The initial growth of sidebranches in ammonium chloride dendrites

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Abstract

We report measurements for the initial stages of sidebranching during the dendritic growth of ammonium chloride from supersaturated aqueous solution. The earliest sidebranches are approximately periodic; they are first evident about 36 times behind the tip, where \( \rho \) is the tip radius, and have an average initial spacing of about 5 times \( \rho \), though both values show considerable variation. The initial sidebranch amplitude grows approximately exponentially, but quickly saturates as sidebranches compete and coarsening sets in. This initial sidebranch growth is reasonably consistent with what would be expected for noise-driven sidebranches, though there are some quantitative differences.

Keywords: A1. Dendrites, A1. Morphological stability, A1. Interfaces, B1. Salts

1. Introduction

Dendritic crystal growth is frequently observed during the crystallization of non-faceted materials from pure melt or supersaturated solution. Common examples include structures formed during the solidification of many metals and metal alloys [1]. For reviews, see Glicksman [2], Jaafar et al. [3], Asta et al. [4], and Boettinger et al. [5].

Dendrites are also more conveniently observed in the crystallization of transparent model compounds; see Akamatsu and Nguyen-Thi [6] and Huang and Wang [7] for overviews. Examples include succinonitrile and pivalic acid [2], rare gases, such as helium [8] and xenon [9], and some salts, such as ammonium bromide [10, 11] and ammonium chloride [12, 13, 14, 15, 16].

Dendritic crystals are characterized by an initially smooth tip that grows at approximately constant speed. Due to the anisotropy of the underlying crystal structure, the tip is not axisymmetric, but instead develops fins along the preferred growth directions. Those fins are unstable, and sidebranches begin to develop on top of them a short distance behind the tip. Much of the beauty of complex crystal structures results from the intricate development and subsequent competition of those sidebranches.

Considerable theoretical and experimental effort has focused on understanding the origin of the sidebranches, measuring the properties of the sidebranch structure, and looking for scaling laws that might govern their ultimate development. Previous extensive studies of sidebranch structure have been reported for succinonitrile [17, 18, 19], pivalic acid [20, 21], ammonium bromide [10, 11], xenon [22, 23], ammonium chloride [21, 24, 25], and succinonitrile and succinonitrile-acetone alloys [26].

In this paper, we focus on the early sidebranches in the dendritic growth of ammonium chloride at low supersaturation, and compare the results to those predicted for noise-driven sidebranches. Specifically, we consider three quantities: the distance to the first sidebranch, \( z_{sbr} \), the initial sidebranch spacing, \( A \), and the amplitude of the initial sidebranch envelope, \( A(z) \). For noise-driven sidebranches, predictions for these quantities were developed by Langer for axisymmetric dendrites [27], and extended to non-axisymmetric dendrites by Brener and Temkin [28]. Details are in the theory section below.

Some of these predictions have been tested for the dendritic growth of pure materials. For succinonitrile [17, 18], the measured values of \( z_{sbr} \) and \( A \) are in accord with the predictions of Ref. [28]. Similarly, for xenon, both the measured value for \( z_{sbr} \) and the sidebranch envelope \( A(z) \) were found to be consistent with the theory. For pivalic acid [20], on the other hand, the measured value of \( A \) is larger than the predicted value.

This paper adds to the range of materials tested by examining the dendritic growth of ammonium chloride from aqueous solution. We find that the measured value for \( z_{sbr} \) is consistent with the theory in Ref. [28], but the measured spacing \( A \) is smaller than expected. The measured sidebranch amplitude \( A(z) \) follows a modified version of the predicted shape, but only for a narrow range of distances \( z \). The underlying causes for these differences remain unclear.

2. Theory

The basic background theory for steady state diffusion-limited dendritic crystal growth is presented in [11]. Solutions incorporating anisotropy in the surface energy, known as microscopic solvability, are presented in [29]. Briefly, for slow growth when kinetic effects may be ignored, the crystal is characterized by a smooth tip of radius \( \rho \) growing at constant speed \( v \). The tip radius and velocity are related to the dimensionless “stability constant” \( \sigma^* \) by

\[
\sigma^* = \frac{2DvD}{\rho v^2}, \tag{1}
\]
where $D$ is the relevant diffusion constant, and $d_0$ is the capillary length, which is related to the solid-liquid interface energy. The predicted value for $\sigma^*$ depends on the anisotropy in the surface energy.

