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## INFLUENCE OF CONVECTION ON FREE GROWTH OF DENDRITE CRYSTALS FROM SOLUTION

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The free growth of dendrites in a uniformly supercooled solution has been examined using cine photography with a Schlieren optical system. Crystals were grown in the bulk of the solution from a centrally located capillary tube, nucleated at the interface with a liquid nitrogen cooled wire. Crystals propagated along the tube, the slower growing orientations eliminated, and emerged at the tip, usually growing parallel to the tube direction. For both sodium sulfate decahydrate from its solution and ice from sodium chloride solution, growth rate and fineness of dendrites increased with supercooling. In sodium sulfate, upward convection of the less dense depleted solution occurs; downward convection was observed for the rejected, more concentrated sodium chloride solution. In both cases, there was a spatial and temporal delay in the release of the convective plume from the moving dendrite tip. The role of this convection on the growth characteristics and the production of secondary crystals is examined. A proposed low-g experiment will examine differences in growth rate, crystal texture and secondary nucleation in a reduced convective regime where molecular diffusion is the dominant transfer process.

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INTRODUCTION

The growth morphology of a crystal is known to depend in a complex way on the environmental conditions: supersaturation or supercooling, physical properties of the fluid, Prandtl and Sherwood number, and the bulk fluid flow around the crystal. These parameters influence the growth of the crystal through heat and mass transport processes, and, most important from the viewpoint of growth rate and crystal habit, through the kinetic processes taking place at the crystal interface. Plane faces appear when layer growth takes place in low index direction in regions of modest supersaturation, with layers originating either from defects or on crystal edges protruding further into the diffusion field and subject to surface nucleation. Skeletal crystals form when these layers fail to reach the crystal center before nucleation of further layers.

Experimental studies aimed at investigating the nature of these dependencies and the molecular detail of the growth mechanism necessarily aim for an idealization experiment to reduce the number of physical variables. For very small growth rates, an isothermal experiment is a practical idealization; rapid stirring prevents local density differentials. For more rapid growth rates, an adiabatic idealization is practical, with crystals growing freely into an infinite, constant condition environment. This latter case is relevant to more extreme growth conditions with large driving force for growth. In all cases, it is necessary to avoid the presence of extraneous surfaces which give spurious heat transfer or nucleation.

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A second feature of crystal growth, especially in the case of these higher driving forces, is the occurrence of secondary crystallization - that is, of the formation of crystals of orientations other than that of an initial single crystal, a phenomenon which gives a differing crystal texture and impurity distribution following complete solidification.

In assessing the role of these different parameters, there are several aspects of the crystal growth to be considered. The habit, the ratio of growth velocity in different low index planes, the absolute growth rate in these directions, the tendency to skeletal growth, and the occurrence of secondary crystals are all important both from the viewpoint of understanding the growth mechanism and from the viewpoint of crystal growth technology.

From the viewpoint of the utility of a low-g environment, there are two aspects of growth selected for study here which are very difficult to investigate in 1-g situations. With dendrites in free growth, the growth rate and dendrite dimension are determined by the ambient supercooling. In 1-g and in an unstirred environment, the release of latent heat and/or depletion of the nearby solution lead to density differences which give rise to local convection. The question arises as to the importance of this self-induced convection on the growth of the dendrite; first, is there an enhancement of dendrite growth because of the motion (it is known that externally imposed motion enhances growth rate), and second is this motion responsible for any secondary crystal nucleation. These questions are relevant for growth in an environment initially at rest with respect to the growing crystal, and not set in motion on the scale of the containing tank. The following experiments were designed to investigate the physical processes occurring in 1-g growth and serve as a basis for assessing the presence of self-induced natural convection by direct comparison with an identical experiment in low-g.

