Sidebranch Development in Free Dendritic Growth

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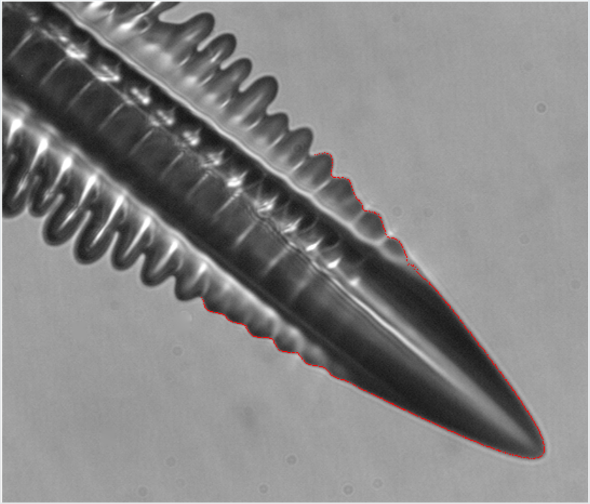
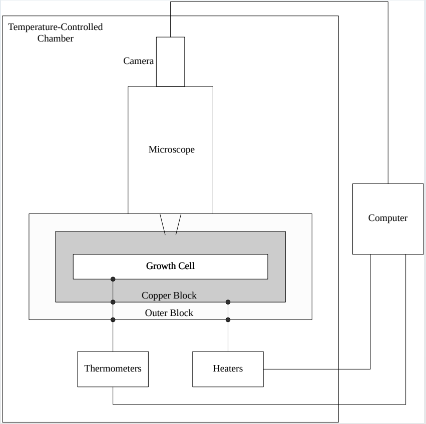
Typical Crystal



NH_4Cl crystal in aqueous solution The image is 400 μm across.

Apparatus



- Growth cell: $40 \times 10 \times 2\,\mathrm{mm}^3$
- Horizontal growth to minimize convection
- Obtain an approximately spherical seed
- Lower temperature $\Delta T \approx 1^\circ\mathrm{C}$ to initiate growth

Theory — I

Diffusion Limited Crystal Growth

u = Dimensionless concentration

$$\begin{aligned} \frac{\partial u}{\partial t} &= D\nabla^2 u \\ u_{interface} &= -d_0 \kappa \\ u_\infty &= -\Delta \\ v_n &= -D\nabla u \cdot \hat{n} \end{aligned}$$

d_0 = capillary length

κ = curvature

Δ = supersaturation

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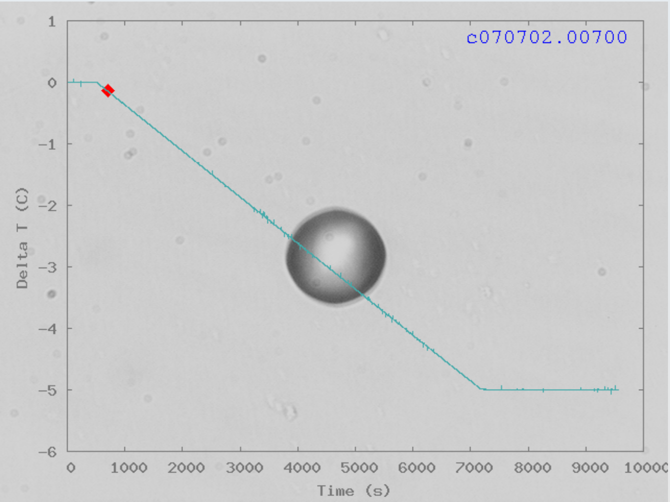
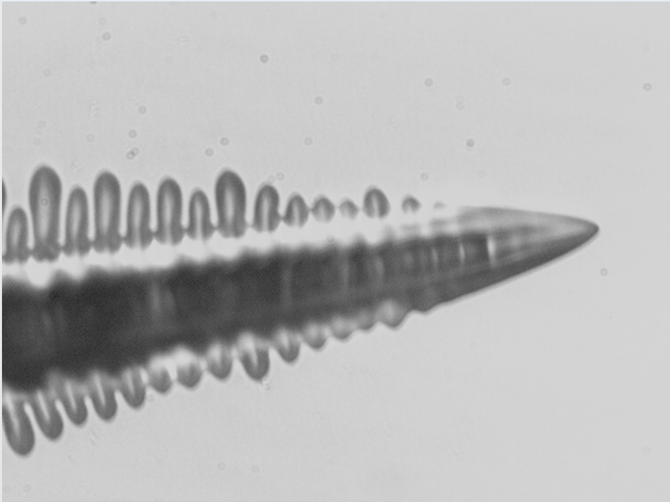
Theory — II

- Two Characteristic Length Scales:
  - $L =$ difusion length $= \dfrac{2D}{v}$ ($\sim$ mm)
  - $d_0 =$ capillary length ($\sim$ nm)
  - Typical scale of pattern is $\sqrt{Ld_0}$ ($\sim \mu$m)
- General Features:
  - Flat interface is unstable
  - Surface tension limits curvature
  - Nonlinear growth and competition leads to structures on a wide range of scales.

