Dendritic crystal growth of ammonium nitrate from aqueous solution

Andrew Dougherty

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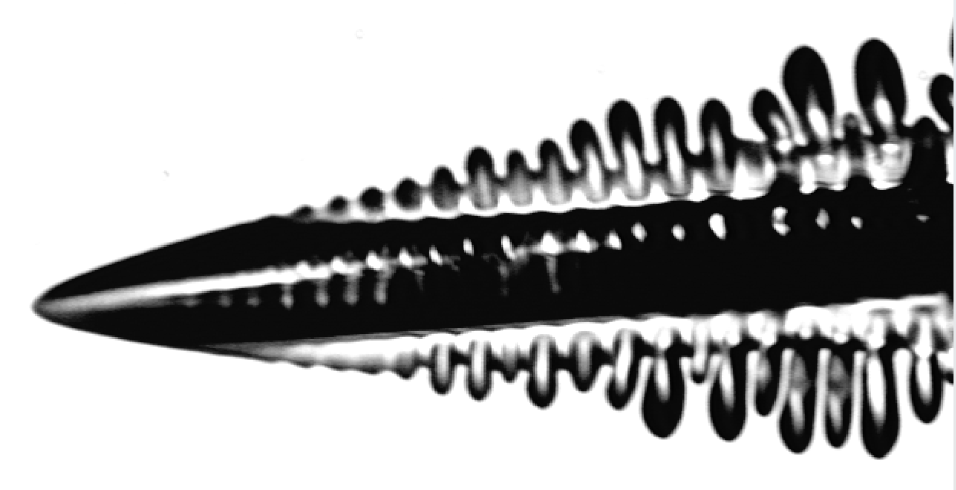
Lafayette College

APS March 2021

LAFAYETTE PHYSICS

Typical Ammonium Chloride Dendrite



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

Theory — I: Diffusion Limited Crystal Growth

u = Dimensionless concentration

D = Diffusion constant

d_0 = capillary length

Δ = supersaturation

κ = curvature

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

Theory — I: Diffusion Limited Crystal Growth

- Two Characteristic Length Scales:
  - $L =$ diffusion 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.

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Apparatus

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

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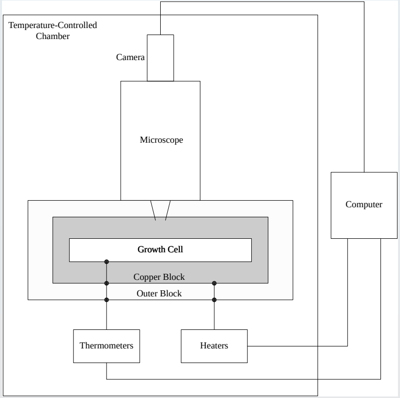

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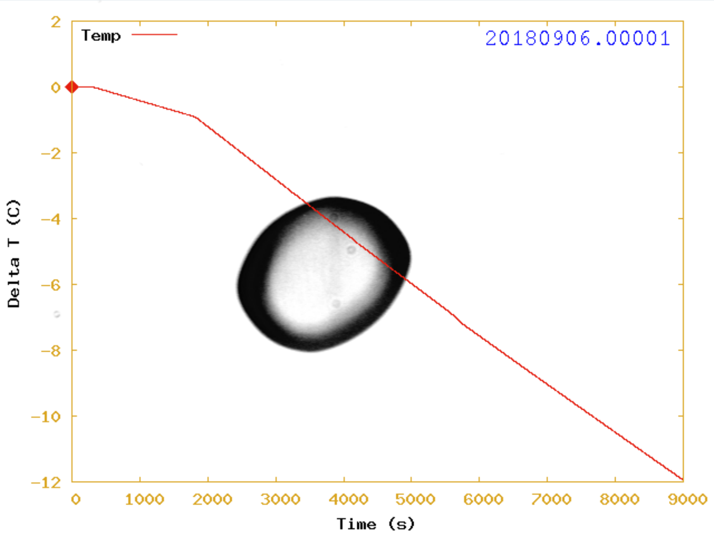

Initial growth of NH_4Cl crystal in aqueous solution.

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Theory — II: Dendritic Growth

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 $\lambda \sim$ few ρ

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  - Value for $\sigma^\star$ (is it even constant?)
  - λ/rho
  - Amplitude of sidebranches
- Which values are peculiar to the handful of materials studied so far, and which are universal?

Ammonium Nitrate Dendrites

Journal of Crystal Growth 128 (1993) 229–233
North-Holland

JOURNAL OF CRYSTAL GROWTH

Growth of ammonium nitrate phase I and II dendrites

C.A. van Driel, A.E.D.M. van der Heijden and G.M. van Rosmalen

Faculty of Chemical Technology and Materials Science, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, Netherlands

Ammonium nitrate (AN) phase I and phase II crystallize as dendrites from a melt containing respectively 0–4.5 and 4.5–12 wt% water. In-situ microscopic measurements show that the, for dendrites, characteristic ratio S/ρ (where S = side branch spacing near the tip and ρ = dendrite tip radius) varies between 2.3 and 5.1 for both AN(I) and AN(II). This agrees reasonably well with the theoretically derived value of 2.8 reported in the literature. The water concentration has a strong influence on the relation between the side branch spacing near the tip, S, and the tip growth rate, v, of the dendrites. The findings satisfy at least qualitatively the theoretically expected relationship between S and v.

