Stability and instability in crystal growth: Symmetric solutions of the Stefan problem

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The stability is studied of the previously known solutions of the equations for the growth of a sphere, cylinder, or plate from the melt. These solutions are shown to be particular cases of a more general formulation, and to be stable against perturbations that retain the initial symmetry. The case of one-dimensional growth of a plate is shown to exhibit neutral stability only at the critical undercooling for which the latent heat of freezing is precisely equal to the amount required to raise the bulk material to the melting point. In conditions of large undercooling kinetic considerations determine the form of the asymptotically stable solutions.

I. INTRODUCTION

The problem of the stability of the growing surface of a crystal solidifying from the melt has been the subject of much recent study. Significant advances have been made in understanding such problems as dendritic growth and pattern formation,[1] and the effects of crystal anisotropy.[2] In an attempt to classify and understand the types of instability that may arise in a condensing system we have performed a number of analytical studies of the solutions of the thermodiffusion problem both in the presence and absence of hydrodynamic effects.

In the present paper we return to the case of symmetric growth of solids from the melt, and reconsider the formation of a sphere, cylinder, or plate. In the simplest thermodiffusion model, in which all hydrodynamic phenomena are ignored, we show that a single expression may be derived that is valid in all three geometries. This general solution is then shown to be stable against perturbations that do not break the symmetry of the initial solidifying shape. The previously formulated solutions[3–5] for these geometries are thus shown to be particular examples of a more general formulation, and, in appropriate coordinate systems, to be asymptotic solutions of a self-similar type. In the final sections of this paper, the problems associated with large undercooling are explored.

II. METHOD

We consider an infinite d-dimensional system in which a symmetrical solid is growing from a liquid initially at a temperature T_∞ that is less than the equilibrium freezing temperature T_M. For an isotropic crystal growing slowly from the melt the governing equations for the flow of heat may be approximated by those of the Stefan problem, namely

$$\partial T_i/\partial t = D_i \nabla^2 T_i, \quad i=1,2 \tag{1}$$

$$k_2 \frac{\partial T_2}{\partial r}\bigg|_{r=R(t)} - k_1 \frac{\partial T_1}{\partial r}\bigg|_{r=R(t)} = \rho\lambda \frac{dR(t)}{dt} . \tag{2}$$

Here T_1 and T_2 are the temperatures of the liquid and solid, respectively, t is the time, and k_i and D_i are the coefficients of thermal conductivity and diffusivity, respectively. The latent heat per unit mass is λ, and ρ is the density of the solid. In order to be able to neglect hydrodynamic phenomena we make the approximation that the liquid density is also equal to ρ. The quantity r measures the distance from the center of the crystal, and takes on the value $R(t)$ at the crystal surface: In three dimensions R is thus the radius of a spherical crystal, in two dimensions the radius of a cylinder, and in one dimension of half-thickness of a plate.

In the absence of appreciable surface tension, the boundary condition at the surface is

$$T_2(R) = T_1(R) = T_M , \tag{3}$$

while

$$\frac{\partial T_2}{\partial r}\bigg|_{r=0} = 0 \tag{4}$$

and

$$T_1(r=\infty) = T_\infty . \tag{5}$$

We now make a transformation to a spatial coordinate that depends on time. This allows us to write the solution to the thermodiffusion equations as functions that are independent of time in the new coordinates. That is, we define

$$\xi \equiv \frac{r}{R(t)}, \quad d\tau \equiv \frac{D_1}{[R(t)]^2} dt . \tag{6}$$

It is also convenient to discuss the dimensionless temperature differences

$$u_i \equiv \frac{C_{v,1}}{\lambda}(T_i - T_M) \tag{7}$$

and

$$\Delta \equiv \frac{C_{v,1}}{\lambda}(T_M - T_\infty) , \tag{8}$$

where $C_{v,i}$ $(i=1,2)$ is the specific heat, equal to $k_i\rho/D_i$, of a phase at constant volume. The velocity v of the freezing surface is related to the dimensionless quantity

$$\beta(t) \equiv \frac{1}{4D_1}\frac{d(R^2)}{dt}\,, \tag{9}$$

which is akin to the Péclet number of fluid dynamics. With these definitions Eq. (1) becomes

$$\frac{\partial u_i}{\partial \tau} - 2\beta\xi\frac{\partial u_i}{\partial \xi} = \frac{D_i}{D_1}\xi^{1-d}\frac{\partial}{\partial \xi}\left[\xi^{d-1}\frac{\partial u_i}{\partial \xi}\right]. \tag{10}$$

