

Nonlinear Three Dimensional Morphological Instability in Directional Solidification — An Integral Approximation

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In this article, we derive a strongly nonlinear evolution equation by using the integral method to study the instabilities in a directionally solidified binary mixture. This equation not only can describe the interfacial behaviors of all the long-wave limits, but also can provide the possibility of strongly nonlinear instability analysis. Three-dimensional weakly nonlinear analysis proceeded from the critical condition is undertaken to investigate the two-dimensional bend-like cells and the three-dimensional hexagonal structures.

KEYWORDS: directional solidification, nonlinear morphological instability, solid-liquid interface, pattern formation, integral approximation

§1. Introduction

A variety of interesting patterns can form during the directional solidification of a dilute binary alloy.^{1,2)} During the solidification, an initially flat interface may develop either a quasi-one-dimensional band-like cell or hexagonal pattern of bulges and depressions which looks very similar to the classic pictures of Bénard convection,^{3,4)} both resulting in unwanted compositional inhomogeneities in the solidified material. This is known as the morphological instability.

The first explanation of the morphological instability was given by Tiller *et al.*⁵⁾ in terms of the mechanism of constitutional supercooling. Mullins and Sekerka⁶⁾ explained the physical nature of this phenomenon by showing that it results from the competition between the destabilizing effect of solute diffusion and the stabilization due to interfacial tension and to the external thermal gradient. They performed a linear stability analysis and calculated the instability threshold, where the bifurcation from the planar to the non-planar front structure occurs.

Wollkind and Segel⁷⁾ presented a weakly nonlinear analysis, up to third order in the front deformation amplitude, which describes the immediate vicinity of the bifurcation. Their two-dimensional treatment only describes two-dimensional band-like cells. Caroli, Caroli, and Roulet⁸⁾ simplified this work and extended it to take account of diffusion in the solid. The effects of latent heat, and hence of nonlinear profiles of temperature, were considered by Alexander, Wollkind, and Sekerka.⁹⁾

The instability of a planar interface to three-dimensional hexagons was investigated by Sriranganathan *et al.*,¹⁰⁾ by Wollkind *et al.*¹¹⁾ and by Kerszberg.¹²⁾ Caroli, Caroli, and Roulet,¹³⁾ extending the works of Wollkind, Sriranganathan, and Oulton,^{10,11)} studied the stability of periodic hexagonal cellular front

patterns against small modulations of the periodic structure.

In the above non-linear analyses, both the concentration of solute and the interfacial amplitude were in advance assumed in forms of perturbation expansion and then were substituted into the governing solute diffusion equation in the melt and the corresponding far-field and interfacial conditions, and eventually in the third order of amplitude the generic Landau-Hopf equations, which describe the dynamics of the amplitude were obtained. However, in the analysis of long-wave morphological stabilities, a simpler way to obtain the amplitude equations can be expected, because some evolution equations have already been derived.

The long-wave morphological instabilities may occur in several limits. Sivashinsky¹⁴⁾ identified a small-segregation-coefficient limit and obtained a weakly-nonlinear evolution equation governing subcritical two-dimensional bifurcation. Brattkus and Davis¹⁵⁾ identified a near-absolute-stability limit and obtained a strongly-nonlinear evolution equation governing supercritical two-dimensional bifurcation. The three-dimensional bifurcation analysis on this equation reveals that, as the segregation coefficient is near unity, stable hexagonal nodes are predictable. Riley and Davis¹⁶⁾ identified a small-segregation-coefficient, large-surface-energy limit and derived another strongly-nonlinear evolution equation linking both of the former and describing the change from the sub- to super-critical two-dimensional bifurcations.

Recently, Hsieh and Hwang,¹⁷⁾ by using an integral technique, have obtained an overall long-wave evolution equation which can reduce to all the long-wave equations mentioned above.¹⁴⁻¹⁶⁾ In the two dimensional analysis of this equation, Hsieh and Hwang had modified Riley and Davis's criterion of the change from the sub- to super-critical bifurcations. However, Hsieh and Hwang did not

continue to undertake the three-dimensional analysis on their equation, and in the meantime, their equation may be further modified by adding one more solution mode to the series of concentration.

So, in this article, we intend to modify Hsieh and Hwang's equation¹⁷⁾ firstly, then based on this newly-derived equation, the overall long-wave three-dimensional developments of solid-liquid interface during solidification will be studied.

§2. Formulation

In this work, behaviors of solid-liquid interface in a directionally - solidified dilute binary mixture is concerned. A physical configuration of directional solidification is shown in Fig. 1, where solidified materials are pulled at a given speed under an imposed constant temperature gradient and are continuously solidified. To simplify and to make the analysis easier, a reasonable mathematical model and some assumptions should be implemented. We consider an infinite one-sided model and neglect diffusion of solute in the solid.³⁾ We also adopt the "frozen-temperature" approximation¹⁾ by assuming that the thermal conductivities, densities and specific heats of both the solid and the melt are equal, and that the latent heat per unit volume of solid is negligible. Under these assumptions, the temperature field decouples from the solute field. If we further assume that the thermal diffusivity in the melt, k_L , is much larger than the solute diffusivity, D , then the temperature could be permanently fixed by

$$T = T_0 + Gz \quad (2.1)$$

where T_0 is the temperature of a planar interface, G is the imposed temperature gradient, and z is the coordinate perpendicular to the planar interface and pointing into the melt, shown in Fig. 1.

If we define C_S and C_L as the concentrations at the interface on the solid and liquid sides, respectively, then the segregation coefficient k is defined by $k = C_S/C_L$. It is clear that if $k < 1$, the solute is rejected by the solid. We further define C_∞ as the concentration of solute in the melt far from the interface.

If lengths are scaled on the solute-diffusional scale D/V , and solute concentration is measured relative to C_∞/k in units of $(k-1)C_\infty/k$, then the scaled equations determining the concentration and the interface position are:

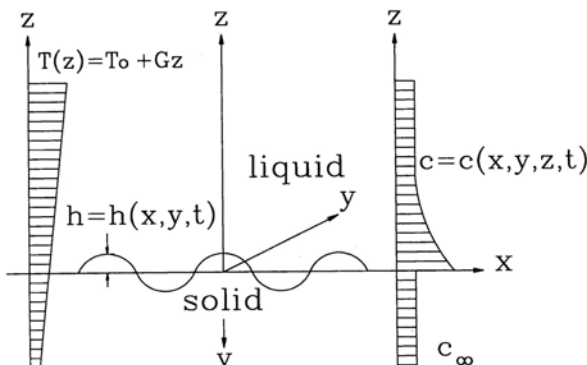


Fig. 1. Physical configuration of the solidification.

$$\nabla^2 C + C_{zz} + C_z = C_t, \quad (2.2)$$

$$[1 + (k-1)C](1 + h_t) = C_z - \nabla h \cdot \nabla C, \quad z = h, \quad (2.3a)$$

$$C - M^{-1}h + \Gamma K = 0, \quad z = h, \quad (2.3b)$$

$$C \rightarrow 1 \quad \text{as} \quad z \rightarrow \infty. \quad (2.4)$$

Here ∇ and ∇^2 are the two-dimensional gradient and Laplacian operators, respectively, K is twice the mean curvature of the interface defined by

$$K = \nabla \cdot [\nabla h / (1 + |\nabla h|^2)^{1/2}], \quad (2.5)$$

M denotes the morphological parameter defined as

$$M = m(k-1)C_\infty V / kDG, \quad (2.6)$$

and Γ denotes the scaled surface energy defined as

$$\Gamma = kT_m \gamma V / DLm(k-1)C_\infty, \quad (2.7)$$

where m is the slope of the liquidus, T_m is the melting temperature of pure material, and γ denotes the surface energy per unit area.