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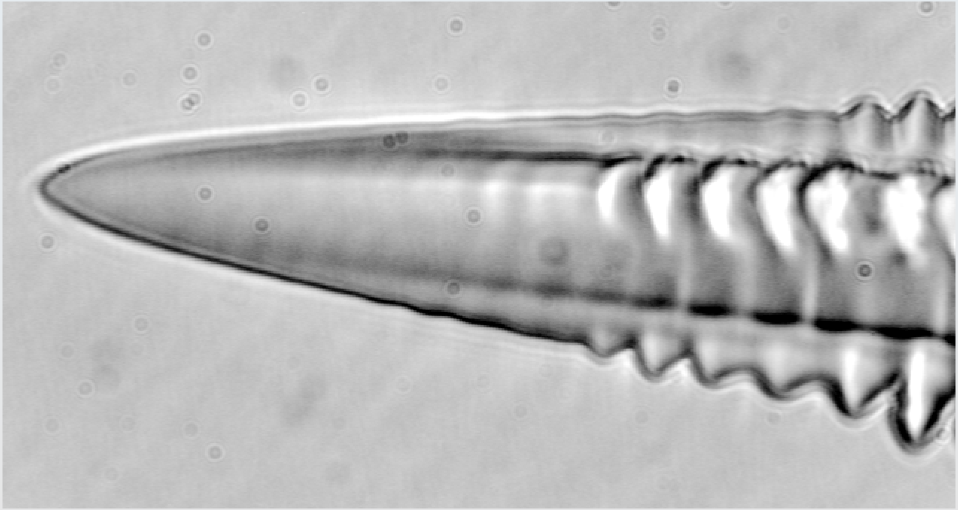
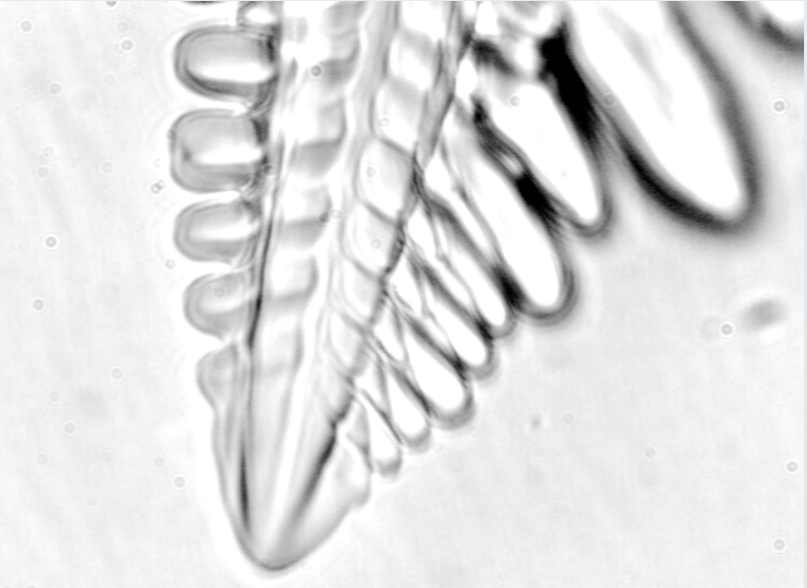


NH_4NO_3 crystal in aqueous solution The image is 200 μm across.

Secondary Ammonium Nitrate Dendrites



Theory — III: Spherical Growth

- Growth of a nearly spherical seed:

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

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- Growth and shrinking of a spherical crystal can be used to measure Dd_0.

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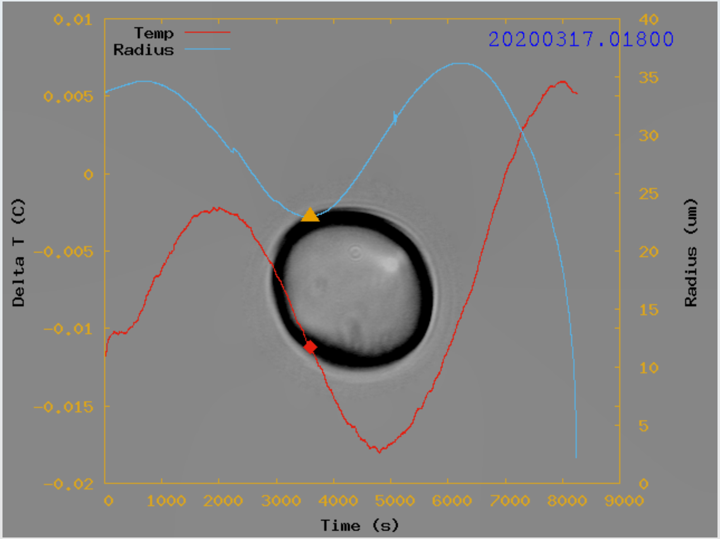
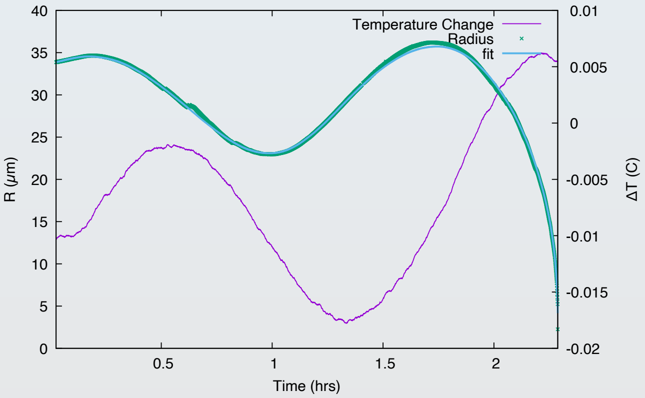
Growth of a Nearly Spherical Seed



Determining the capillary length for ammonium nitrate crystals.

Growth of a Nearly Spherical Seed



- The product $Dd_0 = 3.5 \pm 0.5\,\mu m^3/s$.

