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Impurity effect on dendritic growth

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We consider the effects of impurities on the velocity selection of a needle crystal, in the small thermal and solutal Peclet numbers. As in the case of the growth in a pure melt, steady solutions for needle crystals are found only if surface tension is anisotropic. When anisotropy is small, the variation of σ^* with impurity concentration is found, in agreement with results given by the heuristic model of Lipton *et al.* [Metal. Trans. A **18**, 341 (1987)].

I. INTRODUCTION

Much progress has been made recently in the understanding of dendritic growth rates in undercooled sample of pure fluids. The growth is limited by the diffusion of latent heat released at the interface. The crystal appears as a moving boundary for the temperature field on which thermodynamic relations are applied. The corresponding free boundary problem admits a discrete family of solutions of needle crystals of stationary shape, moving with constant velocity when the surface tension is anisotropic (Meiron,[1] Ben Amar and Pomeau,[2] Barbieri *et al.*,[3] and Ben Amar.[4]) Only the fastest one is linearly stable with respect to the tip-splitting modes (Kessler and Levine,[5] and Bensimon *et al.*[6]) When the undercooling $\Delta=(T_0-T_\infty)/(Q/c_p)$ is small, the velocity of a two-dimensional crystal is given by (Pelcé and Pomeau[7])

$$U\approx(16/\pi^2C)(D_T/d_0)\Delta^4\ . \tag{1}$$

Here, T_∞ is the temperature of the undercooled liquid; T_0, the crystallization temperature of the pure liquid; c_p, the specific heat; and Q, the latent heat released per unit volume of solid. $d_0=\gamma_0c_pT_0/Q^2$ is the capillary length where γ_0 is the mean value of the surface tension. The constant C is an eigenvalue of a nonlinear integrodifferential equation, which is a function of the anisotropy factor β. (β appears in the relation: effective surface tension ($\sigma=\gamma+\gamma''$) versus the growth direction as $\sigma=\sigma_0[1-\beta\cos(4\theta)]$.)

In the case of dendritic growth from an impure liquid (an alloy) one must take into account, in addition, the diffusion of impurities (of solute) partially rejected by the moving interface. This implies the introduction of a new control parameter, the concentration c_∞ of impurities in the liquid, far from the crystal. Measurements of the variation of the crystal velocity when an impurity is added have been performed (Chopra[8]). It appears that, at fixed undercooling with respect to the liquidus temperature, the velocity of the crystal increases when c_∞ increases, reaches a maximum for some finite value of c_∞, and then decreases for a large value of the concentration. Phenomenological models have been proposed (Karma and Langer,[9] Karma and Kotliar,[10] and Lipton *et al.*[11]) which explain qualitatively this behavior. We propose here a more rigorous treatment of the question, by using the same models as in Refs. 9–11, in order to obtain quantitative agreement between theory and experimental data.

In a first part, one introduces the two-dimensional free boundary problem defined by the equations of diffusion of heat and concentration of impurities, with thermodynamic boundary conditions applied at the interface and write, in a second part, the corresponding integral equations. When surface tension effects are neglected, this free boundary problem admits a one-parameter family of Ivantsov parabolas that we determine in a third part. Then, we introduce the effects of surface tension in the problem.

We study the experimentally relevant limit of small thermal and solutal Peclet numbers. In this regime, the solution of the problem appears very close to the case of growth in a pure melt. One derives first an integrodifferential equation for the shape of the crystal in which the velocity appears as an eigenvalue, which has solutions only when surface tension is anisotropic. This equation is studied both analytically, in the Wentzel-Kramers-Brillouin approximation, and numerically. Results are compared with the one obtained by the solvability condition. As shown by Pelcé and Bensimon[12] (see Pelcé[13] also), this condition can be written as the vanishing of an integral in which only the Ivantsov solution and the marginal mode of the dispersion relation for perturbations for the planar interface enter. Then all these theoretical results are compared to experimental data.

II. THE MODEL OF GROWTH

The liquid-solid interface is a region which is in general very small compared to the macroscopic scale (some angstroms). During crystal growth, it is here that the latent heat is released and that the density of the material and the concentration of an impurity vary rapidly. In order to study the dynamics of growth, one can consider the interface as a discontinuity for the fields of temperature and concentration of impurities on which boundary conditions are applied.

