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A NONLINEAR STABILITY ANALYSIS OF THE FREEZING OF A DILUTE BINARY ALLOY

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CONTENTS

An investigation is made of the stability of the shape of a moving planar interface between the liquid and solid phases in the freezing of a dilute binary alloy. A nonlinear model is used to describe an experimental situation in which solidification is controlled so that the mean position of the interface moves with constant speed. The model postulates two-dimensional diffusion of solute and heat such that:

1. Convection in the liquid is negligible.
2. Diffusion of the solute in the solid is negligible.
3. Solute concentration in the liquid is small.
4. The effects of interface attachment kinetics are negligible.
5. The extent of the liquid and solid phases is infinite.
6. $C_S = C_L$ where $C_S(C_L)$ is the specific heat per unit volume of the solid (liquid).
7. $(D/D_{th}) \ll 1$, where D is the diffusion coefficient of the solute in the liquid and D_{th} is the thermal diffusivity in the liquid.
8. $G \approx G_C$ where G is the imposed temperature gradient in the liquid and G_C is the critical value of G at which linear theory predicts the onset of instability.

The analysis is expected to be asymptotically valid as $G \to G_C$. It is found that the interface can be unstable to finite amplitude disturbances even when linear stability theory predicts stability to infinitesimal disturbances. Further, cellular structure can be anticipated for certain ranges of parameter values. These results are in accord with relevant experimental evidence.

1. Introduction and formulation

The classical subject of linear stability theory analyses disturbances to an equilibrium state by neglecting all terms except those which are linear in the perturbations. The resulting class of eigenvalue problems has been under intensive study for many years. Physically, the main fruits of linear theory are the determination of critical conditions at which instability first occurs and the determination of the overall size of disturbances which are most likely to be the first to grow.

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If the spatial pattern of the growing disturbance is to be predicted, if the effect of large disturbances is to be estimated, or if the long-time behaviour of growing perturbations is to be ascertained, then nonlinear terms must be taken into account. The required nonlinear stability theory of phenomena governed by systems of partial differential equations has been the subject of increasingly vigorous investigation in the past two decades. Perhaps the bulk of research has been directed toward understanding certain prototype problems in hydrodynamics. This work has been surveyed by Segel (1966).

Investigators of problems in nonlinear hydrodynamic stability are aware of the fact that their results can be adapted so that they apply to a broad class of physical problems. A member of this class was identified at the conference at which Segel's survey was presented when Kirkaldy (1966) pointed out the similarity between patterns in Bénard convection and cellular patterns observed when an alloy is solidified in a temperature gradient. It is a stability analysis relevant to the latter problem which is the subject of this paper. We are able to carry the investigation far enough to show the unity which underlies the fluid mechanical and metallurgical problems and to illustrate the possible importance of nonlinear effects in solidification instabilities. Such instabilities are of considerable technological importance (Frank, Mullin & Peiser 1968).

Our analysis also provides a concrete discussion of nonlinear effects in a symmetry breaking instability occurring in a dissipative system. Turing (1952), Gmitro & Scriven (1966) and Prigogine & Nicolis (1967) have stressed the importance of such instabilities, particularly in chemical and biological contexts. The metallurgical instability investigated here, with convective terms omitted as relatively unimportant, serves as a good model for pattern-forming instabilities both because it is driven by a 'surface engine' and because diffusive transport is more important than convective transport. Consequently the study reported here may be of interest to some who have no direct concern with the metallurgical problem.

We begin (below) with a formulation of the problem which is a slight generalization of that used by earlier authors. The equilibrium solution (§ 2) describes the uniform advance of a planar interface of solid alloy into the molten metal. Using this solution, we discuss with some care in § 3 the selection of dimensionless variables which seems most appropriate to this complicated problem. (In the present formulation, the phenomenon depends on seven dimensionless parameters.) We proceed in § 4 to a linear stability investigation.

Up to this point we are largely repeating earlier work, although we do include some details which were not spelled out previously, such as a proof of the 'exchange of stabilities' which has heretofore been assumed. Our presentation takes advantage of experience developed by many workers in hydrodynamic stability to present the results in a form which seems more compact and more revealing than forms used heretofore by theoretical metallurgists. In any case, the linear analysis is a necessary preliminary to the nonlinear theory which is based upon it.

Section 5 deals with the adjoint problem whose solution is needed for the nonlinear analysis. Formulation of this problem is simple in principle but turns out to require some sophistication. Section 6 deals with the nonlinear analysis which shows that the amplitude of an initially sinusoidal perturbation is governed by a certain nonlinear ordinary differential equation, the amplitude equation. Those interested in details are referred to the general literature or to Wollkind (1968) where the analysis is presented more fully, but we have tried to outline enough of the calculation so that the general reader can have confidence in its results. We can thus turn in § 7 to a study of the amplitude equation which shows that cellular patterns are to be expected for certain ranges of the governing parameters. For other ranges the interface is unstable to sufficiently

large disturbances in spite of the fact that stability is predicted by linear theory. We suggest that dendritic instabilities are perhaps to be expected in these ranges. We conclude (§ 8) with a discussion of our results.

We now turn to the detailed formulation of the problem. We wish to investigate the stability of the shape of a moving planar interface between the liquid and solid phases in the unidirectional freezing of a dilute binary alloy. We use a nonlinearized version of a mathematical model originated by Mullins & Sekerka (1964) to describe an experimental situation in which solidification is controlled so that the mean position of the interface moves with a constant speed (Sekerka 1968). Our main purpose is to use a nonlinear stability analysis in order to explain more fully the occurrence of both the hexagonal cellular and dendritic structure of the interface which can exist under the appropriate imposed temperature gradients, and the imposed constant rate of solidification.

The mathematical model is developed as follows. Consider a two-dimensional situation in which a stationary or laboratory coordinate system, denoted by $(\tilde{x}, \tilde{z})$, is such that the $\tilde{x}$ axis coincides with the initial mean position at time $\tilde{t} = 0$ of an interface, which satisfies for time $\tilde{t} > 0$, the equation $\tilde{z} = V\tilde{t} + \zeta^*(\tilde{x}, \tilde{t})$. The mean position of this interface is assumed to be moving with a constant speed V in laboratory $(\tilde{x}, \tilde{z})$ coordinates, so that

$$\lim_{L\to\infty} \frac{1}{2L} \int_{-L}^{L} \zeta^*(x, t)\, \mathrm{d}x = 0$$

to lowest order (see § 6).

In writing the equations we shall use the following nomenclature:

V constant mean velocity of the interface,
$\tilde{C}$ concentration of the solute in the liquid,
$\tilde{T}(\tilde{T}')$ temperature in the liquid (solid),
$\tilde{z} = V\tilde{t} + \zeta^*(\tilde{x}, \tilde{t})$ equation of the liquid/solid interface having mean position $\tilde{z} = V\tilde{t}$,
D diffusion coefficient of the solute in the liquid,
$D_{\mathrm{th}}(D'_{\mathrm{th}}) = K_{\mathrm{L}} C_{\mathrm{L}}^{-1}(K_{\mathrm{S}} C_{\mathrm{S}}^{-1})$ thermal diffusivity of the liquid (solid),
$K_{\mathrm{L}}(K_{\mathrm{S}})$ conductivity of the liquid (solid),
$C_{\mathrm{L}}(C_{\mathrm{S}})$ specific heat of liquid (solid) per unit volume,
T_{M} the melting temperature, in degrees Kelvin, of the pure solvent,
Γ σL^{-1} capillary constant,
σ the specific liquid/solid interfacial free energy,
L latent heat of fusion per unit volume,
K distribution coefficient given by the ratio of the equilibrium concentration of solute on the solid side of the interface to that on the liquid side,
$m = \mathrm{d}T_{\mathrm{M}}[0]/\mathrm{d}\tilde{C}$ slope of the liquidus line on the phase diagram,
$\boldsymbol{n}$ unit normal to the interface, $\tilde{z} = V\tilde{t} + \zeta^*(\tilde{x}, \tilde{t})$, pointing into the liquid, and
$\tilde{v}(\tilde{x}, \tilde{t})$ the component of the velocity of the interface in the direction of $\boldsymbol{n}$.

The governing differential equations are (Mullins & Sekerka 1964):

For $\tilde{z} > V\tilde{t} + \zeta^*(\tilde{x}, \tilde{t})$ (in the liquid):

$$D\tilde{\nabla}^2\tilde{C}(\tilde{x}, \tilde{z}, \tilde{t}) = [\partial\tilde{C}/\partial\tilde{t}]\,(\tilde{x}, \tilde{z}, \tilde{t}), \tag{1.1a}$$

$$D_{\mathrm{th}}\tilde{\nabla}^2\tilde{T}(\tilde{x}, \tilde{z}, \tilde{t}) = [\partial\tilde{T}/\partial\tilde{t}]\,(\tilde{x}, \tilde{z}, \tilde{t}), \tag{1.1b}$$

which represent diffusion of solute and heat in the liquid in the absence of convection (see below).

For $\tilde{z} < V\tilde{t}+\zeta^*(\tilde{x},\tilde{t})$ (in the solid):

$$D'_{\mathrm{th}}\tilde{\nabla}^2\tilde{T}'(\tilde{x},\tilde{z},\tilde{t}) = [\partial\tilde{T}'/\partial\tilde{t}]\,(\tilde{x},\tilde{z},\tilde{t}), \tag{1.2}$$

which represents diffusion of heat in the solid. In this model solute diffusion in the solid is neglected and in order to determine the composition ($\tilde{C}_{\mathrm{S}}$) of the solid solution adjacent to the interface, one uses the relation

$$\text{for} \quad \tilde{z} = V\tilde{t}+\zeta^*(\tilde{x},\tilde{t}), \quad \tilde{C}_{\mathrm{S}} = K\tilde{C}.$$

From the outset, we have neglected convection in the liquid phase. Convection will inevitably occur unless the temperature gradient is normal to the interface and parallel to the gravitational field and its influence is certainly of interest (Carruthers 1968; Hamalainen 1968). If the molten metal lies above a horizontal interface, however, the liquid phase is gravitationally stable and only a weak motion is expected, in response to the surface-driven instability. There is little doubt that neglect of convection is justified in an attempt to determine the dominant nonlinear effects in this situation. It is probable that convection will not play a decisive role in other arrangements of constrained crystal growth either, for the morphology of the unstable interface seems largely independent of its orientation with respect to the gravitational field.

In our analysis we explicitly use the following boundary conditions, a nonlinearized alteration of Mullins & Sekerka (1964) [the chief change being the presence of $\partial/\partial n$ instead of $\partial/\partial\tilde{z}$ in (1.3c) and (1.3d)]:

For $\tilde{z} = V\tilde{t}+\zeta^*(\tilde{x},\tilde{t})$ (on the interface):

$$\tilde{T} = \tilde{T}', \quad \tilde{T} = m\tilde{C}+T_{\mathrm{M}}+T_{\mathrm{M}}\Gamma\zeta^*_{\tilde{x}\tilde{x}}(1+\zeta^{*2}_{\tilde{x}})^{-\frac{3}{2}}, \tag{1.3a, b}$$

$$\tilde{v}(\tilde{x},\tilde{t})\,L = K_{\mathrm{S}}\frac{\partial\tilde{T}'}{\partial n}-K_{\mathrm{L}}\frac{\partial\tilde{T}}{\partial n}; \quad \tilde{v}(\tilde{x},\tilde{t})\,(K-1)\,\tilde{C} = D\frac{\partial\tilde{C}}{\partial n}. \tag{1.3c, d}$$

In the above (1.3a) represents the continuity of temperature at the interface, while (1.3b) describes the alteration of the temperature of that interface, $\tilde{T}$, from the equilibrium melting temperature of the pure solvent, T_{M}, due to the presence of solute and the curvature of the interface itself. One can say that

$$\tilde{T} = T_{\mathrm{M}}[\tilde{C}]+\Delta T_{\mathrm{E}}+\delta T,$$

where $T_{\mathrm{M}}[\tilde{C}]$ is the actual *equilibrium* melting temperature of a *planar* interface as a function of the solute concentration of the interface; ΔT_{E} is the correction to that equilibrium melting temperature due to the fact that the interface is curved; and δT is the term that accounts for the fact that the interface temperature must depart from the equilibrium melting temperature because molecular attachment at the interface (interface attachment kinetics) is a 'non-equilibrium' process.

For a dilute alloy, taking the first two terms in a Taylor series

$$T_{\mathrm{M}}[\tilde{C}] \cong T_{\mathrm{M}}[0]+\{\mathrm{d}T_{\mathrm{M}}[0]/\mathrm{d}C\}\,\tilde{C} = T_{\mathrm{M}}+m\tilde{C}.$$

Since $\Delta T_{\mathrm{E}} = T_{\mathrm{M}}\Gamma\kappa$ where κ is curvature and, further, since δT is usually very small for metals and alloys and can be neglected (Tarshis 1967), equation (1.3b) now follows directly. When we use a general balance equation from continuum mechanics for a surface of discontinuity (Wollkind 1968) or a pill box type argument, (1.3c) and (1.3d) follow from conservation of heat and solute respectively at the interface. The right-hand sides of (1.3c) and (1.3d) represent net flux through the interface while the left-hand sides represent heat released by melting and solute rejection at the interface, respectively. The derivation of (1.3c) gives rise to a term, $\tilde{v}(C_{\mathrm{S}}-C_{\mathrm{L}})\,\tilde{T}$,

where $C_S(C_L)$ is specific heat per unit volume in the solid (liquid) phase. Since for such an alloy $C_S \cong C_L$ this term has been neglected.

For an interface of the form presented, $\boldsymbol{n}$ and $\tilde{v}(\tilde{x},\tilde{t})$ are given by

$$\boldsymbol{n} = (-\zeta^*_{\tilde{x}}, 1)\,(1+\zeta^{*2}_{\tilde{x}})^{-\frac{1}{2}} \quad \text{and} \quad \tilde{v}(\tilde{x},\tilde{t}) = (V+\zeta^*_{\tilde{t}})\,(1+\zeta^{*2}_{\tilde{x}})^{-\frac{1}{2}}. \tag{1.4}$$

If we use (1.4) and the fact that $\partial(\tilde{C},\tilde{T},\tilde{T}')/\partial n = \nabla(\tilde{C},\tilde{T},\tilde{T}').\boldsymbol{n}$, and multiply through by $(1+\zeta^{*2}_{\tilde{x}})^{\frac{1}{2}}$, boundary conditions (1.3c) and (1.3d) transform into

$$V+\zeta^*_{\tilde{t}} = \frac{1}{L}\left[K_S\left(\frac{\partial\tilde{T}'}{\partial\tilde{z}} - \zeta^*_{\tilde{x}}\frac{\partial\tilde{T}'}{\partial\tilde{x}}\right) - K_L\left(\frac{\partial\tilde{T}}{\partial\tilde{z}} - \zeta^*_{\tilde{x}}\frac{\partial\tilde{T}}{\partial\tilde{x}}\right)\right] \tag{1.3c*}$$

and

$$(V+\zeta^*_{\tilde{t}})\,\tilde{C}(K-1) = D\left(\frac{\partial\tilde{C}}{\partial\tilde{z}} - \zeta^*_{\tilde{x}}\frac{\partial\tilde{C}}{\partial\tilde{x}}\right). \tag{1.3d*}$$

2. The steady-state planar interface solution

There exists a steady-state solution of (1.1) and (1.2), depending only on z^*, where

$$z^* = \tilde{z} - V\tilde{t},$$

and satisfying boundary conditions (1.3*) for a planar interface, $z^* = \zeta^*(\tilde{x},\tilde{t}) \equiv 0$. This solution is given by

$$\tilde{C} = C^*_0(z^*) = C_0 + (G_0 D/V)\,(1-\exp\{-(V/D)\,z^*\}) \quad (z^* > 0); \tag{2.1a}$$

$$\tilde{T} = T^*_0(z^*) = T_0 + (G^* D_{\mathrm{th}}/V)\,(1-\exp\{-(V/D_{\mathrm{th}})\,z^*\}) \quad (z^* > 0); \tag{2.1b}$$

$$\tilde{T}' = T'^*_0(z^*) = T_0 + (G'^* D'_{\mathrm{th}}/V)\,(1-\exp\{-(V/D'_{\mathrm{th}})\,z^*\}) \quad (z^* < 0); \tag{2.1c}$$

where the various quantities in (2.1) are related by

$$T_0 = mC_0 + T_M, \quad K_S G'^* - K_L G^* = VL \quad \text{and} \quad V = DG_0/C_0(K-1), \tag{2.2}$$

with G^*, G'^*, $m(K-1) > 0$.