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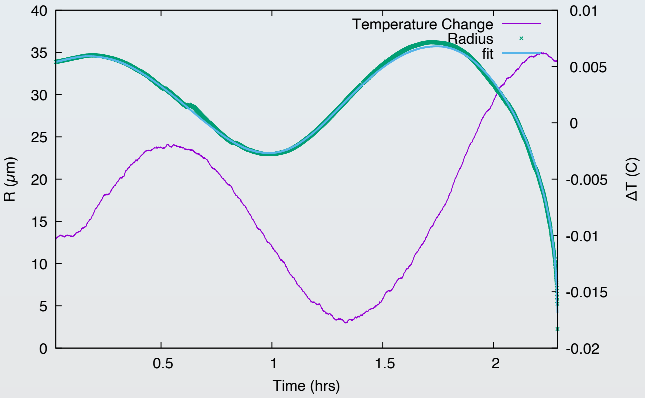
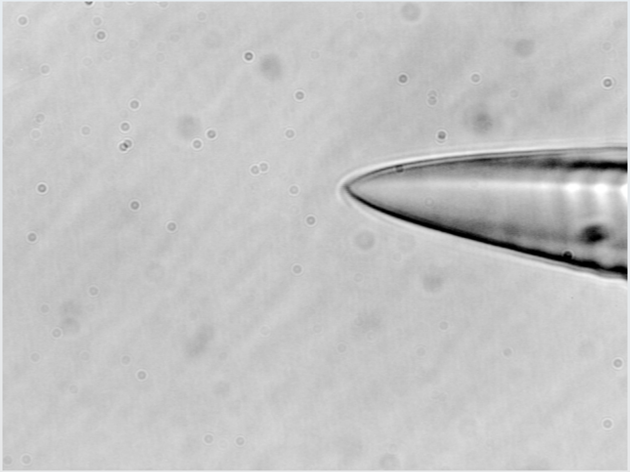


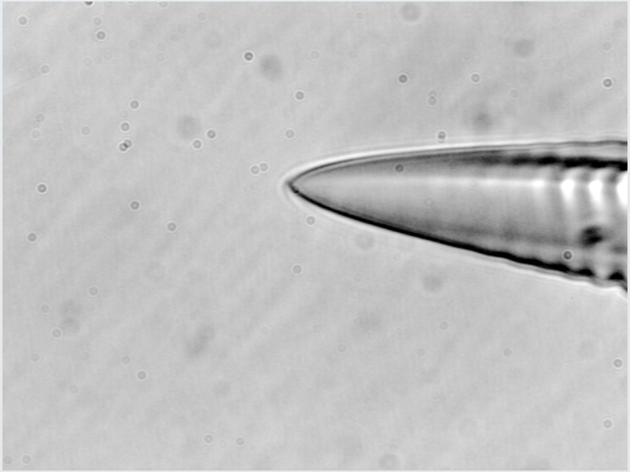
- The product $Dd_0 = 3.5 \pm 0.5\,\mu\text{m}^3/\text{s}$.
- This is about 10x larger than the previous estimate, which was based on an *assumed* value of $\sigma^\star$.

Dendritic Growth



Dendritic growth of ammonium nitrate crystals. The image is 200 μm across, and the time interval is 2 s between images.

Dendritic Growth



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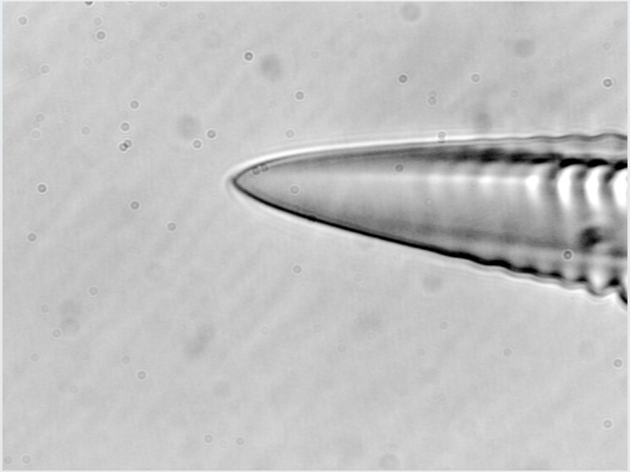

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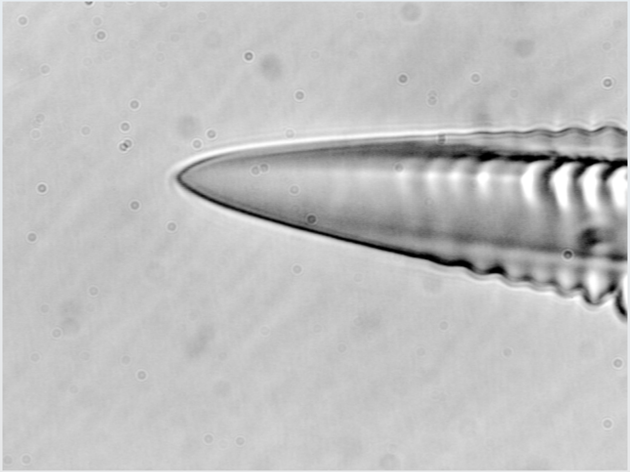

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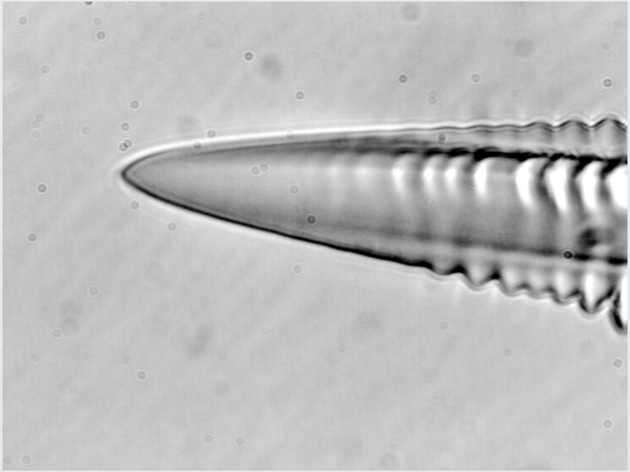

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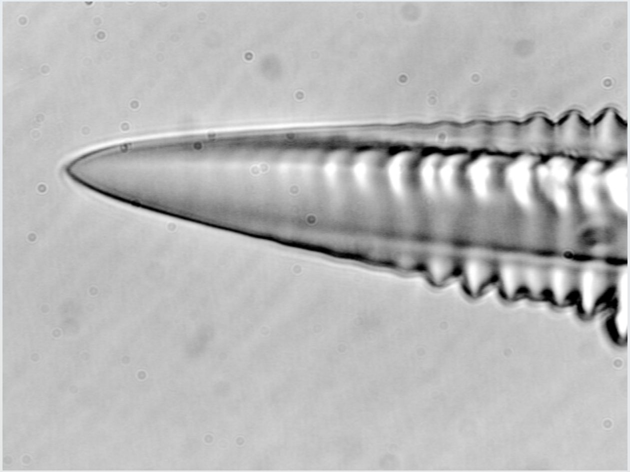