§3. The Evolution Equation

In the previous method of deriving long-wave evolution equations, distinguished limit of parameters should be designated in advance, then standard procedure of the method of perturbation follows. In the present work, we do not constrain ranges of the parameters in advance because the purpose of this article is to derive one equation which can describe interfacial developments in all the long-wave limits. However, we are concerned with the long-wave distribution of the solute concentration. The method of integral approximation was first developed by Kapitza¹⁸⁾ in research on thin-film flows, following an idea first put forth by von Kármán¹⁹⁾ for gaining quantitative information about boundary layers of the flow of a viscous fluid at high Reynolds number past a flat plate. To interpret the physical meaning, this method comes from the concept of solute flux conservation which was also adopted by Weeks and van Saarloos²⁰⁾ in analyzing large amplitude cells for cases of small k and finite Péclet numbers. The procedure of deriving the evolution equation begins with seeking for suitable functions of the distribution of the solute concentration within the liquid. Normally, the suitable functions come from the long-wave solution. Then the distribution of solute concentration, which satisfies the associated boundary conditions, is assumed to be a combination of the chosen functions. The assumed solution usually does not satisfy the governing equation, however, by substituting the assumed solution into the governing equation and then integrating every term of the equation within the whole physical domain along the same direction as that disturbances grow, consequently one will obtain a strongly nonlinear evolution equation.

At the first stage, we look for suitable functions of distribution of the solute concentration by examining the series of solution deduced by Hsieh and Hwang²¹⁾ and find that the solution of the solute concentration can be assumed by:

$$C^* = 1 + P(x, y, t)e^{h-z} + Q(x, y, t)(h-z)e^{h-z} + R(x, y, t)(h-z)^2e^{h-z}, \quad (3.1)$$

which automatically satisfies the far-field condition (2.4). The assumed solute concentration also is required to satisfy the boundary conditions (2.3a), and (2.3b), so we find

$$P(x, y, t) = -1 + M^{-1}h - \Gamma K, \\ Q(x, y, t) = -\left\{ k(M^{-1}h - \Gamma K) + h_t - (M^{-1}h - \Gamma K)h_t + k(M^{-1}h - \Gamma K)h_t + (-1 + M^{-1}h - \Gamma K + M^{-1})|\nabla h|^2 - \Gamma \nabla K \cdot \nabla h \right\} / (1 + |\nabla h|^2). \quad (3.2)$$

The final unknown function, $R(x, y, t)$, can be found by putting the assumed concentration (3.1) into the governing equation (2.2) and letting $z \rightarrow h^+$, thus one has

$$R(x, y, t) = \left\{ P_t + (P + Q)h_t - \nabla^2 P - 2\nabla h \cdot \nabla(P + Q) - (P + Q)\nabla^2 h - (P + Q)|\nabla h|^2 - Q(1 + |\nabla h|^2) \right\} / 2(1 + |\nabla h|^2). \quad (3.3)$$

The choice of C^* , however, does not satisfy the governing equation at all. But as one simply substitutes (3.1)–(3.3) into (2.2) and then integrates every term of (2.2) from $z = h$ to infinite, as shown by the following solute flux conservation equation:

$$\int_h^\infty (\nabla^2 + \partial^2/\partial z^2 + \partial/\partial z - \partial/\partial t)C^* dz = 0, \quad (3.4)$$

eventually one obtains the evolution equation

$$Q(1 + |\nabla h|^2) - \nabla^2 Q + \nabla^2 P + 2\nabla P \cdot \nabla h + P\nabla^2 h + P|\nabla h|^2 - P_t - Ph_t + Q_t - 2R_t + 2\nabla^2 R = 0, \quad (3.5)$$

where P , Q and R are expressed in eqs. (3.2) and (3.3). Since in deriving the evolution equation, h is assumed to be $O(1)$, the evolution equation (3.5) is strongly nonlinear. Meanwhile, if the wave number and the growth rate of the interfacial disturbance and asymptotically small, and terms $\nabla^2 c$ and c_t in (2.2) in turn are small, then the governing equation (2.2) is dominated by c_{zz} and c_z and the choice of the approximate solution (3.1) is straightforward.

Equation (3.5) is in fact very complicated and contains very highly nonlinear terms, but if linear and weakly nonlinear instabilities are concerned, this equation can be re-expressed in a simpler one which contains only linear and weakly nonlinear terms up to third order. In doing this, let's express P , Q and R by the following forms:

$$P(x, y, t) = -1 + M^{-1}h - \Gamma \nabla h^2 + \frac{1}{2}\Gamma \nabla \cdot (\nabla h |\nabla h|^2) + O(h^4), \\ Q(x, y, t) = -h_t - k(M^{-1}h - \Gamma \nabla^2 h) + (1 - k)(M^{-1}h - \Gamma \nabla^2 h)h_t - (-1 + M^{-1}h - \Gamma \nabla^2 h + M^{-1})|\nabla h|^2 + \Gamma \nabla (\nabla^2 h) \cdot \nabla h - \frac{1}{2}k\Gamma \nabla \cdot (\nabla h |\nabla h|^2) + [h_t + k(M^{-1}h - \Gamma \nabla^2 h)]|\nabla h|^2 + O(h^4), \\ R(x, y, t) = \frac{1}{2}\left\{ M^{-1}h_t - \Gamma \nabla^2 h_t + (1 - M^{-1})\nabla^2 h + \Gamma \nabla^4 h + k(M^{-1}h - \Gamma \nabla^2 h) - h_t^2 + [h_t - (1 - k)(M^{-1}h - \Gamma \nabla^2 h)]\nabla^2 h + |\nabla h_t|^2 - (1 - 2k)[M^{-1}|\nabla h|^2 - \Gamma \nabla (\nabla^2 h) \cdot \nabla h] + \left(\frac{\partial}{\partial t} - \nabla^2\right)\left[\frac{1}{2}\Gamma \nabla \cdot (\nabla h |\nabla h|^2)\right] + (h_t - \nabla^2 h) \times [(1 - k)(M^{-1}h - \Gamma \nabla^2 h)h_t + (1 - M^{-1})|\nabla h|^2 + \Gamma \nabla (\nabla^2 h) \cdot \nabla h] - 2\nabla[(1 - k)(M^{-1}h - \Gamma \nabla^2 h)h_t + (1 - M^{-1})|\nabla h|^2 + \Gamma \nabla (\nabla^2 h) \cdot \nabla h] \cdot \nabla h + |\nabla h|^2[(1 - M^{-1})h_t + \Gamma \nabla^2 h_t - (1 - M^{-1})\nabla^2 h - \Gamma \nabla^4 h] + \frac{1}{2}k\Gamma \nabla \cdot (\nabla h |\nabla h|^2) \right\} + O(h^4), \quad (3.6)$$