From the viewpoint of ease of study, the crystallization of sodium sulfate decahydrate from supersaturated solution was chosen. A liter of near saturated solution can readily be supercooled as much as 10C; it is transparent and ideal for optical studies in a convenient range of temperatures, the saturated solution crystallizing at 32.5C. Studies were also carried out of ice crystallizing in sea water (approximately 0.4 M NaCl). The solution was contained in a tank with plate glass viewing windows, dimensions 7 in x 7 in high x 1.5 in thick. It was thermostated to  $\pm 0.2C$  with a similar vertical and horizontal uniformity. An L-shaped Teflon capillary tube was located at the side of the tank (Fig. 1). This arrangement allowed crystallization to be initiated in the bulk of the liquid. A liquid nitrogen-cooled wire was inserted into the capillary; nucleation occurred at the cold spot and crystals grew inside the Teflon tube. The slower growing directions were eliminated, and a fast growth dendrite would usually emerge from the open end to grow horizontally into the liquid. The whole system was inserted into a Schlieren optical system, with the results recorded on still or movie film (Fig. 2). This technique is similar to that employed for the studies of sodium chlorate crystals by Chen et al. (1). Sodium sulfate solution crystallizing to decahydrate gave upward convection of diluted solution; sodium chloride solution crystallizing to ice and rejecting the solute gave a denser solution with downward convection (Fig. 3a,b). In both cases, crystallization velocity increased with supercooling. At large supercooling ( $\gtrsim 10C$  for  $Na_2SO_4$  and  $\gtrsim 5C$  for ice) with velocities  $\sim cm\ s^{-1}$ , the crystal growth kept ahead of any convection and no effects were visible. Very low growth velocities ( $R < 0.01\ cm/sec$ ) at  $\Delta T < 3C$  for  $Na_2SO_4$  and  $\Delta T < 0.25C$  for ice, were complicated by thermal interactions with the walls of the tank. This gives a range of supercooling of about 8 C for  $Na_2SO_4$  and 4 C for ice over which data could be obtained where differences

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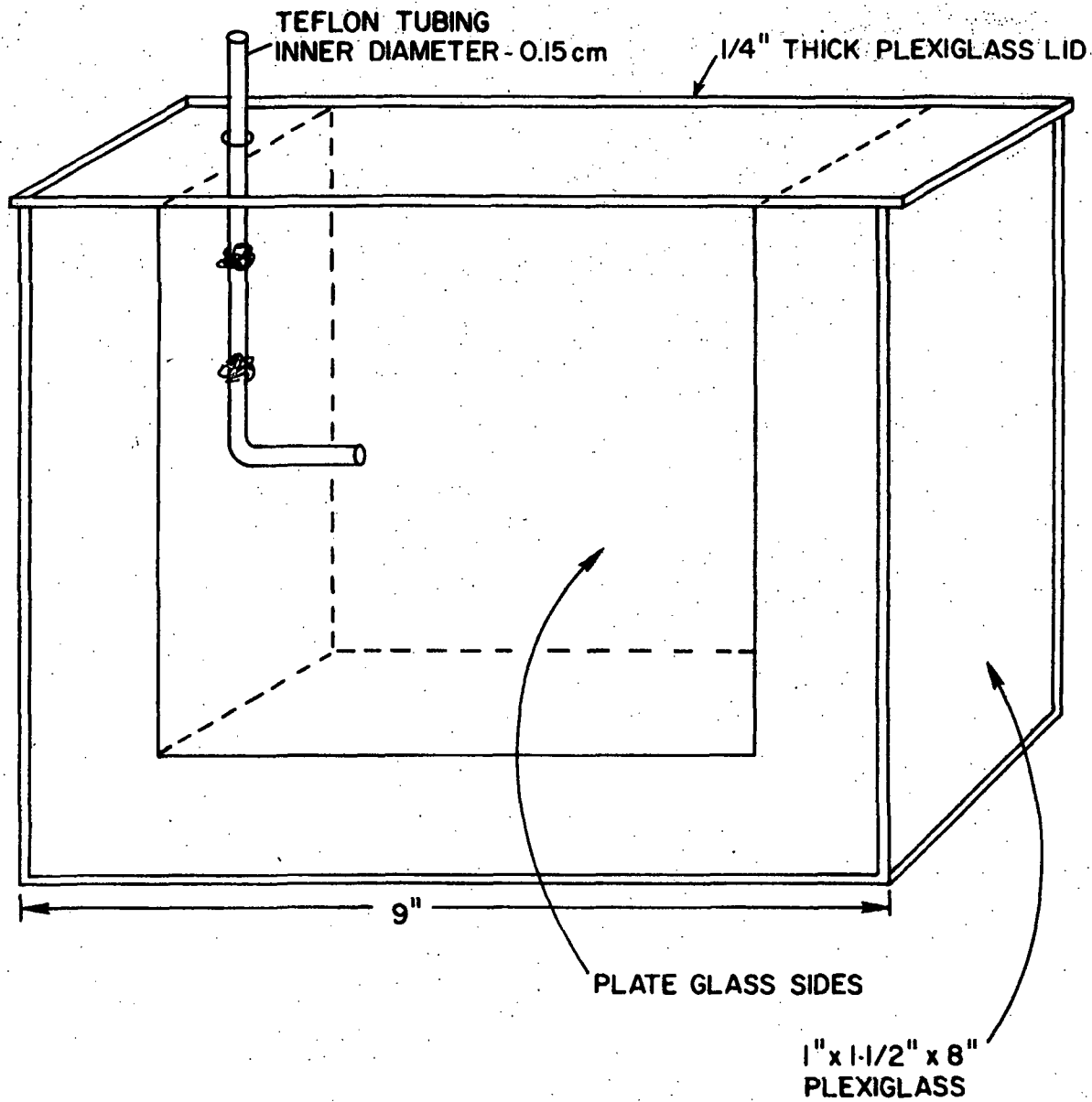


