Stability of the growth of needle dendrites

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(Submitted 30 April 1988)
Zh. Eksp. Teor. Fiz. **94**, 320–329 (December 1988)

We investigate analytically the stability of steady-state growth of two-dimensional needle dendrites in the limit of small anisotropy of the surface energy. We find a discrete spectrum of unstable modes which describe splitting at the tips of the dendrites. Out of the entire set of stationary solutions the only stable one is the one which corresponds to maximal growth velocity. The solutions with smaller growth velocity have unstable modes whose number grows as the velocity decreases. These analytical results are found to be in agreement with the results of numerical calculations.

INTRODUCTION

Needle dendrites, which grow from supercooled melts, constitute one of the simplest modes of crystal growth. The crystallization front of experimentally-observed dendrites is close to parabolic in shape; for this shape, the velocity of growth and the curvature of the dendrite tips are uniquely determined by the supercooling of the melt.[1,2] The fundamental process which controls the growth of these crystals is the transfer of the latent heat of the phase transition from the crystallization front into the supercooled melt via thermal conductivity. Analysis of this process shows that the stationary solutions of Stefan's problem for an isolated two-dimensional dendrite are given by a family of parabolas $y = -x^2/2\rho$; the growth velocity is $v \propto 1/\rho$.[3] The value of ρ remains undetermined in this case by virtue of the absence of any parameter with the dimensions of length in the problem; the dimensionless parameter $p = v\rho/2D$ (i.e., the Péclet number; D is the coefficient of thermal conductivity) is determined by the dimensionless supercooling. This nonuniqueness of ρ is in contradiction with experiments, in which ρ and v are fully determined by the growth conditions. Furthermore, it follows from the solution of the dynamic problem[4] that the entire family of parabolic solutions is unstable. The question then arises: what are the additional factors which select out the unique stable solution? As a result of previous work, it has become generally acceptable to assume that one of these factors is anisotropy of the surface energy at the interphase boundary. Based on numerical[5–8] and analytical[9–12] calculations, the following assertions have been made:

1. When anisotropy of the surface energy is taken into account, it is not possible to obtain a stationary solution to Stefan's problem in the form of a needle dendrite.

2. In the presence of an anisotropic surface energy, a discrete set of stationary solutions can be selected from the continuous-spectrum solutions. The velocity spectrum has a point of accumulation at zero and is bounded by a certain maximum velocity.

3. The crystal grows in the direction of maximum surface energy.[12]

4. According to numerical analysis of the dynamic problem,[6] only the solution with maximum growth velocity is stable. The other solutions are unstable against splitting of the tip of the parabola; as the growth velocity decreases, each member of the sequence (spectrum) of discrete stationary solutions has associated with it one unstable mode more than the previous member.

In this article, we investigate the growth dynamics of needle dendrites in the limit of small surface energy anisotropy, and find the spectrum of unstable modes which describe the splitting of the dendrite tip. Just as in the case of numerical calculations, we find that only the solution with maximum growth velocity is stable, and that the solutions with smaller velocities have unstable modes associated with them whose number grows as the velocity decreases. In this way, we have succeeded in clarifying the analytical structure of the problem; in particular, we find that the surface energy anisotropy, which emerges in the role of a singular perturbation, leads to the selection of a unique stable solution.

The surface energy stabilizes the tip of the dendrite, i.e., the region with maximum curvature. As we depart from the tip, the crystallization front becomes more planar and the stabilizing action of the surface energy decreases. In this case another type of instability emerges, which is connected with the appearance of secondary bulk branches. The character of this instability can be understood by studying the evolution of a wave packet. It is found that in the course of time such a packet is carried away from the dendrite tip along the crystallization front; as it moves, it spreads and grows in amplitude.