In an actual experiment the extent of the liquid and solid phases is naturally finite. A simplifying assumption in this model is that z^* extends to positive and negative infinity. The instability to be considered depends crucially on conditions at the liquid/solid interface but should be virtually unaffected by conditions far from that interface.

Note that as $z^* \to \infty$, $C^*_0(z^*) \to C_0 + G_0 D/V = KC_0$ and $T^*_0(z^*) \to T_0 + G^* D_{\mathrm{th}}/V$ but that as $z^* \to -\infty$, $T'^*_0(z^*) \to -\infty$, which is a consequence of the simplifying assumption that the extent of the phases is infinite (see figure 1). This solution will be referred to as the steady-state 'planar interface' solution. It is the *stability of this solution*, with which we are concerned. In order to investigate this stability we shall consider solutions of the form

$$\tilde{\boldsymbol{v}}(\tilde{x},z^*,\tilde{t}) = \tilde{\boldsymbol{v}}^*_0(z^*) + \tilde{\boldsymbol{v}}_1(\tilde{x},z^*,\tilde{t}), \tag{2.3}$$

or equivalently

$$\begin{bmatrix} \tilde{C}(\tilde{x},z^*,\tilde{t}) \\ \tilde{T}(\tilde{x},z^*,\tilde{t}) \\ \tilde{T}'(\tilde{x},z^*,\tilde{t}) \\ \zeta^*(\tilde{x},\tilde{t}) \end{bmatrix} = \begin{bmatrix} C^*_0(z^*) \\ T^*_0(z^*) \\ T'^*_0(z^*) \\ 0 \end{bmatrix} + \begin{bmatrix} \tilde{C}_1(\tilde{x},z^*,\tilde{t}) \\ \tilde{T}_1(\tilde{x},z^*,\tilde{t}) \\ \tilde{T}'_1(\tilde{x},z^*,\tilde{t}) \\ \zeta^*_1(\tilde{x},\tilde{t}) \end{bmatrix},$$

where $\tilde{\boldsymbol{v}}^*_0(z^*)$ is the planar interface solution and $\tilde{\boldsymbol{v}}_1(\tilde{x},z^*,\tilde{t})$ is a small perturbation. By examining the behaviour of $\tilde{\boldsymbol{v}}_1(\tilde{x},z^*,\tilde{t})$ as $\tilde{t} \to \infty$ for various ranges of the relevant parameters, we can

determine the stability or instability of the planar interface solution. If $\lim_{\tilde{t}\to\infty} \tilde{\boldsymbol{v}}_1(\tilde{x}, z^*, \tilde{t}) = \mathbf{0}$, we say this solution is stable to perturbations of the type $\tilde{\boldsymbol{v}}_1$ and if $\lim_{\tilde{t}\to\infty} \tilde{\boldsymbol{v}}_1(\tilde{x}, z^*, \tilde{t}) \to \infty$, we say it is unstable. It is also possible for $\lim_{\tilde{t}\to\infty} \tilde{\boldsymbol{v}}_1(\tilde{x}, z^*, \tilde{t}) = \tilde{\boldsymbol{v}}_1^*(\tilde{x}, z^*)$, in which case the planar interface solution is unstable to type $\tilde{v}_1$ perturbations but can transform into a finite amplitude equilibrium solution, $\tilde{\boldsymbol{v}}_e = \tilde{\boldsymbol{v}}_0^*(z^*) + \tilde{\boldsymbol{v}}_1^*(\tilde{x}, z^*)$.

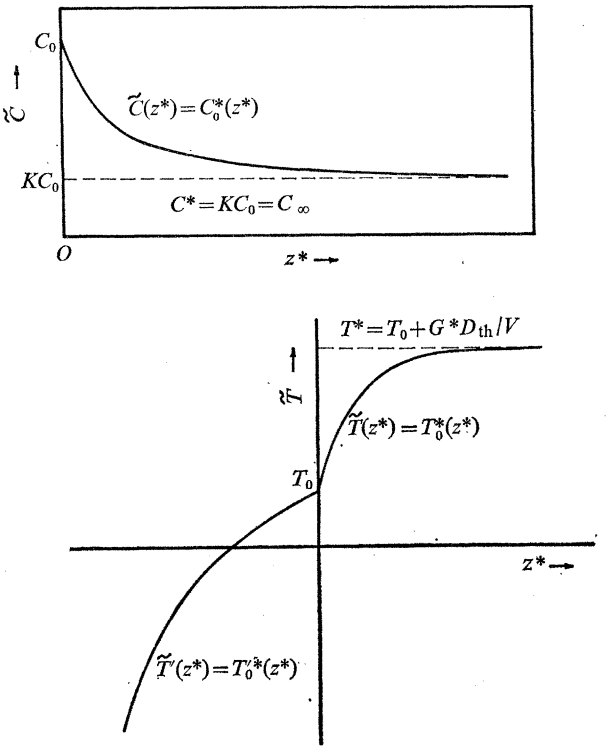

FIGURE 1. The planar interface steady-state solution of (1.1) to (1.3). (*a*) The solute concentration $\tilde{C}(z^*)$ in the liquid. The planar liquid–solid interface has equation $z^* = 0$. (*b*) The temperatures $\tilde{T}'$ and $\tilde{T}$ of the solid and liquid respectively.

We have deferred until now a discussion of the proper boundary conditions to be applied in the liquid and solid phases as $z^* \to \pm\infty$. We expect that far from the interface the influence of the shape of that interface on the solute and temperature fields will become negligible. This means that

$$\left.\begin{aligned} &\tilde{C} \to C_0^*(z^*), \quad \tilde{T} \to T_0^*(z^*) \quad \text{as} \quad z^* \to \infty; \\ &\tilde{T}' \to T_0'^*(z) \quad \text{as} \quad z^* \to -\infty; \end{aligned}\right\} \tag{2.4}$$

where $C_0^*(z^*)$, $T_0^*(z^*)$, and $T_0'^*(z^*)$ comprise the planar interface solution given in (2.1). Equation (2.4) is the proper boundary condition to be applied at $|z^*| \to \infty$, and along with (1.1) and (1.2) and boundary condition (1.3*) constitutes the mathematical formulation of the problem. Also note that for solutions of form (2.3), condition (2.4) implies that

$$\left.\begin{aligned} &\tilde{C}_1 \to 0, \quad \tilde{T}_1 \to 0, \quad \text{as} \quad z^* \to +\infty; \\ &\tilde{T}_1' \to 0 \quad \text{as} \quad z^* \to -\infty. \end{aligned}\right\} \tag{2.5}$$

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3. Scaling and non-dimensional variables

We now discuss the process of scaling as a prelude to the introduction of non-dimensional variables into the governing equations and boundary conditions. Our discussion briefly spells out some matters which are more or less implicit in the usual scaling procedures.

Consider a set of differential equations with dependent variable $f^*(z^*)$, where z^*, the independent variable, is restricted to an interval I^*, which may be finite, semi-infinite, or infinite. We wish to find an f^* scale, F, and a z^* scale, S, so that if we define the non-dimensional scaled variables f and z by

$$z = S^{-1}z^*, \quad f(z) = F^{-1}f^*(Sz), \tag{3.1a, b}$$

then

$$|f(z)|_{\max} = 1 \quad \text{and} \quad |\mathrm{d}f(z)/\mathrm{d}z|_{\max} = 1 \quad \text{for} \quad z \in I, \tag{3.2a, b}$$

where z is in the interval I if and only if z^* is the interval I^*. Now

$$f^*(z^*) = Ff(z), \quad \frac{\mathrm{d}f^*(z^*)}{\mathrm{d}z^*} = \frac{F}{S}\frac{\mathrm{d}f(z)}{\mathrm{d}z}, \tag{3.3a, b}$$

so that this change of variables replaces f^* and $\mathrm{d}f^*/\mathrm{d}z^*$ by fF and $FS^{-1}(\mathrm{d}f/\mathrm{d}z)$ whose maximum absolute values are given by the constant factors F and FS^{-1} respectively. Hence once all the terms in a set of equations are scaled in this preceding manner, one can compare the relative size of each term in a given equation by comparing the relevant constant factors (for subtleties see Lin & Segel 1971).

From the above

$$F = |f^*|_{\max} = \max_{z^* \text{ in } I^*} |f^*(z^*)| \tag{3.4a}$$

and

$$\frac{F}{S} = \left|\frac{\mathrm{d}f^*}{\mathrm{d}z^*}\right|_{\max} = \max_{z^* \text{ in } I^*} \left|\frac{\mathrm{d}f^*(z^*)}{\mathrm{d}z^*}\right|. \tag{3.4b}$$

Thus one makes the following definitions for the scales F and S:

$$F = |f^*|_{\max} \quad \text{and} \quad S = \frac{|f^*|_{\max}}{|\mathrm{d}f^*/\mathrm{d}z^*|_{\max}}. \tag{3.5a, b}$$

If another function of z^*, say $g^*(z^*)$, also appears in the equations, then S is defined as follows:

$$S = \min\left\{\frac{|g^*|_{\max}}{|\mathrm{d}g^*/\mathrm{d}z^*|_{\max}}, \frac{|f^*|_{\max}}{|\mathrm{d}f^*/\mathrm{d}z^*|_{\max}}\right\}. \tag{3.6}$$

In general, higher order derivatives, if they appear in the equations, should be considered in the determination of S but in the problem under consideration no alteration of S is obtained by doing so.

Let us apply the process of scaling just described to the set of equations and boundary conditions, denoted by (1.1), (1.2), (1.3*), and (2.4). The scaling technique developed above assumes knowledge of the very solution we are trying to find. But since only order of magnitudes are required, certain general considerations often suffice to give the required estimates. For example, because (2.3) is a perturbation solution it is reasonable to assume that its dependent variables are of the same magnitude as the dependent variables of the basic solution. We then use this basic solution,

$$\tilde{C} = C_0^*(z^*), \quad \tilde{T} = T_0^*(z^*), \quad \tilde{T}' = T_0'^*(z^*) \quad \text{and} \quad \zeta^* = 0, \tag{3.7}$$

where $C_0^*(z^*)$, $T_0^*(z^*)$ and $T_0'^*(z^*)$ are given by (2.1) and (2.2), in order to calculate the relevant scales and introduce non-dimensional variables.

Recall from § 2 that in the limit as $z^* \to -\infty$, $T_0'^* \to -\infty$, which was a consequence of the simplifying assumption that the extent of the solid phase is infinite. For this reason one cannot consider the $T_0'^*(z^*)$ solution for the purpose of introducing scales. It will now be assumed that the temperature scale for $T_0^*(z^*)$ is also the temperature scale for $T_0'^*(z^*)$. Since $T_0^* = T_0^{*\prime}$ at the interface, one expects this to be a good approximation near the interface.

To find $\mathscr{S}$, $\mathscr{C}$ and $\mathscr{T}$, the length, concentration, and temperature scales respectively it is necessary to calculate various quantities which will be sketched in detail for $\mathscr{C}$. In particular

$$|C_0^*(z^*)|_{\max} = \max_{z^*>0} |C_0 + C_0(K-1)\,(1-\mathrm{e}^{-(V/D)z^*})| = C_0 = C_0^*(0), \tag{3.8a}$$

and

$$\left|\frac{\mathrm{d}C_0^*(z^*)}{\mathrm{d}z^*}\right|_{\max} = \max_{z^*>0} |C_0(K-1)\,V/D\,\mathrm{e}^{-(V/D)z^*}| = C_0(1-K)\,V/D. \tag{3.8b}$$

Hence

$$\frac{|C_0^*|_{\max}}{|\mathrm{d}C_0^*/\mathrm{d}z^*|_{\max}} = \frac{C_0}{C_0(1-K)\,V/D} = \frac{D/V}{1-K}. \tag{3.9}$$

Similarly

$$|T_0^*|_{\max} = \alpha_1 T_{\mathrm{M}} \quad \text{and} \quad \frac{|T_0^*|_{\max}}{|\mathrm{d}T_0^*/\mathrm{d}z^*|_{\max}} = \alpha_2 D_{\mathrm{th}}/V, \tag{3.10}$$

where $\alpha_{1,2} = O(1)$. Since $O(1)$ factors can be neglected in the determination of scales one now chooses $\mathscr{S}$, $\mathscr{C}$ and $\mathscr{T}$ as follows:

$$\mathscr{S} = \min\{D/V, D_{\mathrm{th}}/V\} = D/V, \quad \mathscr{C} = C_0^*(0), \quad \mathscr{T} = T_{\mathrm{M}}. \tag{3.11}$$

The length scale, $\mathscr{S}$, was chosen as above since

$$D/V = O(10^{-4})\,\mathrm{cm} \quad \text{and} \quad D_{\mathrm{th}}/V = O(10^{2})\,\mathrm{cm} \tag{3.12}$$

for typical alloys (Mullins & Sekerka 1964).

We have already made the claim that these various scales are valid for the dependent variables; thus the scales, $C_0^*(0)$ and T_{M} respectively, developed for $\tilde{\boldsymbol{v}}_0^*$, can be applied to $\tilde{\boldsymbol{v}}$. That the length scale of $\tilde{\boldsymbol{v}}_0^*$ can also be used for $\tilde{\boldsymbol{v}}$ is not obvious due to the presence of various perturbation gradients. As a partial justification for this we note that in the Bénard problem, which deals with a buoyancy-driven convection layer confined between parallel plates, and the Taylor problem, which deals with flow between rotating concentric cylinders, the wavelength of the perturbation disturbance is of the magnitude of the gap width (Segel 1966). Also in the work of Scanlon & Segel (1967), concerning a surface tension driven semi-infinite convection layer, the perturbation wavelength is of the same magnitude as the length scale given by the temperature gradient of the basic solution.