Growth from a Nearly Spherical Seed



Ordinary Dendritic Growth



Theory — III

Modeling Dendritic Growth — Approximately parabolic tip

- tip speed v
- tip radius of curvature $\rho = \frac{1}{\sqrt{\sigma^\star}}\sqrt{Ld_0}$
- where the "stability constant" $\sigma^\star = \frac{2d_0 D}{v\rho^2}$
- initial sidebranch spacing $\lambda \sim 4\rho$

Modeling the Dendrite Tip

- First, model the tip, then look for sidebranches as deviations from the initially smooth tip.
- Approximate tip as a parabola

$$z = \frac{x^2}{2\rho}$$

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$$z = \frac{x^2}{2\rho} + A_4 \frac{x^4}{\rho^3}$$

where $A_4 \approx -0.0036$.

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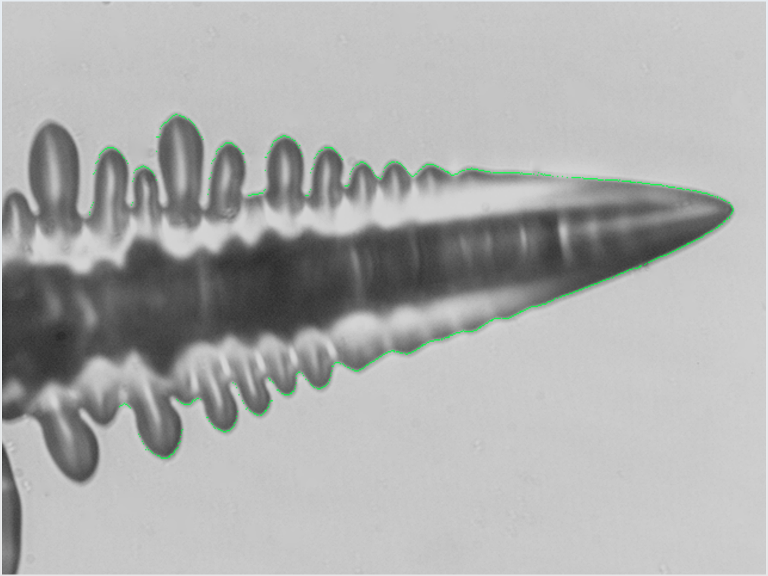
- Or as a power law

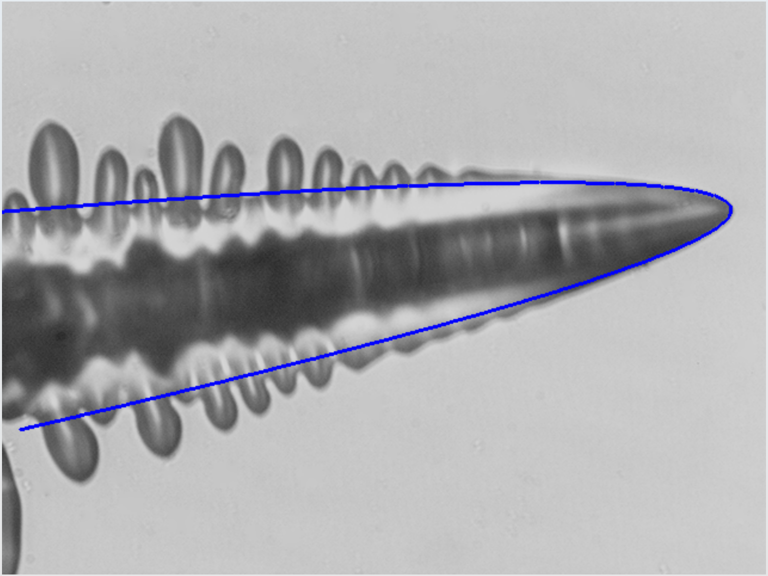
$$x = \frac{z^{\frac{5}{3}}}{(2\rho)^{\frac{2}{3}}}$$

Fitting the Tip



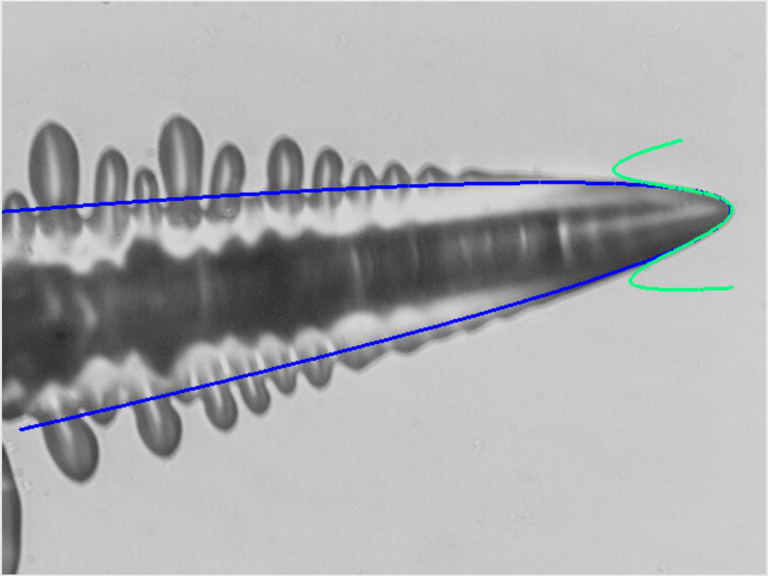
Tip with border points.

