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On morphological stability of planar phase boundaries during unidirectional transient solidification of binary aqueous solutions

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Abstract—This paper deals with the stability of planar phase boundaries during transient solidification of binary aqueous solutions and raises the question of the time and wavenumber characterizing the breakdown of the phase boundaries in these solidification processes. In the first part a linear stability analysis is performed. The central result of this analysis is a dynamical stability criterion that fixes the time of first marginal instability. This criterion is an equivalent formulation to the well-known Mullins–Sekerka criterion, that enables the specific wave number of the first instability to be calculated. In the second part of this paper these criteria are used to determine the breakdown of planar phase boundaries in a special transient freezing situation of an isotonic aqueous solution of sodium chloride.

1. INTRODUCTION

THIS PAPER is to be considered as an immediate follow-up to ref. [1]. In this the transient coupled transport of heat and mass of a binary aqueous salt solution freezing with planar phase boundaries has been discussed. Apart from the specific choice of geometry, the following parameters were taken as essential prerequisites for that problem:

(a) the cooling at the boundaries was linear in time;
(b) total salt particle rejection of the moving phase boundaries.

These assumptions are finally responsible for a specific transient solidification kinetics.

The results obtained there, in particular the partly very high salt concentration gradients building up in front and the moving phase boundaries, led directly to questioning the stability of the planar phase boundaries assumed there. In the present publication, this problem will be discussed in two parts. In the first part, a linear stability analysis is presented which, in quasi-stationary approximation, is applicable to the transient solidification kinetics presented in [1]. Here, essential parts of the calculation are in agreement with the linear stability analysis presented by Wollkind and Segel [2]. In the second part, the general results obtained are applied to the specific system discussed in [1].

The previously indicated methodology of examining, the stability of the planar phase boundaries by quasi-stationary approximation leads necessarily to the question why a further stability analysis should be carried out at all. Following Rutter and Chalmers [3] first formulation of a stability criterion (and the subsequent introduction of constitutional supercooling) which was expressed in quantitative terms by Tiller *et al.* [4], several papers were published [5–14, 2] the results of which might have been applied. However, in these publications, without exception, only systems were considered in which the phase diagram shows a solidus line. This, however, is in contrast to many binary aqueous salt solutions which are the subject of the present paper. Against this background, firstly O'Callaghan's application of the Mullins–Sekerka criterion [7] on a solidifying binary aqueous system is to be considered [15].

2. THEORY

Let us therefore consider a unidirectional solidification process in a binary system, of finite extension, which takes place with planar phase boundary in the direction of the positive x-axis that is characterized by total solute particle rejection at the phase boundary. Moreover, let us assume that the temperature of the solid phase $T_s^p(x,t)$, of the liquid phase $T_l^p(x,t)$ of the solute concentration in the liquid remainder $C^p(x,t)$ and finally the phase boundary kinetics $y(t)$ are known. (In the following the superscript p denotes the corresponding functions as 'planar solutions'.) If an infinitesimally small perturbation $\Phi(w,t)$, w perpendicular to x, is imposed on the planar phase boundary, then, under the assumptions which are extensively explained in [1], the entire system is described by

$$a_s \frac{\partial^2 T_s}{\partial \mathbf{r}^2} + \dot{y}\frac{\partial T_s}{\partial x} = \frac{\partial T_s}{\partial t} \qquad x \leqslant \dot{y}t + \phi \tag{1}$$

$$\left.\begin{aligned} a_l \frac{\partial^2 T_l}{\partial \mathbf{r}^2} + \dot{y}\frac{\partial T_l}{\partial x} &= \frac{\partial T_l}{\partial t} \qquad (2) \\ D\frac{\partial^2 c}{\partial \mathbf{r}^2} + \dot{y}\frac{\partial c}{\partial x} &= \frac{\partial c}{\partial t} \qquad (3) \end{aligned}\right| \quad x \geq \dot{y}t + \phi$$