2. THE DYNAMICAL GROWTH EQUATION

The temperature distribution $T(x,y)$ in a supercooled melt containing a growing crystal is described by the equation of thermal conduction:

$$\partial T/\partial t = D\Delta T. \tag{1}$$

At the crystallization front $y = y(x,t)$ heat is released, and the boundary condition has the form

$$c_p D[\mathbf{n}\nabla T_l - \mathbf{n}\nabla T_c] = -Lv_n, \tag{2}$$

where c_p and D are the heat capacity and coefficient of thermal conductivity, which are the same in both phases, $\mathbf{n}$ is a unit vector normal to the interphase boundary, L is the latent heat of fusion, and v_n is the velocity of the front along the normal; the subscripts l and c refer to the melt and the crystal, respectively. When we neglect kinetic effects at the crystallization front, the equilibrium boundary condition has the form

 0038-5646/88/122574-06$04.00

$$T[x, y(x)] = T_m + (T_m \gamma_E(\theta)/L)\varkappa(x, t), \qquad (3)$$

where T_m is the melting temperature, $\varkappa$ is the front curvature,

$$\varkappa(x,t) = -\frac{\partial^2 y(x,t)}{\partial x^2}\left\{1+\left[\frac{\partial y(x,t)}{\partial x}\right]^2\right\}^{-3/2}.$$

The function γ_E depends on the angle θ between the normal to the surface and the y-axis, and is related to the anisotropy of the surface energy $\gamma(\theta)$ through

$$\gamma_E(\theta) = \gamma(\theta) + d^2\gamma(\theta)/d\theta^2.$$

From the condition of thermodynamic stability it follows that $\gamma_E > 0$. Far from the front, the melt is supercooled and has a temperature $T_0 < T_m$.

According to the boundary condition (2), the latent heat of the phase transition is released at the crystallization front $y(x,t)$, i.e., the front is a line along which heat is released at concentrated (point) sources. As this front moves, the thermal field can be found by using the Green's function of the equation of thermal conduction (1). It then follows that the temperature distribution at the crystallization front, i.e., the left side of Eq. (3), will be determined solely by $y(x,t)$, i.e., the same function that describes the front. Hence, Eqs. (1)–(3) allow us to obtain a single integro-differential equation which describes the dynamics of the crystallization front:

$$\Delta + \frac{d_0(\theta)\varkappa(x,t)}{\rho} = \frac{p}{2\pi}\int_0^\infty \frac{d\tau}{\tau}\int_{-\infty}^\infty dx' \frac{\partial y(x,t-\tau)}{\partial t}\exp\left\{-\frac{p}{2\tau}\left[(x-x')^2 - [y(x,t)-y(x',t-\tau)]^2\right]\right\}. \qquad (4)$$

It is our intent in what follows to investigate the crystallization front dynamics close to a parabolic dendrite undergoing steady-state growth with parabolic parameter ρ; therefore, in Eq. (4) we use the following dimensionless parameters: all lengths are measured in units of ρ, time in units of ρ/v, $p = v\rho/2D$ is the Péclet number, and $\Delta = (T_m - T_0)c_pL^{-1}$ is the dimensionless supercooling. The capillary length $d_0(\theta) = \gamma_E(\theta)T_m c_p L^{-2}$.

In the absence of surface energy ($d_0 = 0$), a solution to Eq. (4) was obtained by Ivantsov in the form of a parabola which moves with constant velocity[3]:

$$y = t - x^2/2,$$

while the Péclet number is determined by the equation

$$\Delta(p) = 2p^{1/2}e^p \int_{p^{1/2}}^\infty e^{-x^2}dx. \qquad (5)$$

In what follows we will be interested in the limit of small supercooling $\Delta \ll 1$, which implies a small Péclet number, i.e., $p \ll 1$. In this case we find from (5) that $p \approx \Delta^2/\pi$.

