# COMPREHENSIVE REVIEWS 

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# Mechanisms of Ice Crystallization in Ice Cream Production 

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#### Abstract

The smoothness and perceived quality of an ice cream depends in large part on the small size of ice crystals in the product. Understanding the mechanisms responsible for producing the disc-shaped crystals found in ice cream will greatly aid manufacturers in predicting how processing and formulation changes will affect their product. Because ice cream mix is opaque, it has not yet been possible to observe ice crystallization in ice cream in situ. Studies to date, therefore, have used analogues or have related observed effects to a hypothesized mechanism. Still, some elements of the crystallization mechanism are well accepted. Because of the large supercooling at the freezer wall, ice nucleates there before being swept into the bulk of the freezer. In the bulk, heat and mass transfer cause some crystals to melt and others to grow. By the time the ice cream reaches the freezer exit, the ice crystals have become small, rounded discs.


Ice cream is a complex food... - H.D. Goff

## Introduction

The delights of ice cream have been known in the western world since Marco Polo returned from Far East Asia in the 13th century bringing with him recipes for water ices. Over time, these water ices evolved into the popular frozen desserts of today. Modern ice cream is a partially-frozen mixture of milk, cream, sugar, stabilizers, and emulsifiers. Its apparent simplicity belies the complicated structure inside America's favorite frozen treat. Ice cream is equally an emulsion, a dispersion, and a foam. The dispersion and emulsion consist primarily of a freeze-concentrated aqueous serum phase containing sugar and the dry matter contents surrounding dispersed ice crystals and fat globules (Marshall and others 2003). Ice crystals range in size from about 1 to over $150 \mu \mathrm{~m}$ in diameter, with an average size of about $35 \mu \mathrm{~m}$ (Berger and others 1972; Caldwell and others 1992; Donhowe and Hartel 1996a; Hagiwara and Hartel 1996; Hartel 1996; Koxholt and others 2000; Marshall and others 2003; Sofjan and Hartel 2004; Inoue and others 2008; Kusumaatmaja 2009). Fat globules are 2 $\mu \mathrm{m}$ or less in diameter (Marshall and others 2003). The foam is formed by pockets of air (about 20 to $50 \mu \mathrm{~m}$ diameter) dispersed throughout the emulsion and is supported by partially-coalesced fat globules (Goff 2002; Marshall and others 2003).
The best ice creams on the market have a smooth and creamy texture. That creamy texture, primarily associated with a high fat content, is also determined, in part, by the average size of the ice crystals. Larger crystals (greater than $50 \mu \mathrm{~m}$ ) impart a grainy

[^0]texture to the ice cream, whereas smaller crystals (around 10 to $20 \mu \mathrm{~m}$ ) give ice cream the desired creaminess (Marshall and others 2003; Eisner and others 2005). With today's consumers becoming more and more health-conscious in their food choices, low-fat ice cream is becoming increasingly popular. The challenge with low-fat ice cream, however, is achieving the same creamy texture of the full-fat version. With less fat, ice cream commonly contains more water and, thus, larger ice crystals (Hartel 1996).

Ice crystal size is also important to ice cream shelf life. As the ice cream sits in storage, the ice crystals continually grow by recrystallization (Donhowe and Hartel 1996b; Hartel 1998a). The temperature fluctuations seen in a frost-free home freezer serve to accelerate this process.

The actual mechanism of ice crystallization in the scrapedsurface heat exchanger remains the subject of research due to the technical difficulties in watching ice form through opaque ice cream mix and inside a scraped-surface freezer. Some basics of the mechanism, however, are generally well accepted. At the wall of the ice cream freezer, and only at the wall, the temperature is cold enough to form new crystals. A layer of ice forms on the wall with properties depending on mix composition and freezer operation. The dasher blade then comes around and scrapes the ice off the wall, dispersing the frozen layer into the bulk of the freezer. According to rates of heat and mass transfer in the center of the freezer, some crystals melt while other crystals grow in a complex process called ripening. The final result at the freezer exit is a distribution of small, disc-shaped crystals.

Understanding how ice forms during the freezing of ice cream will greatly aid manufacturers in predicting the effects of processing and formulation changes. The purpose of this review is to discuss research on how ice crystals form in a scraped-surface freezer and the parameters that affect their growth. Brief descriptions of general crystallization and ice cream manufacture are presented first to provide background.

## Crystallization

Crystallization is the organization of molecules into a solid phase within a fluid. This can occur in several different ways. Vapor can crystallize directly from the gas to solid phase, with the prime example being snow. A solute can be crystallized out of solution, such as in lactose crystallization in dairy products. Alternatively, the solvent can crystallize, as happens when ice forms in ice cream. For a mixture of liquids, lowering the temperature can cause crystallization based on the phase diagram of the mixture, such as in metallurgy (McCabe and others 2005). Since ice crystallization out of a melt is the type of crystallization of concern in ice cream manufacture, it will be the focus of the rest of the discussion on crystallization, though the same general principles apply to other types of crystallization.

The structure of ice determines how the water molecules will be organized after crystallization. Typical ice is categorized as ice lh , which is hexagonal and prismatic in form and occurs below $0^{\circ} \mathrm{C}$ at atmospheric pressure (Fennema 1973). While there are 9 other forms of ice, most exist at pressures greater than 200 MPa . Ice has a hexagonal structure, described by 3 a-axes in one plane and a c-axis normal to that plane (Schwartzberg 1990). Experiments involving freezing sugar solutions on a cold surface have shown the a-axes to grow faster than the c-axis (Schwartzberg 1990). The same is true for snow flakes, which are well-known to exhibit a hexagonal structure (Libbrecht 2005).

Before crystallization can begin, the temperature of the melt must decrease below the freezing point. When the melt is a solution, the solute lowers that freezing point to an extent based on the nature of the solute. Freezing point depression, being a colligative property, is based on the moles of solute present in solution, not on the mass. Therefore, a gram of glucose (with about double the number of moles of sucrose) would lower the freezing point more than a gram of sucrose. Proteins, being very large comparatively, have no measurable effect on freezing point (Marshall and others 2003).