The surface condition, Eq. (2), is transformed into

$$\frac{k_2}{k_1}\frac{\partial u_2}{\partial \xi}\bigg|_{\xi=1} - \frac{\partial u_1}{\partial \xi}\bigg|_{\xi=1} = 2\beta(\tau) \tag{11}$$

and the boundary conditions are

$$u_2|_{\xi=1} = u_1|_{\xi=1} = 0\,, \tag{12}$$

$$\frac{\partial u_2}{\partial \xi}\bigg|_{\xi=0} = 0\,, \tag{13}$$

$$u_1|_{\xi=\infty} = -\Delta\,. \tag{14}$$

III. SOLUTIONS

The valuable property of the equations written in this form lies in the fact that a solution may be found that is independent of the transformed timelike variable τ. The temperature distribution in the solid may immediately by identified as the trivial solution of Eq. (10), namely

$$u_2(\xi) = 0\,, \tag{15}$$

as this satisfies the boundary condition at $\xi=0$. The temperature distribution in the liquid is then the τ-independent solution of Eq. (10) that satisfies the remaining boundary conditions. It is found to be

$$u_1(\xi) = -\Delta + \beta^{d/2}\Psi(\tfrac{1}{2}d, \tfrac{1}{2}d; \beta\xi^2)\exp[\beta(1-\xi^2)]\,. \tag{16}$$

Here Ψ is the confluent hypergeometric function[6] and β is the constant value of the variable defined in Eq. (9). This constant is given by the boundary conditions stated in Eq. (12), and thus satisfies the relation

$$\beta^{d/2}\Psi(\tfrac{1}{2}d, \tfrac{1}{2}d; \beta) = \Delta\,. \tag{17}$$

The solution of this relation for β as a function of Δ has been plotted by Horvay and Cahn.[7] In Fig. 4 of that reference, their Ω is equal to our β, and their U_f is proportional to our Δ. Equation (17) defines β for $0<\Delta<1$; as might be expected, β, which is related to the velocity of the interface, is a monotonically increasing function of the undercooling Δ in this range. For Δ close to unity $\beta \simeq d/2(1-\Delta)$. The behavior for small Δ depends qualitatively on the dimensionality, and is of the form $\beta \simeq \Delta^2/\pi$ for $d=1$, and $\beta \simeq \Delta/2$ for $d=3$. For $d=2$ we find β in this regime to be given as the solution of the equation $\Delta \simeq -\beta(\ln\beta + \gamma)$ with γ the Euler constant, 0.577. . . .

The constancy of β tells us, from its definition in Eq. (9), that the square of the distance, R, of the interface from the origin is increasing uniformly with time. We thus have

$$R = [4\beta D_1(t-t_0)]^{1/2} \tag{18}$$

and

$$v = [\beta D_1/(t-t_0)]^{1/2} \tag{19}$$

with t_0 a constant having the dimensions of time.

It is, incidentally, amusing to note that if we put the dimensionality parameter d equal to zero, then a solution exists only for $\Delta=1$, and β is undetermined in the expression

$$u_1(\xi) = -1 + \exp[\beta(1-\xi^2)]\,. \tag{20}$$

While there is no obvious physical significance to this expression, its similarity to the degenerate solution of the one-dimensional problem at critical undercooling studied in Sec. V is suggestive.

IV. STABILITY

For a given value Δ of the undercooling parameter, Eq. (16) provides the unique asymptotic form of the temperature distribution. To verify that this is a stable solution we study the time development of a small perturbation of the τ-independent solution. We write

$$u_1(\tau,\xi) = u_0(\xi) + u_p(\tau,\xi)\,, \tag{21}$$

$$\beta(\tau) = \beta_0 + \beta_1(\tau)\,. \tag{22}$$

(The solution u_2 is obviously stable and does not need to be considered.)