The presence of a finite surface energy significantly changes the problem, because it leads to the appearance in Eq. (4) of a term with a higher derivative. For small values of the dimensionless parameter

$$\sigma = d_0/p\rho \qquad (6)$$

the correction to the parabolic shape is also small, and can be found explicitly to first order in σ.[12,13] In addition to the regular corrections there are also singular ones which depend exponentially on the parameter $\sigma^{-1/2}$. In the general case the amplitude of these corrections grows as we recede from the tip of the dendrite, so that for an isotropic surface energy there are in general no bounded stationary solutions. An escape from this situation was found by introducing into the investigation a finite anisotropy in the surface energy, for which the simplest model expression is usually used:

$$d_0(\theta) = \bar{d}_0(1 - \alpha\cos 4\theta), \quad \operatorname{tg}\theta = \partial y/\partial x. \qquad (7)$$

When we introduce a new parameter—the anisotropy α—we find that the problem has a bounded solution for a discrete set of velocities v (or the parameter σ). In the limit $\alpha \ll 1$ the spectrum of σ is given by the expression

$$\sigma_n = \alpha^{7/4}/\lambda_n, \qquad (8)$$

where λ_n is a numerical factor which increases with the index n. Thus, solving the stationary problem with the surface energy anisotropy included reveals that a certain discrete spectrum of growth velocities is selected out from the initially continuous spectrum; however, there is no *a priori* reason to prefer any particular one of these velocity values. In order to finally solve the problem of selecting the unique possible growth velocity it is necessary to analyze fully the dynamic stability of these stationary solutions.

The purpose of this article is to investigate the local stability stationary solutions of Eq. (4). To do this we assume that the steady-state problem has been solved and that the spectrum of parameters σ is determined by Eq. (8). It is necessary to study the equation for small perturbations obtained from (4) by substituting into the latter the shape of the front in the form

$$y = t - x^2/2 + \zeta(x)\exp(\Omega\tau)$$

and linearizing with respect to ζ. The equation obtained in this way has a spectrum of eigenvalues Ω; stability corresponds to $\operatorname{Re}\Omega < 0$. Because σ is assumed small, we will neglect corrections to the stationary shape of the front which are linear in σ. As we did in studying the stationary problem, we will use the approximation of small Péclet numbers, i.e., $p \ll 1$. In addition, we will use a generalized quasistatic approximation, namely that the temperature field can adjust far more quickly than the crystallization front can change shape. If this is true, we can neglect the term $\partial T/\partial t$ in the equation for thermal conduction (4); in keeping with this approximation, we replace $\exp[\Omega(t-\tau)]$ by $\exp(\Omega t)$ in the right-hand side of Eq. (4), i.e., we assume that in practice the value $\Omega\tau \ll 1$. The adequateness of this approximation for analysis of dynamic problems of dendrite growth has been discussed before[14]; we will justify it below as applied to investigation of our problem after we find the spectrum and eigenfunctions $\zeta(x)$. In the framework of this approximation, we obtain from (4) the equation

$$\sigma\frac{d^2\zeta}{dx^2}-\frac{3\sigma x}{1+x^2}\frac{d\zeta}{dx}-\frac{(1+x^2)^{1/2}}{2\pi A(x)}\int\limits_{-\infty}^{\infty}\frac{dx'(x+x')[\zeta(x)-\zeta(x')]}{(x-x')[1+(x+x')^2/4]}$$

$$+\frac{(1+x^2)^{1/2}}{\pi A(x)}\Omega\int\limits_{-\infty}^{\infty}dx'\,\zeta(x')\ln\{|x-x'|[1+(x+x')^2/4]^{1/2}\}=0,$$

