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Solvability condition for needle crystals at large undercooling in a nonlocal model of solidification

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We show explicitly that, in a realistic model of diffusion-controlled dendritic solidification, Ivantsov's continuous family of steady-state needle crystals is destroyed by the addition of surface tension. Our starting point is the exact integro-differential equation for the one-sided model, in two dimensions, in a moving frame of reference. In the limit of large undercooling, where the range of the diffusion field is much smaller than the radius of curvature of the tip of the needle, we are able to reduce this problem to a linear, inhomogeneous differential equation of infinite order. We derive a solvability condition for this equation and show that solutions cease to exist for arbitrarily small but finite, isotropic surface tension.

I. INTRODUCTION

Growth of a solid from an undercooled or supersaturated melt gives rise to dendritic pattern formation, a process characterized by propagation of a needle-shaped tip and the persistent emission of sidebranches. A full understanding of the shape of a dendrite, for example, of its degree of self-similarity, is still a completely open problem. Most theoretical investigations of dendritic growth, including the one to be described here, have been attempts to determine from first principles the values of the growth velocity v and the radius of curvature of the tip ρ, two parameters which appear experimentally to be sharply selected by the dendritic growth mechanism.[1,2]

An essential first step toward a modern theory of dendrites was Ivantsov's solution of the "needle-crystal" problem in the limit of zero surface tension.[3,4] A needle crystal, by definition, is a steady-state solution of the solidification problem in which a needlelike solid—a paraboloid of revolution in Ivantsov's case—grows into the liquid at constant speed v, without change of shape, along its axis of symmetry. Ivantsov's solution follows directly from the fact that the diffusion equation in a moving frame of reference is separable in parabolic coordinates; thus, a paraboloidal isotherm at the melting temperature $T=T_M$ is an acceptable solidification front so long as surface tension, via the Gibbs-Thomson condition, does not require T_M to vary with the curvature of the surface.

This analysis at zero surface tension, however, does not produce a unique v and ρ at any given temperature of the melt, as does nature, but rather, produces a continuous family of solutions. To be specific, Ivantsov's solution produces only a single relation between the dimensionless undercooling $\Delta=(T_M-T_\infty)c/L$ and the Péclet number $p=\rho v/2D$. (In these formulas, T_∞ is the temperature of the melt very far from the growing solid, L is the latent heat, c is the specific heat of the fluid, and D is its thermal diffusion constant. Throughout this paper, we shall use only the language of thermally rather than chemically controlled solidification, although much of our discussion will be technically more appropriate to the latter case.) What is happening here is that the Ivantsov problem is missing a length scale. The only quantities in the theory with the dimensions of length are the tip radius ρ and the diffusion length $l=2D/v$; thus, one dimensionless relationship between $p=\rho/l$ and Δ is all that can be expected. It is also not too surprising that the Ivantsov solutions turn out to be manifestly unstable.[5]

This dimensional degeneracy of the Ivantsov problem suggests that capillarity is an essential physical ingredient of the dendritic selection mechanism. A new length scale associated with the surface tension γ is conveniently chosen to be $d_0=\gamma T_M c/L^2$, a quantity which is ordinarily of order angstroms in contrast to l which may be of order millimeters or larger. Of the various attempts to incorporate d_0 into the theory, the one which has been most successful so far in explaining experimental data is the marginal-stability hypothesis.[5] In its most rudimentary form, this theory starts with the observation that the geometric mean $(d_0 l)^{1/2}$ is the characteristic scale of morphological instabilities in solidifying systems, and then makes the guess that this stability length sets the scale of the tip radius ρ. Thus, the ratio $\sigma\equiv d_0 l/\rho^2=2d_0D/v\rho^2$ appears in the theory as a Δ-independent constant whose value provides the extra piece of information required to determine unique values for v and ρ. No rigorous dynamical basis for the marginal-stability hypothesis has yet been discovered.

More recent developments in the dendrite theory have focused attention on the mathematically singular nature of the surface tension as a perturbation of the Ivantsov problem. Work along these lines has been based primarily on simplistic but relatively tractable models[6-9] of solidification in which the fully nonlocal and retarded dynamics of the diffusion field has been replaced by phenomenological local laws governing the motion of a two-dimensional stringlike solidification front. The conclusions from most of these studies[7,9] are that the addition of surface tension causes the Ivantsov family to break up into at most a discrete set of needle-crystal solutions, and that the dynamically selected dendritic tip, if it exists at all, will have the same v and ρ as that of the fastest and sharpest of these solutions. In general, some finite degree of crystalline anisotropy seems to be required either to permit the existence of any needle crystals or to stabilize them.

The important question to which the present paper is addressed is whether the mathematical structure of these local dynamical models carries over to the more realistic nonlocal description of solidification. None of the currently fashionable local models has been derived systematically from first principles. However, the boundary-layer model of Ben-Jacob *et al.*[8,9] is at least couched in the language of solidification theory and appears to have some physical justification in the limit of large Péclet number $p=\rho/l$, where the range of the diffusion field $l=2D/v$ is much smaller than the characteristic length scale ρ of the solidification pattern. This limit can be obtained by letting the undercooling Δ approach its maximum value of unity. ($\Delta > 1$ sometimes can be achieved experimentally, but the physics becomes very different and need not be considered here.) Our strategy has been to look at the realistic nonlocal model in the limit of small $\epsilon \equiv 1-\Delta$ and to ask whether the mathematical structure of the needle-crystal problem in that limit resembles that of the boundary-layer model. We assert that the answer to this question is "yes," that surface tension destroys the family of Ivantsov solutions of the fully nonlocal free-boundary problem and replaces it by, at most, a discrete set of needle crystals for which v and ρ satisfy a solvability condition.

The scheme of this paper is as follows. We start in Sec. II by writing down the exact integro-differential equation for two-dimensional steady-state solutions of the one-sided model of solidification.[1,5,10,11] This is the version of the solidification problem in which no diffusion occurs in the solid phase. We have chosen this version because it most closely corresponds to the boundary-layer model, although it is slightly more complicated mathematically than the symmetric model[12] in which diffusion is the same in both phases. The derivation of the starting equation[11] and a brief description of the solvability condition for the symmetric model have been placed in Appendixes A and B.

The main part of Sec. II is devoted to a formal expansion of the basic equation in powers of the small parameter l/ρ, where ρ may be interpreted for the moment as the radius of curvature at an arbitrary point on the boundary. Our result is a nonlinear differential equation of infinite order. We check that, for zero surface tension, this equation correctly generates the asymptotic expansion of the Ivantsov solution at small ϵ and correspondingly large p.

From this point, our method of analysis proceeds in parallel with recent work by one of the authors on the boundary-layer model,[13] except that the novel form of the equation that we encounter has forced us to invent some techniques that seem plausible to us but which we are unable to justify rigorously. The first and possibly most dangerous of our guesses is that we can linearize our equation for the boundary around the Ivantsov parabola. This linearization was also used in Ref. 13 where it was possible to make a direct check of its validity. The result of this linearization for the present problem is an inhomogeneous linear equation, still of infinite order, which contains two system parameters ϵ and $\nu=d_0/l$.

