an aspect ratio of 10 or less, not 100 or less as suggested above. Furthermore, it is clear that during slow growth (tens of hours for slush) metamorphic processes due to curvature effects on the phase-equilibrium temperature are also important. In the next section we look at the theory of the growth of disk crystals and modify it to account for metamorphism. This is followed by some experimental observations of the growth of single crystals in the melt, at growth rates spanning the range from slush to frazil, to observe the effect of growth rate of morphology.

THEORY

We begin by looking at the established theories for disk growth and then add the effect of metamorphism due to curvature. Since a general theory accounting for all of the processes seems unattainable at this time, we will concentrate on a theory that allows us to think about two of the processes: the rapid growth of disks of a constant

aspect ratio and the transition to the growth of rounded crystals. By analogy with the growth of ice crystals from the vapor (Colbeck 1983), in the melt we might also expect a sudden, rather than a gradual, transition between the growth of disks and well-rounded ice crystals.

Disk growth

The first attempts to model ice crystal growth in an infinite medium used the electrostatic analogy (Marshall and Langrehan 1954), which simulates the potential field, in this case the temperature field, around the growing crystal. This leads to the simple result that, for pure diffusion,

$$\dot{m} = \frac{4\pi C k_w \Delta T}{L} \quad (1)$$

where $\dot{m}$ = mass growth rate

$4\pi C$ = capacitance, which depends on the shape of the particle

k_w = thermal conductivity of water

L = latent heat

ΔT = supercooling.

This approach was reviewed by Hallet (1968). Fujioka and Sekerka (1974) predicted a very differ-

ent temperature field around a disk, one that shows strong temperature gradients only at the tip of the disk, thus accounting for the low growth rates on the faces.

Using the electrostatic approach for a disk, the growth rate for constant thickness is

$$\frac{da}{dt} = \frac{2k_w \Delta T}{\pi b L \rho_i} \quad (2)$$

where a = radius

$2b$ = thickness of the disk

ρ_i = density of ice

t = time.

Using their more sophisticated approach, Fujioka and Sekerka (1974) found that the disk grows as

$$\frac{da}{dt} = \frac{\pi k_w}{b L \rho_i} \frac{\Delta T}{\ln(8ea/b)} \quad (3)$$

These two equations predict similar growth rates for the aspect ratios (a/b) of interest here, but both need to be tested with the appropriate experiments. The observed growth of frazil disks and the experimental observations reported here both suggest that disks thicken as they grow, and thus we extend the theory to the case of a constant aspect ratio. This simply reduces the growth rate given in eq 2 by about one-third, which is not a major change since the equation may only be qualitatively correct anyway. However, the model of a constant aspect ratio is probably more realistic than that of a constant thickness over the range of growth rates of interest here. The major difference

between the two results is that eq 2 predicts a linear increase in disk diameter with time, whereas, if the disk thickens as it grows, the diameter should increase as $t^{1/2}$. The result given by eq 3 falls between these two results, but the assumption of a constant disk thickness is not acceptable at the growth rates of interest here. Because of uncertainty over how good these approximations might be, the models provide only qualitative help for our thinking about slow crystal growth from the melt.

Crystal metamorphism

The effect of curvature on phase-equilibrium thermodynamics is important when the particles are very small or the growth rates are very slow or both. The resulting metamorphism of ice crystals is especially rapid in the melt because the temperature is high and phase change is not rate-limited by the relatively slow process of mass diffusion. Nevertheless, only the slower-growing slush crystals are well rounded, while the faster-growing frazil crystals are distinctly disk-shaped.

