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Needle crystals with nonlinear diffusion

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We study the free-boundary problem of the steady growth of a solid into its undercooled melt, allowing the thermal diffusion coefficient to have an arbitrary temperature dependence. By developing a novel approach to the Ivantsov method, we show that needle-crystal solutions can be found in two and three dimensions. The calculation establishes that the only steadily advancing, shape-preserving solidification fronts the method can produce, for linear or nonlinear diffusion, are parabolas in two dimensions and elliptic (or circular) paraboloids in three dimensions. We discuss the limitations on the Ivantsov method, pointing out that it is only capable of finding families of solutions of the problem, whose members are related by a rescaling of space and time. We show explicitly that including a heat-loss term in the equations causes the method to fail, and argue that any term which introduces a length scale into the problem will, in general, do likewise.

I. INTRODUCTION

Virtually all studies of dendritic crystal growth which adopt the view of the problem as one of macroscopic heat diffusion with a moving solid-liquid interface start with Ivantsov's classic solution[1,2] of the free-boundary problem of the steady growth of an isothermal, paraboloidal dendrite. In this problem the thermal diffusion coefficient is taken to be a constant (at least in the liquid phase) and a constant latent heat is released at the advancing solidification front. In this paper we extend this solution to include an arbitrary temperature-dependent diffusion coefficient. Using a novel geometrical approach to the problem of a steadily advancing, shape-preserving solidification front, we show that the only solutions to this problem accessible to Ivantsov's method—which makes no *explicit a priori* assumption about the shape of the front—have paraboloidal (or, in two dimensions, parabolic) solidification fronts.

A major shortcoming of the Ivantsov model of dendritic growth is the assumption that the entire solidification front is at the equilibrium melting temperature. As a consequence of this assumption, the model has no natural length scale, so that solutions occur only in families related by a dilation transformation. This then leads to the well-known difficulty that the undercooling determines, in this model, only the product of the dendrite's tip radius and growth velocity, not the two quantities separately. In addition, this assumption leads to the solutions' being unstable against infinitesimal perturbations of arbitrarily short wavelengths,[3] which indicates that the problem is ill-posed. This difficulty is still present in the problem with nonlinear diffusion, since the temperature dependence of the diffusion coefficient does not define a length scale. Intense theoretical effort[4–11] has gone into remedying this shortcoming by introducing capillary effects into the problem. Similar effects should also relieve these difficulties in the problem with nonlinear diffusion, but it is not clear how the singular perturbation theory would proceed: existing treatments first eliminate the temperature field from the equations by means of a Green's-function technique; however, this approach is suited only to linear equations and so is not obviously applicable to the problem with nonlinear diffusion.

In principle, the nonuniqueness problem might be remedied by including in the model any effect which suffices to define a length scale, although it is not certain that any particular effect of this sort will in fact remove the nonuniqueness. To investigate this question, we include a heat-loss term, in the form of an arbitrary (linear or nonlinear) function of temperature, in the diffusion equation and again attempt to solve the free-boundary problem. However, we find that with any such heat-loss term present, the Ivantsov method fails to yield solutions.

It does not seem to have been widely appreciated that the Ivantsov method is in fact quite limited. As mentioned above, it makes no explicit assumption about the shape of the solidification front; however, as we will discuss below, it does make an ansatz which virtually forces any solutions the method will find to occur in families related by simultaneous rescaling of space and time. The method certainly leans heavily on the assumption that the solidification front is isothermal, but we argue further that in general the absence of a length scale is needed in order for it to produce solutions.