In Sec. III, we show explicitly that the homogeneous part of this linear equation has solutions which oscillate very rapidly for small ϵ and ν and which grow without bound as one moves away from the tip of the needle. The requirement that these divergent homogeneous solutions not be present in the solution of the inhomogeneous equation leads us in Sec. IV, via another mathematical conjecture, to a solvability condition which becomes a selection criterion for ν as a function of ϵ. Finally, in Sec. V, we evaluate the solvability condition explicitly for the case of an isotropic surface tension and small ν, and show that no needle-crystal solutions survive except at $\nu=0$.[14,15] The search for solutions at larger values of ν or for anisotropic surface tension is left for later investigation. Section VI contains a few concluding comments regarding implications of these results.

II. EXPANSION OF THE STEADY-STATE EQUATION AT LARGE UNDERCOOLING

The defining equations for the two-dimensional one-sided model, written in a frame of reference moving at velocity v in the z direction, are the following. The diffusion equation is

$$\frac{\partial u}{\partial t}=\nabla^2 u+2\frac{\partial u}{\partial z}\ , \tag{1}$$

where $u=(T-T_\infty)c/L$ is the dimensionless thermal field and lengths are measured in units of $l=2D/v$, times in units of l^2/D. Let the position of the interface be $z=\zeta(x,t)$, x being the Cartesian coordinate orthogonal to z. Heat conservation at the interface requires

$$\hat{\mathbf{n}}\cdot\nabla u=-(2+\dot{\zeta})n_z\ , \tag{2}$$

where $\hat{\mathbf{n}}$ is the outward unit normal and $\dot{\zeta}=\partial\zeta/\partial t$. Finally, the Gibbs-Thomson condition is

$$u=\Delta-\nu\mathscr{K}\ , \tag{3}$$

where $\nu=d_0/l$ as before, $\mathscr{K}=-\zeta''/[1+(\zeta')^2]^{3/2}$ is the curvature of the interface, and primes denote differentiation with respect to x.

From Eqs. (1)–(3) one can derive a closed integro-differential equation for $\zeta(x,t)$. This derivation is performed in Appendix A. In the stationary regime to which we restrict ourselves here, this equation reduces to[11]

$$\Delta-\frac{\nu}{2}\mathscr{K}=2\int_0^\infty d\tau\int_{-\infty}^{\infty}dy\,g(y,\tau\,|\,x,0)+\nu\int_0^\infty d\tau\int_{-\infty}^{\infty}dy\,\mathscr{K}(y)\left[1+\frac{\zeta(y)-\zeta(x)-(y-x)\zeta'(y)}{2\tau}\right]g(y,\tau\,|\,x,0)\,, \tag{4}$$

where

$$g(y,\tau\,|\,x,0)=\frac{1}{4\pi\tau}\exp\left[-\frac{1}{4\tau}\{(y-x)^2+[\zeta(y)-\zeta(x)-2\tau]^2\}\right]. \tag{5}$$

We are interested in the regime where the diffusion length l is everywhere small compared with the radius of curvature of the front. This means that, in our reduced units,

$$\zeta''(x)\ll 1\,, \tag{6}$$

and, more generally, because we look for a needle-shaped profile, that $\zeta^{(n)}\ll 1$ for all $n\geq 2$. We are then naturally led, in the integrals of (4), to use the Taylor expansion

$$\zeta(y)-\zeta(x)=Y\zeta'(x)+\sum_{n\,(\geq 2)}\frac{Y^n}{n!}\zeta^{(n)}(x)\,, \tag{7}$$

(where $Y=y-x$) in which we separate out the small terms with $n\geq 2$. We rewrite the diffusion kernel as

$$g(y,\tau\,|\,x,0)=g_0(Y,\tau\,|\,\zeta'(x))(1+\Gamma)\,, \tag{8}$$

where

$$g_0(Y,\tau\,|\,\zeta'(x))=\frac{1}{4\pi\tau}\exp\left[-\frac{1}{4\tau}\{Y^2+[Y\zeta'(x)-2\tau]^2\}\right], \tag{9}$$

and

$$\Gamma=\sum_{p=1}^{\infty}\frac{1}{p!}\left[-\frac{1}{2\tau}\right]^p\left[(Y\zeta'-2\tau)\sum_{n=2}^{\infty}\frac{Y^n}{n!}\zeta^{(n)}(x)+\frac{1}{2}\left[\sum_{n=2}^{\infty}\frac{Y^n}{n!}\zeta^{(n)}(x)\right]^2\right]^p. \tag{10}$$

Expression (8), which is at this stage formally exact, separates a diffusion kernel associated with a locally planar front with space and time ranges of order unity from *a priori* small corrections describing curvature effects. Similarly, we rewrite the expressions inside the second integral in (4) with the help of the Taylor expansion (7). The Y and τ integrations then can be carried out trivially for each term of the resulting infinite expansion.

Taking advantage of the fact that

$$\int_0^\infty d\tau\int_{-\infty}^{\infty}dY\,g_0(Y,\tau\,|\,\zeta')=\tfrac{1}{2}\,, \tag{11}$$

one can formally rewrite (4) as

$$\begin{aligned}-\epsilon+\frac{\nu}{2}\frac{\zeta''}{[1+(\zeta')^2]^{3/2}}=&\,\zeta''[a_0+\tfrac{1}{2}b_0\zeta''+\tfrac{1}{6}c_0(\zeta'')^2+\cdots]+\zeta'''[a_1+b_1\zeta''+\tfrac{1}{2}c_{11}\zeta''+\tfrac{1}{2}c_{12}\zeta'''+\cdots]\\&+\zeta^{(4)}[a_2+b_2\zeta''+\tfrac{1}{2}c_{21}(\zeta'')^2+c_{22}\zeta'''+\tfrac{1}{6}d_{21}(\zeta'')^3+d_{22}\zeta''\zeta'''+\tfrac{1}{2}d_{23}\zeta^{(4)}+\cdots]\\&+\cdots+\zeta^{(n)}[a_{n-2}+b_{n-2}\zeta''+\cdots]+\cdots\,,\end{aligned} \tag{12}$$

where $\epsilon=1-\Delta\ll 1$. In the right-hand side of (12) we have ordered the terms so that the series multiplying $\zeta^{(n)}$ contains all possible combinations of the form $(\zeta'')^{\alpha_2}(\zeta''')^{\alpha_3}\times\cdots\times(\zeta^{(n)})^{\alpha_n}$ (with any set of positive α_i) but no derivative of ζ of order higher than n. The coefficients $a_i,b_i,c_{ij},\ldots$ are functions of $\zeta'(x)$ and also depend on the capillary parameter ν. The reason for this ordering will become clear shortly.

