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Morphological and thermosolutal instabilities inside a deformable solute boundary layer during directional solidification. I. — Theoretical methods

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Résumé. — Nous généralisons l'étude de la stabilité morphologique et thermosolutale au front de solidification d'un alliage binaire pour le cas généralement vérifié en pratique où des mouvements convectifs volumiques sont présents dans le bain liquide. L'analyse linéaire en perturbation est développée par le biais d'un modèle en couche limite déformable Δ. Ceci permet l'obtention sous forme analytique de la condition mathématique de compatibilité pour des instabilités non oscillantes. Une comparaison avec les cas déjà traités dans la littérature (Δ infini) conclut cette première étude.

Abstract. — The linear perturbation analysis of morphological and thermosolutal instabilities at the growth front during directional solidification of a binary alloy is generalized to the case where bulk convection exists in the basic state, as is encountered in most cases, in practice. The model assumes a finite and deformable solute boundary layer Δ. The compatibility condition is obtained in analytical form for the marginal case of exchange of stabilities. The present model is shown to be consistent with literature results in the limiting case of infinite Δ.

1. Introduction.

Solidification of binary alloys has been extensively studied in the last decades because of its numerous industrial applications. One of the most important aims of such an analysis is the prediction of the stability limit of a planar Liquid-Solid interface — i.e. the change in shape when an instability occurs — because the solid structures formed are directly connected with such a phenomenon. The now classical paper by Mullins and Sekerka [1] was the first breakthrough. Considering only pure diffusive transport in the liquid, its main limitation for metallurgy and crystal growth under gravity conditions comes from the disregard of the strong influence of convection [2, 3]. Thus, numerous authors recently tried to analyse the problem of coupling hydrodynamic and morphological instabilities, considering heat, solute and momentum transport in the liquid phase. For such a complex problem, various assumptions should be made : Coriell *et al.* [4], Wollkind [5] and Hurle *et al.* [6] assume pure diffusive liquid as unperturbed state. Since these pioneering studies, various effects including shrinkage at solidification front [7] (due to differences in density between liquid and solid) were added in the models.

However, the strong influence of convection in the liquid bulk has never been considered. Our aim is quite different. To analyse the influence of convection motions, two of us [3] already considered the influence of bulk convection on the solutal field, assuming a « deformable boundary layer » formed close to the interface as a consequence of external forces such as forced or natural convection. Its physical meaning will be emphasized here again. The extent of this layer can easily be estimated by an order of magnitude analysis of continuity equations as explained by Favier and Camel [8]. We now consider the possibility of encountering a thermosolutal instability inside the boundary layer when thermal and solutal gradients present in that region are submitted to a vertical gravity field. Morphological instability governed by bulk convection will now couple with hydrodynamic instability inside this layer.

The present paper can therefore be considered as a generalization of Hurle's paper [6] but should be more realistic as far as comparison with crystal growth experiments is considered. We first describe the physical configuration and propose a mathematical method derived from hydrodynamics [9] to solve the problem analytically. As a test of this theory, the case of an infinite boundary layer extent is calculated and compared with the results of Coriell [4] and Hurle [6]. The complete set of results for variable boundary layer extents as well as the oscillatory case will be presented in the next paper.

2. The physical problem.

We will develop the linear stability analysis of an upward moving solidification front of a binary alloy in a gravity field which is the only external force. Assuming local thermodynamic equilibrium of the solute concentrations C_S^* and C_L^* in both phases taken at the interface Σ, we have :

$$C_S^* \big|_\Sigma = K_0 \, C_L^* \big|_\Sigma \tag{2.1}$$

where K_0 is the equilibrium partition ratio.

A starred quantity means a dimensioned physical quantity. The physical domain we consider here is depicted in figure 1 in the case $K_0 < 1$. The reference surface Σ between both phases is assumed to be a horizontal plane where we attach a reference coordinate system whose normal axis points upwards (Fig. 2a). While the unperturbed system moves upwards with a constant velocity V, the solute is rejected $\left(K_0 < 1\right)$ from the solid into the liquid phase, where it diffuses (Fig. 2b). The first possible instability source, namely constitutional supercooling, appears now if there exists in the liquid phase a region, ahead of the interface, whose temperature is lower than the equilibrium one. This potentially unstable situation explains why the interface can deform itself. Indeed the Gibbs-Thompson law couples there the temperature together with the solute concentration, according to the following relation, where K is the mean curvature of Σ, T_M^* the solidification temperature of the pure solvent, m_L the liquidus slope and Γ a classical capillary parameter :

$$T_M^* + m_L \, C_\Sigma^* \big| - T_M^* \, \Gamma K - T_\Sigma^* = 0 \, . \tag{2.2}$$

Due to the solute contribution on the density various hydrodynamic instabilities may result [4, 6].

But for binary alloys, one has in general :

$$D < \nu < \kappa$$

where D and κ are the solute and thermal diffusivity respectively and ν the kinematic viscosity. This fundamental inequality means that the region influenced by the solute distribution is of a much smaller extent than that influenced by thermal and momentum transport.

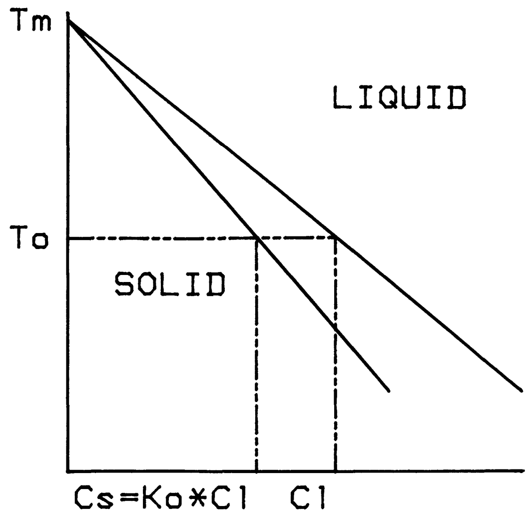

Fig. 1. — The Phase diagram $(T^* C^*)$. The distribution coefficient K is smaller than 1 and both phases are far from the eutectic composition. Cooling a melt of initial temperature T_i^* and concentration C_L^* gives rise to a solid phase $C_S^* = KC_L^*$ at temperature T_0^*.

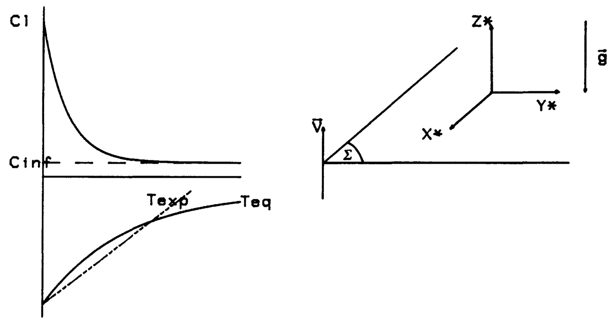

Fig. 2. — (a) The supercooling process. (b) The reference system of coordinates.

This very tiny region, adjacent to the interface, is called the diffusion solutal boundary layer.

