Sidebranching in the Dendritic Crystal Growth of Ammonium Chloride

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Typical Crystal

NH₄Cl crystals in aqueous solution.
Experiments

- NH$_4$Cl growing in aqueous solution
- Growth cell: $40 \times 10 \times 2 \text{ mm}^3$
- Obtain an approximately spherical seed
- Lower temperature $\Delta T \approx 1^\circ\text{C}$ to initiate growth
Apparatus
Diffusion Limited Crystal Growth

$u = \text{Dimensionless concentration}$

$$\frac{\partial u}{\partial t} = D \nabla^2 u$$

$u_{\text{interface}} = -d_0 \kappa$

$u_\infty = -\Delta$

$\nu_n = -D \nabla u \cdot \hat{n}$

$d_0 = \text{capillary length}$

$\kappa = \text{curvature}$

$\Delta = \text{supersaturation}$
Two Characteristic Length Scales:

- \( L = \text{diffusion length} = \frac{2D}{v} \) (\( \sim \) mm)
- \( d_0 = \text{capillary length} (\sim \text{nm}) \)
- Typical scale of pattern is \( \sqrt{Ld_0} \)

General Features:

- Flat interface is unstable
- Surface tension limits curvature
Growth from a Nearly Spherical Seed
Theory — III

Modeling Dendritic Growth — Approximately parabolic tip

- tip speed $v$
- tip radius of curvature $\rho = \frac{1}{\sqrt{\sigma^*}} \sqrt{Ld_0}$
- where the “stability constant” $\sigma^* = \frac{2d_0D}{v\rho^2}$
- initial sidebranch spacing $\lambda \sim \rho$
Origin of Sidebranches

Typical crystal growth—note the long smooth tip and the slightly irregular sidebranches.
Origin of Sidebranches

- Apparent tip oscillations—note the regular sidebranches close to the tip.
Origin of Sidebranches

- Apparent tip oscillations—note the regular sidebranches close to the tip.
- *However*—such patterns are only rarely seen in this experiment, and we have not found any way to repeat them.
Modeling the Dendrite Tip

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

$$z = \frac{x^2}{2\rho}$$
Modeling the Dendrite Tip

- First, model the tip, then look for sidebranches as deviations from the initially smooth tip.
- Approximate tip as a parabola
  \[ z = \frac{x^2}{2\rho} \]
- ... plus a small fourth-order correction
  \[ z = \frac{x^2}{2\rho} + A_4 \frac{x^4}{\rho^3} \]
  where \( A_4 \approx -0.0036 \).
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.
Tip with parabolic fit with fourth-order correction.
Fitting the Tip

Only use data within $6\rho$ of the tip for fit.
Finding the Average Shape

Look for sidebranches as deviation from the smooth tip.
Finding the Average Shape

Try to fit it to a power law.
Average shape is not simple. Over the intermediate range of the sidebranches studied here, the best power-law fit it $w(z)/\rho = 0.95(z/\rho)^{0.67}$. 
Finding the Average Shape

The slope gradually increases with distance from the tip.
Finding the Sidebranch Envelope

Measurements of dendrite tip growth and sidebranching in succinonitrile–acetone alloys

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Abstract

Experiments are carried to investigate free dendritic growth of succinonitrile–acetone alloys in an undercooled melt. The measurements include the steady dendrite tip velocity and radius, the non-axisymmetric amplitude coefficient of the fins near the tip, and the envelope width, projection area, and contour length of the sidebranch structure far from the tip. It is found that the measured dendrite tip growth Péclet numbers agree well with the predictions from a stagnant film model that accounts for thermosolutal convection in the melt. The measured tip selection parameter, σ*, is verified to be independent of the alloy composition, but shows a strong dependence on the imposed undercooling. The universal amplitude coefficient, A1, is measured to be equal to 0.004, independent of the undercooling, but the early onset of sidebranching prevents its accurate determination for more concentrated alloys. For the self-similar sidebranch structure far from the tip, scaling laws are obtained for the measured geometrical parameters. While melt convection causes some widening of the sidebranch envelope, and the early onset of sidebranching for alloy dendrites results in a 25% upward shift of the envelope width, the projection area and, hence, the mean width of a sidebranching dendrite, as well as its contour length in the sidebranch plane, obey universal power laws that are independent of the convection intensity and the alloy composition.
Finding the Sidebranch Envelope

Identify the active sidebranches.
Finding the Sidebranch Envelope

Compute the average sidebranch envelope.
Finding Sidebranches

Sidebranch Envelope

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Active sidebranches
Average envelope
0.80 \((z/\rho)\) 0.73

