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ANOMALOUS GROWTH OF SINGLE CRYSTALS IN SOLUTION

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ABSTRACT

It is shown that major discrepancies exist between experiments and theory for ice crystal growth from solution. Accurate data, taken in a microgravity environment, approximate analytical models, and exact (probably numerical) models all are needed to advance our understanding of ice crystal growth phenomena.

A new approximate semi-empirical theory is presented which predicts that a relatively sharp transition from natural convection control to diffusion control for ice growth in pure water occurs at a subcooling of about 10°C (a reduced temperature difference of about 0.125). No reliable data exist to test this prediction. The theory also predicts qualitatively the growth of ice in NaCl solution in which maxima in the growth rates are observed at various levels of subcooling.

For pure water the exponent on the subcooling (n) predicted by Equation (11) when cast in the form of Equation (1) is 1.9 , which is in reasonable agreement with the experimental value.

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The purpose of the proposed single crystal ice growth experiment is to clarify the roles of thermal and concentration driven convection in crystal growth by measuring growth rates, crystal shape, and temperature and concentration fields in the neighborhood of the single crystal, in the microgravity environment of space, by using shadowgraphs, Schlieren and other optical techniques. It is expected that these data, taken in certain critical ranges of the operating parameters, will help to explain the more serious discrepancies which exist among the various theories of crystal growth and the best available data.

Ice crystal growth rates usually are represented by an equation of the form

$$v = a\Delta T^n \qquad (1)$$

where v is the growth velocity and ΔT is the subcooling. Ivantsov's theory predicts $n = 3$ for parabolic platelets. The best experimental values of n for growth in quiescent water are closer to 2.17. Recent experimental results of Barduhn and Kallungal (1977) have shown ice growth rates to depend on crystal orientation with respect to the gravitational field, and observed rates are an order of magnitude larger than Ivantsov's theory predicts.

Growth rates in the a-axis direction are controlled by heat and mass transfer; crystal formation kinetics play no part. Observed growth rates depend on the salt concentration of the solution and growth rate maxima are observed with about 1% salt solutions. All of this provides convincing evidence that thermal and concentration driven convection play a major role in the growth of ice crystals despite their small size. However, no adequate theory exists to describe these phenomena.

There are fundamental differences between the best data available on ice and succinonitrile and the theories of crystal growth which have been developed. The data of Barduhn and Kallungal (1977) for ice and those of Glicksman, Shaefer and Ayers (1976) for succinonitrile show that the tip radius, R, varies as the reciprocal of under cooling so that

$$R = A\Delta T^m \tag{2}$$

where $m \approx -1$. However the linear stability theory of Langer and Muller-Krumbhaar (1978) predicts a much larger negative value for m which is closer to -2. This is shown in Langer and Muller-Krumbhaar's Figure 4 which, being a log-log plot, tends to make the differences between theory and experiment less obvious. On the other hand the maximum velocity principle predicts $m = -1$, which is in accord with experimental data. Unfortunately the maximum velocity assumption significantly underestimates A.

The Langer-Krumbhaar theory predicts the tip velocity data of Glickman et al. better than the tip radius data with deviations tending to get larger as under cooling increases. This seems to illustrate that linear stability theory often is a useful guide, but seldom is a definitive statement on the quantitative behavior of real systems.

Fernandez and Barduhn (1967), Vlahakis and Barduhn (1974), Simpson et al. (1974), Kallungal and Barduhn (1977) and Huang (1975) have studied various aspects of ice crystal growth in forced convection systems with velocities up to 70 cm/sec. Equation (1) continues to apply here except $n = 3/2$ as predicted by Fernandez using boundary layer theory (and the maximum velocity principle) and observed experimentally provided the forced velocity is large enough. Equation (2) also applies to forced convection; as before m is observed and predicted to be -1. However the maximum velocity principle again predicts values of A which are too low by a factor of 3 or 4 for ice. The data show conclusively that tip radius is independent of forced flow velocity over six orders of magnitude; it also is independent of crystal orientation.

The data on ice growth in a quiescent ambient fluid clearly are influenced by natural convection as evidenced by their sensitivity to crystal orientation. No adequate theory, which includes thermal convection, has ever been proposed to describe ice crystal growth even in pure water and the situation is complicated markedly when the crystals are grown in saline solution. The difficulty of constructing an exact theory, in the

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sense of obtaining exact solutions of the transport equations, is illustrated by the interesting article of Kroeger and Ostrach (1974) on a model which simulates a casting problem and includes forced and natural convection.

