



## DENDRITE TIP GROWTH VELOCITIES OF SETTLING $\text{NH}_4\text{Cl}$ EQUIAXED CRYSTALS

A. Ramani and C. Beckermann  
 Department of Mechanical Engineering  
 The University of Iowa  
 Iowa City, IA 52242

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### Introduction

Dendritic growth is of great practical importance in solidification of metallic materials. The growth and morphology of dendritic crystals influence the grain structure, microstructure, micro- and macro-segregation, porosity and other defects and properties of cast products. Not surprisingly, a great deal of studies have been devoted to measuring or modeling certain aspects of dendritic growth. Much of this work has concentrated on the behavior of a single dendrite tip growing freely into an "infinite" supercooled liquid. In this case, all latent heat and solute released at the advancing solid/liquid interface is diffused and advected into the liquid. Such free growth occurs in equiaxed solidification of both pure materials (thermal only) and alloys. In alloys, solutal transport is usually the rate limiting process because the thermal diffusivity is much larger than the mass diffusivity.

Much of the previous work has concentrated on the limiting case of purely diffusional transport of heat and/or solute in the supercooled liquid, and the effects of flow are neglected. For an isothermal tip with a paraboloid profile, the diffusion field is described by the well known Ivantsov solution (1):

$$\Omega = \text{Pe}_t \exp(\text{Pe}_t) E_1(\text{Pe}_t) \quad (1)$$

where  $E_1$  is the exponential integral. For the solutal case, the tip Peclet number,  $\text{Pe}_t$ , and the dimensionless supercooling,  $\Omega$ , are defined, respectively, as

$$\text{Pe}_t = \frac{V_t R}{2D}; \quad \Omega = \frac{\bar{C}_i - C_o}{\bar{C}_i (1 - \kappa)} \quad (2)$$

where  $V_t$  and  $R$  are the tip velocity and radius, respectively,  $D$  is the mass diffusivity in the liquid,  $\kappa$  is the equilibrium partition coefficient, and  $\bar{C}_i$  and  $C_o$  are the liquid concentrations at the interface and at infinity, respectively. Since Eq.(1) only gives a solution for the product  $V_t R$ , the marginal stability principle (2) is commonly used to provide another relation for the product  $V_t R^2$ . This result can be written as (3)

$$V_t = \frac{4Dm\bar{C}_i(\kappa-1)}{\Gamma/\sigma^*} (Pe_t)^2 \quad (3)$$

where  $\Gamma$  is the Gibbs-Thomson coefficient,  $m$  is the slope of the liquidus line, and  $\sigma^*$  is a stability constant. Langer and Muller-Krumbhaar (4) suggest a value of  $0.025 \pm 0.007$  for  $\sigma^*$ , while Huang and Glicksman (5) measured a value of 0.0194 for pure SCN at high supercoolings. Recently, Liu et al. (6) measured  $\sigma^* = 0.026$  for  $\text{NH}_4\text{Cl}$  crystals growing from an aqueous solution along the [100] direction.

The effect of melt flow on free dendrite tip growth has been studied experimentally by several researchers for the case of pure substances (thermal transport only) (5,7,8,9). Generally it was observed that the growth rate increases with increasing flow velocity and that the stability constant may be different from the diffusion limit. Analytical solutions have been obtained for the case of a uniform flow approaching the dendrite tip from a direction opposite to the growth direction with a velocity,  $U_\infty$ . The solutions are based on the Stokes flow approximation (10), Oseen type rectilinear flow approximation (ORFA), Oseen type viscous flow approximation (OVFA), or potential or inviscid approximations, the details of which can be found in Dash and Gill (11). Recently, a solution was obtained by Xu(12) that is claimed to be valid for all values of the free stream velocity,  $U_\infty$ .

This article reports on experimental free dendrite tip growth velocity data obtained for equiaxed  $\text{NH}_4\text{Cl}$  crystals settling in an infinite, quiescent, supercooled  $\text{NH}_4\text{Cl}-\text{H}_2\text{O}$  solution. The relative velocity between the crystal and the solution, or  $U_\infty$ , is equal to the settling speed and is controlled by the density difference between the solid and liquid phases and the drag of the crystal. Preliminary comparisons are made with an available analytical solution for dendrite tip growth in the presence of convection.

### Experiments

Experiments were performed in a square settling column containing a supercooled solution of ammonium chloride in water, as illustrated in Fig.1. The glass column had inner dimensions of 5 cm  $\times$  5 cm  $\times$  75 cm (length) and was mounted inside a larger column made of Lexan. Water from a constant-temperature bath circulating in the space between the two columns allowed for a precise control (within 0.1°C) of the temperature of the solution. Equiaxed dendritic crystals were generated in a cooled tube above the settling column and were introduced into the supercooled solution through a small hole, which allowed only a few crystals to enter the column. The  $\text{NH}_4\text{Cl}-\text{H}_2\text{O}$  solution was prepared through saturation at a specified temperature (about 22°C). Supercoolings achieved in the various tests ranged from 0.2 to 1.1°C, and initial equivalent crystal diameters were between 1 and 3 mm. During settling, the crystal is approximately in thermal equilibrium with the solution.