then the evolution equation (3.5) is reduced to the following one:

$$h_{tt} + (M^{-1}h_{tt} - \Gamma \nabla^2 h_{tt}) - 2(M^{-1}\nabla^2 h_t - \Gamma \nabla^4 h_t) + (1 + 2k)(M^{-1}h_t - \Gamma \nabla^2 h_t) - (1 + 2k)(M^{-1}\nabla^2 h - \Gamma \nabla^4 h) + k(M^{-1}h - \Gamma \nabla^2 h) + (M^{-1}\nabla^4 h - \Gamma \nabla^6 h) + \nabla^2 h - \nabla^4 h = M^{-1}\nabla \cdot (h\nabla h) - \Gamma \nabla \cdot (\nabla^2 h \nabla h) - k(M^{-1}h - \Gamma \nabla^2 h)h_t$$

$$\begin{aligned}
& + \left(\frac{\partial}{\partial t} - \nabla^2 \right) \{ (1-k)(M^{-1}h - \Gamma \nabla^2 h)h_t + (1-2kM^{-1})|\nabla h|^2 \\
& + 2k\Gamma \nabla(\nabla^2 h) \cdot \nabla h + h_t^2 + (1-k)\nabla^2 h(M^{-1}h - \Gamma \nabla^2 h) - h_t \nabla^2 h - |\nabla h|_t^2 \} \\
& - \frac{1}{2}k\Gamma \nabla \cdot (\nabla h |\nabla h|^2) \\
& + \left(\frac{\partial}{\partial t} - \nabla^2 \right) \left\{ -\frac{1}{2}(1+2k)\Gamma \nabla \cdot (\nabla h |\nabla h|^2) + (k-1)(M^{-1}h - \Gamma \nabla^2 h)|\nabla h|^2 \right. \\
& + h_t |\nabla h|^2 - \left(\frac{\partial}{\partial t} - \nabla^2 \right) \left(\frac{1}{2}\Gamma \nabla \cdot (\nabla h |\nabla h|^2) \right) - (h_t - \nabla^2 h) \\
& \times [(1-k)(M^{-1}h - \Gamma \nabla^2 h)h_t + (1-M^{-1})|\nabla h|^2 + \Gamma \nabla(\nabla^2 h) \cdot \nabla h] \\
& + 2\nabla[(1-k)(M^{-1}h - \Gamma \nabla^2 h)h_t + (1-M^{-1})|\nabla h|^2 + \Gamma \nabla(\nabla^2 h) \cdot \nabla h] \cdot \nabla h \\
& \left. - (1-M^{-1})|\nabla h|^2(h_t - \nabla^2 h) - \Gamma |\nabla h|^2(\nabla^2 h_t - \nabla^4 h) \right\} + O(h^4). \tag{3.7}
\end{aligned}$$

This equation can describe the interfacial behaviors up to third-order nonlinearity in all the distinguished long-wave limits. Examples of the reduction of this equation to all the long-wave evolution equations mentioned before,¹⁴⁻¹⁶⁾ are the same as those shown in the previous work of Hsieh and Hwang.¹⁷⁾

§4. The Amplitude Equations

The evolution equation (3.7) describes the dynamics

of the interface position $h(x, y, t)$. The basic solution of it is obviously the planar interface, i.e., $h = h_0 = 0$. It is the stability of this equation to a particular class of perturbations with which we are concerned in the Segel-Stuart method.²²⁾ We assume that, to third order terms in the amplitude functions $A_1(t)$, $A_2(t)$, and $A_3(t)$, the interface satisfies the equation

$$\begin{aligned}
h(x, y, t) = & \{A_1 + a\bar{A}_2\bar{A}_3 + bA_1^2\bar{A}_1 + dA_1(|A_2|^2 + |A_3|^2)\} \exp(i\mathbf{u}_1 \cdot \mathbf{r}) \\
& + \{A_2 + a\bar{A}_3\bar{A}_1 + bA_2^2\bar{A}_2 + dA_2(|A_3|^2 + |A_1|^2)\} \exp(i\mathbf{u}_2 \cdot \mathbf{r}) \\
& + \{A_3 + a\bar{A}_1\bar{A}_2 + bA_3^2\bar{A}_3 + dA_3(|A_1|^2 + |A_2|^2)\} \exp(i\mathbf{u}_3 \cdot \mathbf{r}) \\
& + f\{A_1\bar{A}_2 \exp(i[\mathbf{u}_1 - \mathbf{u}_2] \cdot \mathbf{r}) + A_2\bar{A}_3 \exp(i[\mathbf{u}_2 - \mathbf{u}_3] \cdot \mathbf{r}) + \\
& \quad A_3\bar{A}_1 \exp(i[\mathbf{u}_3 - \mathbf{u}_1] \cdot \mathbf{r})\} \\
& + e\{A_1^2 \exp(2i\mathbf{u}_1 \cdot \mathbf{r}) + A_2^2 \exp(2i\mathbf{u}_2 \cdot \mathbf{r}) + A_3^2 \exp(2i\mathbf{u}_3 \cdot \mathbf{r})\} \\
& + \frac{1}{2}g\{(|A_1|^2 + |A_2|^2 + |A_3|^2)\} \\
& + c.c. \tag{4.1}
\end{aligned}$$

where $c.c.$ represents complex conjugate, $\bar{A}_i$ is the complex conjugate of A_i ($i = 1, 2, 3$), $\mathbf{u}_1 = \omega(1, 0)$, $\mathbf{u}_2 = \omega(-1/2, \sqrt{3}/2)$, $\mathbf{u}_3 = \omega(-1/2, -\sqrt{3}/2)$, and $\mathbf{r} = (x, y)$. It should be noted that the amplitudes A_i 's generally depend on both spatial and temporal variables. But if the effect of phase-diffusion is ignored, A_i 's can be assumed to depend on the temporal variable only. We now examine (4.1) and conclude that the amplitude functions $A_1(t)$, $A_2(t)$, and $A_3(t)$ satisfy the following amplitude equations to third order

$$\begin{aligned}
dA_1/dt &= \sigma A_1 - \beta \bar{A}_2 \bar{A}_3 - \beta_1 A_1^2 \bar{A}_1 - \beta_2 A_1(|A_2|^2 + |A_3|^2), \\
dA_2/dt &= \sigma A_2 - \beta \bar{A}_3 \bar{A}_1 - \beta_1 A_2^2 \bar{A}_2 - \beta_2 A_2(|A_3|^2 + |A_1|^2), \\
dA_3/dt &= \sigma A_3 - \beta \bar{A}_1 \bar{A}_2 - \beta_1 A_3^2 \bar{A}_3 - \beta_2 A_3(|A_1|^2 + |A_2|^2), \tag{4.2}
\end{aligned}$$

where σ is the growth rate of linear theory, and β , β_1 , and β_2 , are solvability constants to be determined. The

evolutions of A_i 's then are ensured by (4.2) if σ , β , β_1 , and β_2 can be determined. The following procedure of the present analysis begins with the determination of σ , β , β_1 , and β_2 , then in the next section the steady-state solutions of A_i 's will be evaluated and the local stability analysis to these solutions is undertaken to decide whether they are stable or not.