Models which include exact solutions of the relevant transport equations are needed and should be worked on. However, in the meantime it may be possible to gain further insight into crystal growth, including thermal convection, by constructing approximate models which perhaps are viewed best as "order of magnitude estimates" of the real phenomena occurring. One such possible approximate approach, which appears to be new, and which includes both thermal convection and the moving boundary effect will be sketched here.

Consider for illustration a crystal growing as a parabolic platelet. A heat balance on the crystal, which will be assumed to be isothermal, gives

$$v = h \frac{T_i - T_\infty}{\rho_c L} = \text{Nu} \frac{k(T_i - T_\infty)}{R \rho_c L} \tag{3}$$

where Nu = Nusselt number $(\frac{hR}{k})$, k = thermal conductivity of the solution, L = latent heat of fusion, ρ_c = crystal density, T_i and T_∞ = interfacial and ambient temperatures of the fluid. From the Ivantsov theory, as discussed by Horvay and Cahn (1961), if $p << 1$, we find

$$p = \frac{vR}{2\alpha} \simeq [\frac{C_p (T_i - T_\infty)}{L \sqrt{\pi}}]^2 \tag{4}$$

where C_p = heat capacity of the melt and α = thermal diffusivity. Thus, if we assume density differences between the crystal and solution are small, Equations (3) and (4) lead to

$$\text{Nu} = \text{Nu}_{\text{M.B.}} \simeq \frac{2}{\pi} \frac{(T_i - T_\infty)}{L/C_p} \tag{5}$$

where the subscript M.B. denotes moving boundary and this Nusselt number reflects two dimensional heat conduction in the melt with the "apparent convection" created by a moving boundary.

Obviously (5) tells only part of the story; it neglects thermal convection entirely. For a parabolic platelet, even with a fixed boundary, it is a formidable job to solve the thermal convection problem with the two dimensional conduction which must be included in the low Rayleigh number (Ra) systems encountered in crystal growth. However, some information can be obtained very easily from the experimental results of Gebhart and Pera (1970) on heat transfer at low Ra from circular cylinders of very small diameter. These data should be relevant to ice growth if heat transfer at the stagnation point of the tip of the parabolic platelet does indeed control the growth process. The correspondence between Fernandez's forced convection theory, which employs the tip radius as the characteristic dimension, and the experimental growth rate data lends considerable credence to this assumption. One can show (for $Ra < 10^{-4}$) from Gebhart and Pera's data that the Nusselt number due to two dimensional conduction and natural convection is

$$Nu_{N.C.} \simeq 0.47\ Ra^{0.075} \qquad (6)$$

where

$$Ra = \frac{\beta g R^3 (T_i - T_\infty)}{\nu\alpha}$$

β = thermal conductivity, g = gravitational constant, ν = kinematic viscosity.

Equation (6) is very different from the conventional boundary layer result, $Nu_{N.C.} \simeq 0.5\ Ra^{1/4}$, which grossly underestimates heat transfer rates at very low Ra. If one uses the boundary layer approach, then an arbitrarily enlarged length scale is needed to obtain even qualitative agreement between theory and experiment.

Churchill (1977) in numerous papers has discussed the accuracy of combining rules for finding the Nusselt numbers for "mixed mode convection" among other things. Ruckenstein (1978) has provided a theoretical justification for Churchill's procedure. If we consider natural convection and the moving boundary as two processes competing for dominance, which seems plausible but doesn't seem to have been done before, Churchill's work would suggest that a reasonable approximation can be obtained from

$$Nu^3 = Nu^3_{M.B.} + Nu^3_{N.C.}$$

or

$$Nu = [Nu^3_{M.B.} + Nu^3_{N.C.}]^{1/3} \qquad (7)$$

Therefore, one obtains using (3), (5), (6), and (7),

$$v \simeq [(\frac{2}{\pi}\frac{\Delta T}{L/C_p})^3 + 0.10\ (\frac{\beta g R^3 \Delta T}{\nu\alpha})^{0.225}]^{1/3}\ \frac{k\Delta T}{RP_c L} \qquad (8)$$

where $\Delta T = T_i - T_\infty$. Obviously (8) cannot be viewed at this stage as anything more than a plausible speculation. However, Equation (8), and other expressions like it which can be derived in a similar fashion, deserve the effort of being compared with experimental data and perhaps modified accordingly.

