Three-dimensional dendrite tip morphology at low undercooling

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We investigate the three-dimensional morphology of the dendrite tip using the phase-field method. We find that, for low undercoolings, this morphology is ostensibly independent of anisotropy strength except for a localized shape distortion near the tip that only affects the value of the tip radius $\rho$ (which is crudely approximated by $\rho \approx (1 - \alpha)\rho_{iv}$ where $\rho_{iv}$ is the Ivantsov tip radius of an isothermal paraboloid with the same tip velocity and $\alpha$ is the stiffness anisotropy). The universal tip shape, which excludes this distortion, is well fitted by the form $z = -r^2/2 + A_4 r^4 \cos 4\phi$ where $|z|$ is the distance from the tip and all lengths are scaled by $\rho_{iv}$. This fit yields $A_4$ in the range $0.004 - 0.005$ in good quantitative agreement with the existing tip morphology measurements in succinonitrile [LaCombe et al., Phys. Rev. E 52, 2778 (1995)], which are reanalyzed here and found to be consistent with a single $\cos 4\phi$ mode non-axisymmetric deviation from a paraboloid. Moreover, the fin shape away from the tip is well fitted by the power law $z = -a|x|^{5/3}$ with $a \approx 0.68$. Finally, the characterization of the operating state of the dendrite tip is revisited in the light of these results.

I. INTRODUCTION

The shape of crystal dendrites was first suggested by Papapetrou [1] to be parabolic, and slightly more than a decade later Ivantsov demonstrated [2] that a parabola (paraboloid) is an exact solution of the steady-state growth equations in two (three) dimensions when capillary effects are entirely neglected and the interface is isothermal. He derived the well-known relationship

$$\Delta = \frac{P_{iv}}{\rho_{iv} V} \int_{P_{iv}}^\infty ds \frac{\exp(-s)}{s}$$

(1)

between the Peclet number $P_{iv} = \rho_{iv} V/(2D)$ and the dimensionless undercooling $\Delta = (T_{s} - T_{\infty})/(L/c_p)$ for a paraboloid of tip velocity $V$ and tip radius $\rho_{iv}$ where $D$ is the thermal diffusivity, $T_{s}$ is the melting temperature, $T_{\infty}$ is the initial temperature of the undercooled liquid, $L$ is the latent heat of melting, and $c_p$ is the specific heat at constant pressure.

In more recent history, the development of solvability theory [8,9] has led to the additional and crucial understanding that the anisotropic surface energy acts as a singular perturbation that uniquely selects the tip velocity, and also alters the entire dendrite shape [10]. According to this theory, the scaling parameter $\sigma^* = 2 D d_0 / \rho_{iv}^2 V$ (where $d_0$, defined below, is the capillary length) approaches a constant at low undercooling that only depends on the anisotropy strength (denoted here by $\epsilon_a$ for a crystal with an underlying cubic symmetry), and scales as $\sigma^* \sim \epsilon_a^{3/4}$ in the limit of vanishingly small anisotropy. In this same limit, Ben Amar and Brener [11] have predicted that capillary effects lead to a universal four-fold deviation from a paraboloid of the form

$$z = -\frac{r^2}{2} + A_4 r^4 \cos 4\phi,$$

(2)

where $A_4 = 1/88$ is independent of anisotropy strength and $(r, \phi)$ are the polar coordinates in the plane normal to the growth axis $z$ with all lengths scaled by $\rho_{iv}$. The improved prediction $A_4 = 1/96$ has been obtained in a subsequent analysis [12].

To characterize the shape further behind the tip, Brener remarked that the cross-sectional shape of needle crystal dendrites perpendicular to the growth axis can be assumed to evolve with increasing distance $|z|$ from the tip as a two-dimensional growth shape in time ($t = |z|/V$). The area of this shape increases linearly in time, and thus $|z|$, as

$$S(z) = 2\pi \rho_{iv} |z|$$

(3)

where $\rho_{iv}$ is defined by Eq. 1 with $V$ being the actual tip velocity. This area corresponds to the well-known self-similarity solution of a growing circle in two dimensions and is also the exact cross-sectional area of the three-dimensional Ivantsov paraboloid of revolution. The above mapping is presumed to become justified far enough away from the tip where the component of the heat flux along $z$ can be neglected. Using this mapping and the results of a previous analysis of two-dimensional anisotropic Laplacian growth at constant flux [13], he predicted that the width of the four dendrite fins should increase as the $3/5$ power of the distance behind the tip [14], yielding the expression

$$z = - \frac{3}{5} \left( \frac{\sigma^*}{\sigma_2^*} \right)^{1/3} |x|^{5/3},$$

(4)

where $x$ is the interface coordinate normal to the $z$-axis in a $(010)$ section of the tip and $\sigma_2^*$ ($\sigma^*$) is the tip scaling parameter in two (three) dimensions. Moreover, the ratio $\sigma_2^*/\sigma^*$ becomes independent of anisotropy for weak anisotropy with $(\sigma_2^*/\sigma^*)^{1/3} \approx 1$. 