In the Ivantsov limit, $\nu=0$, Eq. (12) yields the parabola $\zeta''=-p^{-1}=$const, with

$$-\epsilon=\zeta''[a_0(\nu=0)+b_0(\nu=0)\zeta''+\cdots]\,. \tag{13}$$

One easily finds that in this limit

$$a_0=\tfrac{1}{2},\quad b_0=\tfrac{3}{2},\quad c_0=\tfrac{45}{4}\,, \tag{14}$$

etc. That is, Eq. (13), which gives $\zeta''\approx -2\epsilon$, precisely represents the first terms of the asymptotic expansion in powers of ζ'' of the two-dimensional Ivantsov relation

$$\Delta=\left[\frac{\pi}{-\zeta''}\right]^{1/2}\exp\left[-\frac{1}{\zeta''}\right]\mathrm{erfc}\left[\left[\frac{1}{-\zeta''}\right]^{1/2}\right]. \tag{15}$$

This result, which can easily be shown[16] to hold to all orders, simply expresses the fact that the Ivantsov parabola exactly solves the integral equation (4) at zero capillarity, as has been shown directly by Pelcé and Pomeau.[15]

A naive interpretation of (12) would seem to indicate that we have already achieved a useful expansion in powers of ϵ of the solution at nonzero ν. Note that, because of the translational invariance of the system, neither x or $\zeta(x)$ appear explicitly in (12). The natural independent variable is ζ', and the function of principal interest

$\zeta''(\zeta')$ is of order ϵ. All higher derivatives can be written in the form

$$\zeta^{(n)}=\left[\zeta''\frac{d}{d\zeta'}\right]^{n-2}\zeta''\approx\left[-2\epsilon\frac{d}{d\zeta'}\right]^{n-2}\zeta'' , \tag{16}$$

and thus appear to be small of order ϵ^{n-1}. One is therefore tempted to truncate the right-hand side of (12) at some finite order in ϵ and then try to solve the resulting differential equation by conventional techniques. The situation is not so simple, however. A differential equation containing operators of the form (16) can generally be expected to have solutions which are essentially singular in ϵ, that is, which are rapidly growing or oscillating functions of ζ' whose speed of variation increases without bound as ϵ becomes small. Such solutions may be of no physical interest; but if, as in the present case, one's interest is to determine whether smooth physical solutions exist, then the possible appearance of singular solutions is of crucial importance.

To investigate this situation in more explicit terms, let us assume that we are close enough to some smooth solution ζ'' that we can linearize around it. For present purposes, the most convenient choice of smooth solution is the Ivantsov parabola for small ϵ, that is, we write

$$\zeta''(x)\simeq-2\epsilon[1+h(\zeta')] . \tag{17}$$

The reason for the ordering on the right-hand side of (12) should now be clear. The factors $\zeta^{(n)}$ outside the square brackets become $(-2\epsilon d/d\zeta')^{n-2}h$, all of which we take to be of order unity and therefore retain. The quantities inside the square brackets each contain a leading term a_n plus corrections of higher orders in ϵ and h. We immediately discard the higher orders in h in the hope that our linearization is legal (see Ref. 13), and keep only the first correction of order ϵ. The result is

$$\frac{1}{2}+\frac{\nu\mu^3}{2}-a_0+\epsilon b_0+O(\epsilon^2)$$
$$=-\frac{\nu\mu^3}{2}h+\sum_{n=0}^{\infty}[a_n-2\epsilon b_n+O(\epsilon^2)]\left[-2\epsilon\frac{d}{d\zeta'}\right]^n h , \tag{18}$$

where

$$\mu\equiv\mu(\zeta')=[1+(\zeta')^2]^{-1/2} . \tag{19}$$

The coefficients a_n and b_n, which are, respectively, the coefficients of $\zeta^{(n+2)}$ and of $\zeta''\zeta^{(n+2)}$ in the expansion of Eq. (4), are found to be given by

$$a_n(\zeta')=\int_0^\infty d\tau\int_{-\infty}^{\infty}dY\,g_0(Y,\tau\,|\,\zeta')\left[\frac{Y^{n+2}}{(n+2)!}\frac{(2\tau-Y\zeta')}{\tau}-\nu\mu^3\frac{Y^n}{n!}\right] , \tag{20}$$

and

$$b_n(\zeta)=\int_0^\infty d\tau\int_{-\infty}^{\infty}dY\,g_0(Y,\tau\,|\,\zeta')\frac{Y^{n+4}}{2(n+2)!}\left[\frac{(Y\zeta'-2\tau)^2}{2\tau^2}-\frac{1}{\tau}\right]$$
$$+\nu\mu^3\int_0^\infty d\tau\int_{-\infty}^{\infty}dY\,g_0(Y,\tau\,|\,\zeta')\left\{\frac{Y^{n+2}}{2\tau}\left[(Y\zeta'-2\tau)\left[\frac{1}{(n+2)!}+\frac{1}{2(n!)}\right]\right.\right.$$
$$\left.\left.+\frac{n+1}{(n+2)!}+\frac{1}{2(n!)}\right]+3\mu^2\zeta'\frac{(n+2)}{(n+1)!}Y^{n+1}\right\} . \tag{21}$$

Finally, using

$$a_0=\frac{1}{2}-\frac{\nu\mu^3}{2} , \tag{22}$$

we rewrite (18) as

$$\left[L_0-2\epsilon L_1-\frac{\nu\mu^3}{2}\right]h(\zeta')=\nu\mu^3+\epsilon b_0 , \tag{23}$$

where

$$L_0=\sum_{n=0}^{\infty}a_n(\zeta')\left[-2\epsilon\frac{d}{d\zeta'}\right]^n , \tag{24}$$

and

$$L_1=\sum_{n=0}^{\infty}b_n(\zeta')\left[-2\epsilon\frac{d}{d\zeta'}\right]^n . \tag{25}$$

III. WKB SOLUTIONS OF THE HOMOGENEOUS EQUATION

Equation (23) is an inhomogeneous linear differential equation which, however, is of infinite order and therefore of a highly nonstandard type. We emphasize once again that the solution we propose here is by no means rigorous.

We start by looking for solutions of the homogeneous part of (23). The form of the linear operator immediately suggests that we try to construct these solutions in the WKB form

$$h_H(\zeta')=\exp\left[\frac{1}{\epsilon}S(\zeta',\epsilon)\right] , \tag{26}$$

where

$$S(\zeta',\epsilon)=S_0(\zeta')+\epsilon S_1(\zeta')+O(\epsilon^2) . \tag{27}$$

The function $\exp[S_1(\zeta')]$ is an ϵ-independent multiplicative factor in (26) which we shall need in our final formula for the solvability condition; it is in order to compute S_1 correctly that we have retained terms of order ϵ in (23). Accordingly, we insert (26) into (23) and use

$$\left[\epsilon \frac{d}{d\zeta'}\right]^n h = \left[(S_0')^n + \epsilon\left[n(S_0')^{n-1}S_1' + \frac{n(n-1)}{2}S_0''(S_0')^{n-2}\right] + O(\epsilon^2)\right] h \ , \quad (28)$$

where $S' \equiv dS/d\zeta'$, to obtain the following equations at the zeroth and first orders in ϵ for S_0 and S_1:

$$L_0(S_0',\zeta') = \frac{\nu\mu^3}{2} \ , \quad (29)$$

$$S_1' \frac{\partial L_0(S_0',\zeta')}{\partial S_0'} + \frac{S_0''}{2}\frac{\partial^2 L_0(S_0',\zeta')}{\partial (S_0')^2} - 2L_1(S_0',\zeta') = 0 \ , \quad (30)$$