We then assume that the time scale τ is given by

$$\tau = \mathscr{S}/V = D/V^2, \tag{3.13}$$

and the length scale, δ, for the interface is defined by

$$\delta = \max|\zeta^*(\tilde{x}, \tilde{t})|. \tag{3.14}$$

We now introduce the following non-dimensional variables and parameters:

$$\left.\begin{aligned} C = \frac{\tilde{C}}{C_0^*(0)}, \quad T = \frac{\tilde{T}}{T_{\mathrm{M}}}, \quad T' = \frac{\tilde{T}'}{T_{\mathrm{M}}}, \quad \zeta = \frac{\zeta^*}{\delta}, \\ (x, z) = \frac{(\tilde{x}, z^*)}{D/V}, \quad t = \frac{\tilde{t}}{D/V^2}, \quad \epsilon = \frac{\delta}{D/V}, \quad \xi = \frac{D}{D_{\mathrm{th}}}, \\ M = \frac{mC_0^*(0)}{T_{\mathrm{M}}}, \quad \gamma = \frac{\Gamma}{D/V} \quad \text{and} \quad n = \frac{K_{\mathrm{S}}}{K_{\mathrm{L}}}. \end{aligned}\right\} \tag{3.15}$$

4. The linear stability problem

Using the dimensionless variables and parameters introduced at the end of the last section (see (3.15)), the basic equations transform into the following:

For $z > \epsilon\zeta$ (in the liquid):

$$\nabla^2 C + \partial C/\partial z - \partial C/\partial t = 0, \tag{4.1a}$$

$$\nabla^2 T = 0. \tag{4.1b}$$

For $z < \epsilon\zeta$ (in the solid):

$$\nabla^2 T' = 0. \tag{4.2}$$

For $z = \epsilon\zeta(x, t)$ (on the interface):

$$T = 1 + MC + \gamma\epsilon\zeta_{xx}(1+\epsilon^2\zeta_x^2)^{-\frac{3}{2}}, \quad T = T', \tag{4.3a, b}$$

$$n\frac{\partial T'}{\partial z} - \frac{\partial T}{\partial z} - \epsilon\zeta_x\left(n\frac{\partial T'}{\partial x} - \frac{\partial T}{\partial x}\right) = 0, \tag{4.3c}$$

$$\frac{\partial C}{\partial z} - \epsilon\zeta_x\frac{\partial C}{\partial x} = (K-1)\,C(1+\epsilon\zeta_t). \tag{4.3d}$$

For $|z| \to \infty$:

$$\left.\begin{aligned} &C \to C_0(z), \quad T \to T_0(z) \quad \text{as} \quad z \to \infty, \\ &T' \to T_0'(z) \quad \text{as} \quad z \to -\infty, \end{aligned}\right\} \tag{4.4}$$

where $C_0(z)$, $T_0(z)$ and $T_0'(z)$ come from the planar interface steady-state solution for *this* system, depending only on z, and satisfying boundary condition (3) for the planar interface $z = \epsilon\zeta \equiv 0$. Thus

$$\left.\begin{aligned} C_0(z) &= 1 + (K-1)\,(1-\mathrm{e}^{-z}), \\ T_0(z) &= 1 + M + Gz, \\ T_0'(z) &= 1 + M + Gn^{-1}z. \end{aligned}\right\} \tag{4.5}$$

In the above we have set the dimensionless parameter ξ, which typically has the very small value of 10^{-6}, equal to zero.

This approximation certainly does not alter any of the fundamental results of the stability analysis that follows and even its quantitative effect is almost always extremely small. (See also remarks under (4.15).)

Proceeding according to the manner outlined in § 2, we investigate the stability of the planar interface solution by considering solutions of the form

$$\boldsymbol{v}(x, z, t; \epsilon) = \boldsymbol{v}_0(z) + \boldsymbol{v}_1(x, z, t; \epsilon), \tag{4.6}$$

or equivalently

$$\begin{bmatrix} C(x,z,t;\epsilon) \\ T(x,z,t;\epsilon) \\ T'(x,z,t;\epsilon) \\ \epsilon\zeta(x,t;\epsilon) \end{bmatrix} = \begin{bmatrix} C_0(z) \\ T_0(z) \\ T_0'(z) \\ 0 \end{bmatrix} + \epsilon \begin{bmatrix} C_1(z) \\ T_1(z) \\ T_1'(z) \\ \zeta_1 \end{bmatrix} \cos\omega x\, \mathrm{e}^{a_0 t}, \tag{4.7}$$

where $\boldsymbol{v}_0(z)$ is the planar interface solution given by (4.5).

We now substitute the vectors of (4.6) and (4.7) into the system (4.1) to (4.4). Then, expanding boundary condition (4.3) in a Taylor expansion about $z = \epsilon\zeta = 0$ and neglecting all terms of

$O(\epsilon^2)$, we obtain the following *linear* problem for $\boldsymbol{v}_1(z) = [C_1(z), T_1(z), T_1'(z), \zeta_1]$ upon cancellation of the common factor $\epsilon \cos \omega x \, e^{a_0 t}$:

$$\left.\begin{aligned} [\mathrm{D}^2 - \omega^2 + \mathrm{D} - a_0]\, C_1(z) = 0, \quad [\mathrm{D}^2 - \omega^2]\, T_1(z) = 0 \quad (z > 0); \\ [\mathrm{D}^2 - \omega^2]\, T_1'(z) = 0 \quad (z < 0;\ D \equiv \mathrm{d}/\mathrm{d}z). \end{aligned}\right\} \tag{4.8}$$

The boundary conditions at $z = 0$ are

$$\left.\begin{aligned} T_1(0) - MC_1(0) + \zeta_1[G + \omega^2\gamma - M(K-1)] = 0, \\ T_1(0) - T_1'(0) + \zeta_1 G(n-1)/n = 0, \\ n\mathrm{D}\, T_1'(0) - \mathrm{D}T_1(0) = 0, \\ \mathrm{D}C_1(0) - (K-1)\, C_1(0) + (1-K)\,(K + a_0)\, \zeta_1 = 0. \end{aligned}\right\} \tag{4.9}$$

As $|z| \to \infty$ we require

$$\left.\begin{aligned} C_1(z) \to 0, \quad T_1(z) \to 0 \quad \text{as} \quad z \to \infty; \\ T_1'(z) \to 0 \quad \text{as} \quad z \to -\infty. \end{aligned}\right\} \tag{4.10}$$

This is an eigenvalue problem with eigenvalue, a_0, and corresponding eigenvector, $\boldsymbol{v}_1(z)$, where a_0 is the *growth rate*. We say that the planar interface solution is *stable*, *unstable*, or *neutrally stable* to this type of disturbance according to whether $\lim_{t\to\infty} e^{a_0 t} \to 0$, ∞, or 1. This in turn depends on the sign of $\mathrm{Re}\,(a_0)$ being less than, greater than or equal to zero. The particular disturbance considered is most likely to lead to instability (see § 8).

Equations (4.8) to (4.10) possess solutions of the form

$$[C_1, T_1, T_1']\,(z) = [A_1, B_1, C_1] \exp\,(-[m_0, m_1, m_2]\, z), \quad \zeta_1 = D_1, \tag{4.11}$$

where A_1, B_1, C_1 and D_1 are constants. We obtain, on substitution into (8) and cancellation of common factors that

$$\left.\begin{aligned} m_0 = \tfrac{1}{2} + (\tfrac{1}{4} + \omega^2 + a_0)^{\frac{1}{2}}, \\ m_1 = |\omega|, \quad m_2 = -|\omega|, \end{aligned}\right\} \tag{4.12}$$

where we have chosen signs in (4.12) so that (4.10) will be satisfied. Substituting (4.11) into (4.9) and making use of (4.12) we obtain:

$$\left.\begin{aligned} MA_1 - B_1 + D_1[M(K-1) - \omega^2\gamma - G] = 0, \\ B_1 - C_1 + D_1 G(n-1)/n = 0, \\ B_1 + nC_1 = 0, \\ [m_0 + (K-1)]\, A_1 + (K-1)\,(K + a_0)\, D_1 = 0. \end{aligned}\right\} \tag{4.13}$$

This is a system of four linear homogeneous equations in four unknowns and if it is to have a non-trivial solution the determinant of the coefficients must vanish. From this condition, after some algebra, we find

$$a_0 = (T - \beta\omega^2)\, g(\omega^2, a_0) - K, \tag{4.14}$$

where

$$T = 1 - W, \quad W = 2G/(1+n)\, M(K-1), \quad \beta = \gamma/M(K-1),$$
$$g(\omega^2, a_0) = m_0(\omega^2, a_0) + K - 1 = K - \tfrac{1}{2} + (\tfrac{1}{4} + \omega^2 + a_0)^{\frac{1}{2}}.$$

(The above dimensionless parameter T should not be confused with the temperature.) The corresponding components of the eigenvectors are

$$C_1(z) = (1-K)\,(T - \beta\omega^2)\, D \exp\{-m_0(\omega^2, a_0)\, z\}, \quad \zeta_1 = D, \tag{4.15}$$

$$T_1(z) = \frac{(1-n)}{1+n}\, GD \exp\{-|\omega|\, z\}, \quad T_1'(z) = \frac{n-1}{n(1+n)}\, GD \exp\{|\omega|\, z\},$$

where D is a constant.

As mentioned, to determine stability we must know the sign of $\mathrm{Re}\,(a_0)$. We first note, as explained in some detail in Wollkind (1968), that by taking the small parameter ξ to be zero in the basic equations we have neglected strongly stable roots of a_0 for which $\mathrm{Re}\,(a_0) < 0$ and $|a_0| \sim \xi^{-1}$ as $\xi \to 0$. Since we are concerned in linear theory with determining the critical conditions at which instability first occurs and in nonlinear theory with the long-time behaviour of the corresponding critical disturbances, we are justified in neglecting terms proportional to ξ in the basic equations.

Next we prove the so-called *principle of exchange of stabilities* for this problem, i.e. we show that in (4.14), $\mathrm{Re}\,(a_0) = 0$ implies $\mathrm{Im}\,(a_0) = 0$. Writing

$$a_0 = \mathrm{Re}\,(a_0) + \mathrm{i}\,\mathrm{Im}\,(a_0) = a_0^{(\mathrm{r})} + \mathrm{i}a_0^{(\mathrm{i})}, \tag{4.16}$$

we substitute (4.16) into (4.14), assume $a_0^{(\mathrm{r})} = 0$, and obtain

$$\mathrm{i}a_0^{(\mathrm{i})} = (T - \beta\omega^2)\,[K - \tfrac{1}{2} + (\tfrac{1}{4} + \omega^2 + \mathrm{i}a_0^{(\mathrm{i})})^{\frac{1}{2}}] - K. \tag{4.17}$$

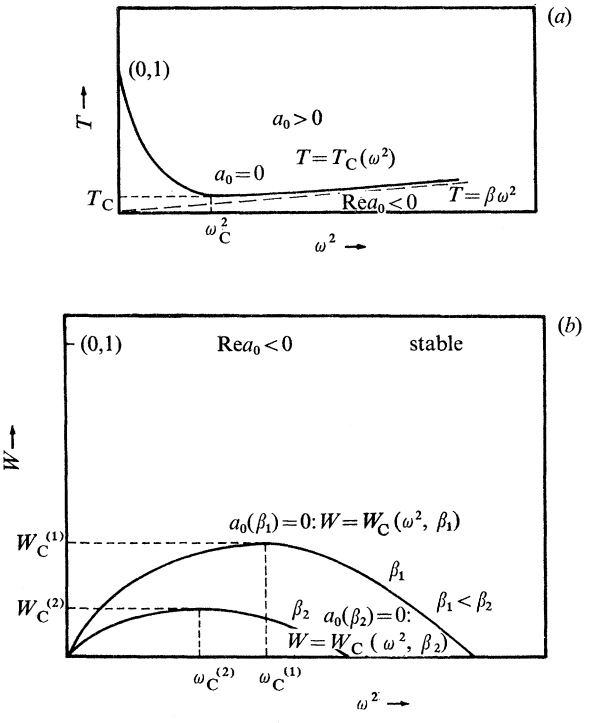

FIGURE 2. (*a*) A plot of $T = 1 - 2G/(1+n)\,M(K-1)$, a dimensionless combination of temperature and concentration gradients, versus ω^2, the square of the wavenumber of the disturbance. From the linear stability analysis, $a_0 = 0$ is the marginal stability curve separating the unstable region, $a_0 > 0$, from the stable region, $\mathrm{Re}\,a_0 < 0$. (*b*) A plot of $W = 2G/(1+n)\,M(K-1)$, a dimensionless combination of concentration and temperature gradients against ω^2. The critical value of the parameters and the marginal stability curves are depicted for two values of β.

Transposing the relevant terms, squaring out, and equating the real and imaginary parts of the resulting expression we find

$$a_0^{(\mathrm{i})}[(\beta\omega^2 + W)\,(2K + T - \beta\omega^2)] = 0, \tag{4.18}$$

$$[K + (T - \beta\omega^2)\,(\tfrac{1}{2} - K)]^2 - (T - \beta\omega^2)^2\,(\tfrac{1}{4} + \omega^2) = a_0^{2(\mathrm{i})}. \tag{4.19}$$

Since the factor multiplying $a_0^{(\mathrm{i})}$ in (4.18) is not identically equal to zero this implies

$$a_0^{(\mathrm{i})} = 0.$$

The existence of an exchange of stabilities means that we can set $a_0 = 0$ in (4.14) in order to investigate neutral stability. Doing this we arrive at the *neutral stability condition*

$$T(\omega^2, 0) = T_C(\omega^2) = \beta\omega^2 + K/g(\omega^2, 0), \tag{4.20}$$

where

$$g(\omega^2, 0) = K - \tfrac{1}{2} + (\tfrac{1}{4} + \omega^2)^{\frac{1}{2}}.$$

$T_C(\omega^2)$ has the properties that

$$T_C(0) = 1 \quad \text{and} \quad T_C(\omega^2) \to \beta\omega^2 \quad \text{as} \quad \omega^2 \to \infty.$$

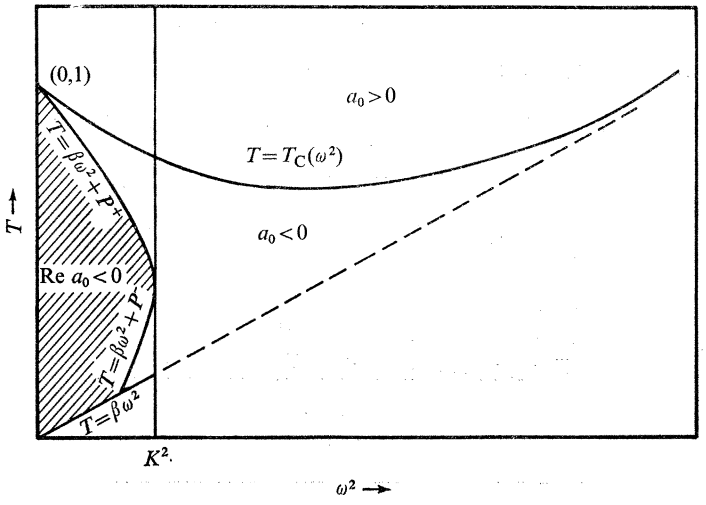

FIGURE 3. The region in the $T-\omega^2$ plane of complex a_0. (The locus is designated by shading.)

