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Mean shape of three-dimensional dendrites: A comparison of pivalic acid and ammonium chloride

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The mean shape of free dendrites of pivalic acid growing from solution is determined. For a three-dimensional axisymmetric needle crystal, the mean width $\bar{w}$ of the dendrites would scale with distance z from the tip according to $w_0 = \sqrt{2\rho z}$, where ρ is the tip radius. For pivalic acid growing from a solution of pivalic acid and ethanol, we find that $\bar{w}$ does not grow as a simple power law in z, and is always larger than w_0. This result reflects the concentration of material into the sidebranching planes due to crystalline anisotropy. A comparison with NH_4Cl in aqueous solution, which has a larger surface tension anisotropy, shows that the magnitude of the crystalline anisotropy does not affect the mean shape. The connections with current three-dimensional theories of dendritic growth are also discussed.

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I. INTRODUCTION

Dendritic growth often occurs when a nonfaceted material crystallizes from an undercooled liquid or supersaturated solution, and the growth is limited by diffusion. Though the patterns that result from this process have been studied for quite some time, there are still many outstanding questions about the mechanisms that determine the overall shape and growth rate as well as the details of the sidebranch development. The two-dimensional steady-state problem appears to be well understood, but the extension to nonaxisymmetric three-dimensional shapes is more difficult. In particular, the asymptotic shape of the steady-state needle crystal and the possible dependence of that shape on the surface tension anisotropy are still open questions.

In this paper, we present measurements of the average shape of three-dimensional free dendrites of pivalic acid grown from supersaturated solution of pivalic acid and ethanol. We find that the average shape is considerably different from the steady-state paraboloid assumed in axisymmetric theoretical treatments. Further, a comparison with previous work on NH_4Cl [1] shows that the average shape is independent of the material used. These findings are consistent with a recent three-dimensional nonaxisymmetric calculation by Brener [2].

The study of the average shape was motivated in part by recent work on a variety of systems, where it has been found that appropriately averaged quantities can be an important probe of the underlying fundamental physics. For very unstable viscous fingering [3], and for two-dimensional dendritic crystal growth and anisotropic viscous fingering [4], the mean shape of the complex patterns was found to be the same as the theoretical steady state for the same conditions. In a similar vein, Gluckman *et al.* found that the time-averaged patterns of chaotic surface waves displayed significant order [5], while Ning *et al.* found that the fluctuations of rotating thermal convection patterns about the averaged state gave important information about the system, such as the instantaneous heat transport [6]. Thus it seems reasonable to suppose that the average shape may contain information about the underlying physical processes.

II. BACKGROUND

In the standard continuum model for free dendritic growth from solution, the growth is assumed to be limited by the diffusion of impurities from the growing interface [7,8]. For a given material, the steady-state tip speed v and radius of curvature ρ are determined uniquely by

the supersaturation Δ. In many cases [9–14], the quantity $\sigma^* = 2\bar{d}_0 D/(v\rho^2)$ is found to be a constant, at least for a range of Δ. Here D is the diffusion constant, and $\bar{d}_0$ is a capillary length (averaged over orientations), proportional to the surface tension [7].

In the absence of surface tension, one theoretical steady state is a parabola in two dimensions, and a paraboloid of revolution in three, but the radius of curvature and tip speed are not uniquely determined. When anisotropic surface tension is included in the two-dimensional or axisymmetric three-dimensional model, a steady-state solution can be obtained by a linearization about the zero surface tension parabola [15].

One of the main predictions of this approach, known as microscopic solvability, is that σ^* depends on the anisotropy in the surface tension. For a two-dimensional crystal with fourfold symmetry, the angular dependence of the capillary length is usually modeled by $d_0(\theta) = \bar{d}_0(1 + \epsilon_4 \cos 4\theta)$, where ϵ_4 is the surface tension anisotropy. Typically, ϵ_4 is small, on the order of 0.01.

Extensions of the model to nonaxisymmetric three-dimensional growth have proven difficult. An initial approach by Kessler and Levine [16] indicated that the tip region is still approximately a paraboloid of revolution, but the asymptotic shape is not. The importance of the asymptotic shape was not clear. Subsequent measurements of NH_4Br dendrite tips were in agreement with the predicted shape corrections near the tip [13].