A. The interface

The interface is assumed to be rough so that the kinetic time of transfer of molecules between solid and liquid is very fast compared to the characteristic diffusion time of heat or of an impurity. Thus one can consider the limiting case where the conditions of growth are out of equilibrium because of the presence of temperature or concentration gradient in the medium, the interface being itself at equilibrium. In these conditions, a thermodynamic relation, the Gibbs-Thomson relation, gives the temperature at the interface, as a function of the local curvature $1/R$ of the front and of the local concentration of impurity. For simplicity, one considers here a two-dimensional model so that the temperature T at the interface is

$$T = T_0 - mc - \frac{T_0}{Q}\frac{\sigma}{R} \ . \tag{2}$$

Here c is the concentration of impurity in the liquid; m, the absolute value of the slope of the liquidus line in the binary phase diagram; σ, the effective anisotropic liquid-solid surface tension; and $1/R$, the curvature of the interface.

B. Diffusion fields

The temperature satisfies the diffusion equation in both liquid and solid:

$$\partial T/\partial t = D_T \Delta T \ , \tag{3}$$

and the concentration of impurity satisfies

$$\partial c/\partial t = D_c \Delta c \tag{4}$$

in the liqud only. At the interface, the conservation of heat and impurities must be satisfied, i.e.,

$$Q\mathbf{v}\cdot\mathbf{n} = D_T c_p (\nabla T_s - \nabla T_l)\cdot\mathbf{n} \tag{5}$$

and

$$c(1-K)\mathbf{v}\cdot\mathbf{n} = -D_c \nabla c \cdot \mathbf{n} \ . \tag{6}$$

Here, $\mathbf{v}\cdot\mathbf{n}$ is the normal velocity of the interface and K the partition coefficient for impurities. D_T and D_c are, respectively, the diffusive coefficients for temperature and concentration, and one has usually $D_c \ll D_T$ (10^{-2} on the order of magnitude). Far at infinity ahead of the crystal, temperature and concentration are uniform and, respectively, equal to T_∞ and c_∞.

III. INTEGRAL EQUATIONS

One first determines the relation between temperature (concentration) and released heat flux (concentration flux) at the stationary interface, moving with constant velocity U. In the case of temperature field, the diffusive coefficients for the temperature can be assumed equal in the liquid and solid phase (symmetic model). Thus the relation between temperature and heat flux at the interface of equation $z = \zeta(x)$ can be written as (see, for instance, Langer and Turski[14])

$$T - T_\infty = D_T \int_{-\infty}^{+\infty} dl' G_T(x,\zeta|x',\zeta')(\nabla' T_s - \nabla' T_l)\cdot\mathbf{n} \ . \tag{7}$$

Here l is the curvilinear coordinate and G_T is the Green function of the diffusion field with coefficient of diffusion D_T, in a frame moving with a constant velocity U. It, satisfies the equation

$$U(\partial/\partial z')G_T(p,p') - D_T \Delta' G_T(p,p') = \delta(p-p') \ , \tag{8}$$

whose solution can be written as

$$G_T(p,p') = (2\pi D_T)^{-1}\exp - [(U/2D_T)(z-z')] \times K_0(U/2D_T|\mathbf{r}-\mathbf{r}'|) \ . \tag{9}$$

Here p is the point of coordinates (x,z), $|\mathbf{r}-\mathbf{r}'| = [(x-x')^2+(z-z')^2]^{1/2}$, and K_0 is the modified Bessel function of zeroth order.

In the case of the concentration field, the coefficient of diffusion is negligible in the solid phase and can be taken as zero (one-sided model). Thus the relation concentration and concentration flux at the interface (see, for instance, Caroli *et al.*,[15]

$$\begin{aligned}\frac{(c-c_\infty)}{2} = & -D_c \int_{-\infty}^{+\infty} dl' G_c(x,\zeta|x',\zeta')\nabla' c\cdot\mathbf{n} \\ & - U\int_{-\infty}^{+\infty} dx'(c-c_\infty)G_c(x,\zeta|x',\zeta') \\ & + D_c \int_{-\infty}^{+\infty} dl'(c-c_\infty)\nabla' G_c(x,\zeta|x',\zeta')\cdot\mathbf{n} \ .\end{aligned} \tag{10}$$