$[\mathbf{r} = (x, w)]$

NOMENCLATURE

a_o	growth parameter
B	cooling function [K]
$\dot{B}$	cooling rate [K s^{-1}]
c	salt concentration [mol mm^{-3}]
C	integration constants
g	abbreviation for gradient
G	functional abbreviation
K	curvature of the phase boundary (mm^{-1})
K^*	gradient combination
m	slope of the liquidus line [K c^{-1}]
M	dimensionless slope of the liquidus line
m_1, m_2, m_3	integration constants
n	dimensionless parameter
q	latent heat of fusion [J mm ^{3}]
$\mathbf{r}$	spatial vector
t	time [s]
T	temperature [K]
T^*	gradient combination
v	velocity of the phase boundary vector component in normal direction [mm s^{-1}]
w, x, z	spatial coordinates [mm]
y	position of planar phase boundaries [mm]
$\dot{y}$	velocity of planar phase boundaries [mm s^{-1}].

Greek symbols

γ	dimensionless capillarity
β	dimensionless heat of fusion
δ	scaling parameter
ϑ	differential operator
Γ	capillarity [mm]
ε	perturbation parameter
ξ	scaling parameter
Φ	perturbed phase boundary [mm]
λ	thermal conductivity [J mm^{-1} s^{-1} K^{-1}].

Constants for calculation in part 2

a_s	thermal diffusivity of ice = 1.364 mm^2 s^{-1}
a_l	thermal diffusivity of liquid = 0.115 mm s^{-1}
D	diffusivity of NaCl in water = 7.8×10^{-4} mm^2 s^{-1}
q	latent heat of fusion = 0.333 J mm^{-3}
T_R	room temperature = 293.15 K
T_o	equilibrium freezing temperature of water = 273.15 K
λ_s	thermal conductivity of ice = 2.34×10^{-3} J mm^{-1} s^{-1} K^{-1}
λ_l	thermal conductivity of liquid = 5.34×10^{-4} J mm^{-1} s^{-1} K^{-1}
Γ	capillarity length = 4.8×10^{-8} mm.

Superscript

p	planar.

Subscripts

c	critical
s	solid
l	liquid
o	marginal stable
Li	liquidus line.

(see also [1] Table 1), while the transition to a two-dimensional description of the diffusion processes has been performed. Equations (1)–(3) refer to a coordinate system moving with the planar phase boundary. (The designation of the coordinate axes have been taken from [1].) The boundary conditions at the perturbed phase boundary undergo the following changes

$$T_s|_\phi = T_l|_\phi = T_o(1+\Gamma K)+mc|_\phi, \tag{4}$$

i.e. the influence of curvature K of the phase boundary on the equilibrium freezing temperature by a Gibbs–Thomson relation (Γ = capillarity constant)

$$qv|_\phi = \lambda_s \frac{\partial T_s}{\partial n}\bigg|_\Phi - \lambda_l \frac{\partial T_l}{\partial n}\bigg|_\Phi \tag{5}$$

the heat balance at the phase boundary in the direction of the surface normal n, v being the phase boundary velocity vector component in this direction.

Consequently, for the total salt particle rejection at Φ

$$-vc|_\Phi = D\frac{\partial c}{\partial n}\bigg|_\Phi \tag{6}$$

appears. Thus, using the relations

$$\mathbf{n} = \left(-\frac{\partial \phi}{\partial w}, 1\right)\left(1+\left(\frac{\partial \phi}{\partial w}\right)^2\right)^{-1/2}, \tag{7}$$

$$v = (\dot{y}+\dot{\phi})\left(1+\left(\frac{\partial \phi}{\partial w}\right)^2\right)^{-1/2} \tag{8}$$

equations (5) and (6) can be written as

$$\dot{y}+\dot{\Phi} = \frac{1}{q}\left[\lambda_s\left(\frac{\partial T_s}{\partial x} - \Phi'\frac{\partial T_s}{\partial w}\right) - \lambda_l\left(\frac{\partial T_l}{\partial x} - \Phi'\frac{\partial T_l}{\partial w}\right)\right], \tag{9}$$

$$-(\dot{y}+\dot{\Phi})c|_\phi = D\left(\frac{\partial c}{\partial x}\bigg|_\phi - \Phi'\frac{\partial c}{\partial w}\bigg|_\phi\right), \qquad \left(\Phi' = \frac{\mathrm{d}\phi}{\mathrm{d}w}\right). \tag{10}$$