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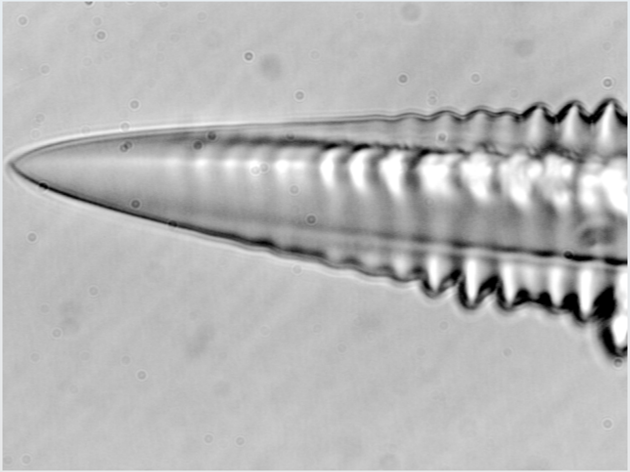

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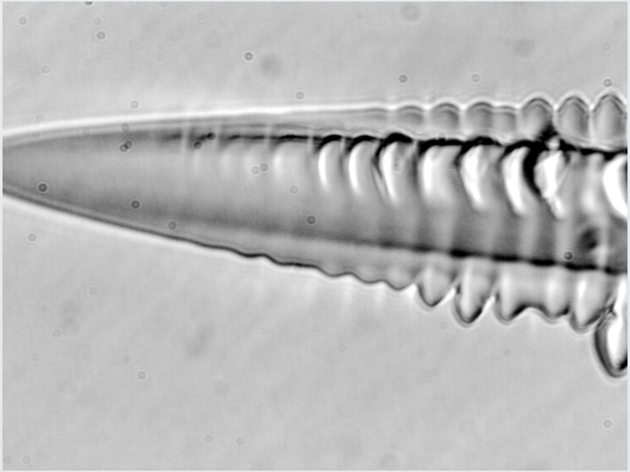

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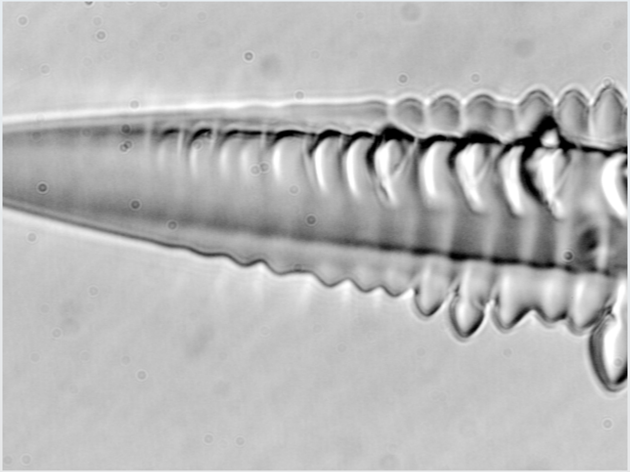

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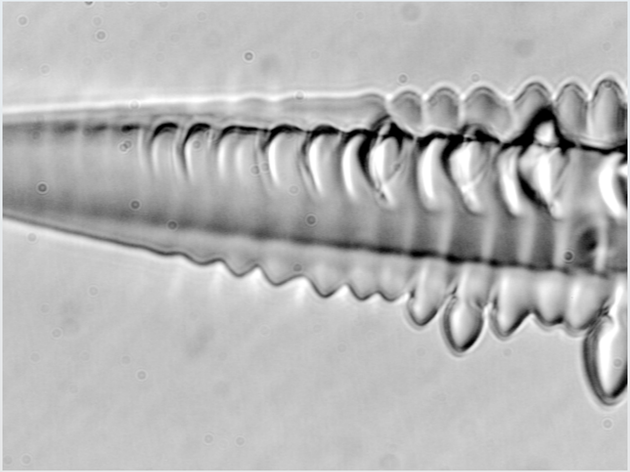

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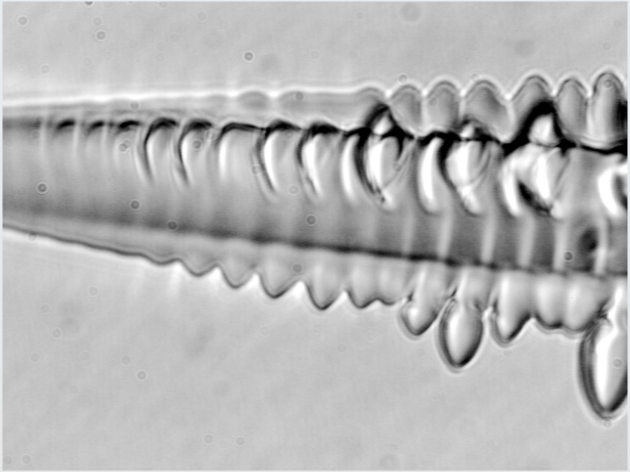

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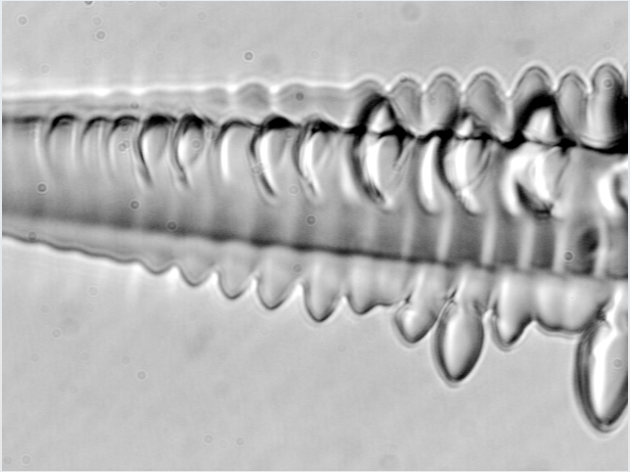

