

Kinetics of Ice Growth in Concrete

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Abstract

Helmuth [1] showed that ice grows in concrete at a rate comparable to the interface-controlled rate measured in thin capillaries. However, the internal temperature of the concrete rose to a value independent of the external temperature, indicating that growth is heat-flow controlled. These are contradictory observations that we have confirmed experimentally. The explanation, revealed by our numerical simulations, is that the ice forms dendrites whose shape allows rapid growth. We speculate that the dendrites in concrete exist on a scale much larger than the pore size, so their curvature is not controlled by surface energy, in contrast to the case of dendrites in free liquid. The implications for freezing stresses in concrete are discussed.

1. Introduction

The mechanism by which freezing causes damage to concrete has been investigated extensively [2,3, 4]. It was originally proposed by Powers that the stress resulted from the increase in volume as water transforms to ice [5]. However, he and Helmuth later proved that this was not the case, and that the real source of stress was crystallization pressure [6]; a detailed discussion of this mechanism is presented in ref. 4. To predict the macroscopic stresses produced by freezing requires a detailed understanding of the distribution of ice within the pore network, together with an appropriate scheme for averaging the effects of the local stresses generated by individual crystals. The latter problem has recently been addressed by Coussy [7]; however, the pattern of ice distribution within concrete during freezing is not adequately understood.

Important evidence for the nature of ice growth through the pores of concrete was obtained by Helmuth [1], from the following experiment. He prepared cylindrical samples of mature cement paste with thermocouples embedded in the interior at uniform intervals along the length. The saturated paste was immersed in a cold bath of kerosene and thermally equilibrated, then cooled. In some cases, ice formed spontaneously (typically at -5 to -15°C) and in other tests it was deliberately initiated by touching the sample with ice. As the crystals grew through the pores, the

heat of fusion released by the ice caused the temperature of the thermocouples (TC) to rise. By recording the time at which each TC responded, the rate of growth could be determined. The rate was found to be about 30-50% of the rate observed by Hillig and Turnbull [8] when ice was grown in thin capillaries. Those authors found that the growth rate, V , was constant in time and increased with undercooling, $\Delta T = T_m - T$ (where T_m is the melting point), according to

$$V \text{ (cm/s)} = 0.16 \Delta T^{1.7} \quad (1)$$

They showed that when the rate of crystal growth is controlled by the kinetics of attachment of molecules to a screw dislocation on the growing surface, then the rate increases as ΔT^2 . They consequently interpreted the exponent of 1.7 as evidence that the ice was growing at a rate controlled by interface attachment kinetics, rather than heat flow.

Helmuth [1] also found that the temperature in the interior of the sample of paste rose to the same value for a given type of paste, independent of the temperature of the surrounding bath. His results are shown in Figure 1. He attributed this to the fact that the heat of fusion released by the ice raises the temperature of the adjacent water to the melting point, so that the temperature inside the sample is the melting point ice in the pores of that paste.

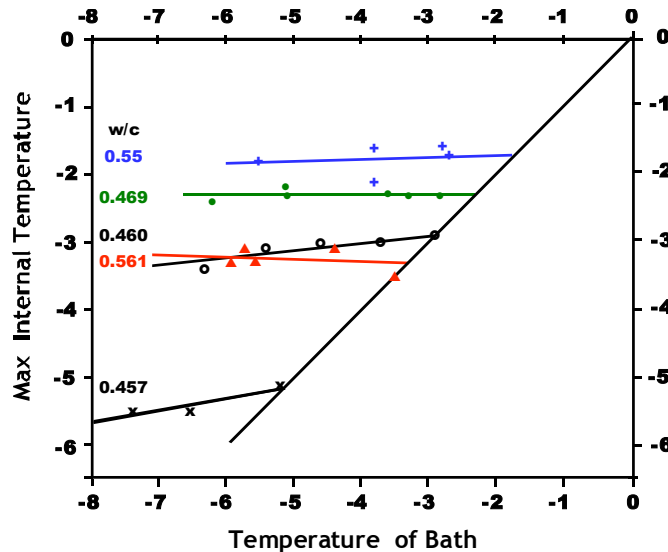


Figure 1. Internal temperature of freezing cement paste (measured by thermocouples) versus temperature of kerosene bath. Water/cement ratio of paste indicated on curves. Redrawn from ref. 1.