The size of a crystal can also affect the freezing point. While ice Ih has a nominal freezing point of $0{ }^{\circ} \mathrm{C}$, smaller ice crystals are known to have a slightly depressed freezing point compared to larger crystals. The same is also true for a sharp point on a crystal surface compared to a flat surface. This phenomenon is due to what is called the Kelvin or radius of curvature effect. Because the small crystals have more surface free energy per volume than do the larger crystals, their freezing point is depressed according to Eq. 1 (Schwartzberg 1990; Hartel 2001).

$$
\begin{equation*}
\Delta T^{\prime}=\frac{2 \sigma T_{\infty}}{\rho_{\mathrm{s}} \Delta H_{\mathrm{fus}} r} \tag{1}
\end{equation*}
$$

Here, $r$ is the crystal radius, $\Delta T^{\prime}$ is the freezing point depression, $T_{\infty}$ is the equilibrium absolute temperature for a crystal of infinite radius, $\sigma$ is the interfacial tension ( 1.5 to $3.2 \times 10^{-2} \mathrm{~J} / \mathrm{m}^{2}$ ) (Hobbs 1974), $\rho_{\mathrm{s}}$ is the density of the crystal ( $917 \mathrm{~kg} / \mathrm{m}^{3}$ for ice) (Fennema 1973; Schwartzberg 1990), and $\Delta H_{\text {fus }}$ is the latent heat of crystallization (Schwartzberg 1990).

Crystallization occurs in 4 steps: supercooling, nucleation, growth, and recrystallization. Supercooling occurs when the temperature of the liquid drops below its freezing point. In general, water molecules are constantly coming together to form clusters held together by hydrogen bonds. These clusters are continually breaking up again due to molecular vibrations, although lower temperatures enhance cluster formation (Schwartzberg 1990; McCabe and others 2005). At a certain level of supercooling, the ice-like clusters gain enough molecules of water that they have an equal chance of surviving or not as crystal nuclei. Thus,
there is a critical radius above which the nuclei will be likely to survive (Schwartzberg 1990).

In a scraped-surface freezer, crystallization conditions can be divided into 2 zones. Close to the wall, the fluid is very cold, so nucleation occurs in that zone only. Far from the wall, in the bulk of the fluid, temperatures are closer to the freezing point, and growth and recrystallization predominate (Cebula and Russell 1998).

## Nucleation

Nucleation is the birth of a crystal (Hartel 2001). In a scrapedsurface freezer, this only occurs at the wall of the freezer where the temperature gradient is high enough to form new crystals. The rate of nucleation is important because it affects the number of crystals in a product, which in turn affects how large each crystal can become. For ice cream, once it exits the freezer, the maximum number of ice crystals is set, and those crystals continue to grow until the amount of ice is in equilibrium with the temperature (Hartel 1996).

The nucleation process starts with the initial cluster of ice as a loose aggregation of molecules. As the cluster loses energy, the molecules become more ordered and a lattice structure begins to form and the cluster becomes an embryo. When the embryo grows large enough to be in thermodynamic equilibrium with the solution and when the embryo overcomes the energy barrier to nucleation, it is a nucleus-the smallest collection of molecules in a crystal lattice that will not redissolve. When the nucleus grows it becomes a crystal (McCabe and others 2005).

Nucleation can occur in several ways. Primary nucleation describes the spontaneous formation of a nucleus from solution, whereas secondary nucleation describes the formation of a nucleus from a preexisting crystal or crystal fragment. There are 2 types of primary nucleation: homogeneous and heterogeneous. In homogeneous nucleation, the nucleus is formed in the bulk of the fluid by molecular accretion (McCabe and others 2005). In heterogeneous nucleation, on the other hand, the nucleus forms on a foreign particle or object, which could be anything from a dust mote to the wall of an ice cream freezer (Hartel 2001). Because heterogeneous nucleation occurs more readily and with less supercooling than does homogeneous nucleation, it is much more common in practical applications (Schwartzberg 1990). Secondary nucleation most commonly occurs in industry as contact nucleation, which is when a crystal collides with another crystal, the wall, or an agitator (McCabe and others 2005).

Several factors affect nucleation. The most important factor is the driving force-the temperature difference between the solution and its freezing point. A greater driving force increases nucleation. However, when the temperature is too low, decreased molecular mobility slows nucleation. Below the glass transition temperature, $T_{\mathrm{g}}$, no nucleation occurs. Agitation can enhance nucleation in a labile (ready-to-nucleate) system. Cooling rate influences nucleation as well. For example, if no nucleation is desired, the solution can be quickly cooled to a temperature below the glass transition before the onset of crystallization (Hartel 2001). In foods, the formulation and ingredients can impact nucleation; for instance, sucrose may slow ice nucleation (Schwartzberg 1990).

## Growth

After ice nucleates at the wall of an ice cream freezer it must grow to become the disc-shaped crystals found in the exit stream. For crystal growth to occur, water must diffuse to the growing crystal surface, solutes must diffuse away from the surface,
water molecules must incorporate themselves into the crystal lattice structure, and latent heat must be removed (Fennema 1973; Schwartzberg 1990; Hartel 2001). While the internal structure of the ice is generally uniform, growth conditions have a profound effect on the external shape and size-the morphology-of the crystal. Generally speaking, slow freezing-slow transport of latent heat-causes fewer nuclei to form per a given volume and time, which allows more space for each crystal to grow in and results in larger crystals. Quick freezing results in a faster nucleation rate and a larger number of small crystals (Schwartzberg 1990; Hartel 2001). Normally, dendritic (tree-like), needle-shaped, and fibrous crystals form with quick freezing, whereas slow freezing allows uniform growth into smoother shapes (Schwartzberg 1990). Dissolved solutes also impact crystal morphology by adsorbing to the crystal surfaces, which interferes with the lattice incorporation step, and by decreasing molecular mobility (increasing viscosity) (Fennema 1973).

Dendritic and branched morphologies are common in crystals made with high supercooling-such as at the wall of an ice cream freezer. Before dendritic structure evolves, a growing ice crystal is approximately circular (Teraoka and others 2002). As one section of the crystal begins to protrude, that tip is surrounded by a higher water concentration, so crystallization is easier at the tip. Dendrites evolve into a branched structure with primary branches developing secondary branches and on to higher-order branches. This positive-feedback loop is called the Mullins-Sekerka instability (Libbrecht 2005).