Let us now calculate the order of magnitude of such a domain where thermosolutal convection can appear. Calling H the geometrical dimension specific of the experiment, we suppose that $D/V < H$ so that the Peclet number $Pe = V \, . \, H/D$ is larger than unity. Due to the no-slip condition at the interface and the incompressibility of the melt, the normal component V_n of the liquid phase velocity in the vicinity of the moving interface is of the form :

$$V_n(Z) \, \frac{H}{\nu} = A \left(\frac{Z}{H}\right)^2 \tag{2.3}$$

where A depends on the convection in the bulk. We supposed here the bulk velocity larger than the interface velocity V.

Inside the solutal boundary layer, solute diffusion plays the dominant role [8]. Its width δ is defined from the balance between solute diffusion and solute convection :

$$\delta = \frac{D}{V_n(\delta)} . \tag{2.4}$$

Combining with (2.3) one has :

$$\frac{\delta}{H} = Sc^{-1/3} A^{-1/3} \tag{2.5a}$$

where $Sc = \nu / D$ is the Schmidt number. The dimensionless boundary layer extent is thus :

$$\Delta = \frac{V}{D} \delta = Pe\, Sc^{-1/3} A^{-1/3} . \tag{2.5b}$$

To analyse such a boundary layer model, subjected to possible morphological and hydrodynamic instabilities, Coriell *et al.* [11] considered the outer boundary to be a rigid surface where the solute disturbances vanish. This model exhibits unexpected abnormal results for high convective regimes, where Δ is very small. This is due to the rigidity of the outer boundary which mathematically induces parasite reflections. So, we choose instead henceforward the model of Favier and Rouzaud [3] which considers a deformable boundary layer (DBL) where this limit is deformed in the same way as the perturbed interface itself. This assumption is justified from a theoretical point of view by the relative diffusion time scales of solute and momentum. We will assume further heat transport to be quasi-steady inside the Δ layer since the Lewis number of both phases is much larger than the Schmidt number. We define dimensionless variables by choosing our scales with respect to the diffusion of solute :

$$t = t^* \frac{V^2}{D} \frac{\rho_S}{\rho} \tag{2.6a}$$

$$\mathbf{r} = \mathbf{r}^* \frac{V}{D} \frac{\rho_S}{\rho} \tag{2.6b}$$

(t^* : time ; $\mathbf{r}^*$: position ; $\rho_S(\rho)$: density of the solid (liquid) phase). The heat balance in both phases is thus given by a time-independent Fourier equation :

$$\nabla^{*2} T_S^* = \nabla^{*2} T^* = 0 . \tag{2.7a}$$

We assume the continuity of temperatures along the interface Σ, the Gibbs-Thomson law (2.2) giving the relation linking temperature and solute distribution along the interface. The difference between the thermal fluxes along the interface provides the energy necessary for the solid to increase at the expense of the liquid phase. It reads :

$$\mathfrak{L} \Omega \mathbf{1}_n = \left\{ K_S \operatorname{grad}^* T_S^* - K_L \operatorname{grad}^* T^* \right\}_\Sigma \tag{2.7b}$$

where $\mathfrak{L}$ is the latent heat of fusion per unit volume, $K_S(K_L)$ the thermal conductivity of the solid (liquid) phase, and Ω the local surface velocity.

In principle, the solute balance introduces another coupling between thermal and solutal profiles, but we will neglect the Dufour and Soret effects and thus the solute balance equation in the liquid phase reduces to :

$$\frac{dC^*}{dt^*} = D \nabla^{*2} C^* \tag{2.7c}$$

where d/dt^* is the substantial time derivative with respect to the laboratory reference frame at rest. One can also neglect the diffusion of solute in the crystal so that the equality between the fluxes entering and leaving the surface Σ is :

$$\left(1 - K_0\right) C^* |_\Sigma \frac{\rho_S}{\rho} \Omega \mathbf{1}_n = - D \operatorname{grad}^* C^* |_\Sigma . \tag{2.7d}$$

Making the assumption of no matter accumulation at the interface, this induces a net velocity u^* of the melt :

$$u^* |_\Sigma = \Omega \left(1 - \frac{\rho_S}{\rho}\right) \mathbf{1}_n . \tag{2.7e}$$

Both phases are incompressible and the gravity is supposed to be the only external force acting on the system. The expression of the state equation depends fundamentally on the thermal and solutal fields :

$$\frac{\rho}{\rho_0} = 1 - \alpha_T [T^*(Z) - T^*(0)] - \alpha_c [C^*(Z) - C^*(0)] \tag{2.7f}$$

where ρ_0 is the reference density whose value is taken along Σ. Since both phases are very different from dilute gases, one can safely apply the Boussinesq approximation [10] so that the momentum balance reads :

$$\frac{du^*}{dt^*} = - \nabla^* \frac{P^*}{\rho_0} + \nu \nabla^{*2} u^* - \frac{\rho}{\rho_0} \mathbf{g} \cdot \mathbf{1}_z \tag{2.7g}$$

where P^* is the dynamic pressure and $\mathbf{g}$ the gravity vector.

3. The linearized perturbed problem.

Let us consider as a reference state the set of steady solutions derived from (2.1 to 2.7g) for the time independent case. Due to the initial geometry we consider the reference surface Σ to be a horizontal plane so that all unperturbed quantities denoted by the superscript 0 will be only Z-dependent. The unperturbed solute concentration is solution of :

$$\left[d^2/dZ^2 + d/dZ \right] \quad C^{*0} = 0 ,$$

if one takes for unit of solute concentration : $\left[- dC^{*0}/dZ \right]_0$, it becomes

$$C^0 = \frac{K_0}{1 - K_0} + e^{-Z} . \tag{3.8a}$$

Considering the thermal field, temperatures will be normalized by the mean gradient of temperature G measured in temperature unit :

$$G = \left[\kappa_L \frac{dT^{*0}}{dZ} + \frac{dT_S^{*0}}{dZ} \kappa_S \frac{\rho_S}{\rho} \right] \Big/ \left(\kappa_L + \kappa_S \frac{\rho_S}{\rho} \right) \quad (3.8b)$$

$$T = \frac{T^*}{G} . \quad (3.8c)$$

Defining

$$g_{SL} = \frac{dT_S^{*0}/dZ}{dT^{*0}/dZ}, \quad y = \frac{\kappa_S \rho_S}{\kappa \rho} \quad \text{and} \quad K_{0S} = \frac{K_S}{K_S + K_L},$$

equation (2.7b) reduces to :

$$\frac{\mathcal{L} D \rho_S}{\left(K_S + K_L\right) g \rho} = \frac{1+y}{1+y g_{SL}} \left[K_{0S}\left(1 + g_{SL}\right) - 1\right] \quad (3.8d)$$

and the Gibbs-Thompson law becomes :

$$\frac{1}{1-K_0} + \mathcal{S}\left[T_M^0 - T_\Sigma^0\right] = 0 \quad (3.8e)$$

where the quantity $\mathcal{S}$ defined as $g \Big/ \left(-m_L \frac{dC^*}{dZ}\Big|_0\right)$ is linked to the morphological stability criterion deduced by Mullins and Sekerka [1]. How does this system now react to a possible infinitesimal disturbance ? In other words we want to know whether it decreases with time (stable case) or not (onset of instability). The classical way to answer such a question is to superpose to the unperturbed solution $f_0(Z)$ of the problem a possible perturbation $\bar{f}(\mathbf{r}, t)$ which is expanded in an infinite series :

$$\bar{f}(\mathbf{r}, t) = \sum_{n=1}^{\infty} \varepsilon^n \bar{f}_n(\mathbf{r}, t) \quad (3.9a)$$

in term of a small parameter ε. The choice of ε is not unique. The *Sc* number being quite large, for most liquid metals a possible candidate could be :

$$\varepsilon = \frac{1}{Sc} . \quad (3.9b)$$

However, we will also consider cases where ε is different from $1/Sc$. Indeed, for particular systems such as Ga doped Ge one may have $1/Sc \cong 0.15$ which is hardly a small quantity.