According to the Gibbs-Thomson equation [9], the melting point is related to the curvature of the crystal/liquid interface, κ_{CL} , by

$$T_m(\kappa_{CL}) = T_m(0) - \frac{\gamma_{CL} \kappa_{CL}}{\Delta S_{fv}} \quad (2)$$

where $T_m(0)$ is the melting point of a flat macroscopic crystal, γ_{CL} is the crystal/liquid interfacial energy, and ΔS_{fv} is the entropy of fusion per unit volume of crystal; for ice, $\Delta S_{fv} \approx 1.2 \text{ J}/(\text{cm}^3 \cdot \text{K})$. In a cylindrical pore, the tip of the advancing crystal can be approximated as hemispherical, so the curvature is

$$\kappa_{CL} = \frac{2}{r_p - \delta} \quad (3)$$

where r_p is the radius of the pore and δ is the thickness of unfrozen water on the surface of the pore; Helmuth estimated this to be about a nanometer. On the basis eqs. (2) and (3), Helmuth estimated the pore radius in the pastes to be on the order of 10 nm. He noted that about 1-10% of the pore water froze initially (contributing to the jump in internal temperature), then water in the smaller pores froze slowly as the temperature continued to drop.

Since Helmuth did not measure the pore size in his samples, we decided to repeat the experiment and to complete it by measuring the pore size by mercury intrusion and nitrogen sorption. Quite similar results were obtained [10], but we realized that there was a contradiction in the data: the internal temperature is identified as the melting point of ice in the pores, which means that the ice is growing under heat-flow control at $T_m(\kappa_{CL})$, but the *rate* of growth is as fast as that of ice in small capillaries where heat is easily removed and interface kinetics control the rate. We therefore ask, how can ice grow so fast, if the undercooling is near zero?

2. Experimental study

Samples of ordinary cement paste were prepared with $w/c = 0.45 - 0.65$, then cured in lime-saturated water for about two weeks. The samples were in the form of rectangular prisms approximately $22 \times 7 \times 5 \text{ cm}$ with thermocouples embedded along the mid-plane every 2.7 cm. The paste blocks were immersed in a kerosene bath at about -5°C and freezing was nucleated by touching the end with ice. The ice would propagate through the sample, causing the temperature to jump at each TC in turn. An example is shown in Figure 2a. A plot of the location of the TC and the

time of the jump yields a straight line whose slope is interpreted as the rate of growth of ice. Occasionally, nucleation would occur spontaneously within the block and spread outward; for example, nucleation might occur between TC 4 and 5, after which temperature jumps would be recorded at TC 3 & 6, then 2 & 7.