where

$$L_0(S_0',\zeta') = \sum_{n=0}^{\infty} a_n(\zeta')(-2S_0')^n \ , \quad (31)$$

$$L_1(S_0',\zeta') = \sum_{n=0}^{\infty} b_n(\zeta')(-2S_0')^n \ . \quad (32)$$

Our next step is to insert the integral formulas for a_n and b_n, Eqs. (20) and (21), into (31) and (32). If we first perform the sum over n inside the integrals, we can then carry out the integrations. The algebra is tedious but straightforward, and yields the results

$$L_0(S_0',\zeta') = \frac{1}{R + (1+2S_0'\zeta')R^{1/2}} - \frac{\nu\mu^3}{2R^{1/2}} \ , \quad (33)$$

$$L_1(S_0',\zeta') = \frac{3}{2R^{5/2}} + \frac{3\nu\mu^3}{2}\left[\frac{(\zeta' - 2S_0')S_0'}{R^{5/2}} + \frac{\zeta'\mu^2}{2S_0'}\left[1 - \frac{1+2\zeta' S_0'}{R^{3/2}}\right]\right] , \quad (34)$$

where

$$R = 1 + 4\zeta' S_0' - 4(S_0')^2 \ , \quad (35)$$

and $R^{1/2}$ is defined as the determination of the square root whose real part is positive when the real part of R is positive. These resummations are unambiguously legitimate only within the domain of convergence of the series (31) and (32). We shall assume that $L_0(S_0',\zeta')$ and $L_1(S_0',\zeta')$ are defined everywhere in the complex S_0' plane by the analytic continuation of expressions (33) and (34).

S_0' now can be obtained from (33) by solving (29). This means solving a quartic equation for S_0' and retaining those of its roots which satisfy (29), an algebraically difficult process that may best be carried out by numerical means. In order to construct an analytic treatment of the problem, which seems necessary to gain some qualitative insight into the effect of capillarity, we shall therefore solve it in the limit of small ν.

We set

$$S_0' = \tfrac{1}{2}\{\zeta' + \psi[1 + (\zeta')^2]^{1/2}\} \ , \quad (36)$$

and notice that the determination of $R^{1/2}$ imposes that, for $0 < \arg\psi < \pi$ and $|\psi| \gg 1$,

$$R^{1/2} = \mu^{-1}(1-\psi^2)^{1/2} = -\frac{i\psi}{\mu}[1 + O(\psi^{-2})] \ ; \quad (37)$$

and for $-\pi < \arg\psi < 0$ and $|\psi| \gg 1$,

$$R^{1/2} = \frac{i\psi}{\mu}[1 + O(\psi^{-2})] \ . \quad (38)$$

Then, for $\nu \ll 1$, one finds that (29) has two solutions

$$S_{0+}'(\zeta') = \frac{i}{\mu\sqrt{2\nu}}\exp\left[-\frac{i}{2}\theta(\zeta')\right] + \tfrac{1}{4}\zeta' - \frac{i}{2} + O(\nu^{1/2}) \ , \quad (39)$$

and

$$S_{0-}'(\zeta') = S_{0+}'^{*}(\zeta') = -S_{0+}'(-\zeta') \ . \quad (40)$$

Here, $\theta = \tan^{-1}\zeta'$ is the angle between the growth direction and the local normal to the solidification front. Integrating (39), we obtain

$$S_{0+}(\zeta') = S_{0-}^{*}(\zeta') = \frac{i}{\sqrt{2\nu}}\int_0^{\tan^{-1}\zeta'} d\theta \frac{e^{-i\theta/2}}{\cos^3\theta} + \tfrac{1}{8}(\zeta')^2 - \frac{i}{2}\zeta' + O(\nu^{1/2}) \ . \quad (41)$$

The associated values of S_1 turn out to be

$$S_{1+}(\zeta') = S_{1-}^{*}(\zeta') = -\frac{3i}{4}\tan^{-1}\zeta' + O(\nu^{1/2}) \ . \quad (42)$$

A crucial point to notice here is that the homogeneous solutions obtained by inserting (41) and (42) into (26) do indeed exhibit the divergent oscillations which were predicted in the previous section. To see this in a particularly useful way note first that the curvature of the Ivantsov parabola is

$$\mathcal{K} = \frac{d\theta}{d\xi} = 2\epsilon\cos^3\theta \ , \quad (43)$$

where ξ is the arclength measured in units of l. Thus, the dominant part of $S(\zeta')$ in the limit of large $|\zeta'|$ and small ν can be written in the form

$$\frac{1}{\epsilon}S_{\pm}(\zeta') \approx \frac{1}{\sqrt{\nu}}(\pm i\xi + |\xi|) \ , \quad (44)$$

which demonstrates that $h_H(\zeta')$ behaves in a physically unacceptable way in the limits $\xi \to \pm\infty$. The length scale associated with this divergence is $\nu^{1/2}$. In physical units this is $\nu^{1/2} l = (d_0 l)^{1/2}$, which is precisely the stability length mentioned in the Introduction.

IV. SOLVABILITY CONDITION FOR THE INHOMOGENEOUS EQUATION

In the absence of a known systematic method for solving the inhomogeneous equation (23), we look for a particular solution $h_P(\zeta')$ in a form which is suggested by the formal solution of a second-order differential equation in the WKB approximation. Our guess is

$$h_P(\zeta')=i\int_{-\infty}^{\zeta} d\eta\,\phi(\eta)F(\eta)\left[\frac{h_+(\zeta')}{h_+(\eta)}-\frac{h_-(\zeta')}{h_-(\eta)}\right], \quad (45)$$

where

$$\phi(\eta)=\nu\mu^3(\eta)+O(\epsilon)\ . \quad (46)$$

h_+ and h_- are the homogeneous solutions associated with S_+ and S_-, respectively, and $F(\eta)$ is an unknown function.

To confirm the validity of (45) and thereby determine $F(\eta)$, we apply to (45) the operator

$$\mathscr{L}=L_0-2\epsilon L_1-\tfrac{1}{2}\nu\mu^3\equiv\sum_{n=0}^{\infty} l_n\left[-2\epsilon\frac{d}{d\zeta'}\right]^n, \quad (47)$$

with

$$l_n=\alpha_n-2\epsilon b_n,\quad \alpha_n=a_n-\frac{\nu\mu^3}{2}\delta_{n,0}\ . \quad (48)$$

Taking advantage of the fact that $\mathscr{L}h_\pm=0$, one obtains

$$\mathscr{L}h=\Lambda_+-\Lambda_-\ , \quad (49)$$

with

$$\Lambda_\pm=\sum_{p=0}^{\infty}\sum_{n=p+2}^{\infty} l_n\left[-2\epsilon\frac{d}{d\zeta'}\right]^p \times\left[(-2\epsilon iF)\phi\frac{1}{h_\pm}\left[-2\epsilon\frac{d}{d\zeta'}\right]^{n-p-1}h_\pm\right]. \quad (50)$$

We are interested in extracting the term in F which is dominant at small ϵ. Noticing that ϕ and $S'_\pm$ are regular functions of ϵ, we can write, to dominant order,

$$i\sum_{p=0}^{\infty}\sum_{n=p+2}^{\infty}\alpha_n[(-2S'_{0+})^{n-p-1}-(-2S'_{0-})^{n-p-1}] \times\left[-2\epsilon\frac{d}{d\zeta'}\right]^p(-2\epsilon F)=1\ . \quad (51)$$

Thus, the equation for $(-2\epsilon F)$ has exactly the same structure as Eq. (23) for h, and the question arises of whether the solution for F itself involves, as does h, an essential singularity in ϵ.