81.30.Fb, 64.70.Dv, 81.10.Aj
Our goal in this paper is to use the phase-field method to obtain a characterization of the dendrite tip morphology that is sufficiently detailed and accurate to test the above theoretical predictions and to make a critical comparison with existing benchmark experiments [11,12]. The present simulations are based on a novel adaptive-step diffusion Monte Carlo method [11,12] that provides an efficient treatment of the large scale diffusion field away from the growing structure. Thus this method allows us to investigate a relatively low undercooling range $\Delta \sim 0.1$ ($P_t \sim 0.03$), in contrast to previous simulations that were limited to Peclet numbers of order unity [13]. As it turns out, and this is one of the main findings in this paper, the tip morphology in this Peclet number range is already ostensibly independent of anisotropy strength and undercooling, except for a localized shape distortion at the tip that is not experimentally relevant. We are therefore able to compare meaningfully this morphology to existing detailed dendrite shape measurements in succinonitrile [8] and xenon [10], even though these measurements were carried out at even smaller $\Delta$.

In the next section, we review the basic equations of the symmetric model of dendritic growth in three dimensions and briefly summarize our numerical methods. The numerical results are then presented in section III and discussed in section IV. Finally, a summary and conclusions are presented in section V.

II. BASIC EQUATIONS

We study the standard symmetric model of solidification in a pure undercooled melt that assumes equal thermal diffusivities in the solid and liquid phases. The basic equations of this model are given by

$$\partial_t u = D \nabla^2 u,$$

$$v_n = D (\partial_n u)|_s - \partial_n u|_l,$$

$$u = -d_0 \sum_{i=1}^2 \left[ a(\hat{n}) + \partial_i^2 a(\hat{n}) \right] \kappa_i,$$

where following common notation, $u = (T - T_m)/(L/c_p)$ is the scaled temperature field that is zero in equilibrium and equal to $-\Delta$ in the liquid far from the interface, $\partial_n u|_l$ ($\partial_n u|_s$) is the normal gradient of $u$ on the liquid (solid) side of the interface, $v_n$ is the normal velocity of the interface, $\theta_i$ are the local angles between the normal $\hat{n}$ to the interface and the two local principal directions on the interface, $\kappa_i$ are the principal curvatures, $d_0 = \gamma_0 T_M c_p/L^2$ is the microscopic capillary length, and $\gamma(\hat{n}) = \gamma_0 a(\hat{n})$ is the anisotropic surface energy where

$$a(\hat{n}) \equiv (1 - 3\epsilon_4) \left[ 1 - \frac{4\epsilon_4}{1 - 3\epsilon_4} (n_x^4 + n_y^4 + n_z^4) \right]$$

for a material with an underlying cubic symmetry, with the $x$, $y$, and $z$ axes chosen parallel to the [100] directions. In writing down the interface condition [11], we have purposely neglected the effect of interface kinetics that is believed to be negligible for the low undercooling range where benchmark shape measurements have been carried out [8,10]. Moreover, theoretical shape predictions to date [2,3] have neglected this effect.

We use two different numerical methods. The first, and main one used here, is the phase-field approach [14,15] that allows us to study the dendrite shape for the full cubic form of the surface energy defined by Eq. 8. In particular, we simulate the time-dependent evolution of a single dendrite arm until steady-state growth is reached. Since we are primarily interested in a low undercooling regime, we use the results of the asymptotic analysis of Karma and Rappel [13] in order to choose the interface width in the phase-field model about an order of magnitude smaller than $\rho$, and thus much larger than $d_0$ for small $\Delta$. This analysis also allows us to choose the model parameters so as to make kinetic effects vanishingly small. Moreover, we use a recently developed Monte Carlo algorithm to integrate efficiently the diffusion equation in the liquid away from the growing structure. In this approach, space is divided into two regions. The first region consists of the solid plus a thin liquid layer surrounding the interface where the deterministic phase-field equations are solved on a cubic lattice with the same choice of computational parameters as in Ref. [13]. The second region is the rest of the liquid where the diffusion equation is solved using an ensemble of random walkers that take progressively larger steps with increasing distance away from the interface. The algorithm used to interface the deterministic and stochastic solutions of the diffusion equation in these two regions and to update the walkers has been summarized in Ref. [13] where it was used to study the early stage of dendritic evolution. It has also been exposed in more details in Ref. [12] together with the results of numerical tests and need not be re-described here.
We exploit the cubic symmetry to reduce simulation time by only integrating a part of a single dendrite arm (the domain \( x > 0, 0 < y < x \) and \( z > x \)), taking advantage of the symmetry planes defined by \( x = 0, y = 0, x = y, \) and \( x = z \). The whole dendrite can then be reconstructed by successive reflections at these planes, and the result of one of our simulations is shown in Fig. 3. These simulations were performed on regular lattices of size \( 240 \times 240 \times 800 \) and each took about 200 hours of CPU time on a 525 MHz DEC-8400 computer. Note that almost no sidebranches can be discerned, although the length of the dendrite arms is more than 40 times the tip radius of curvature. For the analysis of the steady-state shapes, we used only the part of the dendrite grown at a constant tip velocity, which corresponds to about one third of the arm length in Fig. 1. To check whether the shape is well converged, we performed one run in which the dendrite arm growing along the positive \( z \)-direction was “cut off” sufficiently far behind the tip, and its further evolution was simulated in a smaller box moving with the dendrite tip for several diffusion times \((D/V^2)\). No significant change of the shape was observed. In addition, this run (for \( \Delta = 0.1 \) and \( \epsilon_4 = 0.025 \)) yielded data which extend considerably farther behind the tip than for the other parameters, well to within the range where sidebranches are observed in experiments.