Upon entering the supercooled solution, the "test" crystal grew as it settled in the column. The growth velocity of the primary dendrite tips was measured by taking photographs of the crystal at two locations, about 15 cm apart, along the settling path. An enlarged image of a typical  $\text{NH}_4\text{Cl}$  crystal is shown in Fig. 2. The photographs were analyzed to determine the tip to tip length of the primary dendrite arm best visible in the image (correcting for orientation). The tip velocity,  $V_t$  is then equal to half the change in the primary arm length divided by the time elapsed between the two photographs. The relative error in the dendrite tip velocity was estimated to be less than 6%. Despite the fact that the orientation of the dendrite tips with respect to the flow is different for each of the six primary tips and that the flow field around the crystal cannot be expected to be uniform, all crystals grew in a remarkably symmetric fashion (see Fig. 2). This symmetry can be attributed to occasional turning of

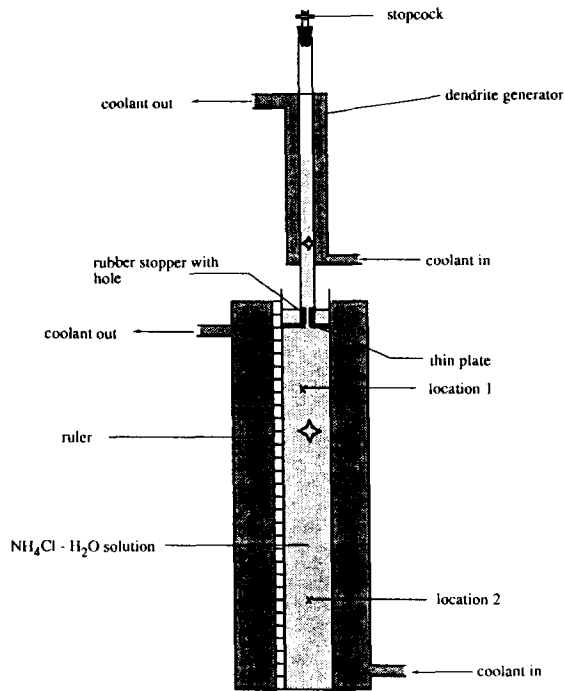


Figure 1. Schematic of the experimental apparatus.

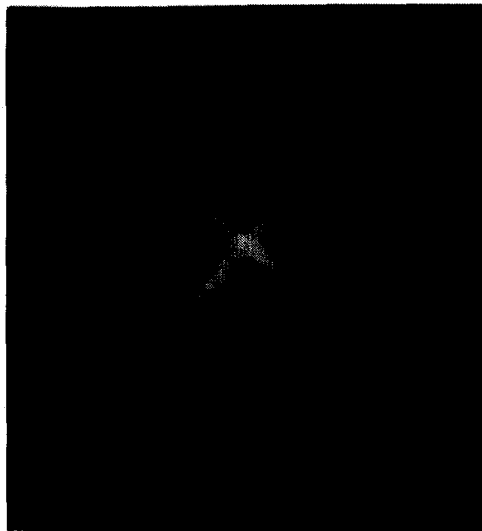


Figure 2. Photograph of a typical settling NH<sub>4</sub>Cl equiaxed crystal (the tip to tip length of the crystal is 3.5 mm).