Fitting the Tip



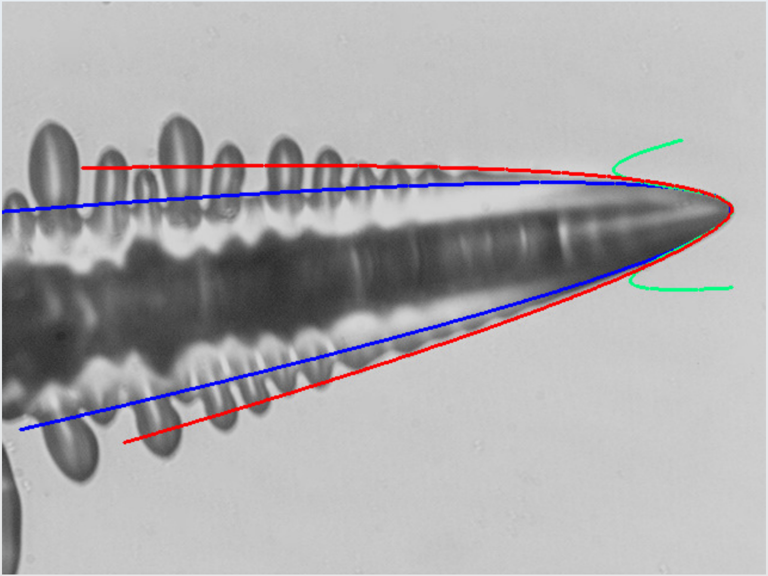
Tip with parabolic fit.

Fitting the Tip



Tip with parabolic fit with fourth-order correction.

Fitting the Tip



Tip with parabolic fit, fit with fourth-order correction, and power law.

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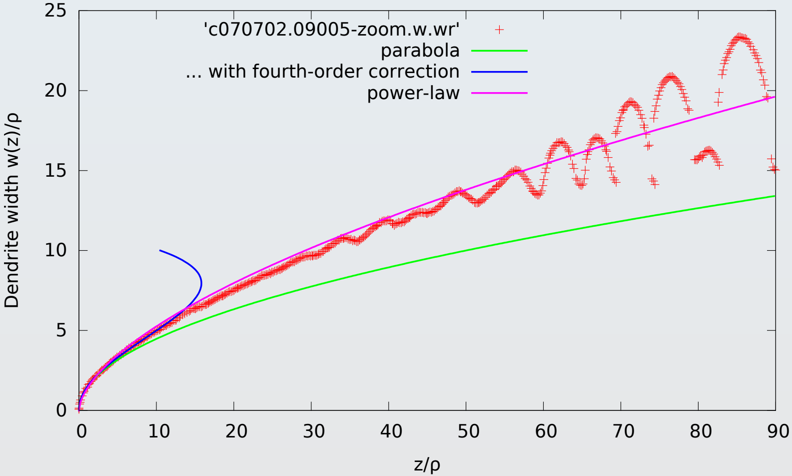
Fitting the Tip



To determine the tip radius ρ, only use data close to the tip, where contamination from the sidebranches is not significant.

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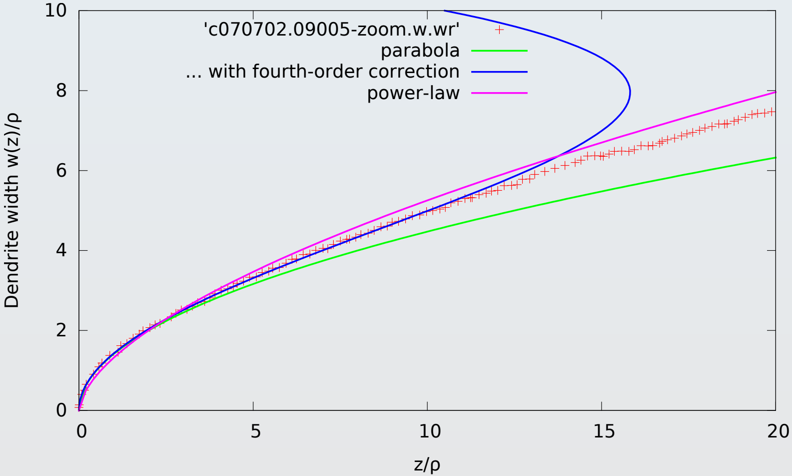
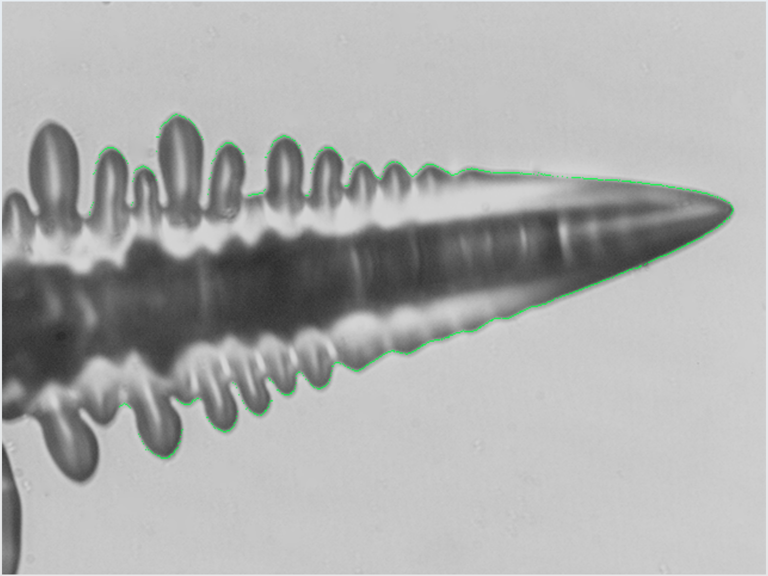
Fitting the Tip