$$A(x)=1+8\alpha x^2/(1+x^2)^2. \qquad (9)$$

This equation contains two small parameters σ and α, which are related by Eq. (8). In analogy with the time-independent problem of finding the spectrum of growth velocities, our procedure for solving Eq. (9) consists of the following: in order to find the function $\zeta(x)$ for a given value of Ω, we can in lowest order set $\alpha=\sigma=0$. Then terms with derivatives drop out, and we obtain an integral equation which depends on the single parameter Ω. We obtain an explicit solution to this equation; it will turn out that for any positive value of Ω there exists a bounded function $\zeta(x)$. This fact implies that the solutions found by Ivantsov are unstable in the absence of surface energy. This result was obtained previously for a one-sided model in which the thermal conductivity of the crystal was neglected.[4] When the terms with derivatives, which are proportional to σ, are taken into account, the eigenfunctions $\zeta(x)$ are changed very little; however, the spectrum of admissible values of Ω is radically altered. This is connected with the fact that in addition to the regular (power-law in σ) corrections there exist singular corrections which depend exponentially on the parameter $\sigma^{-1/2}$. In the general case, for arbitrary values of Ω these corrections diverge at large distances; it is the specific condition that they be bounded which determines the spectrum of admissible values of Ω. If we analyze Eq. (9) only for real values of x, then finding the spectrum of Ω would require that we know its exact solution. In view of the absence of such a solution, we follow earlier work[12] and make use of an approximate approach which comes from the theory of quantum-mechanical reflection over a barrier, which allows us to analyze equations near a singular point in the complex x plane. Actually, it is clear from Eq. (9) that for small σ and α the effect of the derivatives becomes important only in a small region around the singular points $x=\pm i$. In this region Eq. (9) converts to a third-order differential equation. This differential equation and the integral equation obtained by neglecting the derivatives have a common region of applicability, and the condition that their solutions match in this region determines the spectrum of allowable values of Ω.

3. EIGENFUNCTIONS

For $\sigma\ll1$, by neglecting the derivatives in Eq. (9) we obtain the equation

$$\zeta(x)+\frac{1+x^2}{2\pi}\mathrm{P}\int\limits_{-\infty}^{\infty}\frac{(x+x')\zeta(x')dx'}{(x-x')[1+(x+x')^2/4]}$$

$$+\frac{1+x^2}{\pi}\Omega\int\limits_{-\infty}^{\infty}dx'\,\zeta(x')\ln\{|x-x'|[1+(x+x')^2/4]^{1/2}\}, \quad (10)$$

where P denotes an integral in the principal-value sense. After we go over to a Fourier representation

$$\zeta(x)=\int\limits_{-\infty}^{\infty}\zeta(k)\exp(-ikx)\,dk/2\pi$$

this equation becomes a differential equation:

$$\left[\Omega\left(\frac{d^2}{dk^2}-1\right)\frac{1}{|k|}+\mathrm{sign}(k)\frac{d}{dk}\right][\zeta(k)+\exp(-2|k|)\zeta(-k)]$$
$$+\zeta(k)-\exp(-2|k|)\zeta(-k)=0. \qquad (11)$$

Equation (11) has two solutions, one of which is even:

$$\zeta(k)=|k|\exp(-k^2/2\Omega+|k|),$$

and the other odd:

$$\zeta(k)=k\exp(-k^2/2\Omega+|k|).$$

These solutions are bounded only for $\Omega>0$, which confirms the instability of the parabolic solutions in the absence of surface energy. We present as an example the even function $\zeta(x)$ obtained by inverting the Fourier transform:

$$\zeta(x)=\Omega+\Omega(2\pi\Omega)^{1/2}/4$$
$$\times\{(1-ix)\exp[\Omega(1-ix)^2/2]\,\mathrm{erfc}[(\Omega/2)^{1/2}(1-ix)]$$
$$+(1+ix)\exp[\Omega(1+ix)^2/2]\,\mathrm{erfc}[-(\Omega/2)^{1/2}(1+ix)]\}. \qquad (12)$$

Near the tip of the parabola, i.e., for $|x|\ll1$, we obtain from (12)

$$\zeta(x)=2\Omega(2\pi\Omega)^{1/2}\exp(\Omega/2-\Omega x^2/2)\cos\Omega x. \qquad (13)$$

For $\Omega\gg1$ this function is localized at the tip of the parabola and has a number of oscillations of order Ω. This type of instability describes the splitting of the tip of the dendrite. A form analogous to (13) was obtained in Ref. 4 for the eigenfunction $\zeta(x)$ in the course of investigating the one-sided model.

Far from the tip we have for $|x|\gg1$ that

$$\zeta(x)=-1/x^2.$$

In what follows the behavior of the function $\zeta(x)$ in the complex plane will be important. The first term in the curly brackets of (12) is a function which is analytic in the lower half of the complex x-plane, while in the upper half-plane it grows as $\exp[\Omega\mathrm{Im}^2(x)]$; the second term, conversely, is analytic in the upper half-plane and grows in the lower half-plane.