In order to complete the boundary conditions it is considered that the solution of the equation system (1)–(3) should be asymptotically identical (for sufficiently high distances from the phase boundary ϕ) with that of the planar case. If, therefore, a solution in the form of

$$
\begin{aligned}
c(x,w,t) &= c^{\mathrm{p}}(x,t)+\hat{c}(x,w,t),\\
T_{\mathrm{l}}(x,w,t) &= T_{\mathrm{l}}^{\mathrm{p}}(x,t)+\hat{T}_{\mathrm{l}}(x,w,t), \qquad (11)\\
T_{\mathrm{s}}(x,w,t) &= T_{\mathrm{s}}^{\mathrm{p}}(x,t)+\hat{T}_{\mathrm{s}}(x,w,t),
\end{aligned}
$$

is looked for, then $\hat{T}_{\mathrm{s,l}}$ and $\hat{c}$ have to disappear for $x \rightarrow L$, provided ϕ is sufficiently far away from L (see section 3. Here it should be pointed out that, in contrast to other equivalent calculations, the complete time-dependent planar solutions have been incorporated in (11). This means, in the present case, a difference from the classic scheme of stability analysis which always starts from steady-state conditions, reference [16]. However, if at any moment during the transient planar solidification the velocity $\dot{y}$ of the phase boundary and the appropriate functions $T_{\mathrm{s,l}}^{\mathrm{p}}(x,t)$, $c^{\mathrm{p}}(x,t)$ are considered as being constant in time and, based on this assumption, the stability of the planar phase boundary is examined at this moment, it means nothing else but performing a quasi-stationary stability analysis. The subsequent calculations will be carried out on this assumption.

Scaling

The scaling of the parameters used for dimensionless description of the problem can be done in complete agreement with the arguments of Wollkind and Segel [2] because of quasi-stationarity. The following is, therefore, taken over as

$$
\begin{aligned}
&\bar{c}=\frac{c}{c^{\mathrm{p}}|_{\mathrm{o}}}, \quad \bar{T}_{\mathrm{s,l}}=\frac{T_{\mathrm{s,l}}}{T_{\mathrm{o}}}, \quad \bar{\Phi}=\frac{\phi}{\delta},\\
&(\bar{x},\bar{w})=\frac{\dot{y}}{D}(x,w), \quad \bar{t}=\frac{\dot{y}^2}{D}t, \quad \varepsilon=\frac{\dot{y}}{D}\delta,\\
&\xi=\frac{D}{a_{\mathrm{l}}}, \quad M=\frac{mc^{\mathrm{p}}|_{\dot{\mathrm{o}}}}{T_{\mathrm{o}}}, \quad \gamma=\frac{\dot{y}}{D}\Gamma, \qquad (12)\\
&n=\frac{\lambda_{\mathrm{s}}}{\lambda_{\mathrm{l}}}, \quad \delta=\max|\Phi|, \quad \beta=\frac{qD}{\lambda_{\mathrm{l}}T_{\mathrm{o}}}.
\end{aligned}
$$

Thus, equations (1)–(6), (9) and (10) become

$$
\begin{aligned}
&\frac{\partial^2}{\partial\bar{\mathbf{r}}^2}\bar{c}+\frac{\partial\bar{c}}{\partial\bar{x}}-\frac{\partial\bar{c}}{\partial\bar{t}}=0,\\
&\frac{\partial^2}{\partial\bar{\mathbf{r}}^2}\bar{T}_{\mathrm{s,l}}+\xi\frac{\partial\bar{T}_{\mathrm{s,l}}}{\partial\bar{x}}-\xi\frac{\partial\bar{T}_{\mathrm{s,l}}}{\partial\bar{t}}=0\Rightarrow \qquad (13)
\end{aligned}
$$