Substitution of (21) and (22) into (10) and (11) yields

$$\frac{\partial u_p}{\partial \tau} - 2\beta_0\xi\frac{\partial u_p}{\partial \xi} - 2\beta_1\frac{\partial u_0}{\partial \xi} = \xi^{1-d}\frac{\partial}{\partial \xi}\left[\xi^{d-1}\frac{\partial u_p}{\partial \xi}\right] \tag{23}$$

and

$$-\frac{\partial u_p}{\partial \xi}\bigg|_{\xi=1} = 2\beta_1(\tau) \tag{24}$$

with $u_p=0$ at $\xi=1$ and at $\xi=\infty$. It is convenient to use the Laplace transforms

$$\omega(p,\xi) = \int_0^\infty u_p(\tau,\xi)e^{-p\tau}d\tau\,, \tag{25}$$

$$A(p) = \int_0^\infty \beta_1(\tau)e^{-p\tau}d\tau\,, \tag{26}$$

and to define a new space coordinate

$$x = \beta_0\xi^2$$

and the functions

$$Z(x,p) \equiv x^{1/2-\mu}e^{x/2}\omega(p,\xi)\,, \tag{27}$$

$$F(x,p) \equiv x^{-1/2-\mu}e^{x/2} \times \left[A(p)\left[\frac{x}{\beta_0}\right]^{2\mu}\exp(\beta_0 - x) - \frac{u_p(0,\xi)}{4\beta_0}\right], \tag{28}$$

where

$$\mu = \tfrac{1}{2} - \frac{d}{4};\quad \kappa = -\frac{p}{4\beta_0} - \frac{d}{4}\,.$$

The function F contains the initial temperature distribution through the quantity $u_p(0,\xi)$. In terms of these, Eq. (23) becomes

$$\frac{\partial^2 Z}{\partial x^2}+\left[-\frac{1}{4}+\frac{\kappa}{x}+\frac{(\frac{1}{4}-\mu^2)}{x^2}\right]Z=F(x,p) . \quad (29)$$

This has a formal solution in terms of the Whittaker functions, $M(x)$ and $W(x)$, defined in Ref. 6. We find

$$Z(x)=c_1W(x)-gW(x)\int_x^{\infty}M(x)F(x)dx +gM(x)\int_x^{\infty}W(x)F(x)dx , \quad (30)$$

where

$$c_1=\left[-g\frac{M(x)}{W(x)}\int_x^{\infty}W(x)F(x)dx +g\int_x^{\infty}M(x)F(x)dx\right]\Bigg|_{x=\beta_0} \quad (31)$$

and

$$g=-\frac{\Gamma(a)}{\Gamma(c)} \quad (32)$$

with $a=1+p/4\beta_0$ and $c=2-d/2$.

The motion of the phase boundary is governed by the solution

$$A(p)=\frac{\beta_0^{-d/2}\exp(-\beta_0)\int_{\beta_0}^{\infty}u_p(0,\xi)\Psi(a,c,x)\,dx}{4\left[\int_{\beta_0}^{\infty}\exp(-x)x^{c-1}\Psi(a,c,x)dx-\exp(-\beta_0)\beta_0^{c-1}\Psi(a,c,\beta_0)\right]} \quad (33)$$

with Ψ again the confluent hypergeometric function. We see from this that $A(p)$ has singularities whenever the denominator vanishes in Eq. (33). Now it is shown in Ref. 6 that it is a property of Ψ that

$$\frac{d}{dx}[x^{c-1}\Psi(a,c,x)]=-(a-c+1)\Psi(a-c+2,3-c,x) \quad (34)$$

and the right-hand side of this equation is clearly negative[6] if $a-c+1>0$ because $\Psi(a,c,x)>0$ if $a>0$ and $c<3$. It follows that Ψ is a monotonically decreasing function whenever $a-c+1>0$, or, equivalently, whenever $p>-2\beta_0 d$. Thus, if that is the case,

$$\int_{\beta_0}^{\infty}e^{-x}x^{c-1}\Psi(a,c,x)\,dx<\beta_0^{c-1}\Psi(a,c,\beta_0)\int_{\beta_0}^{\infty}e^{-x}dx =e^{-\beta_0}\beta_0^{1-d/2}\Psi(a,c,\beta_0) . \quad (35)$$

The denominator in Eq. (33) can consequently never vanish when p is positive. This absence of poles implies from the definition of $A(p)$ in Eq. (26) that $\beta_1(\tau)$ must always decay exponentially with time. The same holds true for the temperature distribution $u_p(\tau,\xi)$. The decay rate of β_1 and u_p are determined by the smallest negative value of p at which a pole of $A(p)$ occurs.

