The solidification of a disk-shaped crystal from a weakly supercooled binary melt

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Thermodynamic considerations of the solidification of a supercooled aqueous salt solution suggest that the growth of an ice crystal in the basal plane is limited by the diffusive removal of the latent heat of solidification from the solid–liquid interface, while it is limited by attachment kinetics in the perpendicular direction. This leads to the formation of approximately disk-shaped crystals with a low aspect ratio of thickness compared to radius, because radial growth is much faster than axial growth. We model how fast disk-shaped crystals grow in both pure and binary melts, accounting for the comparatively slow axial growth, the effect of dissolved solute in the fluid phase and the difference in thermal properties between solid and fluid phases. Our calculations of diffusive heat and salt transfer demonstrate that certain previous parameterizations, based on scaling arguments, substantially underestimate crystal growth rates by a factor of order 10-100 for low aspect ratio disks. We determine numerically this effect of crystal geometry on heat and salt transfer, and provide a parameterization for use in models of ice crystal growth in environmental settings.

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I. INTRODUCTION

Ice is a particularly rich example of crystallization, with a wide range of crystal shapes formed depending on the environmental conditions [1]. It is also environmentally significant: it forms from the vapour phase in clouds, leading to snow and sleet, and from the liquid phase in rivers and oceans. We study so-called frazil-ice formation from the liquid phase in the environmentally relevant limit of weak supercooling, because this has received comparatively little attention [2]. It also has key applications, both in industrial settings where frazil ice can block the water inlets from rivers and lakes [3], and in geophysical settings where frazil ice forms under floating ice shelves and in open areas of the polar oceans called leads and polynyas [4].

Frazil ice consists of individual crystals as a particular suspension in a supercooled liquid from which the ice grows. This liquid could be freshwater, such as when frazil forms in rivers, or saltwater, such as when frazil forms in the ocean. We study crystal growth from a binary alloy as a simple proxy for saltwater. Crystal growth from a binary alloy has been studied in a variety of geometries, most extensively for spherical and axially-symmetric cylindrical crystals, where morphological instability leading to dendritic growth has been shown to be significant [5, 6].

Crystallization is often an inherently anisotropic process, and macroscopic anisotropy can arise from crystalline anisotropy. Anisotropic surface energy is responsible for the so-called ‘equilibrium Wulff shape’ and anisotropic kinetic attachment is responsible for the ‘kinetic Wulff shape,’ as reviewed by Sekerka [7]. Our focus here is on solidification controlled by the long range diffusive transport of heat and salt, and how this couples with anisotropic kinetic attachment in determining bulk crystal growth from the melt. Frazil ice appears to form axisymmetric disk-shaped crystals, at least for fairly weak supercooling. Slow attachment kinetics limit growth perpendicular to the basal plane of the crystal while growth in the basal plane is limited by diffusion [2, 8].

Previous studies make various approximations in order to determine the growth rate of a disk-shaped crystal in a pure melt. Some proceed by the well known ‘electrostatic analogy’ between ice growth limited by thermal diffusion and electrostatic capacitance [9]. To give an example, Mason [10] uses this method to estimate the mass growth rate of a disk from the vapour phase. In this analogy, temperature is analogous to electrostatic potential, and the crystal growth rate is proportional to the capacitance of a perfect conductor, the surface of which will have a constant potential. Thus, knowing the capacitance of a thin disk and assuming its thickness evolves slowly, the radial growth rate can be estimated. The analogy assumes that the disk is perfectly conducting and infinitesimally thin. We will therefore assess whether the limits of perfectly conducting and infinitely thin can be taken independently.

Other studies note that growth controlled by the diffusive removal of latent heat depends on the ratio of the rate of latent heat release to the rate of thermal transfer away from the interface [8, 11]. These rates can in principle be estimated to within an undetermined dimensionless prefactor using scaling analysis. The success of a scaling approach relies on identifying the most appropriate physical scales.

A more detailed study was made by Fujioka and Sekerka [12], who make the mathematical simplification of assuming that the material properties of the phases are equal and that the growth was purely radial. The authors

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found a separable solution for the temperature field subject to diffusive heat transfer. This model has been used by Yokoyama et al. [13] to explain the experimental observations of Shimada and Furukawa [14] of the growth and stability of ice crystals from a pure melt. The assumption of equal properties of the phases is not entirely accurate for the ice–water system, but might only be expected to make a quantitative difference to the heat transfer, rather than changing the qualitative behaviour. The main limitations, for our purposes, are that their separable solution does not generalize to the combined heat and salt transport problem for growth in a binary alloy, nor does it account for slow axial growth, or differences in thermal properties between solid and liquid. These generalizations break the separable nature of the problem and necessitate a numerical solution of the underlying equations.

In this paper, we first consider the effect of the geometric shape of the crystals by considering the growth of disk-shaped crystals in a pure melt (section II). We then consider the effect of axial growth (section III) and the effect of salt by considering a binary alloy (section IV). Finally, we discuss the implications of our results (section V).