$$\frac{\partial^2}{\partial\bar{\mathbf{r}}^2}\bar{T}_{\mathrm{s,l}}=0 \quad \text{because} \quad \xi\ll 1, \qquad (14)$$

$$\bar{T}|_{\bar{\phi}}=1+M\bar{c}|_{\bar{\phi}}+\gamma\varepsilon\bar{\Phi}''(1+\varepsilon^2\bar{\Phi}'^2)^{-3/2}, \qquad (15)$$

$$\bar{T}_{\mathrm{s}}|_{\bar{\phi}}=\bar{T}_{\mathrm{l}}|_{\bar{\phi}}, \qquad (16)$$

$$n\frac{\partial\bar{T}_{\mathrm{s}}}{\partial\bar{x}}\bigg|_{\bar{\phi}}-\frac{\partial\bar{T}_{\mathrm{c}}}{\partial\bar{x}}\bigg|_{\bar{\phi}}-\varepsilon\bar{\Phi}'\left(n\frac{\partial\bar{T}_{\mathrm{s}}}{\partial\bar{w}}\bigg|_{\bar{\phi}}-\frac{\partial\bar{T}_{\mathrm{c}}}{\partial\bar{w}}\bigg|_{\bar{\phi}}\right)=0,$$

$$\text{because} \quad \beta\ll 1, \qquad (17)$$

$$\frac{\partial\bar{c}}{\partial\bar{x}}\bigg|_{\bar{\phi}}-\varepsilon\bar{\Phi}'\frac{\partial\bar{c}}{\partial\bar{w}}\bigg|_{\bar{\phi}}=-\bar{c}|_{\bar{\phi}}(1+\varepsilon\dot{\bar{\Phi}}). \qquad (18)$$

In order to further develop the system (11), solutions will be looked for by the complete separation formulas

$$
\begin{aligned}
\bar{c}(\bar{\mathbf{r}},\bar{t},\varepsilon) &= c^{\mathrm{p}}(\bar{x},\bar{t})+\varepsilon\dot{c}(\bar{x})\cos(k\bar{w})\,\mathrm{e}^{a_{\mathrm{o}}\bar{t}},\\
\bar{T}_{\mathrm{s,l}}(\bar{\mathbf{r}},\bar{t},\varepsilon) &= \bar{T}_{\mathrm{s,l}}(\bar{x},\bar{t})+\varepsilon\hat{T}_{\mathrm{s,l}}(\bar{x})\cos(k\bar{w})\,\mathrm{e}^{a_{\mathrm{o}}\bar{t}},\\
\varepsilon\bar{\Phi}(w,t,\varepsilon) &= \varepsilon\hat{\Phi}_1\cos(k\bar{w})\,\mathrm{e}^{a_{\mathrm{o}}\bar{t}}. \qquad (19)
\end{aligned}
$$

This provides also a specification of the perturbation as periodic function. Furthermore, the complex parameter a_{o} which is the most important for the entire stability analysis is introduced, the sign of $Re(a_{\mathrm{o}})$ evidently determining whether a planar phase boundary will be stable or not with regard to this specific perturbation.

After insertion in equations (13) and (14)

$$
\begin{aligned}
(\vartheta^2-k^2+\vartheta-a_{\mathrm{o}})\hat{c}(\bar{w}) &= 0,\\
(\vartheta^2-k^2)\hat{T}_{\mathrm{s,l}}(\bar{w}) &= 0 \qquad (20)
\end{aligned}
$$

results, ϑ being the differential operator $\vartheta=\partial/\partial\bar{x}$.