In passing we can again note the unusual behavior of the problem when $d=0$. Then $c=2$ and when $p=0$ then $a=1$; the fact that $\Psi(1,2,x)=x^{-1}$ shows a pole to exist at $p=0$ and the degenerate solution to have neutral stability.

V. THE DEGENERATE SOLUTION

Having established the stability of the general solution for which $\Delta<1$, we now turn to the degenerate solution[1,3] in one dimension that occurs when $\Delta=1$. Then $u_2(\xi)$ is again zero, but in terms of newly defined variables

$$u_1(\xi)=-1+\exp(-2\beta_0\xi) \quad (36)$$

with β_0 now an arbitrary constant related to the velocity of the phase front by

$$\beta_0=\tfrac{1}{2}vR_0/D_1 .$$

We also have

$$R(t)=R_0+vt ,$$

$$\tau=D_1t/R_0^2 ,$$

$$\xi=(x-vt)/R_0 .$$

We now show the uncertainty in velocity to be intimately related to the initial temperature distribution.

We use the same definitions as in Eqs. (21) and (22) to define the perturbations in temperature and front velocity, and their respective Laplace transforms as in Eqs. (25) and (26). The differential equations governing the time development are then

$$\frac{\partial^2\omega}{\partial\xi^2}+2\beta_0\frac{\partial\omega}{\partial\xi}-p\omega=H(\xi,p)\exp(-\beta_0\xi) \quad (37)$$

and

$$-\frac{\partial\omega_1}{\partial\xi}\Bigg|_{\xi=0}=2A(p) , \quad (38)$$

where

$$H(\xi,p)=4\beta_0A(p)\exp(-\beta_0\xi)-u_p(0,\xi)\exp(\beta_0\xi) . \quad (39)$$

The solution for Eqs. (37) and (38) is

$$\omega(p,\xi)=\exp(-\beta_0\xi)\left[c_2Y(\xi)-[2(p+\beta_0^2)^{1/2}Y(\xi)]^{-1}\times\int_{\xi}^{\infty}Y(\zeta)H(\zeta,p)d\zeta+\tfrac{1}{2}(p+\beta_0^2)^{-1/2}Y(\xi)\int_{\xi}^{\infty}[Y(\zeta)]^{-1}H(\zeta,p)d\zeta\right] , \quad (40)$$

where

$$c_2=\tfrac{1}{2}(p+\beta_0^2)^{-1/2}\int_0^\infty H(p,\xi)[Y(\xi)-1/Y(\xi)]d\xi$$

and

$$Y(\xi)=\exp[-(p+\beta_0^2)^{1/2}\xi] .$$

We then also have

$$A(p)=-\frac{[(p+\beta_0^2)^{1/2}+\beta_0]^2}{2p}\times\int_0^\infty u_p(0,\xi)\exp\{-[(p+\beta_0^2)^{1/2}-\beta_0]\xi\}d\xi . \quad (41)$$

The determination of the asymptotic behavior of the temperature distribution at large times is a little more complicated than in the previous case because of the branch cut in the expressions for ω and A. We take the inverse Laplace transforms,

$$u_p(\tau,\xi)=(2\pi i)^{-1}\int_C\omega(\tau,\xi)e^{p\tau}dp$$

and

$$\beta_1(\tau)=(2\pi i)^{-1}\int_C A(p)e^{p\tau}dp$$

by integration along the contour PB_2B_1Q in Fig. 1 and adding the residue from the pole at $p=0$, rather than integrating directly along the straight line PQ. The contributions from the curved regions vanish, leaving only the residue at the origin and the terms involving lines B_2 and B_1. We find

$$u_p(\tau,\xi)=4\beta_0^2\xi\exp(-2\beta_0\xi)\int_0^\infty u_p(0,\xi)d\xi+(2\pi i\tau)^{-1}\exp(-\beta_0^2\tau)\int_0^\infty e^{-x}(\omega_+-\omega_-)dx$$

and

$$\beta_1(\tau)=-2\beta_0^2\int_0^\infty u_p(0,\xi)d\xi-(2\pi i\tau)^{-1}\times\exp(-\beta_0^2\tau)\int_0^\infty e^{-x}(A_+-A_-)dx ,$$