In order to decide this point, let us look for solutions of the homogeneous equation associated with (51) of the following form: $-2\epsilon F_H=\exp[X_0(\zeta')/\epsilon]$. One finds, to dominant order in ϵ,

$$\sum_{p=0}^{\infty}\sum_{n=p+1}^{\infty}\alpha_n(-2X'_0)^p[(-2S'_{0+})^{n-p-1} -(-2S'_{0-})^{n-p-1}]=0\ , \quad (52)$$

which can easily be resummed into

$$H(X'_0)\equiv\left[\frac{1}{S'_{0+}-X'_0}-\frac{1}{S'_{0-}-X'_0}\right]\left[L_0(X'_0,\zeta')-\frac{\nu\mu^3}{2}\right] =0\ . \quad (53)$$

The only roots of the second factor on the left-hand side of Eq. (53) are $X'_0=S'_{0\pm}$, for which

$$\lim_{X'_0\to S'_{0\pm}} H(X'_0)=\mp\left.\frac{\partial L_0(X'_0,\zeta')}{\partial X'_0}\right|_{X'_0=S'_{0\pm}}\neq 0\ . \quad (54)$$

From this, we deduce that the homogeneous part of the equation for $(-2\epsilon F)$ has no solution singular in ϵ, that is, that derivatives of F do not produce inverse powers of ϵ.

We can now calculate F to lowest order in ϵ by retaining only the terms with $p=0$ in (51). The result is, after a little more algebraic manipulation,

$$F(\zeta')=\left[\frac{2}{i\epsilon}\right]\frac{S'_{0+}S'_{0-}}{(S'_{0+}-S'_{0-})(1-2\nu\mu^3)}\ , \quad (55)$$

which completes the determination of $h_P(\zeta')$ in (45). Note that $F(\zeta')$ is a real symmetric function of ζ'.

The general solution of (23) is the sum of the particular solution h_P and any linear combination of the homogeneous solutions $h_\pm$. However, because h_+ and h_- both diverge as $\zeta'\to\pm\infty$, and because we already have chosen the lower limit of integration in (45) so that h_P vanishes as $\zeta'\to-\infty$, we are no longer permitted to add any components of $h_\pm$ to h_P without disqualifying our solution as a physically acceptable capillary correction to the shape of the needle crystal. This criterion also must be applied for $\zeta'\to+\infty$, in which limit we have

$$h_P(\zeta')\approx i[h_+(\zeta')-h_-(\zeta')]I(\epsilon,\nu),\quad \zeta'\to+\infty \quad (56)$$

where

$$I(\epsilon,\nu)=\int_{-\infty}^{\infty}d\eta\frac{\phi(\eta)F(\eta)}{h_+(\eta)}=\int_{-\infty}^{\infty}d\eta\frac{\phi(\eta)F(\eta)}{h_-(\eta)}\ . \quad (57)$$

In writing this last relation, we have used the symmetry of ϕ and F and the fact that $S_+(-\eta)=S_+^*(\eta)=S_-(\eta)$, which implies that I is real and independent of the specification + or −. The major conclusion from all of our analysis is that, in order for h_P to remain well behaved in (56) for $\zeta'\to+\infty$, we must have

$$I(\epsilon,\nu)=0\ . \quad (58)$$

Equation (58) is a solvability condition which must be satisfied if needle crystals are to exist.

Two alternative interpretations of the function $I(\epsilon,\nu)$ are useful for understanding where the solvability condition (58) stands in relation to other work in this area. First, the strategy that has been used for computing the shapes of needle crystals in the various local models[7,9,13] of dendritic growth has been to integrate the (finite-order) steady-state differential equations from $\zeta'=-\infty$ to $\zeta'=0$, and to compute $d\mathscr{K}/d\theta$ at the latter point. In principle, we can imagine having carried out the same procedure here. It is a simple matter to deduce from our preceding equations that

$$\left.\frac{d\mathscr{K}}{d\theta}\right|_{\theta=0}=-2iS'_{0+}(\zeta'=0)I\approx-\sqrt{2/\nu}I\ , \tag{59}$$

where the second form is valid in the limit of small ν. By symmetry, one knows that $d\mathscr{K}/d\theta$ must vanish at $\theta=0$ if a needle crystal is to exist; thus we arrive at the same solvability condition (58) but with a specific interpretation of the quantity I.

The second interpretation is less secure mathematically but possibly more useful for future work. In standard treatments of inhomogeneous linear differential equations such as (23), but of finite order, the equation is said to be solvable if the inhomogeneous term on the right-hand side is orthogonal to the null space of the operator on the left. Apparently the functions $h_{\mp}^{-1}F$ are the left null eigenvectors of this operator—this is exactly what happens for the second-order equations encountered in the local models[13]—in which case (58) is precisely the required orthogonality condition. There are many unresolved mathematical subtleties associated with this interpretation, however, and we shall not pursue the matter beyond the suggestion that it might be a clue to a more general approach to selection problems of this kind.

V. ASYMPTOTIC ESTIMATE FOR $I(\epsilon,\nu)$

We conclude the technical presentation of this paper by describing a few basic properties of the function $I(\epsilon,\nu)$. It appears that there is a great deal to be learned from evaluation of this function, especially if one includes crystalline anisotropy via a prescribed θ or ζ' dependence of the capillary length d_0. However, we shall leave most of these details for later publication.

For the present, let us look only at the special limiting situation in which ν approaches zero while ϵ is held small but fixed. That is, we consider how $I(\epsilon,\nu)$ approaches the Ivantsov limit. In this case, S_{0+} is dominated by the term proportional to $\nu^{-1/2}$ on the right-hand side of (41). It is useful to transform the variable of integration to $\eta'=\tan\theta$ so as to write this function in the form

$$S_{0+}(\eta)\cong\frac{i}{\sqrt{2\nu}}\int_0^{\eta}d\eta'(1-i\eta')^{3/4}(1+i\eta')^{1/4}+O(\nu^0)\ . \tag{60}$$

Note that S_{0+} has stationary points which coincide with branch points at $\eta=\pm i$. The path of deepest descent from $\eta=-\infty$ to $\eta=+\infty$ for the function $\exp[-S_{0+}(\eta)/\epsilon]$ passes through $\eta=-i$, bending through a finite angle there because of the branch point. Because the latter function dominates the integral for I in the limit of interest to us, we can expand it in the region near its peak. Let $\eta=-i+iz/2$, so that

$$S_{0+}(\eta)\cong\frac{a_s}{\sqrt{\nu}}-\frac{z^{7/4}}{7\sqrt{\nu}}\ , \tag{61}$$

where

$$a_s=\frac{1}{\sqrt{2}}\int_0^1 du(1+u)^{1/4}(1-u)^{3/4}\cong 0.4355\ldots\ , \tag{62}$$