The series expansion of the boundary conditions (15)–(18) around $x=0$ and disregarding all terms in ε^2 leads to

$$
\begin{aligned}
&M\hat{c}|_{\mathrm{o}}-\hat{T}_{\mathrm{l}}|_{\mathrm{o}}+\hat{\Phi}_1(M\bar{g}_{\mathrm{c}}-\bar{g}_{\mathrm{l}}-k^2\gamma)=0,\\
&\hat{T}_{\mathrm{s}}|_{\mathrm{o}}-\hat{T}_{\mathrm{l}}|_{\mathrm{o}}-\hat{\Phi}_1(\bar{g}_{\mathrm{l}}-\bar{g}_{\mathrm{s}})=0,\\
&n\frac{\partial\bar{T}_{\mathrm{s}}}{\partial\bar{x}}\bigg|_{\mathrm{o}}-\frac{\partial\bar{T}_{\mathrm{l}}}{\partial\bar{x}}\bigg|_{\mathrm{o}}=0, \qquad (21)\\
&\frac{\partial\hat{c}}{\partial\bar{x}}\bigg|_{\mathrm{o}}+\hat{c}|_{\mathrm{o}}+\hat{\Phi}_1(\bar{g}_{\mathrm{c}}'+\bar{g}_{\mathrm{c}}+a_{\mathrm{o}})=0.
\end{aligned}
$$

In order to achieve better comparability with other publications, in this eigenvalue problem for the eigenvalue a_{o}, the gradients of temperature and salt concentration at the phase boundary were designated by 'g' (it follows that $\bar{g}_{\mathrm{c}}'=\partial^2\bar{c}/\partial\bar{x}^2$). It must, however, be pointed out that $\bar{g}_{\mathrm{s}}$, $\bar{g}_{\mathrm{l}}$, $\bar{g}_{\mathrm{c}}$ and $\bar{g}_{\mathrm{c}}'$ are explicitly time dependent.

The equations

$$
\begin{aligned}
\hat{c}(\bar{x}) &= C_1\exp\{-m_1\bar{x}\},\\
\hat{T}_{\mathrm{s,l}}(\bar{x}) &= C_{2,3}\exp\{-m_{2,3}\bar{x}\}, \qquad (22)\\
\Phi_1 &= C_4
\end{aligned}
$$

when inserted in equation (20) result in

$$
\begin{aligned}
m_1 &= \tfrac{1}{2}+\sqrt{\tfrac{1}{4}+a_{\mathrm{o}}+k^2},\\
m_{2,3} &= \pm|k| \qquad (23)
\end{aligned}
$$

the sign of the root having been selected according to the required asymptotic behaviour.

The determination of the constants C_1–C_4 needed for completing the calculations can be achieved by the solution of the following equation system which is obtained by inserting the equations (22) into the phase boundary system (21).

$$\begin{aligned} MC_1-C_3+(M\bar{g}_c-\bar{g}_l-k^2\gamma)C_4 &= 0,\\ C_2-C_3-(\bar{g}_l-\bar{g}_s)C_4 &= 0,\\ -nm_2C_2+m_3C_3 &= 0,\\ (1-m_1)C_1+(\bar{g}'_c+\bar{g}_l+a_o)C_4 &= 0. \end{aligned} \tag{24}$$

It is known that such a linear system has a non-trivial solution in the case that the determinant of the coefficients vanishes. If this calculation is carried out, an equation for the parameter a_o which is crucial for this stability analysis is finally obtained. Using the equations

$$\begin{aligned} K^* &= \bar{g}'_c+\bar{g}_c,\\ G(a_o,k^2) &= -\tfrac{1}{2}+\sqrt{\tfrac{1}{4}+a_o+k^2},\\ T^*(t) &= \frac{1}{M(1+n)}(\bar{g}_l+n\bar{g}_s)-\bar{g}_c \end{aligned}$$

the result of the determinant calculation is

$$a_o = G(a_o,k^2)\left(T^*-\frac{\gamma}{M}k^2\right)-K^*. \tag{25}$$

Another aim of this linear analysis is the clarification of the question at what time of the transient solidification process, and at which wave number, the breakdown of the planar phase boundaries occurs. This particular question is therefore, essentially different from the stability analysis based on steady planar solutions. In particular, the frequently criticised *ad hoc* assumption of perturbation wave numbers can be dispensed with [17] as it can be expected on the basis of experimental examinations of transient solidification process [18]. The answer to the above question is evidently given by a further examination of the equation (25) in which a_o is obviously dependent on the time-dependent gradient combination K^*, T^* and explicitly on the wave number k, provided $Re(a_o) = 0$. In other words, the conditions for marginal stability will be the subject of the further calculations. The calculations will be considerably facilitated by the so-called 'principle of exchange of stability' which is expressed by