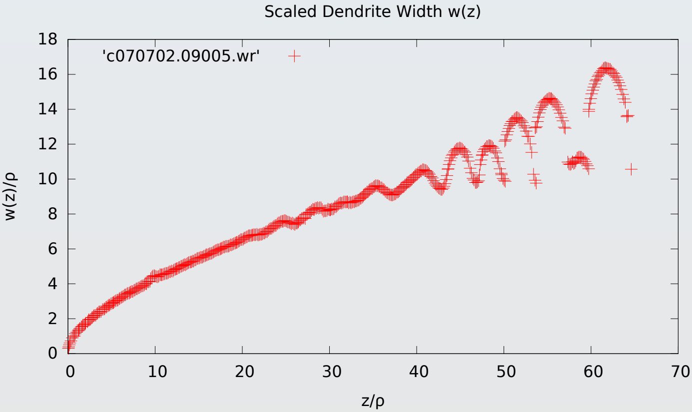
The tip shape is not simple. Near the tip, the fit with the fourth-order correction is the most robust, but it fails for larger distances.

Sidebranch Growth



Return to full set of border points.

- Rotate to make growth horizontal
- Translate all tips to the origin
- Rescale all distances by ρ



Rotated, translated, and scaled dendrite width $w(z)$.

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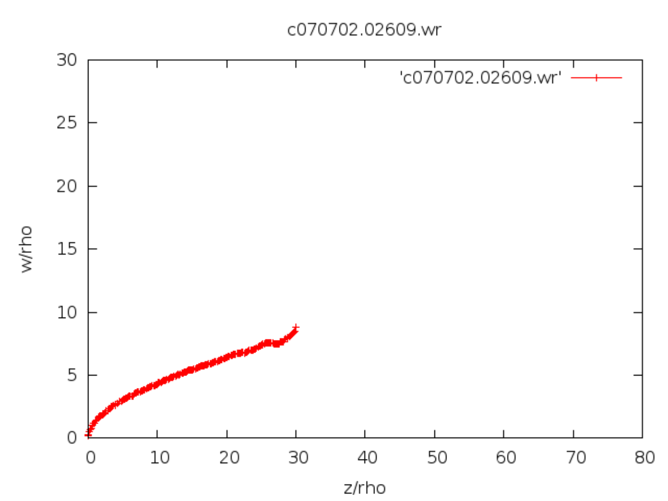
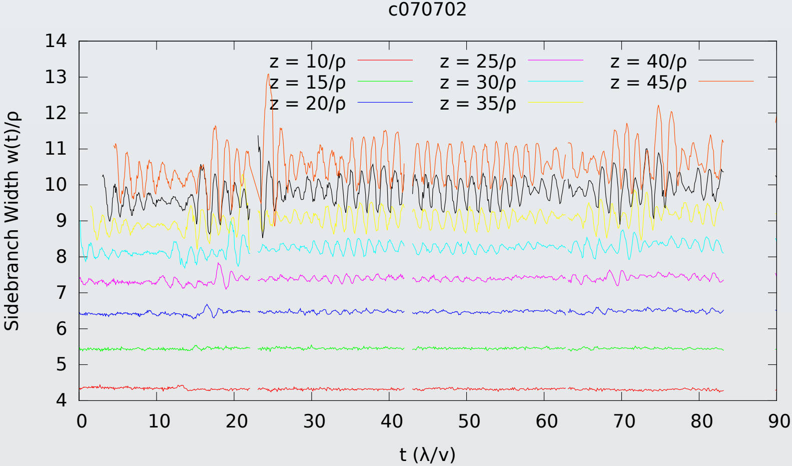
Propagating Sidebranch Waves