To do this, we simply substitute (4.1), together with (4.2), into the evolution equation (3.7), then compare the amplitude in every independent periodic mode. Thus, at the first order of A_i 's, we obtain the dispersion relation which is expressed by

$$\begin{aligned}
(1 + M^{-1} + \Gamma \omega^2)\sigma^2 + (M^{-1} + \Gamma \omega^2)(1 + 2k + 2\omega^2)\sigma \\
+ (M^{-1} + \Gamma \omega^2)(\omega^2 + \omega^4 + k(1 + 2\omega^2)) - \omega^2 - \omega^4 = 0. \tag{4.3}
\end{aligned}$$

It is easy to show that the exchange of stability holds, so with $\sigma = 0$, one has

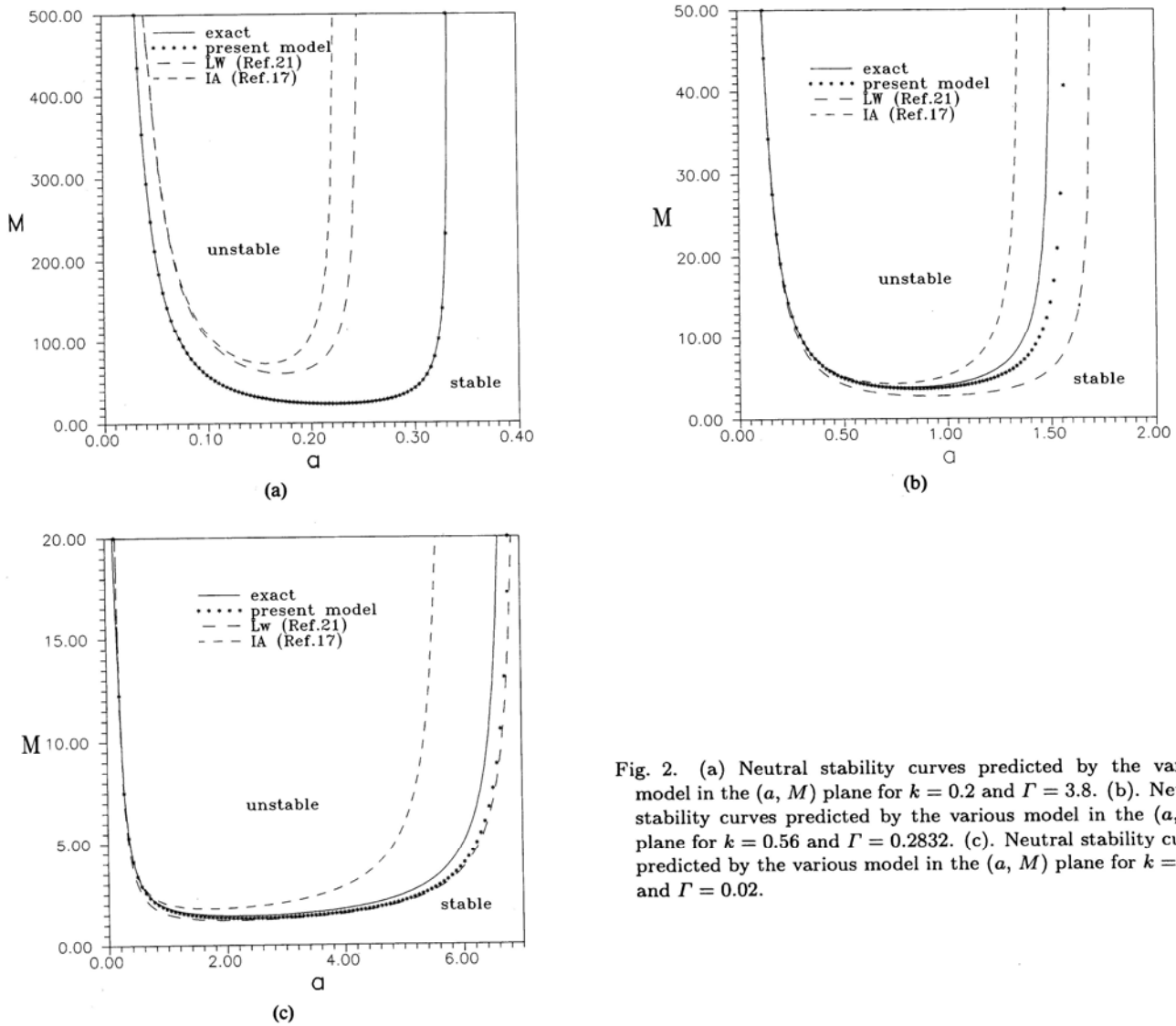


Fig. 2. (a) Neutral stability curves predicted by the various model in the (a, M) plane for $k = 0.2$ and $\Gamma = 3.8$. (b). Neutral stability curves predicted by the various model in the (a, M) plane for $k = 0.56$ and $\Gamma = 0.2832$. (c). Neutral stability curves predicted by the various model in the (a, M) plane for $k = 0.47$ and $\Gamma = 0.02$.

$$M^{-1} = \frac{\omega^2 + \omega^4}{\omega^2 + \omega^4 + k(1 + 2\omega^2)} - \Gamma\omega^2. \quad (4.4)$$

For given Γ and k , M^{-1} varies with ω^2 and has some extreme value. The critical value of ω^2 is defined as the one corresponding to the extreme value of M^{-1} and is denoted by ω_c^2 . Thus, with $dM^{-1}/d\omega^2 = 0$, one finds

$$\Gamma = \frac{k(1 + 2\omega_c^2 + 2\omega_c^4)}{[\omega_c^2 + \omega_c^4 + k(1 + 2\omega_c^2)]^2}. \quad (4.5)$$

With (4.5), the critical value of M can in turn be deter-

mined by (4.4). Figures 2(a), 2(b) and 2(c) display the neutral stability curve in the (a, M) plane for different values of k and Γ . The planar interface is unstable above each curve. It is found that the linear results predicted by the present model are more close to the exact one than those predicted by the other two model of Hsieh and Hwang,^{17,21)} Furthermore, the present model provides very accurate result of the critical condition.