The second numerical method is the standard boundary integral method \([3]\) that can be used to solve directly the sharp-interface steady-state growth equations with the simplified axisymmetric form of surface energy

\[
\alpha(\hat{n}) \equiv (1 - 3\epsilon_4) \left[ 1 - \frac{4\epsilon_4}{1 - 3\epsilon_4} (\cos^4 \theta + \frac{3}{4} \sin^4 \theta) \right], \tag{9}
\]

which is obtained by averaging the full cubic form \([8]\) over the polar angle \( \phi \) in the \( x-y \) plane; \( \theta \) is the angle between the local normal to the solid-liquid interface and the \( z \)-axis. This method only describes axisymmetric tip shapes and is thus only used here as an additional basis of comparison with phase-field results regarding the anisotropy-dependent shape distortion in the tip neighborhood and the selected tip operating state.

III. NUMERICAL RESULTS

A. Equal cross-sectional area shape

The cross-sectional area of solid normal to the growth axis was calculated using the formula

\[
S(z) = \int \frac{1}{2} \psi(x, y, z) \ dv, \tag{10}
\]

where \( \psi(x, y, z) \) is the phase-field that varies from +1 in the solid to −1 in the liquid in the present model \([3]\) and \( \psi(x, y, z) = 0 \) defines the solid-liquid interface. This formula is accurate far enough away from the tip, but of course not at the tip itself, which suffices for the present purposes. Plots of \( S(z) \) vs \( z \) are shown in Fig. 3 for different undercoolings and anisotropy strengths. \( S(z) \) is accurately fitted by a straight line sufficiently away from the tip. This allows us to define the ‘parabolic’ tip radius, \( \rho_p \), of a paraboloid of revolution with the same cross-sectional area as the non-axisymmetric phase-field shape. Such a paraboloid has a cross-sectional area

\[
S_p(z) = 2\pi \rho_p (z_0 - z) \quad \text{for} \quad z < z_0, \tag{11}
\]

where \( z_0 \) is its tip position. By fitting the linear part of \( S(z) \) away from the tip computed from Eq. (10) with Eq. (11), we obtain an accurate estimate of \( \rho_p \) (note that \( z_0 \) need not coincide with the tip position of the full non-axisymmetric shape, see below). The quality of this fit will be illustrated below in Fig. 3, where it is compared to a different method for determining \( \rho_p \).

Remarkably, and in good agreement with theoretical expectation (Eq. 3), \( \rho_p \) coincides to within a numerical accuracy of 1-2 % with the Ivantsov tip radius \( \rho_{IV} \equiv 2DP_{IV}/V \) of the isothermal paraboloid growing with the same tip velocity as the phase-field shape for the different undercoolings and anisotropies investigated here. This indicates that \( \rho_p \approx \rho_{IV} \) is potentially a good scaling parameter for the entire dendrite shape as will be confirmed below. Therefore, unless otherwise stated, all lengths will be rescaled by \( \rho_{IV} \) for the reminder of this paper. The origin of the \( z \)-axis is chosen to coincide with the tip position of the non-axisymmetric dendrite shape.

It is also useful to define the equal cross-sectional area (ECSA) shape

\[
r_0(z) = \left[ \frac{1}{2\pi} \int_0^{2\pi} r^2(z, \phi) \ d\phi \right]^{1/2} \tag{12}
\]

where \( r(z, \phi) \) is the radial coordinate of the full non-axisymmetric shape. This is simply the axisymmetric shape.
shape that has the same cross-sectional area as the full shape, and the above results imply at once that \( r_0(z) \) coincides away from the tip with the Ivantsov paraboloid. The ECSA shape is shown as solid squares in Fig. 3 together with the parabolic fit obtained by using Eqs. (11) and (12). The parabolic fit is extended all the way to its tip position \( z_0 \) for illustrative purposes.

B. Non-axisymmetric tip morphology

Longitudinal sections of the dendrite tip in the \( \phi = 0^\circ \) and \( \phi = 45^\circ \) planes that correspond to the ‘fins’ and ‘valleys’ of the non-axisymmetric shape, respectively, are superimposed in Fig. 3. The two contours coincide in the upper region of the tip, where the shape is essentially axisymmetric, but depart from a paraboloid (dashed line in Fig. 3) in a small region near the tip that will be examined more closely in section III.C. The important point here, especially relevant for comparisons between simulations and experiments, is that aside from this localized tip distortion the entire tip shape scales with \( \rho I_v \) and is ostensibly independent of anisotropy strength and undercooling over the range investigated here. This is clearly demonstrated by the nearly perfect superposition of longitudinal and transverse sections of the various tip shapes shown in Fig. 4 and Fig. 5, respectively. A three-dimensional view of this universal tip morphology is shown in Fig. 6.

