

# Capillary length measurements and noise-driven sidebranches in the dendritic crystal growth of ammonium chloride.

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## Abstract

Dendritic crystal growth is an important example of nonequilibrium pattern formation that involves both nonlinear and noise-driven effects. Testing theoretical models requires careful measurements of the relevant materials parameters. For the growth of ammonium chloride crystals from aqueous solution, previous published estimates of the capillary length have varied by over a factor of 20. We report a new technique for measuring the capillary length for non-faceted materials.

For sidebranches, we find that no simple power law describes either the average sidebranch amplitude or the average sidebranch envelope. Instead, the effective power law exponent appears to increase as a function of distance from the dendritic tip. The branch amplitude is also larger than predicted by simple models of noise-driven sidebranching.

## Introduction

Dendritic crystal growth is commonly observed in the growth of non-faceted materials from a pure melt or supersaturated solution. The crystals are characterized by a smooth, nearly parabolic tip, with sidebranches emerging a short distance behind the tip. Much of the beauty of complex crystal structures results from the intricate development and subsequent competition of these sidebranches. For general reviews, see [1] and [2].

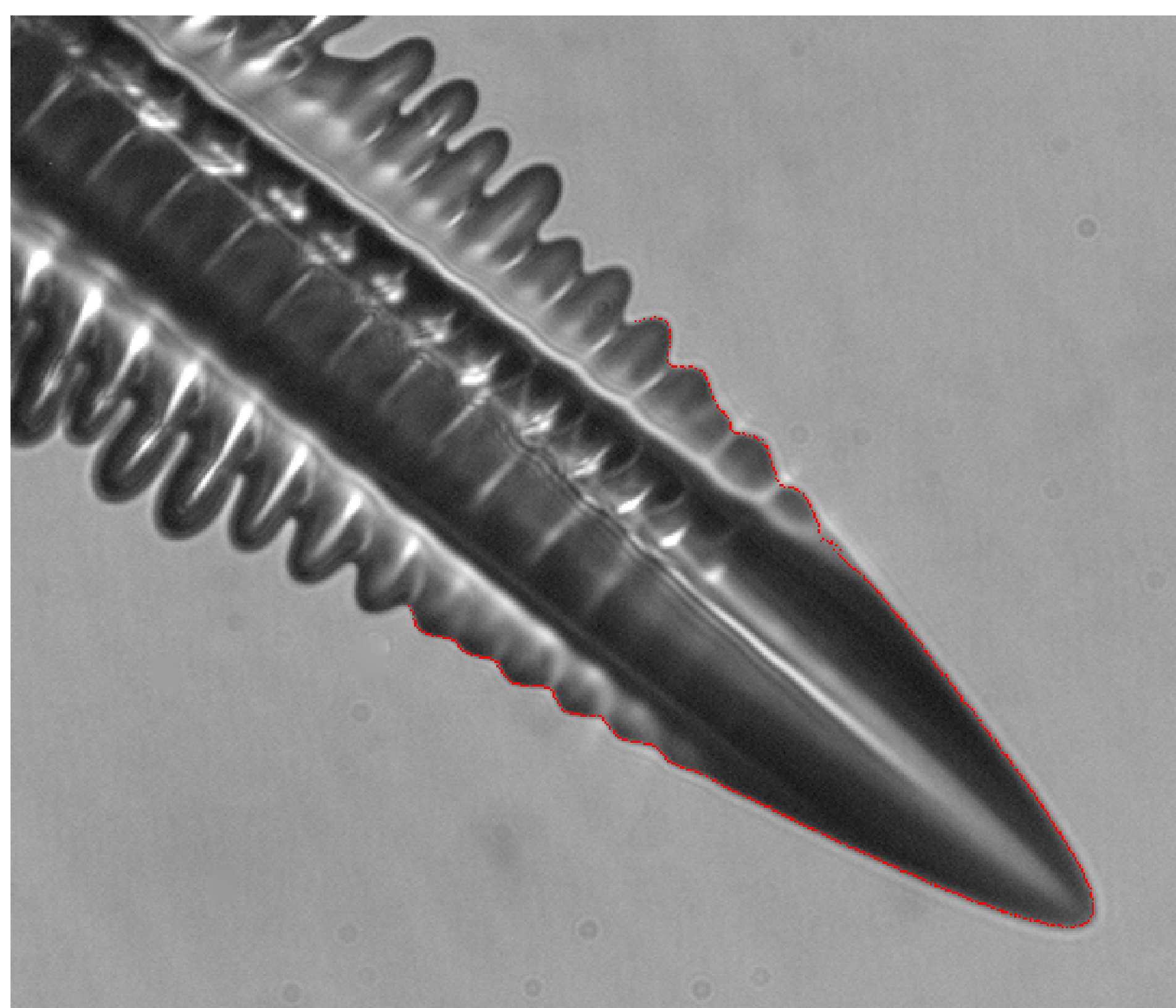


Figure 1: Dendritic crystal of  $\text{NH}_4\text{Cl}$  growing from aqueous solution. The image is approximately  $400\ \mu\text{m}$  across.

Considerable experimental and theoretical effort has focused on measuring the properties of the sidebranch structure, understanding the origin of the sidebranches, and looking for scaling laws that might govern their ultimate development. Previous extensive studies of sidebranch structure have been reported for succinonitrile [3, 4, 5], ammonium bromide [6, 7], Xenon [8], ammonium chloride [9], and succinonitrile and succinonitrile/acetone alloys [10].