When going forward to the second order of A_i 's, one finds

$$e = e(\sigma \rightarrow 0) = \frac{-2\omega^2(M^{-1} + \Gamma\omega^2) + 8k\Gamma\omega^6 - 4(1 - 2kM^{-1})\omega^4 + 4(k - 1)(M^{-1} + \Gamma\omega^2)\omega^4}{(M^{-1} + 4\Gamma\omega^2)[4(1 + 2k)\omega^2 + k + 16\omega^4] - 4\omega^2 - 16\omega^4}, \quad (4.6)$$

$$f = f(\sigma \rightarrow 0) = \frac{-3\omega^2(M^{-1} + \Gamma\omega^2) + 6k\Gamma\omega^6 - 3(1 - 2kM^{-1})\omega^4 + 6(k - 1)(M^{-1} + \Gamma\omega^2)\omega^4}{(M^{-1} + 3\Gamma\omega^2)[3(1 + 2k)\omega^2 + k + 9\omega^4] - 3\omega^2 - 9\omega^4}, \quad (4.7)$$

$$g = g(\sigma \rightarrow 0) = 0, \quad (4.8)$$

and

$$\beta - \sigma a = r(\sigma), \quad (4.9)$$

where

$$\begin{aligned} r(\sigma) = & \frac{\omega^2(M^{-1} + \Gamma\omega^2) + 2\omega^4(M^{-1} + \Gamma\omega^2) - \omega^4}{3(1 + M^{-1} + \Gamma\omega^2)\sigma + (M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)} \\ & + \frac{-2\sigma^3 + [-(1-k) + (M^{-1} + \Gamma\omega^2) - \omega^2]\sigma^2}{3(1 + M^{-1} + \Gamma\omega^2)\sigma + (M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)} \\ & + \frac{[2k(M^{-1} + \Gamma\omega^2) + 2(1+k)(M^{-1} + \Gamma\omega^2)\omega^2 - 2\omega^2 - \omega^4]\sigma}{3(1 + M^{-1} + \Gamma\omega^2)\sigma + (M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)}. \end{aligned} \quad (4.10)$$

According to the analysis of Sriranganathan *et al.*,¹⁰⁾ we should take

$$\beta = \lim_{\sigma \rightarrow 0} r(\sigma) = \frac{\omega^2(M^{-1} + \Gamma\omega^2) + 2\omega^4(M^{-1} + \Gamma\omega^2) - \omega^4}{(M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)}, \quad (4.11)$$

and

$$a = \lim_{\sigma \rightarrow 0} \frac{\beta - r(\sigma)}{\sigma} = -\frac{dr(0)}{d\sigma}. \quad (4.12)$$

Finally, as going further to the third order of A_i 's, one will arrive at

$$\beta_1 - 2\sigma b = r_1(\sigma), \quad (4.13)$$

and

$$\beta_2 - 2\sigma d = r_2(\sigma). \quad (4.14)$$

Thus, similar to the determination of β , we obtain β_1 and β_2 by letting σ approach zero and have

$$\begin{aligned} \beta_1 = & r_1(\sigma \rightarrow 0) \\ = & \left\{ (M^{-1} - 2\Gamma\omega^2)\omega^2 e + M^{-1}\omega^2 g - 4(1 - 2kM^{-1})\omega^4 e + 20k\Gamma\omega^6 e \right. \\ & - (k-1)M^{-1}\omega^4 g - 5(k-1)M^{-1}\omega^4 e - 8(k-1)\Gamma\omega^6 e - \frac{3}{2}k\Gamma\omega^4 \\ & - \frac{3}{2}(1+2k)\Gamma\omega^6 + (1-k)(M^{-1} + \Gamma\omega^2)\omega^4 - \frac{3}{2}\Gamma\omega^8 + 6(1-M^{-1})\omega^6 \\ & \left. - 6\Gamma\omega^8 \right\} / [(M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)], \end{aligned} \quad (4.15)$$

$$\begin{aligned} \beta_2 = & r_2(\sigma \rightarrow 0) \\ = & \left\{ (M^{-1} + \Gamma\omega^2)\omega^2 a + M^{-1}\omega^2(f + g) - (12k - M^{-1})\omega^4(3f + a) + 2k\Gamma\omega^6(6f + a) \right. \\ & - (k-1)M^{-1}\omega^4 g - 4(k-1)M^{-1}\omega^4(f + a) - 6(k-1)\Gamma\omega^6(f + a) - \frac{3}{2}k\Gamma\omega^4 \\ & - \frac{3}{2}(1+2k)\Gamma\omega^6 + 2(1-k)(M^{-1} + \Gamma\omega^2)\omega^4 - \frac{3}{2}\Gamma\omega^8 + 6(1-M^{-1})\omega^6 \\ & - 6\Gamma\omega^8 + (1 + M^{-1} + \Gamma\omega^2)\beta^2 - (1 + 2k + 2\omega^2)(M^{-1} + \Gamma\omega^2)\beta a \\ & - k(M^{-1} + \Gamma\omega^2)\beta + (1-k)(M^{-1} + \Gamma\omega^2)\omega^2\beta + (1 - 2kM^{-1})\omega^2\beta - 2k\Gamma\omega^4\beta \\ & \left. + 2(k-1)(M^{-1} + \Gamma\omega^2)\omega^2\beta \right\} / [(M^{-1} + \Gamma\omega^2)(1 + 2k + 2\omega^2)]. \end{aligned} \quad (4.16)$$

§5. The Steady-State-Solutions and Their Stabilities

As mentioned in the introduction, both of the two-dimension band-like cell and the hexagonal cellular pattern can be observed in the directional solidification. For the analysis of regular patterns, we can assume $A_1 = \bar{A}_1 = A/2$ and $A_2 = \bar{A}_2 = A_3 = \bar{A}_3 = B/4$, then the amplitude equations in (4.2) will reduce to

$$\left. \begin{aligned} dA/dt &= \sigma A - \frac{1}{8}\beta B^2 - \frac{1}{4}\beta_1 A^3 \\ &\quad - \frac{1}{8}\beta_2 AB^2 = F(A, B), \\ dB/dt &= \sigma B - \frac{1}{2}\beta AB - \frac{1}{4}\beta_2 A^2 B \\ &\quad - \frac{1}{16}(\beta_1 + \beta_2)B^3 = G(A, B). \end{aligned} \right\} \quad (5.1)$$

In particular the equilibrium points (A_0, B_0) of

(5.1), which are those points such that $F(A_0, B_0) = G(A_0, B_0) = 0$, can be catalogued as follows:²²⁾

$$\left. \begin{aligned} \alpha_1: A_0 &= B_0 = 0; \\ \alpha_2: A_0 &= \pm 2\sqrt{\sigma/\beta_1}, \quad B_0 = 0; \\ \alpha_{3-1}: A_0 &= [-\beta \pm \sqrt{\beta^2 + 4\sigma(\beta_1 + 2\beta_2)}] \\ &\quad / (\beta_1 + 2\beta_2), \\ B_0 &= 2A_0; \\ \alpha_{3-2}: A_0 &= [-\beta \pm \sqrt{\beta^2 + 4\sigma(\beta_1 + 2\beta_2)}] \\ &\quad / (\beta_1 + 2\beta_2), \\ B_0 &= -2A_0; \\ \alpha_4: A_0 &= -2\beta/(\beta_2 - \beta_1), \\ B_0 &= \pm 4\sqrt{[\sigma - \beta^2\beta_1(\beta_2 - \beta_1)^{-2}]/(\beta_1 + \beta_2)}. \end{aligned} \right\} \quad (5.2)$$