In Sec. II we present the original Ivantsov method and show that it admits a geometrical interpretation when restricted to the problem of steady, shape-preserving growth. Along the way, we show how the Ivantsov method requires the absence of a length scale and so is only capable of finding families of solutions related by a scale transformation. We next make a change of variables, rewriting the problem using temperature as one coordinate, with the other coordinates suggested by the geometry of the problem. In Sec. III we finally make use of the diffusion equation, only the boundary conditions having been used thus far, and show how to obtain the solution of the problem with a temperature-dependent diffusion coefficient in two and three dimensions. We also show that the method cannot find solutions if a heat-loss term, which would introduce a length scale into the problem, is included, and that when such a term is absent the only solutions which can be found are those having parabolic or paraboloidal solidification fronts. This, incidentally, establishes that the solutions obtained by Ivantsov[1] and by Horvay and Cahn[2] in the case of a constant diffusion coefficient are the only steadily advancing, shape-preserving solutions for that problem which are accessible to the method. We discuss the results in the final section.

II. BOUNDARY CONDITIONS AND THEIR EFFECTS

In the standard Ivantsov model of dendritic growth, two boundary conditions are imposed on the solidification front. First, the front must be an isotherm at the equilibrium melting temperature T_M,

$$T(\mathbf{r},t)=T_M=\text{const.} \tag{2.1}$$

on the solidification front. Here $\mathbf{r}(t)$ represents the position of the front at time t. The second condition is the Stefan condition, which states that the rate of advance of the front is governed by how quickly the latent heat released there can be diffused away, so that we have

$$Lv_n=(Dc\hat{\mathbf{n}}\cdot\nabla T)_L^S \ , \tag{2.2}$$

where D is the thermal diffusion coefficient and c the specific heat (both at the melting temperature), L is the latent heat, v_n is the local normal velocity of a point on the advancing solidification front, and $\hat{\mathbf{n}}$ is the unit vector normal to the front and directed into the liquid; the parentheses denote the discontinuity in the bracketed quantity across the front. A final boundary condition is imposed at infinity, namely, that the liquid be undercooled far from the front,

$$T\to T_M-L\Delta/c(T_M) \tag{2.3}$$

at infinity in the liquid, where Δ is a dimensionless measure of the undercooling.

The first place in which the Ivantsov method uses the isothermal front condition (2.1) is in taking the entire solid region to be at the temperature T_M. The temperature gradient in the solid is then zero and so it drops out of the Stefan condition (2.2). Then by differentiating (2.1) with respect to t, we can write the normal velocity v_n of the interface in terms of the derivatives of T at a fixed point in space just on the liquid side of the front. This again makes use of the isothermal condition through its consequence that the temperature gradient at the front is parallel to $\hat{\mathbf{n}}$. The result enables us to rewrite the Stefan condition in the form

$$L\frac{\partial T}{\partial t}=D(T_M)c(T_M)\,|\,\nabla T\,|^2 \tag{2.4}$$

at $T=T_M$ in the liquid, which is the form we will use in subsequent calculations.

The Ivantsov method produces solutions of the original moving boundary problem by promoting the Stefan condition (2.4), which need only hold at the solidification front, to a differential equation which is required to hold throughout the liquid region:

$$\frac{\partial T}{\partial t}=-F'(T)\,|\,\nabla T\,|^2 \ , \tag{2.5}$$

where $F(T)$ is any differentiable function of temperature whose derivative is equal to $-Dc/L$ at $T=T_M$. It is important to realize that this is an ansatz; it is not derived from the diffusion equation, but rather is imposed artificially and so represents a restriction on the solutions the method can produce. Solutions of the original moving boundary problem need not satisfy (2.5), but the method is only capable of finding those solutions which do. This is a very strong limitation on the method—it can only find solutions of the problem for which each isotherm moves with a normal velocity which is proportional to the normal temperature gradient or heat flux through the isotherm (although the constant of proportionality will differ from isotherm to isotherm). To proceed with the method and to investigate further the consequences of the ansatz (2.5), we multiply by $F'(T)$ and use the fact that F can depend on position and time only through T, thus recasting (2.5) into the form