It is worth noting that if $Nu_{M.B.} = 2Nu_{N.C.}$, then $Nu_{M.B.} \approx 0.96Nu$. Even if the factor is 1.25 rather than 2, one gets $Nu_{M.B.} \approx 0.87Nu$. That is, when either of the Nusselt numbers is larger than the other, the mode representing the larger one dominates the process. This can be used to determine the ΔT above which natural convection is negligible by setting $Nu_{M.B.} > Nu_{N.C.}$ and solving for ΔT to obtain $\Delta T \approx 10°C$. If we had used boundary layer theory, we would have obtained $\Delta T \approx 0.5°C$ which, on the basis of Kallungal's data, is too small. Unfortunately, reliable data for ΔT, equal to 10 or more, do not exist to check this prediction. It also is worth noting that $Nu_{N.C.}$, at the very low Ra, is insensitive to the value of Ra. For example, $Nu_{N.C.}$ changes only by a factor of 2, while Ra changes by 10^4. However, depending on ones purposes, this change may be enough, as noted above, to cause Nu to be dominated by $Nu_{M.B.}$.

The forced convection ice crystal growth data for pure water are in good agreement with the theory of Fernandez and Barduhn (1967) if the flow Reynolds number based on tip radius is high enough. However, the experimental values of tip radius are about four times larger than the theory predicts. That is, theory and experiment show that m, in Equation (2), equals minus unity, but the experimental value of $A = 0.6$, is about four times the theoretical one; the reasons for this are unknown.

In the subcooling range of 0°C to 1°C, Kallungal and Barduhn (1977) found experimentally that the forced convection growth theory predicts growth rates in pure water down to a Reynolds number, based on tip radius, of 5×10^{-3}. If one examines carefully the data of Gebhart and Pera (1970) on mixed convection heat transfer to fine wire circular cylinders, one finds that natural convection alters forced convection by about 3% when

$$Re \approx 0.5\ Gr^{1/4}$$

The Grashof number, based on experimental values of ice crystal tip radius, is

$$Gr \approx \frac{0.5 \times 10^{-10}}{\Delta T^2}$$

Thus, for $0.1 \leq \Delta T \leq 1$, one gets

$$1.3 \times 10^{-3} \leq Re \leq 4 \times 10^{-3}$$

Consequently, on the basis of mixed convection heat transfer data, one indeed would expect natural convection to influence forced convection ice crystal growth rates in the Re range where the forced convection theory was found to fail.

The problem of growing ice crystals in saline (NaCl) solution is much more complicated and no theories have been proposed which even describe the experimental data qualitatively. The important facts are: growth rates increase substantially up to salt concentrations of about 1%; the tip radius no longer is inversely proportional to ΔT; the location of the density maximum depends on concentration.

Actually, some simple calculations can shed considerable light on the influence of solute concentration on crystal growth rates. Equation (3), together with its counterpart for mass diffusion, yields

$$\frac{C_\infty}{C_i} = 1 - \left(\frac{Nu}{Sh}\right) \left(\frac{Sc}{Pr}\right) \frac{C_p \; (T_i - T_\infty)}{L} \tag{9}$$

where Sh = Sherwood number $\left(\frac{k_d R}{D}\right)$, Sc = Schmidt number $\left(\frac{V}{D}\right)$, D = diffusion coefficient, k_d = mass transfer coefficient, C_i and C_∞ = interfacial and ambient concentrations of solute. Equation (9) shows that $C_i > C_\infty$ and that this "concentration polarization" increases with subcooling. Obviously then, the extent of freezing point depression increases with subcooling. If forced convection dominates, to a reasonable approximation $(Nu/Sh) \approx (Pr/Sc)^{1/3}$ where $Pr \approx 13.5$, $Sc \approx 2600$ for ice-water-NaCl systems. Since T_i is the equilibrium freezing temperature, corresponding to C_i (taking into account the Gibbs-Thompson curvature effect and freezing point depression), Equation (9) completely determines C_i once T_∞ and C_∞ are specified. Furthermore, the magnitude of C_i increases, as does the freezing point depression, as C_∞ increases. Thus, with pure forced convection, the only effect of the concentration field is to create a freezing point depression, and one expects the growth rate for a given subcooling to decrease as C_∞ increases (subcooling, ΔT is defined as $T_E - T_\infty$, where T_E is the freezing point at C_∞). In effect, as C_∞ increases a greater fraction of ΔT is consumed by the freezing point depression and Gibbs-Thompson curvature and less is left to drive the crystallization process. This is precisely what Huang (1975) has observed experimentally, and the forced flow velocity necessary for forced convection to dominate was between 10 and 60 cm/sec, which is much higher than those necessary in the absence of salt. Below this velocity, maxima were observed in the plots of growth rates versus C_∞.