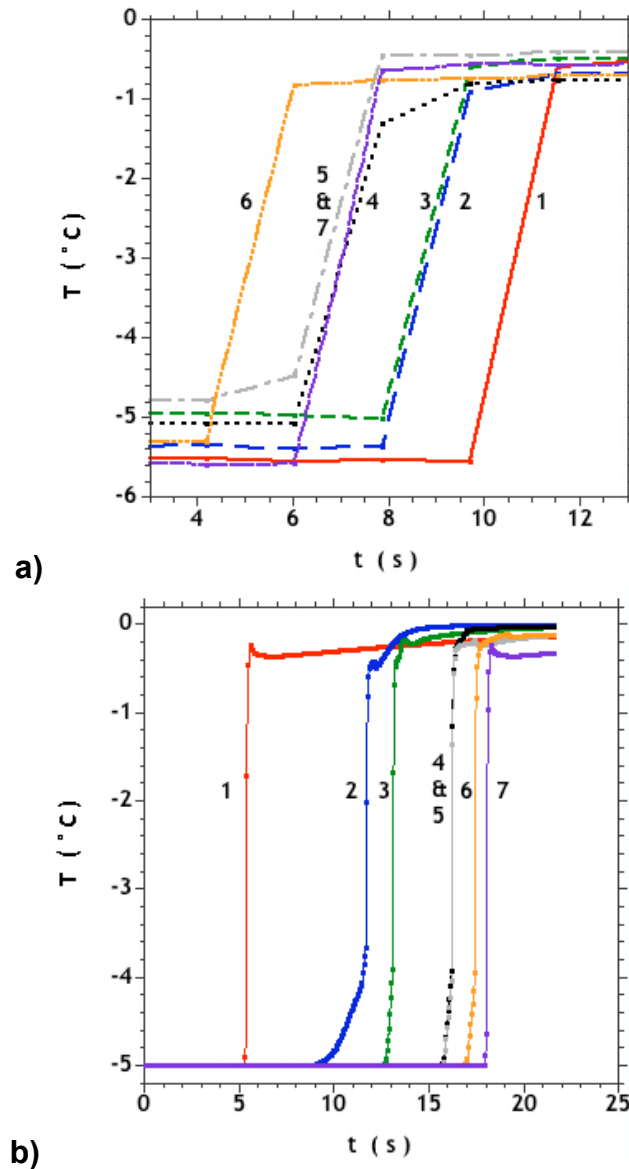


Figure 2. a) Sequential response of thermocouples embedded in sample of cement paste after freezing begins at one end. b) Results of numerical simulation of the experiment, assuming that ice occupies 10% of the volume. Thermocouples are numbered in order.

Recognizing that the temperature would remain low near the surfaces of the sample in contact with the cold kerosene, while it would rise in the interior during crystallization of ice, a 2-d model was built so that we could visualize the process. As shown in Figure 3, it consisted of two clear plastic blocks (each 2.5 x 5 x 12.7 cm) separated by thin (0.079 cm) strips of aluminum along two edges. The other two edges were sealed by vacuum grease. The gap between the blocks was filled with water. The model was put in the cold bath with thermocouples inserted in the gap. If the temperature of the cold bath was below about -5°C , nucleation would occur before the water cooled to the temperature of the bath. In such cases, the ice would race along the aluminum strips (which would remain near the bath temperature), then grow as a smooth layer toward the warmer interior. On the other hand, if the bath was near -4°C , the water would equilibrate at the bath temperature, and freezing could be initiated by touching the edge of the gap with ice. This resulted in rapid dendritic growth of ice throughout the gap.

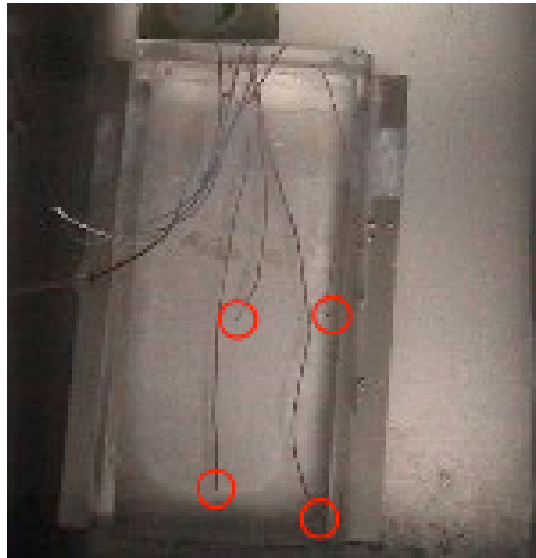


Figure 3. Photo of model with plastic blocks glued to aluminum strips that create a gap which is filled with water. Circles indicate the tips of thermocouples inserted in the gap. The model is immersed in a kerosene cold bath to cause freezing.

3. Numerical simulations

To study the nature of the growth of ice in the pores of cement paste, we

employ the level set method introduced by Osher and Sethian [11] in the form developed by Chen et al. [12]. This is an efficient method for solving the heat flow equation and keeping track of the evolving shape of the liquid/crystal interface during crystallization. Details are provided elsewhere [13]. The simulation is performed on a 2-d grid using physical properties appropriate for water and ice (see). Heat is expelled at the interface as ice forms, so the boundary condition is

$$K_C \left. \frac{\partial T_C}{\partial x} \right|_{x=0} - K_L \left. \frac{\partial T_L}{\partial x} \right|_{x=0} = \frac{\Delta H_f V \phi_C}{v_C} \quad (4)$$

where K_C and K_L are the thermal conductivities of the crystal and liquid, ΔH_f is the molar heat of fusion and v_C is the molar volume of the crystal; ϕ_C is the fraction of the volume that freezes, which may be small in cement or concrete. When simulating freezing of pure water (in the plastic model, for example), we set $\phi_C = 1$; to simulate freezing in cement paste (as in the Helmhuth experiment), we use $\phi_C = 0.1$. The rate of growth at any point on the interface is assumed to depend on the local temperature T_i , so that V is given by eq. (1) with $\Delta T = T_m(K_{CL}) - T_i$. In fact, the radius of the dendrite tip is large enough ($> 0.5 \mu\text{m}$) so that the curvature correction is unimportant.

