

Directional Solidification of Salt Water: Deep and Shallow Cells.

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Abstract. – The common observation of cellular substructure ($(1 \div 10^{-2})$ mm) at the sea-ice-ocean interface is explained by modelling the natural solidification of seawater as that of a dilute H_2O -NaCl solution. Linear and nonlinear perturbation theories reveal that the one-dimensional planar steady state is morphologically unstable, and a bifurcation to cells occurs in geophysically relevant growth regimes. We compute the range of solidification velocity $V_c < V < V_a$ in which the system is unstable for fixed far-field solute concentration C_∞ , and bound the geophysical observations. The system exhibits weak wavelength selection near V_c and the nonlinear theory shows that the bifurcation to cells is subcritical.

Measurements reveal that during growth, mature Arctic Sea ice has a cellular solid-liquid interface [1]. The substructure consists of horizontal c -axes, with random intergrain orientation, and vertical pure ice platelets extending downward, separating regions of concentrated seawater (fig. 1). This two-phase structure influences the bulk mechanical and thermophysical properties of sea ice in much the same way as in binary alloys. A review of the growth and structure of naturally occurring sea ice can be found elsewhere [1]. Other relevant topics include freezing potentials induced by preferential ion incorporation [2], and the influence of bulk solution on acoustic and electromagnetic propagation through the solidified material [3]. Previously, horizontal freezing of ice cylinders from aqueous solutions of concentrations much less than seawater has been investigated [4]. To study the dependence of sea ice platelet spacing on growth parameters, the only approach has been to assume that the stable interfacial growth form is cellular [5]. Qualitatively this approach is useful in studying the transition from cells to dendrites [6], or for long-time simulations of bulk properties in growth from an impure melt [7]. We are interested in the physics responsible for the substructure in this system.

The directional solidification system [8-10] is used in a variety of forms to examine the uni-directional solidification of dilute binary alloys. The alloy is pulled with a constant speed V through an imposed thermal field, and a mean position is established at which the planar solid-liquid interface is located. This state can be maintained for growth velocities V less than a critical velocity V_c , or above an absolute velocity V_a . The influence of the thermal fields and surface tension must overcome the destabilizing effects of solute rejection at the interface to maintain this state [8-10]. Mullins and Sekerka [9] showed that for an alloy solidifying within $V_c < V < V_a$, a bifurcation to cells occurs, because solute diffusion is too slow to remove local

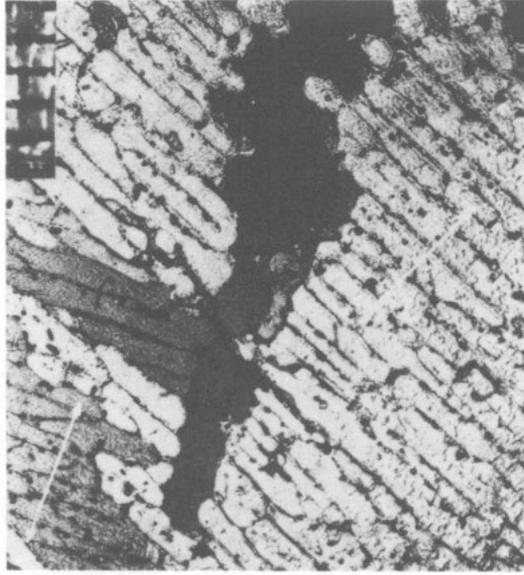


Fig. 1. - Horizontal thin section of Arctic Sea ice exhibiting a substructure of pure ice platelets with uniform intergrain spacing. The crystallographic c -axis (parallel to arrow) is in the plane of the section and oriented perpendicular to the platelet structure of individual crystals. Bulk seawater is trapped between the platelets. The come scale is in mm. (Photograph is courtesy of Dr. A. J. Gow.)

impurity-induced undercooling. The purpose of this letter is to show that the ice platelet substructure results from a diffusive instability, and to call for careful experiments on this transparent system, in this geometry.

As mature sea ice cools, an adverse temperature gradient will develop, so that V approaches V_c from below ($V \rightarrow V_c^-$). For the salt-water system we find that V_c , for the onset of morphological instability, depends weakly on the disturbance wavelength, and that the entire instability range is a one of *subcritical bifurcation*, meaning that cells appear via a jump transition as $V \rightarrow V_c^-$, e.g. [8, 10-12].