We will limit ourselves to a linear perturbation analysis. This is by far not enough to give the full answer of the real system, but it allows determination of the conditions under which the physical system becomes unstable. Due to planar isotropy along x and y, one can consider normal modes under the form : $f_a(Z)\ e^{-pt}$ where a is the wave number. We have to include the specificity of the solidification process. The interface is not rigid any more so that its perturbed shape no longer corresponds to a flat plane. The equation of the perturbed surface is thus :

$$\delta Z = \varepsilon \, . \, Z_{SL} \quad (3.10a)$$

with $Z_{SL} \neq 0$, so that the linear perturbation of any quantity defined along the surface is given by :

$$f(\delta Z) - f^0(0) = f^0(\delta Z) + \bar{f}(\delta Z, t) - - f^0(0) = \varepsilon Z_{SL} \frac{\partial f^0}{\partial Z}\Big|_{Z=0} + \varepsilon \bar{f}\,|_{Z=0} . \quad (3.10b)$$

It depends on 2 terms, one is proportional to the surface deformation and the other is the usual perturbation taken along the reference unperturbed surface. The velocity of the perturbed interface becomes :

$$\Omega - \Omega_0 = \frac{d}{dt^*} \delta Z^* = \frac{\partial}{\partial t^*} \times \delta Z^* = \varepsilon p V Z_{SL} . \quad (3.10c)$$

Since $1/Le = 0\left(\varepsilon^2\right)$, the temperature fluctuations still obey a stationary Fourier equation. Along the surface, the temperatures of both phases remain equal to one another, so that one gets from (2.7a) and (2.7b) :

$$\bar{T}(Z) = Z_{SL}\, \tau\, e^{-aZ} \quad (3.11a)$$

$$\tau = \frac{1+y}{1+y g_{SL}} \left[K_{0S}\left(g_{SL} - 1\right) + + \left(K_{0S}\left(g_{SL} + 1\right) - 1\right) \frac{p}{a}\right] . \quad (3.11b)$$

From (3.7c), one has the perturbed solute distribution as :

$$\left[\frac{d^2}{dZ^2} + \frac{d}{dZ} - \left(a^2 + \frac{p\rho}{\rho_S}\right)\right] \bar{C} = -\bar{u}\, e^{-Z} \quad (3.12a)$$

with the corresponding boundary condition along a deformable boundary layer [3] deduced in a similar manner as (3.10b) :

$$\bar{C}(\Delta) = Z_{SL}\, e^{-\Delta} . \quad (3.12b)$$

This generalizes the previous classical boundary layer models [11, 12] since $\bar{C} \to 0$ when $\Delta \to \infty$ and $\bar{C} \to Z_{SL}$ when $\Delta \to 0$. The Gibbs Thompson law also couples the solute and temperature fluctuations along the interface whose curvature is :

$$K = a^2 \varepsilon Z_{SL} .$$

So that, from (2.2)-(3.10c) and the definition of $\mathcal{S}$, we finally get :

$$\bar{C}\,|_{Z=0} = A_{\mathcal{S}}\, Z_{SL} \quad (3.12c)$$

with

$$A_{\mathcal{S}} = 1 + \mathcal{S}\left[\frac{T_M \Gamma V \rho_S}{D\rho} a^2 + \frac{1+y}{1+y g_{SL}} + \tau\right] \quad (3.12d)$$

and the equality of the solute fluxes along the perturbed interface (2.7d) leads to the boundary condition :

$$\left.\frac{\mathrm{d}\bar{C}}{\mathrm{d}Z}\right|_{Z=0} = B_8 Z_{SL} \quad (3.12e)$$

where

$$B_8 = \left(K_0 - 1\right) A_8 - \left(p + K_0\right). \quad (3.12f)$$

To derive the melt momentum balance, one applies twice the curl operator on equation (2.7g). This leaves us with the following differential equation :

$$\mathfrak{D}_{(4)}\, \bar{u} = a^2\left[Ra_T\, \tau Z_{SL}\, \mathrm{e}^{-aZ} + Ra_c\, \bar{C}\right]. \quad (3.13a)$$

The differential operator $\mathfrak{D}_{(4)}$ is defined as :

$$\mathfrak{D}_{(4)} = \left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - a^2\right)\left[\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - a^2 + \frac{1}{Sc}\left(\frac{\mathrm{d}}{\mathrm{d}Z} - p\right)\right] \quad \text{if} \quad \varepsilon \neq 1/Sc$$

$$\mathfrak{D}_{(4)} = \left(\frac{\mathrm{d}^2}{\mathrm{d}Z^2} - a^2\right)^2 \quad \text{if} \quad \varepsilon = 1/Sc\,.$$

In the last case, one neglects terms proportional to $1/Sc$ since they are now of order ε^2. Beyond its physical relevance, the choice of the definition of ε has mathematical consequences. For $\varepsilon \neq 1/Sc$ the operator $\mathfrak{D}_{(4)}$ has four distinct eigenvalues, and for $\varepsilon = 1/Sc$, the operator $\mathfrak{D}_{(4)}$ has only two distinct ones, each of them being of multiplicity two.

The dimensionless numbers Ra_T and Ra_C are defined by :

$$Ra_T = \frac{\alpha_T\, g}{D\nu}\left(\frac{\rho}{\rho_S}\frac{D}{V}\right)^3 G \quad (3.13b)$$

and

$$Ra_c = \frac{\alpha_c\, g}{D\nu}\left(\frac{\rho}{\rho_S}\frac{D}{V}\right)^3 \left(-\frac{\partial C^{*0}}{\partial Z}\right)_{Z=0}. \quad (3.13c)$$

In the peculiar system of units which we choose, Ra_c is obviously the solutal Rayleigh number but Ra_T is a finite quantity which corresponds to the product of the usual thermal number Ra by the Lewis number [10]. Since there is no accumulation of matter at the interface and since the melt is incompressible, we have the 2 boundary conditions :

$$\bar{u}|_{Z=0} = Z_{SL}\left(\frac{\rho}{\rho_S} - 1\right) p \quad (3.13d)$$

and

$$\left.\frac{\mathrm{d}\bar{u}}{\mathrm{d}Z}\right|_{Z=0} = Z_{SL}\, a^2\left(1 - \frac{\rho}{\rho_S}\right). \quad (3.13e)$$

Let us note that we assume a deformation amplitude of the interface which is different from 0. Indeed if $Z_{SL} = 0$, there is no morphological instability and no temperature fluctuation to consider whatsoever. The problem is thus much simplified. One has then to deal with a classical Rayleigh Benard problem [13]. If Z_{SL} is different from 0, one can still uncouple the thermal field from the convective instability by setting $\alpha_T = 0$ which is a classical assumption [6]. Our approach assumes both $\alpha_T \neq 0$ and $Z_{SL} \neq 0$.