Direct testing of Eq. 1 has proven difficult, in part due to challenges in measuring all of the relevant materials properties to sufficiently high precision, and in part due to the complications introduced by convection in most terrestrial experiments. Moreover, in both microgravity \cite{30, 31} and terrestrial experiments \cite{26, 16}, as well as in phase-field numerical simulations \cite{32, 33}, the value for $\sigma^*$ is not constant, but decreases with increasing undercooling or supersaturation over reasonable ranges of experimental interest. Nevertheless, it still provides a useful dimensionless parameter that at least approximately characterizes the operating state of a dendrite.

### 2.1. Tip Shape

The typical scale for dendritic structures is set by the radius of curvature $\rho$ at the tip. Very close to the tip, the shape is approximately a paraboloid of revolution, but for a cubic material such as NH$_4$Cl, it becomes systematically wider in the planes of the sidebranches and develops fins. The sidebranches ultimately develop on top of those fins. In the present work, we only consider crystals where the sidebranches grow in the plane of the image, as in Fig. 1 below.

For small four-fold anisotropy, Ben Amar and Brener \cite{34} found that the lowest-order correction to the parabolic shape in the plane containing the sidebranches is

$$\frac{z}{\rho} = \frac{1}{2} \left( \frac{w}{\rho} \right)^2 - A_4 \left( \frac{w}{\rho} \right)^4,$$

where the tip is at the origin, $z$ is the distance from the tip along the axis defined by the main dendrite stem, $w$ is the half-width of the dendrite, $\rho$ is the radius of curvature at the tip, and $A_4$ is a small material-dependent parameter. This expression is only valid close to the tip, however. Further back, Brener \cite{35} found that the width of the fins deviates significantly from parabolic and instead scales as a power law

$$\frac{w}{\rho} = a \left( \frac{z}{\rho} \right)^{\beta},$$

where $a = (5/3)^{1/3}$ and $\beta = 3/5$. A more complete description of the three-dimensional shape obtained during phase field simulations is given by Karma, Lee, and Plapp in Ref. \cite{36}.

The net result is that it is challenging to experimentally determine the tip radius. Any estimate of $\rho$ involves fitting data over a finite range of $z$. At small $z$, data may be limited by the experimental resolution, while at larger $z$, incipient sidebranches become more important. Intermediate $z$ values may span the crossover from Eq. 2 to Eq. 3.

In the simulations of Ref. \cite{36}, Karma et al. found that the fitting parameters for both the fourth-order and power-law fits depended on the maximum distance $z$ used in the fit, though that variability also depended on the underlying anisotropy. For xenon dendrites, Bisang and Bilgram \cite{22} found that the power-law shape Eq. 3 provided a more robust fit to the data than Eq. 2.

On the other hand, Lacombe, Koss, and Glicksman \cite{31} found that a hyperbolic shape worked well for pivalic acid dendrites.

For the growth of ammonium chloride crystals at small supersaturation, Dougherty and Lahiri \cite{15} determined that using data up to a distance of $6\rho$ in Eq. 2 gave a more robust fit than the power law, and found $A_4 = 0.004 \pm 0.001$. Melendez and Beckermann \cite{20} found a similar shape correction worked well for succinonitrile-acetone alloys. LaCombe, Brener, and et al. also found a similar shape correction worked well for succinonitrile \cite{37}. In this work, we follow Ref. \cite{15} and use Eq. 2 to estimate the tip radius.

A typical crystal image, along with the fit to Eq. 2, is shown in Fig. 1. Two sets of sidebranches are visible in the plane of the image; two additional sets are growing perpendicular to the plane along the main stem of the dendrite.

![Figure 1: Ammonium chloride dendrite growing from supersaturated aqueous solution. The image is 390 μm across. The tip radius is 3.1 μm and the growth speed is 1.6 μm/s. The inner curve (green) is the best-fit parabola for the tip. The fourth-order fit (Eq. 2) is on the far left in blue; the negative fourth-order term causes the fit to deviate sharply from the tip before the sidebranches become significant. In this image, the first sidebranches are visible approximately 31ρ behind the tip, and have an initial wavelength of approximately 4.6ρ.](image)

### 2.2. Sidebranches

A short distance behind the tip, sidebranches emerge on top of the fins with a characteristic wavelength $\lambda$ that is typically about $3 \sim 6\rho$. These sidebranches start out approximately uniform, but compete in a complex nonlinear coarsening process \cite{17, 10}. Larger branches continue to grow, while shorter ones stop, or even begin to dissolve back, eventually giving rise to structures with a wide range of length scales.