II. GROWTH INTO A PURE MELT

A. Governing equations

We first introduce the equations and boundary conditions that determine the growth of an isolated crystal into a pure melt. Consider an isolated axisymmetric disk-shaped crystal, as shown in figure 1, of radius \( R \) and half-thickness \( H \), such that the aspect ratio \( h = H/R \), which we expect to be small. To aid progress with modelling, we make the simplifying assumption that crystal growth maintains the disk like geometry with uniform growth rates across each individual crystal face. The realism of this approximation is discussed later. We introduce cylindrical polar coordinates \((r, \phi, z)\), where the \( z \)-axis is perpendicular to the basal plane and the origin is the centre of the crystal. The temperature \( T \) obeys the heat equation

\[
\rho c_s \frac{\partial T}{\partial t} = k_s \nabla^2 T, \quad x \in D, \quad (1)
\]

\[
\rho c_l \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = k_l \nabla^2 T, \quad x \not\in D, \quad (2)
\]

where \( D \) denotes the disk-shaped crystal. The density \( \rho \), specific heat capacity \( c \), and thermal conductivity \( k \) take constant values in each phase, whether solid (subscript \( s \)) or liquid (subscript \( l \)), \( u \) is the fluid velocity, and \( t \) is time. The thermal diffusivity \( \kappa = k/\rho c \). We assume that \( T \) approaches a uniform temperature \( T_\infty \) far from the crystal.

We impose a regularity condition at \( r = 0 \) and a symmetry boundary condition at the mid-plane of the disk \( z = 0 \) so that we may restrict attention to \( z \geq 0 \). At the boundary \( \partial D \) of the disk, suitable boundary conditions result from heat conservation and a kinetic condition of thermodynamic disequilibrium, respectively

\[
\rho_s L V_{\text{dim}} = \left[ k \frac{\partial T}{\partial n} \right]_f, \quad x \in \partial D, \quad (3)
\]

\[
V_{\text{dim}} = G(n)(T_m - T_i), \quad x \in \partial D. \quad (4)
\]

The temperature is continuous across the interface and equals \( T_i \). A discontinuity in the heat flux at the interface is associated with the latent heat of fusion \( L \) associated with crystal growth at a velocity \( V_{\text{dim}} \) normal to the interface. Our assumption that the normal growth is uniform across each crystal face is consistent with the simplifying assumption that the crystal remains disk-shaped.

In the second equation, we use a simple linear relationship to describe the role of attachment kinetics, where \( G(n) \) represents the kinetic undercooling and depends on the normal direction \( n \) of the interface. The exact form used is not crucial in what follows in this section where we consider the limit of negligible axial growth, but does impact predictions of weak axial growth in section III.

B. Reduced, non-dimensional model equations for purely radial growth

We make a quasi-steady approximation in which we neglect the explicit time-dependence of the problem in the heat equations (1, 2), and justify this approximation a posteriori in section II E. We neglect externally driven fluid flow, and note that the flow driven by any density difference between the phases can be neglected consistently with our quasi-steady approximation, so \( u = 0 \). We non-dimensionalize lengths with respect to the instantaneous disk radius \( R \), time with the thermal diffusion timescale in the liquid \( R^2/\kappa_l \), and velocities with \( \kappa_l/R \). We define a dimensionless temperature \( \theta = (T - T_\infty)/\Delta T_\infty \), where the supercooling is \( \Delta T_\infty = T_m - T_\infty \).

\[
\frac{\partial T}{\partial t} + u \cdot \nabla T = \kappa \nabla^2 T, \quad x \in D, \quad (1)
\]

\[
\frac{\partial T}{\partial t} + u \cdot \nabla T = \kappa \nabla^2 T, \quad x \not\in D, \quad (2)
\]
Growth is much slower in the direction perpendicular to the crystal basal plane because it is kinetically unfavourable. Thus we introduce anisotropy into the model in a simple limiting form by taking \( G = 0 \) at the top of the crystal \( z = h \) and \( G \to \infty \) at the edge \( r = 1 \). This is a type of faceted crystal growth: the top of the crystal is a singular interface and the edge a vicinal interface, and our formulation of the anisotropic attachment kinetics is equivalent to that of Chernov \([15]\). This leaves the temperature \( T_i \) at \( z = h \) unconstrained, so it can depart from the melting temperature \( T_m \). We consider the effect of slow axial growth \( G > 0 \) later in section III. The simplified boundary conditions are

\[
\frac{\partial \theta}{\partial z}_{z=h^-} = \frac{\partial \theta}{\partial z}_{z=h^+}, \tag{5}
\]

on the top the crystal \((0 \leq r \leq 1)\), and

\[
SV = \frac{\partial \theta}{\partial r}_{r=1^-} - \frac{\partial \theta}{\partial r}_{r=1^+}, \tag{6}
\]

\[
1 = \theta|_{r=1^+}, \tag{7}
\]

don the edge \((0 \leq z \leq h)\).