The T_C against ω^2 curve has an absolute minimum at $\omega = \omega_C$ where ω_C, the *critical wavenumber*, is such that

$$\frac{dT_C}{d\omega^2}(\omega_C^2) = 0 \quad \text{if} \quad \beta \leqslant \frac{1}{K}, \quad \text{which implies} \quad \beta = \frac{K}{2g^2(\omega_C^2, 0)\,(\tfrac{1}{4} + \omega_C^2)^{\frac{1}{2}}} \tag{4.21}$$

or

$$\omega_C = 0 \quad \text{if} \quad \beta > 1/K.$$

Corresponding to ω_C is an associated critical value of the parameter T denoted by T_C (see figure 2) such that

$$T_C(\omega_C^2) = T_C = 1 - W_C = \beta\omega_C^2 + K/g(\omega_C^2, 0). \tag{4.22}$$

We note that

$$0 < T_C \leqslant 1 \quad \text{and} \quad 0 \leqslant W_C < 1.$$

In the plot of T against ω^2, the neutral curve or curve of marginal stability of (20) $T = T_C(\omega^2)$, on which $a_0 = 0$, separates the region of instability where $a_0 > 0$ from that of stability where $\operatorname{Re} a_0 < 0$. In the region where a_0 is real, $a_0 = \alpha(T - T_C) + O(T - T_C)^2$, $\alpha > 0$. Observe that a_0 is complex only in that region of the $T-\omega^2$ plane where

$$P^- < T - \beta\omega^2 < P^+, \quad T > \beta\omega^2 \quad \text{and} \quad \omega^2 < K^2.$$

Here $P^{\pm} = 1 - 2K \pm 2(K^2 - \omega^2)^{\frac{1}{2}}$ (see figure 3). In this region $\operatorname{Re} a_0 < 0$ (Wollkind 1968).

Note from figure 2 that for $T < T_C$ there exist no wavenumbers, ω, such that $a_0 > 0$ and that for $T > T_C$ there exists a band of such wavenumbers corresponding to growing disturbances. This means that for $T > T_C$ or $W < W_C$ one has instability and for $T < T_C$ or $W > W_C$ one has stability.

Since β determines ω_C by relation (4.21) and ω_C determines W_C by relation (4.22) we can speak of

$$W_C[\omega_C^2(\beta)] = W_C(\beta). \tag{4.23}$$

$W = 2G/\rho(1+n)$, where $\rho = M(K-1) = mC_0(K-1)/T_M > 0$, is a dimensionless combination of temperature and concentration gradients. β is equal to γ/ρ, where $\gamma = V\Gamma/D$ is a dimensionless velocity of solidification. For a given alloy of a specific concentration, C_0, the only variable factors involved are G, the temperature gradient in the liquid, and γ. We speak of a critical value of G, G_C, such that

$$G_C = (1+n)\,\rho W_C/2, \quad G_C[\omega_C^2(\gamma/\rho)] = (1+n)\,\rho W_C[\omega_C^2(\gamma/\rho)]/2 = G_C(\gamma). \tag{4.24}$$

Since in terms of G we have stability for $G > G_C$ and instability for $G < G_C$, the curve $G = G_C(\gamma)$ is one of marginal stability in the plot of G against γ represented in figure 4. Note that for $\beta = \gamma/\rho \geqslant 1/K$, $G_C = 0$ and we have stability for any $G > 0$. Thus for $\gamma \geqslant \gamma^* = \rho/K$ we have what metallurgists call *absolute stability*.

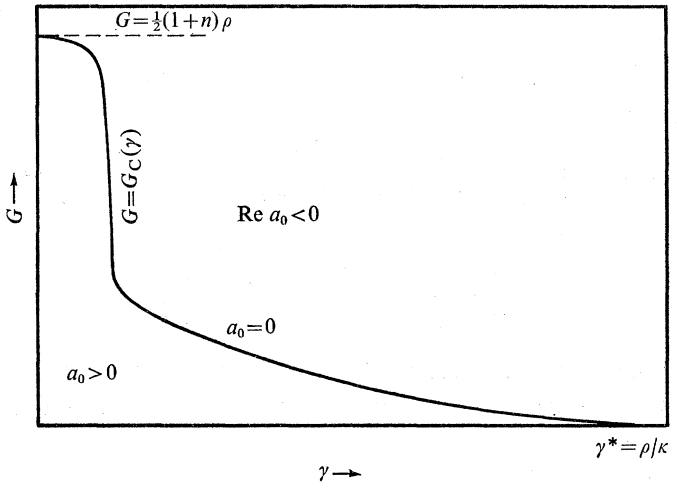

FIGURE 4. A plot of the dimensionless temperature in the liquid against $\gamma = V\Gamma/D$, a dimensionless rate of solidification. $G = G_C(\gamma)$ is the curve of marginal stability and $\gamma^* = \rho/K$ is such that for $\gamma > \gamma^*$ there is stability for any G.

5. THE ADJOINT PROBLEM

Before we can consider the nonlinear stability problem, it is necessary to pose and solve what is called the *adjoint linear eigenvalue problem* (Ince 1956). Owing to the presence of a_0 in boundary condition (4.9), we first put the linear eigenvalue problem, (4.8) to (4.10), in the form

$$\mathscr{L}[\boldsymbol{v}(z)] = a_0 \mathscr{M}[\boldsymbol{v}(z)], \tag{5.1}$$

with boundary conditions on $\boldsymbol{v}(z)$ such that

$$B[\boldsymbol{v}(0)] = \boldsymbol{0}, \quad \boldsymbol{v}(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty. \tag{5.2}$$

$\mathscr{L}[\boldsymbol{v}]$ and $\mathscr{M}[\boldsymbol{v}]$ are to be vector valued operators; $\boldsymbol{v}(z)$ is to be a vector containing $C_1(z)$, $T_1(z)$, $T_1'(z)$ and ζ_1; and $B[\boldsymbol{v}(0)]$ is to be a vector operator evaluated at $z = 0$ which is *independent* of the eigenvalue a_0. Once we have done this we shall formulate the *adjoint problem*

$$\mathscr{L}^+[\boldsymbol{v}^+(z)] = b_0 \mathscr{M}^+[\boldsymbol{v}^+(z)], \tag{5.3}$$

with boundary conditions on $\boldsymbol{v}^+(z)$ such that

$$B^+[\boldsymbol{v}^+(0)] = \boldsymbol{0}, \quad \boldsymbol{v}^+(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty. \tag{5.4}$$

$\mathscr{L}^+[\boldsymbol{v}^+]$, $\mathscr{M}^+[\boldsymbol{v}^+]$ and $B^+[\boldsymbol{v}^+]$ are to be defined such that for all $\boldsymbol{v}$ and $\boldsymbol{v}^+$ satisfying boundary conditions (5.2) and (5.4) mentioned above:

$$(\mathscr{L}[\boldsymbol{v}(z)],\, \boldsymbol{v}^+(z)) = (\boldsymbol{v}(z),\, \mathscr{L}^+[\boldsymbol{v}^+(z)]), \tag{5.5}$$

$$(\mathscr{M}[\boldsymbol{v}(z)],\, \boldsymbol{v}^+(z)) = (\boldsymbol{v}(z),\, \mathscr{M}^+[\boldsymbol{v}^+(z)]), \tag{5.6}$$

where, for the purpose of normalization, we take the common value of (5.6) to be 1; $\boldsymbol{v}^+(z)$ is to be a vector containing $C_1^+(z)$, $T_1^+(z)$, $T_1'^+(z)$ and ζ_1^+; and $(\ ,\ )$ is an appropriate inner product. $\mathscr{L}^+$ and $\mathscr{M}^+$ are the *adjoint operators* of $\mathscr{L}$ and $\mathscr{M}$ respectively.

In order to put the *linear problem* in the form (5.1) and (5.2), we define

$$\mathscr{L}[\boldsymbol{v}(z)] = \begin{bmatrix} (D^2-\omega^2+D)\, C_1(z) \\ (D^2-\omega^2)\, T_1(z) \\ (D^2-\omega^2)\, T_1'(z) \\ nDT_1'(0) - DT_1(0) \\ DC_1(0) - (K-1)\, C_1(0) - K(K-1)\, \zeta_1 \end{bmatrix}, \quad \mathscr{M}[\boldsymbol{v}(z)] = \begin{bmatrix} C_1(z) \\ 0 \\ 0 \\ 0 \\ (K-1)\, \zeta_1 \end{bmatrix} \tag{5.7}$$

for $\boldsymbol{v}(z) = [C_1(z), T_1(z), T_1'(z), \zeta_1, A]$, where A is a constant to be determined. (Note: it is not necessary to distinguish between row and column vectors as they will be used interchangeably.) We define $B[\boldsymbol{v}(0)]$ such that

$$B[\boldsymbol{v}(0)] = \left\{ \begin{matrix} T_1(0) - MC_1(0) + \zeta_1[G + \omega^2\gamma - M(K-1)] \\ T_1(0) - T_1'(0) + \zeta_1 G(n-1)/n \end{matrix} \right\} = \boldsymbol{0}. \tag{5.8}$$

By $\boldsymbol{v}(z) \to \boldsymbol{0}$ as $|z| \to \infty$ we mean

$$\left. \begin{matrix} C_1(z), T_1(z) \to 0 \quad \text{as} \quad z \to \infty; \\ T_1'(z) \to 0 \quad \text{as} \quad z \to -\infty. \end{matrix} \right\} \tag{5.9}$$

In deciding which boundary conditions contain a term proportional to a_0 and hence should be included in $\mathscr{L}$ and $\mathscr{M}$ rather than B, it is essential to consider the ξ-dependent problem and then let $\xi \to 0$ (Wollkind 1968).

We use the *inner product*, $(\boldsymbol{U}, \boldsymbol{V})$, of

$$\boldsymbol{U} = [u_1(z), u_2(z), u_3(z), u_4, u_5]$$

and

$$\boldsymbol{V} = [v_1(z), v_2(z), v_3(z), v_4, v_5]$$

defined by

$$(\boldsymbol{U}, \boldsymbol{V}) = \int_0^\infty [u_1(z)\, v_1(z) + u_2(z)\, v_2(z)]\, \mathrm{d}z + \int_{-\infty}^0 u_3(z)\, v_3(z)\, \mathrm{d}z + u_4 v_4 + u_5 v_5. \tag{5.10}$$

We assume

$$\boldsymbol{v}^+(z) = [C_1^+(z), T_1^+(z), T_1'^+(z), \mathscr{S}_1^+, B],$$

where B is another constant to be determined. Then on inspection of (5.5) and (5.6) it becomes apparent that we should pick

$$B = C_1^+(0), \quad A = C_1(0), \quad B^+[\boldsymbol{v}^+(0)] = \begin{bmatrix} T_1^+(0) + \zeta_1^+ \\ T_1'^+(0) + n\zeta_1^+ \end{bmatrix} = \boldsymbol{0}, \tag{5.11}$$

$$\mathscr{L}^+[\boldsymbol{v}^+] = \begin{bmatrix} (D^2-\omega^2-D)\, C_1^+(z) \\ (D^2-\omega^2)\, T_1^+(z) \\ (D^2-\omega^2)\, T_1'^+(z) \\ DT_1^+(0)\,[M(K-1) - G - \gamma\omega^2] - DT_1'^+(0)\,[M(K-1) - G/n - \gamma\omega^2] - K(K-1)C_1^+(0) \\ DC_1^+(0) - KC_1^+(0) + M[DT_1^+(0) - DT_1'^+(0)] \end{bmatrix}, \tag{5.12}$$

and

$$\mathscr{M}^+[\boldsymbol{v}^+] = [C_1^+(z), 0, 0, (K-1)\, C_1^+(0), 0]. \tag{5.13}$$

We can now formulate the adjoint eigenvalue problem of (5.3) and (5.4), which is

$$\mathscr{L}^+[\boldsymbol{v}^+] = b_0 \mathscr{M}^+[\boldsymbol{v}^+], \quad B^+[\boldsymbol{v}^+(0)] = \mathbf{0}, \quad \boldsymbol{v}^+(z) \to \mathbf{0} \quad \text{as} \quad |z| \to \infty;$$

or

$$(D^2 - \omega^2 - D - b_0)\, C_1^+(z) = 0, \quad (D^2 - \omega^2)\, T_1^+(z) = 0 \quad (z > 0); \tag{5.14}$$

$$(D^2 - \omega^2)\, T_1'^+(z) = 0 \quad (z < 0); \tag{5.15}$$

with boundary conditions

$$\left.\begin{aligned} T_1'^+(0) + \zeta_1^+ = 0, \quad T_1'^+(0) + n\zeta_1^+ = 0, \\ DC_1^+(0) - KC_1^+(0) + M[DT_1^+(0) - DT_1'^+(0)] = 0, \\ DT_1^+(0)\,[M(K-1) - G - \gamma\omega^2] - DT_1'^+(0)\,[M(K-1) - G/n - \gamma\omega^2] \\ - (K-1)\,(K + b_0)\, C_1^+(0) = 0, \end{aligned}\right\} \tag{5.16}$$

and

$$\left.\begin{aligned} C_1^+(z) \to 0, \quad T_1^+(z) \to 0 \quad \text{as} \quad z \to \infty; \\ T_1'^+(z) \to 0 \quad \text{as} \quad z \to -\infty. \end{aligned}\right\} \tag{5.17}$$

We solve this problem in exactly the same manner as we did the eigenvalue problem for a_0 in § 4, obtaining the following equation for b_0:

$$b_0 = (T - \beta\omega^2)\, g(\omega^2, b_0) - K. \tag{5.18}$$

The corresponding eigenvector has components

$$\left.\begin{aligned} C_1^+(z) = M|\omega|\,(n+1)\, D^+ \exp\{-\tilde{m}_0(\omega^2, b_0)\, z\}/g(\omega^2, b_0), \quad \zeta_1^+ = D^+, \\ T_1^+(z) = -D^+ \exp\{-|\omega|\, z\}, \quad T_1'^+(z) = -nD^+ \exp\{|\omega|\, z\}, \end{aligned}\right\} \tag{5.19}$$

where $\tilde{m}_0(\omega^2, b_0) = -\frac{1}{2} + (\frac{1}{4} + \omega^2 + b_0)^{\frac{1}{2}}$ and D^+ is a constant.

Since (5.18) for b_0 is the same as equation (4.14) for a_0 we conclude that

$$a_0 = b_0. \tag{5.20}$$

Note that completeness of both the original and adjoint eigenvectors would imply $a_0 = b_0$. To attempt to prove such completeness would be tangential to our present purposes, so we shall regard (5.20) as an informal check on our work.