There have been several approaches to model the origin of sidebranches. One possibility is that the tip growth itself is actually slightly oscillatory, and the emerging sidebranches reflect that underlying oscillation \cite{38, 39, 40}. Though oscillations were observed in pivalic acid \cite{38}, no such oscillations were detected in xenon \cite{22}, ammonium bromide \cite{10}, or in the present work. Another recent line of analysis by Glicksman \cite{2, 41, 42} considers the importance of capillary-mediated interface perturbations in driving deterministic branching.

The conventional approach is to model sidebranches as arising from microscopic noise. The approximate periodicity of the sidebranches is the result of the selective amplification of that noise \cite{27, 10, 28, 43, 44, 23}.

Several experiments have shown that applied perturbations can produce periodic sidebranches. Directional solidification
experiments with pivalic acid/coumarin alloys have shown that directly applying a pulsing laser to dendritic tips can drive an oscillating tip and produce a sidebranch structure with the corresponding wavelength [45]. Similarly, mechanical vibrations have been shown to induce sidebranches in the free dendritic growth of xenon [23]. Analogous results have also been obtained in viscous fingering experiments [46]. These experiments show that oscillating-tip solutions are possible, but do not address the question of what happens as the amplitude of the applied noise is reduced to zero.

For directional solidification, sidebranches have been observed in bursts that are coherent within a burst, but uncorrelated between bursts [47]. This situation has been extensively studied computationally by Echebarria et al. [48]. They find that in the presence of a thermal gradient, both noise-induced and limit cycle branches are possible, which likely explains the coherent bursts seen in Ref. [47]. In the absence of a thermal gradient, however, as in free dendritic growth, phase field studies such as those by Karma and Rappel [43] show that persistent sidebranches only appear in the presence of noise.

For free dendritic growth, Langer showed how the selective amplification of noise near the dendrite tip could generate trains of sidebranches [27]. For the axisymmetric case, he found that the resulting branches were qualitatively similar to those observed in experiments, but estimated that the predicted amplitude was smaller than observed. Brener and Temkin [28] extended that work to non-axisymmetric growth, where the needle crystal develops fins in the directions favored by anisotropy, and the sidebranches develop on top of those fins. This led to an increased rate of growth. Specifically, they found that the noise-induced sidebranch amplitude $A(z)$ is given by a stretched exponential of the form

$$A(z) = \rho S_0 \exp \left[ \frac{2}{3} \left( \frac{\bar{w}^3(z)}{3\sigma^2 \rho^2} \right)^{1/2} \right].$$

where $\bar{w}(z)$ is the average width of the dendrite given by Eq. [3] and $S_0$ is the dimensionless noise amplitude. For ammonium bromide dendrites growing from supersaturated aqueous solution, Gonzalez-Cinca et al. [49] give $S_0 \sim 6 \times 10^{-3}$ as a conservative over-estimate of the noise value. The distance to the first sidebranch, $z_{obs}$, can then be defined as the distance for which $A(z)$ reaches some arbitrary fraction of $\rho$.

For the initial sidebranch spacing, Brener and Temkin [28] predicted

$$\frac{A(z)}{\rho} = 2\pi \left( \frac{3}{5} \right)^{3/10} \sqrt{3\sigma^2} \left( \frac{\bar{w}}{\rho} \right)^{1/5}. \tag{5}$$

Beyond the initial development of the sidebranches, a number of approaches have been developed to model the interaction and coarsening of sidebranches. Phase field models attempt to incorporate the full physics of the three-dimensional problem [50, 51]. The addition of noise to phase field simulations has also been shown to produce sidebranching structures similar to those observed in experiments [43, 52, 53], though it continues to prove challenging to perform the calculations in the small undercooling and small anisotropy range appropriate for ammonium chloride solution growth [54, 55]. A variety of numerical models and approaches are reviewed in Jaafar et al. [3].

Experimentally, power law behavior has also been reported for a number of integral parameters of dendritic growth, including the sidebranch envelope, contour area, and volume [19, 56, 57, 22, 58, 23]. In contrast, the average width of both pivalic acid and ammonium chloride dendrites was found to follow a simple power law only over a limited range of $z$ values [21]. These results all highlight the complex ways sidebranches interact beyond their initial development.

