Theory of Pattern Selection in Three-Dimensional Nonaxisymmetric Dendritic Growth

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We study the selection of the shape and growth velocity of three-dimensional dendritic crystals in cubically anisotropic materials. In the framework of asymptotics beyond all orders we derive the inner boundary-layer equation for the nonaxisymmetric shape correction to the Ivantsov paraboloid shape. The solvability condition for this equation provides selection for both the velocity and the shape. The comparison with available numerical and experimental results is reasonably good.

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The problem of velocity selection for two-dimensional (2D) needle-crystal growth has been solved both numerically [1] and analytically [2–5]. Contradicting naive physical intuition, it turns out that the steady solutions exist only if the crystalline anisotropy of surface energy is taken into account. The predictions of this steady-state analysis agree with the numerical time-dependent simulations [6] which take into account sidebranching behavior of the tail of the dendrite. Details of this work may be found in [7]. Most experiments, however, are three dimensional (3D) and it is important to extend the previous theory to the three-dimensional case. A simple extrapolation of the 2D case, in which the surface energy is averaged in the azimuthal direction (axisymmetric approach [8]), yields interesting qualitative predictions. But a physical anisotropy, say, with an underlying cubic symmetry, will give rise to a nonaxisymmetric crystal shape, in agreement with experimental observations [9]. Nevertheless, this makes the problem more difficult to solve and, in fact, some doubts about the solvability mechanism were expressed as an explanation for the dynamic behavior of this system [10]. Therefore it seems to us of great importance to bring some new material in the understanding of this theoretical problem which concerns a prototype of growth process. Moreover, we want to stress that this is the first theoretical treatment of a fully 3D pattern. The treatment itself leads to an interesting puzzle. Roughly speaking, in the 2D case or in the axisymmetric case, the velocity selection is given by the solvability condition associated with the smoothness of the dendrite tip. In the 3D nonaxisymmetric case, we must therefore satisfy a solvability condition for each of the azimuthal harmonics. We know of only one attempt to solve a nonaxisymmetric problem. This is the numerical calculation of Kessler and Levine [11]. They made several approximations and finally performed only a two-mode calculation, but the crucial point of their analysis is that they found enough degrees of freedom to satisfy the solvability conditions.

The main aim of this paper is to develop an analytic theory for 3D dendritic growth with an underlying cubic anisotropy. The solvability theory beyond all orders requires the search of singularities in the complex plane for the nonaxisymmetric shape. In their vicinities, called inner regions, one has to establish an inner boundary-layer equation which is a nonlinear differential equation containing derivatives with respect to a fast variable. Because we deal with a function of two variables, the coefficients of the equation should depend also on the smooth variable. The remarkable property of the equation is that all dependences on the smooth variable are combined into a single common factor. The solvability condition requires that this factor be a pure constant. This will provide the selection of the velocity and the anisotropic shape corrections, which are in fact the additional degrees of freedom found in Refs. [11,12]. We would also like to stress an additional problem. In the 2D case, the selected crystal shape is close to the Ivantsov parabola [7] since the anisotropy and surface tension effects are assumed to be small. In the 3D case, the anisotropic shape correction becomes larger than the underlying Ivantsov solution as we move away from the dendrite tip. We will discuss this point at the end of the paper.

Let us study the problem of a free dendrite growing in its undercooled melt. The control parameter is the dimensionless undercooling $\Delta=(T_M-T_\infty)c_p/L$, where T_M is the melting temperature, L the latent heat, and c_p the specific heat. The temperature field satisfies the diffusion equation with the interface, moving with normal velocity v_n, acting as a source of magnitude v_nL/c_p. Together with the Gibbs-Thomson condition at the interface, this leads to a rather complicated integro-differential evolution equation [7]. It is possible to verify [13] that the Ivantsov paraboloid of revolution $\zeta=-r^2/2\rho$ (ρ is the tip radius of curvature), which moves with an arbitrary constant velocity v, satisfies the steady-state equation when the Gibbs-Thomson shift is set equal to zero. The Péclet number $p=v\rho/2D$ (D is the thermal diffusivity) is related to the undercooling by the three-dimensional Ivantsov formula $\Delta=p\exp(p)E_1(p)$, where $E_1(p)$ is the exponential integral function. Adding the Gibbs-Thomson effect, one can expect to have velocity selection [7]. The usual analytical approach to this problem is to linearize the integral term in the evolution equation around the Ivantsov paraboloid, assuming the Gibbs-Thomson effect to be