In this quasi-steady limit, there are only three dimensionless parameters in the problem: the aspect ratio \( h \), the conductivity ratio \( \kappa = k_s/k_l \) and the Stefan number

\[
S = \frac{\rho_s L}{\rho_v c_l \Delta T_\infty}. \tag{8}
\]

Thus the problem reduces to solving Laplace’s equation \( \nabla^2 \theta = 0 \) in the whole domain including the disk subject to the boundary conditions (5–7). Note that \( V \) is determined implicitly as part of the solution. In particular, we calculate a rescaled growth rate

\[
f(h, \kappa) = SV h, \tag{9}
\]

which is a function of the aspect ratio \( h \) and conductivity ratio \( \kappa \) alone. Given that \( R = 1 \) in our nondimensionalization, \( f \) is proportional to the growth rate multiplied by the area of the growing surface.

The boundary conditions contain a subtlety in that equations (6) and (7) are formally inconsistent. This is evident upon studying solutions to Laplace’s equation near the ‘corner’ between the top and edge of the disk [cf. 16]. The inconsistency arises from the simplifying assumption that the crystal remains perfectly disk shaped. In reality, we might expect the crystal shape to evolve via non-uniform growth rates and the regularising impact of surface energy described by the Gibbs-Thomson effect [e.g. 17], with the freezing temperature modified by curvature generated near the ‘corner’ over a length comparable to the capillary length scale. Because our primary interest is in leading order scalings for the macroscopic relief of supercooling and the volumetric rate of ice growth, rather than the detailed microstructure of the crystal edges, we simplify the analysis and neglect these deviations from disk-shaped geometry. We follow Fujioka and Sekerka [12], imposing (6) on \( 0 \leq z \leq h \) but only imposing (7) at \( z = 0 \). We will see later that the dominant thermal gradients driving ice growth scale with the crystal radius \( R \) rather than the disk half-thickness \( H \), and thus we expect the detailed geometry near the disk edges to have a relatively small influence on macroscopic ice growth rates for thin discs with \( h = H/R \ll 1 \). We have also tested the converse approach of applying equation (7) on \( 0 \leq z \leq h \) but only imposing (6) in an integral sense. The difference is negligible for \( h \ll 1 \). We discuss our numerical method in appendix A, and show a typical solution in figure 2.

### C. Comparison with previous models

The function \( f \) represents a crystal growth rate scaled with the Stefan number. To aid comparison, we define equivalent growth rate functions below based on previous published models.

The electrostatic analogy model of Mason [10] gives

\[
f_M = \frac{2}{\pi}. \tag{10}
\]

This is consistent with our function \( f(h, \kappa) \to 2/\pi \) as \( \kappa \to \infty \). Note that the Mason model has no dependence on aspect ratio.

A commonly applied scaling argument of Daly [8], gives

\[
f_D = h \sqrt{2/(1 + 2h)} \sim h \sqrt{2}, \tag{11}
\]

as \( h \to 0 \), which has a strong dependence on aspect ratio and predicts much smaller growth for thin disks than the Mason model.
numerical results for previous models in figure 3. Note that our benchmarked algorithm dependence on aspect ratio. This implies that the growth rate has only a weak, logarithmic dependence on aspect ratio. The red horizontal dashed line shows the Mason [10] model, the solid curve shows the Fujioka and Sekerka [12] model and the much lower dot-dashed curve shows the Daly [8] model.

For equal thermal conductivities ($\kappa = 1$), the model of Fujioka and Sekerka [12] gives

$$f_{FS} = \frac{\pi h}{q_0(h)},$$

(12)

where

$$q_0(h) = 2 \int_0^\infty \frac{\sin(hx)}{x} I_0(x)K_0(x) \, dx,$$

$$\sim h \left[ 1 + 3 \ln(2) - \ln(h) \right],$$

(13)

as $h \to 0$, is the toroidal integral of order zero in which $I_0$ and $K_0$ are the modified Bessel functions of order zero. This implies that the growth rate has only a weak, logarithmic dependence on aspect ratio.

We present our own findings in comparison to these previous models in figure 3. Note that our benchmarked numerical results for $\kappa = 1$ agree with Fujioka and Sekerka [12], and seem to approach the scaling of Mason [10] at high $\kappa$. Crucially, there is a significant difference compared to the scaling of Daly [8]. This is strongly linked to structure of the heat transport, a significant proportion of which occurs through the flat top and base of the disk. An example of the corresponding temperature field is shown in figure 2. We return to this issue in section V C. We give approximate fits to our numerical calculations for practical use in appendix B.