In order to test if the analytical form defined by Eq. 2 provides an accurate description of the non-axisymmetric
tip shape, we determined $A_4$ by minimizing the spatially averaged root-mean-square (rms) deviation $<\delta z^2>^{1/2}$, between the actual shape in the (010)-plane and the polynomial form $z = -r^2/2 + A_4 r^4$ over the interval $1 \leq |z| \leq n$ where $n$ was varied from 4 to 20 in steps of 2. The resulting values of $A_4$ and $<\delta z^2>^{1/2}$ are plotted for the different undercoolings and anisotropy strengths in Fig. 7 and Fig. 8, respectively. Fig. 8 shows that the form (2) provides a good fit of the fin shape for $n$ up to about 10, after which the rms deviation starts to increase rather sharply. Fig. 7, in turn, shows that the fitted value of $A_4$ depends on the fitting length. This means that the polynomial form (2) does not exactly characterize the fin shape. However, the dependence of $A_4$ on $n$ is rather weak: $A_4$ varies between about 0.004 and 0.005 for $n$ between 4 and 10. A comparison of the polynomial fit and the computed fin shape is shown in Fig. 9, showing an excellent overlap up to 10 $\rho I_v$ behind the tip.

We have also fitted the fin shape to the power law $z = -a|x|^\beta$ by minimizing the rms deviation from the computed shape as above. This minimization was carried out both with $a$ and $\beta$ as free parameters and with $a$ as free parameter and $\beta$ fixed to the theoretically expected value 5/3. The values of $a$ and $\beta$ resulting from these two fits are plotted vs the fitting range parameter $n$ in Fig. 11 with the corresponding rms deviations plotted in Fig. 8.
FIG. 9. Comparison of the computed fin shape (open circles) with the polynomial fit for \( n = 10 \) (\( A_4 = 0.004 \), solid line) and the power law fit for \( n = 20 \) and \( \beta = 5/3 \) (\( a = 0.685 \), dashed line).

FIG. 10. Comparison of the computed tip cross-sections for \( \epsilon_4 = 0.025 \), \( \Delta = 0.1 \), and the shape given by Eq. (2) with \( A_4 = 0.004 \). Cross-sections are taken at \( |z|/\rho_{Iv} = 2, 4, 6, 8, \) and 10.

In the two-parameter fit, \( \beta \) is larger than \( 5/3 \) (\( \approx 1.8 \)) for small \( n \) and tends to 1.7 for larger \( n \), which is close to \( 5/3 \). Note that the value of \( a \) is somewhat smaller in the two-parameter fit than in the one parameter fit because of the larger \( \beta \) in the former, and that the two-parameter fit has a smaller rms deviation as one would expect. The two fits, however, become essentially equally good for large \( n \). In this range, the one-parameter fit yields \( a \approx 0.68 \) independent of anisotropy strength. A comparison of the power law fit and the computed fin shape is shown in Fig. 9. In contrast to the polynomial fit, which becomes inaccurate for \( |z| > 10 \rho_{Iv} \), the power law closely fits the fin shape even far away from the tip.

C. Localized tip distortion and tip radius

Let us now return to examine more closely the shape departure from a paraboloid in the region very close to the tip. For this purpose, we show in Fig. 12 a tip magnification of the same curves as in Fig. 3, together with the axisymmetric shape computed by the boundary integral method for an azimuthally averaged surface energy. The latter coincides well with the fins and valleys in the tip neighborhood, but the superposition of these three curves departs from the parabolic fit of the ECSA shape, which represents the interface shape if anisotropic capillary effects were absent. Note also that the boundary integral result starts to deviate noticeably from the phase-field shape rather close to the tip, approximately at \( |z| \approx 0.5 \rho_{Iv} \).

A quantitative measure of this departure is the ratio \( \rho/\rho_{Iv} \), where \( \rho \) is the actual numerically computed tip radius of the phase-field or boundary integral shape and \( \rho_{Iv} \) (recall that \( \rho_{Iv} \equiv 2D_P I_v / V \) where \( P \) is the Peclet number predicted by Eq. 1 and \( V \) is the numerically
computed tip velocity). For the phase-field shape, $\rho$ is computed from the $\phi = 0^\circ$ section using the interpolation scheme that is described in Appendix B of Ref. [13], and which has been tested against exact boundary integral benchmark results in two dimensions.

Figs. 13 and 14 show the variation $\rho/\rho_{Iv}$ as a function of undercooling and anisotropy, respectively. The departure of $\rho$ from the Ivantsov relation increases with anisotropy strength. The same trend was previously found for a higher undercooling ($\Delta = 0.45$) in Ref. [13] and the results of these earlier simulations are also shown in Fig. 14. A new finding here is that this departure becomes independent of undercooling in the low undercooling range studied here as can be seen from the flattening of the curves at small $\Delta$ in Fig. 13. For $\Delta \sim 0.1$, $\rho/\rho_{Iv}$ is already quasi-independent of $\Delta$ and its small $\Delta$ limiting value depends solely on the anisotropy strength. Interestingly, the variation of $\rho/\rho_{Iv}$ with anisotropy is crudely approximated by the relation

$$\rho/\rho_{Iv} \approx 1 - \alpha,$$  

(13)

over an order of magnitude change in anisotropy strength, where $\alpha = 15\epsilon_4$ is the stiffness anisotropy. Since the Gibbs-Thomson condition (7) implies that the steady-state dendrite tip temperature is given by

$$u_{\text{tip}} = -2d_0(1 - \alpha)/\rho,$$  

(14)

Eq. (13) is equivalent to stating that the dendrite tip temperature at a given undercooling is relatively independent of anisotropy strength. The straight line corresponding to Eq. (13) is superimposed as a dashed line in Fig. 14. The numerical results lie slightly above and below this curve for small and large anisotropy, respectively.