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small. This gives [7,11]

$$-\Delta_\mu[\zeta]=\frac{C}{2\pi}\int_0^\infty r_1 dr_1\int_{-\pi}^{\pi}\frac{d\phi_1(r_1^2-r^2)[u(r_1,\phi_1)-u(r,\phi)]}{[r_1^2+r^2-2rr_1\cos(\phi-\phi_1)+(r^2-r_1^2)^2]^{3/2}}. \tag{1}$$

Here u is the correction to the Ivantsov shape; all lengths are reduced by 2ρ; $C=8p\rho/d_0$ is an eigenvalue; $d_0=\tilde{\gamma}T_M c_p/L^2$ is a capillary length proportional to the isotropic part of the surface energy $\tilde{\gamma}$; and $\Delta_\mu[\zeta]$ is the well known [7] Gibbs-Thomson shift from the equilibrium melting point:

$$\Delta_\mu[\zeta]=\frac{1}{R_1}\left(\gamma+\frac{\partial^2\gamma}{\partial\Theta_1^2}\right)+\frac{1}{R_2}\left(\gamma+\frac{\partial^2\gamma}{\partial\Theta_2^2}\right), \tag{2}$$

where R_1,R_2 are the local principal radii of curvature of the surface, Θ_1,Θ_2 are the angles between the normal n and the local principal directions on the surface, and $\gamma(n)$ is the dimensionless anisotropic surface energy [8,11]

$$\gamma(\theta,\tilde{\phi})=1+4\epsilon[\cos^4\theta+\sin^4\theta(\cos^4\tilde{\phi}+\sin^4\tilde{\phi})]=1+4\epsilon(\cos^4\theta+3/4\sin^4\theta+1/4\sin^4\theta\cos4\tilde{\phi}). \tag{3}$$

Here θ and $\tilde{\phi}$ are the Euler angles of the normal vector to the interface. ϵ measures the strength of the cubic anisotropy, giving a maximum of surface energy in the (100) crystal direction. The axisymmetric approximation consists in dropping the last term in Eq. (3). A convenient alternative expression for the Gibbs-Thomson shift is given by Eq. (10) of Ref. [11]:

$$\begin{aligned}-\Delta_\mu=\gamma\nabla\cdot\left(\frac{\nabla\zeta}{\sqrt{1+(\nabla\zeta)^2}}\right)&+\frac{\partial^2\gamma}{\partial\theta^2}\frac{\nabla\theta\cdot\nabla\zeta}{\sqrt{1+(\nabla\zeta)^2}|\nabla\zeta|}+\frac{\partial^2\gamma}{\partial\theta\partial\tilde{\phi}}\frac{\nabla\tilde{\phi}\cdot\nabla\zeta}{\sqrt{1+(\nabla\zeta)^2}|\nabla\zeta|}-\frac{\partial^2\gamma}{\partial\tilde{\phi}^2}\frac{(\nabla\tilde{\phi}\times\nabla\zeta)\cdot\hat{\zeta}}{|\nabla\zeta|^2}\sqrt{1+(\nabla\zeta)^2}\\&-\frac{\partial^2\gamma}{\partial\tilde{\phi}\partial\theta}\frac{(\nabla\theta\times\nabla\zeta)\cdot\hat{\zeta}}{|\nabla\zeta|^2}\sqrt{1+(\nabla\zeta)^2}+\frac{\partial\gamma}{\partial\theta}\frac{\nabla\cdot(\nabla\zeta/|\nabla\zeta|)}{\sqrt{1+(\nabla\zeta)^2}}-\frac{\partial\gamma}{\partial\tilde{\phi}}\frac{\hat{\zeta}\cdot\nabla\zeta\times\nabla(1/|\nabla\zeta|^2)}{\sqrt{1+(\nabla\zeta)^2}},\end{aligned} \tag{4}$$

where ∇ is the two-dimensional gradient operator and $\tan\theta=|\nabla\zeta|$.