Thus

$$\mathscr{L}^+[\boldsymbol{v}^+] = a_0 \mathscr{M}^+[\boldsymbol{v}^+], \quad B^+[\boldsymbol{v}^+(0)] = \mathbf{0}, \quad \boldsymbol{v}^+(z) \to \mathbf{0} \quad \text{as} \quad |z| \to \infty \tag{5.21}$$

and in (5.19) we can replace b_0 by a_0. We now recall that the eigenvectors of the linear problem,

$$\mathscr{L}[\boldsymbol{v}] = a_0 \mathscr{M}[\boldsymbol{v}], \quad B[\boldsymbol{v}(0)] = \mathbf{0}, \quad \boldsymbol{v}(z) \to \mathbf{0} \quad \text{as} \quad |z| \to \infty,$$

are given by (4.15) and use this to evaluate the normalization constant DD^+ such that (5.6) will be satisfied:

$$(\mathscr{M}[\boldsymbol{v}], v^+) = \int_0^\infty \frac{D(1-K)}{g}\,(T - \beta\omega^2)\, M|\omega|\,(n+1)\, D^+ \exp\{-2(\tfrac{1}{4} + \omega^2 + a_0)^{\frac{1}{2}} z\}\,\mathrm{d}z + \frac{D(K-1)M}{g}\,|\omega|\,(n+1)\, D^+ = 1. \tag{5.22}$$

This implies that

$$DD^+ = \frac{2g(\omega^2, a_0)\,(\frac{1}{4} + \omega^2 + a_0)^{\frac{1}{2}}}{M(K-1)\,|\omega|\,(n+1)\,[2(\frac{1}{4} + \omega^2 + a_0)^{\frac{1}{2}} - (T - \beta\omega^2)]}. \tag{5.23}$$

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6. The nonlinear stability problem

In § 4 we examined the stability of the planar interface solution of the basic equations, (4.1) to (4.4), to disturbances satisfying the *linearized* perturbation equations (*infinitesimal disturbances*). In this section we investigate the stability of the planar interface solution to disturbances satisfying the full *nonlinear* perturbation equations (*finite amplitude disturbances*).

Generalizing § 4, we consider solutions of the basic equations of the form of (4.6) where now

$$\boldsymbol{v}'(x, z, t; \epsilon) = \sum_{n=1}^{\infty} \epsilon^n \boldsymbol{v}_n(x, z, t), \tag{6.1}$$

with

$$\boldsymbol{v}_n(x, z, t) = [C_n(x, z, t),\ T_n(x, z, t),\ T'_n(x, z, t),\ \zeta_n(x, z, t)]. \tag{6.2}$$

We wish to determine the spatial and time dependence of the quantities $\boldsymbol{v}_n$. In an attempt to motivate the formal procedure which we shall follow, we substitute the type of solution introduced above into boundary condition (4.3*b*):

$$T(x, \epsilon\zeta, t) = T'(x, \epsilon\zeta, t). \tag{6.3}$$

We then obtain, using (4.5), (6.1), (6.2) and (6.3),

$$\begin{aligned} 1 + M + G\epsilon\zeta + \epsilon T_1(x, \epsilon\zeta, t) + \epsilon^2 T_2(x, \epsilon\zeta, t) + \epsilon^3 T_3(x, \epsilon\zeta, t) + \ldots \\ = 1 + M + Gn^{-1}\epsilon\zeta + \epsilon T'_1(x, \epsilon\zeta, t) + \epsilon^2 T'_2(x, \epsilon\zeta, t) + \epsilon^3 T'_3(x, \epsilon\zeta, t) + \ldots. \end{aligned} \tag{6.4}$$

Making use of the fact that

$$\epsilon\zeta(x, t; \epsilon) = 0 + \sum_{n=1}^{\infty} \epsilon^n \zeta_n(x, t),$$

expanding the quantities T_n and T'_n of (6.4) in Taylor series about $z = \epsilon\zeta = 0$, collecting terms of like powers of ϵ and equating these to zero, we obtain

$$O(1): \quad 0 = 0, \tag{6.5}$$

$$O(\epsilon): \quad T_1(x, 0, t) - T'_1(x, 0, t) + \zeta_1(x, t)\, G(n-1)/n = 0, \tag{6.6}$$

$$O(\epsilon^2): \quad T_2(x, 0, t) - T'_2(x, 0, t) + \zeta_2(x, t)\, G(n-1)/n = [dT'_1(x, 0, t) - dT_1(x, 0, t)]\, \zeta_1(x, t), \tag{6.7}$$

$$\begin{aligned} O(\epsilon^3): \quad & T_3(x, 0, t) - T'_3(x, 0, t) + \zeta_3(x, t)\, G(n-1)/n \\ & = [dT'_1(x, 0, t) - dT_1(x, 0, t)]\, \zeta_2(x, t) + \tfrac{1}{2}[d^2T'_1(x, 0, t) - d^2T_1(x, 0, t)]\, \zeta_1^2(x, t) \\ & \quad + [dT'_2(x, 0, t) - dT_2(x, 0, t)]\, \zeta_1(x, t), \end{aligned} \tag{6.8}$$

where $d = \partial/\partial z$.

Note that (6.5) is satisfied identically, which is a consequence of $\boldsymbol{v}_0(z)$ being an exact solution of the basic equations. Also note that the left-hand sides of (6.6), (6.7) and (6.8) are of the same form and that (6.6) is homogeneous while (6.7), (6.8) are inhomogeneous.

We assume

$$\boldsymbol{v}_1(x, z, t) = A(t) \cos \omega x \boldsymbol{v}_{11}(z), \tag{6.9}$$

where $\boldsymbol{v}_{11}(z) = [C_{11}(z), T_{11}(z), T'_{11}(z), \zeta_{11}]$, and $A(t)$ is an unknown amplitude function such that

$$\max_t |A(t)| = 1.$$

Owing to the presence of nonlinear terms such as those in (6.7) and (6.8) it is not possible to make use of the superposition principle. We therefore cannot expect that a study of (6.9) will allow us to draw conclusions concerning an arbitrary periodic disturbance in x as it does with the linear

problem. By examining the $\cos \omega x$ spatial term we then determine the nonlinear stability behaviour resulting from a disturbance consisting primarily of just this *one* component. Thus the nonlinear analysis is not as general as is the linear one.

Placing (6.9) into (6.6) we arrive at

$$T_{11}(0) - T'_{11}(0) + \zeta_{11} G(n-1)/n = 0 \tag{6.10}$$

upon cancellation of $A(t) \cos \omega x$. Note that this is the same equation $T_1(z)$, $T'_1(z)$ and ζ_1 satisfied for the linear problem (equation (4.9)).

Substituting (6.9) into (6.7) we obtain

$$T_2(x, 0, t) - T'_2(x, 0, t) + \zeta_2(x, t)\, G(n-1)/n = \tfrac{1}{2}[D T'_{11}(0) - D T_{11}(0)]\, A^2(t)\, (1 + \cos 2\omega x). \tag{6.11}$$

It turns out that the inhomogeneous terms for *all* the $O(\epsilon^2)$ boundary conditions have the form of the right side of (6.11) so we look for $\boldsymbol{v}_2(x, z, t)$ of the form

$$\boldsymbol{v}_2(x, z, t) = A^2(t)\, [\boldsymbol{v}_{20}(z) + \boldsymbol{v}_{22}(z) \cos 2\omega x], \tag{6.12}$$

where from now on we use the notation

$$\boldsymbol{v}_{nm}(z) = [C_{nm}(z), T_{nm}(z), T'_{nm}(z), \zeta_{nm}].$$

Substituting (6.9) and (6.12) into (6.8) and collecting terms we obtain

$$T_3(x, 0, t) - T'_3(x, 0, t) + \zeta_3(x, t)\, G(n-1)/n = A^3(t)\, [f_1 \cos \omega x + f_3 \cos 3\omega x], \tag{6.13}$$

where f_1, f_3 are functions of $\boldsymbol{v}_{20}(0)$, $\boldsymbol{v}_{22}(0)$ and $\boldsymbol{v}_{11}(0)$.

This leads us to look for $\boldsymbol{v}_3(x, z, t)$ of the form

$$\boldsymbol{v}_3(x, z, t) = A^3(t)\, [\boldsymbol{v}_{31}(z) \cos \omega x + \boldsymbol{v}_{33}(z) \cos 3\omega x]. \tag{6.14}$$

Thus from (6.9), (6.12) and (6.14) we deduce that

$$\begin{aligned} \boldsymbol{v}(x, z, t; \epsilon) = {} & \epsilon A(t)\, \boldsymbol{v}_{11}(z) \cos \omega x + \epsilon^2 A^2(t)\, [\boldsymbol{v}_{20}(z) + \boldsymbol{v}_{22}(z) \cos 2\omega x] \\ & + \epsilon^3 A^3(t)\, [\boldsymbol{v}_{31}(z) \cos \omega x + \boldsymbol{v}_{33}(z) \cos 3\omega x] + \sum_{n=4}^{\infty} \epsilon^n A^n(t)\, \boldsymbol{v}_n(x, z). \end{aligned} \tag{6.15}$$

Using (6.15) and being motivated by the forms of the five component vectors of § 5, we seek solutions of the basic equations (4.1) to (4.4) of the form

$$\begin{aligned} \boldsymbol{g}(x, z, t; \epsilon) = {} & \boldsymbol{g}_0(z) + \epsilon A(t)\, \boldsymbol{g}_{11}(z) \cos \omega x + \epsilon^2 A^2(t)\, [\boldsymbol{g}_{20}(z) + \boldsymbol{g}_{22}(z) \cos 2\omega x] \\ & + \epsilon^3 A^3(t)\, [\boldsymbol{g}_{31}(z) \cos \omega x + \boldsymbol{g}_{33}(z) \cos 3\omega x] + \sum_{n=4}^{\infty} \epsilon^n A^n(t)\, \boldsymbol{g}_n(x, z), \end{aligned} \tag{6.16}$$

where

$$\boldsymbol{g}(x, z, t; \epsilon) = \begin{bmatrix} C(x, z, t; \epsilon) \\ T(x, z, t; \epsilon) \\ T'(x, z, t; \epsilon) \\ \epsilon\zeta(x, t; \epsilon) \\ C(x, 0, t; \epsilon) \end{bmatrix}, \quad \boldsymbol{g}_0(z) = \begin{bmatrix} C_0(z) \\ T_0(z) \\ T'_0(z) \\ 0 \\ C_0(0) \end{bmatrix}, \quad \boldsymbol{g}_{ij}(z) = \begin{bmatrix} C_{ij}(z) \\ T_{ij}(z) \\ T'_{ij}(z) \\ \zeta_{ij} \\ C_{ij}(0) \end{bmatrix}, \tag{6.17}$$

and

$$\epsilon\, \mathrm{d}A(t)/\mathrm{d}t = \epsilon \dot{A}(t) = a_0 \epsilon A(t) - a_1 \epsilon^3 A^3(t) + \sum_{n=2}^{\infty} a_n [\epsilon A(t)]^{2n+1}. \tag{6.18}$$

In order to motivate (6.18), we note that when (6.16) and (6.17) are substituted in the basic equations the time dependence appears as $\epsilon \dot{A}(t)$ and powers of $\epsilon A(t)$. Hence it is natural to assume an expansion for $\epsilon \dot{A}(t)$ in powers of $\epsilon A(t)$. Another means of motivating (6.18) is to note that in

the linear development of § 4, $A(t)$ is such that $\epsilon\dot{A}(t)/\epsilon A(t) = \sigma$ where σ, the growth rate, is a constant. For nonlinear stability we assume that σ is a slowly varying time-dependent function such that

$$\sigma(t) = a_0 + \sum_{n=1}^{\infty} \tilde{a}_n \epsilon^n A^n(t).$$

There are no even powers of $\epsilon A(t)$ in the expansion of $\epsilon\dot{A}(t)$ given in (6.18). If we assumed a full power series expansion, solvability conditions for the systems to be developed below would show that the coefficients of $[\epsilon A(t)]^{2K}$, $K = 1, 2, 3, \ldots$, were zero.

For additional discussion of some of the finer points of this approach see Eckhaus (1965) and Segel (1966). In introducing extra components evaluated at $z = 0$, we have followed Scanlon & Segel (1967).

If use is made of (6.16) to (6.18), and the boundary conditions are expanded in a Taylor series about $z = \epsilon\zeta(x, t) = 0$, then there results after some tedious computation a set of differential equations and boundary conditions for each ϵ^n; $n = 1, 2, 3$. The system for $n = 0$ is satisfied identically since $\boldsymbol{g}_0(z)$ is the exact planar interface solution with components

$$C_0(z) = 1 + (K-1)\,[1 - \exp(-z)], \quad T_0(z) = 1 + M + Gz, \quad T_0'(z) = 1 + M + Gn^{-1}z, \quad \zeta_0 = 0.$$

We define the following operators

$$\mathscr{L}_p[\boldsymbol{g}_{ij}(z)] = \begin{bmatrix} (D^2 - p^2\omega^2 + D)\, C_{ij}(z) \\ (D^2 - p^2\omega^2)\, T_{ij}(z) \\ (D^2 - p^2\omega^2)\, T'_{ij}(z) \\ nD\,T'_{ij}(0) - DT_{ij}(0) \\ DC_{ij}(0) - (K-1)\,C_{ij}(0) - (K-1)\,K\zeta_{ij} \end{bmatrix} \quad (p = 0, 1, 2, \ldots), \tag{6.19}$$

$$\mathscr{M}[\boldsymbol{g}_{ij}(z)] = \begin{bmatrix} C_{ij}(z) \\ 0 \\ 0 \\ 0 \\ (K-1)\,\zeta_{ij} \end{bmatrix}; \quad B_p[\boldsymbol{g}_{ij}(0)] = \begin{bmatrix} T_{ij}(0) - MC_{ij}(0) + \zeta_{ij}[G + p^2\omega^2\gamma - M(K-1)] \\ T_{ij}(0) - T'_{ij}(0) + \zeta_{ij}G(n-1)/n \end{bmatrix},$$

$$(p = 0, 1, 2, \ldots); \tag{6.20}$$

and by $\boldsymbol{g}_{ij}(z) \to \boldsymbol{0}$ as $|z| \to \infty$ we mean

$$C_{ij}(z), T_{ij}(z) \to 0 \quad \text{as} \quad z \to \infty \qquad \text{and} \qquad T'_{ij}(z) \to 0 \quad \text{as} \quad z \to -\infty. \tag{6.21}$$

Using these operators we can write the differential equations and boundary conditions for the various orders of ϵ as follows:

For $O(\epsilon)$ one problem results proportional to $A(t)\cos\omega x$ of the form

$$\mathscr{L}_1[\boldsymbol{g}_{11}(z)] = a_0\mathscr{M}[\boldsymbol{g}_{11}(z)], \quad B_1[\boldsymbol{g}_{11}(0)] = \boldsymbol{0}, \tag{6.22}$$
$$\boldsymbol{g}_{11}(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty.$$

For $O(\epsilon^2)$ two problems result, one proportional to $A^2(t)$ and the other to $A^2(t)\cos 2\omega x$, of the forms

$$\mathscr{L}_0[\boldsymbol{g}_{20}(z)] - 2a_0\mathscr{M}[\boldsymbol{g}_{20}(z)] = \boldsymbol{r}[\boldsymbol{g}_0(0), \boldsymbol{g}_{11}(0)];$$
$$B_0[\boldsymbol{g}_{20}(0)] = \boldsymbol{h}[\boldsymbol{g}_0(0), \boldsymbol{g}_{11}(0)]; \qquad \boldsymbol{g}_{20}(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty, \tag{6.23}$$

and

$$\mathscr{L}_2[\boldsymbol{g}_{22}(z)] - 2a_0\mathscr{M}[\boldsymbol{g}_{22}(z)] = \boldsymbol{b}[\boldsymbol{g}_0(0), \boldsymbol{g}_{11}(0)];$$
$$B_2[\boldsymbol{g}_{22}(0)] = \boldsymbol{h}[\boldsymbol{g}_0(0), \boldsymbol{g}_{11}(0)]; \qquad \boldsymbol{g}_{22}(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty; \tag{6.24}$$

respectively. In (6.23) and (6.24) $\boldsymbol{b}$, $\boldsymbol{r}$ and $\boldsymbol{h}$ are vectors containing components of $\boldsymbol{g}_0(z)$ and $\boldsymbol{g}_{11}(z)$ and their derivatives evaluated at $z = 0$. The explicit forms of (6.23) and (6.24) are given in Wollkind (1968).