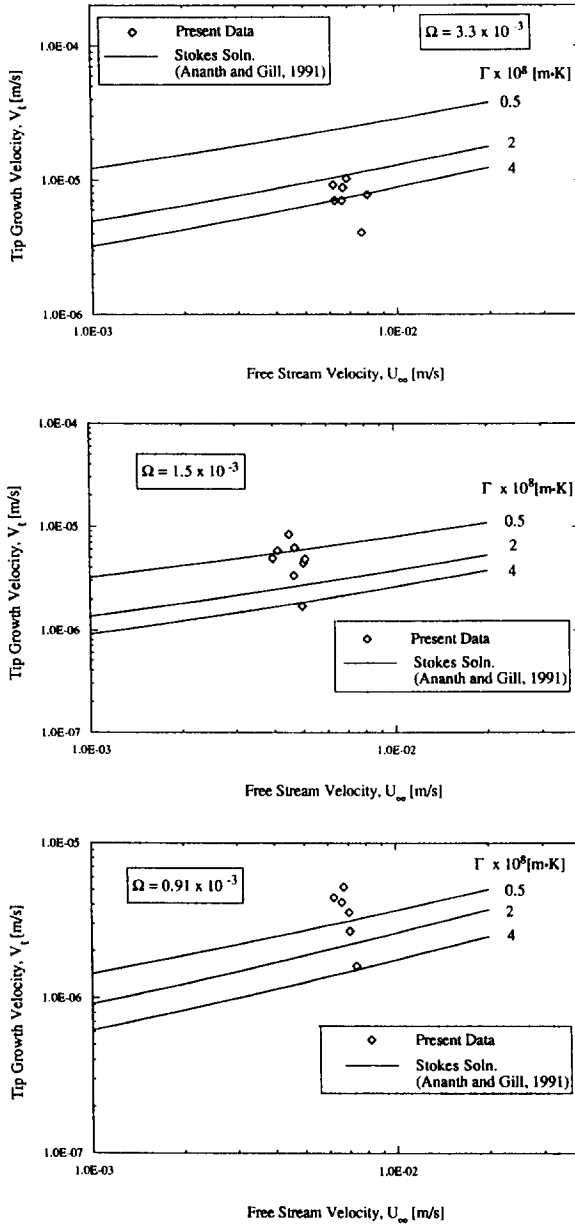


Figure 3. Measured and predicted tip growth velocities as a function of the relative velocity between the crystal and the liquid. (a)  $\Omega = 3.3 \times 10^{-3}$ , (b)  $\Omega = 1.5 \times 10^{-3}$ , (c)  $\Omega = 0.91 \times 10^{-3}$ .

the crystal in the flow. Therefore, the measured tip velocities can only be interpreted as average velocities for the entire crystal.

The instantaneous settling velocity,  $U_\infty$ , of the crystal was measured using a video camera. Because of the increase in the size of the crystal, the settling velocity increased by 2 to 20% (depending on the supercooling) between the two measurement locations. The velocity increase was almost linear in time, and only the mean settling velocity is reported here. A reduction in the distance between the measurement locations (15 cm) was not possible due to the small tip velocities at small supercoolings

TABLE 1  
Properties and Parameters Used in the Calculations

Parameter	Value
mass diffusivity, D	$2 \times 10^{-9} \text{ m}^2/\text{s}$
partition coefficient, $\kappa$	0
liquidus slope, m	- 4.8 K/wt%
stability constant, $\sigma^*$	0.025
Schmidt number, Sc	511
initial concentration, $C_0$	72 wt%
Gibbs-Thomson coefficient, $\Gamma$	$0.5 \text{ to } 4.0 \times 10^{-8} \text{ Km}$

and limits in the resolution of the dendrite arm length measurements (about 0.1 mm). In some experiments, the distance was doubled, and for the same supercooling and average settling velocity, the dendrite tip velocity was found to be the same within experimental scatter. The simple settling experiment of the present study allowed for no control over the relative velocity between the crystal and the liquid, and all velocities fell between 3 and 9 mm/s, depending on the initial crystal size.

### Results and Discussion

Measured tip growth velocities are plotted against the settling velocity of the crystals in Figs. 3a to 3c for three different dimensionless solutal supercoolings (see Eq.(2)). For each supercooling, significant scatter ( $\pm 30\%$ ) can be observed in the measured tip velocities. Similar scatter has recently been reported by Miyata and Tanaka (9) in their forced convection experiments for pure succinonitrile with a fixed dendrite, and may be attributed to varying orientations of the tips with respect to the settling direction as well as to measurement uncertainties (see above). As expected, the tip velocity generally increases with increasing supercooling.

Also shown in Figs. 3 (lines) is the Stokes solution by Ananth and Gill (10) for free growth of an isolated dendrite tip with a uniform flow approaching the tip opposite to the growth direction. All parameters and properties used in the calculations are listed in Table 1. The largest uncertainty exists in the value of the Gibbs-Thomson coefficient,  $\Gamma$ , for  $\text{NH}_4\text{Cl}$ , and no values were found in the literature. Values for  $\Gamma$  between  $0.5 \text{ to } 4.0 \times 10^{-8} \text{ Km}$  give reasonable agreement of the measured data with the Stokes solution, with  $2 \times 10^{-8} \text{ Km}$  being an approximate mean. Note that any uncertainty in the value of the stability constant  $\sigma^*$  is overshadowed by the uncertainty in  $\Gamma$ . The present differences between the data and theory are not uncommon, even for pure substances (13). More generally, there is considerable doubt about the applicability of the Stokes solution for an isolated dendrite tip to the present experiments, because the flow field at the tips is influenced by the presence of the entire equiaxed crystal (regardless of orientation). Furthermore, the Stokes solution does not take into account the density difference between the solid and liquid, which is about 30% for the  $\text{NH}_4\text{Cl-H}_2\text{O}$  system.

### Summary

Dendrite tip growth velocities were measured for equiaxed  $\text{NH}_4\text{Cl}$  crystals settling in a supercooled aqueous solution. Data are reported as a function of the relative velocity between the crystal and the solution and several supercoolings. The tip velocities are more than two orders of magnitude higher than those in a purely diffusive environment. The data show considerable scatter, which can be attributed to orientation effects, measurement uncertainties, or other unknown influences (such as the

varying overall structure of the crystals). Preliminary comparisons with the Stokes solution of Ananth and Gill (10) for a single dendrite tip growing into an approaching uniform flow show that the measured tip velocities can be approximately predicted. However, uncertainties with regard to the Gibbs-Thomson coefficient of  $\text{NH}_4\text{Cl}$  are large. It can be concluded that more accurate theories are needed to predict dendrite tip growth velocities for equiaxed crystals in the presence of convection.

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