A simple model of the rounding of a particle by metamorphism is constructed here to estimate the magnitude of this effect on the shape of growing crystals of varying growth rates. Consider a crystal growing with the shape of an oblate spheroid, such as that shown in Figure 4. At the tip, where the curvature is high, the melting temperature is low; on the face, where the curvature is low, the melting temperature is high. Therefore, heat flows from the face to the tip, with a consequent

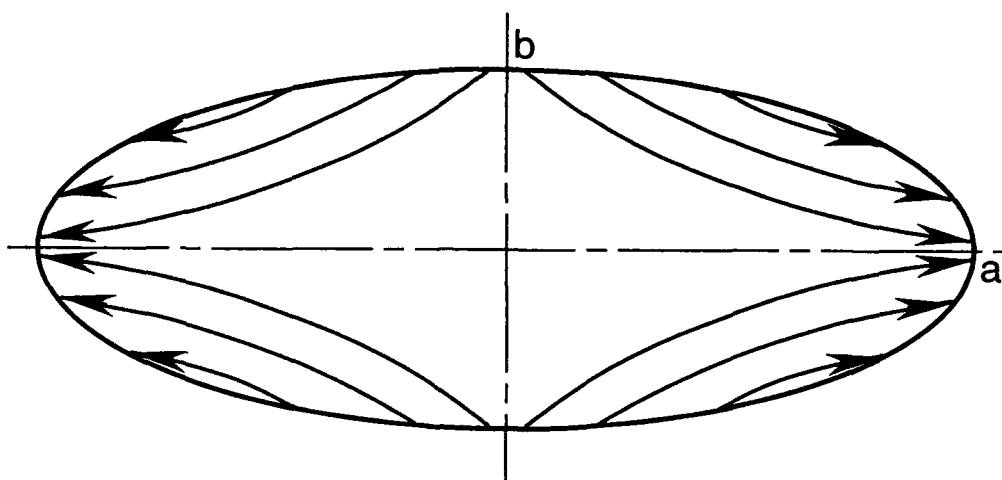


Figure 4. Model of an ice crystal undergoing metamorphism. This oblate spheroid would melt at the edge and grow on the face as it becomes rounder.

loss of ice from the tip and gain on the face. By this mechanism the crystal is rounded such that, if this process is fast enough, disks would become sphere-like. However, if the rate at which this process takes place is much smaller than the rate of growth along the a -axis, the shape will be determined by the kinetics of the growth process and metamorphism can be ignored. With the model of this process constructed here, an attempt is made to determine if metamorphism is important over this range of growth rates.

The temperature difference ΔT_m driving the metamorphic process can be approximated by

$$\Delta T_m = \frac{2T_0\sigma}{\rho_i L} \left(\frac{1}{b} - \frac{1}{a} \right) \quad (4)$$

where T_0 = melting temperature

σ = ice-water interfacial energy

a and b = major and minor axes of the spheroid and the b/a ratios come from the curvatures of a spheroid on the major and minor axes. The phase change and thickening are balanced when

$$2\pi a^2 L \rho_i \frac{dB}{dt} = \pi abq \quad (5)$$

where dB/dt is the thickening rate due to metamorphism only. The heat flow q is approximately $2k_i \Delta T_m / a$, where k_i is the thermal conductivity of ice. The rate of thickening due to metamorphism, or alternatively the rate of shrinking of the diameter of the spheroid dA/dt , is then given by

$$\frac{dA}{dt} = -\frac{k_i T_0 \sigma}{(\rho_i L)^2} \frac{1}{a^2} \left(\frac{a}{b} - 1 \right). \quad (6)$$

This suggests that metamorphism is important when the aspect ratio a/b is large or when the disk is small or both. Thus large, rapidly growing disks should not experience metamorphism because of the long heat flow path along their length. Also, for large, rapidly growing disks, the temperature field calculated by Fujioka and Sekerka (1974) would overwhelm this effect. However, for slow growth rates the effect is important, as will be shown later.