We next must evaluate the other ingredients of the integrand. Our results are

$$\exp[-S_{1+}(\eta)]=\left[\frac{1+i\eta}{1-i\eta}\right]^{3/8}\cong\left[\frac{4}{z}\right]^{3/8}\ , \tag{63}$$

$$F(\eta)\cong-\frac{1}{\epsilon\sqrt{\nu}(1-2\nu\mu^3)\mu(1+\mu)^{1/2}}\cong-\frac{z^{9/4}}{\epsilon\sqrt{\nu}(z^{3/2}-2\nu)}\ , \tag{64}$$

and

$$\phi(\eta)=\nu\mu^3\cong\frac{\nu}{z^{3/2}}\ . \tag{65}$$

Note that the first-order correction to the WKB formula, Eq. (63), makes a leading-order contribution to I. Combining terms, we find

$$I\approx\frac{i\sqrt{\nu}}{2^{1/4}\epsilon}\exp\left[-\frac{a_s}{\epsilon\sqrt{\nu}}\right]\int_C dz\frac{z^{3/8}\exp\left[\dfrac{z^{7/4}}{7\epsilon\sqrt{\nu}}\right]}{(z^{3/2}-2\nu)}\ , \tag{66}$$

where the contour of integration C runs from $-i\infty$ to $+i\infty$ and stays to the right of the pole at $z=(2\nu)^{2/3}$. In the limit $\nu^2\ll\epsilon^3$, this pole merges with the branch point at $z=0$, and we find

$$I(\epsilon,\nu)\approx-\frac{2^{11/4}\pi\nu^{13/28}}{(7\epsilon)^{15/14}\Gamma(15/14)}\exp\left[-\frac{a_s}{\epsilon\sqrt{\nu}}\right]\ . \tag{67}$$

Several remarks are now in order. I vanishes rapidly in the Ivantsov limit $\nu\to 0$, but has no other zeros within the range of values of ϵ,ν for which (67) is valid; thus the Ivantsov family of solutions disappears completely for small but finite isotropic surface tension. The fact that I has an essential singularity in ν at $\nu=0$ means that no technique for computing the correction to the shape of the Ivantsov parabola as a power series in ν can give any information whatsoever about whether the corrected shape is actually a solution of the needle-crystal problem. The dimensionless parameter that characterizes the singular behavior of I is the product $\epsilon\sqrt{\nu}$. Because $\epsilon\cong l/\rho$ in our solution, this product is the same as $(d_0 l)^{1/2}/\rho=\sigma^{1/2}$, where σ is the parameter identified in the Introduction as playing a fundamental role in stability-related theories of dendritic pattern selection.[5] We do not yet claim to understand the implications of this fact.

VI. CONCLUDING REMARKS

We have shown here, in the limit of large undercooling—and with the proviso that our mathematics be legitimate—that surface tension acts as a singular perturbation on the capillarity-free Ivantsov solutions of the needle-crystal problem. That is, whatever its magnitude, surface tension breaks the degeneracy of the Ivantsov family of solutions and, under some circumstances, causes those solutions to disappear altogether. Our result is expressed in terms of the solvability condition (58) which, when it can be satisfied at all, is an equation determining the dimensionless capillary length $\nu=d_0/l=d_0v/2D$ as a function of the dimensionless undercooling $\Delta=1-\epsilon$. This equation, together with the relation $-\zeta''(0)=l/\rho\approx 2\epsilon$, predicts both the tip radius ρ and growth velocity v as independent functions of the undercooling.

This result has been obtained in the one-sided model. In order to show that it does not depend crucially on the absence of thermal diffusion on the solid side of the solidification front, we have performed the same analysis for the symmetric model, that is, for the case where the two phases have the same thermal properties.[12] This analysis is summarized briefly in Appendix B, where we show that the mathematical structure of the symmetric problem is the same as for the one-sided model. In particular, the homogeneous equation for the departure from the parabolic shape has two solutions, both of which diverge at $\zeta'\to\pm\infty$. One therefore obtains a solvability condition in the form (58) where the only difference between the one-sided and symmetric models appears in the detailed expressions for the functions $S_0(\zeta')$, $S_1(\zeta')$. It appears that this kind of capillary-induced breakdown of steady-state solutions must be a commonly occurring feature of pattern-selection problems.

Another question of some interest is the extent to which the mathematical structure discovered here is actually consistent with what we know about the local models. The latter models, after all, provided the rationale for the present investigation; and the boundary-layer model is supposed to have some physical validity in the limit of small ϵ. We do not yet have a detailed answer to this question but are able to see some aspects of what is happening. At the most basic level, our solvability condition with its exponential dependence on $\nu^{-1/2}$ is identical to that of the boundary-layer model.[13] The underlying equations for the shape of the needle crystal look superficially quite different, however. In particular, the analog of (23) for the boundary-layer model is a second-order differential equation (which can easily be written as an equation for h as a function of ζ') in which the capillary parameter ν multiplies the derivatives instead of the undifferentiated term.[13] Something much closer to the structure of the boundary-layer model is obtained, however, if one operates on (23) from the left by the inverse of the operator $L_0+\epsilon L_1$ and then expands the resulting equation to second order in $-2\epsilon d/d\zeta'$. In this way, one is approximating the branch cut singularities in $L_0+\epsilon L_1$ by poles. Much of the structure of the realistic diffusion problem is lost in this procedure, but it remains to be seen how crucial these losses may be.

By far the most important unresolved question is how much the existence of a solvability condition tells us about dendritic pattern selection. It seems possible that we shall be able, in the not too distant future, to carry out time-dependent numerical simulations of the one-sided or symmetric models of solidification and check whether needle crystals which satisfy solvability conditions do, in fact, identify the dynamically selected modes of growth. This is what has been discovered to happen in the relatively more tractable local models.[7,9] If we had a better understanding of how realistic the latter models are, for example, and if we could answer the questions raised in the last paragraph, we might be quite confident about proposing the same selection mechanism for real dendrites. In any case, we shall eventually have to deal with the dynamical properties of the realistic models studied in this paper. We know that in both the geometric and boundary-layer models there occur needle-crystal solutions, with small but finite anisotropy, which satisfy solvability conditions but which are unstable against tip-splitting deformations. Such solutions are not physically realizable dendritic growth modes. Thus, even if the analogy between local models and real physics turns out to be complete, a technique for studying dynamical stability will be an essential part of any theory of dendrites. The intriguing appearance of stability-related parameters in the present investigation gives us hope that the techniques we have been exploring will also yield some dynamical information.

APPENDIX A: DERIVATION OF THE INTEGRO-DIFFERENTIAL EQUATION FOR THE ONE-SIDED MODEL

Let us introduce the following notation: $v=(\rho,t)$, $p=(\mathbf{r},t)$, $p_s=(v,\zeta(v))$, $\rho=x\hat{\mathbf{i}}+y\hat{\mathbf{j}}$, $\mathbf{r}=\rho+z\hat{\mathbf{k}}$, where $z=\zeta(v)$ is the position of the interface. Lengths are measured in units of $l=2D/v$, times in units of l^2/D.