The solidification of seawater is approximated as that of a dilute H_2O -NaCl solution, since NaCl is the major impurity species. We analyze a thermally nonsymmetric (thermal conductivities of both phases differ), chemically one-sided model (solute diffusion in the solid is negligible). Because the intergrain platelet spacing is uniform (fig. 1), we focus on a single crystal grain, and ignore grain boundary energy effects. Convective transport of heat or solute is prescribed, because the critical wavelength for convective instability is two orders of magnitude greater than that of morphological instability. The reference frame is attached to the solidification front which is moving with a speed V into the liquid. The planar interface is disturbed as $h(x, t)$, along the direction x , perpendicular to the direction of V . The lengths and times in the problem are scaled on the solute diffusion scales z , $x = (z', x') V/D$ and $t = t' V^2/D$, where the primed quantities have dimensions, and D is the diffusivity of solute in the liquid. The temperature and solute scales are $T_{L,S} = (T'_{L,S} - T'_0)/G^* D/V$, and $C = [C'k - C_\infty]/(k - 1)C_\infty$, where the far-field solute concentration is C_∞ and k is the segregation coefficient, giving the ratio of the solute in the solid to that in the liquid. The low solubility of salt in ice is represented by $k < 1$. These are related to the scales from a thermally symmetric zero-latent-heat analysis [13], but here we include latent heat. The subscripts L, S denote the liquid and solid phases, and T'_0 is the reference temperature of the planar interface. The dimensional temperatures $T'_{L,S} = T_{L,S}^* - T_m$ are measured relative to

the bulk melting temperature of ice T_m . The quantity $G^* = (2G'_L + LV/k_L)/(1 + n)$ is the average temperature gradient at the interface. The dimensional liquid temperature gradient is G'_L , the latent-heat per unit volume is L , and the ratio of solid-to-liquid thermal conductivity is $n = k_S/k_L$.

Using the above scales, the dimensionless diffusion fields obey the following two-dimensional equations and boundary conditions:

for the liquid, $z > h(x, t)$

$$\nabla^2 T_L = 0, \tag{1a}$$

$$\nabla^2 C + C_z = C_t; \tag{1b}$$

for the solid, $z < h(x, t)$

$$\nabla^2 T_S = 0. \tag{1c}$$

At $z = h(x, t)$,

$$T_L = T_S = MC + M\Gamma h_{xx}(1 + h_x^2)^{-3/2}, \tag{2}$$

$$l(1 + h_t) = n(T_{Sx} - h_x T_{Sx}) - (T_{Lz} - h_x T_{Lx}), \tag{3}$$

$$(1 + h_t)[1 + C(k - 1)] = C_z - h_x C_x, \tag{4}$$

where the subscripts x, z, t denote partial differentiation. Equations (1a)-(1c) represent the limit $\{D/\kappa_L, D/\kappa_S\} \rightarrow 0$, where κ_L (κ_S) is the liquid (solid) thermal diffusivity. Condition (2) is the impurity-corrected Gibbs-Thomson relation, and in condition (3) the latent-heat parameter is $l = LV/G^*k_L$. In the far field as $z \rightarrow \infty$, $T_L \rightarrow T_{L0}$, $C \rightarrow C_0$, and as $z \rightarrow -\infty$, $T_S \rightarrow T_{S0}$, so the steady-state planar solutions T_{L0} , C_0 , and T_{S0} are unaffected by interfacial disturbances. The morphological number $M = mG_c/G^* = mC_\infty(k - 1)V/(DkG^*)$, and surface energy parameter $\Gamma = T_m \gamma_{iw}kV/LDmC_\infty(k - 1)$ are the nondimensional numbers appearing in (2). m is the liquidus slope, taken from a locally linear binary phase diagram, G_c is the steady-state solute gradient at the interface, and γ_{iw} is the ice-water interfacial surface tension [14]. It is important to recognize that here $M = M(V)$, implicitly through G^* , which is not the case in a model without latent heat. Equations (1) through (4), and the far-field conditions define the mathematical problem for the unknown functions $C, T_{L,S}$, and h .

We perturb the planar interface states as $z = h(x, t) = \exp[\sigma t + iax]$, and keep track of their temporal behavior. When solving the resulting eigenvalue problem for the growth rate σ using a standard procedure (e.g., [8-10]) a characteristic equation is obtained

$$\sigma = \frac{a[MR(1 + n) - (2G_L + l)(R + k) - a^2M\Gamma(R + k)(1 + n)]}{l(R + k) + Ma(1 + n)}, \tag{5}$$

in which $R = (1/4 + a^2 + \sigma)^{1/2} - 1/2$ is a wave number parameter. If $\text{Re } \sigma = 0$, then $\text{Im } \sigma = 0$, since there is an exchange of stabilities for the finite latent-heat system [15]. When $\text{Re } \sigma > 0$ the planar interface loses stability to nonoscillatory disturbances, and when $\text{Re } \sigma < 0$ it is stable. We can examine the neutrally stable modes by setting $\sigma = 0$. The topological behavior of the resulting equation has been studied elsewhere [16].