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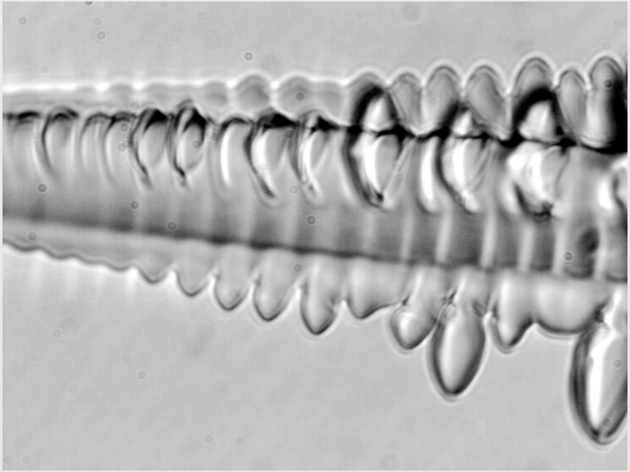

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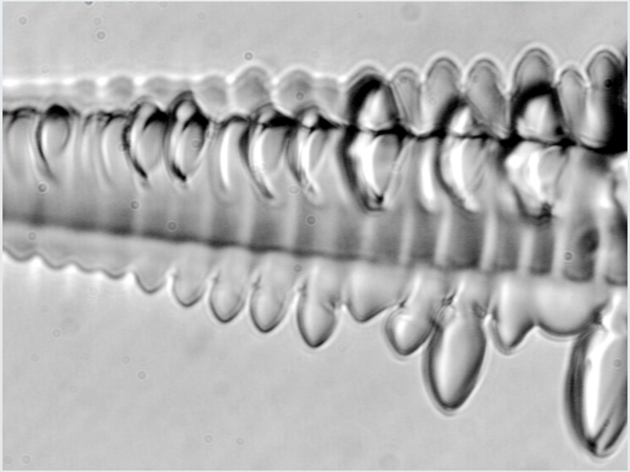

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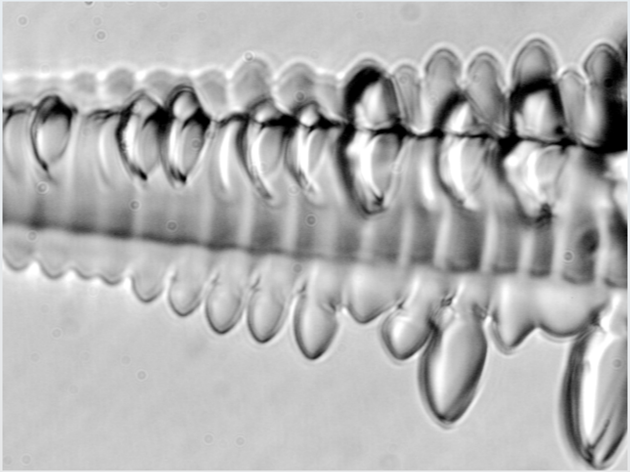

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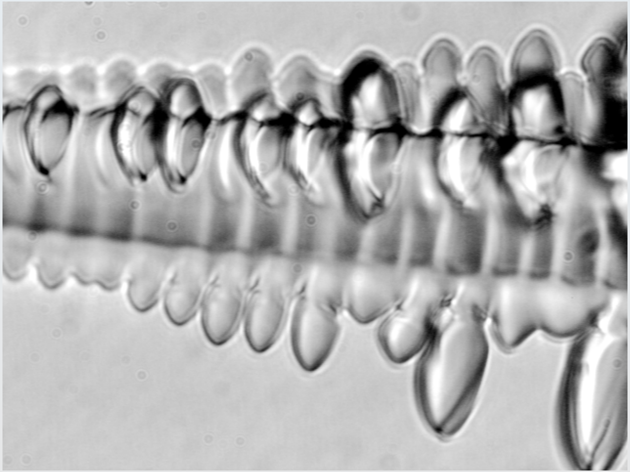

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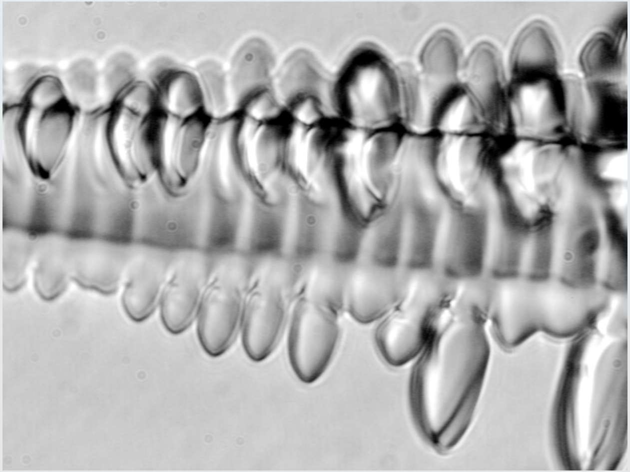

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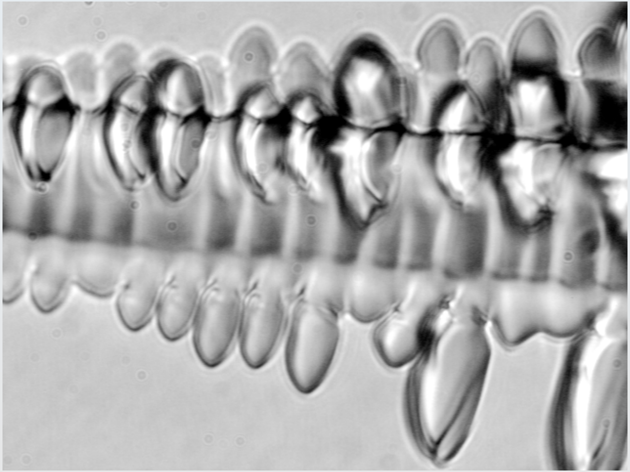