EXPERIMENTS

Suspended ice crystals were grown in pure water at growth rates that spanned the range from those for slush to those for frazil. These rates were achieved by suspending small ice seeds on a nylon string in pure water, which itself was surrounded

by a saline, ice-water bath. The supercooling of the pure water and therefore the growth rates of the suspended crystals increased with the salinity of the ice-water bath. However, the crystal growth rate and the salinity are not highly correlated because multiple crystals grew from the seeds, not just one crystal, as was desired. Also, the supercooling was not measured directly since it was too low to resolve accurately (-0.001 to -0.05°C), but it was calculated from the measured salinity of the ice-water bath. As a result the quality of the data given in Table 1 is poor, but the trend to larger disks with larger aspect ratios can clearly be seen, just as expected from the observed differences between slush and frazil. The most rapidly growing disks (e.g. Fig. 5) had the highest aspect ratios, and the slowest growing ones (e.g. Fig. 6) had the lowest aspect ratios. All of the crystals were disks; the slower growing ones were not sphere-like, which was expected because the growth rate of at least one disk was in the range of slush. Likewise, the more rapidly growing disks had a wide range of aspect ratios and were not confined to the fairly narrow range found for frazil (Daly and Colbeck 1986).

The average growth rate $\overline{dm}/dt$ was computed from the final thickness and diameter of each disk ($2b_f$, d_f) and length of each test; this is shown in Figure 7 vs $d_f \Delta T$. This data set is reasonably described by

$$\overline{dm}/dt = 0.00296 d_f \Delta T \quad (7)$$

with an r^2 of 0.86. However, the observed growth rates are significantly less than expected from the electrostatic theory for disks with a constant aspect ratio, which is also shown on Figure 7. The expected growth rate was calculated by integrating eq 1 over the growth period and assuming that the final diameter was twice its average value. Much of the difference between expected and observed sizes is probably due to competition among the growing crystals, as described above. Unfortunately this suggests caution in use of ΔT as a parameter in interpreting these results, but other results based on shape and size should still be useful. Since the crystals did not grow into semi-infinite surroundings but tended to grow while crowded by neighbors, there is no clear effect of ΔT .

Several crystals were recovered and measured at most supercoolings. The results shown in Figure 8 suggest that the average growth rate increased as about the fourth power of size. This is a

Table 1. Measured values.

Diameter (mm)	Thickness (mm)	Time (hr)	ΔT (°C)	$\bar{m} \times 10^5$ (g/hr)	Aspect
8.21	0.235	44.75	—	25.5	34.9
2.03	0.760	49.75	—	4.53	2.67
5.68	0.604	65.00	—	21.60	9.40
4.58	0.703	192.0	0.0104	5.51	6.51
3.92	0.600	192.0	0.0104	3.45	6.53
4.865	0.5305	192.0	0.0104	4.71	9.17
2.25	0.5068	192.0	0.0104	0.963	4.44
1.10	0.4932	192.0	0.0104	0.222	2.22
4.90	1.04	314.0	0.00225	5.29	4.71
2.77	1.23	314.0	0.00225	2.14	2.25
3.54	0.833	314.0	0.00225	2.39	4.25
7.20	0.625	314.0	0.00225	7.45	11.52
3.01	0.411	263.5	0.00143	1.021	7.33
3.22	0.6575	263.5	0.00143	1.86	4.90
3.625	0.370	263.5	0.00143	1.33	9.80
3.40	0.616	263.5	0.00143	1.95	5.52
4.43	0.677	27.0	0.0470	35.5	6.55
13.0	0.492	27.0	0.0470	223.0	26.5
2.06	0.447	90.0	0.0302	1.517	4.60
4.71	0.581	90.0	0.0302	10.32	8.10
4.41	0.512	90.0	0.0302	7.95	8.61
3.545	0.465	90.0	0.0302	4.68	7.62
2.75	0.329	53.5	0.023	3.34	8.35
3.175	0.235	53.5	0.023	3.19	13.5
2.42	0.329	53.5	0.023	2.60	7.36
2.43	0.513	53.5	0.023	4.08	4.74
2.76	0.184	53.5	0.023	1.89	15.00
3.26	0.290	53.5	0.023	4.13	11.25



Figure 5. Rapidly growing disk crystal in these experiments.



Figure 6. Slowly growing disk crystal in these experiments.