Dendrite width \(w(z)/\rho\)

\(z/\rho\)

\(0 10 20 30 40 50 60 70 80 90\)
Average envelope is also not simple. The best power law fit over the range $10 < z/\rho < 85$ is $env(z)/\rho = 0.80(z/\rho)^{0.73}$. 
Finding Sidebranches

The slope gradually increases with distance.
Dendritic sidebranching with periodic localized perturbations: Directional solidification of pivalic acid–coumarin 152 mixtures

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We have studied the response of the sidebranches of pivalic acid dendrites, growing by directional solidification, to localized periodic thermal perturbations. The perturbations were generated by a laser beam focused near the tip of a single dendrite growing in a glass capillary, with the pulse duration, repetition rate, and intensity controlled separately. The perturbation dramatically altered the sidebranch structure, producing ordered sidebranches of well-defined wavelength, synchronous with the perturbation, which were strongly correlated on the two sides of the dendrite. The dependences of the sidebranch amplitude on the frequency of the perturbation and on the distance from the dendrite tip were compared to the predictions of Barber, Barbieri, and Langer [Phys. Rev. A 36, 3340 (1987)] and found to be in qualitative agreement. The value of the selection parameter $\sigma$ found from these fits to the theory is compared to a value, obtained from material parameters also determined in this experiment, and to a value deduced from the initial Mullins-Sekerka instability of the planar crystal-melt interface.

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FIG. 2. Video images of dendrites grown by directional solidification from a mixture of pivalic acid and 0.44 wt.% coumarin 152. \( v = 3.7 \ \mu m/s \). (a) No perturbation; (b) 1-s laser pulses with a repetition rate of \( \tau_r = 15 \) s; (c) repetition rate of \( \tau_r = 19 \) s, which is close to the natural period; (d) repetition rate of \( \tau_r = 26 \) s.
Sidebranching induced by external noise in solutal dendritic growth

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We have studied sidebranching induced by fluctuations in dendritic growth. The amplitude of sidebranching induced by internal (equilibrium) concentration fluctuations in the case of solidification with solutal diffusion is computed. This amplitude turns out to be significantly smaller than values reported in previous experiments. The effects of other possible sources of fluctuations (of an external origin) are examined by introducing nonconserved noise in a phase-field model. This reproduces the characteristics of sidebranching found in experiments. Results also show that sidebranching induced by external noise is qualitatively similar to that of internal noise, and it is only distinguished by its amplitude.

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The sidebranching amplitude is predicted to be

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

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

\[ \sigma^* = \frac{2d_0 D}{\nu \rho^2} \]
Sidebranch Amplitude

➢ The sidebranching amplitude is predicted to be

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

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\[ \sigma^* = \frac{2d_0D}{v\rho^2} \]

➢ The noise amplitude \( S_0 \) is given by

\[ S_0^2 = \frac{2CL^{eq}D}{(\Delta C^{eq})^2 \rho^3v} \approx 6 \times 10^{-5} \]
Generically, if \( w_{ave}(z) \) scales as a power law with \( z \), the amplitude of the sidebranches is predicted to scale

\[
A(z) = S_0 \exp \left( \frac{z}{s} \right)^\alpha
\]
Sidebranch Amplitude

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

$$A(z) = S_0 \exp \left( \frac{Z}{S} \right)^{\alpha}$$

- where $\alpha$ is predicted to be 0.4 if $w_{ave} \sim z^{3/5}$,
Sidebranch Amplitude

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

$$A(z) = S_0 \exp \left( \frac{z}{s} \right)^{\alpha}$$

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

Define sidebranch amplitude as rms variation around the average shape.
The fit is poorly constrained.
The fit is poorly constrained.

\[ S_0 = 0.0044, \ \alpha = 0.375, \ s = 0.590. \]
The fit is poorly constrained.

- $S_0 = 0.0044, \alpha = 0.375, s = 0.590.$
- $S_0 = 6.43 \times 10^{-6}, \alpha = 0.18, s = 2.6 \times 10^{-5}.$
Key uncertainty is at very small amplitudes that are difficult to resolve well.

Is consistent with initial exponential growth with no onset.
Key uncertainty is at very small amplitudes that are difficult to resolve well.

- Is consistent with initial exponential growth with no onset.
Sidebranch Amplitude

Tip Shape

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parabola
... with fourth-order correction
Summary

- No simple scaling law describes
  - the tip shape
  - average crystal width
  - sidebranch envelope
  - sidebranch amplitude

- Instead, seem to see continual transition from
  - smooth tip
  - initial branches
  - competing branches
  - independently growing new dendrites