We are interested in the ice platelet spacing, so we use eq. (5) to draw a dimensional neutral stability curve in the (V, λ) -plane for $C_\infty = 35$ p.p.t. Figure 2 shows the entire neutral curve, and the inset shows the bottom of the curve close to V_c . The value of G'_L is small compared to that used in atomic metals, but is rarely much greater under a natural ice sheet [17]. Increasing G'_L increases V_c . Near critical, we see the weak dependence of V on λ noted by other investigators [11, 12]. There are low (due to surface tension) and high (due to the finite interaction range of the solute field) λ cut-offs, bounding the allowable scale of the substructure. The dashed curve is the fastest growing disturbance, and corresponds to $\max(\sigma)$. The most striking implication of this result is that the interface will always develop a

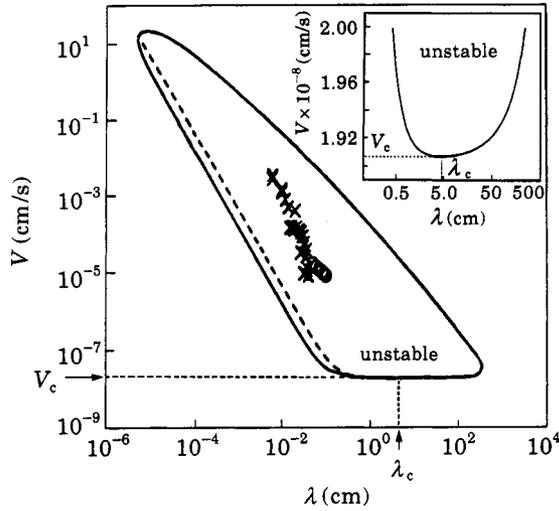


Fig. 2. - The dimensional V - λ neutral stability curve for an H_2O - $NaCl$ system with $C_\infty = 35$ p.p.t. = 0.035 wt.%, $k = 0.3$, $n = 3.57$, $G'_L = 3.57 \text{ Km}^{-1}$, $\gamma_{iw} = 33 \text{ mJ m}^{-2}$ [14], and $L = 3.06 \cdot 10^8 \text{ J m}^{-3}$. The planar interface is unstable interior to the curve. The inset is the neutral curve near critical (V_c, λ_c). The crosses are from Lofgren and Weeks [5], and the average number of platelets measured to obtain each data point was 223. The circles are from Nakawo and Sinha [5]. There are no estimates of G'_L , but it is believed to be small.

platelet substructure (consistent with observation [1]), since naturally occurring sea ice grows in the range $(10^{-8} \div 10^{-4}) \text{ cm s}^{-1}$. The data are the platelet spacing beyond critical, so linear theory bounds the observed substructure, and is qualitatively consistent with the observed [5] power law dependence $\lambda \propto V^{-12}$. Experiments have not investigated the critical platelet spacing, since the lowest laboratory velocities shown here are higher than is typically found in mature sea ice, and greater than V_c . Naturally occurring sea ice will never obtain a $V > V_a \approx 21 \text{ cm s}^{-1}$.

To examine the weakly nonlinear evolution of a single perturbation with itself near critical, a Landau-like amplitude equation

$$\frac{dA}{dt} = \sigma A - a_1 A |A|^2, \tag{6}$$

can be derived [8, 10, 15]. Here, the linear growth rate is σ , and a_1 is the Landau coefficient. Thus, the nonlinear self-interaction of the most unstable mode may generate harmonics that can moderate its slow exponential growth. The equilibrium cell amplitude $A_e = (\sigma/a_1)^{1/2}$ will evolve slowly if $a_1 > 0$ as $V \rightarrow V_c^-$. Then, bifurcation to cells is termed *supercritical*. If $a_1 < 0$, cells will appear abruptly, as the disturbance jumps to a finite amplitude through a *subcritical* bifurcation. For Al-Cu, Alexander *et al.* [15] found that nonlinear behavior is strongly affected by the inclusion of latent heat as $n \rightarrow 1$. For SCN-acetone, Merchant and Davis [18] used these results to show that the latent-heat effect extends the region of supercritical bifurcation into experimentally accessible parameter ranges. For $V \approx V_c$, the Landau coefficient can be written in terms of Γ as

$$a_1 \sim \frac{1 - n + (1 + n)I^{-1}}{\Gamma(1 + n)(1 + I^{-1})} + O[(4k/\Gamma)^{2/3}], \tag{7}$$

where $I = (1 + n)k_L m C_\infty (k - 1)/kLD$ [18].