Here, G_c is the same Green function as before [see Eq. (9)] but with a coefficient of diffusion equal to D_c. In the particular case where c is constant on the interface, Eq. (10) can be simplified by using an integral relation that satisfies the Green function G_c. When one integrates Eq. (8), one obtains the equation

$$\begin{aligned}\tfrac{1}{2} = & \ U\int_{-\infty}^{+\infty} dx' G_c(x,\zeta|x',\zeta') \\ & - D_c \int_{-\infty}^{+\infty} dl' \nabla' G_c(x,\zeta|x',\zeta')\cdot\mathbf{n} \ .\end{aligned} \tag{11}$$

Thus, if c is constant on the interface, by using (10) and (11), one gets the equation

$$c - c_\infty = -D_c \int_{-\infty}^{+\infty} dl' G_c(x,\zeta|x',\zeta')\nabla' c\cdot\mathbf{n} \ , \tag{12}$$

which is similar to Eq. (7). This property comes from the fact that, when c is constant on the interface, it is uniform in the whole solid, and thus the fact that the concentration diffuses or not in the solid has no importance.

By using Eqs. (5) and (6) giving the different fluxes released at the interface, one can rewrite Eqs. (7) and (10) as

$$T - T_\infty = \frac{UQ}{c_p}\int_{-\infty}^{+\infty} dx' G_T(x,\zeta|x',\zeta') \tag{13}$$

and

$$\frac{(c-c_\infty)}{2}=U(1-K)\int_{-\infty}^{+\infty}dx'cG_c(x,\zeta|x',\zeta')-U\int_{-\infty}^{+\infty}dx'(c-c_\infty)G_c(x,\zeta|x',\zeta')+D_c\int_{-\infty}^{+\infty}dl'(c-c_\infty)\nabla'G_c(x,\zeta|x',\zeta')\cdot\mathbf{n}\ . \tag{14}$$

Thus the free boundary problem to solve is given by Eqs. (13) and (14) with the boundary condition (2) at the interface. Far at infinity, ahead of the finger, $T=T_\infty$ and $c=c_\infty$.

IV. THE CASE WITHOUT SURFACE TENSION

In this case [$\sigma=0$ in Eq. (2)], $T-T_0$ is simply proportional to c at the interface. A family of exact solutions can be found when T and c are constant on the interface $T=T_i$, $c=c_i$. It corresponds to the family of the Ivantsov-Horway-Cahn parabolas,[16,17] $\zeta(x)=-x^2/2\rho$, where associated thermal and solutal Peclet numbers, respectively, $P_T=\rho U/2D_t$ and $P_c=\rho U/2D_c$ satisfy the relations

$$\Delta_T=\frac{(T_i-T_\infty)c_p}{Q}=\left[\frac{4}{\sqrt{\pi}}\right]P_T\int_0^\infty dx\frac{\exp(-x^2/4)}{(x^2+4P_T)}\ , \tag{15}$$

$$\Delta_c=\frac{(c_i-c_\infty)}{c_i(1-K)}=\left[\frac{4}{\sqrt{\pi}}\right]P_c\int_0^\infty dx\frac{\exp(-x^2/4)}{(x^2+4P_c)}\ . \tag{16}$$

Thus, when c_∞ and T_∞ are given, one has three unknown T_i, c_i, and ρU, which are determined by Eqs. (15), (16), and (2). As is the case for the crystallization in a pure liquid, the velocity of the crystal is not determined at this level, thus leading to the existence of a one parameter family of homothetic parabolas. Usually, thermal undercooling Δ_T is small compared to unity so that Eq. (15) can be rewritten as

$$P_T\approx\Delta_T^2/\pi\ , \tag{17}$$

and thus the thermal Peclet number is small. Similarly, in the case of the solute, one has

$$P_c\approx\Delta_c^2/\pi\ . \tag{18}$$

By using Eq. (2), (17), and (18), one deduces

$$P_T=(\Delta_{\text{eff}}^2/\pi)[1+mc_\infty(1-K)c_p/Q(D_T/D_c)^{1/2}]^2\ . \tag{19}$$