In order to find the solution of the diffusion equation (1):

$$\left[\frac{\partial}{\partial t}-2\frac{\partial}{\partial z}-\nabla^2\right]u(p)=0,\quad \lim_{z\to\infty}u(p)=0 \tag{A1}$$

we introduce the retarded Green's function $G(p,p')$, defined by

$$\left[\nabla_{\mathbf{r}'}^2-2\frac{\partial}{\partial z'}+\frac{\partial}{\partial t'}\right]G(p,p')=-\delta(p-p')\ ,$$

$$G(p,p')\equiv 0\ \text{ for } t-t'<0 \tag{A2}$$

so that

$$G(p,p')=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{e^{i\omega(t-t')+i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{i\omega+k^2-2ik_z} \tag{A3}$$

or

$$G(p,p')=\frac{\Theta(t-t')}{[4\pi(t-t')]^{3/2}}\exp\left[-\frac{A^2}{4(t-t')}\right], \quad (A4)$$

where Θ is the unit step function, and

$$A^2=|\boldsymbol{\rho}-\boldsymbol{\rho}'|^2+[z-z'+2(t-t')]^2 . \quad (A5)$$

Hence

$$G(\mathbf{r},t;\mathbf{r}',t_-)=\lim_{\epsilon\to 0}G(\mathbf{r},t;\mathbf{r}',t-\epsilon)=\delta(\mathbf{r}-\mathbf{r}') . \quad (A6)$$

Note that, setting

$$\mathbf{k}=\mathbf{q}+k_z\hat{\mathbf{k}} \quad (A7)$$

in (A3) and integrating over k_z, one obtains

$$G(p,p')=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{i\omega(t-t')}\int\frac{d\mathbf{q}}{(2\pi)^2}\frac{e^{i\mathbf{q}\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')}}{2[m(q,\omega)-1]}\exp(-\{z-z'+|z-z'|[m(q,\omega)-1]\}) , \quad (A8)$$

where

$$m(q,\omega)=1+(1+i\omega+q^2)^{1/2} , \quad (A9)$$

with $\mathrm{Re}(1+i\omega+q^2)^{1/2}>0$.

Using Green's theorem, one finds from (A2)

$$-\int_{-\infty}^{t_-}dt'\int dS'\hat{\mathbf{n}}'\cdot\nabla_{\mathbf{r}_s'}G(p,p_s')-2\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\int_{\zeta(v')}^{\infty}dz'\frac{\partial}{\partial z'}G(p,p') + \int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\int_{\zeta(v')}^{\infty}dz'\frac{\partial}{\partial t'}G(p,p')=0 , \quad (A10)$$

where $\hat{\mathbf{n}}$ is the unit vector normal to the interface pointing from the solid $[z<\zeta(v)]$ into the liquid $[z>\zeta(v)]$, and $\int dS'$ denotes an integration over the interface. Moreover,

$$\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\int_{\zeta(v')}^{\infty}dz'\frac{\partial}{\partial t'}G(p,p')=\int_{-\infty}^{t_-}dt'\left[\frac{d}{dt'}\int_{[z'>\zeta(v')]}d\mathbf{r}'G(p,p')+\int d\boldsymbol{\rho}'\dot{\zeta}(v')G(p,p_s')\right]$$
$$=1+\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\dot{\zeta}(v')G(p,p_s') , \quad (A11)$$

where use has been made of (A6) and of $\lim_{t'\to-\infty}G(p,p')=0$.

On the other hand, one can write

$$\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\int_{\zeta(v')}^{\infty}dz'\frac{\partial}{\partial z'}G(p,p')=\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\left[\lim_{z_1\to\infty}G(p;\boldsymbol{\rho}',z_1,t')-G(p,p_s')\right] . \quad (A12)$$

In order to evaluate the first term in the right-hand side of (A12), we note that because $G(p;r',t+\epsilon)=0$, we can write with the help of (A8),

$$\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'\lim_{z_1\to\infty}G(p;\boldsymbol{\rho}',z_1,t')$$
$$=\lim_{z_1\to\infty}\int_{-\infty}^{\infty}dt'\int d\boldsymbol{\rho}'\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{i\omega(t-t')}\int\frac{d\mathbf{q}}{(2\pi)^2}\frac{e^{i\mathbf{q}\cdot(\boldsymbol{\rho}-\boldsymbol{\rho}')-(z-z_1)[2-m(q,\omega)]}}{2[m(q,\omega)-1]}=\frac{1}{2} . \quad (A13)$$

Substituting relations (A11) through (A13) into (A10), we find

$$\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'[2+\dot{\zeta}(v')]G(p,p_s')-\int_{-\infty}^{t_-}dt'\int dS'\hat{\mathbf{n}}'\cdot\nabla_{\mathbf{r}'}G(p,p_s')=0 . \quad (A14)$$

Returning to Eqs. (A1) and (A2), multiplying them by $G(p,p')$ and $u(p')$, respectively, adding and integrating, we find with the help of Green's theorem

$$\int_{-\infty}^{t_-}dt'\int_{[z'>\zeta(v')]}d\mathbf{r}'\frac{\partial}{\partial t'}[G(p,p')u(p')]=2\int_{-\infty}^{t_-}dt'\int_{[z'>\zeta(v')]}d\mathbf{r}'\frac{\partial}{\partial z'}[G(p,p')u(p')]$$
$$-\int_{-\infty}^{t_-}dt'\int dS'\hat{\mathbf{n}}'\cdot[G(p,p_s')\nabla_{\mathbf{r}'}u(p_s')-u(p_s')\nabla_{\mathbf{r}'}G(p,p_s')] , \quad (A15)$$

so that, because $\lim_{z\to\infty}u(p)=0$,

$$u(p)=-\int_{-\infty}^{t_-}dt'\int d\boldsymbol{\rho}'[2+\dot{\zeta}(v')]u(p_s')G(p,p_s')-\int_{-\infty}^{t_-}dt'\int dS'\hat{\mathbf{n}}'\cdot[G(p,p_s')\nabla_{\mathbf{r}'}u(p_s')-u(p_s')\nabla_{\mathbf{r}'}G(p,p_s')] . \quad (A16)$$

We then get, from (A14) and (A16)

$$u(p)=\int_{-\infty}^{t^-}dt'\int d\rho'[2+\dot{\zeta}(v')][1-u(p_s')]G(p,p_s')-\int_{-\infty}^{t^-}dt'\int dS'[\hat{\mathbf{n}}'\cdot\nabla_{r'}u(p_s')]G(p,p_s')$$
$$+\int_{-\infty}^{t^-}dt'\int dS'[u(p_s')-1]\hat{\mathbf{n}}'\cdot\nabla_{r'}G(p,p_s')\ . \qquad \text{(A17)}$$

The $\dot{\zeta}$ appearing in the first term of (A17) is absent from the analogous equation derived by Dee and Mathur[10] for directional solidification. It is clear that this term must be present because (A17) must be Galilean invariant. The error in Ref. 10, which affects only dynamical predictions and not the results of that paper, stems from overlooking the time dependence of the position of the interface in the derivation of (A16).