IV. DISCUSSION

A. Comparison with analytical theories

Let us first compare our results with the analytical theories reviewed in the introduction. We have found that Eq. (2) provides a good fit of the tip shape up to a distance of about eight to ten $\rho_{Iv}$ behind the tip. Moreover, for low undercooling, this shape is independent of anisotropy strength (at least over the range investigated here) which is in qualitative agreement with the prediction of linear solvability theory [5,6]. The value of $A_4$ found here, however, is about twice smaller than the value $A_4 = 1/96 \approx 0.0104$ [6] predicted by this theory. One possible reason for this discrepancy is that the existing solvability calculations [5,6] are carried out in the limit of vanishing anisotropy, whereas in the present computations the anisotropy is finite. We have seen, however, that even for a short fitting distance behind the tip, $A_4$ increases from about 0.004 to 0.005 when the anisotropy is lowered from 2.5% to 1.25%, which does not appear
consistent with an extrapolation of $A_4$ to its theoretically predicted value in the limit that $\epsilon_4 \rightarrow 0$. It seems also difficult to explain this discrepancy by the fact that existing calculations are based on linearizing the steady-state growth equations around a paraboloid of revolution. We find indeed a localized tip distortion that depends strongly on anisotropy strength, and which is not accounted for in these theories. The rest of the tip shape, however, departs only weakly from a paraboloid and is accounted for in these theories. The rest of the tip shape, however, departs only weakly from a paraboloid and is well fitted by the form (2) independently of anisotropy. Therefore, the origin of this discrepancy remains to be understood.

In contrast, the predicted power law (Eq. 3) for the fin shape away from the tip is in relatively good quantitative agreement with the present simulations. We find a good fit of the fin shape with a fixed exponent $\beta = 5/3$ and a prefactor $a \approx 0.68$ that is independent of anisotropy strength and only about 15% larger than theoretically predicted, or with a slightly higher exponent $\beta = 1.7$ and a lower $a \approx 0.65$. It is interesting to note that the mapping with two-dimensional growth shapes [7] implies that Eq. 2 should only strictly hold in a region far behind the tip where the cross-sectional shape contains four well-developed arms. It is therefore rather remarkable, and perhaps coincidental, that it also holds closer to the tip in a region where the fins are not yet well developed.

Finally, we note that our results indicate a smooth cross-over from a polynomial form to a power law form for the fin shape with increasing $|z|$ as indicated by the excellent overlap of these two forms in an intermediate distance range behind the tip (Fig. 3).

**B. Comparison with experiments**

On the experimental side, the most detailed shape measurements to date have been carried out by LaCombe et al. who analyzed the full three-dimensional tip morphology in succinonitrile (SCN) [9] and by Bisang and Bilgram who studied the fin shape in xenon [11].

On the basis of their measurements on SCN dendrites, Lacombe et al. reported that the tip shape can be fitted by the form

$$z \approx -\frac{r^2}{2} - Q(\phi) r^4,$$  \hspace{1cm} (15)

where lengths are in units of the tip radius. The values for the function $Q(\phi)$ reported by these authors and the associated error bars are reproduced here in Fig. 15. It can be seen that $Q(\phi)$ differs from a cosine function, and they concluded that the tip morphology cannot be described by a pure $\cos 4\phi$ mode, in apparent disagreement with solvability theory and the present results. This function, however, was constructed from projected shapes obtained by taking photographs of the dendrite tip from different azimuthal angles $\phi$. We point out here that Eq. 15 with $Q(\phi)$ obtained from projected shapes does not correctly represent the actual non-axisymmetric tip morphology from which these projections are obtained. The reason is that the projected shape observed from a given azimuthal angle $\phi$ differs from the cross-sectional shape at this angle. To illustrate this point, we have drawn in Fig. 16 a cross-section of the tip shape normal to the growth direction and rotated it by an angle $\phi$ with respect to the viewing direction chosen parallel to the Y-axis. The projected shape appears wider than the 'true' contour of the dendrite at that orientation. Therefore, the dendrite cross-sections (Fig. 11 in Ref. [9]) reconstructed by LaCombe et al. using Eq. 15 are not representative of the true cross-sections.

It is nonetheless possible to relate our results to the experimental measurements of these authors by calcu-
Fitting numerically the function $Q(\phi)$ that corresponds to the tip morphology characterized by a single $\cos 4\phi$ mode (Eq. 3). As mentioned earlier, Eq. 3 with $A_4 = 0.004$ provides a good fit to our simulated tip morphology up to $10 \rho_{f}$, behind the tip and is therefore adequate for the purpose of this comparison (neglecting small corrections due to higher azimuthal harmonics). To obtain $Q(\phi)$, we must first calculate numerically the projected shape, and thus relate the apparent width $w(\phi, z)$ of the dendrite at a given distance $z$ behind the tip to the true width $r(-\phi, z)$, which is the intersection of the fixed $X$-axis with the interface. Using the definitions of Fig. 16 and purely geometrical considerations, it is simple to obtain the relation

$$w(\phi, z) = r(\psi - \phi, z) \cos \psi$$

where $\psi(\phi, z)$ is defined implicitly by the relation

$$\psi = \arctan \left[ \frac{\partial_{\psi}r(\psi - \phi, z)}{r(\psi - \phi, z)} \right].$$