Here Δ_{eff} is the effective supercooling with respect to the liquid temperature:

$$\Delta_{\text{eff}}=(T_0-mc_\infty-T_\infty)c_p/Q\ . \tag{20}$$

As the ratio D_T/D_c is large, but $mc_\infty c_p/Q$ small, the factor $mc_\infty c_p/Q(D_T/D_c)^{1/2}$ is not larger than unity and P_T is of order Δ_{eff}^2. As $P_c=(D_T/D_c)P_T$, the condition for small solutal Peclet numbers is that

$$0<\Delta_{\text{eff}}\ll(D_c/D_T)^{1/2}\ . \tag{21}$$

Let us discuss here the axisymmetric case before going further. In the small-Peclet-number limit Eqs. (17) and (18) become

$$P_T\approx[-\Delta_T/2\ln(\Delta_T)]\ , \tag{22}$$

$$P_c\approx[-\Delta_c/2\ln(\Delta_c)]\ , \tag{23}$$

so that Eq. (19) becomes

$$P_T\approx\Delta_{\text{eff}}/2\{\ln(\Delta_{\text{eff}})[1+mc_\infty(Q/c_p)^{-1}\times(1-K)(D_T/D_c)]\}\ . \tag{24}$$

From this it follows that P_c is small if

$$0<\Delta_{\text{eff}}\ll D_c/D_T\ . \tag{25}$$

V. EFFECT OF SURFACE TENSION

When effects of surface tension are introduced, temperature and concentration of impurity are no longer constant on the interface and a parabolic shape is no longer a solution of the free boundary problem. One must come back to the integral equations (13) and (14) and to Eq. (2).

A. The eigenvalue equation

The procedure is similar to the one developed by Pelcé and Pomeau.[7] The radius of the crystal is small compared to the corresponding diffusive length and one can solve the integral equations with a matched asymptotic expansion procedure. Far from the tip, the curvature effects due to surface tension are negligible and the shape of the crystal is an Ivantsov parabola of tip radius ρ, growing with the same velocity as the considered needle crystal. In this region, the temperature T_i and the concentration c_i are constant and determined by Eqs. (15) and (2), in which the surface tension effects have been neglected. Close to the tip, the integral equations (13) and (14) can be simplified as follows: first one substracts from (13) and (14) the equivalent relation obtained with the Ivantsov solution. If one writes $T=T_i+\delta T$ and $c=c_i+\delta c$, one has

$$\delta T=\frac{UQ}{c_p}\int_{-\infty}^{+\infty}dx'[G_T(x,\zeta|x',\zeta')-G_T(x,\zeta_{iv}|x',\zeta'_{iv})]\ , \tag{26}$$

$$\frac{\delta c}{2}=U(1-K)\int_{-\infty}^{+\infty}dx'[(c_i+\delta c)G_c(x,\zeta|x',\zeta')-c_iG_c(x,\zeta_{iv}|x',\zeta'_{iv})]-U\int_{-\infty}^{+\infty}dx'\delta cG_c(x,\zeta|x',\zeta')+D_c\int_{-\infty}^{+\infty}dl'\delta c\nabla'G_c(x,\zeta|x',\zeta')\cdot\mathbf{n}\ . \tag{27}$$

The integrals are noticeably different from zero only around the tip so that lengths can be scaled by 2ρ and the Green functions can be expanded for small values of the argument. One uses Eq. (9) for small values of the argument and obtains

$$G(x,\zeta|x',\zeta')\approx -(1/2\pi D)\ln(U/2D|\mathbf{r}-\mathbf{r}'|)\ , \tag{28}$$

so that Eqs. (26) and (27) can be rewritten at dominant order

$$\delta T=-\frac{1}{\pi}\frac{\rho U}{D_T}\frac{Q}{c_p}\int_{-\infty}^{+\infty}dx'\ln\left[\frac{|\mathbf{r}-\mathbf{r}'|}{|\mathbf{r}_{\rm iv}-\mathbf{r}'_{\rm iv}|}\right]\ , \tag{29}$$

where $\zeta_{iv}(x)=-x^2$ and

$$\frac{\delta c}{2}=-\frac{1}{\pi}\frac{\rho U c_\infty(1-K)}{D_c}\int_{-\infty}^{+\infty}dx'\ln\left[\frac{|\mathbf{r}-\mathbf{r}'|}{|\mathbf{r}_{\rm iv}-r'_{\rm iv}|}\right]+\frac{1}{2\pi}\int_{-\infty}^{+\infty}dx'\delta c\frac{(\zeta-\zeta')-(x-x')(\partial\zeta/\partial x')}{(x-x')^2+(\zeta-\zeta')^2}\ . \tag{30}$$