Dendrite morphology is dependent on the behavior at the crystal tips. This behavior is characterized by the dendrite growth velocity and the tip radius (the radius of a circle fitting the curvature at the tip), which are in turn a function of the supercooling and the solids concentration (Hindmarsh and others 2005). A perfect dendrite will have a hexagonal shape, but at higher growth velocities (higher supercooling) an increased number of dislocations can cause crystals that have extra branches parallel to the 6 main branches (Teraoka and others 2002). The spacing between dendrites has been found to be proportional to the freezing rate to the $-\frac{1}{2}$ power (Schwartzberg 1990), which means that dendrites formed at higher supercooling have closer (and thinner) branches. As well, higher solute concentration produces thinner branches (Teraoka and others 2002). Between 2 branches, there will be stagnant regions with high solute concentration and low freezing point. As a dendrite ripens these branches may become thicker and more widely spaced (Huang and Glicksman 1981a). The branches in dendrites are observed to be at $60^{\circ}$ angles, indicating that the a-axes of the ice grow faster than the c-axis (Schwartzberg 1990). This has been observed in hexagonal ice crystals growing laterally out of a sucrose solution before growing vertically (Si 2000).

While an instability easily results in branch formation, the freezing point at the tip is also lower, so dendritic growth is only favored with high supercooling (Schwartzberg 1990). The heat being removed from the crystal tip is conducted away mainly through the ice because ice is about four times as conductive as water (McCabe and others 2005). At steady state, the dendritic stability criterion states that the tip's growth velocity times the square of the tip radius is constant (Huang and Glicksman 1981b).
A negative thermal gradient at the freezing front can result in irregular or dendritic crystal growth. In this case, temperature decreases from the interface both into the liquid and into the solid (temperature is highest at the interface). This may occur if the rate of heat removal is greater than the rate of crystallization (Fennema 1973). The heat of crystallization can then be conducted away through both the crystal and the liquid. Also, because the temper-


Figure 1-Conditions for constitutional supercooling (Fennema 1973).
ature is lower farther away from the interface, there is a stronger driving force for a protuberance from the crystal to grow into the solution. Secondary protuberances will cause the branches typical of dendritic crystals (Fennema 1973; Zheng 2006).

A positive temperature gradient on the other hand, where temperature continues to increase from the solid to the interface and into the liquid, discourages dendritic growth. The heat of crystallization is conducted away through the crystal only, so any protruding crystal will not only be in a warmer location but will also need to conduct its heat of crystallization farther back to the main crystal (Fennema 1973; Zheng 2006).

At the crystallization front, the solution will be more concentrated due to counter-diffusion of solutes. As a result of the higher concentration, the freezing point temperature is reduced at the surface, with a gradient that levels off to the bulk freezing point farther away from the crystal surface. If at the same time the temperature in the solution increases from the freezing point at the crystal surface to the bulk temperature more slowly than the freezing point increases, the result will be constitutional supercooling, as shown in Figure 1 (Fennema 1973; Zheng 2006). Constitutional supercooling differs from normal supercooling in that it is due to a solute concentration gradient. Within the region of constitutional supercooling, protrusions may grow into a dendritic form, as with a negative temperature gradient (Fennema 1973; Zheng 2006). If 2 crystals are close together, the higher solute concentrations at each interface may overlap, flattening and lowering the freezing point curve such that the constitutional supercooling region disappears and melting occurs. Fast solidification and low solute diffusivity, as found in ice cream freezing, favor constitutional supercooling (Zheng 2006).

## Recrystallization

Recrystallization, also called ripening or coarsening, is the final stage of crystallization describing a change in the shape and size of the individual crystals while keeping the total crystal mass constant. It can occur both during a crystallization process, such as during initial ice cream freezing, and after the process, such as during storage of ice cream. Recrystallization, like growth, is a function of heat- and mass-transfer, as well as the Kelvin effect. It occurs because a system tends towards an equilibrium with minimal free energy (Schwartzberg 1990). Also, because of the Kelvin effect, small crystals and sharp points on a crystal (greater freezing point depression) melt faster than larger, rounder crystals at a given temperature (Hartel 1998b).

The 3 main types of recrystallization are isomass, migratory, and accretive recrystallization. Isomass recrystallization is the change in shape of a crystal without change in mass.

Migratory recrystallization, or Ostwald ripening, describes large crystals growing at the expense of small crystals. Accretion is 2 crystals joining together to form 1 crystal (Fennema 1973; Donhowe and Hartel 1996b).

Recrystallization is often modeled according to Eq. 2, where $\bar{r}$ is the average radius of a spherical particle at time $t, \bar{r}_{0}$ is the initial average radius, and $\tau$ and $n$ depend on the mechanism (Hartel 1998b; Flemings 2005).

$$
\begin{equation*}
\bar{r}^{n}=\bar{r}_{0}^{n}+t / \tau \tag{2}
\end{equation*}
$$

For long times, recrystallization can be modeled according to Eq. 3, where $R$ is the rate of recrystallization (Hartel 1998b).

$$
\begin{equation*}
\bar{r}=\bar{r}_{0}+R t^{1 / n} \tag{3}
\end{equation*}
$$

The value of $n$ can reveal the mechanism of recrystallization. For $n=3$, ripening is said to be limited by diffusion of the solute from the bulk in a stagnant system (Lifshitz and Slyozov 1961; Wagner 1961). A value of 2 for $n$ indicates either that ripening is controlled by the lattice incorporation (Jain and Hughes 1978) or surface reaction step (Mullin 1993) or that convective diffusion limits growth (Kahlweit 1975). When $n=4$, "grain boundary diffusion" has been found to be limiting; that is, the grain boundaries serve as the active sites for diffusion from the solution (Jain and Hughes 1978). The rate of recrystallization itself is a function of the system properties, such as composition and temperature. For hardened ice cream in storage, recrystallization follows Eq. 3 with $n$ equal to 3 and the rate of recrystallization has an Arrhenius-type dependence on temperature (Donhowe and Hartel 1996a).

Recrystallization is not only a function of time, however. The crystal size distribution can also play a role. For a given distribution at a given temperature, there may be a few crystals whose radii put them in perfect equilibrium with the bulk temperature. Other crystals will be either smaller or larger than the equilibrium radius, and the small crystals will tend to melt due to their lower freezing point, and the large crystals will grow (Smith and Schwartzberg 1985). Melting the small crystals takes energy out of the solution, and this heat removal, in turn, provides a heat sink for the latent heat of crystallization given off from the growing larger crystals. While growth is governed by heat and mass transfer and lattice incorporation kinetics, crystal dissolution or melting is mainly governed by heat and mass transfer. Manipulation of the size distribution can affect how fast the system ripens (Smith and Schwartzberg 1985; Sutton and others 1994). For example, a size distribution where every crystal was within a couple microns of the equilibrium radius would ripen very slowly, whereas a very wide distribution would ripen faster because the crystals at each extreme will have a larger driving force for recrystallization.