Since we consider a linear problem in the perturbed quantities, they are defined up to a common multiplying constant. We will thus define new dimensionless quantities u, T, C as :

$$u = \frac{\bar{u}}{Z_{SL}} \quad (3.14a)$$

$$T = \frac{\bar{T}}{Z_{SL}} \quad (3.14b)$$

$$C = \frac{\bar{C}}{Z_{SL}}. \quad (3.14c)$$

We will call these new perturbation quantities velocity, temperature and concentration, respectively. This transformation enables us to deal with the perturbed boundary layer as a straight ribbon of width Δ and thus we are still defining an inner and an outer region in a straightforward way. The linear perturbation analysis has one further advantage which we will use now. Inside the inner region (the Δ layer) one might define the velocity u as the sum of 2 components (see Fig. 4) :

$$u = f_1(Z) + f_2(Z)\,. \quad (3.15)$$

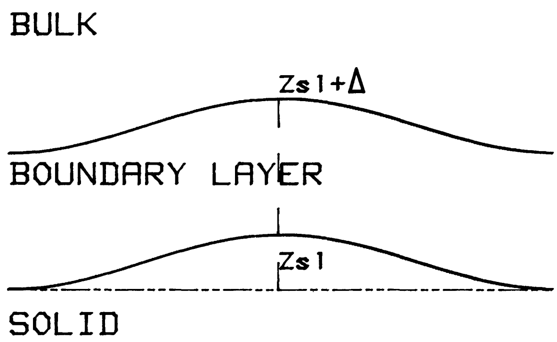

Fig. 3. — The perturbed diffusion boundary layer.

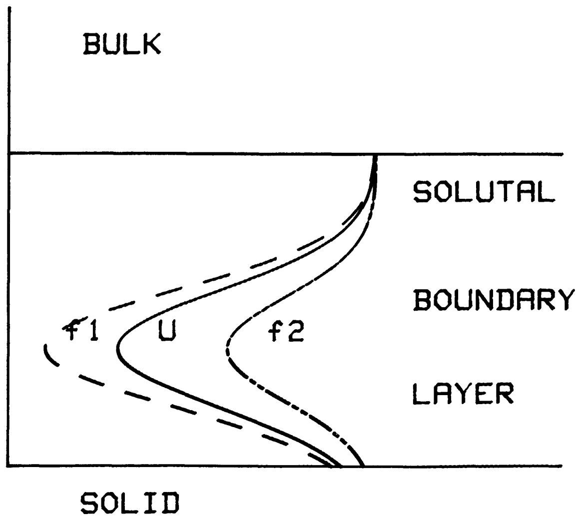

Fig. 4. — The velocity v as a sum of two components.

The first contribution $f_1(Z)$ is the part of velocity fluctuations which acts in all the liquid (Δ layer and bulk) and is due to the temperature fluctuation. The other part $f_2(Z)$ is linked to the solute profile and is thus zero outside the Δ layer. Also one has to match the solutions of the motion along the outer frontier of the Δ layer, coming from either side of it. Thus one is led to introduce the following equations due to the continuity equation of the velocity and to the incompressibility condition :

$$f_2(Z)\,\big|_{\Delta} = 0 = \frac{d}{dZ} f_2(Z)\,\big|_{\Delta}. \qquad (3.16)$$

4. The compatibility condition inside the Δ layer

We will neglect the shrinkage and use as boundary conditions, together with (3.16),

$$C\,|_{Z=0} = A_g \qquad (4.17a)$$

$$\left.\frac{dC}{dZ}\right|_{Z=0} = B_g \qquad (4.17b)$$

$$C\,|_{Z=\Delta} = e^{-\Delta} \qquad (4.17c)$$

$$f_2\big|_{Z=0} = 0 \qquad (4.17d)$$

$$\left.\frac{d}{dZ} f_2\right|_{Z=0} = 0\,. \qquad (4.17e)$$

The quantity $f_1(Z) + f_2(Z)$ obeys the momentum balance :

$$\mathfrak{D}_{(4)}\left[f_1(Z) + f_2(Z)\right] =$$

$$= a^2\left[Ra_T\,\tau e^{-aZ} + Ra_c\,C\right] \quad Z \in [0, \Delta] \quad (4.18a)$$

where, by its very nature, $f_1(Z)$ is the analytical solution of :

$$\mathfrak{D}_{(4)}\, f_1(Z) = Ra_T\,\tau a^2 e^{-aZ} \quad z \in [0, \infty]. \quad (4.18b)$$

The solution of this equation is derived by the classical method of constants variation [14] :

$$f_1(Z) = \frac{Ra_T\,\tau Z^2}{8} e^{-aZ} \quad \text{for} \quad \varepsilon = \frac{1}{Sc} \quad (4.18c)$$

$$f_1(Z) = \frac{Ra_T\,\tau Sc}{2}\left[\left(\frac{1}{\alpha + a} + Z\right) e^{-aZ} - \frac{1}{\alpha + a} e^{\alpha Z}\right]$$

$$\text{for} \quad \varepsilon \neq \frac{1}{Sc} \quad (4.18d)$$

where $\alpha = -\frac{1}{2\,Sc}\left(1 + \left(1 + 4\,a^2 Sc^2\right)^{1/2}\right)$.

Using (4.18c) or (4.18d) we now have to solve :

$$[L]\begin{bmatrix} f_2(Z) \\ C \end{bmatrix} = \begin{bmatrix} 0 \\ -f_1(Z)\,e^{-Z} \end{bmatrix} \quad Z \in [0, \Delta] \quad (4.19a)$$

where the differential operator L is given by :

$$[L] = \begin{bmatrix} \mathfrak{D}_{(4)} & -a^2 Ra_c \\ e^{-Z} & \mathfrak{D}_{(2)} \end{bmatrix} \quad (4.19b)$$

with

$$\left.\begin{aligned} &\mathfrak{D}_{(4)} \text{ already defined in (3.13a)} \\ &\mathfrak{D}_{(2)} = \left(\frac{d^2}{dZ^2} + \frac{d}{dZ} - a^2 - p\,\frac{\rho}{\rho_S}\right) \end{aligned}\right\}. \quad (4.19cd)$$

The condition of compatibility of system (4.17), (4.19) is now easy to determine. Here lies the main interest of this linear analysis since it gives the analytical relationship between all the physical parameters of the problem. We will limit ourselves to the non-oscillatory marginal case where :

$$\text{Re}\,(p) = \text{Im}\,(p) = 0\,. \qquad (4.20)$$

The differential operator L is then a real one, of order six but the system is over-determined since we have seven boundary conditions (4.16) and (4.17a-e) to be simultaneously satisfied. One uses the Fredholm alternative theorem of the general operator theory [15]. As usual, one looks first for the adjoint differential operator $\tilde{L}$ of the operator L, defining the norm in the real Hilbert space :

$$\langle \omega, \omega \rangle = \int_0^{\Delta} \omega\omega\, dZ \quad Z \in [0, \Delta]$$

one uses the extended Green equality [15, 16, 9]

$$\int_0^{\Delta} \left[\omega L v - (\tilde{L}\omega)\, v\right] dZ = \left[F(\omega, v)\right]_0^{\Delta}. \quad (4.21a)$$