By using Eqs. (2), (29), and (30), one finally obtains

$$(1-\beta\cos4\theta)\frac{\zeta_{xx}}{(1+\zeta_x^2)^{3/2}}=\frac{C}{2\pi}\left[1+\frac{2mc_\infty(1-K)c_p}{Q}\left[\frac{D_T}{D_c}\right]\right]\int_{-\infty}^{+\infty}dx'\ln\left[\frac{|\mathbf{r}-\mathbf{r}'|}{|\mathbf{r}_{\rm iv}-\mathbf{r}'_{\rm iv}|}\right]+\frac{1}{\pi}\int_{-\infty}^{+\infty}dx'\Psi(x,x')\left[\int_{-\infty}^{+\infty}dx''\frac{C}{2\pi}\ln\left[\frac{|\mathbf{r}''-\mathbf{r}'|}{|\mathbf{r}''_{\rm iv}-\mathbf{r}'_{\rm iv}|}\right]+(1-\beta\cos4\theta')\frac{\zeta_{x'x'}}{(1+\zeta_{x'}^2)^{3/2}}\right]\ , \tag{31}$$

where

$$\Psi(x,x')=[(\zeta-\zeta')-(x-x')\partial\zeta/\partial x']\times[(x-x')^2+(\zeta-\zeta')^2]^{-1}$$

and C, the eigenvalue $(4\rho^2U)/D_Td_0$. (C is related to σ^*, used in Ref. 11, but is not in general simply inversely proportional to it. Here C is defined with the tip radius of the parabola towards which the shape of the crystal is asymptotic far from the tip, and σ^* is defined with the tip radius R. In general, the shape of the tip is not a parabola and the tip radius R is different from ρ. When C is large, the shape of the tip is close to the parabola and C and σ^* become inversely proportional.)

B. The eigenvalue problem in the WKB limit

First, we propose a WKB analysis of Eq. (31), valid in the limit of large C values. We sum up the main steps of the demonstration since analogous treatments of nonlinear and nonlocal equations have been extensively explained by Ben Amar and Pomeau[2] and Ben Amar[4] for the symmetric model of solidification [which corresponds to $\Psi(x,x')=0$ in (31)] and extended to the one-sided model by Misbah[18] [which formally means that the first term in the integrand of the second integral in the right-hand side of Eq. (31) is equal to zero]. This method consists of solving Eq. (31) in the complex plane (variable z) and focuses on the calculation of the first derivative of ζ at the origin, since the solvability condition requires

$$d\zeta(C)/dx=0 \quad \text{at } x=0\ .$$

We choose an integration path in the complex plane coming from $-\infty$, on the negative real axis, passing across an internal region located at $i/2$, where ζ is singular, and going to zero along the imaginary axis. The first step of this analysis requires the asymptotic behavior of Φ, the deviation of ζ from the Ivantsov parabola

$$\Phi(z)=\zeta(z)+z^2\ .$$

We expect Φ to decrease more quickly than $\zeta_{iv}(x)=-x^2$ as x goes to $-\infty$. As a consequence, Eq. (31) can be linearized around ζ_{iv} and one derives a slightly different inhomogeneous integral equation when compared to the symmetric model for which $\Psi=0$. If only the largest terms are taken into account, we obtain

$$-\frac{2}{(1+4x^2)^{3/2}}-\frac{2}{\pi}\int_{-\infty}^{+\infty}dt\frac{1}{[1+(x+t)^2](1+4t^2)^{3/2}}=\frac{C\Gamma}{2\pi}\int_{-\infty}^{+\infty}dt\frac{\Phi(x)-\Phi(t)}{x-t}\frac{x+t}{1+(x+t)^2}\ , \tag{32}$$

where $\Gamma=1+2mc_\infty(1-K)c_p(D_T/D_c)Q$. From Eq. (32), one can notice that $\Phi(x)$ is defined up to an arbitrary additive constant. One can choose a function $\Phi(x)$ decreasing faster than any constant at infinity. In that case, one expands Eq. (32) at large x and obtains, from the terms in $1/x^2$,

$$\int_{-\infty}^{+\infty}\Phi(x)dx=\frac{4}{C\Gamma}\ . \tag{33}$$

Anyway, this additional term does not modify the singular behavior of $\Phi(z)$ when

$$z=x+i/2-i\epsilon \quad \text{with } \epsilon>0\ ,$$

which is given by $(1/C\Gamma)(ix)^{3/2}$ and is crucial for the matching of Φ in the internal region. In this region, around $i/2$, we adopt a stretching transformation

$$\Phi(z)=C^{-\alpha}F(C^{\beta}u) \quad \text{with } z=i/2+u \quad \text{and } \alpha,\beta>0\ . \tag{34}$$

We assume that we can linearize the integral terms and only keep the nonlinearities of the local curvature term.