$$\frac{\partial F}{\partial t}=-\,|\,\nabla F\,|^2 \ . \tag{2.6}$$

We immediately see that this equation is invariant under simultaneous rescaling of length by a factor b and time by a factor b^2 (or, equivalently, velocity by a factor b^{-1}). Thus if we find a solution $F(\mathbf{r},t)$ which describes a solidification front advancing with velocity $\mathbf{v}$, then $F(b\mathbf{r},b^2t)$ is also a solution describing a front whose velocity is $\mathbf{v}/b$. Since the diffusion equation is also invariant under these rescalings, any solution of the full problem which corresponds to growth at one velocity is related by a rescaling to solutions for growth at any other velocity. If another term is included in the diffusion equation which breaks this invariance, then we could conceivably find a family of solutions $F(b\mathbf{r},b^2t)$ of (2.6) of which only one member (or discretely many members) satisfies the modified diffusion equation. However, when we include a heat-loss term in the diffusion equation, we will find instead that the method simply fails to give any solutions at all.

In order to solve Eq. (2.6), Ivantsov used separation of variables to find a general time-dependent linear solution[1] and then found special solutions by envelope formation.[2] Since ours is the less ambitious goal of finding only shape-preserving solutions which advance with constant velocity, we will develop a more elegant method which finds *all* such solutions of the full moving boundary problem which are consistent with the ansatz (2.5). For a solution which advances steadily at velocity $\mathbf{v}$, we have $\partial F/\partial t=-\mathbf{v}\cdot\nabla F$ and so (2.6) becomes

$$|\,\nabla F\,|^2-\mathbf{v}\cdot\nabla F=0 \ , \tag{2.7}$$

or, after completing the square,

$$|\,\nabla F-\tfrac{1}{2}\mathbf{v}\,|^2=\tfrac{1}{4}\,|\,\mathbf{v}\,|^2 \ . \tag{2.8}$$

We may choose the x axis to point in the direction of $\mathbf{v}$. Using the notation $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ to denote unit vectors in the directions of the Cartesian axes, we find that (2.8) is equivalent to

$$\frac{2}{|\mathbf{v}|}\nabla F=\hat{\mathbf{x}}+\hat{\xi}(\mathbf{r}) \ , \tag{2.9}$$

where $\hat{\xi}(\mathbf{r})$ is any irrotational *unit* vector field. An irrotational unit vector field, however, is a rather restricted object. We can see how it is restricted by noting that since its curl vanishes, we have *a fortiori* $\hat{\xi}\times(\nabla\times\hat{\xi})=0$; using vector identities and the fact that $\hat{\xi}$ has constant magnitude, we can reduce this to

$$(\hat{\xi}\cdot\nabla)\hat{\xi}=0 \ , \tag{2.10}$$

which means that $\hat{\xi}$ does not change in the direction of $\hat{\xi}$, i.e., $\hat{\xi}$ is constant along lines radiating outward from the interface.

At this point we have a good deal of information about the geometry of the isotherms. We know that the vector field $\hat{\mathbf{x}}+\hat{\xi}$ is everywhere normal to surfaces of constant F, which, since F is a function of T only, are isotherms. In addition, we have a simple characterization of the unit vector field $\hat{\xi}$. Motivated by this knowledge about the geometry of the isotherms, we proceed to set the problem up in the hodograph coordinates T, θ, and ϕ, where θ and ϕ are two angles which specify the direction of $\hat{\xi}$. To do this we first choose an arbitrary reference surface $\mathbf{r}=\mathbf{r}_0(\theta,\phi)$, most conveniently located within the solid region, such that the point $\mathbf{r}_0(\theta,\phi)$ on this surface is the point where the line of constant $\hat{\xi}$ whose coordinates are θ and ϕ would cross the reference surface. We then define the unknown function $R(T,\theta,\phi)$ to be the distance along this line of constant $\hat{\xi}$ from $\mathbf{r}_0(\theta,\phi)$ to the isotherm at temperature T. Thus the location of a general point in space is given by

$$\mathbf{r}(T,\theta,\phi)=\mathbf{r}_0(\theta,\phi)+R(T,\theta,\phi)\hat{\xi}(\theta,\phi) \ . \tag{2.11}$$

At this point there is a considerable amount of arbitrariness in the choice of $\mathbf{r}_0$ and R; as the calculation progresses, we will discover convenient ways of making these arbitrary choices.