Since, in our case, L is a matrix operator whose elements are differential operators, one obtains its adjoint by systematically applying the classical rules of integration by parts (see Appendix). The adjoint homogeneous system is :

$$\tilde{L}\omega = 0 \qquad (4.21b)$$

$$\tilde{L} = \begin{pmatrix} \tilde{\mathfrak{D}}_{(4)} & e^{-Z} \\ -a^2 . Ra_c\,\mathfrak{D}_{(2)} \end{pmatrix} \qquad (4.21c)$$

with

$$\tilde{\mathfrak{D}}_{(2)} = \frac{d^2}{dZ^2} - \frac{d}{dZ} - a^2$$

and

$$\tilde{\mathfrak{D}}_{(4)} = \left(\frac{d^2}{dZ^2} - a^2\right)\left(\frac{d^2}{dZ^2} - \frac{1}{Sc}\frac{d}{dZ} - a^2\right) \quad \text{if} \quad \varepsilon \neq \frac{1}{Sc}$$

$$\tilde{\mathfrak{D}}_{(4)} = \mathfrak{D}_{(4)} = \left(\frac{d^2}{dZ^2} - a^2\right)^2 \quad \text{if} \quad \varepsilon \neq \frac{1}{Sc}$$

To find the homogeneous boundary conditions associated to (4.21a-b) one calculates the concomitant $[F(\omega, v)]$ and replaces the conditions (4.17a-e) by their homogeneous equivalent. To put the concomitant equal to 0 gives us a certain number of conditions on the $\boldsymbol{\omega}$ components and their derivatives. The minimum number of conditions we have to keep is five. After calculations we have :

$$\omega_1\big|_0 = \left.\frac{d\omega_1}{dZ}\right|_0 = \omega_1\big|_{\Delta} = \left.\frac{d\omega_1}{dZ}\right|_{\Delta} = 0 \quad (4.21d)$$

$$\omega_2\big|_{\Delta} = 0\,. \qquad (4.21e)$$

The adjoint homogeneous system (4.21a-d) is thus an undetermined one. The compatibility condition is thus deduced from the Green extended equality using (4.18) and (3.12d) (see Appendix) :

$$\left[\frac{d\omega_2}{dZ}\bigg|_0 - \omega_2\big|_0\right] A_8 - \omega_2\big|_0 B_8 = \frac{d\omega_2}{dZ}\bigg|_\Delta e^{-\Delta} - \int_0^\Delta f_1(Z)\,\omega_2(Z)\,e^{-Z}\,dZ \qquad 0 \le \Delta < \infty$$

$$= 0 \quad \text{when} \quad \Delta \to \infty\,. \qquad (4.22)$$

The analysis can immediately be compared to Hurle's work for which Δ is infinite [6]. Indeed we have used Fredholm alternative theorem to determine the necessary and sufficient condition for a non-trivial solution to exist for the non-homogeneous differential system (4.17a) linked to the non-homogeneous boundary conditions (4.17a-e). When Δ tends towards infinity and $\alpha_T = 0$, the contribution of the right hand side of (4.22) vanishes while the boundary conditions (4.17a-e) remain, giving rise to the left hand side of equation (4.22). The physical problem considered by Hurle is identical to (4.17-4.18) putting the right hand side in (4.18) equal to zero, since $Ra_T = 0$. Hurle solves this problem in a direct way using the boundary conditions and the eigenvectors of the operator L, to get an algebraic linear homogeneous system of 3 equations and 3 variables. So that he has a non-trivial solution if, and only if, the determinant of the system is zero. Both methods considering the same physical problem provide one and only one necessary and sufficient condition. So they must be equivalent. An analytical verification in the case $\varepsilon = 1/Sc$ is given in the Appendix.

5. The adjoint system.

We must show that there is only one compatibility condition. Thus one studies the undetermined homogeneous adjoint system (4.21a-b) and shows that it has an infinity of solutions differing from one another by a multiplying constant. We begin first by eliminating ω_1 from the system (4.21e-d) and expressing the boundary conditions in terms of ω_2 we get :

$$\left[\tilde{\mathfrak{D}}_{(4)}\,\tilde{\mathfrak{D}}_{(2)} + a^2 Ra_c\,e^{-Z}\right]\omega_2 = 0 \qquad (5.23a)$$

$\tilde{\mathfrak{D}}_{(2)}\,\omega_2 = 0$ and

$$\frac{d}{dZ}\tilde{\mathfrak{D}}_{(2)}\,\omega_2 = 0 \quad \text{at} \quad Z = 0, \Delta\,. \qquad (5.23b)$$

Due to (4.21d) we have now a sixth condition :

$$\tilde{\mathfrak{D}}_{(4)}\,\tilde{\mathfrak{D}}_{(2)}\,\omega_2 = 0 \quad \text{at} \quad Z = \Delta\,. \qquad (5.23c)$$

Introducing the following change of variables :

$$s = a^2 Ra_c\,e^{-Z} \qquad (5.24a)$$

$$-\frac{d}{dZ} = s\frac{d}{ds} = \delta\,. \qquad (5.24b)$$

One obtains instead of (5.23a) :

$$\left\{\prod_{i=1}^{6}\left[\delta + C_i\right] + s\right\}\omega_2 = 0 \qquad (5.25a)$$

where the C_i are any cyclic permutation of the six quantities b_i defined below. Let us note that the definition of ε is of utmost importance in their values (see Table I).

Table I

	$\varepsilon \neq 1/Sc$	$\varepsilon = 1/Sc$
b_1	a	a
b_2	$-a$	$-a$
b_3	$\frac{1}{2Sc}[1 + \sqrt{1 + 4a^2 Sc^2}]$	$+a$
b_4	$\frac{1}{2Sc}[1 - \sqrt{1 + 4a^2 Sc^2}]$	$-a$
b_5	$\frac{1}{2}[1 + \sqrt{1 + 4a^2}]$	$\frac{1}{2}[1 + \sqrt{1 + 4a^2}]$
b_6	$\frac{1}{2}[1 - \sqrt{1 + 4a^2}]$	$\frac{1}{2}[1 - \sqrt{1 + 4a^2}]$

(5.25b)

Equation (5.25a) is a well known differential equation of the sixth order whose solutions are the Meijer functions G defined in the present case as [14, 17] :

$$G_{0,6}^{2t+1,0}\left(s; -C_1, -C_2, -C_3, -C_4, -C_5, -C_6\right) = \frac{1}{2\pi i}\int_L \frac{\prod_{j=1}^{2t+1}\Gamma\left(-C_j - y\right)}{\prod_{j=2t+2}^{6}\Gamma\left(+C_j + 1 + y\right)}\,s^y\,dy \qquad t = 0, 1, 2 \quad (5.26a)$$

where L is a loop starting and ending at $+\infty$ and including all the poles of the $2t+1$ functions $\Gamma\left(-C_j - y\right)$ only once in a clockwise direction. The problem reduces to choose six linearly independent solutions of (5.23a) from all the possible functions given by (5.26a). To do this we apply in a systematic way the residue theorem to equation (5.26a). The $\Gamma\left(-C_j - y\right)$ functions are single valued analytical functions everywhere except at their poles which are defined at

$$y = -C_j + n \quad j = 1, 2t+1 \qquad (5.26b)$$

where n is a non-negative integer. Near to such a pole the series expansion is given by [18] :

$$\Gamma\left(-C_j-y\right)=\frac{(-1)^{n-1}}{n!}\left[\frac{1}{y+C_j-n}-\Psi(n+1)+0\left(\left|-C_j+n-y\right|\right)\right]. \quad (5.26c)$$