Fig. 1. Tank for initiating crystallization in the bulk of the supercooled liquid. The tip of a stainless steel wire was cooled in liquid  $N_2$  and then inserted into the Teflon tube as far as the bend. Dendrites grew from the tube tip into the liquid.

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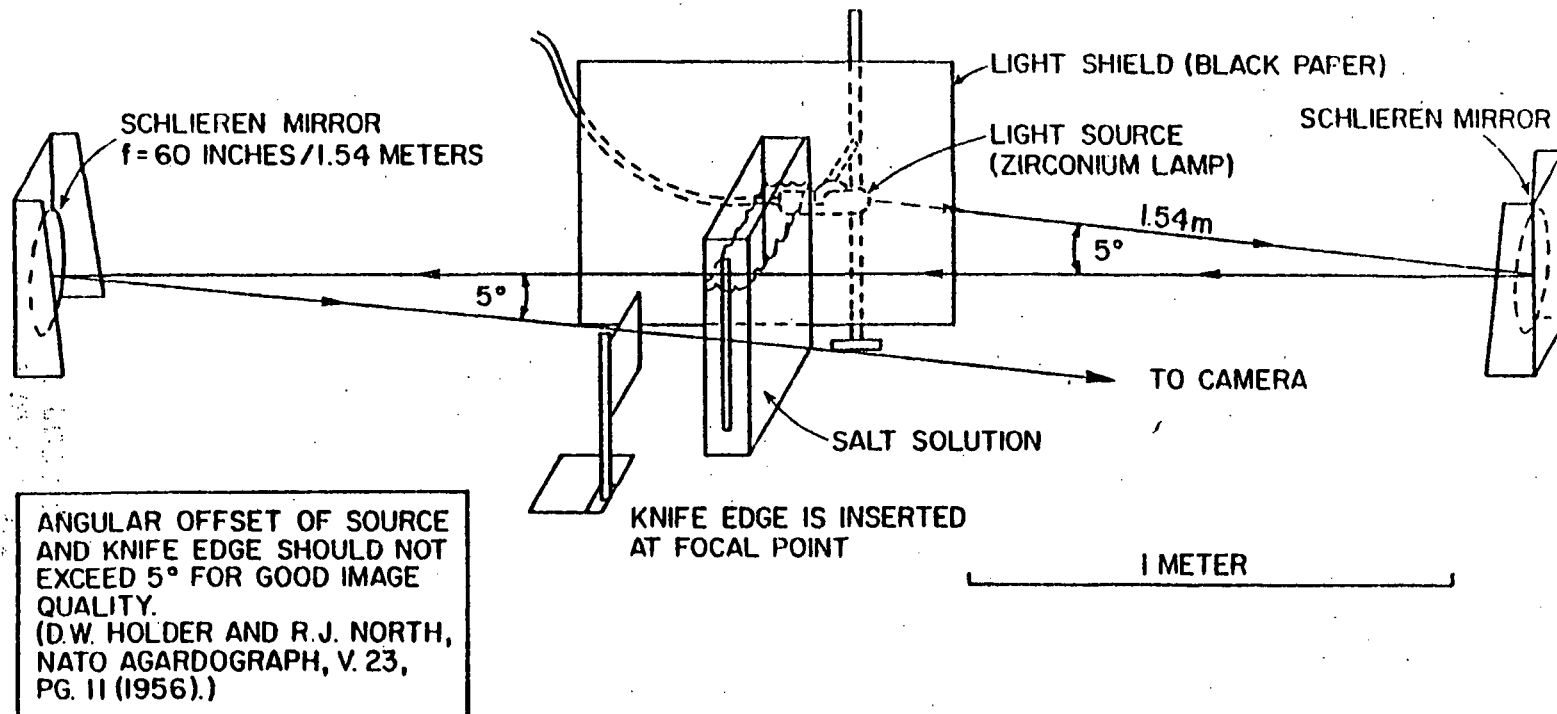
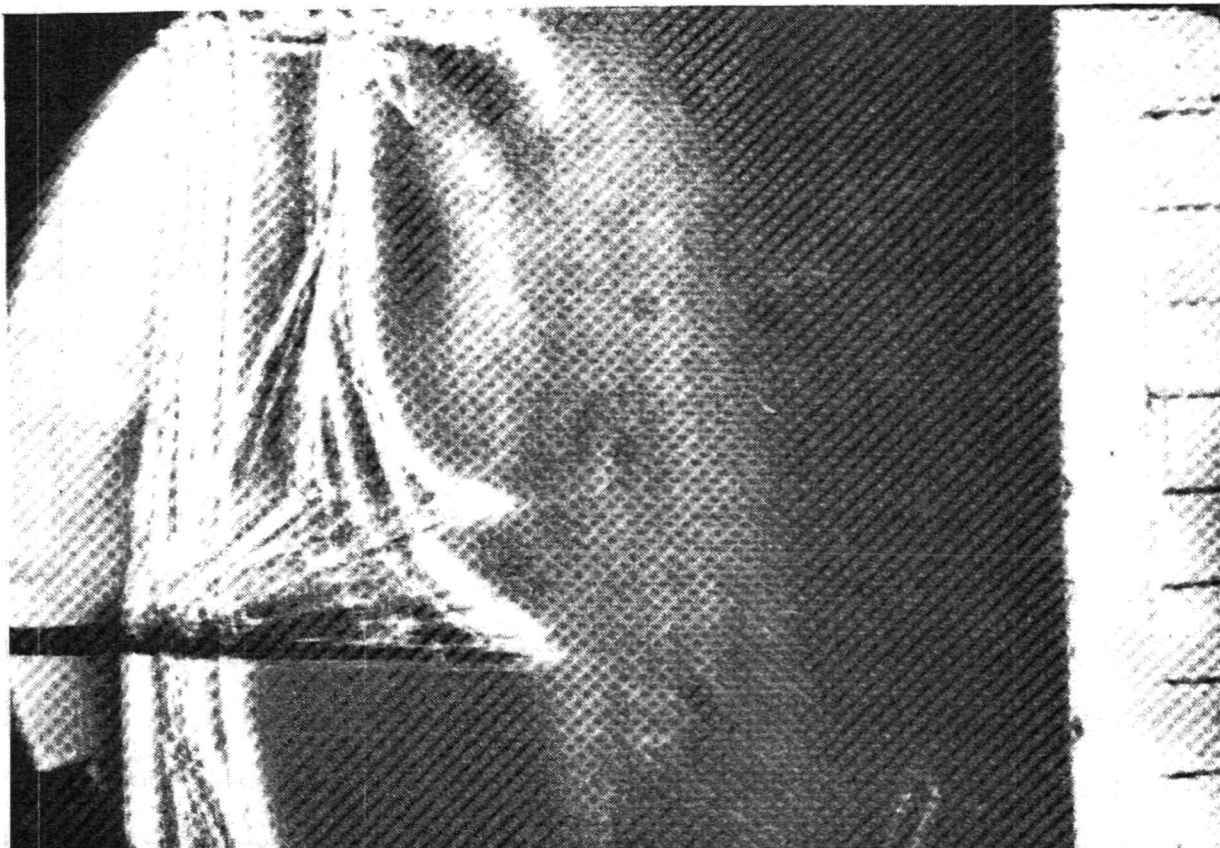


Figure 2. The Schlieren System. The light source is a 10 watt Zirconium arc lamp.