Eq. 17 follows directly from the condition that the point on the true contour that corresponds to the apparent (perceived) edge of the solid tip (point A in Fig. 16) be the one of maximum width as a function of $\psi$. For a fixed $\phi$, the corresponding $\psi$ can be simply obtained by setting equal to zero the derivative of the right-hand-side of Eq. 16 with respect to $\psi$. The angle $\psi$ defined implicitly by Eq. 17 is then the polar coordinate of this point measured from the fixed $X$-axis in Fig. 16, and $-\psi$ measures the angle between the line OA and the (010) plane. Note that at this point, Eqs. 16 and 17 can be used to construct the projected shape that corresponds to an arbitrary true shape whose transverse sections are convex. To proceed further, we now restrict our attention to the case where the true shape is given by Eq. 3, or equivalently

$$r(\phi, z) = \left[ 1 - \frac{1 - 16A_4 \cos 4\phi}{4A_4 \cos 4\phi} \right]^{1/2}$$

(18)

Combining Eqs. 16 through 18, we obtain numerically the projected shape $z(\phi, w)$ that is the inverse of $w(\phi, z)$ at fixed $\phi$. We finally obtain $Q(\phi)$ by following the same procedure as LaCombe et al. that consists of fitting these shapes to a fourth order polynomial of the form

$$z \approx -w^2/2 - Q(\phi)w^4$$

for different values of $\phi$. This procedure yields a function $Q(\phi)$ that differs from $\cos 4\phi$ and is superimposed as a dashed line in Fig. 15. This function fits well through the data points for $Q(\phi)$ reported by LaCombe et al. We therefore conclude that, within experimental error bars, our simulated universal tip morphology dominated by a single $\cos 4\phi$ mode with an amplitude $A_4 \approx 0.004$ agrees quantitatively well with the true underlying tip morphology of SCN dendrites.

A few additional remarks should be made. Firstly, in drawing the above conclusion we have implicitly assumed that the inverse problem that consists of reconstructing the true shape from its projections has a unique solution. It can indeed be shown that this solution is unique \cite{17}, such that this assumption is valid. That is if we were to calculate the true shape from the projections defined by Eq. 19 we would recover a tip shape that is well fitted by Eq. 2. Moreover, an explicit solution to this inverse problem can be obtained analytically by cleverly noting \cite{17} that it is exactly analogous to the one of constructing a two-dimensional equilibrium crystal shape, with the role of the anisotropic surface energy being played here by $w(\phi, z)$ at fixed $z$. This is the well-known Wulff construction \cite{18} and the application of the $\xi$-vector formalism of Calm and Hoffman \cite{19} yields that the distance $AB$ in Fig. 16 is equal to $|\partial_{\phi}w(\phi, z)|$, and thus that the solution to this inverse problem is given by

$$r(\psi - \phi, z) = \sqrt{[w(\phi, z)]^2 + [\partial_{\psi}w(\phi, z)]^2},$$

(20)

$$\psi = -\arctan \left[ \frac{\partial_{\psi}w(\phi, z)}{w(\phi, z)} \right].$$

(21)

It should therefore be in principle possible to reconstruct the higher azimuthal harmonics from the experimental data. At present, however, such an analysis is precluded by the magnitude of the error bars in the measurements, especially in view of the small amplitude of such harmonics predicted by our simulations. Lastly, we note that in the present example the exact (numerically computed) projected shapes $z(\phi, w)$ defined by Eqs. 16-18 are only approximately fitted by fourth order polynomials in $w$, even though the underlying true shapes defined by Eq. 3 are exact fourth order polynomials in $r$. It is simple to see why this is so by using Eqs. 16-18 to derive an analytical expression for the projected shape in powers of $A_4$ (valid close to the tip), and by noting that this expansion generates terms $\sim w^6$ at $O(A_4^2)$. Nonetheless,
the form (Eq. 19) provides a reasonably accurate global fit of the projected shape over the range $0 < |z| < 10$ and is therefore quantitatively adequate to interpret experimental results.

In xenon, Bisang and Bilgram have reported that they cannot accurately fit the fin shape with a low order polynomial. They find, instead, a good fit with a power law $|z| = ax^\beta$ with $a = 0.58 \pm 0.04$ and $\beta = 1.67 \pm 0.05$, that extends rather close to the tip. Our present results differ from theirs in that both for the polynomial and the power law fit, the fitting parameters vary with the fitting length, including the exponent $\beta$ which increases when the fit is restricted to a region close to the tip. On the other hand, in agreement with their findings, the polynomial fit becomes inaccurate for larger fitting lengths, whereas the power law fits the fin shape even far behind the tip. While the exponents obtained from our simulations and their measurements are very close, we find here a slightly larger prefactor $a \approx 0.68$, independently of anisotropy. Note, however, that this discrepancy might be simply due to the choice of the rescaling length. Bilgram and Bisang use the actual tip radius as a scaling length, whereas we use the Ivanitsov tip radius. Taking this into account, their prefactor $a'$ and our prefactor $a$ should be related by $a' = a(\rho/\rho_t)^{-\beta}$. As $\rho$ is smaller than $\rho_t$, our prefactor should indeed be larger than theirs. It would be interesting to re-examine the experimental data using $\rho_t$ as the scaling length.