For $t=0$, equation (5.26) has only poles of order one at $y=-C_1+n$, so that we obtain for this choice of the C_1 (see 5.25b) :

$$G_{0,6}^{1,0}\left(s;\left\{-C_i\right\}\right)=\frac{s^{-C_1}}{\prod_{j=2}^{6}\Gamma\left(1+C_j-C_i\right)}\times {}_0F_5\left(-s;\left\{1+C_j-C_1\right\}\right) \quad (5.26d)$$

where we introduce the hypergeometric generalized function [17, 18]

$${}_0F_5\left(-s;\left\{1+C_j-C_1\right\}\right)=\sum_{n=0}^{\infty}\frac{(-s)^n}{n!}\frac{1}{\prod_{j=2}^{6}\left(C_j-C_1+1\right)_n} \quad (5.26e)$$

where

$$\left(C_j-C_1+1\right)_n=\frac{\Gamma\left(1+C_j-C_1+n\right)}{\Gamma\left(1+C_j-C_1\right)}. \quad (5.26f)$$

If ε is chosen different from $1/Sc$, there are six different values possible for C_1 (see 5.25b). The cyclic permutation of the C_i gives us six linearly independent Meijer functions which are solution of the adjoint problem.

$$G_i(Z)=\frac{\left(a^2 Ra_c\,\mathrm{e}^{-Z}\right)^{-C_i}}{\prod_{j=1}^{5}\Gamma\left(\beta_j^{(i)}\right)}\times {}_0F_5\left(-a^2 Ra_c\,\mathrm{e}^{-Z};\left\{\beta_j^{(i)}\right\}\right) \quad (5.27a)$$

where

$$\beta_j^{(i)}=1+C_K-C_i$$

$$\begin{aligned} K&=6-j && \text{if } i=6\\ K&=6+i-j && \text{if } j\in i,\dots 5\\ K&=i-j && \text{if } j\in 1,\dots i-1. \end{aligned} \quad (5.27b)$$

Let us note that for Δ going to infinity the six $G_i(Z)$ reduce to three physically meaning ones since the odd b_i imply that $G_i(Z)$ diverge at infinity. The other solutions offer striking similarity with the three hypergeometric functions derived by Hurle [6] (see Eq. (68)).

If $\varepsilon=1/Sc$, there are only four different values of G_i (see (5.25b) and we have to look for two more linearly independent solutions $(i=3,4)$ which will be deduced from :

$$G_{0,6}^{3,0}\left(s;\left\{-C_i\right\}\right)=\frac{1}{2\pi i}\int_L\frac{\Gamma^2\left(-C_1-y\right)\Gamma^2\left(-C_3-y\right)}{\prod_{j=4}^{6}\Gamma\left(1+C_j-y\right)}s^y\,\mathrm{d}y \quad (5.28a)$$

where $C_1=C_2$ so that the integrand has poles of order 2 at $y=-C_1+n$ and poles of order 1 at $y=-C_3+n$. Applying again the residue theorem we obtain :

$$\begin{aligned} G_{0,6}^{3,0}\left(s\middle|\left\{-C_i\right\}\right)=&\frac{\Gamma\left(C_1-C_3\right)s^{-C_1}}{\prod_{j=4}^{6}\Gamma\left(1+C_j-C_1\right)}\times\left\{\left[\Psi\left(C_1-C_3\right)+\sum_{j=4}^{6}\Psi\left(1+C_j-C_1\right)-\log s-2\gamma\right]\times\right.\\ &\times{}_0F_5\left(-s\middle|\left\{\delta_j^{(1)}\right\}\right)+\sum_{m=0}^{\infty}\frac{(-s)^m}{m!\prod_{j=3}^{6}\left(1+C_j-C_1\right)_m}\times\\ &\left.\times\left[\sum_{e=1}^{6}\left(\Psi\left(1+C_j-C_1+m\right)-\Psi\left(1+C_j-C_1\right)\right)\right]\right\}+\frac{\Gamma^2\left(C_3-C_1\right)s^{-C_3}}{\prod_{j=4}^{6}\Gamma\left(1+C_j-C_3\right)}{}_0F_5\left(-s\middle|\left\{\delta_j^{(3)}\right\}\right) \end{aligned} \quad (5.29a)$$

with $\delta_j^{(i)}=1+C_j-C_1$, $j=1\dots 6$ and $j\neq i$.

To obtain $G_{i+2}(Z)$ explicitly one replaces C_1 by b_i and C_3 by b_{i+4} in (5.28a), for $i=1$ and $i=2$ respectively. It is clear that the $G_{i+2}(Z)$ are linearly independent from $G_i(Z)$ $(i=1,2)$ since they contain terms which are proportional to $G_i(Z)\,.\,Z$. Thus we have six linearly independent solutions of equations (5.23a) since by construction [18] they are solution of (5.25a) for every Z and in peculiar at $Z=\Delta$.

Condition (5.23c) is thus identical with equation (4.21d). Since the general solution of (5.23a) is given by $\omega_2 = \sum_{i=1}^{6} A_i\, G_i\,(Z)$ we have only five independent conditions to determine 6 amplitudes A_i given by (5.23b) and (4.21d). There are thus an infinite number of sets of six A_i, each being different from the other by a multiplying constant, which proves our initial thesis.

6. Results and conclusions.

The only results presented here concern the comparison of our model with the recent work of Coriell *et al.* [47, 19] and Hurle [6] who both assume pure diffusive transport in the liquid $(\Delta \rightarrow \infty)$. The influence of convection will be given in a following paper (Δ finite). By setting the thermal expansion coefficient equal to 0 and assuming the diffusion boundary layer Δ to be infinite, we were brought back, for $\varepsilon \neq 1/Sc$, to Hurle's Pb-Sn configuration [6] and we definitely obtained identical results. Our results are compared with the numerical analysis of Coriell *et al.* although the minor stabilizing effect of thermal gradient is taken into account in the last analysis. This is clearly shown in table II for the critical-wave number at the marginal state as well as for the prediction of the onset of instability. A typical numerical solution is shown in figure 5 by plotting the critical concentration in the bulk. C_∞, *versus* the perturbation wavenumber for the vertical unidirectional solidification of a doped Pb-Sn alloy at a constant rate of 2×10^{-3} cm/s under a one g gravity. The first minimum (at low wave number $\equiv$ high wavelength) corresponds to the onset of hydrodynamic instability and the second one (low wavelength) to Mullins-Sekerka morphological instability. Our model seems consequently a powerful tool to analyse the influence of convection on hydrodynamic and morphological instabilities. A parametric study for various solutal boundary layer extents is just now in progress and will be dealt with in a further paper.