Clearly, the maxima in the growth rates must be due to natural convection induced by concentration differences. Much larger density differences are created by concentration than temperature differences and concentration differences increase with C_∞ for a given subcooling. Also, the Rayleigh number for mass diffusion is about 200 times that for heat transfer if they both are based on the same density difference. All of this means that natural convection created by concentration differences will be very strong and will increase with C_∞. Consequently, a competition is set up between the freezing point depression effect, which decreases growth rates, and the augmented transfer by natural convection, which increases growth rates. Apparently, natural convection wins at C_∞ less than 1% and freezing point depression prevails about 1% salt by weight.

In the low ΔT region, natural convection dominates and this is augmented by concentration differences. To describe this mathematically, first note that

$$T_i - T_\infty = (T_E - T_\infty) - [K_f (W_{S_i} - W_{S_\infty}) + \frac{273.2\ \gamma}{\rho L R}] \qquad (10)$$

where $K_f = 31.8$ is the freezing point depression constant, W_{S_i} and W_{S_∞} are the mass fractions of solute at the interface and in the bulk solution, and γ is the interfacial tension.

Equations (9) and (10) enable one to calculate W_{S_i} which then can be used to determine the growth velocity from

$$v = \frac{D}{R} \mathrm{Sh} \, [1 - \frac{W_{S_\infty}}{W_{S_i}}] \qquad (11)$$

To use Equations (9), (10), and (11), one must know Nu, Sh, and have a relationship between R and ΔT. Realistic theoretical expressions for Nu and Sh are badly needed, but it is a formidable job to obtain them. One can get a rough estimate for these expressions by assuming that the analogy between heat and mass transfer holds and that Equation (6) applies with the Grashof number given by

$$Gr = \frac{gR^3}{\nu^2} \left(\frac{\rho_i - \rho_\infty}{\rho_\infty}\right) \qquad (12)$$

where $\frac{\rho_i - \rho_\infty}{\rho_\infty}$ reflects both temperature and concentration differences. This leads to $(Nu/Sh) \approx (Pr/Sc)^{0.075}$. Thus, all necessary parameters are known once T_∞ and W_{S_∞} are specified.

If one uses (11) with these crude assumptions and the experimental expression for R in terms of ΔT, the results when compared with experimental growth data are encouraging. Equation (11) predicts maxima in the growth versus W_{S_∞} curves, as are observed experimentally. Also, the magnitudes of v predicted are reasonably close to the experimental values. However, the theoretical maxima are not as pronounced as the experimental ones. Predicted rates are somewhat too high near $W_{S_\infty} = 0$ and somewhat too low at concentrations between 1 and 2 weight percent. When one casts (11) in the form of (1), one finds $n = 1.9$ for $W_{S_\infty} = 0$ and $n = 2.1$ for $W_{S_\infty} = 0.02$, which are in reasonable agreement with the experimental values.

It is not clear why $m = -1.5$ in Equation (2) for the tip radius as observed by Vlahakis and Barduhn (1974) when growth is in a 0.15% NaCl. Hydrodynamic effects do not seem likely to account for this because in pure water $m = -1$ over a change of 10-fold in ΔT and six orders of magnitude for the forced velocity of pure water. This question needs further study.

It is clear that some very important aspects of crystal growth are clouded by thermal and concentration driven convection. Accurate data, taken in a microgravity environment, approximate analytical models, and exact (probably numerical) models all seem to be needed to understand better the important problem of crystal growth.

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