Since, by construction, the vector $\hat{\mathbf{x}}+\hat{\xi}$ is normal to isotherms and the vectors $(\partial\mathbf{r}/\partial\theta)_T$ and $(\partial\mathbf{r}/\partial\phi)_T$ are tangent to isotherms, we find

$$\partial R/\partial\theta=-(\hat{\mathbf{x}}+\hat{\xi})\cdot(\partial\mathbf{r}_0/\partial\theta+R\,\partial\hat{\xi}/\partial\theta)/(1+\hat{\xi}\cdot\hat{\mathbf{x}}) \ , \tag{2.12}$$

and similarly for $\partial R/\partial\phi$. Using these results, we can see that the new unknown function

$$u=(1+\hat{\xi}\cdot\hat{\mathbf{x}})R(T,\theta,\phi) \tag{2.13}$$

will play a special role in the calculation. This comes about because differentiating u with respect to θ and applying (2.12) yields

$$\partial u/\partial\theta=-(\hat{\mathbf{x}}+\hat{\xi})\cdot(\partial\mathbf{r}_0/\partial\theta) \ , \tag{2.14}$$

which is independent of T. A similar result is obtained for $\partial u/\partial\phi$. Thus we see that u can be written as the sum of two functions, one of which depends *only* on T, the other *only* on the angles θ and ϕ. However, we can absorb the function of angles into the reference point $\mathbf{r}_0$ in (2.11) and so without loss of generality we can take u to be a function of T only. This implies in turn, through (2.14) and its counterpart for $\partial u/\partial\phi$, that both $\partial\mathbf{r}_0/\partial\theta$ and $\partial\mathbf{r}_0/\partial\phi$ are orthogonal to $\hat{\mathbf{x}}+\hat{\xi}$.

Next we will rewrite the Stefan condition (2.4) in terms of u. First note that for steady growth, (2.4) becomes

$$\frac{\partial T}{\partial x}=-\frac{Dc}{Lv}|\nabla T|^2 \ \text{ at } T=T_M \ . \tag{2.15}$$

Since $\hat{\mathbf{x}}+\hat{\xi}$ must be orthogonal to isotherms, the gradient of T must be parallel to it, so we have

$$\nabla T=(\hat{\mathbf{x}}+\hat{\xi})/(\hat{\mathbf{x}}+\hat{\xi})\cdot(\partial\mathbf{r}/\partial T)=(\hat{\mathbf{x}}+\hat{\xi})/u' \ , \tag{2.16}$$

where the prime denotes a derivative with respect to T. Substituting this into the Stefan condition (2.15) yields

$$u'(T_M)=-2D(T_M)c(T_M)/Lv \ , \tag{2.17}$$

so the Stefan condition becomes simply a condition on the derivative of the new variable u.

The original free-boundary problem has now been reduced to the problem of finding a function $u(T)$ which satisfies the boundary condition (2.17) and, to satisfy (2.3), diverges as T approaches $T_M-L\Delta/c(T_M)$ from above. This function, together with the reference surface $\mathbf{r}_0(\theta,\phi)$ and the unit vector field $\hat{\xi}(\theta,\phi)$, must also allow a solution to the diffusion equation. We now examine how this restricts the possible solutions further.