This hypothesis, already used in Refs. 2 and 4, must be checked once the scaling exponents α, β are calculated. Once linearized, the double integral in Eq. (31) simply reads

$$\frac{C}{2\pi}\int_{-\infty}^{+\infty} dt\, \Phi(t) \frac{4z^2t^2+3z^2-4zt-4t^4-7t^2+6}{[1+(z+t)^2][4+(z-t)^2](1+4t^2)} . \tag{35}$$

When the integration is performed on the real axis (variable t), one can notice that this term is never singular as z approaches $i/2$. Therefore, we do not need to take it into account in the internal region. The last integral involving the curvature term is already present in the one-sided model of solidification, so we conclude that we can reduce Eq. (31) in the internal region in the same way as for the one-sided model, with the same exponents ($\alpha=\frac{4}{11}$) and $\beta=\frac{2}{11}$). Finally, we can linearize completely Eq. (31) around ζ_{iv} on the imaginary axis and neglect the nonlocal term involving the curvature since it is not multiplied by C. We notice that the additional term (35) is purely real as $z=it$. Therefore, focusing on the imaginary part of Φ, we derive the same equation as in Ref. 18. Consequently, the solvability condition of Eq. (31) is exactly the same as for the symmetric model and is due to a turning point located on the imaginary axis and introduced by the anisotropic surface-tension effects. We conclude that Eq. (31) has an infinite discrete set of solutions, such that

$$C_n = \frac{C_n^s}{1+\dfrac{2mc_\infty(1-K)c_p}{Q}\dfrac{D_T}{D_c}} , \tag{36}$$

C_n^s being the eigenvalue set of the symmetric model of solidification. One can reasonably expect that, as is the case for the growth in a pure melt, only the first eigenvalue ($n=1$) is relevant in experimental situations.

In order to make a more quantitative comparison with the experiments (more precisely, Fig. 3 of the work by Lipton *et al.*,[11] let us introduce the dimensionless quantity

$$\sigma^*(c_\infty)=\frac{D_T d_0}{R^2U} , \tag{37}$$

where R is the tip of radius. Lipton *et al.*[11] found that

$$\frac{\sigma^*(c_\infty)}{\sigma_0}=1+2m\frac{c_\infty(1-K)c_p}{Q}\frac{D_T}{D_c} , \tag{38}$$

i.e., a formula identical to (36) if one identifies R and ρ. As can be seen from the eigenvalue equation (31), this is true only if C is large, i.e., when the WKB approximation applies. When C is large, the integral of the logarithm must be very small in order that the other terms balance and thus $\mathbf{r}$ is very close to $\mathbf{r}_{\text{iv}}$. As can be deduced from the relation (36) this occurs when C^S is large since the denominator is of order unity, or when the anisotropy is small.[2,3] This is the case of the succinonitrile-acetone mixture which is used for experiments in Ref. 11.

C. Solvability condition method

1. Stability analysis of a planar interface moving with constant velocity

Consider first the motion of a planar interface moving at constant velocity V in the z direction. The stationary profiles of temperature and concentration of impurity are, respectively,

$$\bar{T}_l=T_\infty+\frac{Q}{c_p}\exp\left[-z\frac{V}{D_T}\right],\quad \bar{T}_s=T_\infty+\frac{Q}{c_p} , \tag{39}$$

$$c=c_\infty+c_i(1-K)\exp\left[-z\frac{V}{D_c}\right] . \tag{40}$$

Consider now a small deformation of the interface $\zeta(x)=A\exp(\omega t+ikx)$. The corresponding perturbations for the temperature and concentration fields are, respectively,

$$\begin{aligned} T_1' &= B\exp(\omega t+qz+ikx) , \\ T_s' &= C\exp(\omega t+q'z+ikx) , \\ c' &= D\exp(\omega t+q''z+ikx) . \end{aligned} \tag{41}$$