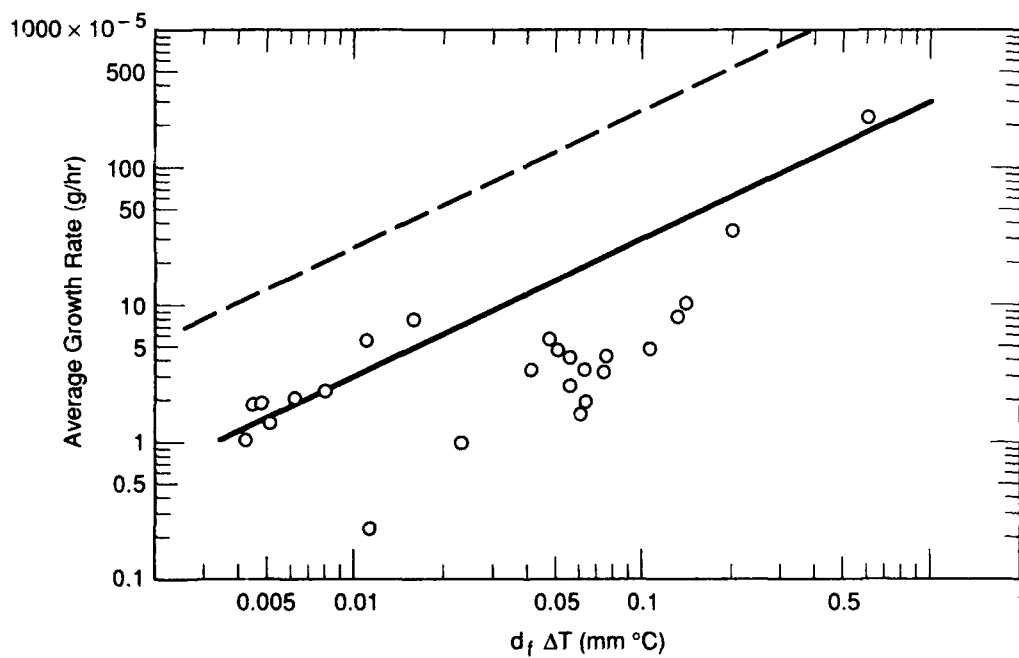


Figure 7. Average mass growth rate vs the product of size and ΔT . The data are described by a least-squares fit, with r^2 of 0.86. The theoretically derived line is also shown.