4. DISCRETE SPECTRUM OF INCREMENTS Ω

In the previous section the function $\zeta(x)$ was found by neglecting the surface energy, i.e., terms which contain derivatives, in Eq. (9). For finite but still small σ and α, there arises the necessity of investigating the full equation (9) near the points $x=\pm i$. In this region the integro-differential equation reduces to a differential equation. In this case, as in the earlier Ref. 12, we cast the function $\zeta(x)$ in the form

$$\zeta(x)=\zeta_+(x)+\zeta_-(x),$$

where the functions $\zeta_+(x)$ and $\zeta_-(x)$ are analytic in the upper and lower halves of the complex x-plane:

$$\zeta_\pm(x)=\pm\frac{1}{2\pi i}\int\frac{\zeta(x')dx'}{x'-x\mp i0}.$$

In this representation the first of the integrals in (9) is calculated by the method of residues. The second integral in (9) is calculated analogously, if we first do an integration by parts and introduce the function

$$\varphi_\pm(x)=\int_{-\infty}^{x}\zeta_\pm(x')dx'.$$

In summary, from Eq. (9) we obtain a differential-differences equation for the functions $\varphi_\pm(x)$:

$$\begin{aligned}&\sigma A(x)[\varphi_+'''(x)+\varphi_-'''(x)]\\&\quad-3\sigma A(x)x(1+x^2)^{-1}[\varphi_+''(x)+\varphi_-''(x)]\\&\quad-i(1+x^2)^{1/2}\{[(x+i)\varphi_+'(x)+(x-i)\varphi_-'(-x-2i)]\\&\qquad-[(x+i)\varphi_+'(-x+2i)+(x-i)\varphi_-'(x)]\}\\&\quad+i\Omega(1+x^2)^{1/2}[\varphi_-(x)-\varphi_+(x)+\varphi_-(-x-2i)\\&\quad-\varphi_+(-x+2i)]=0.\end{aligned}\tag{14}$$

Let us investigate this equation near the point $x=i$, at which the coefficients of the equation are singular. As earlier in Ref. 12, the important x are those for which $|x-i|\sim\alpha^{1/2}\ll 1$. It is possible to simplify Eq. (14) in view of the fact that the scales of the functions $\varphi_+(x)$ and $\varphi_-(x)$ near the point $x=i$ are quite different. Actually, if we retain in the equation only terms which contain $\varphi_-(x)$, then in making the resulting equation dimensionless we find a characteristic scale $\Omega\sim\alpha^{-1/2}\gg 1$. The relative scale of the functions φ_+ and φ_- can be explicitly seen if we investigate expression (12), in which the first term in curly brackets corresponds to $\zeta_-(x)$, the second to $\zeta_+(x)$. At $x=i$ we have $\zeta_-\propto\exp(2\Omega)$ while ζ_+ reduces to zero linearly in $|x-i|$. In agreement with this, for $\Omega\gg 1$ the magnitude of $\varphi_-(i)$ is exponentially large in comparison to $\varphi_+(i)$, and also in comparison to $\varphi_-(-3i)\propto\varphi_+(3i)$. In this way, Eq. (14) becomes a differential equation for $\varphi(x)=\varphi_-(x)$. Making the substitution

$$x=i(1-\alpha^{1/2}z),\quad \Omega=\omega\alpha^{-1/2}$$

and assuming that the small parameters σ and α are connected by Eq. (8), which follows from the condition that the stationary problem is solvable, we obtain from Eq. (14) the equation

$$\frac{d^3\varphi}{dz^3}-\frac{3}{2z}\frac{d^2\varphi}{dz^2}-\frac{2^{1/4}\lambda_n z^{1/2}}{z^2-2}\left(\frac{d\varphi}{dz}+2\omega\varphi\right)=0.\tag{15}$$