The equilibrium points of α_1 correspond to a planar interface while the equilibrium solutions of α_2 represent equivalent observable two-dimensional band-like structures. The equilibrium points of α_{3-1} and α_{3-2} yield equivalent observable hexagonal morphologies of interface. Since the stability analysis to the solutions of α_{3-1} and α_{3-2} will depend on B_0^2 and thus will reveal identical result, we will only discuss the steady-state solutions of α_{3-1} . For alloys having $k < 1$, hexagonal structures with $A_0 > 0$ correspond to cells with dome-shaped centers projecting into the liquid and higher solute concentrations at the boundaries while those with $A_0 < 0$ correspond to a close-packed arrangement of nodes or circular depressions of solute rich liquid into the solid; see *e.g.* (2.3b). The points α_4 represent cells bounded by some closed non-hexagonal contour, which are not what we are concerned with. So we will cancel the discussion of these points in later analysis. In the meantime, for convenience of investigation on these equilibrium points, later in the next section, we will use superscript (1) to denote the "+" solution and (2), the "-" solution.

To study the local stability of these steady-state solutions, we assume solutions of (5.1) be in the form

$$A(t) = A_0 + \epsilon X \exp(\rho t) + O(\epsilon^2), \quad (5.3a)$$

$$B(t) = B_0 + \epsilon Y \exp(\rho t) + O(\epsilon^2), \quad (5.3b)$$

where $|\epsilon| \ll 1$. A somewhat limited nature of following stability analysis should be mentioned here because no spatial dependence is performed in eqs. (5.2). Aside this, anyway, the analysis that is about to be undertaken is useful for the present situation. Substituting these solutions into (5.1), neglecting terms of $O(\epsilon^2)$, and canceling the common factor $\epsilon \exp(\rho t)$, one will obtain two linear homogeneous equations in the constants X and Y . To ensure the existence of X and Y , we should require that ρ satisfies:

$$\rho^2 + p\rho + q = 0, \quad (5.4)$$

where

$$p = -2\sigma + \frac{1}{2}\beta A_0 + \frac{1}{4}(3\beta_1 + \beta_2)A_0^2 + \frac{1}{16}(3\beta_1 + 5\beta_2)B_0^2, \quad (5.5a)$$

$$q = \left(\sigma - \frac{3}{4}\beta_1 A_0^2 - \frac{1}{8}\beta_2 B_0^2 \right) \left[\sigma - \frac{1}{2}\beta A_0 - \frac{1}{4}\beta_2 A_0^2 - \frac{3}{16}(\beta_1 + \beta_2)B_0^2 \right] - \frac{1}{8}B_0^2(\beta + \beta_2 A_0)^2. \quad (5.5b)$$

The equilibrium point (A_0, B_0) is said to be locally stable if the real part of ρ is negative, thus the criterion for deciding whether (A_0, B_0) is stable is simply

$$p > 0 \quad \text{and} \quad q > 0. \quad (5.6)$$

It should be mentioned here that, in what follows, typical weakly nonlinear theory suggests we should consider the condition that is only slightly exceeded the critical condition, in other words, all the constants such as β , β_1 , β_2 , f and e should be chosen according to the critical condition. Furthermore, we choose M as the bifurcation parameter and define

$$M^{-1} = M_c^{-1} - \mu, \quad (5.7)$$

where μ should better be $O(\sigma)$. If we do so, then from the dispersion relation (4.3), we will arrive at

$$\mu = \frac{(M_c^{-1} + \Gamma\omega_c^2)(1 + 2k + 2\omega_c^2)}{\omega_c^2 + \omega_c^4 + k(1 + 2\omega_c^2)}\sigma + O(\sigma^2). \quad (5.8)$$

§6. Results and Discussion

In this section, we shall respectively study the stabilities of the equilibrium points of α_1 , α_2 , and α_{3-1} . The corresponding bifurcation structures of the two-dimensional band-like cell and the three-dimensional hexagonal solution will also be shown.

We first note that for equilibrium point α_1

$$p = -2\sigma \quad \text{and} \quad q = \sigma^2. \quad (6.1)$$

Hence the planar interface is locally stable provided $\sigma < 0$. For equilibrium point α_2 , we rearrange the relation (5.4) and show

$$\begin{aligned} p &= \frac{1}{4}A_0[(\beta_1 + \beta_2)A_0 + 2\beta] \\ q &= \frac{1}{8}\beta_1 A_0^3[2\beta - (\beta_1 - \beta_2)A_0]. \end{aligned} \quad (6.2)$$

For equilibrium point α_{3-1} , we have

$$\begin{aligned} p &= \frac{1}{2}A_0[(2\beta_1 + \beta_2)A_0 - \beta] \\ q &= \frac{1}{4}A_0^2[(\beta_1 + 2\beta_2)A_0 - \beta][(\beta_1 - \beta_2)A_0 - 2\beta]. \end{aligned} \quad (6.3)$$

After detail examination on (6.2) and (6.3), we find that stabilities of equilibrium points α_2 and α_{3-1} are determined by whether β_1 , $\beta_1 + \beta_2$, $\beta_1 + 2\beta_2$, and $\beta_1 - \beta_2$ are positive or not. Noting that in most of the applicable parameter range of evolution equation (3.7), $\beta > 0$, we thus consider the following possibilities.

- (1) $\beta_2 < \beta_1 < 0$: We find that both two-dimensional cell $A_0^{(1)}$ and $A_0^{(2)}$ are unstable, and three-dimensional structures $A_0^{(1)}$ and $A_0^{(2)}$ are unstable, as well. The

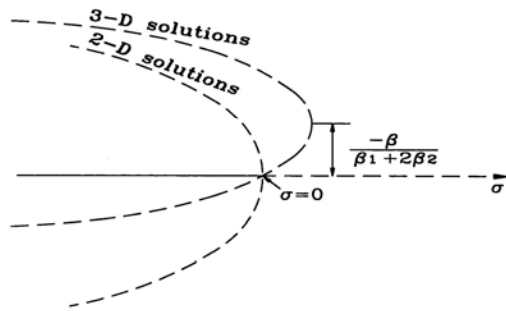


Fig. 3. Bifurcation diagrams for $\beta_2 < \beta_1 < 0$. Solid lines represent the stable solution while dashed lines denote the unstable solution.

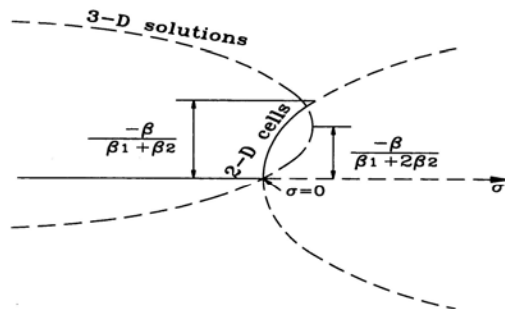


Fig. 4. Bifurcation diagrams for $\beta_2 < 0 < \beta_1$, and $\beta_1 + \beta_2 < 0$. Solid lines represent the stable solution while dashed lines denote the unstable solution.