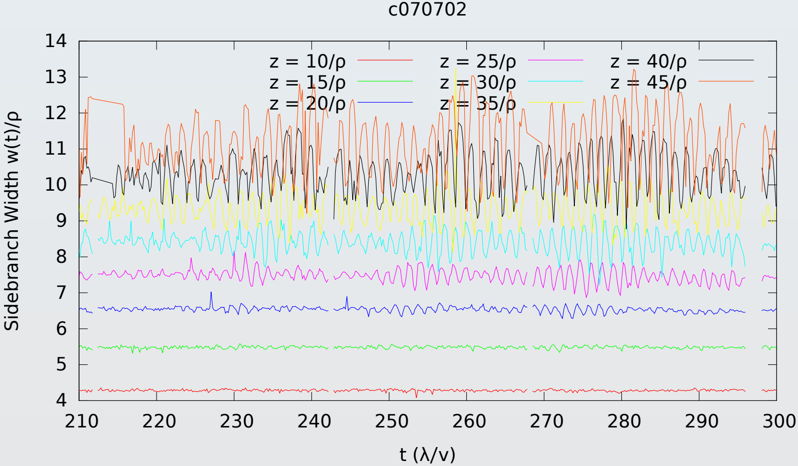


Analyze width time series



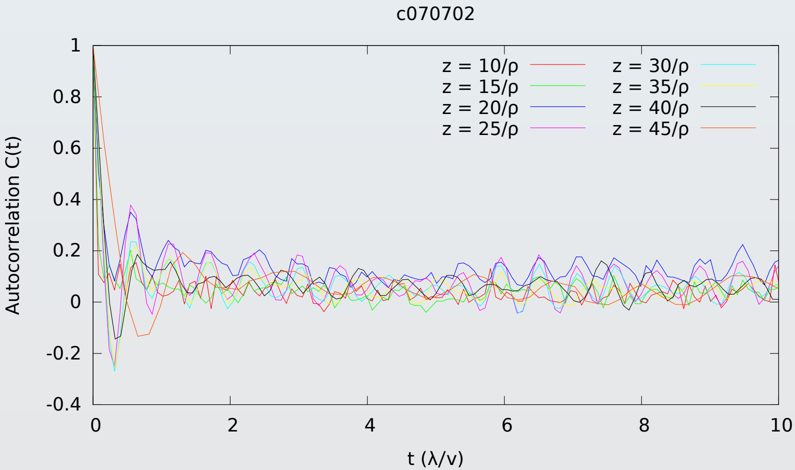
Sample $w(z, t)$ at various fixed z.

Analyze width time series



Same crystal at a later time segment

Autocorrelation



Correlations fall off fairly quickly, particularly for the larger branches

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Correlations

- Do see some “bursts” of sidebranches

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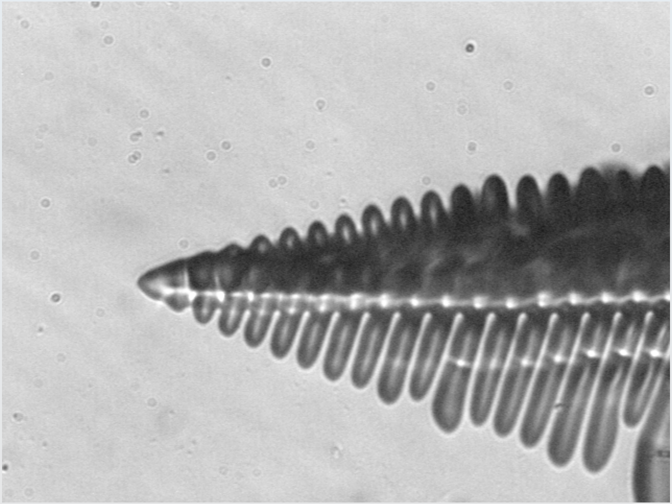
- Correlations die off quickly—even within a burst, branches aren’t strictly periodic
- Correlations drop off more rapidly for large branches, where competition is more significant

Unusual Strongly Periodic Sidebranch Growth



Occasionally, we will see very regular branches. This appears to be an interaction with the cell floor boundary.

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- Steady state growth has approximately constant tip size and speed

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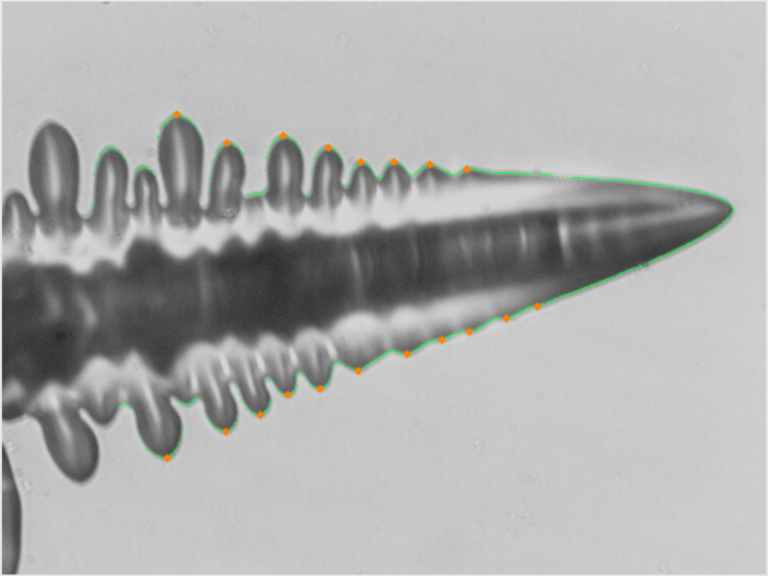
- Steady state growth has approximately constant tip size and speed
- with somewhat regular, but noisy, sidebranches initially emerging
- Measurements of tip size and speed are contaminated by earliest sidebranches
- Measurements of early sidebranches are affected by tip size and shape measurements.
- Bursts of sidebranches do occur
- ... but even they are weakly correlated.
- Both sidebranch amplitude and timing suggest that even if there is a weak underlying oscillatory driving, noise plays a central role even in the earliest stages.

Finding the Sidebranch Envelope



Identify the active sidebranches.