3. Materials and Methods

The experiments were performed with a solution of ammonium chloride (Fisher Scientific, 99.99%) in water (Fisher Scientific, HPLC grade, filtered through a 0.1 $\mu$m filter). The concentration was approximately 36% NH$_4$Cl by weight, for a saturation temperature of approximately 66.7°C. The solution was placed in a 40 $\times$ 10 $\times$ 2 mm$^3$ glass spectrophotometer cell sealed with a Teflon stopper held in place by epoxy. The cell was mounted in a temperature-controlled copper block, surrounded by a temperature-controlled outer aluminum block, and placed on an insulated microscope stage. The entire apparatus was enclosed in a temperature-controlled insulated Plexiglas box. The rms temperature fluctuations of the copper block were approximately $2 \times 10^{-4}$ °C. Temperature gradients were estimated to be less than 0.001 °C/mm. Additional details of the experimental apparatus and protocol are given in Ref. [59].

The solution was heated to dissolve all the solids, stirred to eliminate concentration gradients, and then cooled. Upon cooling, many crystals would nucleate. The system was then warmed until only one seed remained. That seed was held in equilibrium and then cooled at a rate of $-6.0 \times 10^{-4}$ °C/s to allow a single dendrite to develop and grow. Once that crystal became well-established, the cooling rate was increased to $-1.6 \times 10^{-3}$ °C/s. Because the finite cell became depleted as the crystal grew, it was necessary to continually lower the temperature to maintain growth throughout the 10 000 s run. Even at the given cooling rate, however, the crystal did slow significantly; overall the tip velocity varied from 7.2 $\mu$m/s to 0.8 $\mu$m/s. The change in velocity was generally quite slow, however. Over the typical distance and time scales corresponding to the initial growth of sidebranches, the velocity changes were between 1% and 4%.

Although the temperature varied slowly during the course of a run, we still model the growth as that of an isothermal mixture limited by chemical diffusion. For ammonium chloride solutions [60], the thermal diffusion constant is approximately $\alpha = 1.3 \times 10^{5}$ $\mu$m$^2$/s, while we estimate [59] the chemical diffusion constant to be approximately $D \approx 2500$ $\mu$m$^2$/s. The Lewis number is then $\alpha/D \approx 50$, indicating that the process is dominated by chemical diffusion.

3.1. Imaging

Images were obtained at 1-second intervals from a charged coupled device (CCD) camera attached to the microscope and
acquired directly into the computer via a Data Translation DT3155 frame grabber with a resolution of 640 × 480 pixels. The resolution of the images was $0.628 \pm 0.010 \mu m/pixel$. A typical crystal image, with $\rho = 3.1 \mu m$ and $v = 1.6 \mu m/s$, is shown above in Fig. 1.

The interface position was determined by an iterative process, described in detail in Ref. [15]. Briefly, the image intensity was scanned on lines roughly perpendicular to the interface. Over the range of about 4 pixels, the intensity dropped rapidly from the outside to the inside of the crystal. In that transition region, a straight line was fit to the intensity function, and the border was interpolated as the position where that fit intensity equaled the average of the intensity just outside and just inside the crystal. Those border points were used to make initial estimates of the tip position, orientation, $\rho$ and $A_4$. Those initial estimates were then used to run a new set of image scans perpendicular to the interface, and the process was iterated until it converged. A final set of scans was run along the full length of the dendrite to measure the dendrite width $w(z)$.

To fit to Eq. 2 only data with $z \leq z_{max} = 6\rho$ was used. As was shown in Ref. [15], this is a compromise value. Although Eq. 2 applies close to the tip, the small and highly-curved tip is the most difficult part to image accurately, so fits with a small $z_{max}$ tend to be less robust. On the other hand, fits with larger $z_{max}$ may start to include early sidebranches, and also enter a regime where Eq. 2 is no longer appropriate. (See also Ref. [26] for a similar discussion for succinonitrile-acetone alloys.)

4. Results

The width of the early sidebranch region of the crystal from Fig. 1 is shown in Fig. 2 along with the measured average shape $\bar{w}(z)$ for all crystals grown under similar conditions. All distances have been scaled by the tip radius $\rho$.