When freezing ice cream, dendrites may form initially (Schwartzberg and Liu 1990); however, by the time the ice cream exits the freezer, the crystals-whatever their initial form-have become disc-shaped. How dendrites recrystallize has been wellstudied in the field of metallurgy for solidification of metal alloys. As a dendrite coarsens, branches separate from their trunks, the thinnest branches melt away, the trunks increase in width, and all the points become more rounded. Dendrites are known to ripen in 3 ways (Flemings 2005). First, large dendrite arms may grow at the expense of small dendrite arms. Second, the arms may "coalesce" as the space between the dendrite arms fills in and the dendrite starts becoming rounder. Third, the number of dendrites, but not the mass, may multiply as the crystal breaks apart. Fluid motion in the early stages of solidification causes dendrites to break up, although increasing fluid velocity does not always raise the breakup rate (Flemings 2005; Mullis 2006). After the
arms separate, they become disc-shaped (Flemings 2005). One possible mechanism for dendrite breakup is that the dendrites separate at their branch points, which is where the radius of curvature is high and the crystal is prone to melting (Flemings 2005; Mullis 2006). In quiescent systems, dendrites may exist intact for a long time. However, any perturbation may cause the dendrite to break apart by partial melting and arm detachment (Mullis 2006). Often, many dendrite arms will detach at once, possibly due to a small energy input, such as slight agitation, driving the system farther from equilibrium and increasing the melting rate (Mullis 2006). Convection then takes away any superheat into the bulk along with the dendrite fragments (Flemings 2005).

When quantitatively characterizing dendrites, the distance between secondary dendrite arms (branch spacing) and the dendrite tip radius are common measurements of fineness. A finer, thinner dendrite will have arms spaced close together and a smaller tip radius. As the dendrite coarsens, the arms will become fewer and farther apart and the tip radius will increase. Dendrite coarsening has also been modeled with Eq. 3 with $n$ equal to 3 and $r$ as the tip radius (Glicksman and Voorhees 1984).

## Manufacture of Ice Cream

To produce ice cream in the typical commercial process, the ingredients are first mixed together, then pasteurized, homogenized, cooled, and aged for at least 4 h at a temperature of about $4{ }^{\circ} \mathrm{C}$. Flavoring is then added before the mix is pumped into the scraped-surface freezer (SSF), where about $50 \%$ of the water is frozen and air is incorporated into the product. Upon exiting the SSF, inclusions and variegates may be added, and the soft product, at about -5 to $-6^{\circ} \mathrm{C}$, is filled into its retail container. The ice cream is sent to harden until the core reaches a specified temperature, usually about $-18^{\circ} \mathrm{C}$. As the temperature drops and more ice crystallizes, the remaining water contains more and more sugar, which depresses the freezing point so that in the final, hardened product, about $75 \%$ of the water is frozen. The finished product is stored between -18 and $-30^{\circ} \mathrm{C}$ (Ben-Yoseph and Hartel 1998), depending on the plant, distributed, and sold (Hartel 1996; Marshall and others 2003). In the supermarket, temperatures in certain types of freezer cabinets (particularly open-faced cabinets) can reach $-9{ }^{\circ} \mathrm{C}$, and in frost-free consumer freezers, temperatures can vary quite widely during the frost-free cycle (Ben-Yoseph and Hartel 1998).

Initial freezing in the SSF is arguably the most important step in creating ice cream. This is the only step in which ice crystals are formed. During hardening, the crystals formed in the SSF grow to accommodate the increased crystal mass. Assuming an equilibrium ice content in the draw (exit) stream of the SSF, the more ice crystals there are at draw, the more ice crystals will be preserved during hardening, leading to a smaller average crystal size. Because of this, it is critical to product quality to control and optimize ice nucleation, growth, and ripening in the SSF. Ideally, the ice crystals will be kept as small as possible to enhance creaminess and extend shelf life.

A typical SSF consists of a cylindrical barrel with a refrigerant, such as vaporizing ammonia or Freon, surrounding it. Inside the barrel is a rotating shaft, or dasher, with scraper blades attached to it. Typically, the barrel and dasher assembly are made of stainless steel (Marshall and others 2003). Ice cream may be frozen either in a batch or continuous process. A batch process may take on the order of 10 to 20 min to freeze. A continuous freezer, common to large operations, has a residence time on the order of 1 to 2 min (Goff and Hartel 2006). The temperature profile inside a continuous freezer is not uniform. Radially, the temperature increases from -26 to $-28{ }^{\circ} \mathrm{C}$ at the wall, where the refrigerant temperature is about $-30^{\circ} \mathrm{C}$, up to the bulk fluid temperature at


Figure 2 - Three-dimensional schematic diagram of ice crystallization and fluid flows through a scraped-surface heat exchanger for ice cream manufacture. The scraper blade removes a slush of ice crystals and concentrated ice cream mix from the barrel wall in flocs, the dasher breaks apart these ice flocs, and the warm bulk liquid melts the flocs apart into disc-shaped crystals. Near the inlet, the warm bulk temperatures melt the majority of the ice. As freezing continues more ice crystals survive in the bulk. Close to the exit, the bulk crystals are larger; the wide size range causes many small new crystals to melt.
the center (Hartel 1996). Axially, from the inlet to the outlet along the barrel center, the temperature has been shown to decrease rapidly in the first $15 \%$ of the barrel to between -3 and $-7{ }^{\circ} \mathrm{C}$ and then decrease linearly to just before the freezer exit, where the temperature increases by about $1{ }^{\circ} \mathrm{C}$ (Hartel 1996; Russell and others 1999).

Initial freezing is a dynamic process: the mix is frozen while being agitated, which whips in the air, destabilizes the fat, and scrapes ice into the bulk fluid (Goff 1997; Marshall and others 2003). As illustrated in Figure 2, cold ice cream mix enters the freezer, with the refrigerant absorbing the heat in the mix until the supercooling at the wall is great enough to initiate ice nucleation. As ice crystals form at the wall, the dasher blades scrape the surface layer from the wall about every 0.075 s , assuming 4 blades with a dasher speed of 200 rpm , and propel the ice layer, at a temperature of -20 to $-25{ }^{\circ} \mathrm{C}$ (Hartel 1996), into the bulk of the freezing ice cream mix. This is pictured schematically in Figure 2, with a larger, cross-sectional view shown in Figure 3. In the bulk, the warmer temperatures cause the ice crystals to ripen into disclike shapes. The details on how the ice crystals actually form and ripen is still the subject of research, although several theories have been proposed (see next section). When the ice cream exits the freezer, it is usually around -5 to $-6^{\circ} \mathrm{C}$, and close to half of the water is frozen. From a survey of recent studies, the average ice crystal size exiting an ice cream freezer is 20 to 30 $\mu \mathrm{m}$ (Donhowe and Hartel 1996a; Hartel 1996; Russell and others 1999; Chang 2000; Windhab and Wildmoser 2002; Marshall and others 2003; Sofjan and Hartel 2004; Drewett and Hartel 2007).