C. Tip distortion

The tip distortion analyzed in section III.C can be interpreted to result from capillary effects at the tip that persist even in the limit of low undercooling. It may appear at first counter-intuitive that such effects remain important in this limit since the magnitude of capillary corrections to the tip temperature vanishes due to the increase of the tip radius, i.e. $d_0/\rho \to 0$ as $\Delta \to 0$. One must recall, however, that the tip velocity and thus the temperature gradient at the tip also vanishes in this limit. Thus the correct measure of the relative importance of capillary effects is the ratio of the magnitudes of the normal gradient of $u$ in the tip region induced by capillary variations, $(\partial_n u)_c \sim d_0/\rho^2$, and by heat diffusion, $(\partial_n u)_d \sim V/D$, or $(\partial_n u)_c/(\partial_n u)_d \sim Dd_0/(\rho^2V) \sim \sigma^*$. The constancy of $\sigma^*$ implies that capillary effects can produce a non-negligible tip distortion that persists in the low undercooling limit.

With regard to the tip radius, Eq. 13 can be crudely interpreted to be the simplest linear interpolation between the isotropic limit where the tip radius approaches its isothermal value, and the limit $\alpha \to 1$ ($\epsilon_4 \to 1/15$) which marks the appearance of cusps at the $[100]$ orientations of the equilibrium shape where $\rho$ vanishes. There is, of course, no obvious reason why this linear interpolation should exactly hold in between these two limits and Fig. 14 shows that our numerical results do not lie exactly on it. Eq. 13 should only be considered a reasonable first estimate of the actual tip radius.

D. Operating state

Traditionally, the operating state of the dendrite tip has been characterized in terms of two independently measurable parameters, the tip radius $\rho$ and velocity $V$, from which one defines the scaling parameters

$$P = \frac{\rho V}{2D}$$

$$\sigma^* = \frac{2Dd_0}{\rho^2V}$$

It is clear, however, from the present results that an accurate measurement of the ‘true’ tip radius is most likely not experimentally feasible. Such a measurement would require a very high resolution of the localized shape distortion near the tip that is already barely noticeable on the scale of Fig. 2 for a 2.5% anisotropy, and with the interface and the reference parabola represented by thin lines that are finer than the experimental resolution.

The present results show that, outside the small region very close to the tip where this distortion is noticeable, the entire tip shape is well fitted by a paraboloid with a small non-axisymmetric four fold deviation, and that the rest of the dendrite shape further away from the tip scales with the tip radius $\rho_0$ of this paraboloid. Therefore, a better definition of the tip operating state is to use $\rho_0$ instead of $\rho$ and to define accordingly the dimensionless parameters

$$P_\rho = \frac{\rho_0 V}{2D}$$

$$\sigma^* = \frac{2Dd_0}{\rho_0^2V}$$

which are actually the ones that have been traditionally measured in experiments. In addition, the definition of $\sigma^*$ used in solvability theories (see section I) coincides with the latter definition with the further assumption that $\rho_0 = \rho_t$. For a weakly anisotropic material such as SCN $\rho$ is not too different from $\rho_t$ such that the two definition sets (Eqs. 22 and 24) are roughly equivalent. In contrast, for a more strongly anisotropic material such as pivalic acid (PVA), $\rho_0$ can be about two to five times larger than $\rho$, and concomitantly $\sigma^*$ four to twenty-five times smaller than $\sigma^*$ if we assume that $\epsilon_4$ is somewhere in the range $0.025 - 0.05$, where the lower limit has been measured by Muschol et al. and the upper one by Glicksman and Singh.

If we adopt Eqs. 22 and 24 as a definition of the tip operating state, three questions remain to be addressed. Firstly, what is the best way to measure $\rho_0$? Secondly, how accurately does linear solvability predict the tip operating
state as compared to the present simulations? Lastly, does \( \rho_p \) necessarily equal \( \rho_{1v} \), as found here and assumed in solvability theory?

In our simulations, we have obtained \( \rho_p \) in section III.A from a plot of the cross-sectional area of the dendrite versus distance from the tip, exploiting the fact that, away from the tip, \( \rho_p \) is simply the slope of this curve divided by 2\( \pi \). This provides a very accurate procedure, as can be demonstrated by plotting the resulting value for \( \rho_p \) versus the fitting range (Fig. 17): for \( n \) between 4 and 10, \( \rho_p \) varies by less than one percent. The dendrite cross-section, however, is not easy to measure as the true dendrite shape is difficult to reconstruct from longitudinal projections for the reasons emphasized in section IV.B. The best data are obtained for the fin shape [9,10]. One way to extract \( \rho_p \) is therefore to fit the un-rescaled fin shape with a fourth order polynomial,

\[
z = -(r/\rho_p)^2/2 + A_4 (r/\rho_p)^4, \tag{26}
\]

over a varying distance from the tip where both \( \rho_p \) and \( A_4 \) are allowed to vary, which is the method used by LaCombe et al. in SCN [3]. We have carried out this same procedure on our computed fin shapes and the results are shown in Fig. 17 for two different anisotropies. (Note that this fit differs from the one carried out in section III.B where we fixed \( \rho_p \) to its value \( \approx \rho_{1v} \) extracted from the cross-section measurement, and only varied \( A_4 \).)