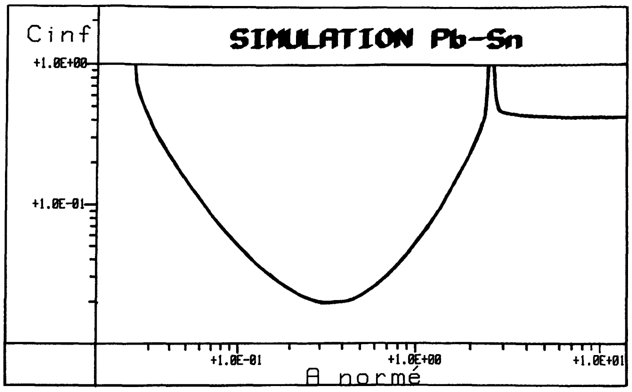

Fig. 5. — Critical concentration in the bulk *versus* perturbation wave number. (The first minimum for a low wave number corresponds to hydrodynamic instability, the flat second one to morphological instability.)

In conclusion, we presented here a general mathematical method to predict the onset of instabilities in solidification processes. It derives from a classical technique currently used in hydrodynamic theoretical studies. The transposition of governing equations in the adjoint space led to an analytical compatibility condition which could be rapidly solved by a small desktop computer. Although the generality

Table II

	Velocity v (cm/s)	C_∞^{**} (wt %)		$a = \omega D/v$		$C_{\infty \mathrm{M.S.}}$ (wt %)		$a_{\mathrm{M.S.}}$	
		Coriell *et al.*	This work	Coriell *et al.*	This work	Coriell. *et al.*	This work	Coriell. *et al.*	This work
$g = g_0$	10^{-3}	3.1×10^{-3}	2.54×10^{-3}	0.4	0.345	0.804	0.804	12.6	12.8
	2×10^{-3}	1.89×10^{-2}	1.88×10^{-2}	0.36	0.353	0.412	0.42	7.85	7.8
	3×10^{-3}	6.4×10^{-2}	6.56×10^{-2}	0.35	0.353	0.281	0.29	6.28	6.15
	4×10^{-3}	0.186	0.209	0.34	0.345	0.215	0.219	5.24	5.18
	5×10^{-3}	0.175	0.175	4.5	4.68	0.175	0.175	4.71	4.68
	8×10^{-3}	0.116	0.118	3.4	3.45	0.116	0.118	3.4	3.45
$g = 10^{-4}\, g_0$	2.5×10^{-4}	3.63×10^{-1}	0.34	0.34	0.345	1.97	not calculated	35.9	not calculated

$G_L = 200$ K/cm.

of the method allows it to be applied to various systems (for instance organic fluids), we focused our attention on the metallurgical alloys assuming $Le \gg Sc$. We also solved the case $1/Sc = 0$ which appeared more complicated due to the linear dependence of basic hypergeometric functions. The simple solution corresponding to Sc not strictly infinite has been checked with models available in the literature for very simplified configurations ($\Delta \to \infty$, $Ra_T = 0$). This method allows us to study more realistic metallurgical cases by taking into account a pre-existent bulk convection through a boundary layer model. We chose the deformable boundary layer model [3] which gives, for high convective regimes, a better agreement with experimental data. Moreover, our analysis can be generalized in the complex plane to predict oscillatory states. However a rather not limitative assumption of our model is that the liquid is completely quiescent in the layer close to the interface [20]. So, a future interesting extension is the introduction of a shear flow near the interface to study the width Δ as a function of a Couette flow already used for a layer of infinite extent by Coriell *et al.* [21].

Appendix

DEMONSTRATION OF THE COMPATIBILITY CONDITION AND EQUIVALENCE WITH HURLE'S MODEL. — We have the original differential system :

$$[L]\begin{bmatrix} f_2(Z) \\ C \end{bmatrix} = \begin{bmatrix} 0 \\ -f_1(Z)\,\mathrm{e}^{-Z} \end{bmatrix} \qquad \text{(I)}$$

with

$$[L] = \begin{pmatrix} \mathfrak{D}_{(4)} & -a^2 Ra_c \\ \mathrm{e}^{-Z} & \mathfrak{D}_{(2)} \end{pmatrix}.$$

Let us define in accordance with the norm of Hilbert space for real functions

$$\langle \omega, Lv \rangle = \sum_{i,j} \int_0^{\Delta} \omega_i\, L_{ij}\, v_j \,\mathrm{d}Z$$

$$\langle \tilde{L}\omega, v \rangle = \sum_{i,j} \int_0^{\Delta} \left(\tilde{L}_{ij}\,\omega_j\right) v_i \,\mathrm{d}Z\,.$$

Since each operator L_{ij} acts on a function v_j as

$$L_{ij}\, v_j(Z) = \sum_{K=0}^{r} A_{ij}\left[p_K(Z)\,\frac{\mathrm{d}^K}{\mathrm{d}Z^K} v_j(Z)\right]$$

the index r being linked to the couple (i, j), a systematic use of integration by parts gives us :

$$(\tilde{L})_{ji}\,\omega_i(Z) = = \sum_{K=0}^{r} A_{ij}\left[\frac{\mathrm{d}^K}{\mathrm{d}Z^K}(-1)^K p_K(Z)\,\omega_i(Z)\right].$$

Defining the bilinear concomitant :

$$F(\omega, v) = \sum_{i,j} A_{ij} \sum_{K=0}^{r}\sum_{j=0}^{K-1} \frac{\mathrm{d}^j}{\mathrm{d}Z^j}\left[p_k(Z)\,\omega_i(Z)\right] \times \frac{\mathrm{d}^{K-1-j}}{\mathrm{d}Z^{K-1-j}}\left[(-1)^j v_j(Z)\right]$$

and using extended Green identity we are reduced to :

$$\int_0^{\Delta}\left\{\left[\omega_1\,\mathfrak{D}_{(4)}\,v_1 - v_1\,\mathfrak{D}_{(4)}\,\omega_1\right] + \left[\omega_2\,\tilde{\mathfrak{D}}_{(2)}\,v_2 - v_2\,\tilde{\mathfrak{D}}_{(2)}\,\omega_2\right]\right\}\mathrm{d}Z = \left[F\left(\omega_1, \omega_2, v_1, v_2\right)\right]_0^{\Delta}.$$

Then one replaces all the boundary conditions (3.16) and (4.17a-e) by their homogeneous counterpart, and the concomitant becomes :

$$\omega_1\left[\frac{\mathrm{d}^3}{\mathrm{d}Z^3} f_2\right]_0^{\Delta} + \omega_2\Big|_{\Delta}\frac{\mathrm{d}C}{\mathrm{d}Z}\Big|_{\Delta} - \left[\frac{\mathrm{d}\omega_1}{\mathrm{d}Z}\frac{\mathrm{d}^2 f_2}{\mathrm{d}Z^2}\right]_0^{\Delta}.$$

The minimum number of conditions on ω_1 and ω_2 needed to put this expression equal to 0 is 5 :

$$\omega_1\Big|_0 = \frac{\mathrm{d}\omega_1}{\mathrm{d}Z}\Big|_0 = \omega_1\Big|_{\Delta} = \frac{\mathrm{d}\omega_1}{\mathrm{d}Z}\Big|_{\Delta} = \omega_2\Big|_{\Delta} = 0 \qquad \text{(II)}$$

which are the boundary conditions on the homogeneous adjoint system. Using the real boundary conditions (3.16) and (4.17a-e) the Green identity reduces to :

$$\langle \omega, Lv \rangle - \langle L\omega, v \rangle = \left[\frac{\mathrm{d}\omega_2}{\mathrm{d}Z}\Big|_0 - \omega_2\Big|_0\right] \times A_8 - \omega_2\Big|_0 B_8 - \frac{\mathrm{d}\omega_2}{\mathrm{d}Z}\Big|_{\Delta}\mathrm{e}^{-\Delta}. \qquad \text{(III)}$$