![Figure 2: Width of a portion of the crystal in Fig. 1 as a function of distance back from the tip. All distances are scaled by the tip radius $\rho$, and only the first few sidebranches are shown. The solid line is the measured scaled width averaged over all crystals grown under similar conditions.](image)

4.1. Tip Radius and Velocity

As the cell became depleted over the course of the run, the tip velocity gradually changed from $7.2 \mu m/s$ to $0.8 \mu m/s$, while the tip radius varied from $1.5 \mu m$ to $4.0 \mu m$. The value of the combination $Dd_0$ for this material was previously reported [59] to be $Dd_0 = 0.78 \pm 0.07 \mu m/s$. The resulting values for $\sigma^*$ in Eq. 1 are shown in Fig. 3. There is a downward trend with velocity, as was seen in previous experiments [30, 31, 26, 16] as well as phase field simulations [32, 33]. For this work, we used the average value $\sigma^* = 0.10 \pm 0.02$.

![Figure 3: Variation of the parameter $\sigma^*$ with growth speed. The error bars indicate one standard deviation. There is a small downward trend with velocity.](image)

4.2. Sidebranches

In Fig. 2 the first sidebranches are visible starting around $z \approx 31\rho$, and the initial spacing is $\lambda = 4.6\rho$. Beyond $z \sim 50\rho$, significant competition between sidebranches clearly affects their growth.

We first measured the envelope of active sidebranches, as in Refs. [23] and [26]. A sidebranch was considered “active” if it was larger than all other sidebranches on the same side closer to the tip. A sidebranch also had to be at least a distance $\rho$ away from the previous branch in order to be considered a new branch.

The average sidebranch wavelength $\lambda$ was estimated by performing a linear fit to the positions of adjacent early sidebranches vs. sidebranch number. The results are shown in Fig. 4. There was considerable variation in spacing from image to image, but the overall mean value was $\lambda = (5.05 \pm 0.01)\rho$, where the uncertainty is the standard deviation of the mean.

![Figure 4: Mean sidebranch wavelength as a function of growth speed. Error bars indicate one standard deviation. There is a very slight downward trend with velocity, but the typical variations at any speed are larger than the overall trend.](image)
We also estimated the distance $z_{sbr}$ to the first detectable sidebranch. Since the identification of the first branch tended to be significantly affected by noise, the following procedure was adopted: The position and amplitude of the first 4 branches were found and fit to a straight line. The amplitude was found by measuring the deviation of the width $w(z)$ from the measured average shape $\bar{w}(z)$. The distance $z_{sbr}$ was taken to be the distance at which the fit sidebranch amplitude would equal an arbitrary threshold of 0.25$\rho$. For the crystal in Fig. 2, this gives $z_{sbr} = 32.8, but there was considerable variation throughout the run. Results for all crystals are shown in Fig. 5. Overall, the average distance was $z_{sbr} = (35.8 \pm 0.1)\rho$, where the uncertainty is one standard deviation of the mean.

Using this value for $z$ in Eq. 5, we would expect $\lambda(z_{sbr}) = (6.1 \pm 0.3)\rho$, somewhat larger than the measured value of $5.05 \pm 0.01$. Conversely, constraining $\lambda$ to the measured value in Eq. 5 would require $z_{sbr} \sim 14\rho$. (Since Eq. 5 depends only weakly on $z$, the dominant uncertainty is in $\sigma^*$.)

![Figure 5: Position of first sidebranch as a function of growth speed. Error bars indicate one standard deviation. There is a slight downward trend with velocity, although the typical variations at any speed are comparable to the overall trend.](image)

Finally, we considered the amplitude of early sidebranches, and compared with the theoretical noise prediction from Eq. 4. Since most of the sidebranch parameters vary only slowly with growth speed, we scaled all crystals by the appropriate tip radius $\rho$.

To estimate $A(z)$, we computed the root mean square (rms) deviation of the measured shape around $\bar{w}(z)$. For $\bar{w}(z)$, we considered several models, including the power law of Eq. 3, a parabola $\sqrt{2\rho z}$ with higher-order corrections, and a hyperboloid, but none fit the data sufficiently well over the range of interest. Instead, we used the actual measured average shape.