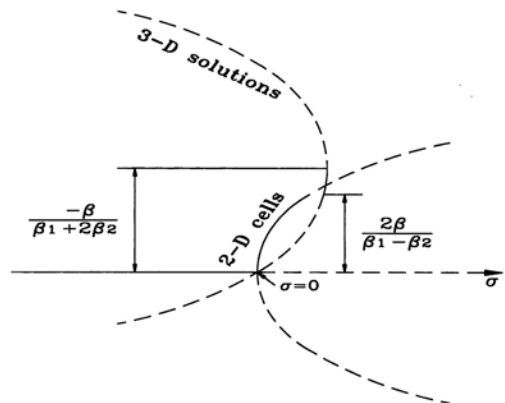


Fig. 5. Bifurcation diagrams for $\beta_2 < 0 < \beta_1$, $\beta_1 + \beta_2 > 0$, and $\beta_1 + 2\beta_2 < 0$. Solid lines represent the stable solution while dashed lines denote the unstable solution.

associated bifurcation diagram is shown in Fig. 3.

- (2) $\beta_2 < 0 < \beta_1$, and $\beta_1 + \beta_2 < 0$: We find that the two-dimensional cell $A_0^{(1)}$ is stable if $A_0^{(1)} < -2\beta/(\beta_1 + \beta_2)$ while both the three-dimensional solutions $A_0^{(1)}$ and $A_0^{(2)}$ are unstable. The associated bifurcation diagram is shown in Fig. 4.
- (3) $\beta_2 < 0 < \beta_1$, $\beta_1 + \beta_2 > 0$, and $\beta_1 + 2\beta_2 < 0$: We conclude that the two-dimensional cell $A_0^{(1)}$ is stable if $A_0^{(1)} < 2\beta/(\beta_1 - \beta_2)$, and the three-dimensional $A_0^{(1)}$ is stable if $2\beta/(\beta_1 - \beta_2) < A_0^{(1)} < -\beta/(\beta_1 + 2\beta_2)$. The associated bifurcation diagram is shown in Fig. 5.

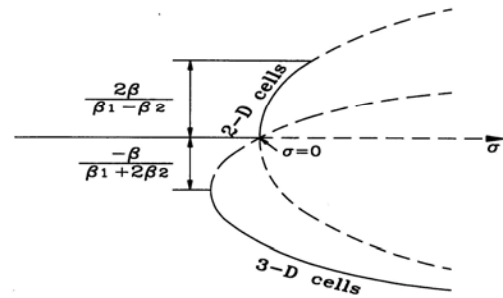


Fig. 6. Bifurcation diagrams for $\beta_1 > 0$, $\beta_1 > \beta_2$, and $\beta_1 + 2\beta_2 > 0$. Solid lines represent the stable solution while dashed lines denote the unstable solution.

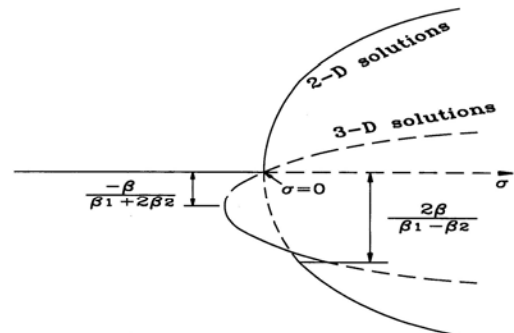


Fig. 7. Bifurcation diagrams for $0 < \beta_1 < \beta_2$. Solid lines represent the stable solution while dashed lines denote the unstable solution.

- (4) $\beta_1 > 0$, $\beta_1 > \beta_2$, and $\beta_1 + 2\beta_2 > 0$: We find that two-dimensional cell $A_0^{(1)}$ is stable if $A_0^{(1)} < 2\beta/(\beta_1 - \beta_2)$ or from (5.2) $0 < \sigma < \sigma_1$, where $\sigma_1 = \beta^2\beta_1/(\beta_1 - \beta_2)^2$, and the three-dimensional $A_0^{(2)}$ is locally stable. The associated bifurcation diagram is shown in Fig. 6.
- (5) $0 < \beta_1 < \beta_2$: We observe that the two-dimensional cell $A_0^{(1)}$ is stable and $A_0^{(2)}$ is stable only if $A_0^{(2)} > 2\beta/(\beta_1 - \beta_2)$ or $0 < \sigma < \sigma_2$, where $\sigma_2 = \beta^2(2\beta_1 + \beta_2)/(\beta_1 - \beta_2)^2$. The associated bifurcation diagram is shown in Fig. 7.

In summary, in our prediction, two-dimensional cells can be found only in area (5), where $0 < \beta_1 < \beta_2$, when $\sigma > \sigma_1$, while three-dimensional nodes can be found in area (4), where $\beta_1 > 0 > \beta_2$ and $\beta_1 + 2\beta_2 > 0$, when $\sigma > 0$ or in area (5) when $0 < \sigma < \sigma_2$. Note that in the above discussion, the equilibrium amplitude should be small to assure the amplitude equation (5.1) to be converge. So, in the limit that Riley and Davis¹⁶⁾ considered, only the three-dimensional $A_0^{(1)}$ near $\sigma = 0$ had been analyzed by them, while in the limit near absolute stability the result is identical to that obtained by Brattkus and Davis.¹⁵⁾

In Figs. 8 and 9, the marginal stability curves and the curves representing $\sigma = \sigma_1$ and $\sigma = \sigma_2$ for alloys Al-Zn ($k = 0.47$) and Al-Mn ($k = 0.79$) are shown in the M^{-1} - Γ plane, respectively. On each marginal stability curve of Figures 8 and 9, we have marked the special points which represent from left to right, $\beta_1 - \beta_2 = 0$, $\beta_1 + 2\beta_2 = 0$, $\beta_1 + \beta_2 = 0$, and $\beta_1 = 0$, respectively, and divide the curve into five portions. Thus if the parameter

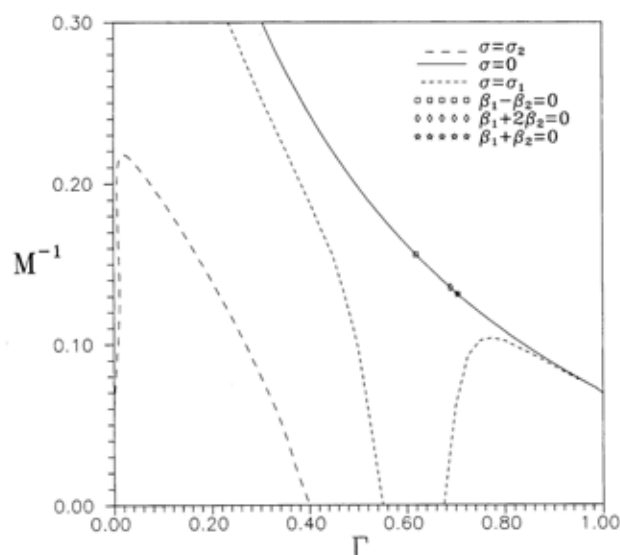


Fig. 8. The marginal stability curve and the curves of $\sigma = \sigma_1$, $\sigma = \sigma_2$ for alloy Al-Zn, $k = 0.47$.