Let us look for a solution of Eq. (1) of the form $\zeta=\zeta_0+u(r,\phi)$, where

$$\zeta_0=-r^2+\sum A_m r^m\cos(m\phi). \tag{5}$$

This is possible at least formally, because none of the terms $r^m\cos(m\phi)$ contributes to the integral in Eq. (1) [11,12]. Kessler and Levine [11] proposed that these degrees of freedom are exactly those needed to satisfy the solvability conditions for the smoothness of the dendrite tip. They truncated the linear version of Eq. (1) to the first nonaxisymmetric mode $\cos(4\phi)$ and solved this equation numerically. They found C to be close to the value of the axisymmetric version and also found the coefficient A_4 to be small but not zero. Of course formula (5) cannot describe the true needle-crystal solution. It is clear that the linear approximation must break down eventually as we move away from the tip because the shift $r^m\cos(m\phi)$ grows at a faster rate than the underlying solution.

From the point of view of the general structure of the analytic theory [2,7,14], which has been developed only for the 2D and 3D axisymmetric cases, we must look, first of all, at the regular theory of perturbation for Eq. (1) with respect to the small parameter $1/C$. It is possible to prove that, for each mode, the regular theory of perturbation exists. Because the starting point of the perturbation theory implies to drop $u(r,\phi)$ in the Gibbs-Thomson shift $\Delta_\mu[\zeta]$, then one has to deal with linear inhomogeneous integral equations. A necessary condition for the existence of a solution is that the inhomogeneous term must be orthogonal to the null eigenvector of the adjoint operator. The crucial point here is that the solution of the adjoint integral operator simply does not exist. According to the general theorem of existence of the solution for the singular integral operator [15] we reach the conclusion that the solution of the regular theory of perturbation exists for each mode without any additional conditions and, moreover, the solutions are smooth at the origin.

We turn now to the problem of the selection of the C and A_m. As we mentioned before, the solvability condition appears only beyond all orders; in order to handle it properly we have to derive the local equation near the singularities in the complex plane. The location of the singularities of this Gibbs-Thomson shift is given by the condition

$$1+(\nabla\zeta_0)^2=0. \tag{6}$$

This equation describes the singularities line in the complex plane: $r=r_s(\phi)$. The function ζ_0 is given by Eq. (5) and, for example, for the pure Ivantsov shape we have $r_s=i/2$. We will derive the inner equation of $u(r,\phi)$ by imposing a smoothness condition in ζ_0. We do not assume that this function is close to the pure Ivantsov solution. In the close vicinity of the line of the singularities we can keep only the local singular contribution in the integral term and the most singular piece in the Gibbs-Thomson shift which contains the factor $[1+(\nabla\zeta)^2]^{-3/2}$. This greatly simplifies Eq. (1). Let us start with the Gibbs-Thomson shift. The most singular contribution

comes from the first and second terms in Eq. (4). Using the definition $\tan\theta=|\nabla\zeta|$, we find

$$-\Delta_\mu \approx \left(\gamma+\frac{\partial^2\gamma}{\partial\theta^2}\right)\frac{\nabla\zeta\cdot\nabla(|\nabla\zeta|)}{[1+(\nabla\zeta)^2]^{3/2}|\nabla\zeta|} \tag{7}$$

and

$$\gamma+\frac{\partial^2\gamma}{\partial\theta^2}\approx 1-\frac{7\alpha[1+(1/7)\cos4\tilde{\phi}]}{[1+(\nabla\zeta)^2]^2}, \tag{8}$$