The numerical model can be tested by comparison to some simple analytical cases. For example, for a planar crystal/liquid interface, if the coordinate system moves with the interface, the temperature of the liquid is described by

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + V \frac{\partial T}{\partial x} \quad (5)$$

where α is the thermal diffusivity. Assuming that the growth rate is constant and the heat diffuses only into the liquid, the solution of eq. (5) indicates that the temperature of the interface increases as

$$T_i(t) = T_\infty + \lambda \left[\sqrt{\frac{t}{\pi \tau}} \exp\left(-\frac{t}{4\tau}\right) - \frac{t}{2\tau} + \left(1 + \frac{t}{2\tau}\right) \text{erf}\left(\sqrt{\frac{t}{4\tau}}\right) \right] \quad (6)$$

where T_∞ = temperature far from the interface, $\tau = \alpha l^2$, $\lambda = \Delta H_f / (v_C c_p \rho)$, c_p = heat capacity, and ρ = density of liquid. On the other hand, if the growth rate decreases as $V = V_0 / t^{1/2}$, then the temperature of the interface is constant, and is given by

$$T_i = T_\infty + \sqrt{\pi} \lambda \mu \exp(\mu^2) \operatorname{erfc}(\mu) \quad (7)$$

where $\mu = u_0/\alpha^{1/2}$. Simulations of these two cases, shown in Figure 4 yield very satisfactory results. (For these tests, we assumed $\phi_C = 1$.)

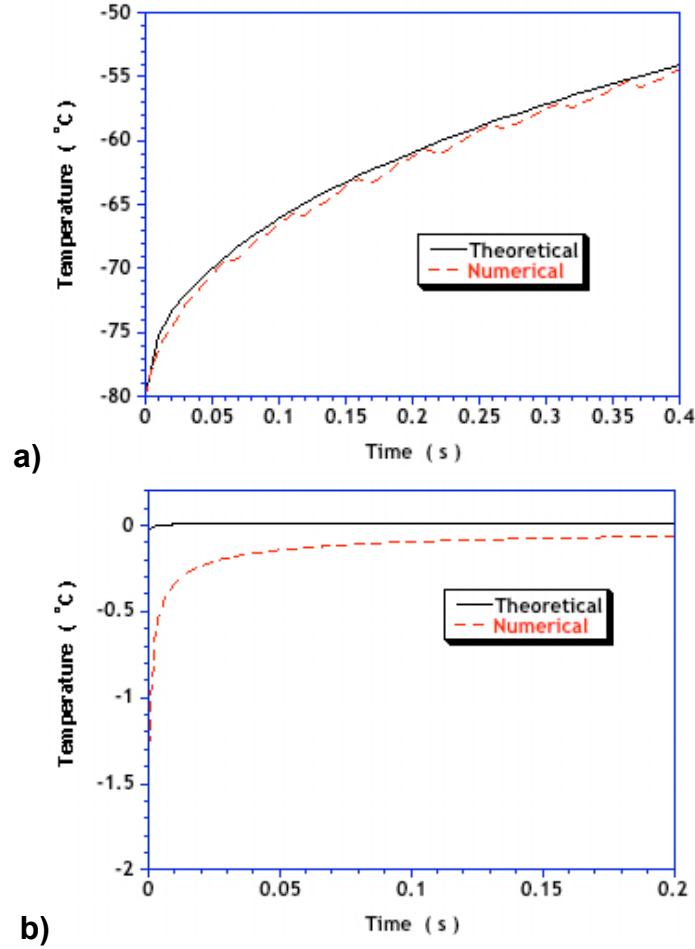


Figure 4. a) Interfacial temperature of flat crystal growing at $V = \text{constant}$, according to the simulation (symbols) and eq. (6) (Theoretical); b) when growing with velocity $V = V_0/t^{1/2}$, simulation (symbols) quickly approaches value predicted by eq. (7) (theoretical).

To simulate Helmuth's experiment, we set $\phi_C = 0.1$ and use a sample size of 5 x 15 cm (two-dimensional) with the initial internal temperature of the sample at -5°C and the edges held at a bath temperature of -7°C .

Nucleation is initiated at one edge and the crystals begin to grow at a rate given by eq. (1). As shown in Figure 5, one large dendrite emerges from the site of nucleation, and intersects the first TC. Ice also races down the long edges, where fast growth is driven by the low temperature, and dendrites then grow inward from the edge. Except for the first two, all the TC are engulfed by dendrites from the edges of the sample.