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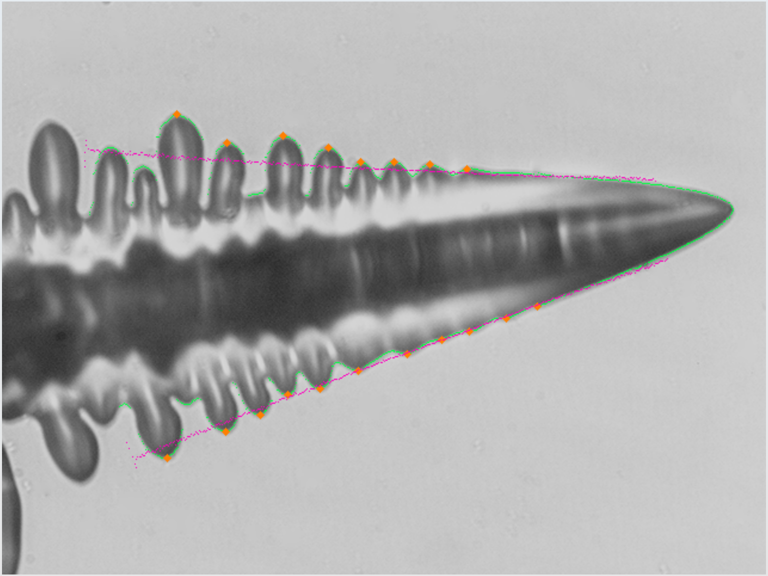
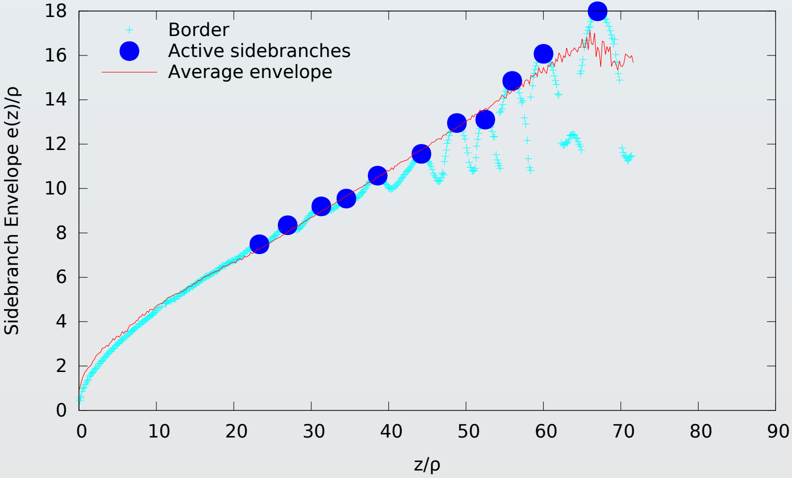
Finding the Sidebranch Envelope



Identify the active sidebranches and compute the average sidebranch envelope.

Finding Sidebranches



Sidebranch Amplitude

- One prediction for the sidebranching amplitude is

$$A(z) = S_0 \exp\left(\frac{2}{3}\left(\frac{w_{ave}^3(z)}{3\sigma^* z\rho^2}\right)^{1/2}\right)$$

where z is the distance back from the tip, ρ is the tip radius, $w_{ave}(z)$ is the average shape of the dendrite, and

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- The noise amplitude S_0 is given by

$$S_0^2 = \frac{2CL^{eq}D}{(\Delta C^{eq})^2\rho^3 v} \approx 6 \times 10^{-5}$$

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Sidebranch Amplitude

- Generically, if $w_{ave}(z)$ scales as a power law with z, the amplitude of the sidebranches is predicted to scale

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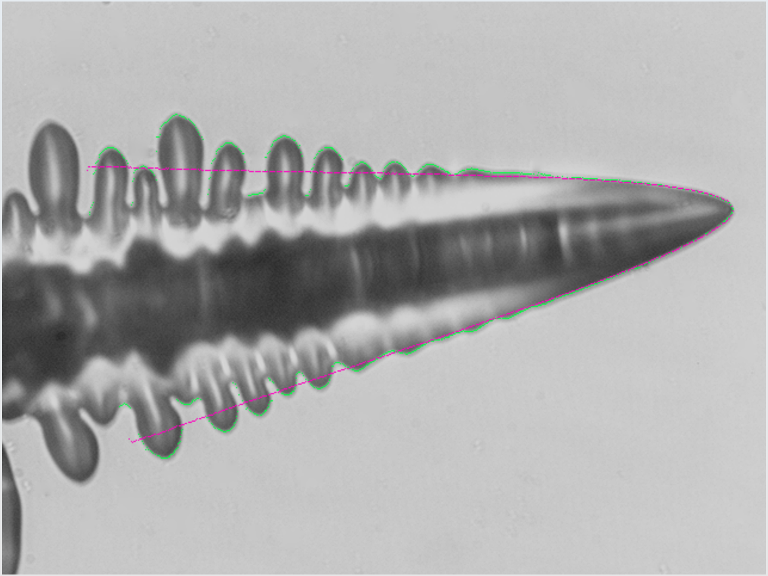
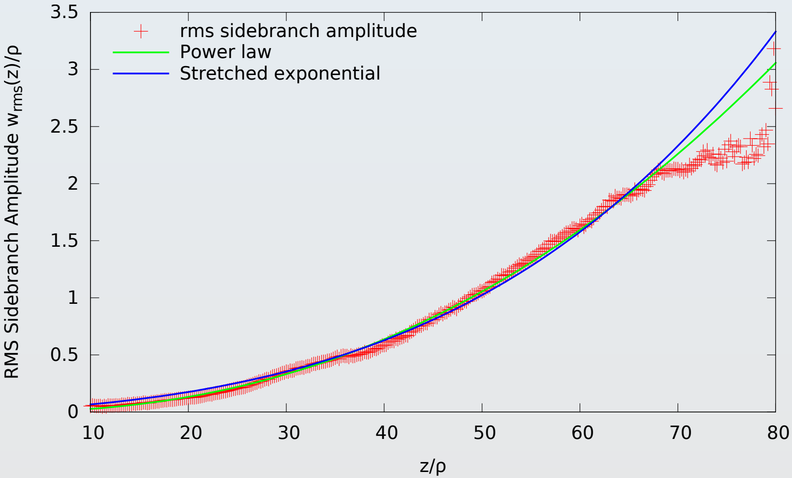
- where α is predicted to be 0.4 if $w_{ave} \sim z^{3/5}$,
- or 0.5, based on the w_{ave} fit found above.

