1987

Development of sidebranching in dendritic crystal growth

A. Dougherty

P. D. Kaplan

Jerry P. Gollub
Haverford College

Development of Side Branching in Dendritic Crystal Growth

A. Dougherty, P. D. Kaplan, and J. P. Gollub
Physics Department, Haverford College, Haverford, Pennsylvania 19041, and
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 19 December 1986)

The growth of dendritic crystals of NH_4Br from supersaturated solution has been studied in a way that allows high-resolution measurements of the early stages of side branching. The branches are found to be nonperiodic at any distance from the tip, with apparently random variations in both phase and amplitude. Side branches on opposite sides of the dendrite are imperfectly correlated. The rms side-branch amplitude is an exponential function of distance from the tip, with no apparent onset. The implications of these results for several theories of the stability of growing dendrites are discussed.

PACS numbers: 68.70.+w, 61.50.Cj, 81.30.Fb

The problem of explaining the convoluted shapes of dendritic crystals is particularly challenging.[1-4] Dendrites growing from a supercooled melt or supersaturated solution are characterized by smooth, nearly parabolic tips growing at constant velocity with fairly regular side branches (for example, see Fig. 1). These branches compete with each other through the diffusion field in the liquid phase. Smaller ones are screened and cease growing or even begin to dissolve, while larger ones accelerate. This coarsening process is important in determining the large-scale grain structure of solidifying materials.

Much is known about the tip shape and velocity, the mean initial side-branch spacing, and the importance of crystalline anisotropy, from earlier experimental and theoretical studies.[1-5] However, the processes that determine the side-branching frequency and amplitude, and the subsequent coarsening, are still the subject of controversy. In this paper we present a study of the growth of free dendrites of ammonium bromide from supersaturated aqueous solution. Our experiment allows the side-branch amplitudes to be measured to a precision of 2% of the tip radius, and is hence particularly sensitive to the dynamics of the side-branching process. We find that the side-branch amplitude is surprisingly noisy, and comment on the implications of this fact for theoretical models.

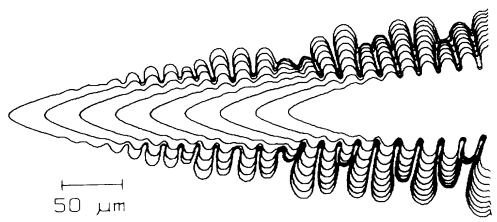

FIG. 1. Contours of an ammonium bromide dendrite growing from supersaturated solution. The contours are obtained by digital processing of microscope images taken at 20-s intervals. Supersaturation $\Delta \approx 0.007$; tip radius $\rho = 4.0\ \mu$m; tip speed $v = 1.44\ \mu$m/s; initial side-branch spacing $\lambda = 16\ \mu$m.

In the standard continuum approximation, growth from solution is controlled by the diffusion of solute towards the interface. The control parameter is the dimensionless supersaturation $\Delta = (C_\infty - C_{eq})/(C_s - C_{eq})$, where C_{eq} is the equilibrium concentration of NH_4Br at the operating temperature, and C_s and C_∞ are the concentrations in the solid and in the solution far from the interface. The parameter Δ relates the concentration gradient in the solution to the concentration discontinuity across the interface. In the absence of surface tension and crystalline anisotropy, and ignoring side branching, the steady-state, or Ivantsov, solutions to the diffusion equation are paraboloids of revolution with tip radius ρ, moving at constant velocity v. These solutions fix only the Péclet number, $\mathcal{P} = \rho v/2D$, where D is the diffusion constant of the crystallizing material.[1] Experimentally, however, the dendrite grows at a unique velocity. More recent work indicates that when surface tension and anisotropy (but not side branching) are included, this continuous family breaks down into a discrete set of nearly parabolic solutions.[4] Of these solutions, only the one with the highest velocity is believed to be linearly stable.[6] However, these theoretical results have not yet been adequately tested experimentally.

To investigate the origin of side branching, which is the primary goal of this work, we look for deviations from the steady-state shape. Specifically, we measure the half-width $w_z(t)$ of the dendrite (from the center to one side) *at a fixed distance z behind the tip,* as a function of time. This amounts to viewing the dendrite in a frame of reference moving with the tip. The width oscillates as the side-branching waves pass by the observation point. Measured over long times, $w_z(t)$ gives a statistically stationary measure of the side-branching activity at that fixed location z. The measurement process is repeated for various values of z in order to characterize the initiation and subsequent development of side branches.

The experiments are conducted in a glass cell of dimensions $60 \times 6 \times 0.3$ mm^3, filled with a known concen-

tration of NH_4Br. After the solid has been dissolved, the cell is cooled to a uniform temperature that determines Δ. A crystal nucleates at random; only experiments yielding a single free dendrite are used. The growth process is observed through a microscope with a video camera and recorded on video tape for later digital analysis.