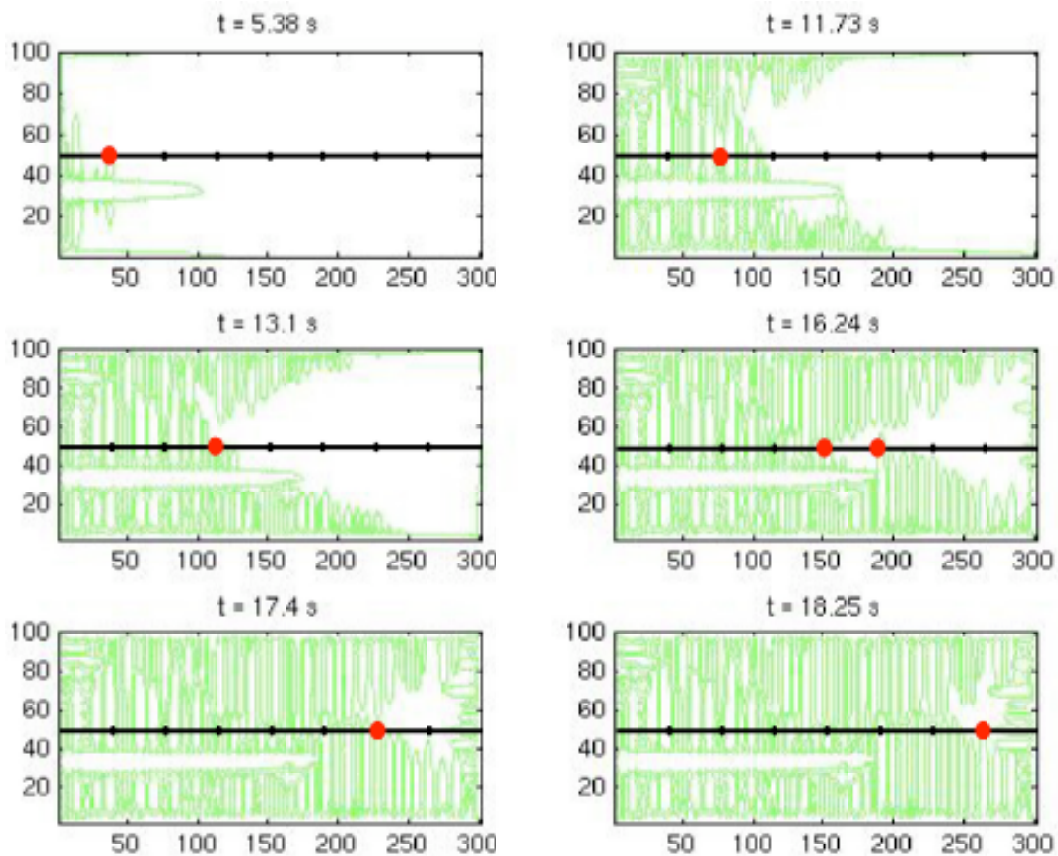


Figure 5. Simulation of dendritic growth in cement paste, where ice fills 10% of the sample volume. The dots along the axis of the sample are thermocouple locations, and the large dot is the one that reports a jump in temperature at the indicated time. Except for the first two, the TC are engulfed by dendrites growing in from the edge.

Dendrites form because a flat crystal is unstable in the presence of a temperature gradient: if a perturbation allows a portion of the interface to jut out ahead of the plane, the tip of the perturbation is in cooler liquid, so it grows more rapidly. This is an unstable situation that results in the

formation of dendrites. Helmuth [1] proposed that dendrites would propagate through a network of larger pores, but it is not realistic to imagine that an unstable interface would form within a 20 nm pore, because the surface energy would suppress such small structures. We believe that the dendrites within the porous matrix of cement paste are much larger than the pores.

The change in temperature of each TC is shown in Figure 2b; just as in the experimental case shown in Figure 2a, the TC sequentially jump up to the melting temperature as the ice arrives. Figure 6 shows a plot of TC location versus the time at which the jump occurs, and it yields a constant “growth rate” comparable to the values seen experimentally by Helmuth [1], and in our own experiments [10]. However, it is clear from Figure 5 that the TC are *not* recording the actual growth rate of the ice. Examination of individual dendrites indicates that the actual growth rate was about 0.5-0.7 cm/s.