III. DIFFUSION EQUATION

So far, we have only used the boundary conditions on the free-boundary problem and the ansatz (2.5). We now consider the diffusion equation in the liquid region, which for steady-state growth reads

$$0=\nabla\cdot[D(T)\nabla T]+v\frac{\partial T}{\partial x}-\Gamma(T) \ , \tag{3.1}$$

where $\Gamma(T)$ is a heat-loss term which has an arbitrary temperature dependence. For example, we could take Γ to be $\sigma\epsilon(T)(T^4-T_\infty^4)$, with T_∞ the ambient temperature and ϵ the emissivity of the liquid, thus describing radiation. This term, whatever it may be, has units of (temperature/time) and so can be used to define a natural length scale for the problem. However, we will show that in order for the Ivantsov method to lead to solutions of the problem, Γ must be identically zero.

We will first work the problem out in two dimensions. The unit vector field $\hat{\xi}$ now depends only on the single coordinate θ. We define this coordinate by writing

$$\hat{\xi}=\hat{\mathbf{x}}\cos\theta+\hat{y}\sin\theta \ . \tag{3.2}$$

Note that θ is not necessarily the angular coordinate appearing in ordinary cylindrical coordinates, but rather is a general coordinate which gives the orientation of the unit vector field $\hat{\xi}$. Since, as we saw above, $d\mathbf{r}_0/d\theta$ must be orthogonal to $\hat{\xi}+\hat{\mathbf{x}}$, and since the vector $(d/d\theta)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$ is orthogonal to $\hat{\xi}+\hat{\mathbf{x}}$, we can write

$$d\mathbf{r}_0/d\theta=Q(\theta)(d/d\theta)[\hat{\xi}/(1+\hat{\xi}\cdot\hat{\mathbf{x}})] \ , \tag{3.3}$$

where Q is an unknown function of θ. We have already written the gradient of T explicitly in Eq. (2.16). It is now a standard problem in tensor analysis[12] to write the second-derivative term in (3.1) in the (nonorthogonal) coordinates T and θ, starting with the expression (2.11) for the position vector, differentiating and using (2.14) and (3.3) to find the components of the metric tensor. After a certain amount of manipulation we find that the diffusion equation (3.1) takes the explicit form

$$0=D+\left\{-2\frac{Du''}{u'^2}+2\frac{D'}{u'}+v-\frac{\Gamma(T)u'}{1+\cos\theta}\right\}[u(T)+Q(\theta)] \; . \tag{3.4}$$

By solving (3.4) for $Q(\theta)$, differentiating with respect to T, and noting that the result must vanish identically, we see that (3.4) can hold only if we have $\Gamma=0$. Thus the heat-loss term, which would have introduced a length scale into the problem, must in fact be absent in order for the Ivantsov method to yield solutions.

We now look for solutions of (3.1) with $\Gamma=0$, but still keeping an arbitrary diffusion coefficient $D(T)$. The only θ dependence remaining in the diffusion equation (3.4) is then in $Q(\theta)$ and so Q must be a constant. Thus $d\mathbf{r}_0/d\theta$ must be a constant multiple of the vector $(d/d\theta)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$. However, according to (2.11), this can be absorbed into $u(T)$ by simply adding the constant Q to it. Thus without loss of generality we may take $\mathbf{r}_0(\theta)$ to be a constant. This implies that all the lines of constant $\hat{\xi}$ appear to radiate from a single point (which we may take to be the origin), and leaves us with the result

$$\mathbf{r}(T,\theta)=u(T)(\hat{\mathbf{x}}\cos\theta+\hat{\mathbf{y}}\sin\theta)/(1+\cos\theta) \; , \tag{3.5}$$

which shows that the isotherms are parabolas with vertices along the positive x axis and foci at the origin. Note that the vector $(d/d\theta)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$ which we used in setting up the calculation is singular only at $\theta=\pi$, which is safely inside the solid region.

Now that we have found the isotherms, the final step of the solution is to label them with temperature values by solving for $u(T)$. We will defer the discussion of this final step, however, until after we have looked at the three-dimensional problem.