$$Re(a_o) = 0 \Rightarrow Im(a_o) = 0. \tag{26a}$$

If, therefore, $a_o = Re(a_o)+Im(a_o)$ is inserted in equation (25) it can easily be shown that (26) is met. Because of the simplicity of this evidence it will not be further discussed. The advantage mentioned consists in the possibility to express $a_o = 0$ for examining marginal stability.

Thus, the marginal stability criterion is formulated as follows:

$$0 = G(o,k^2)\left(T^*_c-\frac{\gamma}{M}k^2\right)-K^*_c. \tag{26b}$$

Because of the common summand $\bar{g}_c$, K^*_c in the above equation can be replaced by a term in T^*_c, so that equation (26) defines a function $T^*_c(k^2,\bar{t})$ which carries in itself the conditions for marginal stability

$$T^*_c(k^2,\bar{t}) = \frac{1}{M(\frac{1}{2}+\sqrt{\frac{1}{2}+k^2})} \times\left[M\bar{g}'_c+\frac{1}{1+n}(\bar{g}_l+n\bar{g}_s)+\gamma k^2(\tfrac{1}{2}-\sqrt{\tfrac{1}{4}-k^2})\right]. \tag{27}$$

By using the equation $T^*_c(k^2,t) = T^*(t)$, a solution set k^2_v ($v = 0, 1, 2,\ldots$) is generally obtained of those wave numbers for which, at a fixed time $\bar{t}$, the gradients considered fulfil the marginal stability criterion. This solution set can have a maximum of two elements (cf. [2] and note the structure of T^*_c). It may, however, also be empty. As can be seen from Wollkind and Segel [2], both wave numbers form, in the first case, the boundaries of a closed k-band in which $Re(a_o) > 0$, i.e. instability of the planar phase boundary. The second case implies the absolute stability of the planar phase boundary, independent of k.

If, therefore, a unidirectional transient solidification process takes place initially with a planar phase boundary, the question posed above as to the time $\bar{t}_o$ of the first instability and its corresponding wave number k_o is expressed by the equivalent formulation.

We are looking for the condition for which the equation

$$T^*_c(k^2,\bar{t}) = T^*(\bar{t}) \tag{28}$$

provides only one solution $k^2_o \neq 0$. It can easily be verified that this is the case when $K^*_c = 0$, or

$$\bar{g}'_c(\bar{t}_o)+\bar{g}_c(\bar{t}_o) = 0. \tag{29}$$

From this it follows for the wave number k_o

$$\gamma k^2_o = \frac{1}{1+n}(\bar{g}_l+n\bar{g}_s)-M\bar{g}_c. \tag{30}$$

Equations (29) and (30) are the general result of the present quasi-stationary stability analysis. The moment at which the first instability occurs is primarily determined by the concentration of the dissolved substance, provided there is total rejection of solute by the moving phase boundary. As $\bar{g}_c < 0$ and $\bar{g}'_c > 0$ always applies, stability at the planar phase boundary is maintained as long as

$$\bar{g}'_c > |\bar{g}_c| \tag{31}$$

holds. In other words, $\bar{g}'_c$ is a stabilizing factor for planar phase boundaries, in contrast to $\bar{g}_c$, as is generally known. Applying the condition for total particle rejection of solute (cf. [1]), it can be demonstrated, after cancelling the scaling procedure and using some algebra, that equation (29) possesses an equivalent formulation in

$$\frac{c^p|_o}{D}\dot{y}^2 = \dot{c}^p|_o. \tag{32}$$

Thus, the formulation of a *dynamic* stability condition is established.