Sidebranch Amplitude



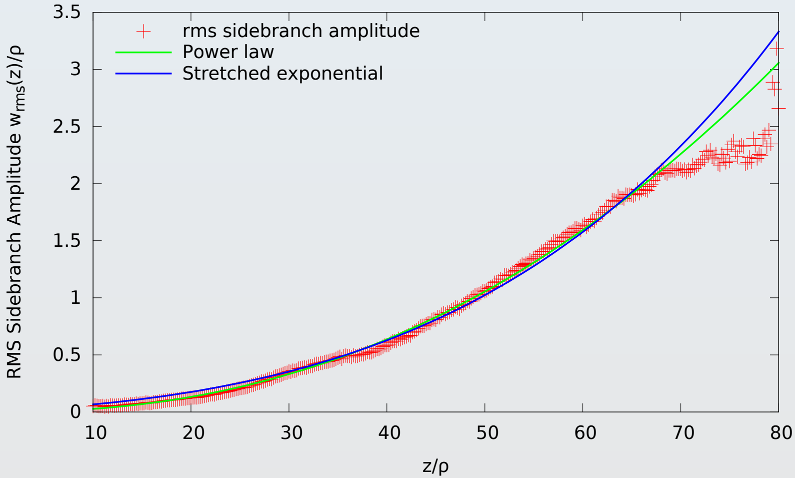
Define sidebranch amplitude as rms variation around the average shape.

Sidebranch Amplitude



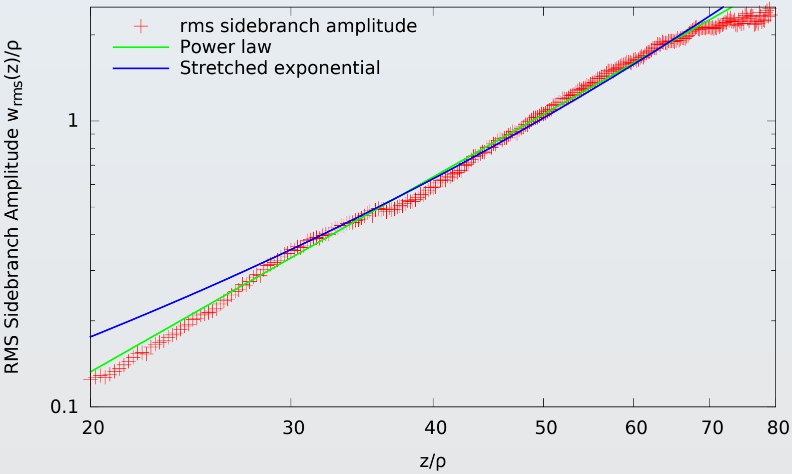
- The fit is poorly constrained.

Sidebranch Amplitude



- The fit is poorly constrained.
- $S_0 = 0.0023 \pm 0.0015$, $\alpha = 0.37 \pm 0.04$, $s = 0.40 \pm 0.33$.

Sidebranch Amplitude



- Key uncertainty is at very small amplitudes that are difficult to resolve well.

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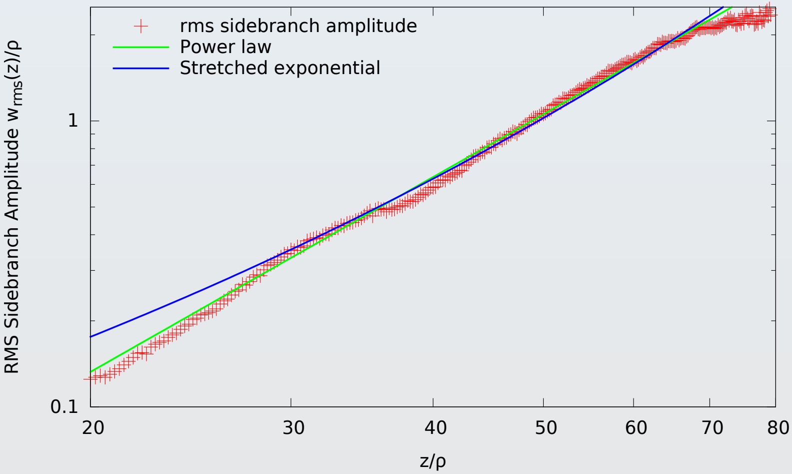

- Key uncertainty is at very small amplitudes that are difficult to resolve well.
- Noise level is higher than expected from thermal noise.