## Theory

The basic theory for steady state diffusion-limited dendritic crystal growth is presented in [11]. For growth from solution, the growth is limited by the diffusion of impurities. The driving is typically expressed in terms of a dimensionless supersaturation,  $\Delta$ . In this experiment, the typical temperature variations are less than  $\pm 0.02^\circ\text{C}$ , so we adopt a simple linear model for  $\Delta$ , namely

$$\Delta = c_T(T_{eq} - T)$$

where  $T_{eq}$  is the temperature at which a flat interface would be in equilibrium, and  $c_T$  is to be determined empirically.

## Theory for a Spherical Crystal

The theory for diffusion-limited growth of an isotropic spherical crystal in an isothermal solution is developed in Ref. [11]. The central result used here is that the radial growth velocity,  $dR/dt$ , is given by

$$\frac{dR}{dt} = \frac{D}{R} \left( \Delta - \frac{2d_0}{R} \right) \quad (1)$$

where  $R$  is the radius of the crystal,  $D$  is the diffusion coefficient for  $\text{NH}_4\text{Cl}$  in aqueous solution,  $d_0$  is the capillary length, and  $\Delta$  is the dimensionless supersaturation.

## Experiment

An aqueous solution of ammonium chloride was placed in a glass cell mounted in a massive copper block, surrounded by an outer aluminum block, and placed on a microscope enclosed in a temperature-controlled insulating box. The temperature of the system was then oscillated to cause the crystal to grow and dissolve. Fits to Eq. 1 were used to determine the product  $Dd_0$  and  $c_T$ .

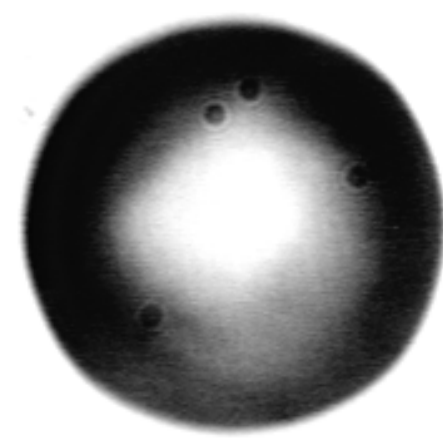


Figure 2: Spherical crystal of  $\text{NH}_4\text{Cl}$  held in unstable equilibrium. The radius is  $26\ \mu\text{m}$ .