D. Dependence on thermal conductivity ratio

Interestingly, even quite large changes in the thermal conductivity ratio have only a modest effect on the radial growth of crystals, with $f(h, \kappa)$ changing by less than factor of 2 as $\kappa$ varies over 3 orders of magnitude (figure 3). Whilst a higher solid phase conductivity transports latent heat away from the interface more efficiently, the heat flux through the solid depends on the product $h\kappa$, which is typically small, and the heat must in any case be transported away from the disk. The Mason [10] model corresponds to large $h\kappa$, and so represents a limit which is inappropriate for frazil-ice growth in the ocean, but much more appropriate for ice formation in clouds (its original purpose) because ice is very much more thermally conductive than air. Calculations at very high values of $\kappa$, shown in figure 4, demonstrate that the Mason [10] model does indeed obtain the correct limiting behaviour, provided $h\kappa \geq O(1)$.

E. Validity of the quasi-steady approximation

The quasi-steady approximation is generally taken to hold provided the Stefan number $S \gg 1$ [5]. However, while the standard requirement is appropriate for the growth of a spherical crystal, it must modified for the growth of a disk crystal. In particular, we may neglect the explicit time dependence in equation (2) if $V \ll 1$. Thus using equation (9) we firstly require $Sh \gg 1$, given that $f = O(1)$ throughout the parameter range of interest. This is another reminder of the differences that arise from the geometry of crystal growth. Second, the dimensionless flow induced by density differences between the phases is negligible provided $S \rho_1/(\rho_1 - \rho_3) \gg 1$, because the induced flow is proportional to solidification rate and the density difference. Third, we may neglect the time dependence in the heat equation for the solid phase (1).
provided $ShR/κ_1 ≫ 1$. For ice–water disk crystals, these latter requirements are satisfied provided the first is satisfied.

III. NON-ZERO AXIAL GROWTH

In the previous section, we introduced an extreme form of anisotropy into the model by requiring that the disk remained at constant thickness through imposing a kinetic attachment coefficient $G = 0$ on the top of the disk. In our non-dimensionalization of equations (3) and (4), the dimensionless kinetic coefficient is

$$G = G\rho_s LR/κ_1,$$

where $G$ is the dimensional kinetic coefficient. Thus as the crystal radius increases $G$ may become $O(1)$. Note also that $G$ is independent of the supercooling $∆T$.

We investigate the potential effect of axial growth by allowing $G > 0$ in directions perpendicular to the basal plane, and define a rescaled axial growth rate $f_2(h, k, G) = SW$, where $W$ is the uniform dimensionless growth rate of the top of the disk. The function $f_2$ is proportional to the product of the growth rate and the growing surface area. The kinetic undercooling law (4) is applied in a radially averaged sense, and our numerical method is discussed in appendix A. The latent heat release associated with axial growth also affects the radial growth, and so the rescaled radial growth function $f_1(h, k, G) = SVh$ depends on $G$. Note that $f_1(h, k, 0) = f(h, k)$ as defined previously. In this section, we illustrate results relevant to frazil-ice formation from liquid water, so fix $k = 4$ and investigate the dependence on aspect ratio and kinetic coefficient.

Firstly, axial growth inhibits radial growth. Thus $f_1$ decreases as $G$ increases across the whole parameter space (figure 5a). Axial growth releases latent heat, which increases the temperature of the top of the disk and so reduces conduction through the disk interior away from the radially growing edge of the disk. This is especially significant because the disk is a good thermal conductor and a significant fraction of the removal of latent heat for solidification at the disk edges occurs via transport through the solid disk interior.

Secondly, axial growth increases with $G$, and this effect is stronger at moderate aspect ratios $G ≲ 10$ (figure 5b). However, this observation depends on the choice of rescaling for $f_2$. To eliminate this dependence, we investigate the rate of change of aspect ratio. Using our quasi-steady predictions of heat transfer to predict instantaneous growth rates $V$ and $W$ for given values of $R$ and $H$, we derive a simple autonomous system for the kinetic coefficient $G$ and the aspect ratio $h = H/R$,

$$\dot{G} = Gf_1/h,$$

$$\dot{h} = f_2 - f_1,$$

where a dot represents a derivative with respect to the slow timescale $τ = t/S$. In figure 5(c), we highlight the critical curve $\dot{G} = G_c(h, k)$ on which the aspect ratio is constant ($h = 0$). Throughout we take $k = 4$. Note that the changes in the gradient of $f_2$ at relatively large values of $h$ are well resolved features that do not occur in the case $k = 1$.