where $\alpha=15\epsilon$ and ϵ is the anisotropy coefficient in Eq. (3) (assumed to be small). The function ζ contains two pieces. The first one, ζ_0, is smooth and the second one, u, is assumed to be small, but varies rapidly with respect to the fast variable: $t=1+i|\nabla\zeta_0|$ [we can choose, for example, ϕ as a smooth variable because r and ϕ are connected to each other by Eq. (6)]. More precisely, and this will be checked self-consistently later, we assume that $u\sim\alpha$, the derivative $u_t\sim t\sim\sqrt{\alpha}$ and $u_{tt}\sim 1$. In principle, the ensuing calculations are quite straightforward; all we need to do is to keep the main term with respect to the small quantity α. Using the fact that $\nabla u\approx u_t\nabla t$ and $\nabla u_t\approx u_{tt}\nabla t$, we find after some algebra

$$1+(\nabla\zeta)^2\approx 2t+2\nabla\zeta_0\cdot\nabla u=2(t-qu_t) \tag{9}$$

and

$$\nabla\zeta\cdot\nabla(|\nabla\zeta|)|\nabla\zeta|^{-1}\approx q(1-qu_{tt}), \tag{10}$$

where

$$q=\nabla\zeta_0\cdot\nabla(|\nabla\zeta_0|)|\nabla\zeta_0|^{-1}. \tag{11}$$

Next, we perform a stretching transformation for both the variable $t=\tilde{\alpha}^{1/2}\tau$ and the function $u=-\tilde{\alpha}f/q$, and combine everything into the final formula for the Gibbs-Thomson shift:

$$-\Delta_\mu=\frac{q}{2\sqrt{2}\tilde{\alpha}^{3/4}}\left(1-\frac{1}{(\tau+f_\tau)^2}\right)\frac{1+f_{\tau\tau}}{(\tau+f_\tau)^{3/2}}, \tag{12}$$

where $\tilde{\alpha}=(7\alpha/4)(1+\frac{1}{7}\cos4\tilde{\phi})$. Using the definition of $\tilde{\phi}$ as a spherical angle made by the normal vector to the interface, we find $\tilde{\phi}=\phi+\beta$, where

$$\sin\beta=-\frac{\partial\zeta/\partial\phi}{r|\nabla\zeta|}\approx\frac{i}{r}\frac{\partial\zeta_0}{\partial\phi}. \tag{13}$$

We note that the structure of the Gibbs-Thomson shift [Eq. (12)] is very close to the one found in the 2D and 3D axisymmetric cases [2,7], except for the prefactor which depends now on the smooth variable.

Let us discuss the behavior of the integral term in Eq. (1) in the singular region. Because the function u is singular, we need keep only the local contribution. Therefore, we can write the integral term, which we call J, in the form $J=-CBu/2$. In the nonaxisymmetric case a careful analysis, which takes into account both the pole term and the set of logarithmic singularities, gives

$$B=\frac{1}{1+4r^2}+\frac{2ir}{(1+4r^2)\{1+[(1+4r^2)/r^2](dr_s/d\phi)^2\}^{1/2}}, \tag{14}$$

which transforms into the usual [2,7] expression if the location of the singularities r_s is ϕ independent. Finally the local inner equation (which in fact is simply $-\Delta_\mu=J$) can be written as

$$\left(1-\frac{1}{(\tau+f_\tau)^2}\right)\frac{1+f_{\tau\tau}}{(\tau+f_\tau)^{3/2}}-f\lambda=0, \tag{15}$$