## Results: Growth of a Spherical Crystal

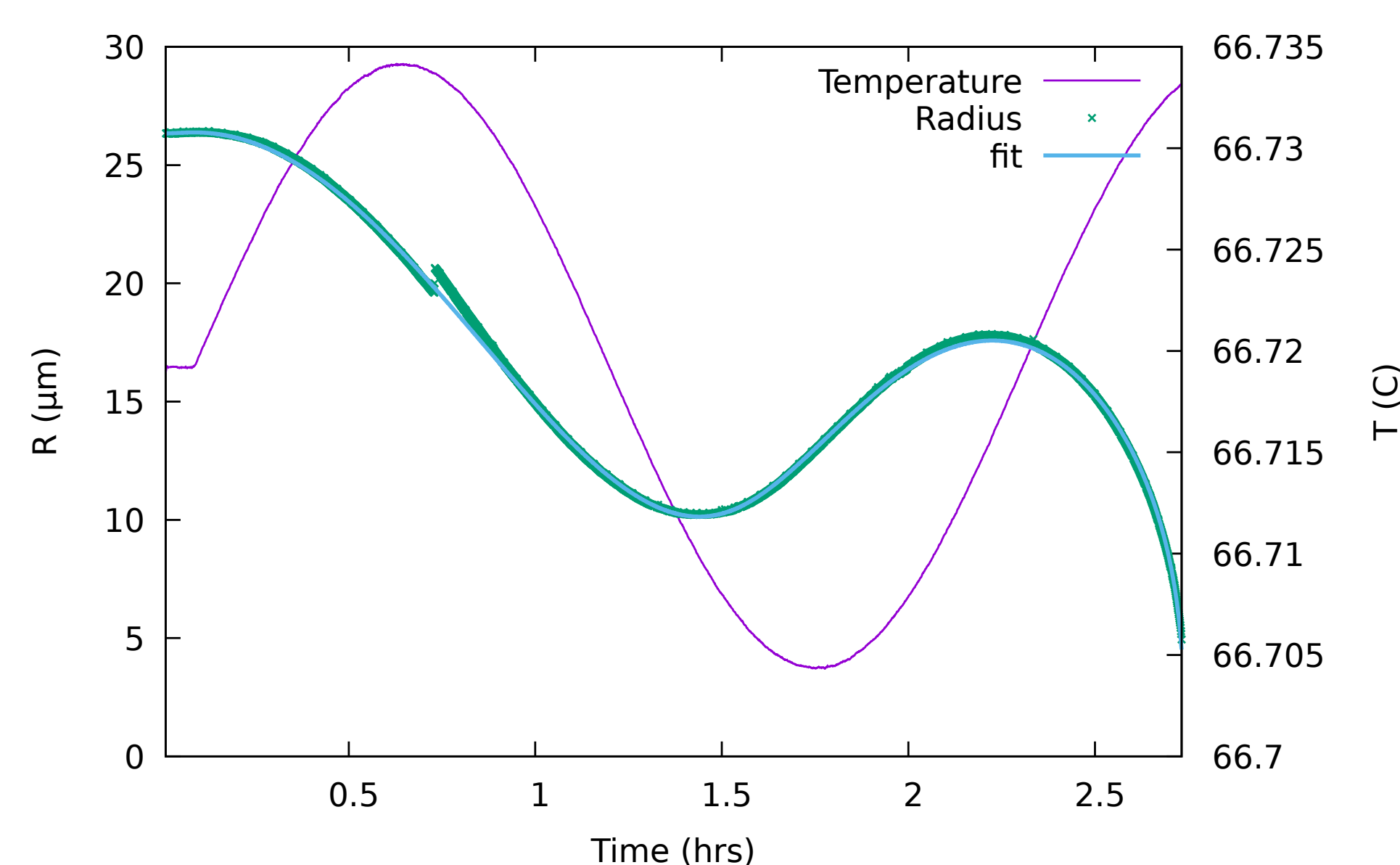


Figure 3: Radius vs. time for a spherical crystal subject to an oscillating temperature (shown in purple). The solid curve is a fit to Eq. 1. At the end of the run, the crystal was dissolving rapidly and eventually completely dissolved.