For $|z|\gg 1$ this equation has the particular solution

$$\varphi(z)=\exp(-2\omega z),\tag{16}$$

which agrees with the solution to (12) in the region of their common applicability $\alpha^{1/2}\ll|x-i|\ll 1$. Hence, the complete solution of the problem will be found if we succeed in obtaining a solution to Eq. (15) with the asymptotic form (16). This condition selects out the discrete spectrum of ω. The situation here is completely analogous to finding the discrete spectrum λ_n for the solution to the stationary problem. The point is that the general solution to Eq. (15) for $|z|\gg 1$ grows as

$$\varphi\propto\exp[(4/7)2^{1/4}\lambda_n^{1/2}z^{7/4}],$$

if $\arg z=0$, and as

$$\varphi\propto\exp[-(4/7)2^{1/4}\lambda_n^{1/2}z^{7/4}],$$

if $\arg z=\pm 4\pi/7$. In order to suppress this growth along the three rays mentioned above and arrive at the asymptotic form (16), we must have available three free parameters. In keeping with the fact that (15) is a linear homogeneous third-order equation, it is possible to suppress growth along two of the above rays by using two constants of integration; then the condition on the third ray determines the spectrum. The eigenvalues ω are denoted by $\omega_j(n)$. the value of n indicates the number of the stationary solution, while the subscript j is the index number of the unstable mode for a given n. The number n determines the value of λ_n; therefore, $\omega_j(n)$ constitutes a set of numbers of order unity. The results of numerical solution of Eq. (15) for the conditions given above, together with the spectrum λ_n calculated earlier,[12] are listed in the table.

The important qualitative features of the spectrum so obtained consist of the following: the unique stable solution corresponds to the minimum value λ_0, i.e., the maximum of the possible growth velocities. The number of unstable modes which correspond to splitting of the dendrite tip equals the index number of the stationary solutions. These results are obtained in the limit of small surface energy anisotropy ($\alpha\ll 1$) by reducing the original integro-differenital equation (9) to the differential equation (15), which does not contain the parameters. The qualitative outlines of the spectrum found this way coincide with those of the spectrum obtained by direct numerical solution of the original problem.[6]

To conclude this section, we point out the conditions of applicability for the quasistatic approximation. The time derivative in the equation for heat conduction can be neglected for $p\Omega\ll k^2$, where k is a characteristic wave vector of the inhomogeneity. From Eq. (6) it is clear that $k\sim\Omega$. The growth rates Ω we have found are of order $\alpha^{-1/2}$. Hence, the quasistatic condition takes the form $p\alpha^{1/2}\ll 1$. Let us note that the spectrum (8) for σ_n in the stationary case was obtained using these very conditions.[12]

5. SPECTRUM OF GROWTH RATES ω FOR LARGE λ_n

In the table we present the spectrum $\omega_j(n)$ for the first four values of n. For large n ($\lambda_n\gg 1$) Eq. (15) can be investigated analytically. In this case we are able to solve the problem completely near the upper bound of the spectrum, when $\omega\sim\lambda_n^{1/2}$. In order to simplify Eq. (15) for $\omega\gg 1$, we rewrite it in the form

$$\left(\frac{d}{dz}+3\omega\right)^2\left(\frac{d}{dz}-6\omega\right)\varphi+[27\omega^2-f(z)]\left(\frac{d}{dz}+2\omega\right)\varphi-\frac{3}{2z}\frac{d^2\varphi}{dz^2}=0,\tag{17}$$

TABLE I. Table of values of λ_n and $\omega_j(n)$.

λ_n	n/j	1	2	3
0.48	0	–	–	–
5.8	1	0.92	–	–
17.2	2	1.22	1.88	–
34.6	3	1.45	2.25	2.8

where

$$f(z)=2^{1/2}\lambda_n z^{7/2}/(z^2-2).$$

If we assume that $d\varphi/dz\sim\omega\varphi$, then the first two terms are of order $\omega^3\varphi$, while the last is of order $\omega^2\varphi$, so that to first approximation the latter need not be included. Assuming now that in the region of interest for z the inequality $|27\omega^2-f(z)|\ll\omega^2$ is fulfilled, we obtain a solution for φ in the form

$$\varphi_{1,2}\propto\exp(-3\omega z),\quad \varphi_3\propto\exp(6\omega z).$$

The solution φ_3 must be rejected, since it flows along the ray $\arg z=0$. This allows us to lower the order of Eq. (17) if, after substituting