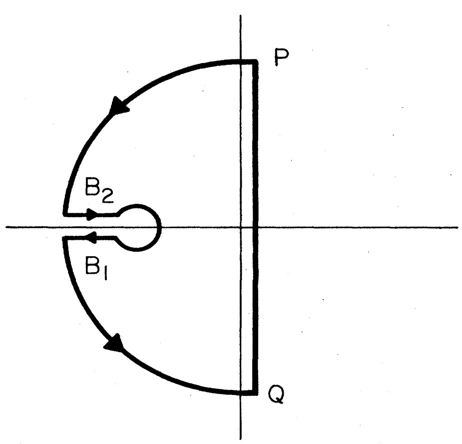

FIG. 1. Contour for integration of the inverse Laplace transform of u_p and β_1.

where $\omega_\pm(x)$ is defined as $\omega(p,\xi)$ evaluated at

$$p=-\beta_0^2+\tau^{-1}xe^{\pm\pi i} ,$$

and $A_\pm(x)$ is $A(p)$ evaluated similarly. In the limit of large times $\tau\gg\beta_0^{-2}$, and these contributions from the branch cut vanish. We are then left with the asymptotic result arising only from the residue at the origin, giving

$$\beta_1(\tau)\simeq-2\beta_0^2\int_0^\infty u_p(0,\xi)\,d\xi$$

and

$$u_p(\tau,\xi)\simeq4\beta_0^2\xi\exp(-2\beta_0\xi)\int_0^\infty u_p(0,\xi)d\xi=-2\beta_1\xi\exp(-2\beta_0\xi) .$$

The total temperature distribution in the liquid is then

$$u_1(\tau,\xi)\simeq-1+(1-2\beta_1\xi)\exp(-2\beta_0\xi) ,$$

which, because of the assumed smallness of $u_p(0,\xi)$ and hence of β_1, can be written as

$$u_1(\tau,\xi)\simeq-1+\exp[-2(\beta_0+\beta_1)\xi] .$$

The initial perturbation of u_1 is thus incorporated into the asymptotic solution, which now represents an alternative self-similar solution of the Stefan problem, but with β_0 replaced by $\beta_0+\beta_1$. In terms of the original coordinates

$$T_1(x,t)=T_M+\frac{\lambda}{C_v}(-1+e^{-v(x-vt)/D_1}) ,$$

where now the perturbed velocity v of the phase front is changed from its original value v_0 to be

$$v=v_0-(v_0^2R_0/D_1)\int_0^\infty u_p(0,\xi)d\xi .$$

In one dimension the moving phase front at critical undercooling thus represents a situation of neutral stability.

VI. EXTREME UNDERCOOLING

We have now explored the general symmetric solutions for the cases where the undercooling parameter Δ is less than unity, and for the special case where $\Delta=1$. What, we now ask, will be the behavior in the situation of extreme undercooling where $\Delta>1$?

The first point to note here is that the temperature of the phase boundary between liquid and solid will no longer be the equilibrium melting temperature T_M. Because there is not sufficient energy in the system for the bulk solid to be raised to T_M, the phase boundary will in general be at some lower temperature. This fact poses the difficulty that we lose one of the boundary conditions for the solution of the differential equations.

We illustrate this by considering the one-dimensional case shown in Fig. 2, in which a nucleating thermal reservoir at temperature $T_0<T_M$ is plunged into a supercooled liquid at temperature $T_\infty<T_M-\lambda/C_{v,1}$. Equations (10) and (11) continue to apply in the version in which $d=1$, but the boundary conditions are altered. If we redefine u_i as

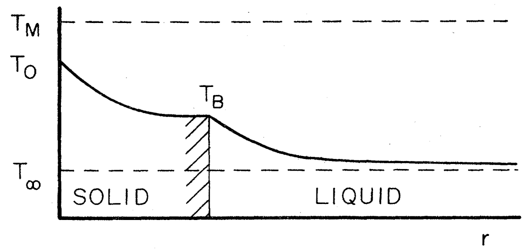

FIG. 2. This figure illustrates an example of large undercooling.