Applying to (A17) the theorem on the discontinuity of the heat potential of a double layer,[10,17] according to which

$$\lim_{z\to\zeta(x)+0}\int_{-\infty}^{t^-}dt'\int dS'f(p_s')\hat{\mathbf{n}}'\cdot\nabla_{r'}G(p,p_s')=\tfrac{1}{2}f(p_s)+\int_{-\infty}^{t^-}dt'\int dS'f(p_s')\hat{\mathbf{n}}'\cdot\nabla_{r'}G(p_s,p_s')\ , \qquad \text{(A18)}$$

we find

$$u(p_s)+1=2\int_{-\infty}^{t^-}dt'\int d\rho'[2+\dot{\zeta}(v')][1-u(p_s')]G(p_s,p_s')-2\int_{-\infty}^{t^-}dt'\int dS'[\hat{\mathbf{n}}'\cdot\nabla_{r'}u(p_s')]G(p_s,p_s')$$
$$+2\int_{-\infty}^{t^-}dt'\int dS'[u(p_s')-1]\hat{\mathbf{n}}'\cdot\nabla_{r'}G(p_s,p_s')\ . \qquad \text{(A19)}$$

Finally, using Eqs. (2) and (3) and applying (A14) to (A17), we obtain the following closed integro-differential equation for the position of the interface:

$$\Delta-\frac{\nu}{2}\mathcal{K}(v)=\int_{-\infty}^{t^-}dt'\int d\rho'[2+\dot{\zeta}(v')]G(p_s,p_s')+\nu\int_{-\infty}^{t^-}dt'\int d\rho'[2+\dot{\zeta}(v')]\mathcal{K}(v')G(p_s,p_s')$$
$$-\nu\int_{-\infty}^{t^-}dt'\int dS'\mathcal{K}(v')\hat{\mathbf{n}}'\cdot\nabla_{r'}G(p_s,p_s')\ , \qquad \text{(A20)}$$

where $\mathcal{K}(v)$ is the curvature of the interface at the point $(v,\zeta(v))$.

In the two-dimensional stationary case studied in this paper, $\dot{\zeta}(v)=0$; $\zeta(v)\equiv\zeta(x)$. The function $G(p_s,p_s')$, when integrated over x', yields the two-dimensional Green's function defined by (5), and (A20) finally reduces to (4).

APPENDIX B: THE SYMMETRIC MODEL

For the symmetric model, the integral equation for the stationary interface is[1,12]

$$\Delta-\nu\mathcal{K}(x)=2\int_0^{\infty}d\tau\int_{-\infty}^{\infty}dy\,g(y,\tau\,|\,x,0)\ . \qquad \text{(B1)}$$

One can perform on the right-hand side of (B1) the same ϵ expansion around the Ivantsov solution as that performed in Sec. II for the one-sided model. Noticing that the right-hand side of (B1) is the $\nu=0$ limit of the right-hand side of (4), one immediately finds that the departure from the parabolic interface must satisfy

$$(L_0^{(0)}-2\epsilon L_1^{(0)}-\nu\mu^3)h(\zeta')=\nu\mu^3+\epsilon b_0^{(0)}\ , \qquad \text{(B2)}$$

where

$$L_0^{(0)}=\sum_{n=0}^{\infty}a_n^{(0)}(\zeta')\left[-2\epsilon\frac{d}{d\zeta'}\right]^n\ , \qquad \text{(B3)}$$

$$L_1^{(0)}=\sum_{n=0}^{\infty}b_n^{(0)}(\zeta')\left[-2\epsilon\frac{d}{d\zeta'}\right]^n\ , \qquad \text{(B4)}$$

and $a_n^{(0)}(\zeta')$ and $b_n^{(0)}(\zeta')$ are given by expressions (20) and (21) with $\nu=0$.

We then look for solutions of the homogeneous equation associated with (B2) in the form given by (26). S_0' must be the solution of

$$L_0^{(0)}(S_0',\zeta')\equiv\frac{1}{R+(1+2S_0'\zeta')R^{1/2}}=\nu\mu^3\ . \qquad \text{(B5)}$$

In the small-ν limit, this equation yields the approximate solutions

$$S_{0+}'=S_{0-}'^{*}=\frac{i}{2\mu\sqrt{\nu}}\exp\left[-\frac{i\theta(\zeta)}{2}\right]+\frac{\zeta'}{2}\ , \qquad \text{(B6)}$$

from which $S_{1\pm}$ can be computed with the help of (30).

It is clear that, as in the one-sided case, the homogeneous solutions $h_{\pm}(\zeta')$ both diverge at $\zeta'\to\pm\infty$. One may then carry out the analysis along the same lines as in Sec. III, arriving at (57) and the solvability condition (58), the only difference being that S_0, S_1, and F must now be calculated using (B6) instead of (39).

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[1]J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980).
[2]S. C. Huang and M. E. Glicksman, Acta Metall. **29**, 701 (1981); **29**, 717 (1981).
[3]G. P. Ivantsov, Dokl. Akad. Nauk SSSR **58**, 567 (1947); A. Papapetrou, Z. Kristallogr. **92**, 108 (1935).
[4]G. Horvay and J. W. Cahn, Acta Metall. **9**, 695 (1961).
[5]J. S. Langer and H. Müller-Krumbhaar, Acta Metall. **26**, 1681 (1978); **26**, 1689 (1978); **26**, 1697 (1978).
[6]R. Brower, D. Kessler, J. Koplik, and H. Levine, Phys. Rev. Lett. **51**, 1111 (1983); Phys. Rev. A **29**, 1335 (1984).
[7]D. Kessler, J. Koplik, and H. Levine, Phys. Rev. A **30**, 3161 (1984).
[8]E. Ben-Jacob, N. D. Goldenfeld, J. S. Langer, and G. Schön, Phys. Rev. Lett. **51**, 1930 (1983); Phys. Rev. A **29**, 330 (1984).
[9]E. Ben-Jacob, N. D. Goldenfeld, B. G. Kotliar, and J. S. Langer, Phys. Rev. Lett. **53**, 2110 (1984).
[10]G. Dee and R. Mathur, Phys. Rev. B **27**, 7073 (1983).
[11]An independent derivation of the integro-differential equation for the one-sided model has been given by A. Karma, Ph.D. Thesis, University of California, Santa Barbara (1985), and also by A. Karma and M. Marder (unpublished).
[12]J. S. Langer, Acta Metall. **25**, 1121 (1977).
[13]J. S. Langer, preceding paper, Phys. Rev. A **33**, 435 (1986).
[14]This result is consistent with very recent numerical calculations by D. Meiron (private communication).
[15]An analysis which leads in the direction of a similar result in the limit of small undercooling Δ has been presented by P. Pelcé and Y. Pomeau (unpublished).
[16]C. D. Graham, Met. Prog. **71**, 75 (1957).
[17]M. Gerney, J. Math. Pures Appl. **9**, 6 (1913); L. I. Rubinstein, *The Stefan Problem* (American Mathematical Society, Providence, Rhode Island, 1977); W. Pogorzelski, *Integral Equations and their Applications* (Pergamon, New York, 1966).