3a



3b

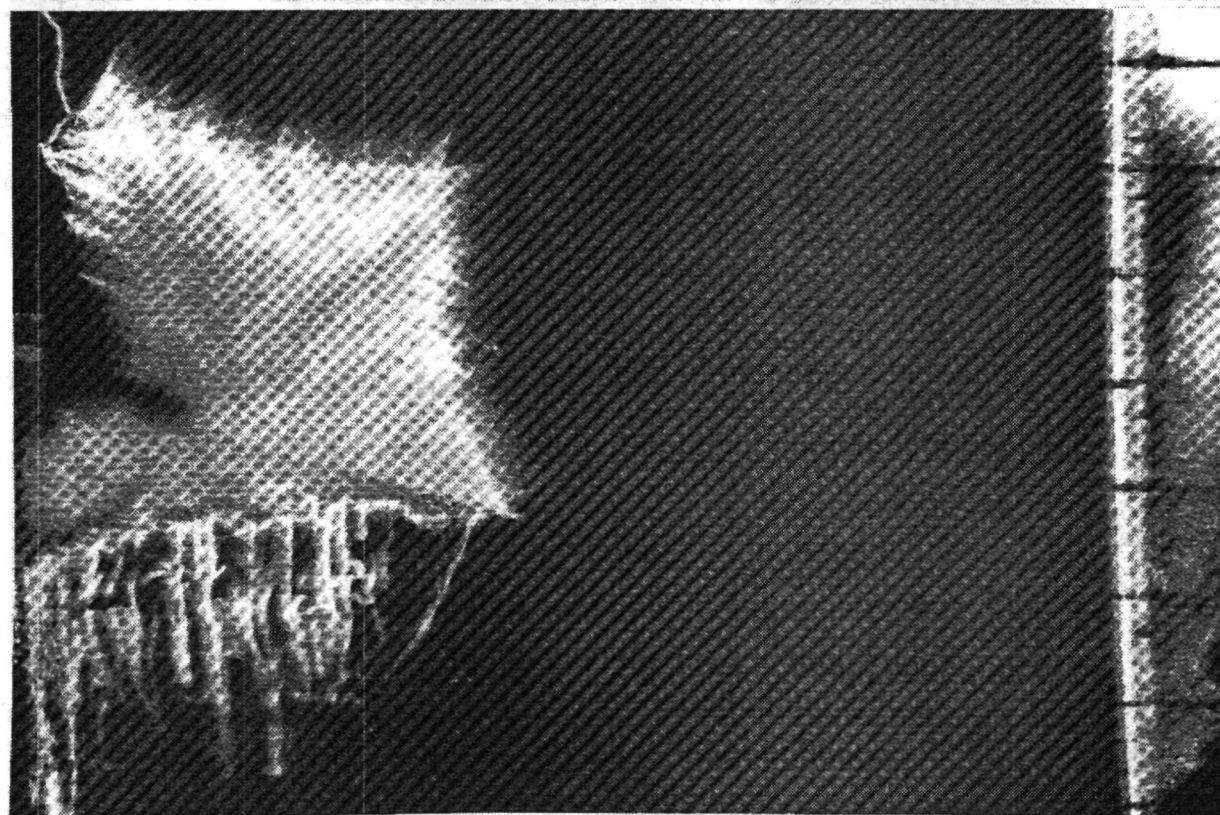


Figure 3. Crystallization of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  from solution and ice in sea-water. Both pictures were taken with Tr-X film utilizing the tank and Schlieren system shown in Figs. 1 and 2. The plume from growing  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  dendrites (3a) convects upward at  $\sim 0.2 \text{ cm s}^{-1}$  (2.7 M,  $\Delta T = 5.5 \text{ C}$ ). The plume from the ice dendrites (3b) convects downward at  $\sim 0.01 \text{ cm s}^{-1}$  ( $\Delta T = 0.5 \text{ C}$ ). Scale divisions on the right are 1 cm.

are expected because of natural convection. Within this range, it was necessary to examine the growth only during the period that the convection had not set up a general circulation in the tank - some 2 to 30 s.