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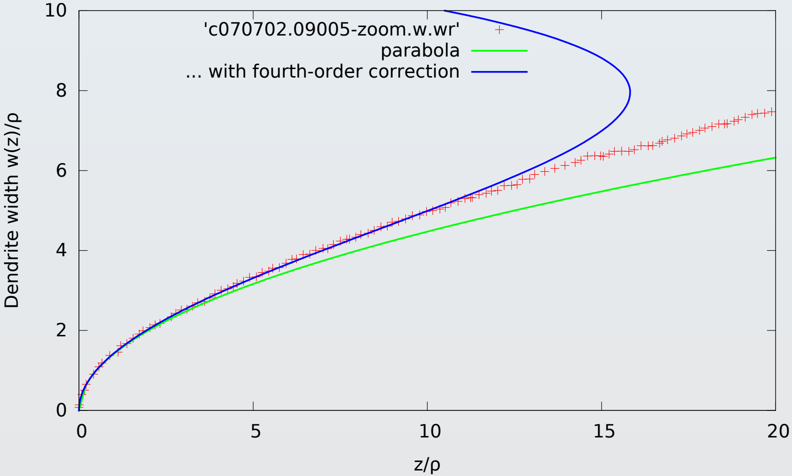
Sidebranch Amplitude



Determination of initial sidebranch amplitudes depends critically on shape assumed for average underlying shape.

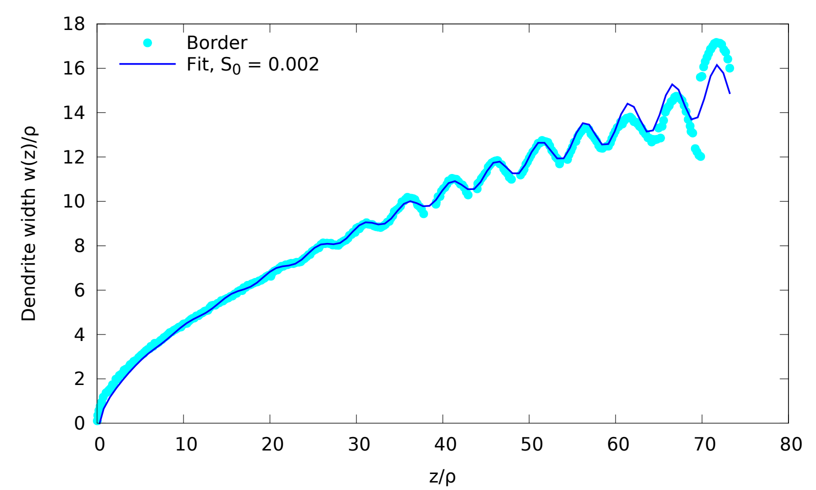
Amplitude of Individual Sidebranches

- Model scaled dendrite width by

$$w(z) = \bar{w}(z) + S_0 \exp\left(\frac{z}{s}\right)^{\alpha} \sin\left(\frac{2\pi}{\lambda} z + \phi\right)$$

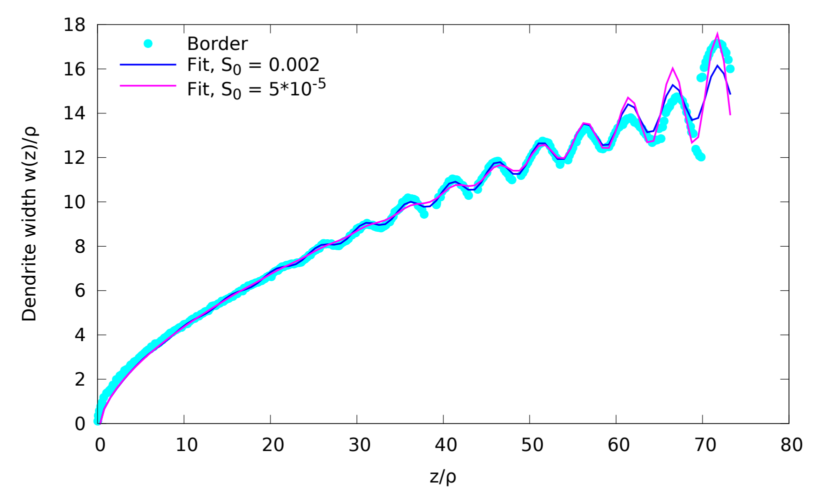
λ is sidebranch wavelength.

Amplitude of Individual Sidebranches



Shape is consistent with large “noise” value S_0.

Amplitude of Individual Sidebranches



Forcing S_0 to a smaller value closer to the theoretical expectation does not yield as good a fit.

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Summary

- No simple scaling law describes
  - the tip shape
  - average crystal width
  - sidebranch envelope
  - sidebranch amplitude
- Instead, seem to see continual transition from
  - $\Rightarrow$ smooth tip
  - $\Rightarrow$ initial branches
  - $\Rightarrow$ competing branches
  - $\Rightarrow$ independently growing new dendrites

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