FIG. 5. Contours of: (a) the radial growth rate $f_1$, (b) the axial growth rate $f_2$, and (c) the rate of change in aspect ratio, $\dot{h}$. In the latter, we highlight the critical curve $\dot{G} = G_c(h, k)$ on which the aspect ratio is constant ($h = 0$). Throughout we take $k = 4$. Note that the changes in the gradient of $f_2$ at relatively large values of $h$ are well resolved features that do not occur in the case $k = 1$. 


ence between $\mathcal{G} = 0$ and $\mathcal{G} > 0$. When $\mathcal{G} = 0$, $\dot{h} < 0$ for all $h$ (the thickness is fixed but the radius increases so the aspect ratio decreases). However, when $\mathcal{G} > 0$, there is a critical aspect ratio below which $\dot{h} > 0$. This can be used to interpret crystal size evolution. Soon after a crystal nucleates, $\mathcal{G}$ will be small but the aspect ratio will be $O(1)$. As the crystal radius increases, the aspect ratio decreases towards the critical curve, but $\mathcal{G}$ will increase. Thus, at sufficiently late time, the aspect ratio will eventually start to increase. Some such trajectories are shown in figure 6. It is important to note that the timescale used in the non-dimensionalization is proportional to $R^2$ and so the evolution of a crystal in phase space slows down as the crystal radius $R$ increases.

The autonomous system of equations (15–16) significantly simplifies the parameter space. For example, we have scaled out the dependence on supercooling, which is hard to hold constant experimentally. Thus this is a potentially powerful way to interpret experimental data by plotting time series of experimental observations in this parameter space. Observing a minimum aspect ratio and the radius at this aspect ratio could be used to infer the dimensional kinetic coefficient $\mathcal{G}$. We show a phase portrait of this autonomous system in figure 6.

Numerically, we observe that the critical curve, $\mathcal{G} = \mathcal{G}_c(h, k)$, on which $\dot{h} = 0$, approaches zero as $h \to 0$. In the particular case $k = 1$, we can average the solution (equation 7a) of Fujioka and Sekerka [12] over the surface of the disk, to show that

$$\mathcal{G}_c \sim \frac{\pi}{\log(h^{-1}) - 3(1 - \log 2)}.$$  

(17)

Convergence is exponentially slow as $h \to 0$, but this nevertheless illustrates the important result that $\mathcal{G}_c \to 0$ as $h \to 0$, which affects the range of possible trajectories in phase space.

IV. COMBINED HEAT AND SALT TRANSFER

Crystal growth in a supercooled binary alloy is affected by the presence of solute through two related physical mechanisms. Firstly, it reduces the overall driving temperature difference between the interfacial temperature (which is reduced in the presence of solute) and the far-field temperature. Secondly, the ice-crystal growth rejects solute, which can build up at the interface, so further inhibiting growth. We here focus on their impacts on disk shaped crystal growth, noting that in certain circumstances these effects may also promote morphological instability. We return to the latter possibility in the concluding discussion.

A. Extended problem formulation

We extend our method by additionally solving for the solute concentration field $C$ outside the disk, assuming that the concentration inside the disk $C_i$ is constant because diffusion of salt through the solid phase is slow relative to diffusion through the liquid phase. We outline the method more briefly. The main difference is that we require a condition relating the interfacial temperature $T_i$ to the concentration $C_i$ at the interface to couple the heat and salt problems. Thus on the growing edge we impose

$$T_i = T_L(C_i) \equiv T_m - m(C_i - C_s),$$  

(18)

where $m$ is the gradient of the (assumed linear) liquidus relationship $T_L(C)$ and $T_m = T_L(C_s)$ is the melting temperature of solid with concentration $C_s$. We assume $C$ approaches a uniform concentration $C_\infty$ far from the crystal.

We use a dimensionless concentration $\Theta = (C - C_\infty)/\Delta C_\infty$, where $\Delta C_\infty = C_i - C_\infty$. Note that the non-dimensionalization involves $C_i$, which must be determined as part of the solution. In the coupled problem we redefine $\theta = (T - T_\infty)/(T_i - T_\infty)$ and $S = \rho_i L/\rho c_i (T_i - T_\infty)$, which depend on $(C_i - C_s)$ through the liquidus relationship (18). We define $C = C_i - C_s)/C_i - C_\infty$ which is the compositional analogue of the Stefan number and again must be large for the quasi-steady approximation to hold (section II E). Note that the thermal problem takes the same form as before, but with $S = S(C)$.

Thus we must additionally solve $\nabla^2 \Theta = 0$ outside the disk subject to the following boundary conditions, which are analogous to equations (5–7),

$$\frac{\partial \Theta}{\partial z} \bigg|_{z = h^+} = 0,$$  

(19)
on the top of the disk \((0 \leq r \leq 1)\) where we set \(G = 0\), and

\[
Le CV = -\frac{\partial \Theta}{\partial r} \bigg|_{r=1+}, \tag{20}
\]

\[
\Theta_{r=1+} = 1, \tag{21}
\]
on the growing edge \((0 \leq z \leq h)\). As before, equation (21) is only applied at \(z = 0\). The Lewis number,

\[
Le = \frac{\kappa_l}{D_t}, \tag{22}
\]
is the ratio of diffusivity of heat \(\kappa_l\) to solute \(D_t\) in the liquid phase.