It has to be pointed out that equations (29) and (30) are equivalent presentations. As is to be expected for this type of analysis, equation (30) presents the central Mullins–Sekerka equation (7). The essential fact here consists in finding in equation (29) and equation (32) respectively an equivalent dynamic condition, independent of k, which fixes the moment of the solidification process at which following the Mullins–Sekerka criterion, the wave number k_0 of the first instability can be determined.

3. SPECIAL RESULTS AND DISCUSSION

Now, in analogy to [1], the following geometrical arrangement is considered: two parallel plane walls that are at a fixed distance of $2L$ from each other and that extend into infinity in z- and w-directions bound the region under further consideration (Fig. 1).

This region is filled entirely and homogeneously with an aqueous solution of sodium chloride (concentration C_0) initially being held at room temperature T_R. The 'cooling' of this salt solution shall be performed by a spatially independent linear function

$$B(t) = T_R + \dot{B}t, \quad \dot{B} = \text{const.} < 0$$

that is defined in the planes (o, w, z) and $(2L, w, z)$. Now, the planar solidification of the salt solution that starts as soon as the temperature of these planes is lower than the equilibrium freezing temperature $T_{Li}(C_0)$ can be completely described by special numerical techniques [1]. This means $T_s^p(x,t)$, $T_l^p(x,t)$, $C^p(x,t)$ and $y(t)$ are known, clarifying the transient character of this special freezing process.

Although the situation described seems to be a good approximation to a real solidification process, there does to date unfortunately not exist, as far as the authors are aware, any possibility of comparing the model calculation with experimental findings.

The application of equation (29) on this planar solution leads to Fig. 2, in which the moment of first instability of the planar phase boundary is plotted vs the cooling rate $\dot{B}$.

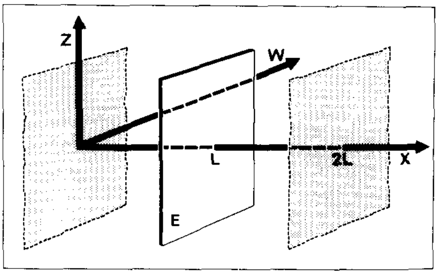

FIG. 1. Definition of geometrical arrangement.

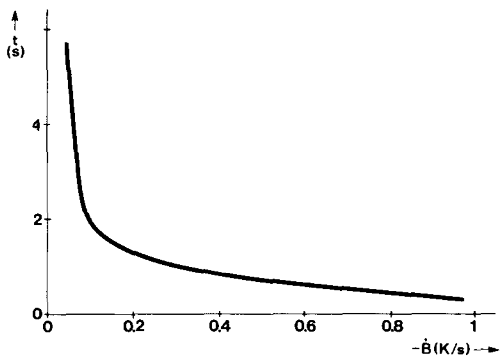

FIG. 2. The time of first marginal stability vs cooling rate.

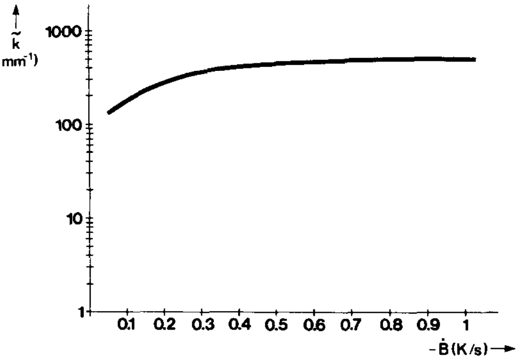

FIG. 3. The wave number of first marginal stability vs cooling rate.

In general it can be said that planar phase boundaries remain, in this particular case, stable only for a relatively short time. In other words, the solidifying salt solution 'reacts' relatively quickly to the imposed cooling B by a higher order phase boundary structure. This is due to the missing inclusion of the saline in the solid phase. As can be expected, this effect is small at high cooling rates and vice versa. However, caution should be applied for the transition $-\dot{B} \rightarrow 0$. At very slow cooling rates, a homogeneous supercooling of the system may occur. This case is excluded in [1] and does not necessarily result in unidirectional solidification.