Subsequently, Ben Amar and Brener studied the nonaxisymmetric three-dimensional model [17] and found that the asymptotic shape indeed diverges from a paraboloid, but that the divergence appears to be irrelevant to the selection of the tip radius and speed. This agrees with the earlier work of Kessler and Levine [16]. Further, Ben Amar and Brener found that, for small anisotropy, the shape correction near the tip is independent of the value of the anisotropy.

Recently, Brener [2] extended this work and presented a solution for both the tip shape and the intermediate and asymptotic tail shapes for nonaxisymmetric growth. Near the tip, the dendrite is described by the axisymmetric microscopic solvability theory, and is approximately the same as the Ivantsov parabola. The width w of the crystal near the tip grows as $z^{1/2}$, were z is the distance back from the tip. Further from the tip, the effects of crystalline anisotropy cause material to concentrate in the four sidebranching planes. There is an intermediate range of z where $w \propto z^{3/5}$, and an eventual crossover to a regime where $w \propto z^1$. When all lengths are scaled by ρ, this shape is independent of both supersaturation and crystalline anisotropy, at least for small values of ϵ_4.

Comparison of dendritic growth theory with experiments has proven difficult [18], both because convection is often present [9,13], and because there is considerable uncertainty in the value of ϵ_4. For pivalic acid, for example, reported values for ϵ_4 are $\epsilon_4 = 0.006$ [19], 0.025 [20], and 0.05 [11]. There are also differing reports for σ^* for the growth of NH_4Br from solution [10,13] that might be due to differences in convection in the solution.

In this work, we report measurements of the average shape of free three-dimensional dendrites. If we assume that the average shape is related to the underlying theoretical steady state, then these measurements can also be used to test the theoretical steady-state predictions. In particular, by comparing NH_4Cl and pivalic acid, we can test whether the shape is independent of the value of the crystalline anisotropy.

III. EXPERIMENTS

The experiments were performed with pivalic acid with approximately 1% ethanol added as an impurity. This amount of impurity was sufficient to ensure that the growth was limited by the transport of impurity from the interface. The saturation temperature was approximately 26 °C.

The solution was placed in a $45 \times 12.5 \times 1$ mm^3 glass cell and sealed with a Teflon stopper. The cell was mounted in a massive temperature-controlled copper block surrounded by an insulated temperature-controlled aluminum block. The entire apparatus was enclosed and controlled to ± 1 °C, and could be cooled to keep the system below room temperature. The copper block was controlled by an ac bridge, and the operating temperature could be set by computer. The resulting temperature stability of the sample was better than ± 1 mK.

The solution was heated to dissolve all the crystals, stirred to eliminate concentration gradients, and then cooled to initiate growth. Typically, many crystals would nucleate. An automated process was set up to slowly adjust the temperature until all but the largest crystal had dissolved. Only isolated dendrites that grew with both the tip velocity and the sidebranches in the plane of view were considered. After an initial transient, the growth velocity would remain approximately constant until the dendrite tip neared one of the walls of the cell. Data were only recorded for the portion of the experiment during which the growth speed and tip radius remained approximately constant. A typical pivalic acid dendrite with $v = 2.4$ μm/s and $\rho = 6.2$ μm is shown in Fig. 1.
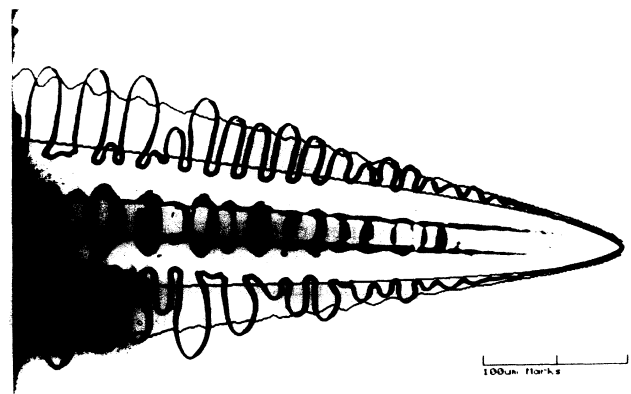

FIG. 1. A pivalic acid dendrite growing in a solution of pivalic acid and ethanol. The tip speed is $v = 2.4$ μm/s and the tip radius is $\rho = 6.2$ μm. The inner solid line is the parabola fitted to the tip. The outer solid line is the average shape for all dendrites grown under the same conditions.