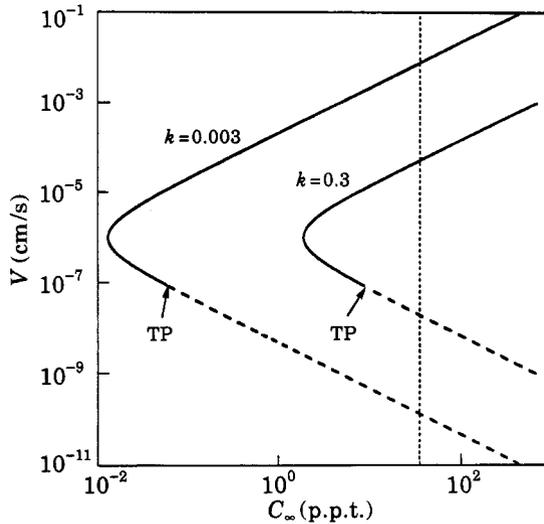


Fig. 3. - The dimensional $V-C_\infty$ neutral stability curves at λ_c . The dotted vertical line is $C_\infty = 35$ p.p.t. and $n = 1.286$. The transition point (TP) divides regions of subcritical bifurcation (dashed line) from regions of supercritical bifurcation (solid line). For $k = 0.3$, TP is $C_\infty = 8.28$ p.p.t., $V = 8.52 \cdot 10^{-8}$ cm s $^{-1}$. For $k = 3.0 \cdot 10^{-3}$, it is $C_\infty = 5.81 \cdot 10^{-2}$ p.p.t., $V = 8.51 \cdot 10^{-8}$ cm s $^{-1}$.

For the geophysical G'_L , we present the $V-C_\infty$ neutral curve in fig. 3 for two k values. Above the high-velocity branch surface tension stabilizes solute rejection, and below the lower branch the thermal fields stabilize solute rejection [9]. Between these branches the planar interface is unstable. The transition point subcritical (dashed curve) and supercritical (solid curve) bifurcation is defined as the point on the neutral curve where $a_1 = 0$ [18]. Here, the linear theory is insensitive to changes in n , as has been noted for metal and transparent organic systems [15, 18]. However, the nonlinear results are very sensitive to changes in n . For $n = 3.57$, the entire curve for both values of k is a region of subcritical bifurcation, implying that in naturally occurring sea ice the breakdown of the interface will always evolve as a jump transition. For $n = 1.1$, the entire $V-C_\infty$ neutral curve is a region of supercritical bifurcation, where shallow cells will appear through the slow evolution of infinitesimal disturbances.

As $n \rightarrow 1$, finite-amplitude disturbances are suppressed, but infinitesimal disturbances are unaffected. Viewing subcritical bifurcations as true jump transitions from the planar state to finite amplitude ($\geq A_e$) cells, and supercritical bifurcations as slow, continuously evolving infinitesimal disturbances ($\ll A_e$), we distinguish the two types of bifurcations based on amplitude near $V = V_c$. The length scale dependence relates to that of the undercooling felt by various disturbances. Close to critical, using the dimensional version of eq. (3), the increase in planar-state solid temperature gradient, G'_S , associated with a decrease in n from n_1 to n_2 can be written as

$$\Delta G'_S = \left(\frac{LV_c}{k_L} + G'_L \right) [n_2^{-1} - n_1^{-1}]. \tag{8}$$

For fixed $G'_L = 3.57 \cdot 10^{-2}$ K cm $^{-1}$, $n_1 = 3.57$, $n_2 = 1.29$, and $V_c = 1.907 \cdot 10^{-8}$ cm s $^{-1}$, then $\Delta G'_S = 0.018$ K cm $^{-1}$. When $n \rightarrow n_2$, a perturbation of amplitude $A_a = 0.1$ cm ($A_b = 0.001$ cm) will experience a decrease in temperature of approximately $\delta T_a = 2.83 \cdot 10^{-3}$ K ($\delta T_b = 2.83 \cdot 10^{-5}$ K) at its minima.