The results are shown in Fig. 6, along with a fit to the prediction in Eq. 4 from Ref. 28, with a noise amplitude of $S_0 = (5.6 \pm 0.1) \times 10^{-5}$. It is clear that the amplitude grows more rapidly than the model in the early sidebranch regime, so we also considered a modified fit, where we included an additional dimensionless term $s$ in the exponential factor:

$$A(z) = S_0 \exp \left[ \frac{2}{3} \left( \frac{n^3(z)}{3\pi^2} \right)^{1/2} \right],$$

where all distances have been scaled by $\rho$. The best-fit parameters are $S_0 = (1.1 \pm 0.2) \times 10^{-6}$ and $s = 1.72 \pm 0.03$. The value for $S_0$ is less than the conservative over-estimate of $S_0 \sim 6 \times 10^{-5}$ given by Gonzalez-Cinca et al. 49, but the value for $s$ is not in agreement with the expected value of 1 in Eq. 4.

It is worth emphasizing that the fit is only applicable over a rather narrow range of $z$ values. At small distances, $z \lesssim 20\rho$, the measurements are dominated by noise, while at larger distances, $z \gtrsim 40\rho$, competition among sidebranches slows down their growth. Similar constraints were also apparent in the study of xenon sidebranches 23, where the theoretical fit worked well only in the range of $8 \sim 15\rho$.

As an additional check, we extended Eq. 6 to include an oscillatory term so that it could be applied to individual images, such as Fig. 2.

$$w(z) = \bar{w}(z) + A(z) \sin \left( \frac{2\pi}{\lambda} + \phi \right),$$

where $\lambda$ is the wavelength for that particular image and $\phi$ is the phase. The best fit, with $\lambda = 4.6$, is shown in Fig. 7. The results from these individual fits were consistent with the global average fit above.

![Figure 6: Semi-log plot of the measured sidebranch amplitude as a function of distance from the tip, along with the best fit to Eq. 4 and a fit to the modified prediction in Eq. 6. Beyond about $z = 40\rho$, competition among the sidebranches becomes more important and Eq. 6 no longer applies.](image)

![Figure 7: Width of one side of the crystal from Fig. 2 along with a fit to Eq. 7. At larger distances, as in Fig. 6, the sidebranches enter a nonlinear competitive regime where the fit is not applicable.](image)

5. Discussion

We have considered the early stages of sidebranching in the growth of ammonium chloride dendrites from supersaturated aqueous solution. When all distances are scaled by the tip radius, the overall features vary only slightly with growth speed,
and are roughly consistent with what would be expected if the sidebranches are due to the selective amplification of noise.

A stretched exponential of the form of Eq. 5 does provide a reasonable fit to the sidebranch amplitude data, but that fit requires an additional factor $s$ in the exponential. The noise amplitude $\sigma_0$ is consistent with that estimated for intrinsic noise [49], and the resulting distance to the first sidebranch, $z_{sbr}$, is also consistent with the theory.

By contrast for xenon, Wittwer and Bilgram [23] found good agreement for Eq. 4 without any additional factor $s$. The reason for the difference is not clear, but it is worth noting that the value for $\sigma^* = 0.10 \pm 0.02$ found in the present work is five times the value $\sigma^* = 0.02$ used in Ref. [23], and the distance to the first sidebranch $z_{sbr}$ in ammonium chloride is roughly twice the value $z_{sbr}/\rho = 17.5 \pm 3$ reported for xenon [23]. Whether these discrepancies are due to different material properties, solution $vs.$ thermal growth, or some other factor, is unclear.

The measured mean sidebranch wavelength $\lambda = (5.05 \pm 0.01)\rho$ for ammonium chloride is slightly smaller than the predicted value of $(6.1 \pm 0.3)\rho$ from Eq. 5. For succinitonitrile [17, 27, 28], the measured value was consistent with the theory, while for pivalic acid, the measured value was slightly larger than predicted [20]. The source of these small differences remains unclear.

It is important to recognize that the range of applicability of Eq. 6 is quite limited, so the fitted function is not particularly well-constrained. At small $z$, there are two main issues. First, emerging sidebranches are potentially masked by measurement noise. Second, measurements of the tip itself (and hence all distances scaled by $\rho$) are also potentially contaminated by early sidebranches. These effects are particularly problematic near the tip because the concentration gradients and corresponding optical distortions are largest there. Measurements of the very early sidebranches and tip shape are thus inextricably intertwined. At larger $z$, the increasing nonlinear competition among sidebranches leads to changes in the expected scaling behavior. At even larger $z$, it is no longer possible to characterize the structure by a single-valued width function $w(z)$. These constraints make it much more challenging to identify whether there are simple underlying scaling laws that govern the origin and initial growth of sidebranches.

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