We calculate a rescaled growth rate \(g(h) = LeCVh\) for the salt diffusion problem (shown in figure 7), and eliminate \(V\) using (9) from the thermal problem to obtain

\[
LeC = \frac{g(h)}{f(h, k)} S(C), \tag{23}
\]

### B. Results

There are three independent temperature scales in the problem

\[
\Delta T_\infty = T_m - T_\infty, \quad \Delta T_L = \rho s L / \rho c_t, \quad \Delta T_C = m (C_\infty - C_s). \tag{24}
\]
The remaining parameters only appear in the group \(g(h)/f(h, k)Le\). In order to group separately what might be considered material and geometry-dependent parameters versus experimental parameters, we define

\[
\hat{S} = \frac{\Delta T_L}{\Delta T_C Le f(h, k)} \frac{g(h)}{1 + \hat{S}}, \tag{25}
\]
representing the importance as the crystal grows of the diffusive removal of the latent heat released during crystal growth to the diffusive removal of rejected solute and the resulting freezing point depression. When \(k = 4\), the ratio \(g(h)/f(h, k)\) shows only weak variation with \(h\), as shown in figure 7. Thus \(\hat{S}\) could reasonably be treated as a material constant during disk growth, to leading order.

We also define the dimensionless supercooling \(\alpha\) through

\[
\Delta T_\infty = \Delta T_C (1 + \alpha), \tag{26}
\]
where \(\alpha > 0\) ensures supercooling in the far-field. Indeed, there is supercooling everywhere in the liquid, and equilibrium is only achieved on the growing ice–liquid interface. This follows by applying the maximum principle to Laplace’s equation \(\nabla^2 [T - T_L(C)] = 0\), noting that the liquidus relation \(T_L(C)\) is linear. Using equations (24) and (25), to express equation (23) in terms of \(C\) yields a quadratic equation with solution

\[
C = 1 + \frac{1 + \hat{S} - \alpha + \sqrt{(1 + \hat{S} - \alpha)^2 + 4\alpha}}{2\alpha}, \tag{27}
\]

where we take the positive square root since \(C > 1\) from the definition. Note that we actually require \(C \gg 1\) for the quasi-stationary approximation to hold, consistent with \(\alpha \ll 1\).

To gain insight into the impact of solute on the growth rate, we investigate the factor \(V\) by which salt modifies crystal growth relative to growth into a pure melt with supercooling adjusted for the salt

\[
V = \frac{V}{(f(h, k)/h) \cdot (T_L(C_\infty) - T_\infty) / \Delta T_L} = \frac{\hat{S}}{\alpha C}. \tag{28}
\]

In the physically relevant limit of small supercooling \(\alpha \to 0\),

\[
V \sim \frac{\hat{S}}{1 + \hat{S}} - \alpha \frac{\hat{S}}{(1 + \hat{S})^2} + \alpha \frac{\hat{S}(1 - \hat{S})}{(1 + \hat{S})^3} + O(\alpha^3). \tag{29}
\]

We can subsequently take limits of the leading order term for small and large \(\hat{S}\):

\[
V \sim \hat{S} \quad (\hat{S} \to 0), \tag{30}
\]
\[
V \sim 1 \quad (\hat{S} \to \infty),
\]

which we interpret in the discussion below.

### V. DISCUSSION AND CONCLUSIONS

We now apply the theoretical results from the preceding sections to infer physical consequences for predictions of crystal growth, and evaluate some previous more approximate parameterisations.
A. Dimensional results for purely radial growth

The purely radial growth rate of a disk-shaped crystal into a pure melt, in dimensional terms, is

\[ V_{\text{dim.}} = \frac{1}{H} \frac{k_l \Delta T_{\infty}}{\rho_s L} f(h, k) \]  

(31)

For a binary alloy, we recover the pure melt case in the limit of large \( \tilde{S} \) (equation 30) with an adjusted driving temperature difference \( \Delta T_{\infty} = T_L (C_{\infty}) - T_{\infty} \), so

\[ V_{\text{dim.}} \approx \frac{1}{H} \frac{k_l \Delta T_{\infty}}{\rho_s L} f(h, \tilde{k}) \]  

(32)

This means that if the dimensionless group \( \tilde{S} \) is sufficiently large, a good modelling assumption is to use formulae appropriate to a pure melt but adjust the freezing temperature when calculating supercooling to account for the solute impurity. Growth is controlled by the diffusive removal of the latent heat released during solidification. However, for small \( \tilde{S} \) (equation 29) we find

\[ V_{\text{dim.}} \approx \frac{1}{H} \frac{D_l \Delta T_{\infty}}{\Delta T_C} g(h) = \frac{1}{H} D_l \log(h), \]

(33)

which means that growth is no longer controlled by the thermal diffusion of latent heat released at the interface but rather by the slow diffusion of solute rejected there.