Here, q and q' are the roots with, respectively, negative and positive real parts of

$$\omega-Vq=D_T(q^2-k^2) \tag{42}$$

and q'' the root of Eq. (4.2) with negative real part, where D_T is changed by D_c. Then, by using Eqs. (2), (5), and (6), one finally obtains

$$\begin{aligned} C=B-\frac{V}{D_T}\frac{Q}{c_p}A=-m&\left[D-\frac{V}{D_c}c_i(1-K)A\right] \\ &-\sigma_0\frac{T_0}{Q}(1-\beta)Ak^2 , \end{aligned} \tag{43}$$

$$Q\omega A=D_Tc_p\left[q'C-qB\left[\frac{V}{D_T}\right]^2\frac{Q}{c_p}A\right] , \tag{44}$$

and

$$\begin{aligned} c_i(1-K)\omega A=&-D[V(1-K)+q''D_c] \\ &-c_i(1-K)\frac{V^2}{D_c}A , \end{aligned} \tag{45}$$

from which one deduces the two coupled relations (the coupling parameter is $h=D/A$)

$$\begin{aligned} \omega=&-Vq+V(q'-q)\frac{mc_p}{Q}c_i(1-K)\frac{D_T}{D_c} \\ &-d_0(1-\beta)D_Tk^2(q-q') \\ &-\frac{V^2}{D_T}+D_T\frac{mc_p}{Q}(q-q')h \end{aligned} \tag{46}$$

and

$$\omega = -h\left[\frac{V}{c_i} + \frac{D_c q''}{c_i(1-K)}\right] - K\frac{V^2}{D_c}\ . \tag{47}$$

The dispersion relation $\omega(k)$ is obtained by eliminating the coupling parameter h between relations (46) and (47) and by writing q, q', and q'' as a function of k and ω [see Eq. (42)].

2. *The solvability condition*

As mentioned in Ref. 12, the solvability condition can be written as

$$\int_{-\infty}^{+\infty} dl\, G[X_0(l)]\exp\left[i\int_0^1 k_m(l')dl'\right] = 0\ . \tag{48}$$

Here, $X_0(l)$ is the Ivantsov parabola function of the curvilinear coordinate l; G, the curvature operator; and k_m, the local nonzero marginal mode of the conjugate dispersion relation, written in a frame moving with constant velocity U in the z direction (frame at rest with respect to the unperturbed solution).

Consider now a planar interface moving with constant velocity U in the z direction, but tilted at an angle θ. One considers first a frame with axis normal and tangent to the interface and whose origin moves normally to the interface at the velocity $V = U\cos\theta$. Because of the rotational symmetry of the system, a perturbation of wave number k grows with the growth rate $\omega(k)$ determined by Eqs. (46) and (47). If now the origin of the frame moves in the z direction with the constant velocity U, the growth rate of the same perturbation will be $\omega(k) + iU\sin\theta k$, due to the tangential velocity of the new frame $U\sin\theta$. Thus the marginal mode k_m which appears in relation (48) satisfies $\omega(k_m) = iU\sin\theta k_m$, since it is a zero of the conjugate of the dispersion relation written in the frame moving with constant velocity U in the z direction.

In the small-Peclet-number limit (thermal and solute), relevant wave numbers are large compared to the inverse of the diffusive lengths, and the quasistationary approximation applies. It follows from Eq. (42) that $q' \approx -q \approx -q''\{k\}$, where $\{k\} = k$ if $\mathrm{Re}k > 0$ and $-k$ if $\mathrm{Re}k < 0$. By eliminating h between relations (46) and (47) and by neglecting V/D compared to k, one finally obtains

$$-iU\sin\theta k_m\left[1 + \frac{2mc_p}{Q}c_i(1-K)\frac{D_T}{D_c}\right] + \{k_m\}\left[U\cos\theta\left[1 + \frac{2mc_p}{Q}c_i(1-K)\frac{D_T}{D_c}\right] - 2D_T d_0(1-\beta\cos4\theta)k_m^2\right] = 0\ . \tag{49}$$

It follows that

$$k_m = k_m^s\left[1 + \frac{2mc_p c_i(1-K)}{Q}\frac{D_T}{D_c}\right]^{1/2}, \tag{50}$$

where k_m^s is the marginal mode obtained in the symmetric model for growth in a pure melt. Thus computation of the integral (48) involves the same steps as the one described in the pure case.[3,12,13] As in the small solutal Peclet-number limit, $c_i \approx c_\infty$, the solvability condition leads to relation (36).