The left hand of this equation reduces to $\langle \omega, Lv \rangle$ since $\tilde{L}\omega = 0$. If v is a solution of the system (4.18)

$$\langle \omega, Lv \rangle = \int_0^{\Delta} -\omega_2\, f_1(Z)\,\mathrm{e}^{-Z}\,\mathrm{d}Z \qquad \text{(IV)}$$

and thus one obtains (4.22) using (4.18) and (3.12-f)

$$\left(\frac{\mathrm{d}\omega_2}{\mathrm{d}Z}\Big|_0 - \omega_2\Big|_0\right) A_8 - \omega_2\Big|_0 B_8 = \frac{\mathrm{d}\omega_2}{\mathrm{d}Z}\Big|_{\Delta} \times \mathrm{e}^{-\Delta} - \int_0^{\Delta} f_1(Z)\,\omega_2(Z)\,\mathrm{e}^{-Z}\,\mathrm{d}Z\,. \qquad \text{(V)}$$

When $\alpha_T = 0$ and $\Delta \to \infty$ one obtains back the problem studied by Hurle since the previous equation reduces to :

$$\left(\frac{\mathrm{d}\omega_2}{\mathrm{d}Z}\Big|_0 - \omega_2\Big|_0\right) A_8 - \omega_2\Big|_0 B_8 = 0\,. \qquad \text{(VI)}$$

But

$$\omega_2 = -\,\mathrm{e}^{-Z}\,\tilde{\mathfrak{D}}_{(4)}\,\omega_1 \qquad \forall Z$$

Thus equation (V) is equivalent to :

$$\left[\frac{\mathrm{d}}{\mathrm{d}Z}-\frac{B_g}{A_g}\right]\tilde{\mathfrak{D}}_{(4)}\ \omega_1\big|_0=0 \qquad \text{(VII)}$$

which, for $\varepsilon = 1/Sc$, is exactly Hurle's equation (62b) since :

$$\frac{B_g}{A_g}=H=\frac{mG_c-(1-K)\left(G+Ba^2\right)}{G-mG_c+Ba^2}$$

according to the formalism used in [6].

Let us consider the adjoint homogeneous system :

$$\tilde{\mathfrak{D}}_{(4)}\ \omega_1+\mathrm{e}^{-Z}\,\omega_2=0$$

$$\tilde{\mathfrak{D}}_{(2)}\ \omega_2-a^2\,Ra_c\,\omega_1=0$$

and let us multiply the first equation by the operator $\mathfrak{D}_{(2)}$. It follows :

$$\mathfrak{D}_{(2)}\ \tilde{\mathfrak{D}}_{(4)}\ \omega_1+\mathfrak{D}_{(2)}\left[\mathrm{e}^{-Z}\,\omega_2\right]=$$

$$=\mathfrak{D}_{(2)}\ \tilde{\mathfrak{D}}_{(4)}\ \omega_1+Ra_c\,a^2\,\mathrm{e}^{-Z}\,\omega_1=0\,. \qquad \text{(VIII)}$$

But for $\varepsilon = 1/Sc$

$$\tilde{\mathfrak{D}}_{(4)}=\mathfrak{D}_{(4)}\,.$$

Introducing Hurle hypothesis in (I), eliminating C, and using we get :

$$f_2(Z)\rightarrow u \quad f_1(Z)\rightarrow 0$$

we get :

$$\mathfrak{D}_{(2)}\ \mathfrak{D}_{(4)}\ u+\mathrm{e}^{-Z}\,a^2\,Ra_c\,u=0\,. \qquad \text{(IX)}$$

So that u and ω_1 are solutions of the same differential equation and obey the same boundary conditions, since (4.17d-e) become respectively :

$$u\,|_0=0 \qquad \frac{\mathrm{d}}{\mathrm{d}Z}u\,|_0=0\,.$$

The boundary conditions (4.17a-b) become

$$\frac{\mathrm{d}}{\mathrm{d}Z}\mathfrak{D}_{(4)}\ u\,|_0=a^2\,Ra_c\,B_g \qquad \mathfrak{D}_{(4)}\ u\,|_0=a^2\,Ra_c\,A_g$$

and thus :

$$\left[\frac{\mathrm{d}}{\mathrm{d}Z}-\frac{B_g}{A_g}\right]\mathfrak{D}_{(4)}\ u\,|_0=0$$

which is equivalent to (VI).

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References

[1] MULLINS, W. W., SEKERKA, R. F., *J. Appl. Phys.* **34** (1963) 323.
[2] FLEMINGS, M., *Solidification Processing* (Mac Graw Hill) 1974.
[3] FAVIER, J. J., ROUZAUD, A., *J. Crystal Growth* **64** (1983) 367.
[4] CORIELL, S. R., CORDES, M. R., BOETTINGER, W. J., SEKERKA, R. F., *J. Crystal Growth* **49** (1980) 13.
[5] WOLLKIND, D. J., SEGEL, L. A., *Philos. Trans. R. Soc. London* **A 268** (1970) 351.
[6] HURLE, D. T. J., JAKEMAN, E., WHEELER, A. A., *J. Crystal Growth* **58** (1982) 163.
[7] CAROLI, B., CAROLI, C., MISBAH, C. and ROULET, B., *J. Physique* **46** (1985) 401.
[8] CAMEL, D., FAVIER, J. J., *J. Crystal Growth* **67** (1984) 42 and 57 and submitted to *J. Physique.*
[9] LANCZOS, C., *Linear Differential Operators* (Ed. Van Nostrand, N.Y.) 1961.
[10] CHANDRASEKHAR, S., *Hydrodynamic and Hydromagnetic Stability* (Oxford University Press London) 1961.
[11] CORIELL, S. R., HURLE, D. T. J., SEKERKA, R. F., *J. Crystal Growth* **32** (1976) 1.
[12] BURTON, J. A., PRIM, R. C., SLICHTER, W. P., *J. Chem. Phys.* **21** (1953) 1987.
[13] NIELD, D. A., *J. Fluid Mech.* **29** (1967) 545.
[14] SMIRNOV, S., *Cours de Mathématiques Supérieures* (Ed. Mir Moscou) 1973.
[15] NAYFEH, A. H., *Introduction to Perturbation Techniques* (Ed. J. Wiley and sons, N. Y.) 1981.
[16] STAKGOLD, T., *Green's Functions and Boundary Value Problems* (Wiley Interscience, N. Y.) 1979.
[17] ABRAHMOWITZ, J., STEGUN, I., *Tables of Mathematical Functions* (Dover, N. Y.) 1974.
[18] ERDELYI, A., *Higher Transcendantal Functions* (Mac Graw Hill) 1960.
[19] CORIELL, S. R., SEKERKA, R. F., *Physicochem. Hydrodyn.* **2** (1981) 281.
[20] HURLE, D. T. J. (private discussion).
[21] CORIELL, S. R., MACFADDEN, BOISVERT, R. F. and SEKERKA, R. F., *J. Crystal Growth* **69** (1984) 15.