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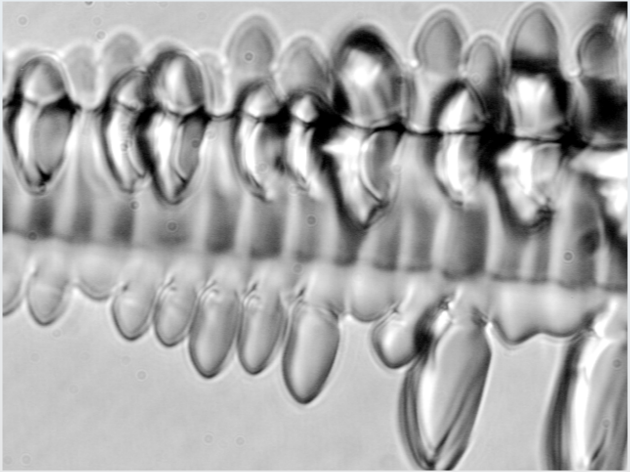

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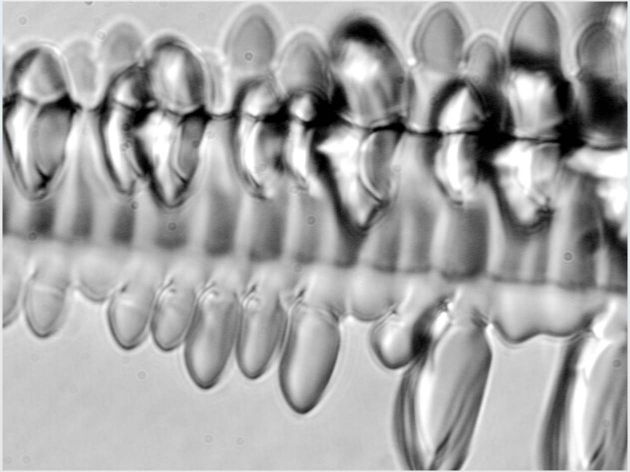

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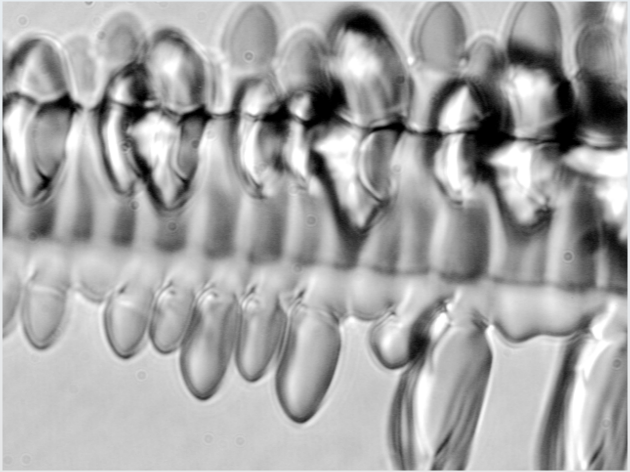

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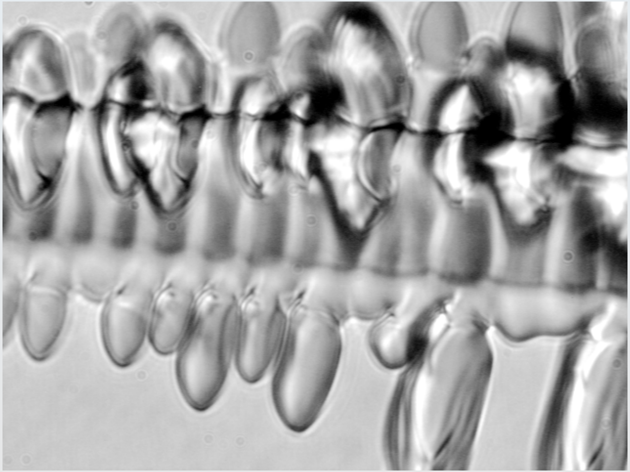

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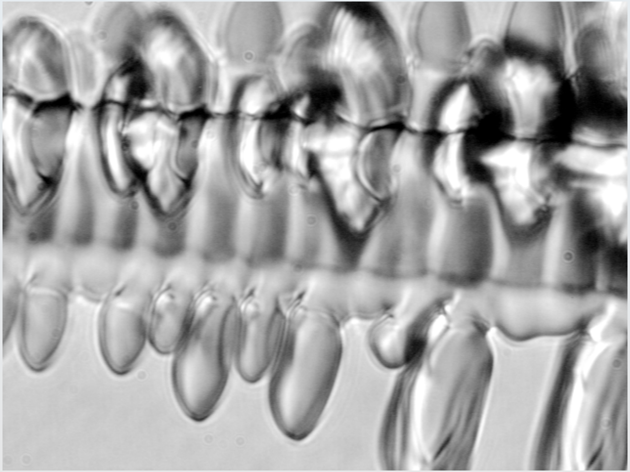

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- First, model the tip, then look for sidebranches as deviations from the initially smooth tip.
- Approximate tip as a parabola

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  - where $A_4 \approx -0.004$ for ammonium chloride.
  - Or $A_4 \approx -0.002$ for ammonium nitrate.