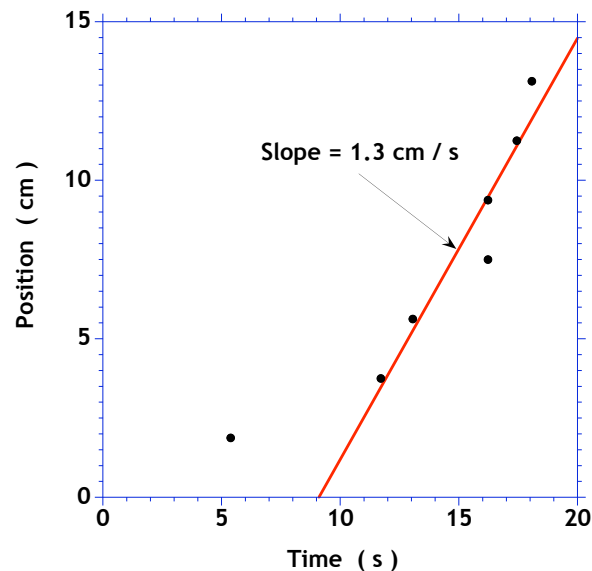


Figure 6. TC position versus time at which the temperature jump occurs; values taken from Figure 2b. The apparent growth rate is $V = 1.3$ cm/s, but the actual growth rate of the dendrites is slower (~ 0.5 - 0.7 cm/s).

4. Conclusions

Helmuth [1] offered an insightful interpretation of the growth of ice in cement paste, arguing that the pore liquid would be raised to the melting

point by the heat of fusion, but that T_m would be different from 0°C , because of the curvature of the ice crystals in the small pores of the paste. However, if the growth rate is controlled by heat flow, there are two possible outcomes: a) a stable interface advances at a decelerating rate, $V = V_0 / \sqrt{t}$, or b) dendrites grow at a constant rate, but the interfacial temperature is below the melting point. Based on the high and constant growth rates measured by Helmuth and by Kumpf, together with the simulations presented here, we conclude that ice propagates through the pores of concrete in the form of dendrites. These grow rapidly, because their acute shape permits the heat of fusion to diffuse away rapidly. However, the heat accumulates between the dendrites, so that the temperature is close to the melting point at a short distance behind the tips of the leading dendrites.

Our simulations reveal that the apparent growth rate found from the temperature jumps by a series of thermocouples is misleading. The rapid advance of the temperature wave arises from fast propagation of ice along the cold surfaces in contact with the kerosene bath; subsequently, dendrites grow inward from the lateral surfaces. It is the growth of the latter dendrites that triggers the TC. The temperature quickly rises to the melting point, because of the latent heat contained *between* the dendrites. The melting point is indeed shifted according to the Gibbs-Thomson equation, eq. (2), as explained by Helmuth, and this explains the constancy of the internal temperature during freezing, revealed in Figure 1.

It is important to recognize that the dendrites within the porous matrix of cement paste are unlike those commonly seen in free liquids. Helmuth proposed dendritic growth, but he seems to have meant that dendrites would form within the individual pores. This is improbable, because the pore diameters in paste are on the order of tens of nm, while the typical radius of curvature of a free dendrite is hundreds or thousands of nm [14]. Therefore, we conclude that the dendrites in paste are much larger than the scale of the pores; that is, the thermal instability favors the formation of a narrow "dendrite" that incorporates many crystallites, but sheds heat more efficiently than a planar interface. Whereas the curvature of the individual crystallites corresponds to the pore radius, and leads to a substantial change in melting point, the curvature of the envelope bounding the polycrystalline dendrite is so large that it does not produce significant capillary effects. What, then, are the factors that control the radius of the dendrite? For free dendrites, there are many theories [15], among the most successful of which is the idea of marginal stability proposed by Langer and Müller-Krumbar [16]. They argue that the tip

radius of a dendrite is equal to the largest stable wavelength obtained from a Mullins-Sekerka [17] stability analysis: larger wavelengths grow, and smaller ones are suppressed by surface energy, so the tip of the dendrite hovers near the critical size. For dendrites in a porous medium, no theory yet exists. We suggest that the force driving instability is the temperature gradient, as in a free liquid; the force opposing instability may be related to the connectivity of the pores. If a dendrite becomes too narrow, the larger pores may not percolate within it, so the growth of ice will be arrested. To explore this possibility, we will use pore network models in which the dendrite size can be compared to spatial correlation functions, and other indices of pore size and connectivity.

Acknowledgment

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