### RESULTS

For dendrites of both sodium sulfate decahydrate and ice, a convective plume was evident coming from just behind the advancing tip. A starting plume began as growing crystals emerged from the capillary, with velocity  $\sim 0.2 \text{ cm s}^{-1}$  for sodium sulfate and  $0.01 \text{ cm s}^{-1}$  for ice in sea-water (Fig. 4). As this moved away from the tip, the  $\text{Na}_2\text{SO}_4$  plume retained shape similarity with respect to the tip and became approximately parabolic, as can be seen from Fig. 3 for both ice and sodium sulfate. There is a spatial delay in the visible plume detaching from the dendrite, which increases with the crystal growth velocity (Fig. 5). To a first approximation, the time for detachment is independent of the growth velocity and is 10 s for sodium sulfate and 20 s for ice. There is an asymmetry in the growth velocity of dendrites with direction which is a complicated function of both crystal habit and convection velocity. In  $\text{Na}_2\text{SO}_4$  solution (Fig 3a), dendrites will grow more slowly into the disturbed solution with the fastest growing crystal being horizontal, while the ice crystal is distinctly inhibited in the convecting region (3b). Growth of dendrites into undisturbed fluid is aided by convection as can be clearly seen in these figures.

For sodium sulfate, secondary nucleation of crystals occurs for supercoolings between 3 and 6C. These small crystals rise with the buoyant fluid, grow, and produce yet more crystals as they fall out. For ice, larger crystals occasionally break away at supercooling  $>1 \text{ C}$  to give other orientations. Ice, being less dense than the solution, rises - decahydrate being more dense finally sinks relative to the fluid motion. In each case, the crystals move into fresh



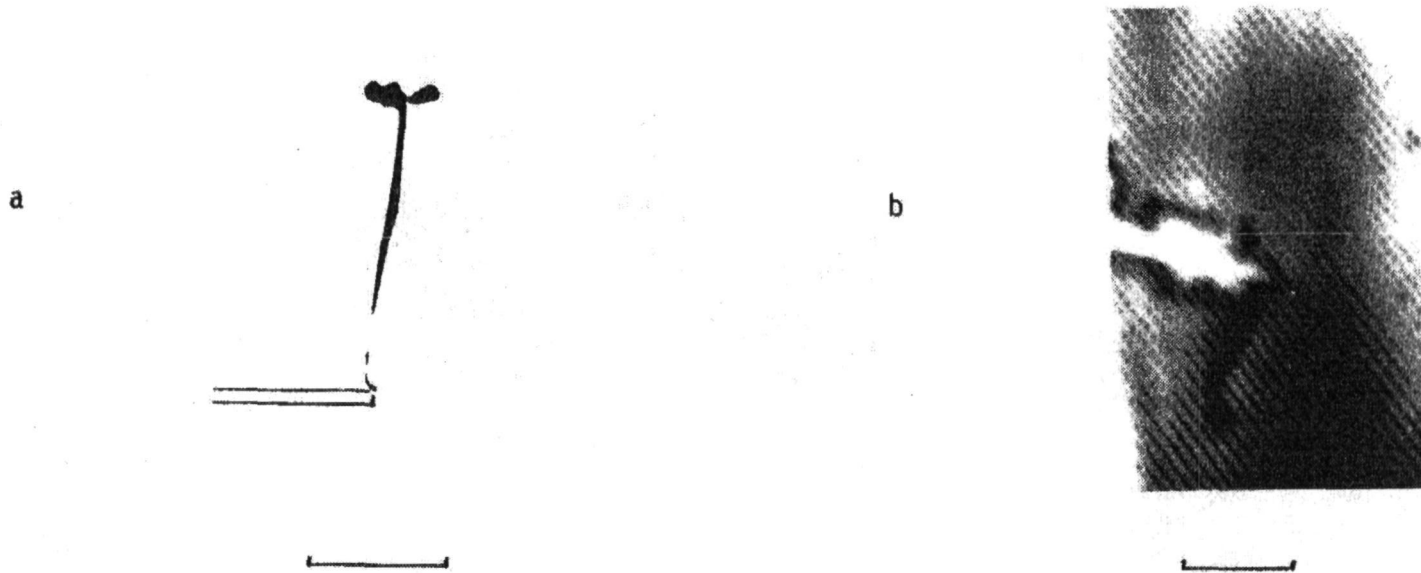


Figure 4. Initial plume from crystal issuing from end of Teflon tube.