At $O(\epsilon^3)$ two problems result, one proportional to $A^3(t)\cos\omega x$ and the other to $A^3(t)\cos 3\omega x$. We shall only consider the first of these, which is of the form

$$\mathscr{L}_1[\boldsymbol{g}_{31}(z)] - 3a_0\mathscr{M}[\boldsymbol{g}_{31}(z)] + a_1\mathscr{M}[\boldsymbol{g}_{11}(z)] = a_0\begin{bmatrix}0\\0\\0\\0\\d_0\end{bmatrix} + \begin{bmatrix}0\\0\\0\\d_2\\d_3\end{bmatrix}, \tag{6.25a}$$

$$B_1[\boldsymbol{g}_{31}(0)] = \begin{bmatrix}d_1\\d_4\end{bmatrix}, \quad \boldsymbol{g}_{31}(z) \to \boldsymbol{0} \quad \text{as} \quad |z| \to \infty, \tag{6.25b}$$

where $d_i = d_i[\boldsymbol{g}_0(0), \boldsymbol{g}_{11}(0), \boldsymbol{g}_{20}(0), g_{22}(0)]$, $i = 0, 1, 2, 3, 4$ (see Wollkind 1968). We shall investigate each of these problems.

The $O(\epsilon)$ problem

Except for notation the $O(\epsilon)$ problem is the same as the linear stability problem. If one compares the form of the operators in (6.22), as defined by (6.19) to (6.21), with those of the linear eigenvalue problem of § 5 it will be seen that $\mathscr{L}_1 = \mathscr{L}$, $\mathscr{M} = \mathscr{M}$, and $B_1 = B$. Thus (6.22) is an eigenvalue problem for a_0 with associated eigenvectors $\boldsymbol{g}_{11}(z)$ and is identical in form to that of the linear problem. Therefore a_0 satisfies (4.14), or

$$a_0 = (T - \beta\omega^2)\, g(\omega^2, a_0) - K, \tag{6.26}$$

with, as in (4.15), associated eigenvector $\boldsymbol{g}_{11}(z) = \boldsymbol{v}_1(z)$. Noting that

$$\epsilon\zeta(x,t) = \epsilon DA(t)\cos\omega x + O(\epsilon^2) \quad \text{as} \quad \epsilon \to 0,$$

we wish to normalize in such a manner that ϵ is the coefficient of $\cos\omega x$ to any order of ϵ. We require

$$\max_t |\epsilon\zeta(x,t)|_m = \epsilon \quad \text{where} \quad |\epsilon\zeta(x,t)|_m = \lim_{L\to\infty}\frac{1}{L}\left|\int_{-L}^{L}\epsilon\zeta(x,t)\cos\omega x\,\mathrm{d}x\right|; \tag{6.27}$$

this implies that $D = 1$. We now choose for a_0 that root of (6.26) such that for $T > T_C$, $a_0 > 0$.

Since (6.22) is equivalent to the linear eigenvalue problem, the adjoint problem for (6.22) is equivalent to the adjoint eigenvalue problem of § 5. In what follows we will designate $\mathscr{L}^+$, B^+ and $\boldsymbol{v}^+(z)$ of that section by $\mathscr{L}_1^+$, B_1^+ and $\boldsymbol{g}_{11}^+(z)$ respectively. Note that the associated adjoint eigenvector $\boldsymbol{g}_{11}^+(z)$ is given explicitly by (5.19).

The $O(\epsilon^2)$ problems

First we consider the system (6.23) for the so-called mean motion terms at order ϵ^2. The quantity $\epsilon^2A^2(t)\,\boldsymbol{g}_{20}(z)$ represents the alteration of the mean of the basic solution due to the type of perturbation of § 6. Writing out the differential equations for $\boldsymbol{g}_{20}(z)$ we obtain

$$[D^2 + D - 2a_0]\,C_{20}(z) = 0, \quad D^2T_{20}(z) = 0 \quad \text{for} \quad z > 0; \qquad D^2T'_{20}(z) = 0 \quad \text{for} \quad z < 0. \tag{6.28}$$

Equation (6.28) has solutions

$$\left.\begin{aligned} C_{20}(z) &= A_{20}\,\mathrm{e}^{-n_0 z}, \quad n_0 = \tfrac{1}{2} + (\tfrac{1}{4} + 2a_0)^{\frac{1}{2}},\\ \zeta_{20} &= D_{20}, \quad T_{20}(z) = B_{20}z + C_{20}, \quad T'_{20}(z) = B'_{20}z + C'_{20}, \end{aligned}\right\} \tag{6.29}$$

where n_0 has been chosen to satisfy $C_{20}(z) \to 0$ as $z \to +\infty$ and A_{20}, B_{20}, C_{20}, B'_{20}, C'_{20} and D_{20} are constants. We also must satisfy the conditions $T_{20}(z) \to 0$ as $z \to +\infty$ and $T'_{20}(z) \to 0$ as $z \to -\infty$. Before we consider them however, we shall examine the boundary conditions at $z = 0$. We obtain upon substitution of (6.29) into these boundary conditions the following:

$$MA_{20} - C_{20} + D_{20}[M(K-1) - G] = \tfrac{1}{2}M(K-1)\,[\tfrac{1}{2} - m_0(T - \beta\omega^2)] + |\omega|\,G(n-1)/2(n+1), \quad (6.30a)$$

$$nB'_{20} - B_{20} = 0, \quad (6.30b)$$

$$[n_0 + K - 1]\,A_{20} + D_{20}[(K-1)\,(2a_0 + K)]$$
$$= \tfrac{1}{4}(K-1)\,[K - 2a_0(K-1)] + \tfrac{1}{2}[(K-1)\,(T - \beta\omega^2)\,\{(K-1)\,a_0 - m_0 g + \omega^2\}], \quad (6.30c)$$

$$C_{20} - C'_{20} + D_{20}[(n-1)\,G/n] = -|\omega|\,G(n-1)^2/2n(n+1). \quad (6.30d)$$

In order for the solution of (6.29) to satisfy the remaining boundary condition as $|z| \to \infty$ it would be necessary for

$$B_{20} = C_{20} = B'_{20} = C'_{20} = 0. \quad (6.31)$$

If we assume that (6.31) is true, the four equations of (6.30) will reduce to three equations ((6.30b) is satisfied identically) in the two unknowns A_{20} and D_{20}. If this procedure is to be valid, the reduced system must be consistent to $O(1)$. Later we shall show that

$$a_0 = O(\epsilon^2), \quad (6.32)$$

hence
$$A_{20}(a_0) = A_{20}(0) + O(\epsilon^2), \quad D_{20}(a_0) = D_{20}(0) + O(\epsilon^2). \quad (6.33)$$

Noting that
$$n_0 + K - 1 = K + O(a_0), \quad (6.34)$$

and neglecting all terms proportional to a_0 in (6.30) we obtain

$$MA_{20}(0) + D_{20}(0)\,[M(K-1) - G] = \tfrac{1}{2}M(K-1)\,[\tfrac{1}{2} - m_0(T - \beta\omega^2)] + |\omega|\,G(n-1)/2(n+1), \quad (6.35a)$$

$$KA_{20}(0) + D_{20}(0)\,[(K-1)\,K] = K(K-1)/4 + \tfrac{1}{2}[(K-1)\,(T - \beta\omega^2)\,(\omega^2 - m_0 g)], \quad (6.35b)$$

$$D_{20} = |\omega|\,(1-n)/2(n+1). \quad (6.35c)$$

In the above, such conditions as $m_0 = m_0(\omega^2, a_0)$ and $g(\omega^2, a_0)$ are to be understood, when contained in (6.35) and (6.36), as evaluated at $a_0 = 0$. Solving for $A_{20}(0)$ and $D_{20}(0)$ from (6.35a) and (6.35b) we find that

$$A_{20}(0) = |\omega|\,(n-1)\,(K-1)/2(n+1) + \tfrac{1}{4}(K-1) - \tfrac{1}{2}m_0(K-1)\,(T - \beta\omega^2), \quad (6.36)$$

$$D_{20}(0) = |\omega|\,(1-n)/2(n+1), \quad (6.37)$$

where use has been made of the relations $g = m_0 + K - 1$ and $m_0^2 - m_0 - \omega^2 = 0$. Thus system (6.35) is consistent.

$\boldsymbol{g}_{20}(z)$ has components to $O(\epsilon^2)$

$$C_{20}(z) = A_{20}(0)\,\mathrm{e}^{-z}, \quad T_{20}(z) = 0, \quad T'_{20}(z) = 0, \quad \zeta_{20} = D_{20}(0), \quad (6.38)$$

where $A_{20}(0)$ and $D_{20}(0)$ are given by (6.36) and (6.37). The mean of $\boldsymbol{g}(x, z, t; \epsilon)$ is given by

$$\lim_{L\to\infty} \frac{1}{2L}\int_{-L}^{L} \boldsymbol{g}(x, z, t; \epsilon)\,\mathrm{d}x = \boldsymbol{g}_0(z) + \epsilon^2 \boldsymbol{g}_{20}(x) + O(\epsilon^4),$$

as mentioned at the start of this section. From (6.38) the mean of the temperature gradients for the liquid and solid at $z = 0$ are given to $O(\epsilon^2)$ by G and G/n respectively, while the mean position of the interface is now at

$$z = \epsilon^2 A^2(t)\,D_{20}(0) = \epsilon^2 A^2(t)\,|\omega|\,(1-n)/2(n+1). \quad (6.39)$$

Since $n \simeq 2$, the quantity on the right of (6.39) is negative. Thus a nonlinear effect is that the mean position of the interface lags behind its position of $z = 0$ as determined by linear theory.

The second $O(\epsilon^2)$ system is that given by (6.24) for $\boldsymbol{g}_{22}(z)$. $\boldsymbol{g}_{22}(z)$ has components:

$$\left.\begin{aligned} C_{22}(z) &= A_{22}\,\mathrm{e}^{-p_0 z}, \quad p_0 = \tfrac{1}{2} + (\tfrac{1}{4} + 4\omega^2 + 2a_0)^{\frac{1}{2}}, \\ T_{22}(z) &= B_{22}\,\mathrm{e}^{-2|\omega| z}, \quad T'_{22}(z) = C_{22}\,\mathrm{e}^{2|\omega| z}, \quad \zeta_{22} = D_{22}. \end{aligned}\right\} \tag{6.40}$$

As in the system for $\boldsymbol{g}_{20}(z)$ we note that

$$[A_{22}, B_{22}, C_{22}, D_{22}]\,(a_0) = [A_{22}, B_{22}, C_{22}, D_{22}]\,(0) + O(\epsilon^2).$$

For explicit values of these constants see Wollkind (1968).

The $O(\epsilon^3)$ problem

As mentioned earlier in this section we shall only consider the problem for $\boldsymbol{g}_{31}(z)$ given by (6.25). Applying the usual Fredholm conditions (Ince 1956) to this problem we take the inner product of (6.25a) with the adjoint eigenvector

$$\boldsymbol{g}^{+}_{11}(z) = [C^{+}_{11}(z), T^{+}_{11}(z), T'^{+}_{11}(z), \zeta^{+}_{11}, C^{+}_{11}(0)] \tag{6.41}$$

and obtain

$$\begin{aligned}(\mathscr{L}_1[\boldsymbol{g}_{31}(z)],\, \boldsymbol{g}^{+}_{11}(z)) - 3a_0(\mathscr{M}[\boldsymbol{g}_{31}(z)],\, \boldsymbol{g}^{+}_{11}(z)) + a_1(\mathscr{M}[\boldsymbol{g}_{11}(z)], \boldsymbol{g}^{+}_{11}(z)) \\ = a_0 d_0 C^{+}_{11}(0) + d_2\zeta^{+}_{11} + d_3 C^{+}_{11}(0).\end{aligned} \tag{6.42}$$

We recall that

$$\mathscr{L}^{+}_1[\boldsymbol{g}^{+}_{11}(z)] = a_0\mathscr{M}^{+}[\boldsymbol{g}^{+}_{11}(z)], \quad (\mathscr{M}[\boldsymbol{g}_{11}(z)],\, \boldsymbol{g}^{+}_{11}(z)) = 1. \tag{6.43}$$

Integrating by parts and using (6.25b) one can show that

$$(\mathscr{L}_1[\boldsymbol{g}_{31}(z)],\, \boldsymbol{g}^{+}_{11}(z)) = d_1 D T^{+}_{11}(0) - (d_1 - d_4)\, D T'^{+}_{11}(0) + (\boldsymbol{g}_{31}(z),\, \mathscr{L}^{+}_1[\boldsymbol{g}^{+}_{11}(z)]). \tag{6.44}$$

By substituting (6.44) into (6.42), making use of (6.43), and noting that

$$(\mathscr{M}[\boldsymbol{g}_{31}(z)],\, \boldsymbol{g}^{+}_{11}(z)) = (\boldsymbol{g}_{31}(z), \mathscr{M}^{+}[\boldsymbol{g}_{31}(z)]),$$

we obtain

$$\begin{aligned}-[2(\mathscr{M}[\boldsymbol{g}_{31}(z)],\, \boldsymbol{g}^{+}_{11}(z)) + d_0 C^{+}_{11}(0)]\, a_0 + a_1 \\ = -d_1 D T^{+}_{11}(0) + (d_1 - d_4)\, D T'^{+}_{11}(0) + d_2\zeta^{+}_{11} + d_3 C^{+}_{11}(0) = S_{31}.\end{aligned} \tag{6.45}$$

Taking the limit of (6.45) as $T \to T_{\mathrm{C}}$ and $\omega \to \omega_{\mathrm{C}}$, and making use of the fact that in the above limit $a_0 \to 0$, we arrive at the following determination of a_1:

$$a_1 = \lim_{\substack{T \to T_{\mathrm{C}} \\ \omega \to \omega_{\mathrm{C}}}} S_{31} = \lim_{\substack{T \to T_{\mathrm{C}} \\ \omega \to \omega_{\mathrm{C}}}} \{-d_1 D T^{+}_{11}(0) + (d_1 - d_4)\, D T'^{+}_{11}(0) + d_2\zeta^{+}_{11} + d_3 C^{+}_{11}(0)\}. \tag{6.46}$$

We find after some algebra

$$\begin{aligned}S_{31} = D^{+}|\omega|\,\{&[\tfrac{1}{2}M(K-1)\,(1-K/g) + 2|\omega|\,(n-1)\,G/(1+n)^2 - M(K-1)\,\omega^2(T-\beta\omega^2)/g]\,D_{22} \\ &- \tfrac{1}{8}[3\gamma\omega^4 + M(K-1)\,\{1 - K/g - 2\omega^2 m_0(T-\beta\omega^2)/g\}] \\ &+ M[\tfrac{1}{2}p_0(1-\tilde{g}/g) + \omega^2/g]\,A_{22} + M(K-1)\,(1-K/g)\,D_{20} + M(1-K/g)\,A_{20}\},\end{aligned} \tag{6.47}$$

where $\tilde{g} = p_0 + K - 1$.