We model the liquid region between the perturbation minima and $h = 0$ as a sphere of fluid, and compare the curvature- and impurity-induced undercooling to $\delta T_{a,b}$, to estimate

the relative thermodynamic potential for freezing. The sum of the curvature and impurity undercoolings is denoted $\delta T_{a,b}^{ci}$. We find $\delta T_a^{ci}/\delta T_a = 2$, and $\delta T_b^{ci}/\delta T_b \approx 10^{-3}$, so the driving force to freeze back the large (small) amplitude minima is sufficient (insufficient). There will be a crossover where $\delta T^{ci} = \delta T$, and the associated disturbance amplitude will demarcate the scale dependence of this n -induced stabilization. Therefore, the increase in G'_S has a negligible effect on the evolution of shallow cells, and a profound effect on that of deep cells.

A cellular substructure at the sea-ice-ocean interface will exist for all geophysically accessible growth rates, and it will appear as a subcritical bifurcation. Careful experiments are needed to examine the theory close to critical, and the transparency of the H_2O -NaCl system, like the commonly studied SCN-acetone system, makes it appealing for many applications. For example, studies of how freezing potentials [2] depend on the interfacial configuration. The present work focuses on the role of hydrodynamics in controlling microstructure in this system. The n -dependent stabilization suggests that orientational differences in n by a factor of at least two may result in a crystallographic preference for shallow or deep cells. Ice has only about a five percent conductivity anisotropy, so suppression of subcritical bifurcations must be controlled differently. Of course, in the laboratory such control can be maintained by radiative heating or varying solute concentration, but nature provides a paucity of geophysical control parameters.

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REFERENCES

- [1] WEEKS W. F. and ACKLEY S. F., in *Geophysics of Sea Ice*, edited by N. UNTERSTEINER (Plenum, New York, N.Y.) 1986.
- [2] BRONSHTEYN V. L. and CHERNOV A. A., *J. Cryst. Growth*, **112** (1991) 129.
- [3] WILLIAMS K., GARRISON G. R. and MOURAD O. D., submitted to *J. Acoust. Soc. Am.*; VANT M. R., RAMSEIER R. O. and MAKIOS V., *J. Appl. Phys.*, **49** (1978) 1264.
- [4] HARDY S. C. and CORIELL S. R., *J. Cryst. Growth*, **20** (1973) 292.
- [5] LOFGREN G. and WEEKS W. F., *J. Glaciol.*, **8** (1969) 153; WEEKS W. F. and LOFGREN G., in *Physics of Snow and Ice*, edited by H. OURA, Vol. 1, Pt. 1 (Hokkaido, Japan) 1967; NAKAWO M. and SINHA N. K., *Atmos. Ocean.*, **22** (1984) 193.
- [6] KARMA A. and PELCÉ P., *Phys. Rev. A*, **41** (1990) 6741; *Europhys. Lett.*, **9** (1989) 713.
- [7] HUPPERT H. E., *J. Fluid Mech.*, **212** (1990) 209.
- [8] WOLLKIND D. J. and SEGAL L. A., *Philos. Trans. R. Soc. London*, **268** (1970) 351.
- [9] MULLINS W. W. and SEKERKA R. F., *J. Appl. Phys.*, **35** (1964) 444; CORIELL S. R., MCFADDEN G. B. and SEKERKA R. F., *Annu. Rev. Mater. Sci.*, **15** (1985) 119.
- [10] LANGER J. S., in *Chance and Matter*, edited by J. SOULETIE, J. VANNIMENUS and R. STORA (North Holland, New York, N.Y.) 1987.
- [11] BENNETT M. J. and BROWN R. A., *Phys. Rev. B*, **39** (1989) 11705.
- [12] MERCHANT G. J. and DAVIS S. H., *Phys. Rev. B*, **40** (1989) 11140.
- [13] MERCHANT G. J. and DAVIS S. H., *Acta Metall.*, **38** (1990) 2683.
- [14] KETCHUM W. M. and HOBBS P. V., *Philos. Mag.*, **19** (1969) 1161; HARDY S. C., *Philos. Mag.*, **35** (1977) 471.
- [15] ALEXANDER J. I. D., WOLLKIND D. J. and SEKERKA R. F., *J. Cryst. Growth*, **79** (1986) 849.
- [16] WETTTLAUFER J. S., *Bull. Am. Phys. Soc.*, **36** (1991) 2690.
- [17] WETTTLAUFER J. S., *J. Geophys. Res.*, **96** (1991) 7215.
- [18] MERCHANT G. J. and DAVIS S. H., *Phys. Rev. Lett.*, **63** (1989) 573.