Based on the axial temperature profile in a SSF, ice cream freezing generally follows the solid-liquid equilibrium curve on an ice cream mix phase diagram. Figure 4 shows an approximate phase diagram for ice cream mix. The actual freezing point for an ice cream mix can be calculated from published equations (Bradley 1984; Marshall and others 2003) and is based on the type and content of sweeteners and other solids in the mix. As freezing begins, the ice crystals formed are purely frozen water (Omran and King 1974), which leaves the solutes dissolved in less water than before. As freezing continues and the serum phase is further concentrated, the freezing point decreases until the target temperature has been achieved. If the ice cream is fur-


Figure 3-Two-dimensional view looking down the length of the dasher showing a larger view of ice crystallization near the freezer exit. At this stage, the ice crystals ripening in the bulk are mostly larger than the ice discs formed from the material scraped off the freezer wall, likely resulting in the large crystals growing at the expense of the smaller crystals. For clarity, the size of the crystals inside the slush and ice flocs has been exaggerated.
ther cooled to below the glass transition temperature, $T_{g}^{\prime}$, it has reached the maximal freeze concentration and becomes a glass. However, because ice cream is stored at temperatures above the glass transition temperature, normal storage is between -10 and $-20{ }^{\circ} \mathrm{C}$, the ice can continue to change and recrystallize, mainly by isomass rounding and accretion (Donhowe and Hartel 1996b; Hartel 1996).

Although no new ice crystals nucleate after the freezer (heat transfer is not fast enough), the existing ice crystals continue to grow as the product cools from the draw temperature to $-18{ }^{\circ} \mathrm{C}$. Typically during hardening, ice crystals grow by about $30 \%$ to $40 \%$ (Marshall and others 2003) to an average size of about 25 to $45 \mu \mathrm{~m}$ (Berger and others 1972; Caldwell and others 1992; Donhowe and Hartel 1996a; Hagiwara and Hartel 1996; Koxholt and others 2000; Sofjan and Hartel 2004; Inoue and others 2008; Kusumaatmaja 2009). Because higher temperatures accelerate recrystallization, quick hardening limits the growth of the ice crystals (Hartel 1996; Marshall and others 2003).


Figure 4 -Sample phase diagram for ice cream mix containing 10\% milk solids nonfat, $\mathbf{1 6 \%}$ sucrose, and $\mathbf{3 8 \%}$ total solids; $T_{\mathbf{g}}^{\prime}$ is the glass transition temperature at maximal freeze concentration, $T_{m}^{\prime}$ is the end of the freezing point curve, and $C_{g}^{\prime}$ is the maximal freeze concentration (Hartel 1996; Marshall and others 2003; Schawe 2006). The dashed lines indicate that there is a degree of uncertainty when predicting the glass transition curve and the freezing curve for ice cream mix with high solids.

## Freezing Mechanisms

The specific mechanisms of ice crystal formation in a scrapedsurface heat exchanger during ice cream manufacture remain somewhat elusive. No one has yet been able to observe ice crystals forming while making ice cream, mainly because ice cream mix is opaque and the freezer barrel is enclosed. Various studies, therefore, have resorted to either using sucrose solutions as model systems for ice cream (Omran and King 1974; Stocking and King 1976; Schwartzberg and Liu 1990; Sodawala and Garside 1997; Jacobsen 1999; Si 2000; Lian and others 2006; Zheng 2006) or to examining cause-and-effect relationships when making ice cream in an SSF (Cebula and Russell 1998; Russell and others 1999; Drewett and Hartel 2007).

Crystal morphology is of fundamental importance to describing how ice forms in an SSF. If the crystals are initially disc-shaped, they will ripen differently than if the ice leaves the freezer wall in dendritic form. Numerous studies have attempted to define the initial ice crystal shape formed in an SSF. In freezing sugar solutions, disc-shaped crystal morphologies were observed at very low supercooling (under 100 mK ). At higher supercoolings, such as in an SSF, however, dendritic or needle-like morphologies occurred (Stocking and King 1976). In quiescently-frozen sugar solutions, as well, dendritic growth is well-known to occur (Macklin and Ryan 1966; Omran and King 1974). At constant supercooling, increasing the sugar concentration delays nucleation and causes crystal size to decrease (Omran and King 1974; Schwartzberg 1990). For dendrites, increasing sugar content also causes thinner branches (Schwartzberg 1990).

Based on the principles of dendrite formation, Schwartzberg proposed the "lawnmower model." Schwartzberg's experiments involved observation of sucrose solution quiescently-frozen on a chilled surface (Schwartzberg and Liu 1990). Because the experiments used quiescent freezing, dendritic growth was observed. However, he suggested that due to the high supercooling at the
wall in an ice cream freezer, dendritic ice growth is likely there, as well. In this model, dendrites grow normal to the freezing surface, and when a scraper blade comes around, it cuts off the budding dendrites at their base on the wall. Fluid motion transports the dendrites into the bulk of the freezer, where they ripen into disc-shaped ice crystals (Schwartzberg 1990).

The heat input during scraping may also affect ice formation in an SSF. Schwartzberg (1990) calculated that the dasher inputs a large amount of frictional heat into the freezer-as much as $50 \%$ of the total heat removed-which will cause some crystals to melt and will slow the freezing process. Russell and others (1999) measured the actual energy input from the dasher, which showed that about $15 \%$ to $40 \%$ of the heat removed was frictional heat, depending on the dasher speed and draw temperature. Clearly the dasher inputs a high amount of heat into the freezer, which likely has a significant, yet largely unknown, effect on ice formation in an SSF.