The calculation for needle crystals in three dimensions parallels that for two dimensions. We specify θ and ϕ by choosing $\hat{\xi}$ to have the explicit form

$$\hat{\xi}=\hat{\mathbf{x}}\cos\theta+\hat{\mathbf{y}}\sin\theta\cos\phi+\hat{\mathbf{z}}\sin\theta\sin\phi \; . \tag{3.6}$$

We then note that the vectors $(\partial/\partial\theta)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$ and $(\partial/\partial\phi)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$ are both orthogonal to $\hat{\xi}+\hat{\mathbf{x}}$, and are singular only at $\theta=\pi$. Then since, as we have seen, $\partial\mathbf{r}_0/\partial\theta$ and $\partial\mathbf{r}_0/\partial\phi$ must be orthogonal to $\hat{\xi}+\hat{\mathbf{x}}$, we may write

$$\partial\mathbf{r}_0/\partial\theta=Q_{11}\partial/\partial\theta[\hat{\xi}/(1+\hat{\xi}\cdot\hat{\mathbf{x}})] +Q_{12}\partial/\partial\phi[\hat{\xi}/(1+\hat{\xi}\cdot\hat{\mathbf{x}})] \; , \tag{3.7a}$$

$$\partial\mathbf{r}_0/\partial\phi=Q_{21}\partial/\partial\theta[\hat{\xi}/(1+\hat{\xi}\cdot\hat{\mathbf{x}})] +Q_{22}\partial/\partial\phi[\hat{\xi}/(1+\hat{\xi}\cdot\hat{\mathbf{x}})] \; , \tag{3.7b}$$

where the Q_{ij} are as-yet undetermined functions of θ and ϕ. After a tedious calculation, the diffusion equation (3.1) can now be put in the form

$$0=D[2u+f(\theta,\phi)]+\left\{-2\frac{Du''}{u'^2}+2\frac{D'}{u'}+v-\frac{\Gamma(T)u'}{1+\cos\theta}\right\}\times[u^2+f(\theta,\phi)u+h(\theta,\phi)] \; , \tag{3.8}$$

where f and h are given by

$$f(\theta,\phi)=Q_{11}+Q_{22} \; , \tag{3.9a}$$

$$h(\theta,\phi)=Q_{11}Q_{22}-Q_{12}Q_{21} \; . \tag{3.9b}$$

As in the two-dimensional calculation, we next solve (3.8) for h. We then differentiate the resulting equation with respect to T; since h is independent of T, this leaves us with an equation in which h does not appear and which we can then solve for f. We then differentiate this second equation with respect to T, thus obtaining a third equation in which the only terms depending on angles come from the Γ term in (3.8). From the form of this third equation, we see that Γ must vanish for the three-dimensional calculation to go through, just as it had to vanish in two dimensions. The second equation then forces f to be constant and the first in turn implies that h must also be constant. In the Appendix we observe that f can be taken to be zero and show that the compatibility condition for Eqs. (3.7a) and (3.7b) and the conditions that f and h be constant force h to be negative and imply that the reference surface $\mathbf{r}_0$ must be given by

$$\mathbf{r}_0(\theta,\phi)=(C/2)\tan(\theta/2) \times[-\hat{\mathbf{x}}\tan(\theta/2)\cos2\phi+2\hat{\mathbf{y}}\cos\phi-2\hat{\mathbf{z}}\sin\phi] \; , \tag{3.10}$$

where we have chosen $\mathbf{r}_0$ $(\theta=0)$ to be the origin and set

$$h=-C^2 \; . \tag{3.11}$$

With this form for $\mathbf{r}_0$, the isotherms are easily seen to be elliptic paraboloids. The eccentricity of the elliptical cross section of the isotherm at temperature T is $[2C/u(T)+C]^{1/2}$, with the major axis in the y direction and the minor axis in the z direction. In order for the line $\theta=\pi$, along which the tangent vectors used in (3.7) are singular, to lie entirely within the solid region, we must also choose $C<u(T_M)$.