D. Numerical computation of the eigenvalues

Let us now come back to experiments.[11] The plot (σ^*/σ_0) versus c_∞ is clearly checked at small c_∞ values, but seems not to be valid as soon as Γ is of order 1.5. Our result, consistent with the heuristic models proposed by Lipton *et al.*[11] and Karma and Langer[10] cannot explain the abrupt rise of σ^* as $\Gamma \approx 4$, so we perform a numerical analysis of Eq. (31) in order to check the assumptions of the analytical treatment. The main lines of our code, for the symmetric model, have been published elsewhere;[19] we have added both integral terms in (31), using exactly the same method as in Ref. 19. In Table I, we give the numerical values obtained for $C\Gamma$ as c_∞ varies, for three different values of the anisotropy coefficients. First of all, we must mention a slightly different numerical eigenvalue between the symmetric (C^S) and one-sided (C^{OS}) model of solidification, although the previous WKB treatment predicts identical results for the two models. This discrepancy comes from a contribution of the nonlocal curvature term, neglected on the imaginary axis because it is not multiplied by C. The $C\Gamma$ values describe the narrow interval between $[C^S, C^{OS}]$, confirming the validity of our WKB treatment for large C values. As expected, our numerical results based on our model do not explain the experimental results. The latest seem to have been obtained at small thermal and solute Peclet numbers, which correspond to the main assumption of our analysis. We have no explanation of this behavior since we cannot invoke a different result in three dimensions, if we refer to Ref. 4.

When the eigenvalues are known, growth rates are obtained by using relation (19) and the definition of C. One obtains

TABLE I. Calculated eigenvalues $C\Gamma$ for different values of the anisotropy coefficient β.

	β			
a[a]	0.05	0.075	0.1	0.15
S[b]	1203.44	672.14	449.42	261.76
0.1	1204.31	672.98	450.23	262.49
1.0	1208.25	676.76	453.92	266.03
5.0	1211.81	680.19	457.22	269.22
10.0	1212.68	681.02	458.02	269.99
OS[c]	1213.72	682.04	459.02	270.95

[a] $a = 2mc_\infty(1-K)/(Q/c_p)D_T/D_C = 2C_0D_T/D_c$. C_0 has been defined in Ref. 11; also, $a = \Gamma - 1$.

[b] Eigenvalue of the pure thermal model (symmetric model of solidification).

[c] Eigenvalue of the pure impurity model (one-sided model of solidification).

$$U=\frac{16}{C}\frac{D_T}{d_0}P_T^2 \ . \tag{51}$$

In the two-dimensional (2D) model, in the case of small thermal and solutal Peclet numbers, and in the case of small anisotropy in surface tension, relations (19) and (36), respectively, apply and one obtains

$$U=\frac{16}{\pi^2}\beta^{7/4}\frac{D_T}{d_0}\frac{\left[1+\dfrac{2mc_\infty(1-K)c_p}{Q}\dfrac{D_T}{D_c}\right]^2}{\left[1+\dfrac{mc_\infty(1-K)c_p}{Q}\left[\dfrac{D_T}{D_c}\right]^{1/2}\right]^4}\Delta_{\text{eff}}^4 \ , \tag{52}$$

so that the growth rate has a maximum for some finite value of the concentration of impurity, as observed in experiments.

VI. CONCLUSION

We studied the effect of the presence of impurities on dendritic growth rates in the limit of small thermal and solutal Peclet numbers.

As in the case of growth in a pure melt, steady solutions of needle crystals are found only if surface tension is anisotropic. The shape of the crystal is a parabola far from the tip and satisfies an eigenvalue equation close to the tip.

When surface anisotropy is small, the whole shape is close to a parabola and the corresponding eigenvalue C can be computed by using WKB approximation. The results obtained are in agreement with the previous work of Lipton *et al.*,[11] i.e., the ratio of the first eigenvalues $C^s/C(c_\infty)$, which in this case is the same as the ratio $\sigma^*(c_\infty)/\sigma_0$, is a linear increasing function of the concentration.

For anisotropy of order unity, the eigenvalues are computed numerically and behave similarly. In the frame work of this model, no abrupt rise of σ^* was found for some finite value of the concentration, as is the case in experiments.

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