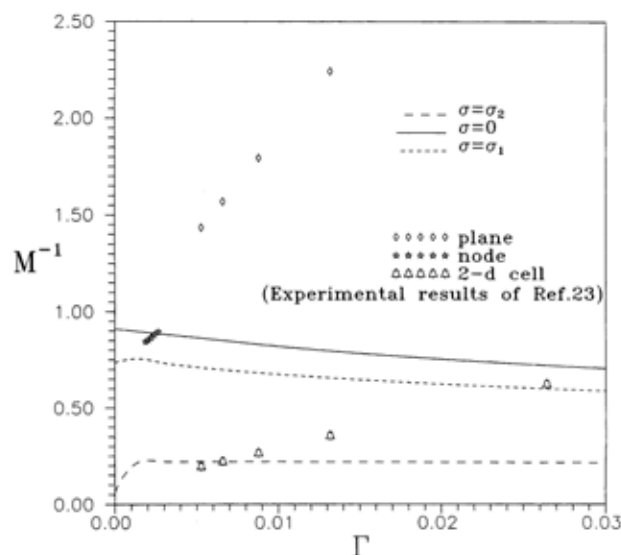


Fig. 10. Part of area (5) for Al-Zn alloy. The experiment results are obtained from Takahashi *et al.*²³⁾ under the conditions shown in Table I.

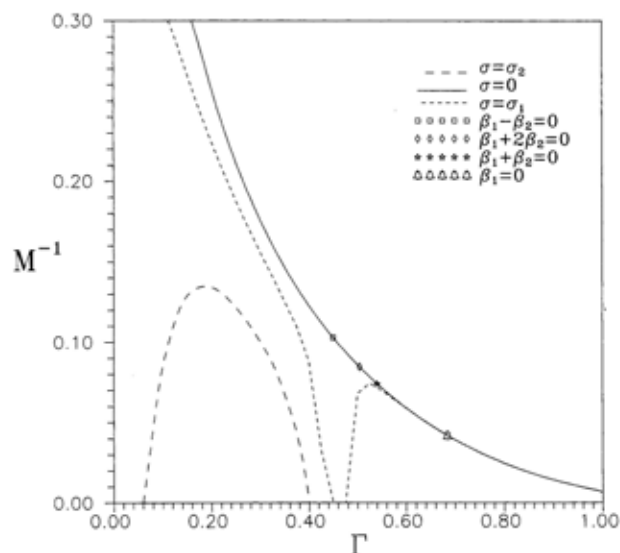


Fig. 9. The marginal stability curve and the curves of $\sigma = \sigma_1$, $\sigma = \sigma_2$ for alloy Al-Mn, $k = 0.79$.

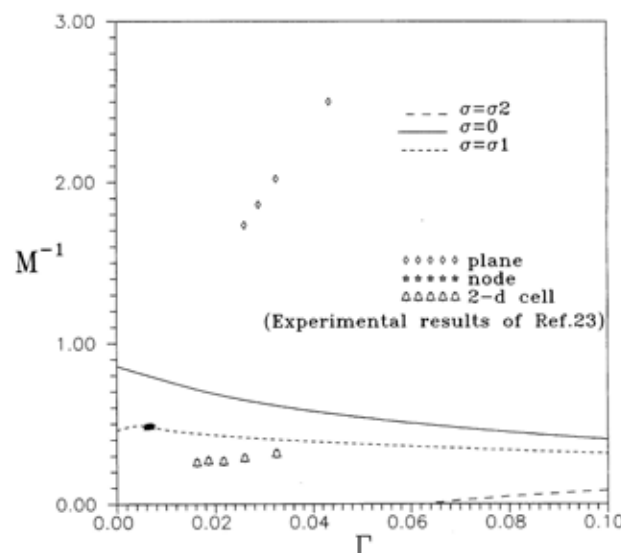


Fig. 11. Part of area (5) for Al-Mn alloy. The experiment results are obtained from Takahashi *et al.*²³⁾ under the conditions shown in Table I.

Table I. Physical constants of Al-Zn and Al-Mn alloys. Note $G = 2G_L/(1+n)$ and $n = k_S/k_L$, where G_L is the real temperature gradient in the melt.

Parameter	Al-Zn	Al-Mn	Units
k	0.47	0.79	
C_∞	0.5	0.1	wt%
m	-0.55	-1.65	K/wt%
$(T_M\gamma/L) \times 10^7$	1.2	1.2	Km
$D \times 10^9$	2.6	2.1	m ² /s
k_L	95	95	J/sKm
k_S	210	210	J/sKm

M is chosen as the bifurcating parameter, then the area left to the mark of $\beta_1 - \beta_2 = 0$ is area (5), the area between the marks of $\beta_1 - \beta_2 = 0$ and $\beta_1 + 2\beta_2 = 0$ is area (4), the area between the marks of $\beta_1 + 2\beta_2 = 0$ and $\beta_1 + \beta_2 = 0$ is area (3), the area between the marks of

$\beta_1 + \beta_2 = 0$ and $\beta_1 = 0$ is area (2), and the area right to the mark of $\beta_1 = 0$ is area (1). Since almost the binary alloys under normal freezing rate possess very small Γ , morphologies of such alloys can be found almost only in area (5). So, in Figs. 10 and 11, we have enlarged the areas (5) of alloys Al-Zn and Al-Mn. Some morphologies observed by Takahashi *et al.*²³⁾ are also marked on these figures to show the validity of our theory.

§7. Conclusion

In this article, we have modified the evolution equation that Hsieh and Hwang recently have obtained¹⁷⁾ and have derived a new strongly nonlinear evolution equation by using the method of integral approximation. The approximate form of the interfacial amplitude adopted here is from the long-wave result deduced in a previous

work of Hsieh and Hwang,²¹⁾ so the present evolution equation has connected all the long-wave equations derived by Sivashinsky,¹⁴⁾ by Brattkus and Davis,¹⁵⁾ and by Riley and Davis.¹⁶⁾

Three-dimensional analysis to the newly-derived evolution has been undertaken. The possible equilibrium solutions and their stability analyses are also demonstrated. As compared to the exact results, the transition points are extremely accurately evaluated, except in the case of small- Γ and $M \approx 1$, which in other words corresponds to large wave number. Some morphologies of alloys Al-Zn and Al-Mn observed by Takahashi *et al.* are also shown in Figs. 10 and 11 to prove the validity of our theory.

The present evolution equation is very complex and contains many high-order nonlinear terms which are higher than cubic nonlinearity. Although in this work we have only undertaken the weakly nonlinear analysis, the possibility that this equation can contribute to analyze strongly nonlinear instabilities, at least, by a numerical simulation, should be emphasized.

Acknowledgement

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