Cebula and Russell (1998) considered ice cream freezing in an SSF to occur in 2 distinct zones: a wall zone and a bulk zone. In the wall zone, they found, by spreading mix over a cold plate and then examining a cross-section with a scanning electron microscope, that globular crystals formed in the vicinity of the surface and that columnar crystals formed farther away. The columnar crystals did not attach themselves to the wall, however, but grew out from small nuclei near the cold wall. When the surface was scraped, it was observed that remaining ice debris served as secondary nuclei for new crystal growth. The new ice grew in roughly hexagonal shapes, which may have had time to grow into a unified layer depending on the length of time between scrapes. Investigating the bulk zone, Cebula and Russell (1998) varied the dasher speed, which varied the specific net energy dissipated by the freezer, while keeping residence time constant, and found that increasing the total energy input greatly increased the average crystal size. This likely occurred because the extra energy in the system would have melted many of the smallest (and least stable) crystals, leaving fewer and larger crystals in the product. They concluded that, in the wall zone, the mechanism of ice formation is probably somewhere between heterogeneous nucleation at the wall and nucleation from ice debris and that, in the bulk zone, the total energy input into the system is critical to the final crystal size distribution.

A subsequent study by Russell and others (1999) showed that product residence time in the freezer had a more important impact on final crystal size distribution than did initial nucleation rate. Ice creams made by varying the wall temperature while keeping the residence time constant gave very similar crystal size distributions, whereas ice creams made with a constant exit temperature (constant heat removal) or a constant coolant temperature with varied residence time gave different distributions. A shorter residence time gave a smaller average crystal size (Russell and others 1999). The fact that residence time had a more significant impact on the final average crystal size than did the wall temperature indicates that ripening is more significant than nucleation. A similar study by Drewett and Hartel (2007) also concluded that residence time had the greatest impact on final crystal size distribution, followed by draw temperature and dasher speed.

Sodawala and Garside (1997) observed freezing of a $10 \%$ sucrose solution with a videomicroscope in a flowcell simulating a scraped-surface heat exchanger. The flowcell contained a flat stainless steel surface cooled underneath by a coolant and a sharp-edged blade that scraped the surface at intervals while sucrose solution flowed over the metal surface. After a scrape, islands of ice grew parallel to the freezing surface before merging and continuing to grow normal to the surface. At low scraping frequencies, flocs of ice were scraped off the cold surface into the
bulk of the solution. Higher scraping frequencies generated more heat, which reduced both nucleation and growth rates; they also resulted in smaller flocs being scraped off.

Studying ice crystallization from a sucrose solution in a slush freezer, Jacobsen (1999) found that oblong ice crystal sheets were initially scraped off the heat-exchange surface by the blade. Agitation within the warmer bulk fluid then broke apart these crystal sheets, which ripened into rounded ice crystals within 10 min . After 16 h in the slush freezer, pellet-shaped crystals had formed, as opposed to the typical flat disc-shaped crystals found in hardened ice cream.

Ice crystallization and transformation were observed under many different experimental conditions in an effort to elucidate how ice forms in an SSF (Si 2000). Sucrose solution was frozen on a microscope slide placed over a small glass flowcell containing refrigerant inside a refrigerated enclosure. A hightemperature driving force between the refrigerant and the slide caused dendritic crystals to grow. Without agitation at a constant temperature, the dendrites did not become discs. In another experiment, $40 \%$ sucrose solution was frozen without stirring in a chilled, jacketed glass beaker. It was observed that at a low wall temperature, the dendrites grew closer together and that near $-25{ }^{\circ} \mathrm{C}$ some even looked glassy. Subsequent warming from -20 to $-10^{\circ} \mathrm{C}$ caused dendrites to subsequently melt into many, discshaped crystals. A subsequent experiment observed ice crystallization in a scraped-surface heat exchanger with a sucrose and gelatin solution. Large ( 100 to $450 \mu \mathrm{~m}$ ) hexagonal crystals were seen to form initially and remain for about 20 s before changing into a dendritic form. The hexagonal crystals grew quickly for the first 5 s, after which crystal growth was slower. The scraper blades then broke the dendrites into shreds (Si 2000). For a short time the shreds and dendrites could coexist. Then, the shreds partially melted in the bulk of the freezer and eventually rounded into discs (Si 2000).

More recently, using a flowcell equipped with a scraper blade and a chilled surface, Zheng (2006) studied heat transfer during ice crystallization from a sucrose solution. Zheng observed that many nuclei rapidly grew from ice debris remaining after each scrape and continued growing along the cooling surface before merging and growing vertically, as also seen by Sodawala and Garside (1997). It was then concluded that, for crystallization, the most significant effect of the scraper is to cause secondary nucleation at the surface. By monitoring the heat flux through the cold surface, Zheng (2006) showed that crystallization at the surface greatly enhanced heat transfer because the heat could travel directly from the crystal, through the wall, and to the refrigerant, without having to travel through the liquid. The frozen layer at the cold surface was determined to be effectively a slush composed of both ice and concentrated sucrose solution. This was concluded when thermal conductivity measurements of the frozen layer yielded a value close to the average thermal conductivity, weighted by volume fraction, of ice and the concentrated sucrose solution. A slush requires less power to scrape than a layer of solid ice, which suggests reduced scraping power might be possible (Zheng 2006).

Lian and others (2006) modeled ice crystallization in an SSF for sucrose solution. They used computational fluid dynamics coupled with crystal population balance to predict the ice crystal size distribution, assuming only nucleation and growth and no aggregation, breakage, or back-mixing. The model results matched the shape of the ice crystal distribution curve, but overestimated the mean crystal size (Lian and others 2006). It is possible that the overestimation is a result of not accounting for effects that would shrink crystal size, such as breakage and melting.

Pulling together the findings from these diverse studies, a basic mechanism for ice crystal formation in a scraped-surface freezer
may be hypothesized. First, an ice layer forms on the wall, and the scraper blade removes the ice layer into the bulk. Exactly how this layer forms is still debatable. Depending on how well the scraper blade removes ice from the wall, there may be a little residual ice left behind, if only in microscopic crevices, to seed the next round of crystal nucleation, or there may a relatively thick layer of ice left behind that would simply keep growing. Another factor is what happens when, after a scrape, the icecontaining bulk fluid comes in contact with the wall. Perhaps the cold wall-zone temperatures cause the existing ice to grow at an accelerated rate, possibly in a dendritic fashion. Based on video images from the research of both Zheng (2006) and Sodawala and Garside (1997), it is likely that the ice growing at the wall grows parallel to the freezing surface. Given enough time for the ice growths to converge, the ice would then begin to grow normal to the surface. Regardless of exactly how it forms, the ice layer scraped off the wall is probably a slush containing dendrites and entrapped, concentrated ice cream mix. Once the scraper blade disperses the slush layer at the wall into the warmer bulk medium, the result would be the crystals melting apart into many disc-shaped crystals. Toward the freezer entrance, much, if not all, of the ice dispersed into the warmer bulk fluid is likely to melt and bring down the bulk temperature. Farther along the length of the freezer, more ice would survive. By the freezer exit, the bulk ice crystals would be much larger than the new crystals being transported from the wall. This wider crystal size distribution would accelerate ripening and encourage the large crystals to grow at the expense of the small crystals. Energy input from the dasher, due to friction at the wall and viscous dissipation, also can contribute significantly to crystal melting and ripening.