Fits to Eq. 1 do not give independent measures of  $D$  and  $d_0$ ; instead we find that the product

$$Dd_0 = 0.58 \pm 0.04\ \mu\text{m}^3/\text{s}.$$

Using a typical estimate [12, 13] of  $D = 2500\ \mu\text{m}^2/\text{s}$ , we estimate  $d_0 = 0.23 \pm 0.02\ \text{nm}$ . This value is between the values of  $0.065\ \text{nm}$  in Ref. [12] and  $1.59\ \text{nm}$  in Ref. [13].

## Theory for Dendritic Growth

A growing dendrite is characterized by a smooth, nearly parabolic tip of radius  $\rho$  growing at constant speed  $v$ . The tip radius and velocity are related to the "stability constant"  $\sigma^*$  by

$$\sigma^* = \frac{2d_0D}{v\rho^2}, \quad (2)$$

A short distance behind the tip, sidebranches emerge with a characteristic wavelength  $\lambda$  that is typically  $\sim 3\rho$ . These sidebranches start out approximately uniform, but compete in a complex nonlinear coarsening process [3, 6].

## Results: Sidebranches

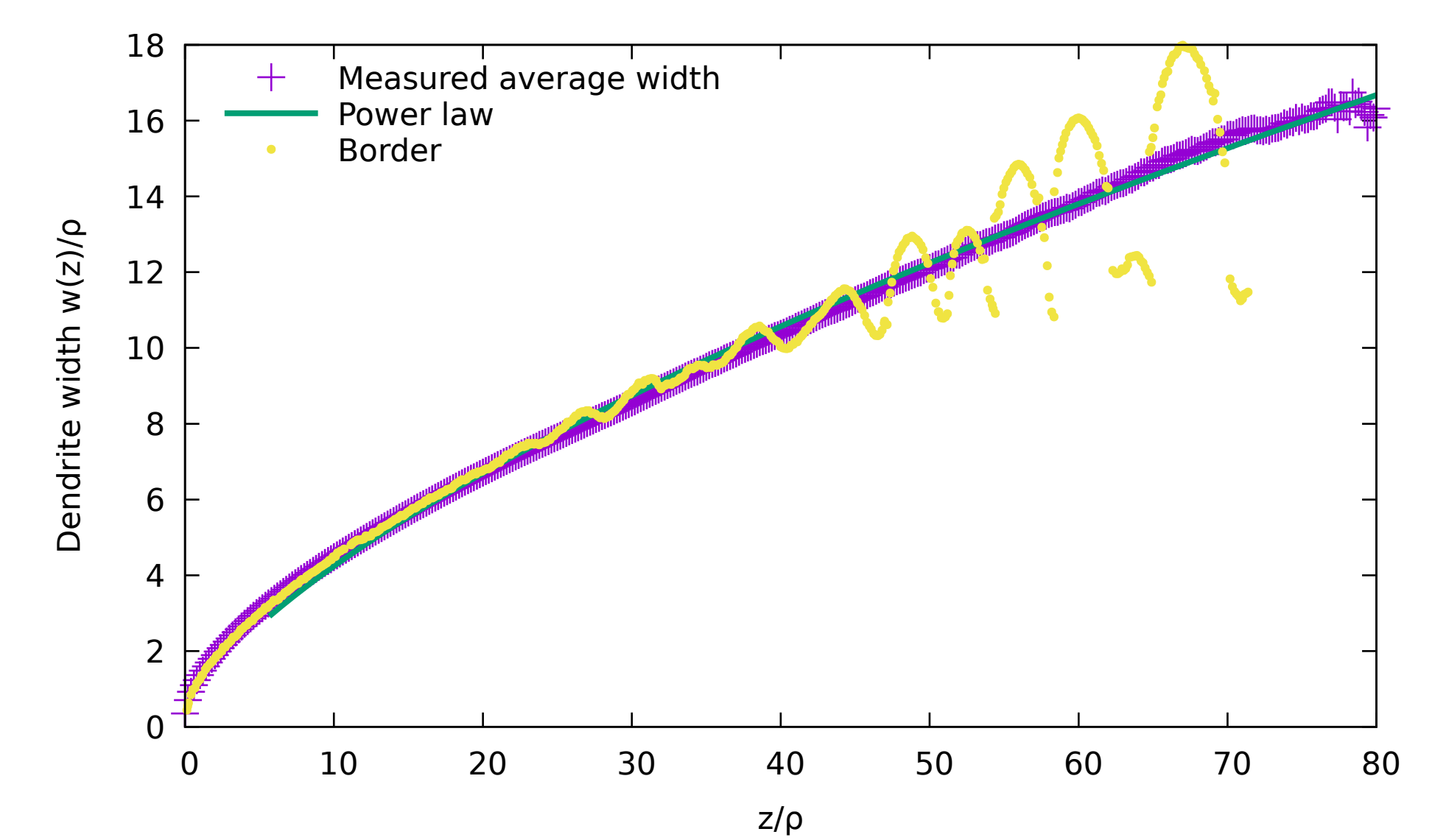


Figure 4: Width of a dendrite as a function of distance away from the tip. All distances are scaled by the tip radius  $\rho$ . Shown for comparison are the average width for all images from the same run, as well as a power-law fit to that average.

The average width is shown in Fig. 4 along with a power-law fit with exponent  $0.658 \pm 0.002$ . For reference, the width from one single image is also included. A log-log version is shown in Fig. 5; it is clear that the width is not well-described by a single power law. Instead, there is a gradual transition from a power law of roughly  $\frac{1}{2}$  close to the tip to a much larger value further away. Sufficiently far back from the tip, the largest branches grow as independent dendrites, so the slope will approach 1.