We thus arrive at the following expression for the Landau constant, a_1,

$$\begin{aligned} a_1 = {} & 2g(\tfrac{1}{2}+\omega_C^2)\,[2(\tfrac{1}{4}+\omega_C^2)-(T_C-\beta\omega_C^2)]^{-1}\{[(T_C-4\beta\omega_C^2)\,\tilde{g}-K]^{-1} \\ & \times([\tfrac{1}{2}(1-K/g)+(n-1)\,\omega_C(1-T_C)/(1+n)-\omega_C^2(T_C-\beta\omega_C^2)/g]\,[-\tfrac{1}{4}K \\ & +\tfrac{1}{2}(m_0 g+\omega_C^2)\,(T_C-\beta\omega_C^2)+\tilde{g}\{\tfrac{1}{4}-\tfrac{1}{2}m_0(T_C-\beta\omega_C^2)\}] \\ & +[\tfrac{1}{2}p_0(1-\tilde{g}/g)+\omega_C^2/g]\,\{[\tfrac{1}{4}K-\tfrac{1}{2}(m_0 g+\omega_C^2)\,(T_C-\beta\omega_C^2)]\,[T_C-4\beta\omega_C^2] \\ & +K[-\tfrac{1}{4}+\tfrac{1}{2}m_0(T_C-\beta\omega_C^2)]\})+\tfrac{1}{8}[2\omega_C^2 m_0(T_C-\beta\omega_C^2)/g]-\tfrac{3}{8}\beta\omega_C^4 \\ & +(1-K/g)\,[\tfrac{1}{8}-\tfrac{1}{2}m_0(T_C-\beta\omega_C^2)]\}, \end{aligned} \tag{6.48}$$

where quantities such as $[g, m_0, \tilde{g}, p_0]$ (ω^2, a_0) in (6.48) are understood to be evaluated at $\omega = \omega_C$ and $a_0 = 0$.

With the value of a_1 chosen as in (6.48), which was determined from the solvability condition for system (6.25), we can find a particular solution denoted by $\boldsymbol{g}_{31}^{(P)}(z)$ which satisfies (6.25). The total solution of (6.25) is then

$$\boldsymbol{g}_{31}(z) = \boldsymbol{g}_{31}^{(C)}(z) + \boldsymbol{g}_{31}^{(P)}(z), \tag{6.49}$$

where the *complementary* solution denoted by $\boldsymbol{g}_{31}^{(C)}(z)$ satisfies (6.25) for *homogeneous* conditions or

$$\mathscr{L}_1[\boldsymbol{g}_{31}^{(C)}(z)] - 3a_0\mathscr{M}[\boldsymbol{g}_{31}^{(C)}(z)] = 0, \tag{6.50a}$$

$$B_1[\boldsymbol{g}_{31}^{(C)}(z)] = 0, \qquad \boldsymbol{g}_{31}^{(C)}(z) \to 0 \quad \text{as} \quad |z| \to \infty. \tag{6.50b}$$

For the $O(\epsilon^2)$ systems we implicitly assumed $\boldsymbol{g}_{20}^{(C)}(z) = \boldsymbol{g}_{22}^{(C)}(z) = 0$. Note in this system that except for the presence of the '3' in (6.50*a*), (6.50) is identical with the $O(\epsilon)$ problem. It therefore has a solution $\boldsymbol{g}_{31}^{(C)}$ with components

$$\zeta_{31}^{(C)} = C, \quad C_{31}^{(C)}(z) = C(1-K)\,(T-\beta\omega^2)\,\mathrm{e}^{-m_0(\omega^2,\,3a_0)z},$$

$$T_{31}^{(C)}(z) = C(1-n)\,G^1\,\mathrm{e}^{-|\omega|z}/(1+n), \quad T_{31}^{(C)\prime}(z) = C(n-1)\,\mathrm{e}^{+|\omega|z}/n(1+n).$$

To satisfy (6.27) we must take $C = -\zeta_{31}^{(P)}$.

7. The amplitude equation

The equation which the amplitude function $A(t)$ satisfies to order ϵ^3 is

$$\epsilon\dot{A}(t) = a_0\epsilon A(t) - a_1\epsilon^3 A^3(t). \tag{7.1}$$

In order to investigate the stability of the planar interface solution to the type of perturbations of § 6 we must examine the behaviour of $A(t)$ as $t \to \infty$. We shall consider (7.1) in the form

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(\epsilon A)^2 = a_0(\epsilon A)^2 - a_1(\epsilon A)^4 \equiv f(A). \tag{7.2}$$

We shall consider the four cases represented by the possibility of a_0, the growth rate, and a_1, the Landau constant, being either positive or negative. We shall examine the critical points of (7.2), i.e. those A_0 such that $f(A_0) = 0$—and determine their stability in the respective cases.

These cases are portrayed schematically in figure 5 in which $\mathrm{d}(\epsilon A)^2/\mathrm{d}t$ is plotted against $(\epsilon A)^2$. The arrows denote how an initial disturbance will behave as time increases. The cases are as follows:

(*a*) $a_0 > 0$, $a_1 > 0$. In this case $\mathrm{d}(\epsilon A)^2/\mathrm{d}t = 0$ where $(\epsilon A)^2 = a_0/a_1$. By studying (*a*) of figure 5 it

can be seen that this is a *stable equilibrium solution*. Another way to show this is to consider the solution

$$\epsilon A e = (a_0/a_1)^{\frac{1}{2}}, \tag{7.3}$$

and do a local linear stability analysis of it by substituting

$$\epsilon A(t) = \epsilon A e + \epsilon A'(t), \tag{7.4}$$

into (7.1) and neglecting all but linear terms in $A'(t)$. We then obtain

$$\mathrm{d}[(\epsilon A'(t)]/\mathrm{d}t = -2a_0 \epsilon A'(t), \quad \text{so} \quad \epsilon A'(t) = \epsilon A'(0)\, \mathrm{e}^{-2a_0 t}. \tag{7.5}$$

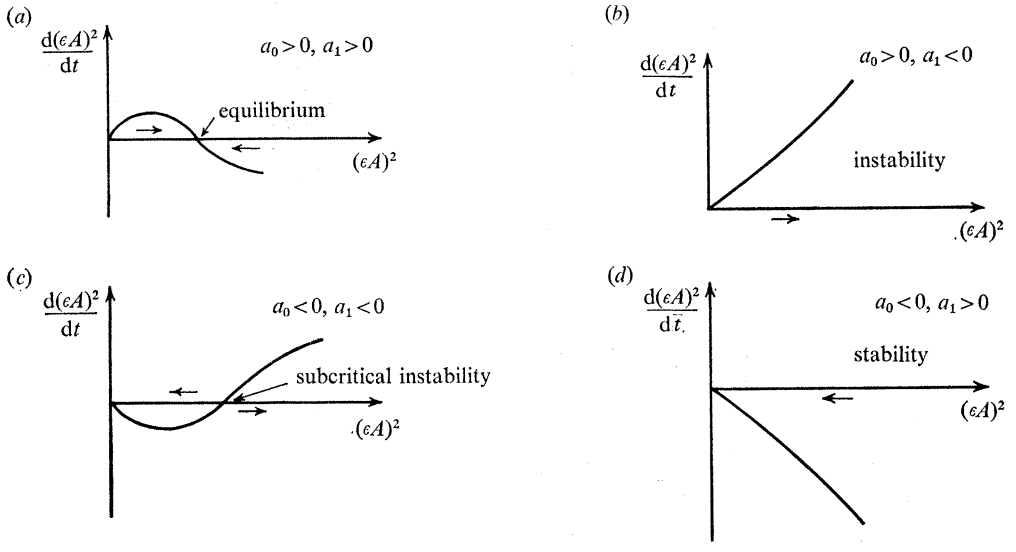

FIGURE 5. A plot of $\mathrm{d}(\epsilon A)^2/\mathrm{d}t$ against $(\epsilon A)^2$, showing the four possible qualitative behaviours of solutions to (7.1).

A' approaches zero as $t \to \infty$, showing that (7.3) is a stable equilibrium solution. Since

$$a_0 > 0 (T > T_C),$$

linear theory would predict instability, whereas a nonlinear analysis shows the existence of a *finite amplitude stable equilibrium solution.*

(*b*) $a_0 > 0$, $a_1 < 0$. There is no *finite amplitude* equilibrium solution and from figure 5 it can be seen that the nonlinear effects act to reinforce the destabilizing tendency shown by linear theory.

(*c*) $a_0 < 0$, $a_1 < 0$. Here

$$\mathrm{d}(\epsilon A)^2/\mathrm{d}t = 0 \quad \text{where} \quad (\epsilon A)^2 = a_0/a_1 > 0.$$

From figure 5, or by doing a local linear stability analysis as in (*a*), it can be seen that this equilibrium solution is unstable. This case is said to show *subcritical instability* of the unperturbed state $A = 0$. The reason is that for $T < T_C$ (since $a_0 < 0$), where linear theory predicts stability to infinitesimal disturbances, nonlinear theory shows that the solution $A = 0$ is unstable to finite amplitude disturbances whose magnitude ϵA satisfies $\epsilon^2 A^2 > a_0/a_1$.

(*d*) $a_0 < 0$, $a_1 > 0$. As in (*b*) there is no finite amplitude equilibrium solution but from figure 5 it can be seen that the nonlinear effects act to reinforce the stabilizing tendency shown by linear theory.

In order to analyse the stability of the planar interface solution to finite amplitude perturbations we must determine the signs of a_0 and a_1 in the amplitude equation. In § 4 we showed that

$$a_0 > 0 \quad \text{for} \quad G < G_C, \qquad a_0 = 0 \quad \text{for} \quad G = G_C, \qquad a_0 < 0 \quad \text{for} \quad G > G_C, \tag{7.6}$$

where $G_C = G_C(\gamma)$ is the marginal curve as represented in figure 4.

Thus we need only analyse the expression for a_1 given in (6.48). We note that for a given alloy with fixed concentration the parameters appearing there either determine ω_C (such as β) or are determined by it (such as T_C, g, $\tilde{g}$, m_0, p_0, $\tilde{m}_0$). Thus a_1 can be thought of as a function of ω_C.

TABLE 1. RESULTS, FOR $K = 0.2$, OF a_1 AND γM^{-1} AGAINST ω_C

ω_C	a_1	γ/M
10	-390	8.47×10^{-5}
8	-196	1.68×10^{-4}
6	-80.1	4.06×10^{-4}
4	-22.2	1.43×10^{-3}
2	-2.19	1.25×10^{-2}
1	-0.153	0.107
0.9	-9.51×10^{-2}	0.146
0.8	-5.35×10^{-2}	0.205
0.7	-2.54×10^{-2}	0.296
0.6	-8.14×10^{-3}	0.443
0.5	9.09×10^{-4}	0.683
0.4	4.21×10^{-3}	1.08
0.3	4.06×10^{-3}	1.71
0.2	2.39×10^{-3}	2.61
0.1	7.01×10^{-4}	3.56

However, since ω_C is a function of γ, then a_1 can be thought of as a function of γ. We wish to know the value of a_1 for different ω_C and for a number of values of K. To compute a_1 we used a computer and evaluated a_1 for $\omega_C = 10$ to 0.1 by tenths and from 0.1 to 0.01 by hundredths. We did this for $K = 0.1, 0.2, \ldots, 0.9$. A sample of the results of this computation is given in table 1 and corresponds to $K = 0.2$. We define ω_C^* so that

$$a_1 > 0 \quad \text{for} \quad \omega_C < \omega_C^*; \qquad a_1 < 0 \quad \text{for} \quad \omega_C > \omega_C^*. \tag{7.7}$$

If $\gamma_C \equiv \gamma(\omega_C^*)$ is the corresponding value of γ, then

$$a_1 > 0 \quad \text{for} \quad \gamma > \gamma_C; \qquad a_1 < 0 \quad \text{for} \quad \gamma < \gamma_C. \tag{7.8}$$

From table 1, when $K = 0.2$,

$$0.5 < \omega_C^* < 0.6, \quad 0.44M < \gamma_C < 0.68M.$$

The behaviour of a_1 for different values of K is similar to that for $K = 0.2$ (see table 2).

TABLE 2. THE VALUES OF ω_C^* AND γ_C FOR DIFFERENT K

Note. The numbers on the left and right of the 2nd and 3rd columns give, for different K values, upper and lower bounds for ω_C^* and $\gamma_C M^{-1}$ respectively.

K	ω_C^*		γ_C/M	
0.1	0.3	0.4	1.2	2.3
0.3	0.6	0.7	0.28	0.40
0.4	0.7	0.8	0.18	0.24
0.5	0.8	0.9	0.12	0.15
0.6	1.0	1.1	5.8×10^{-2}	7.2×10^{-2}
0.7	1.1	1.2	3.6×10^{-2}	4.4×10^{-2}
0.8	1.3	1.4	1.7×10^{-2}	2.0×10^{-2}
0.9	1.5	1.6	6.2×10^{-3}	7.3×10^{-3}

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We plot the marginal curve for a_0, $G = G_C(\gamma)$, and also the 'marginal curve' for a_1, $\gamma = \gamma_C$, on the same graph (see figure 6). This then separates the $\gamma - G$ plane into four regions, each corresponding to one of the cases presented above. Figure 6 is drawn for $K = 0.2$ where

$$\left.\begin{aligned} \gamma_C = 0.7\rho(\rho = M(K-1) = 4|m|\, C_0/5T_M), \quad \omega_C^* = 0.55, \\ G_C(\gamma_C) \equiv \bar{G}_C = [1-\gamma_C\omega_C^{*2}/\rho - K/g(\omega_C^{*2}, 0)]\,(1+n)\,\rho/2 = 0.3(1+n)\,\rho/2. \end{aligned}\right\} \tag{7.9}$$

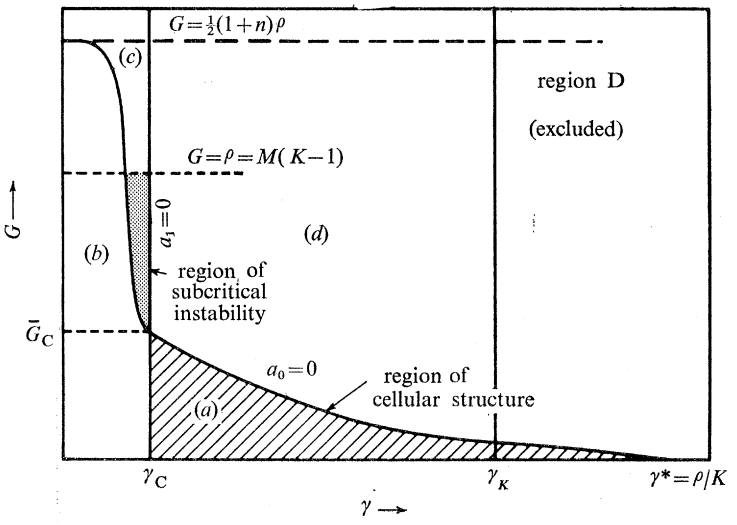

FIGURE 6. A plot of G against γ showing the regions corresponding to the cases given in the text for the four possible combinations of sign of a_0 and a_1 in the amplitude equation (7.1).