where λ is given by

$$\lambda=\sqrt{2}C\tilde{\alpha}^{7/4}Bq^{-2}. \tag{16}$$

Here, λ is to be evaluated on the line of singularities $r=r_s(\phi)$, and this depends on the smooth variable ϕ only. The crucial point is that Eq. (15) has precisely the same structure as in the 2D case [2,7] and the dependence on the smooth variable is entirely contained in the single factor λ. Therefore, as in the 2D and 3D cases [2,7], Eq. (15) is an eigenvalue equation: Transcendental small corrections must disappear in its asymptotics when $\tau\to\infty$. So λ must be a pure constant which belongs to a discrete spectrum. The independence of λ with respect to ϕ represents the new 3D solvability condition which provides the selection of C and A_m. The consideration of the leading order with respect to δ in Eq. (16), simply derived by linearization, can help the reader to make this new solvability condition more explicit. First we note that C obeys the usual 2D scaling relation: $C=a\alpha^{-7/4}$. Then, Eq. (16) does not contain any small parameters, which means that α and A_m should be pure numbers. The axisymmetric approach to this complicated nonlinear equation simply consists in neglecting the dependence on ϕ in Eq (8). In this case we can set A_m equal to zero and find the usual discrete spectrum of the eigenvalues a; only the solution which corresponds to the smallest value of a is a stable one [1,4]. Let us consider the axisymmetric approach as an approximation of zero order with respect to the "small" parameter $\delta=1/7$ [see Eq. (8)]. Because of this small parameter, we can expect that for the stable solution, a should be only slightly different from its value in the pure axisymmetric approach. It is clear that the correction to a appears only at the second order with respect to δ (a change of sign of δ means simply the change of the origin of ϕ). This might explain that the numerics [11] give a selected value of C which is close to the value found in the axisymmetric approach. In the linear approximation we can satisfy the solvability condition by the correction $A_4r^4\cos(4\phi)$ to the Ivantsov shape. A simple but tedious calculation, which involves linearization of Eq. (16) with respect to δ and A_4, gives $A_4=7\delta/11=1/11$. To leading order in α, the tip shape is given by

$$\zeta_0=-r^2+\tfrac{1}{11}r^4\cos(4\phi). \tag{17}$$

So, in the limit of small α, we predict that the shape correction is independent of the anisotropy parameter α, once written in units of ρ contrary to the tip radius ρ itself. We note that this universal shape correction for cubic material is close to the only published experimental determination in Ref. [9]. Concerning the numerics, this number is about a factor of 2 smaller than the number given in Ref. [11]. This difference can be explained by the fact that several different approximations have been made in both calculations. Unfortunately, in Ref. [11], the calculation has been performed only for a single anisotropy value, so we cannot make a comparison at this point. We hope that our result will suggest new experiments and numerical simulations on the 3D dendrite shape. In principle, we can go further in the expansion (5) and see, for example, that A_{4m} should be small at least like δ^m. But what is more important is the fact that the number of degrees of freedom available are precisely those we need to satisfy the solvability condition.

We discussed the growth in the direction (100), which corresponds to the most common situation of a maximum of the surface energy (3) with positive ϵ. If it occurs that ϵ is negative, then the direction (100) corresponds to the minimum and the direction (111) corresponds to the maximum of the surface energy. In this case, the theory predicts that the dendrite will grow in the direction (111), if we assume this model for the surface energy.

As we mentioned before the linear approximation breaks down eventually as we move away from the tip because the shift vector $r^m \cos m\phi$ grows at a faster rate than the underlying Ivantsov solution. This means that our approximation of linearizing the integral term is valid in the tip region only. This is the crucial difference between the 3D nonaxisymmetric case and the 2D case where the selected needle-crystal shape is close to the Ivantsov parabola everywhere if the anisotropy is small. What does it mean? We think that the complete treatment of the 3D dendritic shape requires two different steps. Our paper is concerned with the first one: the selection mechanism by a fully anisotropic surface tension and the determination of the tip shape. Since the shape correction cannot be extended to all distances, a further analysis is required to complete the description of the needle crystal. A correct treatment requires a matching between the tip and the tail via an intermediate range of r values where the nonlinear effects cannot be neglected. From a purely theoretical point of view, this analysis will differ completely from the selection problem which is concerned with short distances near the tip and where an analytical extension in the complex plane is useful. Once the shape correction is established, one can always include time-dependent sidebranching nonaxisymmetric modes as in Ref. [16]. Perhaps these modes are important in the matching treatment but we think as in Ref. [16] that they are irrelevant to the selection process itself.

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