B. A simple way to account for the presence of salt

Salt is significant to frazil ice growth in the ocean. To see this, we estimate typical values \( \Delta T_L = 80^\circ \text{C} \), \( \Delta T_C = 2^\circ \text{C} \), and \( Le = 200 \) to 1 significant figure, using material properties estimated at 0°C, ocean water of salinity \( C_{\infty} = 35 \text{ g kg}^{-1} \) and pure ice with \( C_s \approx 0 \). Thus \( \tilde{S} \approx 0.16 \) which is an intermediate case with \( \tilde{S} \lesssim O(1) \), but rather closer to the limit dominated by solute rejection. Thus both the dependence of freezing temperature on salinity and solute rejection are important, and significant errors result from neglecting either. There is large error in assuming that growth is controlled by the removal of released latent heat alone.

In larger scale models that parameterize frazil-ice growth, it is very common to adjust the freezing temperature with salinity, and some models also investigate the effect of salt rejection and diffusion. For example, Holland and Feltham [18] multiply the growth rate by 0.2 as a way of testing for the sensitivity to salt. Galton-Fenzi et al. [19], extending Holland and Jenkins [20], multiply their growth rate by a factor of \( 1/(1 + Le \Delta T_C/\Delta T_L) \) which is typically about 0.2. Now at small supercooling, equation (28) gives

\[ \frac{1}{V} \sim 1 + Le \frac{\Delta T_C}{\Delta T_L} f(h, k) g(h), \]

(34)

which is a similar expression since the ratio \( g(h)/f(h, k) \) is of order 1. Therefore, the approach of Galton-Fenzi et al. [19] is likely to capture correctly the leading order behaviour for the salinity dependence of growth, although using equation (34) with the numerical dependence on aspect ratio from equation (B4) could give slightly better results.

C. Growth rate of crystal mass and scaling analysis

An instructive way to express disk crystal growth when the crystal grows both radially and axially is in terms of growth rate of crystal mass. We write

\[ L \frac{dM}{dt} = A \frac{k_l \Delta T_{\infty}}{R} m(h, k, G), \]

(35)

where \( M \) is the mass of the crystal, \( A \) is the total surface area, and the effective total growth rate factor \( m = (2 f_1 + f_2)/(1 + 2h) = O(1) \), as shown in figure 8. As a crude simplification, it is possible to take \( m = 1 \). If the aspect ratio is small, \( A \approx 2\pi R^2 \), so a simple formula for frazil-ice growth in a pure melt is

\[ L \frac{dM}{dt} \approx 2\pi R k_l \Delta T_{\infty}, \]

(36)

which can also be modified for salt as discussed previously. To within a factor of \( 4/\pi \), equation (36) yields the same growth rate as equation (2) of Mason [10].

Equation (35) has a simple physical interpretation in terms of the scaling arguments introduced in section I. Firstly, heat transfer occurs across the whole surface area \( A \). For example, even when only the edges of the disk are growing, there is still a key contribution to the removal of latent heat from conduction through the solid from the growing edge and escaping through the crystal faces. Indeed the transfer through the faces dominates when \( k h \gg 1 \). Secondly, the length scale of the thermal
boundary layer scales with the radius of the crystal, not its thickness (see figure 2), since \( k_l \Delta T_{\infty} / R \) is a heat flux.

In our opinion, the implications of the work of Fujioka and Sekerka [12] have not been fully appreciated, because these scales could have been inferred from their mathematical model. We have extended their work to investigate the effect of axial growth, different conductivity ratios, and salt. Many papers incorrectly estimate these scales controlling crystal growth. In some papers, for example [11, 18, 19, 21, 22], \( A \sim 4\pi R H \) is taken to be the area of the edge of the crystal rather than the total surface area, whilst the thermal boundary layer is correctly assumed to have thickness proportional to \( R \). The resulting heat transfer thereby significantly underestimates crystal growth by a factor between 10 and 100. Alternatively, in other earlier papers, for example [23], the correct order of magnitude for the growth rate is obtained by erroneously using the area of the crystal edge \( A \sim 4\pi R H \) combined with a thermal boundary layer thickness proportional to \( H \), two errors in the derivation that cancelled to produce the correct order of magnitude for the final result. Moreover, in models that use a distribution of crystal sizes following [21], our results suggest that there has been an underestimation of evolution towards the larger crystal sizes, an area of research we are actively pursuing.

D. Implications and limitations

We have identified order of magnitude errors in predictions of ice growth, or equivalently the timescale over which the initial supercooling of a melt is relieved. While all of this analysis is confined to diffusive growth, much carries through relatively straightforwardly to the case of relatively weak turbulence [24]. That the boundary layer scales like the crystal radius means that discs of radius comparable to the Kolmogorov length will have a slightly enhanced growth rate compared to the purely diffusive prediction. It is therefore important to characterize correctly the diffusive growth of crystals, and our calculations have rationalized this process and allowed us to test the assumptions inherent in models of frazil-ice dynamics. Our methodology can account for axial growth as well as radial growth. The weak dependence of growth rate on aspect ratio is likely to be important in more detailed models of frazil-ice dynamics that account for evolution in crystal-size distribution [21].