$$u_i \equiv \frac{C_{v,1}}{\lambda}(T_i - T_\infty)$$

and define

$$\Delta_1 \equiv \frac{C_{v,1}}{\lambda}(T_0 - T_\infty); \quad \Delta_2 \equiv \frac{C_{v,1}}{\lambda}(T_0 - T_b)$$

with T_b the temperature of the phase boundary then Eqs. (12), (13), and (14) are changed to

$$u_2 \mid_{\xi=1} = u_1 \mid_{\xi=1} = \Delta_1 - \Delta_2 ,$$

$$u_2 \mid_{\xi=0} = \Delta_1 ,$$

and

$$u_1 \mid_{\xi=\infty} = 0 .$$

The solutions are

$$u_1(\xi) = (\Delta_1 - \Delta_2)\frac{\exp(-\beta\xi^2)\Psi(\frac{1}{2},\frac{1}{2},\beta\xi^2)}{\exp(-\beta)\Psi(\frac{1}{2},\frac{1}{2},\beta)}$$

and

$$u_2(\xi) = \Delta_1 - \Delta_2 \left[\frac{\Gamma(\frac{1}{2}) - \exp(-\beta\xi^2/\alpha)\Psi(\frac{1}{2},\frac{1}{2},\beta\xi^2/\alpha)}{\Gamma(\frac{1}{2}) - \exp(-\beta/\alpha)\Psi(\frac{1}{2},\frac{1}{2},\beta/\alpha)} \right] ,$$

where $\alpha = D_2/D_1$, the ratio of thermal diffusivities in solid and liquid.

The difference between this solution and that obtained for modest undercooling lies in the fact that Δ_2 is an unknown quantity. With two second-order differential equations and only three boundary conditions, the quantities β and T_b remain undetermined. The resolution of this problem requires a reexamination of the microscopic freezing process.

The rate at which atoms or molecules from the liquid are entrapped at the solid surface and the rate at which molecules from the solid escape into the liquid are both functions of temperature, and are equal at T_M. At temperatures slightly below T_M the rate of deposition exceeds that of dissolution, and the phase boundary moves at a rate proportional to $T_M - T$. The analysis of the preceding sections is thus not entirely correct, as the motion of the phase boundary corresponding to a finite β must imply a temperature different from T_M. However, this effect may reasonably be assumed negligibly small when $\Delta < 1$, as in this case the speed of the interface is limited by thermal conduction.

When $\Delta > 1$, on the other hand, there is no such limitation, and we must expect the speed of the phase boundary to be determined by these kinetic considerations. We thus require a solution in which the velocity v of the phase front is constant, and does not decrease with time in the manner given by Eq. (19). This fact obliges us to turn to a variant of the degenerate solutions discussed in the preceding section, since they have the desired property. The requirement of the preceding section that Δ be equal to unity translates in the present context to the condition $\Delta_2 = 1$. The asymptotically stable solutions are then

$$u_2 = 1 \quad (x \gg D_1/v) ,$$

$$u_1 = \exp[-v(x - vt)/D_1] ,$$

with v determined by kinetic considerations arising from the condition

$$T_b = T_\infty + \lambda/C_{v,1} .$$

(For small x, the quantity u_2 must rise to Δ_1 to satisfy the boundary conditions.)

Because v is much larger in this case than when $\Delta < 1$, the temperature gradients are correspondingly severe, and we must also expect nonlocal effects to modify the equations for thermal conduction. These effects, however, lie outside the scope of the present paper.

VII. CONCLUSIONS

We have shown that it is possible to express symmetric solutions of the Stefan problem in the absence of hydrodynamic effects in terms of confluent hypergeometric functions. These solutions are stable against perturbations that retain the symmetry of the phase front. The particular case of a solidifying plate exhibits degenerate solutions for a certain critical undercooling, and these are of neutral stability.

At larger undercooling kinetic considerations determine the temperature of the interface, and the speed with which it moves. In succeeding papers in this series we shall explore the nature of the instabilities that arise when the restrictions to symmetric solutions and to the absence of hydrodynamic effects are lifted.

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