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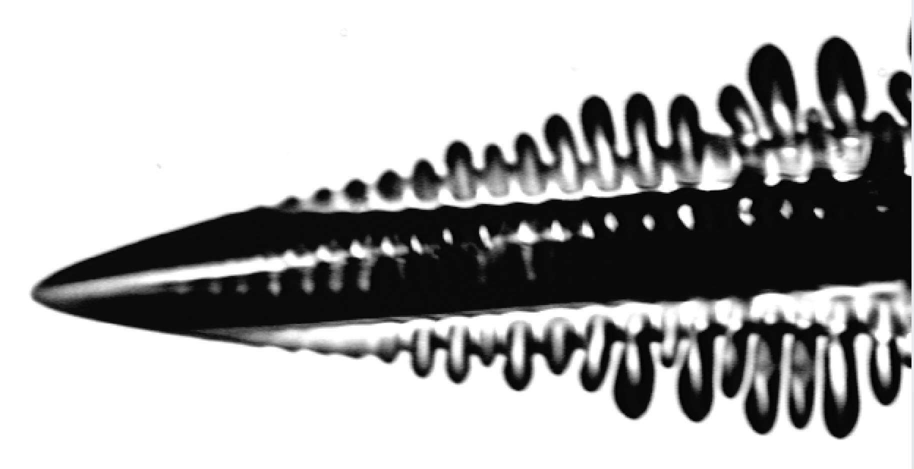
Fitting the Tip—Ammonium Chloride



Ammonium chloride tip.

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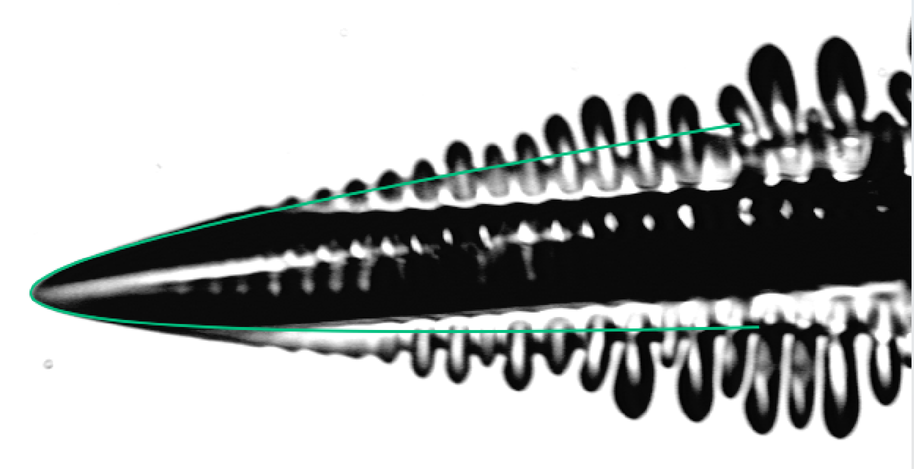

Ammonium chloride tip with parabolic fit.

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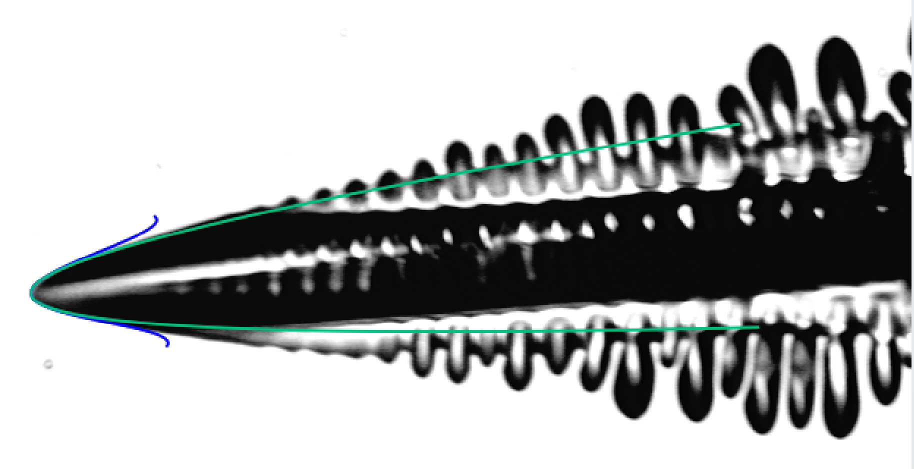
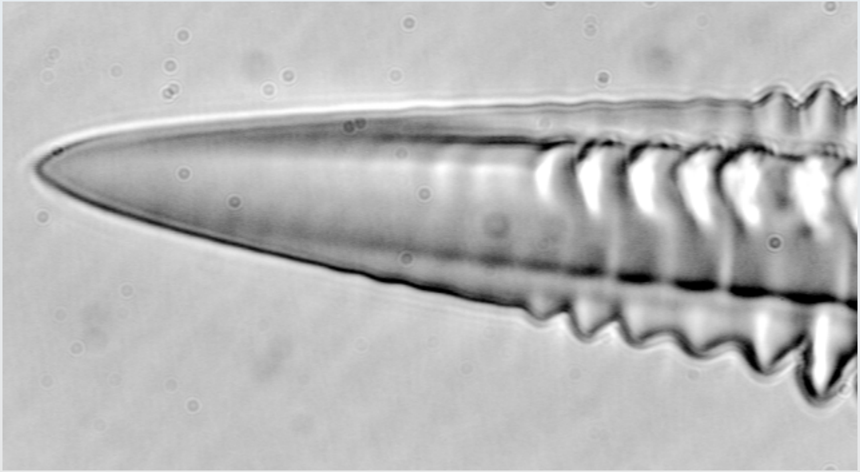


Ammonium chloride tip with parabolic fit and fourth-order correction.

Fitting the Tip—Ammonium Nitrate Comparison



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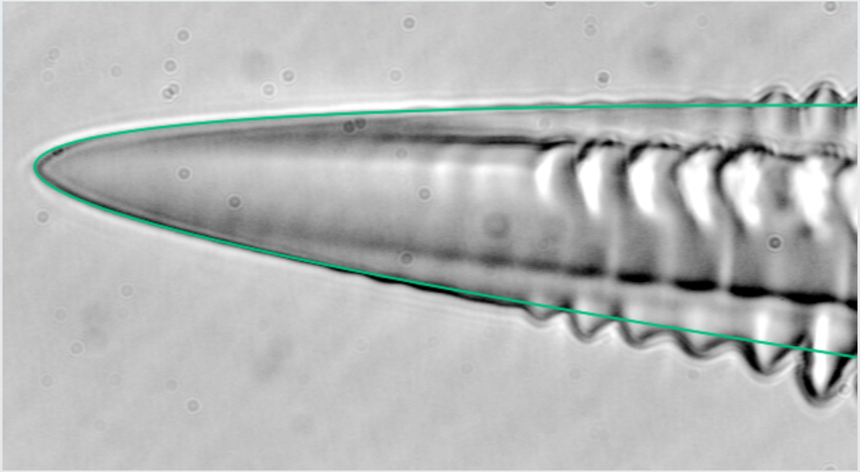