One can see that \( \rho_p \) increases with the fitting distance \( (\approx n \rho_{1v}) \) behind the tip, which renders a precise determination of \( \rho_p \) difficult. This trend was observed by Bisang and Bilgram in xenon dendrites [10]. On the other hand, for SCN, where \( \epsilon_4 \) is about twice smaller than the lowest anisotropy studied here, LaCombe et al. find that \( \rho_p \) is almost constant when \( n \) varies between 4 and 10. It is therefore possible that this fitting procedure improves for lower anisotropies. Fig. 17 also shows that the departure of the fitted radius from \( \rho_{1v} \) is of the order of a few percent for fitting ranges around \( n = 10 \), such that this method can provide a reasonable estimate.

We compare in Table I the values of \( \sigma^* \) predicted by the linear solvability theory of Barbieri and Langer [23] with the values corresponding to the non-axisymmetric shapes of the phase-field model and the axisymmetric shapes computed by the boundary integral method for an azimuthally averaged surface energy. We list as well the \( \sigma^* \) values corresponding to these shapes. Note that \( \rho_p = \rho_{1v} \) both for the paraboloid assumed in solvability theory and for the computed non-axisymmetric and axisymmetric shapes, such that comparing \( \sigma^*_p \) values is equivalent here to comparing scaled velocity values \( Vd_0/D = 2\sigma^*_pP^2_{1v} \). One remarkable fact is that the linear solvability theory predicts relatively accurately \( \sigma^*_p \) even though it does not describe the localized tip distortion that causes \( \rho \) to depart from \( \rho_p \). Thus, we can conclude from this comparison that this distortion does not strongly affect the selection of the velocity. A reexamination of the phase-field results of Ref. [13] in terms of \( \sigma^*_p \) show, however, that the linear solvability theory becomes increasingly inaccurate for larger anisotropy values \( (\epsilon_4 > 0.03) \).

Finally, McFadden et al. [22] have recently carried out a perturbative analysis of the diffusion field around a non-axisymmetric isothermal shape defined at leading order in \( A_4 \) by Eq. 2 where \( A_4 \) is treated as an expansion parameter. Since their analysis neglects capillary effects, their tip radius \( \rho \) should be compared to \( \rho_p \) here. They derived a correction to the Ivantsov relation (Eq. 1) that can become significant in the limit of very low undercoolings. For the lowest undercooling studied here \( (\Delta = 0.1) \), this correction is of the order of a percent and thus comparable to the accuracy at which \( \rho_p \) was determined numerically. Our results are therefore not in contradiction with their predictions. We note, however, that the universal non-isothermal shape found here starts to deviate from the isothermal one they consider only a short distance away from the tip where the fins develop under the action of anisotropic surface tension. Simulations at substantially lower undercooling would be necessary to

| \( \Delta \) | \( \epsilon_4 \) | \( \sigma^* \) | \( \sigma^*_p \) |
|-----|-----|-----|-----|
| Phase-field | 0.2 | 0.025 | 0.171 | 0.0565 |
| Linear Solvability | 0.1 | 0.025 | 0.181 | 0.0611 |
| Boundary Integral | | | 0.155 | 0.059 |
| Phase-field | 0.2 | 0.0125 | 0.0447 | 0.0282 |
| Linear Solvability | | | 0.0294 | |
| Boundary Integral | | | 0.0394 | 0.0265 |
test if this difference between the isothermal and non-isothermal shapes affects their predictions.

V. CONCLUSIONS

We have studied the three-dimensional morphology of the dendrite tip using recent improvements of the phase-field method \( \phi \) that make it possible to carry out quantitatively accurate simulations are relatively low undercoolings. Our main finding is that the experimentally measurable low undercooling tip morphology is independent of anisotropy strength and thus universal under the assumption that kinetic effects are negligible, in qualitative agreement with solvability theory \( \phi \). The non-axisymmetric deviation of this morphology from a paraboloid is well fitted by a single \( \cos 4\phi \) mode with an amplitude that is about twice smaller than predicted by solvability theory and in good agreement with existing shape measurements in SCN \( \phi \). Moreover, these measurements were reanalyzed here and found to be consistent with a non-axisymmetric tip shape dominated by a single \( \cos 4\phi \) mode as in our simulations.

The fins are well described away from the tip by the power law derived by Brener on the basis of the analogy \( \phi \) between three-dimensional steady-state shapes and two-dimensional time-dependent growth shapes \( \phi \), albeit with a slightly larger prefactor than predicted. Interestingly, the validity of this power law extends remarkably close to the tip. Our findings are also in good agreement with experimental data on xenon dendrites \( \phi \).

Finally, we conclude that the ‘true’ tip radius is not an experimentally adequate parameter to characterize the tip operating state since the anisotropy-dependent shape distortion near the tip that fixes this radius is most likely not measurable. In contrast, the tip radius of the paraboloid which underlies the rest of the tip morphology (excluding this distortion) is both measurable and a good scaling parameter for the entire dendrite shape. The latter tip radius is indistinguishable from the Ivantssov prediction over the range of undercooling studied here, which does not exclude differences between these two radii to be present at even lower undercoolings \( \phi \).

It would be interesting in the future to extend the present study to investigate how the anisotrop kinetic of molecular attachment at the interface alters the tip morphology. The detailed study of the tip morphology, and in particular its departure from the universal shape characterized here, may actually provide a sensitive probe of interface kinetic effects.

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