a.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; 3.0 M,  $\Delta T = 6.5 \text{ C}$  .

b. Ice in sea-water, 28‰,  $\Delta T = 0.5 \text{ C}$  .

Negative prints from Plus-X Reversal film.

All scales show 1 cm.

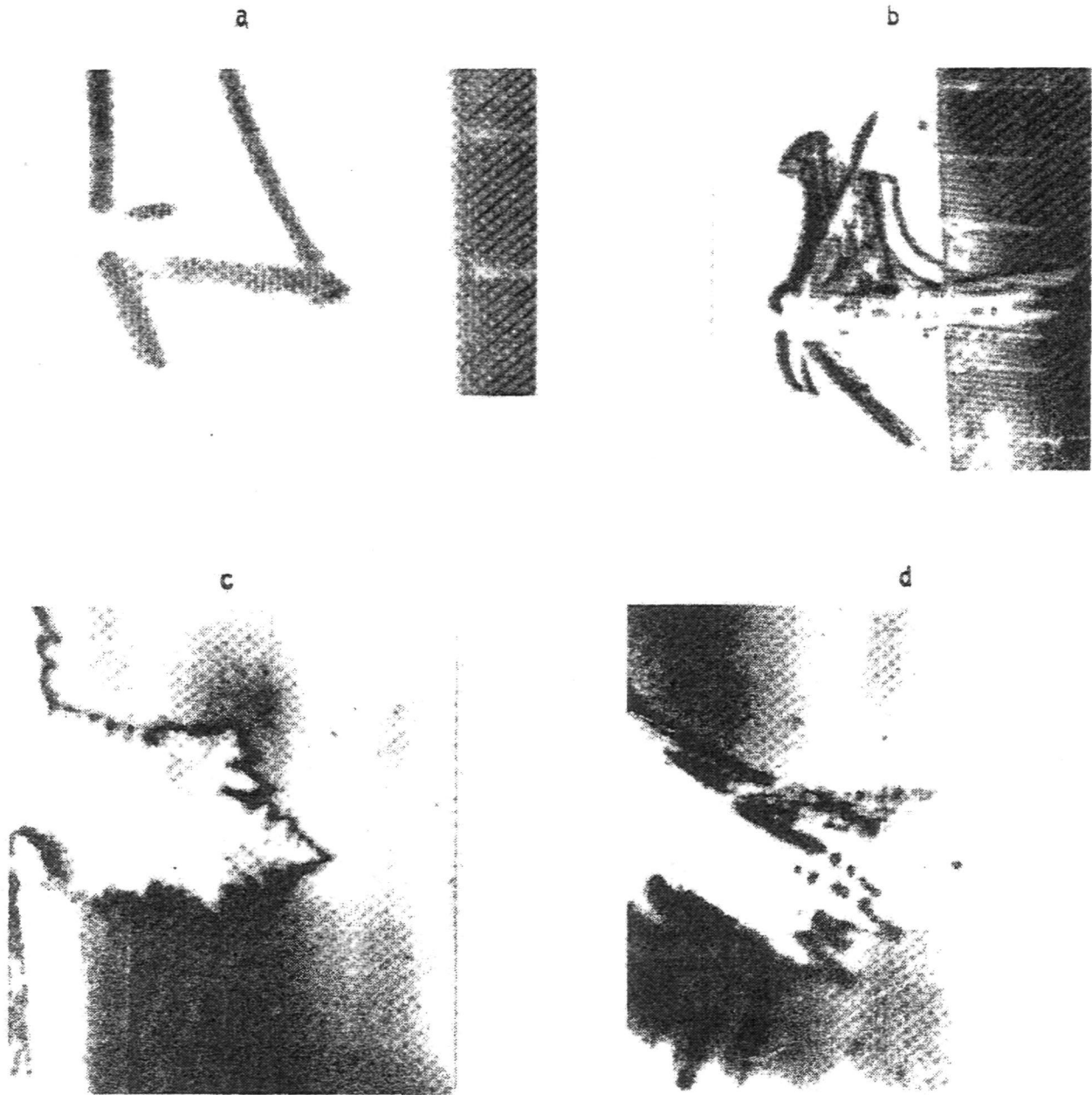


Figure 5. Spatial delay in the separation of the plume from the crystal increases with increased velocity. a and b are 3.0 M  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  dendrites with  $V = 0.02$  cm/sec, spatial delay = 0.16 cm and  $V = 0.2$  cm/sec, delay = 1.7 cm. c and d are 28% salinity sea water dendrites with  $V = 0.008$  cm/sec, delay = 0.16 cm and  $V = 0.025$  cm/sec, delay = 0.5 cm.

environmental fluid. As supercooling is increased, the morphology of the dendrites change, the branches becoming finer and apparently more fragile.

### DISCUSSION

Convective flow is sufficiently slow that the regime is laminar for all situations examined, with  $Re \lesssim 20$ . The convective velocity is consistent with the expected density differences. It increases as  $\Delta\rho^n$  ( $n \sim 1$  to a first approximation). The growth velocity of the dendrites on the other hand increases as  $\Delta\rho^m$  ( $m \sim 2-3$  to a first approximation) so that beyond a critical excess the growth is sufficiently rapid to mitigate any effect of 1-g convection. An estimate of Grashoff number ( $Gr$ ) is difficult, since the dimension to be taken as relevant for convection is not obvious, and the physical properties of the fluids under the experimental conditions are not known very precisely; a crude estimate is in the range 500 to 5000. A reduction of gravity by  $10^4$  would reduce  $Gr$  in proportion, with a corresponding overall reduction in mass heat transfer and velocity.

The role of increasing fineness of dendrites with supercooling is to be assessed in terms of their likelihood of breaking in the local flow or self-induced buoyancy (O'Hara and Tiller) (2). One might expect their strength to increase as  $d^4$  ( $d =$  diameter) with both buoyancy forces and drag force increasing approximately  $d^2$ , so finer dendrites would be more likely to fracture. On the other hand, finer dendrites might be expected to contain fewer defects; there is probably an optimum size for maximum fracture probability.