Images were recorded with a charge coupled device (CCD) camera onto video tape and later digitized with a resolution of 512 × 480 pixels and an overall scale of 1.3 μm/pixel. After subtraction of a background image, the interface position was determined in the same manner as in Ref. [10]. The intensity in the image was measured on a line perpendicular to the interface. Over the range of a few pixels, the intensity changed rapidly from bright to dark. In the transition region, we fitted a straight line to the intensity profile. We defined the interface as the location where the fitted intensity was the average of the high value outside the crystal and the low value just inside the crystal. This fitting procedure interpolates intensity values and allows a reproducible measure of the interface to better than one pixel resolution. It is also insensitive to absolute intensity levels and to variations in intensity across a single image.

For each image, a parabola of the form $z - z_{\text{tip}} = (x - x_{\text{tip}})^2/(2\rho)$ was fitted to the tip, where $(x_{\text{tip}}, z_{\text{tip}})$ is the location of the tip, z is the distance back from the tip along the stem of the dendrite, and ρ is the tip radius. The velocity was determined by measuring the displacement of the tip over known time intervals. The parabola given by $w_0 = \sqrt{2\rho z}$ is shown by the inner solid line on Fig. 1.

The width $w(z)$ of the crystal in the plane of the side-branches (from the center to one side) was then measured as a function of the distance z back from the tip. Overhangs were ignored. The result for the top branches in Fig. 1 is shown in Fig. 2.

The mean width $\bar{w}(z)$ was then determined by averaging the results from a large number of images under similar conditions. In order to obtain measurements for large z, the dendrite tip was allowed to grow off the edge of the screen and the tip position was extrapolated. The result is shown as the outer solid line in Fig. 1.

When all measurements are scaled by ρ, we find that $\bar{w}(z)$ is approximately independent of both growth speed and material used. The results are shown in Fig. 3 for pivalic acid dendrites with $v = 1.3$ μm/s and 3.9 μm/s, and for NH$_4$Cl dendrites with $v = 0.93$ μm/s (from Ref. [1]). For comparison, the parabola fitted to the tip is shown by the lower solid line.

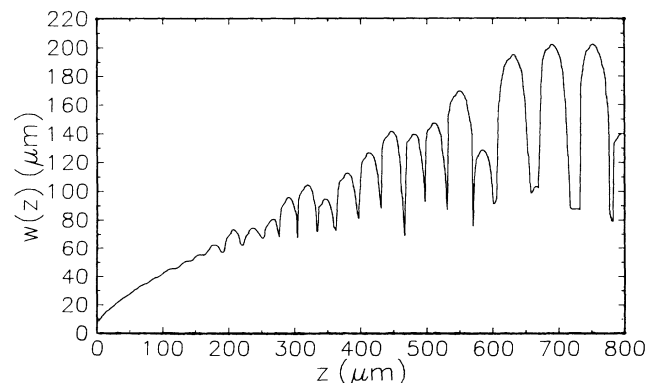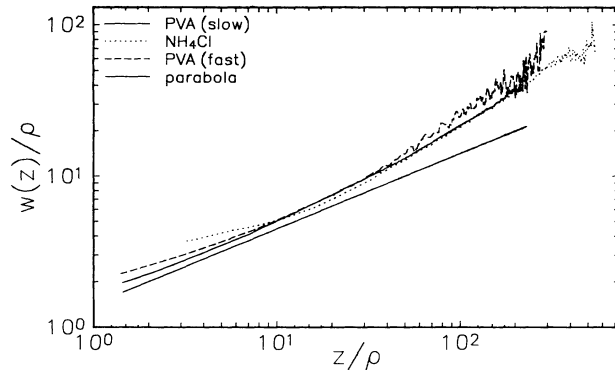Near the smooth tip, we expect $\bar{w}(z) = w_0 \propto z^{1/2}$, but