The one remaining task is to solve the diffusion equation (3.4) for the two-dimensional problem or (3.8) for the three-dimensional problem, with Γ and f equal to zero and h constant in (3.8). Both of these equations can be rewritten in the form

$$0=\frac{u''}{u'}-\frac{u'(dW/du)}{2W(u)}-\frac{D'}{D}-\frac{vu'}{2D} \; , \tag{3.12}$$

where $W(u)$ is u for the two-dimensional problem or $u^2+fu+h=u^2-C^2$ for the three-dimensional problem. The similarity between the equations for two- and three-dimensional needle crystals suggests that the diffusion equation will take the form (3.12) in any number of dimensions, with $W(u)$ being the secular determinant of the matrix Q_{ij} defined by analogy with (3.7). We have not attempted to confirm this conjecture.

For the standard problem of constant D, Eq. (3.12) can immediately be integrated once; then after using the Stefan condition (2.17) to fix the constant of integration, we may integrate again to find

$$T=T_M-L\Delta/c(T_M)+\frac{Lv}{2Dc}\sqrt{W[u(T_M)]}e^{vu(T_M)/2D}\times\int_u^\infty e^{-vu/2D}[W(u)]^{-1/2}du\ , \tag{3.13}$$

which reproduces the results of Ivantsov[1] and of Horvay and Cahn.[2]

When $D(T)$ is not constant, there is no analytical first integral of (3.12). However, we can maneuver it into a more familiar-looking form by changing variables back from T to u, which, according to (2.11) and the discussion following it, is proportional to the positions of the x intercepts of the isotherms. Equation (3.12) takes the form

$$0=\frac{d}{du}\left[D(T)\frac{dT}{du}\right]+\frac{1}{2}\left[v+D(T)\frac{d\ln W}{du}\right]\frac{dT}{du}\ , \tag{3.14}$$

with the boundary conditions $T\to T_M-L\Delta/c$ for $u\to\infty$ and $dT/du=-Lv/2Dc$ at the value of u for which $T=T_M$. Here $d\ln W/du$ is $1/u$ for the two-dimensional problem and $2u/(u^2-C^2)$ for the three-dimensional problem. Thus one can solve the two- and three-dimensional problems by solving the nonlinear ordinary differential equation (3.12) or by solving the one-dimensional free-boundary problem (3.14).

IV. DISCUSSION

One of the first steps in the Ivantsov solution of the moving boundary problem of solidification of an undercooled liquid is the positing of the ansatz (2.5), which eventually leads to a relation between the isotherms obtained for different interface velocities. Moreover, the form of (2.5) implies that any isotherm, for any solution produced by the method, is a valid candidate for the solidification front. If we now imagine assigning temperatures to these isotherms, starting at infinity and working our way back toward the dendrite, we see that any isotherm will actually be the solidification front for some suitable undercooling. Thus the method actually locates *families* of solutions, rather than individual solutions of the problem. Viewed in this light, it is not surprising that it is possible to solve for needle crystals with nonlinear diffusion, since having a temperature dependence of the diffusion coefficient would only change the labeling of the isotherms, but would not change the isotherms themselves.

The fact that any isotherm found by the Ivantsov method will be the solidification front for some undercooling, combined with the dilation symmetry of (2.5), strongly suggests that the method will fail to produce solutions if any term is included in the equations which breaks this dilational symmetry and defines a length scale. Indeed, we have seen explicitly that if we include heat loss in the problem by adding an arbitrary function of temperature to the diffusion equation, then the Ivantsov method fails to find solutions of the free-boundary problem for steady growth of a shape-preserving dendrite.