$$\varphi=\exp(-3\omega z)\psi(z)$$

we neglect terms in $d\psi/dz$ compared to $\omega\psi$. Omission of the term $d^3\psi/dz^3$ compared to $\omega d\psi/dz^2$ corresponds to omitting solutions of the type φ_3. In sum, we obtain from Eq. (17) the equation

$$d^2\psi/dz^2+[3\omega^2-(1/9)f(z)]\psi=0. \tag{18}$$

Equation (18) has the form of a Schroedinger equation; the function $\psi(z)$ is localized near the minimum of the function $f(z)$, i.e., near $z=z_0=(14/3)^{1/2}$. Expanding $f(z)$ near $z=z_0$ up to quadratic terms, we obtain the equation

$$d^2\psi/dz^2+3(\omega^2-\omega_{ext}^2)\psi-(27/16)\omega_{ext}^2(z-z_0)^2\psi=0, \tag{19}$$

where

$$\omega_{ext}^2=f(z_0)/27=7(7/6)^{3/4}\lambda_n/27.$$

Previously, the selection of ω was accomplished by invoking the boundary conditions on the rays $\arg z=0$, $\pm 4\pi/7$. In the case under discussion, this is equivalent to the condition that ψ decay along the rays $\arg(z-z_0)=\pm\pi/2$. In keeping with the harmonic-oscillator character of Eq. (19), we obtain the equidistant spectrum

$$\omega_j(n)=\omega_n(n)-3^{1/2}(n-j)/4, \tag{20}$$

where

$$\omega_n(n)=\frac{1}{3}\left(\frac{\pi}{2}\right)^{1/2}\left(\frac{3}{7}\right)^{15/8}\frac{\Gamma(7/8)}{\Gamma(3/8)}\left(n+\frac{4}{11}\right)$$
$$-\frac{3^{1/2}}{8}\left[1+\left(\frac{2}{7}\right)^{1/2}\right]$$

is the maximum value of the growth rate for a given n. In the spectrum (2) we have included a shift in the limiting frequency $\omega_n(n)$ because of the last term in Eq. (19), and have substituted in the value of $\omega_{\rm ext}$; we have also used the asymptotic form of the expression for λ_n (see Ref. 12). We remark that Eq. (10) describes the distant region of the spectrum, because it was also obtained under the assumption that $\omega_{\rm ext}-\omega\ll\omega_{\rm ext}$, i.e., $n-j\ll n$.

Let us illustrate briefly the method of finding the spectrum $\omega_j(n)$ in regions where it is not equally spaced, i.e., for $n-j\sim n$. Investigating Eq. (17) by the WKB method, we replace d/dz by k and obtain a cubic for $k(z)$. For $\omega<\omega_{\rm ext}$, the function $k(z)$ has two complex-conjugate branch points in the z-plane, i.e., two turning points. In the limit $n-j\ll n$ investigated previously, these were two oscillatory turning points located close to $z=z_0$:

$$z=z_0\pm i(4/3)2^{1/2}[(\omega_{ext}-\omega)/\omega_{ext}]^{1/2}.$$

The spectrum of ω is obtained from the quantization condition on the integral of the difference of the two roots of $k(z)$ between the turning points. We note that the contour of integration should not intersect the cut $(-\infty,\sqrt{2})$. For $j\gg 1$ and $n-j\ll n$, when we apply the oscillatory equation and the WKB approximation at the same time, both approaches give the spectrum (20).