The discussion that follows is based on a detailed analysis of a particular experimental run characterized by the following parameters: $\Delta \approx 0.007$, $\rho = 4.0 \pm 0.2$ μm, $v = 1.44 \pm 0.08$ μm/s, $D = (2.6 \pm 0.2) \times 10^{-5}$ cm^2/s, $\mathcal{P} = 0.0011$, and λ (the mean side-branch spacing near the tip) $= 16 \pm 1$ μm. (The surface tension and its anisotropy are not known for this system. However, qualitative observations of the dendritic shapes suggest that the anisotropy is somewhat larger than that of succinonitrile.) The growth was recorded for 36 min, yielding a dendrite more than 3 mm long with approximately 200 side branches. To obtain $w_z(t)$, about 14000 video frames were digitized to a resolution of 512×480 pixels, with each pixel being 0.64 ± 0.01 μm.

The character of the side branches near the tip is shown in Fig. 2, where $w_z(t)$ and its power spectrum $P_z(f)$ are shown for $z = 32$ μm. (The actual data record used to compute the spectrum is six times the length shown.) The side branching is only approximately periodic, and the amplitude has an unanticipated intermittent character. The spectrum contains a peak at the characteristic side-branching frequency of 0.09 Hz, but the peak has a standard deviation $\sigma = 0.007$ Hz when fitted by a Gaussian, indicating the presence of a range of frequencies.

This noisy behavior is also reflected in the cross-correlation function

$$C(\tau) = \langle [w_{Lz}(t+\tau) - \bar{w}_{Lz}][w_{Rz}(t) - \bar{w}_{Rz}] \rangle / \sigma_L \sigma_R,$$

where $w_{Lz}(t)$, $w_{Rz}(t)$, σ_L, and σ_Z are the width functions and their standard deviations for the two sides of the dendrite at the same z. We find that $C(0)$ is less than 0.4 for any z, and $C(\tau)$ drops to zero (within the measurement precision) for $\tau \gtrsim 66$ s, the time to nucleate six side branches. Similar behavior is seen for the autocorrelation function, so that side branches separated by more than about 6λ are essentially uncorrelated with each other. There are apparently random fluctuations in both the phase and amplitude of $w_z(t)$ that destroy any long-range correlations.

The character of the side branches for $z = 95$ μm (Fig. 3) is similar to that near the tip except for the obvious presence of competition. The side-branch amplitude is larger, but the spectral peak has essentially the same mean frequency and width as it had at $z = 32$ μm. The coarsening process has increased the overall noise level in the spectrum at all frequencies, including those below the peak. Beyond about 150 μm, the spectral peak stops growing and the background noise level continues to rise,

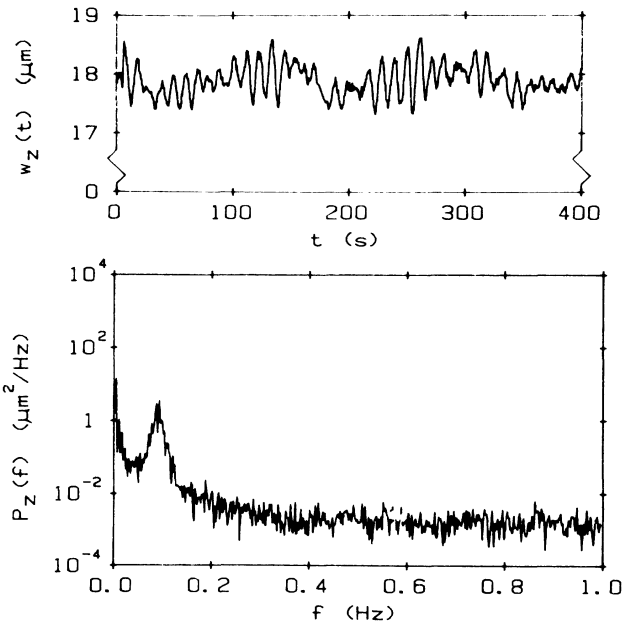

FIG. 2. Portion of the dendrite width function $w_z(t)$ and its power spectrum $P_z(f)$, for $z = 32$ μm behind the tip. The intermittency of the side-branching process is evident.