## Factors Affecting Crystallization

The course of crystallization is determined by many factors that interact with and depend upon one another. Ice cream formulation can affect ice crystallization by influencing the freezing point and/or the crystallization mechanism. The sugars and milk salts in ice cream mix affect the freezing point of the mix, which affects the degree of supercooling for a given coolant temperature (Marshall and others 2003). Fat can reduce ice crystal size by taking the place of water. In this case, for a given number of nuclei formed in ice cream that is hardened to a given temperature, there will be less water to freeze when fat replaces some of the water (Hartel 1996). Partial coalescence of fat globules may also have a role in keeping ice crystals small (Barfod 2001). Proteins, having a high molecular weight, diffuse more slowly than other solutes, which could cause them to interfere with the lattice incorporation step of ice crystallization. The air cells may act as an insulator, mitigating temperature fluctuations (Sofjan and Hartel 2004), and may physically impede ice crystal growth.

Stabilizers in ice cream attenuate the effects of recrystallization during storage, but have no significant effect in the freezer itself (Goff 1997; Bolliger and others 2000). They neither change the thermodynamics of the ice cream mix nor alter ice nucleation kinetics, though they do slow down crystal growth during heat shock (Muhr and others 1986; Marshall and others 2003). Emulsifiers help destabilize fat, incorporate more and smaller air bubbles, and form thinner lamellae between air bubbles, all of which are physical impediments to ice crystal growth (Marshall and others 2003). In the SSF, emulsifiers have been shown to lower the average ice crystal size (Hartel, unpublished).

Ice structuring proteins, ISPs (Regand and Goff 2006), and propylene glycol monostearate (PGMS) (Aleong and others 2008) are emerging as new options to limit ice crystal growth and recrystallization. Taken from freeze-tolerant plants, ISPs are believed to act by adsorbing to the ice crystal surface and thus interfering
with the normal kinetics of water diffusion and adsorption at the ice crystal-solution interface (Regand and Goff 2006). PGMS is also thought to directly interfere with the lattice incorporation step of crystallization and to retard ice crystal growth even more strongly than ISPs (Aleong and others 2008).

Faster freezing results in smaller ice crystals. To that end, the length of time that the ice cream spends in the SSF greatly impacts the final ice crystal size distribution. A longer residence time means that, for a given draw temperature, the ice cream mix is slower to reach its exit temperature. It also gives the ice crystals in the warmer bulk of the fluid more opportunity to recrystallize and grow larger (Russell and others 1999; Drewett and Hartel 2007). Additionally, a wide residence time distribution causes some of the ice cream mix to spend a longer time in the freezer and grow larger (Russell and others 1997). Decreased dasher speed, fewer or smaller gaps between the dasher blades, and increased shear thinning consistency in the fluid all are known to decrease axial mixing within the freezer and to narrow the residence time distribution. Ideally, no backmixing via plug flow would give the narrowest distribution (Russell and others 1997).

To achieve a high cooling rate, heat transfer at the wall must be as efficient as possible. Because heat travels more slowly through ice than stainless steel, ice building up on the barrel wall acts as an insulator and slows its own growth. Efficient scraping, by keeping the blade sharp and close to the wall, ensures that heat transfer remains fast, giving smaller ice crystals (Marshall and others 2003).

The wall temperature has a direct effect on the cooling rate of the mix: a higher driving force speeds initial nucleation and growth. While wall temperature may not be the dominant factor in determining the final ice crystal size distribution, lower wall temperatures can lower the bulk temperature of the ice cream faster, reducing residence time and improving the ice crystal size distribution (Russell and others 1999; Drewett and Hartel 2007).

Dasher speed is known to have an effect on the final ice crystal size; however, literature sources are not in agreement as to this effect. Increasing dasher speed has been found to increase (Russell and others 1999), slightly increase (Drewett and Hartel 2007), not to affect (Koxholt and others 2000), and to have mixed effects (Inoue and others 2008) on ice crystal size. Crystal size could increase with dasher speed because of the extra mechanical energy and frictional heat being put into the system via the rotation of the dasher, which accelerates recrystallization (Russell and others 1999). Conversely, increasing dasher speed could help reduce ice crystal size by scraping off a thinner ice layer. According to Schwartzberg's theory (Schwartzberg 1990), a higher scraping rate should interrupt crystal growth and result in smaller crystals being mixed into the bulk, but he also acknowledged that scraping produces frictional heat and that a dasher must input some power into the freezer to agitate the product. It is possible that dasher speed itself is not a direct predictor of ice crystal size, instead the actual frictional heat generation may give a better correlation with ice crystal size. This case suggests an optimum balance between rotation rate and heat generation, which would depend on the individual freezer and ice cream mix composition to produce the smallest ice crystals.

Dashers are made in a variety of displacements, the percentage of the freezer barrel volume occupied by the dasher. Solid dashers have high displacement, typically about $80 \%$, whereas open dashers have low displacement and often include beaters (Marshall and others 2003). The effect of having a high displacement dasher is to bring all the ice cream mix closer to the wall by making the mix pass through an annular space, which can also reduce the residence time within the freezer and speed heat transfer. High displacement, therefore, theoretically results in a smaller ice crystal size (Marshall and others 2003). Using differ-
ent dasher displacements with a constant exit or wall temperature has not been found, however, to have a significant effect on the resulting ice crystal size distribution (Russell and others 1999).

Draw temperature is determined by the transport properties of the system: heat transfer rates, extent of crystallization, frictional heating, and so forth. A lower draw temperature results in less time for hardening and, thus, smaller ice crystals. With conventional ice cream freezing, however, if the draw temperature is too low, the ice cream will be too viscous to package into its retail container (Marshall and others 2003). Also, a lower wall temperature lowers the bulk temperature inside the freezer, reducing ripening (Koxholt and others 2000; Drewett and Hartel 2007).