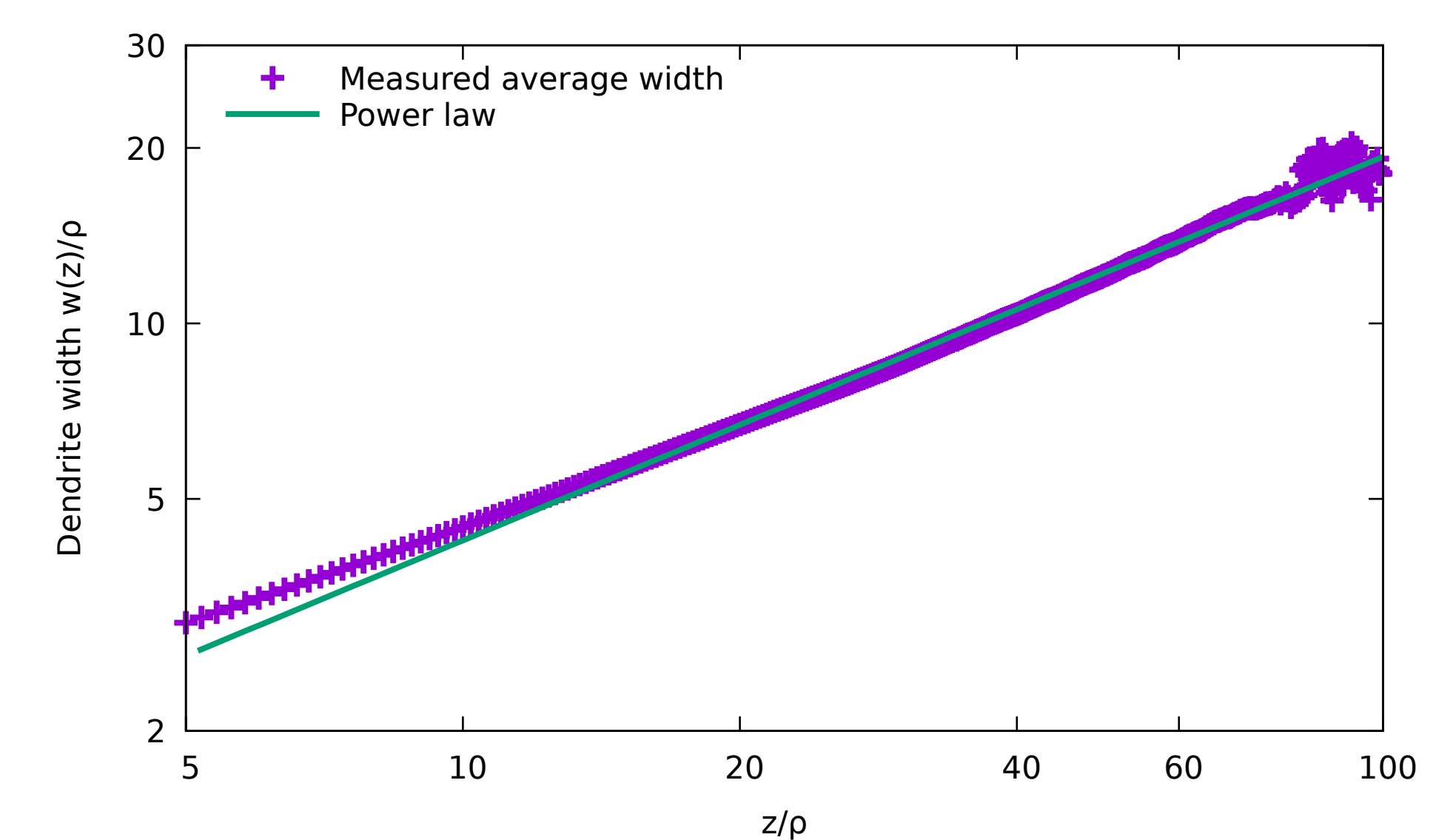


Figure 5: A log-log plot of dendrite width, along with a power-law fit.

## Discussion

No single power-law adequately describes the development of dendritic sidebranches. The results above are for the average crystal width, but similar results hold for other measures, including the RMS sidebranch amplitude and the envelope of active sidebranches.

One remaining question is the extent to which these intricate sidebranching patterns reflect intrinsic oscillatory instabilities versus forcing due to external noise. Our preliminary assessment is that the sidebranches are generally larger than would be anticipated solely due to thermal noise.

## References

- [1] W. J. Boettinger, et al. (2000) *Acta Materialia* 48 (1):43.
- [2] M. Asta, et al. (2009) *Acta Materialia* 57 (4):941 ISSN 1359-6454.
- [3] M. E. Glicksman, et al. (1981) *Acta Metall* 29:717.
- [4] D. P. Corrigan, et al. (1999) *Phys Rev E* 60 (6 Part B):7217.
- [5] Q. Li, et al. (1998) *Phys Rev E* 57 (3):3176.
- [6] A. Dougherty, et al. (1987) *Phys Rev Lett* 58:1652.
- [7] Y. Couder, et al. (2005) *Phys Rev E* 71 (3):031602.
- [8] O. Wittwer, et al. (2006) *Phys Rev E* 74 (4, Part 1):041604 ISSN 1539-3755.
- [9] K. Kishinawa, et al. (2008) *Phys Rev E* 77:030602.
- [10] A. J. Melendez, et al. (2012) *J Cryst Growth* 340 (1):175 ISSN 0022-0248.
- [11] J. Langer (1980) *Rev Mod Phys* 52:1.
- [12] T. Sawada, et al. (1995) *Phys Rev E* 51:R3834.
- [13] A. Tanaka, et al. (1992) *J Cryst Growth* 125 (1-2):59.