FIG. 3. Dependence of the mean dendrite width $\bar{w}(z)/\rho$ on z/ρ, where z is the distance from the tip. Curves are shown for pivalic acid (PVA) with $v = 1.3$ μm/s, $\rho = 8.1$ μm (solid), NH$_4$Cl with $v = 0.93$ μm/s, $\rho = 1.5$ μm (dotted), and PVA with $v = 3.9$ μm/s, $\rho = 4.8$ μm (dashed). The lower solid line is the parabola fitted to the tip, given by $w_0 = \sqrt{2\rho z}$.

this is near the resolution limits of the measurements and does not show up clearly in Fig. 1. For larger values of z, $\bar{w}$ increases much more rapidly than w_0. Although we do not find strict power-law behavior, we do find that for $z \gtrsim 30\rho$ the slope of the $\log_{10}(w/\rho)$ vs $\log_{10}(z/\rho)$ graph typically increases smoothly from about 0.6 to about 0.8. In some runs, there is evidence of an eventual crossover to a slope near 1. This behavior seems at least roughly consistent with the asymptotic needle-crystal shape found by Brener [2].

The variations in amplitude among the curves shown are typical of all those obtained, both in the present work and in the previous work on NH$_4$Cl. To within the sensitivity of the measurements, this average shape appears to be independent of both supersaturation and crystalline anisotropy.

The range of available supersaturations for the present work is somewhat limited. At low supersaturation, the crystals are quite large, and it is difficult to obtain measurements for many sidebranches large distances from the tip. In addition, the finite size of the cell becomes a factor as the diffusion length D/v becomes comparable to the cell dimensions. Convection may also be a significant problem at low supersaturation [19,9]. At high supersaturation, the crystals are quite small and growth is very rapid. This makes quantitative imaging difficult.

Although the mean width in the plane of the side-branches diverges from the Ivantsov parabola, it is important to note that the axially averaged growth shape is still consistent with the Ivantsov parabola, as was found in Ref. [1]. This simply reflects the fact that the growth is limited by diffusion. Thus, while the tip grows with constant speed, the axially averaged width grows as $t^{1/2}$, or as $z^{1/2}$.

IV. CONCLUSIONS

The main results of this work are shown in Fig. 3. First, the mean asymptotic shape of three-dimensional nonaxisymmetric dendrites diverges strongly from a

FIG. 2. Width $w(z)$ of the crystal in Fig. 1, from the center line to the branches on the top side.

paraboloid of revolution. Instead, the material is concentrated by crystalline anisotropy into the sidebranching planes. Second, that mean shape is independent of both the growth conditions and the crystalline anisotropy ϵ_4 of the materials used. Although no power-law scaling was observed, these results are roughly consistent with the asymptotic needle-crystal shape found by Brener [2].

This work has addressed the mean shape only over a limited range of distances, where the sidebranches still actively compete. Eventually, the spacing between active sidebranches becomes sufficiently large that they must grow as essentially free dendrite tips. It remains to be seen whether the present picture holds even for such large distances, or whether the overall growth envelope might indeed depend on supersaturation, as appears to be the case for some mean-field models of diffusion-limited growth [21]. It is also not clear whether similar results would hold for systems such as ^{3}He where the sidebranch activity is apparently very weak [22].

ACKNOWLEDGMENTS

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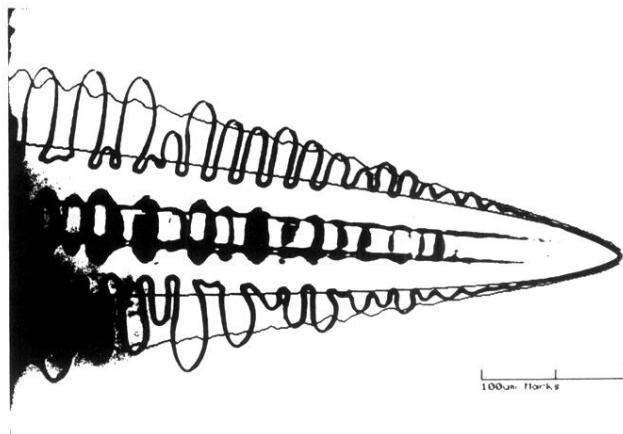[22] Etienne Rolley, Sebastien Balibar, and Francois Graner (unpublished).

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