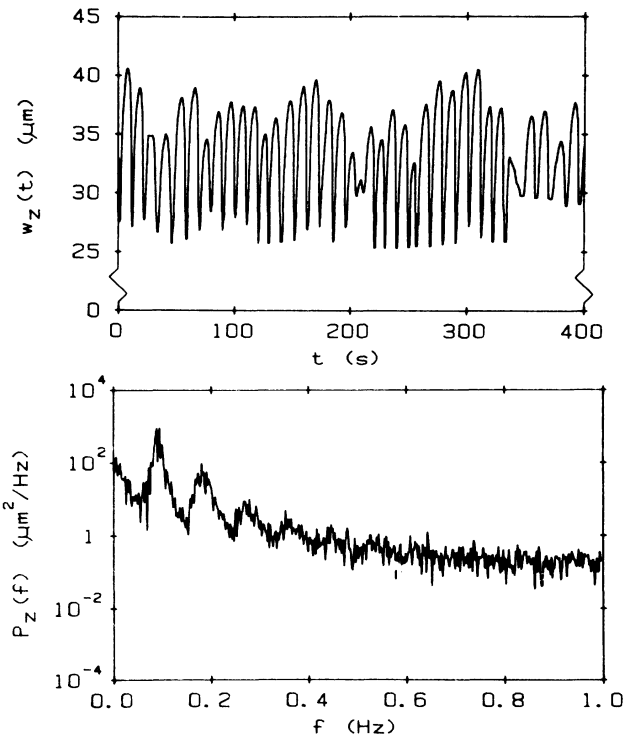

FIG. 3. Portion of $w_z(t)$ and its power spectrum $P_z(f)$ farther from the tip at $z = 95$ μm. Note the change of scales for $w_z(t)$.

yielding a relatively featureless spectrum with noise at all frequencies.

It is worth emphasizing that although these are optical measurements, they are reproducible to considerably less than the optical wavelength. The resolution limit of the microscope objective is about 1.9 μm, and the dendrite edge is actually spread over about 4 μm in the digitized image. However, interpolation over the edge region (and signal averaging) improves the effective resolution dramatically. In particular, for $z=32$ μm, where the root mean square variation in the side-branch amplitude is only 0.32 μm, the measurement precision is about 0.05 μm.

A possible source of systematic error is the concentration gradients which locally change the index of refraction, and slightly reduce (by less than 5%) the apparent radius of curvature. This would occur even without side branches, but the distortion in that case would be static in the tip frame and thus have no effect on the spectral measurements. However, the side branches are accompanied by local enhancements of the concentration gradients, leading to a possible periodic distortion estimated to be about 0.08 μm. This is generally much smaller than the side-branch amplitudes measured.

It will be important to test whether mechanisms other than diffusion, such as convection, are significant for the dendritic growth in this system. However, preliminary estimates indicate that this is unlikely because the value for Δ obtained from the Ivantsov solution with the measured ρ and v is in approximate agreement with the measured Δ, so that diffusion is the dominant transport mechanism.

Despite the apparently restricted geometry, the dendrites in this experiment are not two-dimensional. The diffusion field around a parabolic dendrite decreases very sharply, as the exponential integral $E_1(x/l)$, where x is the distance perpendicular to the growth direction and $l=2D/v$ is the diffusion length (about 3.6 mm in this case). Even though the cell thickness d is only about $0.08l$, the concentration deviation $[C(x)-C_{eq}]$ at $x=d/2$ is about $0.56(C_\infty-C_{eq})$. Thus the growth is not as strongly constrained in the third dimension as one might expect from the geometry. (This view is substantiated by experiments on directional solidification of a dilute binary alloy,[7] in which Somboonsuk, Mason, and Trivedi determined that the dendrite tip radius and initial side-branch spacing were independent of d for $d \gtrsim 0.06l$.)

Theoretical models at present offer little insight into the dynamics of side branching. Even for the purely local models that have been extensively studied, it is not clear whether persistent side branching occurs.[8-10] However, several possible scenarios have been suggested.

According to one hypothesis, the dendrite tip is not actually a stationary point in the tip frame of reference; rather, its position and curvature oscillate, forming a limit cycle at the side-branching frequency.[8] If this is correct, the side-branch amplitude would be periodic, and the two sides almost perfectly correlated, since noise should be ineffective in the presence of a limit cycle. Neither feature is observed in the present experiment. We have also made careful measurements of the tip velocity, and found it to be constant. In a bandwidth of 0.1 Hz around the side-branching frequency, the velocity fluctuations are less than 0.05 μm/s, or 3.5%. This is consistent with most previous experiments on free dendrites,[2] although tip oscillations have been seen in two-dimensional growth for very low supersaturation.[11] We conclude from these observations that a dynamical limit cycle involving the tip is unlikely to be an essential ingredient of the side-branching process, at least in this system.

Alternatively, the tip could be a stable structure, with side branches resulting from the amplification of finite microscopic noise.[9,12] In this view, noise (e.g., concentration fluctuations in the solution near the tip) gives rise to small interfacial perturbations. In the tip frame of reference, these perturbations propagate away from the tip and grow approximately exponentially with distance. This may be qualitatively similar to the growth of a disturbance as it is convected downstream in some hydrodynamic systems such as pipe flow.[13] In this "noise-induced side-branching" scenario, the structure is expected to be nonperiodic, and branches on opposite sides of the dendrite imperfectly correlated, as is observed. It is not implausible that concentration fluctuations could be significant, since the fractional fluctuations in Δ in a 1 $(\mu m)^3$ volume due to Poisson statistics are about 10^{-3} in this experiment.