The lag of convection in detaching from a growing dendrite is to be interpreted in terms of a sufficient dimension being required to enable the buoyant fluid to separate - to be interpreted analytically in terms of a critical Rayleigh number. The possibility exists that there is a convective plume ahead of the visible plume which cannot be detected by the Schlieren technique.

This is limited by the optical path difference caused by the width of the convective plume ( $\sim$  mm), and the refractive index differential ( $\sim 10^{-3}$ ). This gives an order of magnitude refractive index gradient of  $10^{-2} \text{ cm}^{-1}$  overall; the detail of the local gradient is somewhat masked by the nature of the path length integration accomplished by the Schlieren system.

### CONCLUSION

The optical technique used in this experiment gives immediate qualitative information on the nature of the induced fluid flow around free growing dendrites. In the two systems investigated, new crystal orientations appear. In sodium sulfate this occurs only beyond a critical supercooling, and can be hypothesized as being associated with local shear resulting from natural convection. In the case of ice, new orientations apparently result from buoyant displacement of the larger crystals. A better understanding of these physical mechanisms will come from studies over a wider range of environmental conditions than has been attempted so far. In particular, a low-g experiment in which convective velocities are substantially reduced should yield a comparison situation in which no secondary crystals are produced and where growth velocities are uninfluenced by the fluid flow; in this case the optical system should yield detail of the molecular diffusion properties in a stationary environment around the growing dendrite. A candidate material for a study is sodium acetate - a trihydrate with a convenient melting temperature of 58 C.

The comparison study will give a better understanding of the mechanism of dendrite growth and its application in higher velocity crystallization, situations which often occur in metals (3) and solutions.

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### ACKNOWLEDGEMENT

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