The assumption of small supercooling has entered this analysis at a number of stages. The quasi-steady approximation requires that the supercooling is small compared to \( \Delta T_{\infty} \approx 80^\circ \text{C} \) for growth from pure water, and, for the case of ocean water of salinity \( C_{\infty} = 35 \text{ g kg}^{-1} \), the supercooling must be small compared to \( \Delta T_{\infty} \approx 2^\circ \text{C} \). Another assumption regarding morphological stability is more subtle. Experimental observations and stability analyses [13, 14] suggest that disk-shaped crystals are morphologically stable provided the thickness is less than about 100 times greater than the nucleation radius, which is inversely proportional to the supercooling. The supercooling in the ocean is typically rather small (for example, the largest supercooling recorded by Skogseth et al. [25] in an Arctic polynya was 0.037°C), and so our assumption to neglect morphological instability appears to be appropriate for frazil ice in the ocean. For stronger supercooling, a range of crystal morphologies occur and a more complex study of heat transfer is required.

The long range, diffusive transport of heat and salt plays an important role in the solidification of disk-shaped crystals from a binary melt. We have identified the physical scales that determine the bulk growth rate. We used a simple, thermodynamically motivated, anisotropic kinetic coefficient consistent with a disk-shaped morphology, and neglected anisotropic surface energy. In doing so we provided a complementary perspective on crystal growth to that of ‘kinetic Wulff shapes,’ which allowed us to highlight the importance of diffusion to the formation of frazil ice in oceans and rivers.

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Appendix A: Numerical method

We adopt a straightforward numerical method. We solve the axisymmetric form of Laplace’s equation in \((r,z)\) space using a Finite-Element-Method with adaptive meshing, which concentrates the mesh near the disk corner, where most resolution is needed. We used the MATLAB Partial Differential Equation Toolbox. We use linear basis functions on triangular elements. We truncate our domain at spherical radius \( \hat{r} = \hat{R} \), following the method of Bayliss et al. [26]. Setting \( \theta = 0 \) on this outer boundary gives an \( O(1/\hat{R}) \) error. Thus, motivated by the well-known multipole expansion for far-field behaviour of the solutions of Laplace’s equation, we instead set

\[
\frac{\partial \theta}{\partial \hat{r}} + \frac{\theta}{\hat{r}} = 0. \quad (\hat{r} = \hat{R})
\]  

(A1)

This has an \( O(1/\hat{R}^2) \) error.

In order to implement the jump boundary condition equation (6), we introduce a notch of thickness \( \epsilon \) at the growing edge of the disk, in which we impose a volumetric heat source. The notch becomes a line source in the limit \( \epsilon \to 0 \). We investigated the dependence of \( f(h,\hat{R}) \) and hence the growth rate on \( \epsilon \) and \( \hat{R} \). We ensure
we solve iteratively, using a Newton-Raphson method. Produces a nonlinearity into the system of equations, which introduces a notch. The crucial difference to the purely radial growth case is that equation (A3) introduces a nonlinearity into the system of equations, which we solve iteratively, using a Newton-Raphson method.

\[ SW = \left[ k \frac{\partial \theta}{\partial z} \right]_l, \quad (A2) \]

\[ W = 2G \int_0^1 (1 - \theta_i) r dr \quad (A3) \]

from equations (3) and (4). In equation (A3), we have averaged the supercooling over the face of the disk, consistent with our assumption that the crystal remains disk-shaped. We solve equation (A2) in the same way as (6), by introducing a notch. The crucial difference to the purely radial growth case is that equation (A3) introduces a nonlinearity into the system of equations, which we solve iteratively, using a Newton-Raphson method.

**Appendix B: Practical formulae derived from fits to numerical calculations**

Motivated by the asymptotic form of the toroidal integral (equation 13), we look for fits of the form \(1/(b - c \log(x))\), for \(b, c\) constant, to the numerically calculated results presented in figures 3 and 7. We obtain

\[ f(h, k = 1) \approx 1/(0.9675 - 0.3160 \log(h)), \quad (B1) \]

\[ f(h, k = 4) \approx 1/(0.9008 - 0.2634 \log(h)), \quad (B2) \]

\[ g(h) \approx 1/(1.100 - 0.4146 \log(h)). \quad (B3) \]

The absolute errors in these formulae are typically very small, and are entirely negligible compared to the modelling uncertainties. Depending on the range of \(h\) of interest, different formula can be obtained, but these are practical for \(10^{-3} < h < 1\).

For the ratio \(g(h)/f(h, k = 4)\) important to the combined heat and salt calculation, a very accurate formula is

\[ \frac{g(h)}{f(h, k = 4)} = \frac{0.9457h^2 + 2.775h + 18.08}{h^2 + 1.574h + 21.79}. \quad (B4) \]

A simpler alternative with slightly diminished accuracy is to use a constant value as mentioned in the main text, for example 0.73.