The growth of the branches as a function of distance z from the tip is given by the square root of the area under the spectral peak (Fig. 4). This growth appears exponential at very small z, but saturates at large z. (The data are also consistent with another suggested growth law, $\exp\sqrt{s}$, where s is the arclength.[12]) This exponential growth of the side-branch amplitude in the tip frame

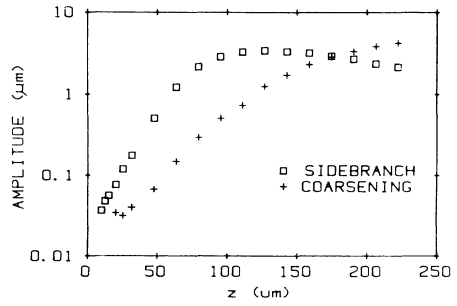

FIG. 4. Squares: rms variations in the side-branch amplitude vs distance z from the tip. Crosses: Coarsening noise (see text).

appears consistent with noise-induced side branching. There is no clear onset; the amplitude simply falls below the measurement noise level for $z < 10\ \mu$m, despite the precision of the measurements.

The development of coarsening is manifested as a rise in the low-frequency power with increasing z. Though the coarsening occurs at all wave numbers less than that of the spectral peak, we use, as a measure of the coarsening, the square root of the spectral power in a bandwidth of 0.025 Hz centered at half the side-branching frequency. Its growth as a function of z (Fig. 4) is slower than that of the side-branching instability, but is important rather close to the tip. This observation emphasizes the need to make measurements very close to the tip to explore the origin of side branching.

In summary, our measurements are consistent with the hypothesis that the amplification of microscopic noise is important to the side-branching process. To determine whether the structure is dependent on the noise intensity, the growth of larger dendrites (lower Δ) should be studied. Experiments along these lines are currently under way.

It may ultimately be necessary to consider the origin of side branches as a nucleation problem which is very sensitive to conditions on the atomic scale (for example, the presence of grain boundaries).[14] Continuum models may not be adequate to describe fully the stability of dendrites.

This work was supported by National Science Foundation Low Temperature Physics Grant No. DMR-8503543. Seed funds were previously provided by the National Science Foundation Materials Research Laboratory program under Grant No. DMR-82-16718. We appreciate helpful conversations with M. Glicksman, N. Goldenfeld, and H. Levine, and also the opportunity for extensive discussions at the Aspen Center for Physics.

[1]For a review, see J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980), and references therein.

[2]S.-C. Huang and M. E. Glicksman, Acta Metall. **29**, 701, 717 (1981); H. Honjo and Y. Sawada, J. Crystal Growth **58**, 297 (1982).

[3]R. Trivedi and K. Somboonsuk, Acta Metall. **33**, 1061 (1985).

[4]D. A. Kessler, J. Koplik, and H. Levine, Phys. Rev. A **33**, 3352 (1986); B. Caroli, C. Caroli, B. Roulet, and J. S. Langer, Phys. Rev. A **33**, 442 (1986).

[5]F. Heslot and A. Libchaber, Phys. Scr. **T9**, 126 (1985).

[6]D. A. Kessler and H. Levine, Phys. Rev. Lett. **57**, 3069 (1986).

[7]K. Somboonsuk, J. T. Mason, and R. Trivedi, Metall. Trans. A **15A**, 967 (1984).

[8]See, for example, E. Ben-Jacob, N. Goldenfeld, B. G. Kotliar, and J. S. Langer, Phys. Rev. Lett. **53**, 2110 (1984); D. Kessler, J. Koplik, and H. Levine, Phys. Rev. A **30**, 3161 (1984).

[9]R. Pieters and J. S. Langer, Phys. Rev. Lett. **56**, 1948 (1986); G. Li, D. Kessler, and L. Sander, Phys. Rev. A **34**, 3535 (1986).

[10]N. Goldenfeld, private communication.

[11]H. Honjo, S. Ohata, and Y. Sawada, Phys. Rev. Lett. **55**, 841 (1985). Tip oscillations have also been reported in directional solidification: L. R. Morris and W. C. Winegard, J. Crystal Growth **1**, 245 (1967).

[12]D. A. Kessler and H. Levine, private communication.

[13]R. J. Diessler, J. Stat. Phys. **40**, 371 (1985), and Physica (Amsterdam) **18D**, 467 (1986); J. M. Chomaz, P. Huerre, and L. G. Redekopp, Bull. Am. Phys. Soc. **31**, 1696 (1986).

[14]R. J. Schaefer and M. E. Glicksman, Metall. Trans. **1**, 1973 (1970).