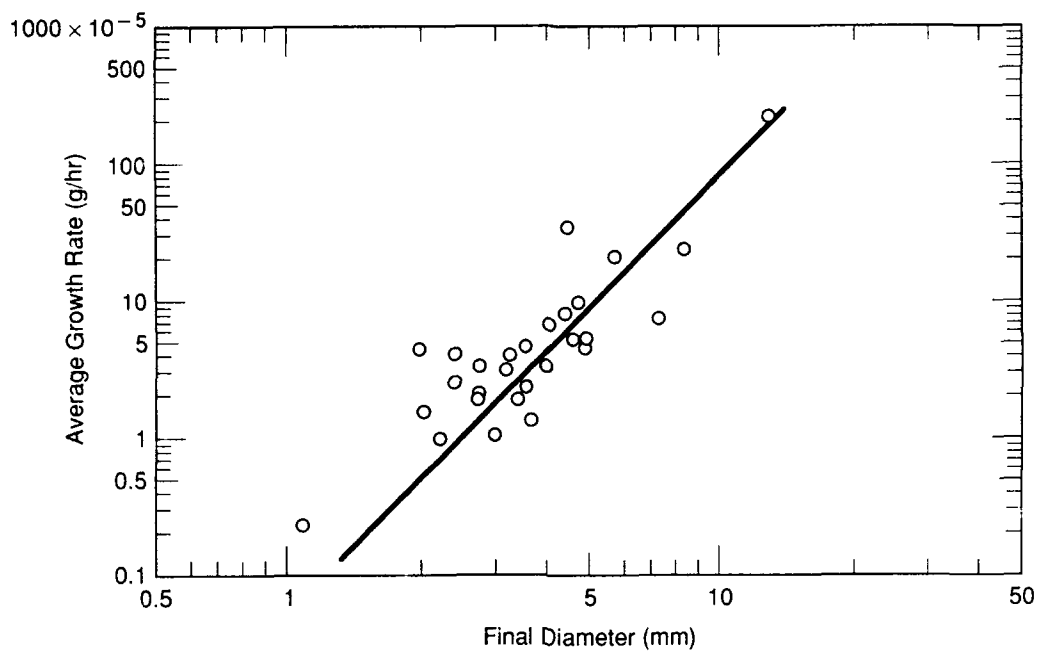


Figure 8. Average mass growth rate vs size. The data are described by a least-squares fit, with r^2 of 0.97.

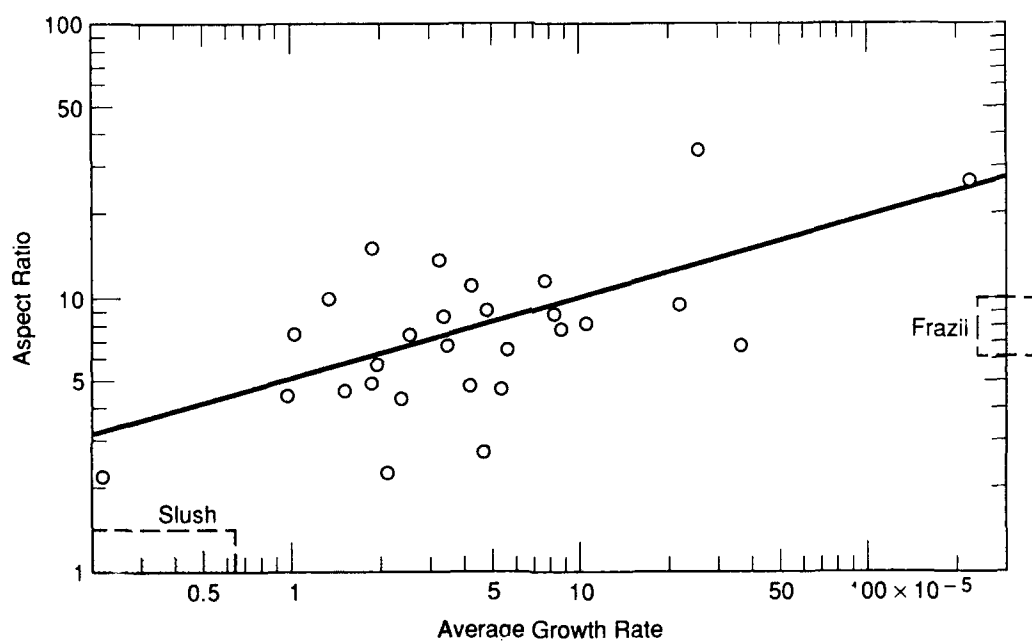


Figure 9. Aspect ratio vs average mass growth rate. The observed ranges for slush and frazil are shown, and the data are described by a least-squares fit, with r^2 of 0.78.