A new technology for reducing draw temperature and eliminating the need for hardening is cold extrusion (Windhab and Wildmoser 2002). The process reportedly improves both the sensory and shelf-life properties of the ice cream. The lowtemperature extruder is placed after the normal scraped-surface freezer and can bring the draw temperature down to -15 to $-18{ }^{\circ} \mathrm{C}$ (Windhab and Wildmoser 2002). The extruder may be in either a single-screw configuration, which churns the ice cream around the screw, or a twin-screw configuration, which kneads and churns the ice cream between 2 parallel screws. Both operate at a rotational rate of about 15 rpm (Kunzig 2004). In the extruder, high homogeneous local shear breaks up the fat globules, ice crystals, and air cells into smaller units. Because of the smaller dispersion sizes, ice cream flowability is maintained. For ice crystals, the low temperatures and high ice-cream viscosity in the extruder not only help form additional secondary nuclei, but the shear breaks apart ice aggregates, too. Most importantly, fast heat transfer helps prevent local ice remelting of small crystals and recrystallization. Compared to conventional ice cream freezing and hardening, including a twin-screw cold extruder reduces ice crystal and air cell size by a factor of 2-3 (Windhab and Wildmoser 2002). The single-screw setup only had a small effect on ice crystal size, but still impacted air cell size similar to the twin-screw (Wildmoser 2004). The smaller fat globule aggregates resulting from the high shear in the cold extruder impart a creamy texture to the ice cream without a buttery defect, making the technology useful for low-fat formulations (Windhab and Wildmoser 2002).

One potential modification to the typical ice cream freezing process is to recirculate a portion of the product stream back to the freezer inlet stream. The benefit of this practice is mainly for start-up, where recirculation minimizes production of unused unfrozen product. The recirculation stream brings existing ice crystals into the mix where they can serve as seed crystals and can continue to grow in size (Hartel 1996). This results in a wider residence time distribution with a higher average residence time and, thus, a larger, wider crystal size distribution (Schwartzberg 1990; Hartel 1996; Levenspiel 1998; Kusumaatmaja 2009). Recirculation does have a beneficial effect on the air cell size, however, because the extra whipping-provided by the increased residence time-breaks the air cells into smaller bubbles (Chang and Hartel 2002; Goff 2002; Thakur and others 2005).

Preaeration, or prewhipping, is the practice of whipping the ice cream mix to incorporate air and begin destabilizing the fat before the mix is frozen (Marshall and others 2003). Preaeration reportedly gives a slightly smaller air bubble size and improves perceptions of creaminess and smoothness (Burmester and others 2005). Smaller air cells pack more tightly, which leaves smaller spaces between bubbles for ice to grow in, and the ice crystals, consequently, are smaller in size (Barfod 2001). Smaller air bubble size, in addition to small ice crystal size, can function as a fat replacer (Tharp 1997). A recent study (Kusumaatmaja 2009), however, found little correlation between pre-aeration and ice crystal size or air cell size. Air cell size likely did not decrease
significantly with preaeration due to relatively low shear before the mix was frozen compared to the higher shear experienced inside the freezer barrel. The fact that air cell size did not change with preaeration was likely why ice crystal size did not change either (Kusumaatmaja 2009). Also, without the ice crystals present to provide viscosity and stability to the ice cream structure, air bubbles are prone to coalescence, reducing the impact of preaeration (Windhab and Wildmoser 2002).

An emerging technology in ice cream that has yet to be fully developed is the use of ultrasonic waves to decrease ice crystal size (Zheng and Sun 2006). High intensity ultrasound causes cavitation-negative acoustic pressure causing the liquid to fracture and form bubbles-and microstreaming-vigorous circulation of the cavitation bubbles through the fluid causing eddies. Cavitation can help increase nucleation and help prevent ice encrustation on the wall, and microstreaming can improve heat and mass transfer. The acoustic stress also causes ice crystals to fracture, creating smaller crystals. It was suggested that ultrasound could be applied to ice cream production by attaching a transducer coupling to the external surface of the SSF barrel (Zheng and Sun 2006).

## Conclusions

The final structure and sensory properties of ice cream are a function of many different processing and formulation variables that tend to be a complex function of one another. Ice cream companies today already are able to produce high-quality ice cream. However, with the ongoing quest to make products healthier, longer-lasting, cheaper, and/or of higher quality, understanding the effects of the numerous variables and their interactions helps both scientists and engineers. This understanding allows scientists to better predict the effects of processing and formulation changes and allows engineers to optimize plans and to make improved assumptions in models.

Existing research has made great strides in elucidating the mechanisms of ice crystallization in the ice cream freezer, though more research is still needed to obtain the definitive model. The vast majority of research has looked at ice crystallization in model solutions in model systems. Ideally, scientists will one day be able to piece together how ice forms in ice cream mix in its actual system.

## Nomenclature

| Roman letters |  |
| :---: | :---: |
| $C=$ Concentration, g solute/g solution; $C_{g}^{\prime}$, maximum freeze concentration |  |
|  | $n=$ Variable parameter, dimensionles |
| $r=$ Radius, $\mathrm{m} ; \bar{r}$, average radius; $\bar{r}_{0}$, initial average radius |  |
| $R=$ Recrystallization rate, $\mathrm{m} / \mathrm{s}^{1 / n}$ |  |
| $t=$ Time, s |  |
| Temperature, $\mathrm{K} ; \mathrm{T}_{\mathrm{g}}$, glass transition temperature; $T_{g}^{\prime}$, glass transition temperature at maximum freeze concentration; $T_{m}^{\prime}$, onset of melting at maximum freeze concentration; $T_{\infty}$, temperature at infinite radius |  |
| Greek letters |  |
| $\Delta H_{\text {fus }}=$ Latent heat of crystallization, $\mathrm{J} / \mathrm{kg}$ <br> $\Delta T^{\prime}=$ Freezing point depression, K |  |
| $\rho_{\mathrm{s}}=$ Crystal density, $\mathrm{kg} / \mathrm{m}^{3}$ |  |
| $\begin{aligned} & \sigma=\begin{array}{l} \text { Interfacial tension (surface free energy per unit } \\ \text { area), } \mathrm{J} / \mathrm{m}^{2} \text { or } \mathrm{N} / \mathrm{m} \end{array} \end{aligned}$ |  |
|  | $\tau=$ Variable parameter, $\mathrm{s} / \mathrm{m}^{n}$ |

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