In Fig. 3, according to equation (30), the wave number $\tilde{k}$ at the moment of first instability is also plotted vs the cooling rate. In this presentation, it is remarkable that the system reacts to increasing cooling rates with increasing distinct wave numbers. This reaction is more pronounced in the range of slow cooling rates. However, it is stagnating at higher cooling rates.

This finding, which is somewhat surprising, raises the question as to another way (different from breaking down at a defined moment with fixed wave numbers) in which a planar phase boundary may react to imposed cooling rates. It seems evident that this question is not answered by the linear stability analysis presented here; elucidation of this problem could rather be expected from a subsequent examination of the further growing of the disturbed phase boundary.

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SUR LA STABILITE MORPHOLOGIQUE DE FRONTIERES PLANES ENTRE PHASES PENDANT LA SOLIDIFICATION UNIDIRECTIONNELLE TRANSITOIRE DE SOLUTIONS BINAIRES AQUEUSES

Résumé—On Considère la stabilité de frontières planes pendant la solidification transitoire de solutions binaires aqueuses et on soulève la question du temps et du nombre d'onde qui caractérisent la rupture des interfaces dans ces mécanismes de solidification. Dans la première partie, on conduit une analyse linéaire de stabilité. Le résultat principal de l'étude est un critère de stabilité dynamique qui fixe le temps de la première instabilité marginale. Ce critère est une formulation équivalente à celle du critère connu de Mullins–Sekerks qui fournit le nombre d'onde spécifique de la première instabilité. Dans la seconde partie du texte, ces critères sont utilisés pour déterminer la rupture des interfaces planes dans une situation spéciale du gel d'une solution aqueuse isotonique de chlorure de sodium.

ÜBER DIE MORPHOLOGISCHE STABILITÄT PLANARER PHASENGRENZEN WÄHREND DER GERICHTETEN INSTATIONAREM ERSTARRUNG BINÄRER WÄSSRIGER LÖSUNGEN

Zusammenfassung—Der vorliegenden Arbeit liegt die Frage zugrunde, zu welchem Zeitpunkt und mit welcher Wellenzahl planare Phasengrenzen in instationär verlaufenden Erstarrungsvorgängen binärer wässriger Lösungen zusammenbrechen. Im ersten Teil wird, unter der Voraussetzung von Quasistationarität eine lineare Stabilitäts-analyse für solche Systeme durchgeführt. Das zentrale Ergebnis dieser Analyse ist ein dynamisches Stabilitätskriterium, das den Zeitpunkt der ersten marginalen Instabilität bestimmt. Dieses Kriterium ist eine äquivalente Formulierung des Mullins–Sekerka Kriteriums, das die Bestimmung der gesuchten Wellenzahl ermöglicht. Im zweiten Teil der Arbeit finden diese Kriterien eine Anwendung auf einen speziellen instationären Erstarrungsvorgang einer isotonen wäßrigen Kochsalzlösung.

О МОРФОЛОГИЧЕСКОЙ СТАБИЛЬНОСТИ ПЛОСКИХ ФАЗОВЫХ ГРАНИЦ ПРИ ОДНОНАПРАВЛЕННОМ ПЕРЕХОДНОМ РЕЖИМЕ ЗАТВЕРДЕВАНИЯ БИНАРНЫХ ВОДНЫХ РАСТВОРОВ

Аннотация—В работе исследуется стабильность плоских фазовых границ при переходном режиме затвердевания бинарных водных растворов, находится время и волновые числа, характеризующие разрушение плоских фазовых границ при процессах затвердевания. В первой части дан линейный анализ устойчивости, в результате которого получен критерий динамической устойчивости, определяющий время первой маргинальной неустойчивости границ. Полученный критерий эквивалентен хорошо известному критерию Муллинса–Секерки, применяемому для расчета характерного волнового числа первой неустойчивости. Во второй части оба критерия используются для определения условий разрушения плоской границы в особом случае фазы переходного замораживания изотонического водного раствора хлорида натрия.