For our present nonlinear analysis to be valid, a_0 must be real. For $T > T_C$, a_0 is always real. A sufficient condition to ensure that a_0 is real for $T < T_C$ is that

$$\omega_C > K \quad \text{or} \quad \gamma < \gamma_K = \frac{K}{2g(K^2, 0)\,(\frac{1}{4}+K^2)^{\frac{1}{2}}}. \tag{7.10}$$

Hence in figure 6 we have excluded region D, where $\gamma > \gamma_K$ and $G > G_C(\gamma)$. This region corresponds to the possibility of a_0 being complex, and is comparatively uninteresting, so we have not felt it worth while to include it by making the required extension of our nonlinear analysis.

We now examine the physical behaviour in each of the regions:

(*a*) $a_0 > 0$, $a_1 > 0$. This is the finite amplitude stable equilibrium case. Since we have dealt only with a one-dimensional disturbance to the planar interface

$$\epsilon\zeta = \epsilon A(t)\cos\omega x + \ldots$$

we can only conclude that stable *bands*, a one-dimensional periodic structure, can be present in this region. However, in cellular convection driven by gravity (Segel 1966) or surface tension (Scanlon & Segel 1967) a two-dimensional analysis has shown that stable hexagons existed where a one-dimensional analysis predicted bands. It is observed that for dilute alloys under the proper conditions the planar interface solution becomes unstable and a transition to domed-shaped regular five- or six-sided cells occur. To demonstrate conclusively that this is the cellular region it would be necessary to carry out a two-dimensional analysis and thereby show the existence of stable hexagons. At present, due to the analogy with cellular convection, we tentatively (but with some confidence) refer to the region where a_0 and a_1 are positive as the *cellular régime*.

(*b*) $a_0 > 0$, $a_1 < 0$. This is the region where the planar interface solution is unstable to infinitesimal disturbances. Finite amplitude effects enhance disturbance growth.

(*c*) $a_0 < 0, a_1 < 0$. This is the region of subcritical instability. It may well correspond physically to dendritic growth. O'Hara (1966) put forth two criteria for what he termed metastable growth of dendrites. These were that the planar interface be stable by linear stability considerations ($a_0 < 0$) and that $G < \rho = M(K-1)$. The region in this sector which corresponds to these criteria, namely

$$0.45\rho = \bar{G}_C < G < \rho, \tag{7.11}$$

has been shaded in figure 6. (We have taken $n = 2$, an excellent approximation in most situations.)

(*d*) $a_0 < 0$, $a_1 > 0$. This is the region where the planar interface is stable to both infinitesimal and finite amplitude disturbances.

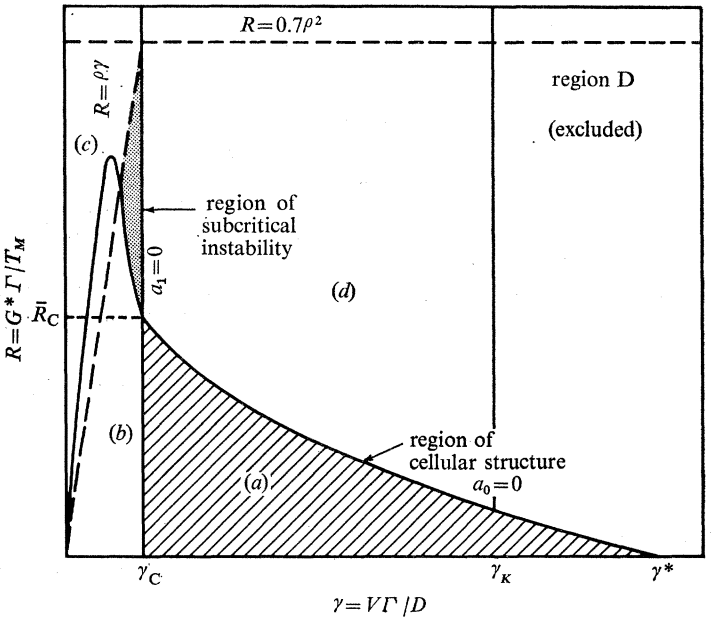

FIGURE 7. A schematic plot of R against γ. $R = G\gamma = G^*\Gamma/T_M$ has the advantage of being a dimensionless temperature gradient independent of V. The regions are to be interpreted as in figure 6.

Recall that $G = G^*D/T_M V$ and $\gamma = V\Gamma/D$. Since G is a function of V it might be useful to consider a dimensionless quantity containing G^* that is independent of V. For this purpose we define

$$R = G\gamma = G^*\Gamma/T_M. \tag{7.12}$$

We plot schematically R against γ for $K = 0.2$ in figure 7. For this case

$$\gamma_C = 0.7\rho, \quad \bar{R}_C = \bar{G}_C\gamma_C = 0.32\rho^2, \quad R_C(\gamma) = \gamma G_C(\gamma). \tag{7.13}$$

The regions in figure 7 are to be interpreted just as they were for figure 6. Note that $G = \rho$ transforms into $R = \rho\gamma$. This type of plot is an aid to experimentalists since R is proportional to G^* and γ is proportional to V for a given alloy.

As an example, we now specialize our results so that they apply to a particular dilute binary

alloy, the tin-lead system. It has the following values for relevant parameters (Rutter 1957; Mullins & Sekerka 1964):

$$T_M = 505\,\mathrm{K}, \quad K = 0.2, \quad m = -2\,\mathrm{K\ per\ weight\ \%\ lead},$$
$$D = 5\times 10^{-5}\,\mathrm{cm^2/s}, \quad \Gamma = 10^{-8}\,\mathrm{cm}, \quad n = 2. \tag{7.14}$$

Thus
$$\beta = \gamma/\rho = \frac{V\Gamma T_M}{mC_0(K-1)D} = 0.063\,V/C_0. \tag{7.15}$$

From (7.9), $\gamma_C = 0.7\rho$. Using $\beta = \gamma/\rho$ we find $\beta_C = 0.7$. Hence for this alloy

$$(V/C_0)_C = 11\,\frac{\mathrm{cm/s}}{\%\ \mathrm{Pb\ (by\ wt.)}}, \tag{7.16}$$

where as above, a subscript C on a quantity refers to its critical value. For a given concentration, C_0, then
$$V_C = 11 C_0\,\mathrm{cm/s}, \tag{7.17}$$
$$\bar{R}_C = \bar{G}_C\gamma_C = 0.32\rho^2 = 0.32[mC_0(K-1)/T_M]^2.$$

To put this in dimensional form we recall from (7.12) that $R = G^*\Gamma/T_M$; thus

$$G^*_C = 0.32m^2C_0^2(K-1)^2/\Gamma T_M = 1.6\times 10^5\,C_0^2\,\mathrm{K/cm}. \tag{7.18}$$

For $C_0 = 0.01\%$ Pb then $V_C = 0.11$ cm/s and $G^*_C = 16$ K/cm. Using these values we note that subcritical instability will occur for finite amplitude disturbances whose magnitude, ϵ, satisfies

$$\epsilon^2 > 6\times 10^{-2}(G^* - G^*_C). \tag{7.19}$$

Earlier we stated that it would be shown that $a_0 = O(\epsilon^2)$. In this section we investigated the amplitude equation to $O(\epsilon^3)$ and arrived at the following equilibrium solution when $a_1, a_0 > 0$:

$$\epsilon Ae = (a_0/a_1)^{\frac{1}{2}}.$$

It can be shown that $A(t)$ increases monotonically. Since we made the convention $\max_t |A(t)| = 1$ we must have $Ae = 1$ and

$$|\epsilon|^2 a_1 = a_0. \tag{7.20}$$

All our analysis has tacitly assumed that $a_1 = O(1)$ with respect to ϵ. We now consider one further term in the amplitude equation or

$$\epsilon\dot{A}(t) = a_0A(t)\,\epsilon - a_1\epsilon^3A^3(t) - a_2\epsilon^5A^5(t). \tag{7.21}$$

In order to have neglected the $\epsilon^5A^5(t)$ term of (7.21) in our previous work it is necessary that

$$|\epsilon|^2 \ll a_1/a_2. \tag{7.22}$$

Equations (7.20) and (7.22) together imply the condition

$$a_0 \ll a_1^2/a_2. \tag{7.23}$$

Computation of a_2 is a formidable task so we shall limit ourselves to the statement that the relation $a_0 = O(T - T_C)$ indicates that our calculations will be valid when the imposed temperature gradient is sufficiently close to its critical value.

8. Discussion

Our two major nonlinear results are that:

1. The interface can be unstable to finite amplitude disturbances when linear theory predicts stability to infinitesimal disturbances. This is called subcritical instability and is closely connected with the possibility of dendritic growth.

2. Cellular structure can be anticipated for certain ranges of parameter values.

A nonlinear effect shown by our analysis is that when the temperature gradients in the solid and liquid at infinity are required to remain the same as the gradients of the basic solution, then the mean position of the interface lags behind its position in unidirectional freezing.

Comparing our analysis with previous work we first note that the original (Tiller & Rutter 1956) qualitative supercooling criterion for instability, $G^* < mG_0$, becomes in our non-dimensionalized variables either

$$G < \rho = M(K-1) \quad \text{or} \quad R < \rho\gamma. \tag{8.1}$$

Our linear theory results, arrived at by a standard linear perturbation analysis of the full-time dependent equations, are equivalent to those obtained by Mullins & Sekerka (1964) using a 'steady-state' approximation. In order to show this we recall that their stability criterion was

$$\frac{nG'^* + G^*}{mG_0(1+n)} > \mathscr{S}(A, K). \tag{8.2}$$

Transforming into dimensionless variables and making use of $nG' = G$ we obtain

$$\frac{2G}{M(K-1)(1+n)} = W > \mathscr{S}(A, K). \tag{8.3}$$

We now observe that $\mathscr{S}(A, K)$ is equal to what we have called $W_C(\beta)$ and that $A = K\beta$. Hence our linear stability criterion is equivalent to (8.2).

Mullins & Sekerka arrived at their criterion by assuming time dependence of the form $\delta = \delta(t)$ and neglecting time derivatives except in ζ_t. They then determined their stability criterion by setting $\dot{\delta}/\delta = 0$. Thus they calculated the marginal condition for instability by tacitly assuming exchange of stabilities which we have demonstrated in § 4. Their analysis is correct for the marginal case. Their work on maximum growth rates is incorrect since the time derivatives in the diffusion equations are neglected. When ξ is small, this is permissible in the temperature equations but it is never permissible in the concentration equation.

Sekerka (1967) and Delves (1966) reworked the problem for time dependent diffusion equations by using transform techniques. We have used a normal mode or separation of variables approach. The normal mode method analyses the discrete or point spectrum of the linear problem while transform methods analyse the continuous spectrum *and* the point spectrum. From the work of Sekerka (1967) and Delves (1966), however, it can be concluded that for this problem one can predict the onset of instability by determining where the point spectrum eigenvalues a_0 satisfy $\mathrm{Re}\,(a_0) > 0$ for a disturbance proportional to $e^{a_0 t}$. Thus we say that the normal modes, considered here, are the 'most dangerous' modes.

Let us examine our predicted regions of cellular structure and subcritical instability in the light of previous results. As stated earlier, O'Hara's criteria for dendritic structure for constrained crystal growth are in our notation

$$a_0 < 0, \quad G < M(K-1). \tag{8.4}$$

In figures 6 and 7 this region is shaded in the area of subcritical instability ($a_0 < 0, a_1 < 0$). We observe that the second condition of (8.4) is merely the old constitutional supercooling criterion for instability. Supercooling is expected to be destabilizing and the additional factors of curvature and temperature gradients, are expected to be stabilizing. It is thus not surprising that a finite amplitude disturbance chiefly confined to the concentration might result in an instability where linear theory predicts stability to infinitesimal disturbances (for which normal mode concentration disturbances are inevitably accompanied by disturbances of the same magnitude in all other variables).

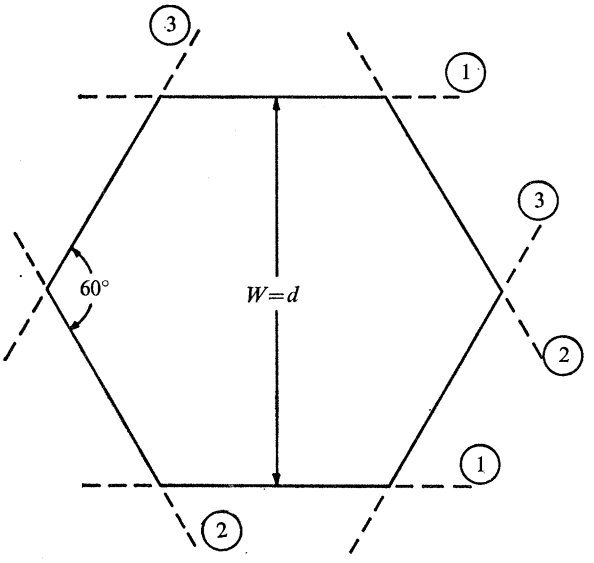

FIGURE 8. The formation of a hexagonal cell from three rolls. Note that the width of a roll, W, is equal to the diameter of the cell, d.

The typical diameter of a cell on the interface between the two phases of a dilute binary alloy ranges from 60 to 90 μm (Tarshis 1967). It has been found in nonlinear studies of the Bénard problem that cells exhibit a width similar to the wavelength associated with the critical wave number. We note that hexagons are made up of the superposition of three bands meeting at 60° and their diameter coincides with the width of a band (figure 8). In our analysis we have shown that λ_C, the critical dimensional wavelength of a roll, is such that

$$\lambda_C = \frac{2\pi}{\omega_C} D/V = f(V). \tag{8.5}$$

From our analysis in § 7 for an alloy with $K = 0.2$ the maximum wavenumber at which one can have cellular structure is $\omega_C^* = 0.55$. In the case of the particular alloy handled in § 7,

$$D/V = 5 \times 10^{-4}\,\text{cm};$$

hence the dimensional wavelength corresponding to this is

$$\lambda_C^* = \left(\frac{2\pi}{0.55}\right)(5 \times 10^{-4})\,\text{cm} \cong 57 \times 10^{-4}\,\text{cm} = 57\,\mu\text{m}, \tag{8.6}$$

which compares favourably with the 60 μm lower cellular limit mentioned earlier. The maximum λ_C for which cellular structure can occur by our analysis is $\lambda_C \to \infty (\omega_C = 0)$. This corresponds to

a very large value of V. The maximum observed λ_C is presumably associated with the largest experimentally feasible value of V.

To recapitulate, we have considered a nonlinearized version of the Mullins and Sekerka mathematical model for the constrained growth of a dilute binary alloy. We have carried out a systematic linear stability analysis of the planar interface solution by a normal mode approach. We have used a nonlinear stability analysis of a Stuart–Watson nature (Segel 1966) and expect this to be asymptotically valid as $G \to G_C$. Our principal results are predictions of subcritical instability and equilibrium cellular structure.

The work done on this paper was largely completed while one of us (D. J. W.) was a graduate student in the Department of Mathematics, Rensselaer Polytechnic Institute, and was partially supported by funds from the Army Research Office (Durham) and the National Aeronautics and Space Administration. The authors wish to thank Dr Lemuel Tarshis of General Electric for his explanations and helpful suggestions on the physical metallurgical aspects of this problem and Dr Lester Rubenfeld of Rensselaer Polytechnic Institute for his comments concerning the complex nature of the growth rate. An abstract of this work appeared in Frank *et al.* (1968).

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