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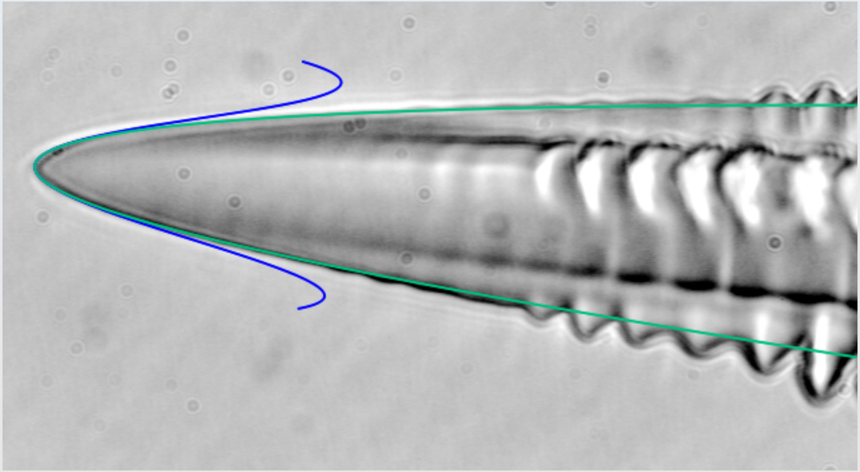

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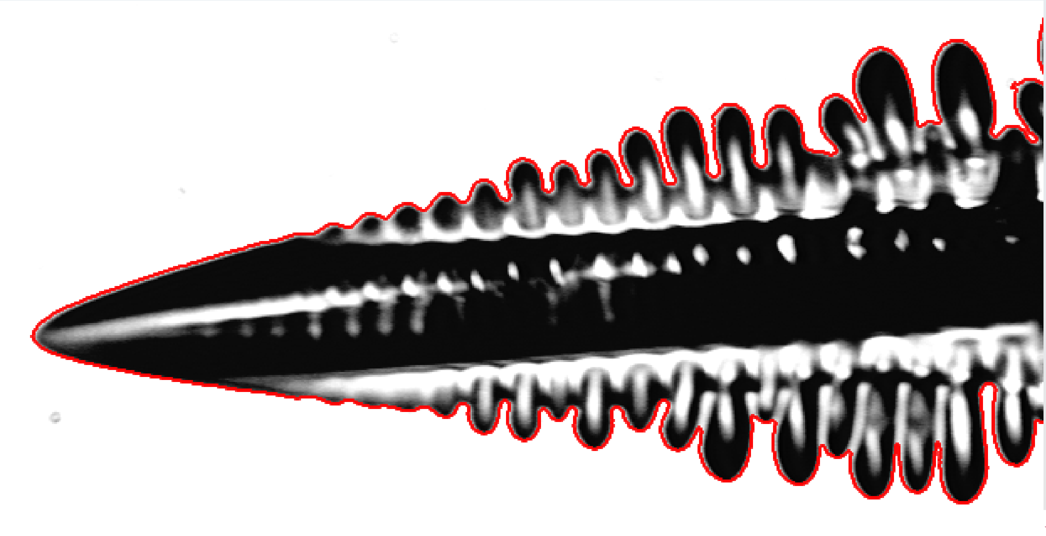
Sidebranch Growth



Consider the width $w(z)$ of the dendrite as a function of distance z back from the tip.

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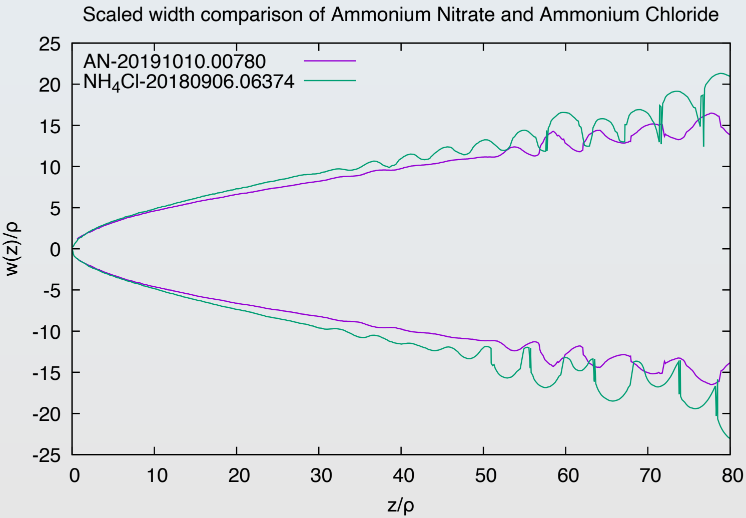
- Rotate to make growth horizontal
- Translate all tips to the origin
- Rescale all distances by ρ



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Preliminary Results

	NH_4Cl	NH_4NO_3
Dd_0	$0.78 \pm 0.07\,\mu m^3/s$	$3.0 \pm 0.1\,\mu m^3/s$
A_4	-0.004 ± 0.001	-0.002 ± 0.001
σ^*	0.10 ± 0.02	0.17 ± 0.02
λ/ρ	5.05 ± 0.01	5.6 ± 0.2

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- New material to test theories
- Dendritic growth for T over about 90 °C.
- Approximately same tip shape as ammonium chloride
- Larger value for σ^*
- Sidebranches appear suppressed.
- Transition to a different dendritic phase at even higher temperatures.

Lafayette Student Collaborators

- Ian Crawley ('15)
- Scott Skinner ('11)
- Tom Nunnally ('07)
- Mayank Lahiri ('05)
- James Reeder ('03)

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