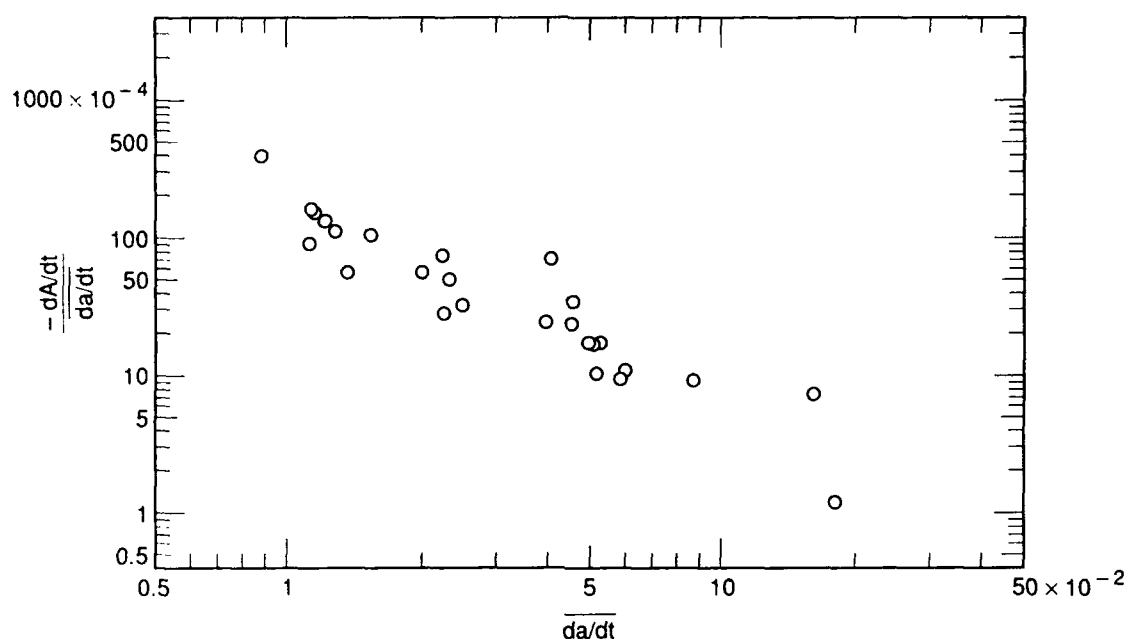


Figure 10. Ratio of metamorphic growth rate to average growth rate vs average growth rate.

much stronger dependence on size than is suggested by eq 1. The result should be viewed with some caution, however, since it is highly dependent on one crystal. If the largest crystal is ignored, the dependence on crystal size decreases markedly.

Figure 9 shows that aspect ratio increased with growth rate and shows the approximate regions into which slush and frazil would fall. However, there is no clear distinction between rapidly growing disks and slowly growing spheres, as might be expected from observations of slush and frazil and as was observed for growth from the vapor (Colbeck 1983). Although one crystal grew at a rate similar to that of slush, it was clearly disk-shaped with an aspect ratio of over two; it had rounded edges but had distinctive flat faces. While even the most rapidly growing crystals had rounded edges, frazil crystals are generally quite sharp. Thus, simulation of the growth of either slush or frazil was imperfect using this technique.

From eq 6 we expect that metamorphism should be relatively important for the smallest crystals. This is clearly shown in Figure 10, where the ratio of metamorphic shrinking to measured growth rate is plotted vs measured growth rate. This ratio increases as the growth rate decreases but never approaches a value of one in the lower

range of growth rates from the experimental results. Thus, even for particles growing in the range of slush crystals, the rate of thickening due to metamorphism appears to have no effect on the overall growth characteristics of the particles, so the kinetics of crystal growth must control the shape of crystals over this entire range of growth rates. Again, there is no suggestion of a sudden transition from disk growth to sphere-like growth.

CONCLUSION

Ice crystals were grown on a line suspended in supercooled water at rates spanning the range from those of slush to those of frazil ice. Their growth should be described by the classic theory for crystal growth in an infinite medium, but the theory overpredicts the growth rate, probably because multiple crystals grew at each location in the supercooled water. A simple model of crystal thickening by metamorphism was also constructed, and this suggests that the crystals do not thicken by this mechanism, even at the lowest growth rates observed. Thus, thickening by curvature-controlled metamorphism is not important for the crystals grown here, although it does appear to be important in the crowded environment in which

slush grows. The aspect ratio increased with growth rate, as was expected from observations of slush and frazil, but there was no sharp transition between them, as is observed with vapor-grown crystals. The aspect ratios observed in these experiments were larger than expected in the growth ranges for both slush and frazil. While these experiments were somewhat successful in simulating the growth of frazil and slush crystals, some clear departures from both theory and observations in nature were noted. These might be changed by a more carefully controlled set of experiments where only one crystal grew from each seed and where the slight supercoolings were measured. However, it could also indicate a failure of the theory, which has never before been tested.

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