6. INVESTIGATION OF STABILITY BASED ON THE LOCAL SPECTRUM $\Omega(k,x)$

Let us investigate a perturbation of the crystallization front $\zeta(x)$ with characteristic wave vector k_s tangent to the front which is much larger than the curvature of the unperturbed front. Then from Eq. (9) we can obtain the local spectrum $\Omega(k,x)$ by taking the Fourier transform in x and assuming the coefficients of the equation are constant:

$$\Omega(k,x)=|k_s|[(1+x^2)^{-1/2}-\sigma A(x)k_s^2$$
$$+3\sigma A(x)ik_sx(1+x^2)^{-3/2}]+ik_sx(1+x^2)^{-1/2}, \tag{21}$$

in which

$$k_s=k(1+x^2)^{-1/2},\quad A(x)=1+8\alpha x^2/(1+x^2)^2.$$

The first two terms in (21) describe the unstable Mullins-Sekerka spectrum for the original planar front, taking into account the surface energy. The third term includes the distortion of the originally parabolic front. The last term includes the tangential component of the velocity of the liquid relative to the unperturbed front in a system of coordinates moving with the dendrite tip.

In Ref. 15, a theory was developed for stability of inhomogeneous states based on the local spectrum. This approach makes use of a representation of the Green's function of the equation under study in the form of a functional integral

$$G(x,x',t)=\int\exp\left[\int_0^t\Omega(k,x)\,d\tau-i\int_{x'}^{x}k\,dx\right]D\{k(\tau)\}D\{x(\tau)\}, \tag{22}$$

where the integration is carried out over all paths $k(\tau)$, $x(\tau)$ subject to the condition $x(0)=x'$, $x(t)=x$. In the case of perturbations with short wavelengths, the functional integral can be computed by the method of steepest descent, and the behavior of the Green's function will be determined by the extremal paths, which satisfy Hamilton's equation:

$$\frac{dx}{d\tau}=-i\frac{\partial\Omega(k,x)}{\partial k},\quad \frac{dk}{d\tau}=i\frac{\partial\Omega(k,x)}{\partial x}. \tag{23}$$

These equations are useful for finding the discrete spectrum of the original equation and for studying the evolution of wave packets.

The discrete spectrum of the equation is determined by the asymptotic form of the Green's function $G(x,x',t)$ as $t\to\infty$. Therefore, we must investigate the paths which return to the original point after a long time.[15] The simplest of these paths is the fixed point k_0, x_0 determined by the equations

$$\partial\Omega(k,\ x)/\partial k=0,\quad \partial\Omega(k,\ x)/\partial x=0. \tag{24}$$

For small values of α, σ there are two fixed points lying close to $x = \pm i$. After investigating (24) near $x = i$, by substituting $x = i(1-\alpha^{1/2}z)$, $\Omega = \omega\alpha^{-1/2}$, $k = \tilde{k}\alpha^{-1/2}$ we obtain for $\lambda_n \gg 1$

$$z_0=(^{14}/_3)^{1/2},\quad \tilde{k}_0=3\omega_{ext},\quad \omega_{ext}^2=\omega^2(k_0,x_0)=7(^7/_6)^{3/4}\lambda_n/27,$$

which is found to be in full agreement with the results presented in the previous section. In order to find the points of the discrete spectrum which are close $\omega_{\rm ext}$, it is necessary to carry out an expansion in the exponent along paths which are close to the points k_0, x_0, which gives the usual Gaussian integral for the harmonic-oscillator Green's function. The eigenfrequency ν_0 of this oscillator can easily be found from the equation of motion (23) linearized in the vicinity of k_0, x_0:

$$\nu_0=3^{1/2}/4.$$

Using the asymptotic expression for the oscillator Green's function,[16] we obtain the equidistant spectrum (20). As before, this answer is valid for large values of λ_n and ω close to $\omega_{\rm ext}$.

In order to investigate the evolution of a wave packet, we must find that solution of Eq. (23) in the complex plane which proceeds from the real point x' to the real point x in a finite time. In this case, the amplitude of a packet $\zeta(x,t)$ will be proportional to the exponent in (22) calculated on this extremal path. Because of the drift term in the spectrum (21), the packet will be localized at large times near $x = (2t)^{1/2}$. As the packet drifts, its amplitude grows exponentially:

$$\zeta\propto\exp[(^2/_3)^{3/2}(2t)^{1/4}\sigma^{-1/2}],$$

and the packet itself spreads. The detailed development of this type of drifting instability, and its possible connection with the appearance of bulk branches of the dendrite, were studied previously by somewhat different methods.[14]

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Translated by Frank J. Crowne