McFadden and Coriell[13] have extended the Ivantsov problem in three dimensions to include fluid flow induced by a density difference between the solid and liquid phases. Their solution was obtained by assuming that the interface remains paraboloidal; the incompressible Navier-Stokes equations were then written in terms of a velocity potential and separated in parabolic coordinates. This introduces an extra dimensionless parameter, the density ratio, into the equations, but does not give rise to a length scale and so does not break the dilational symmetry of the problem. It should also be possible to include this effect in the calculation presented above.

The calculations presented here also give the somewhat surprising result that the parabolic dendrite in two dimensions and the elliptic paraboloid in three dimensions, which have already been found for constant diffusion coefficients by Ivantsov[1] and Horvay and Cahn,[2] are in fact the only shapes of steadily advancing needle crystals which the method can find, either for linear or nonlinear diffusion. This is not to say that other shapes, such as three-dimensional "paraboloids" with more complicated cross sections, do not exist in steady state. However, it does establish that such solutions, if they exist, cannot be found by Ivantsov's method with the ansatz (2.5). It may be possible to find such putative solutions if one can work out the calculation using a different ansatz, or it may be necessary to develop some different approach to the free-boundary problem.

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APPENDIX: REFERENCE SURFACE FOR THREE-DIMENSIONAL NEEDLE CRYSTALS

We first note that since $Q_{11}+Q_{22}$ is forced to be constant, we may set it to zero by adding an appropriate constant to $u(T)$. This satisfies the condition on f. Next, we write out the compatibility condition for Eqs. (3.7a) and (3.7b) by equating the ϕ derivative of the first and the θ derivative of the second. This yields a vector equation, from which we may extract three distinct pieces of information by forming its scalar product with three linearly independent vectors. Having made the explicit choice of coordinates θ and ϕ embodied in Eq. (3.6), we choose these three vectors to be $\hat{\xi}+\hat{\mathbf{x}}$, $\hat{\mathbf{x}}$, and $(\partial/\partial\phi)(\hat{\xi}/1+\hat{\xi}\cdot\hat{\mathbf{x}})$. The first gives us

$$Q_{21}=Q_{12}\sin^2\theta\ . \tag{A1}$$

Then, using this and $Q_{11}=-Q_{22}$, we obtain from the other two

$$(\partial Q_{22}/\partial\phi)+\sin^2\theta(\partial Q_{12}/\partial\theta)+(2+\cos\theta)(\sin\theta)Q_{12}=0\ , \tag{A2}$$

$$\sin\theta[(\partial Q_{22}/\partial\theta)-(\partial Q_{12}/\partial\phi)]+2Q_{22}=0\ . \tag{A3}$$

The condition on h now reads

$$Q_{22}^2+Q_{12}^2\sin^2\theta=C^2\ , \tag{A4}$$

where C is an arbitrary constant; the constant value of h is $-C^2$. Differentiating this with respect to ϕ, substituting for the ϕ derivatives of Q_{12} and Q_{22} using (A2) and (A3), and integrating over θ leads to

$$Q_{22}=Q_{12}(\sin\theta)p(\phi)\ , \tag{A5}$$

where the arbitrary function p arises as a constant of integration. Together with (A4) this gives

$$Q_{12}=C/\sin\theta(1+p^2)^{1/2},\quad Q_{22}=Cp/(1+p^2)^{1/2}\ . \tag{A6}$$

Note that Q_{22} depends only on ϕ. To determine $p(\phi)$, we substitute these expressions into (A3), obtaining the equation

$$p[(dp/d\phi)+2(1+p^2)]=0\ . \tag{A7}$$

The solution $p=0$ must be discarded, since it fails to satisfy (A2). Integrating (A7) then gives

$$p(\phi)=\tan[2(\phi-\phi_0)]\ , \tag{A8}$$

where ϕ_0 is a constant of integration which can be set to zero by rotating the y and z axes through an angle ϕ_0. Thus we have obtained explicit equations for $\partial\mathbf{r}_0/\partial\theta$ and $\partial\mathbf{r}_0/\partial\phi$ which, when integrated, yield (3.10).

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