

Three-dimensional cellular instabilities in directional solidification considering interfacial kinetics

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(Received 1 April 1996; revised manuscript received 19 August 1996)

In this work, three-dimensional cellular instabilities in directional solidification are investigated. Local thermodynamic nonequilibrium at the solid-liquid interface is taken into account by applying a model of velocity-dependent segregation coefficient and attachment kinetics developed by Boettinger, Aziz, and Jackson *et al.* The infinitely one-sided model and the frozen-temperature approximation are adopted in the analysis. An evolution equation was first derived by an integral technique. Then the Segel-Stuart method was used to determine the solvability constants of the amplitude equations. The equilibrium solutions associated with different morphologies were evaluated and the stability analysis of them to three-dimensional disturbances was studied. Finally, five stability basins of bifurcation were addressed. The result shows that the interface morphologies depend on which basin the chosen critical condition is located in and how far the operating point is exceeded from the critical condition. The presence of disequilibrium can stabilize the steady cellular mode, cause the wave number to be smaller, and affect the location of the chosen critical condition in the basin of bifurcation. [S0163-1829(97)06401-1]

I. INTRODUCTION

A variety of interesting patterns can form during the directional solidification of a dilute binary alloy.^{1,2} During the solidification, for example, an initially flat solid-liquid interface may develop either a quasi-one-dimensional bandlike cell or a 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 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 interface tension and the external thermal gradient. They posed local thermodynamic equilibrium at the interface and studied the linear stability of the planar front in directional solidification. They found that the interface is susceptible to steady cellular instabilities that occur at nonzero wave numbers. Further, they found that at sufficiently high pulling speeds the instability is suppressed by surface energy at the absolute-stability boundary.

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 analysis only treated two-dimensional bandlike 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, Wollkind, and Oulton,¹⁰ by Wollkind, Sriranganathan, and Oulton,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 nonlinear 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 instabilities, a simpler way to obtain the amplitude equations can be expected, and some evolution equations have already been derived.

The long-wave morphological instability 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 equation governing supercritical two-dimensional bifurcation. In this limit stable hexagonal nodes are predictable as the segregation coefficient is near unity. 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 sub- to supercritical two-dimensional bifurcations. They suggested that stable, steady hexagonal nodes should exist in this limit. 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 just mentioned.^{14–16} References 14–17, following Mullins and Sekerka,⁶ in common considered local equilibrium at the interface and adopted the frozen-temperature approximation (FTA), which decouples the temperature field from the solute field by assuming equal thermal conductivities, zero latent heat release at the interface, and the solute diffusivity is much less than the heat diffusivity. Also, these works in common adopted the one-sided model, in which the solute diffusion in the solid phase is ignored; this is appropriate for many materials such as metals and some organic compounds. It should be pointed out, however, that the one-sided model may produce cusp singularity, i.e., steep-sided grooves can be found in the formation of cellular structure. Numerical solutions of the Sivashinsky equation on periodic domains even exhibit blowup in finite time. To avoid this singularity, and for more general situations, i.e., when diffusion in the solid phase is as important as in the liquid, especially when solidifications of liquid crystal are discussed, diffusion in the solid phase should be allowed to perform in the simulation. Ungar and Brown,¹⁸ applying two-sided model, showed deep two-dimensional cells by a finite-element method and examined the influence of the ratio of solid to liquid diffusivities on the cell shape and the adjacent concentration field. Kessler and Levine¹⁹ used an integral formulation for steady-state growth within a symmetric model of directional solidification. Saito, Misbah, and Müller-Krumbhaar²⁰ analyzed the transition from cells to dendrites numerically by a Green's-function method. Brattkus and Misbah²¹ derived a phase equation from the front integral equation and studied the phase instability. They found a strong deviation from the Ginzburg-Landau theory even very close to threshold. Kassner, Misbah, and Müller-Krumbhaar²² studied the long-wave limit and showed evidence for new branches of bifurcation, parity-breaking and oscillating breathing, and transition to chaos; see also Kassner *et al.*²³

All the works mentioned above treated the situation when the material is solidified at the low rate and, therefore, assumed local thermodynamic equilibrium at the solid-liquid interface. Local nonequilibrium at the interface, however, should be considered when the pulling speed is high enough in the directional solidification. For this, many investigators of rapid solidification used a model developed by Boettinger and co-workers,^{24,25} Aziz,²⁶ and Jackson *et al.*,²⁷ which allows for nonequilibrium effects on the interface through a velocity-dependent segregation coefficient and attachment kinetics. Merchant and Davis²⁸ performed a linear stability analysis using the FTA. They found in addition to the Mullins and Sekerka⁶ cellular branch an oscillatory branch due to the presence of disequilibrium effects. The onset of this instability occurs at zero wave number and so relates to a pulsatile mode. Braun and Davis^{29,30} have analyzed the weakly nonlinear behavior of both the cellular and oscillatory modes just past their thresholds and obtained amplitude equations describing the bifurcation structure. Merchant *et al.*³¹ performed a strongly nonlinear analysis of the oscillatory mode

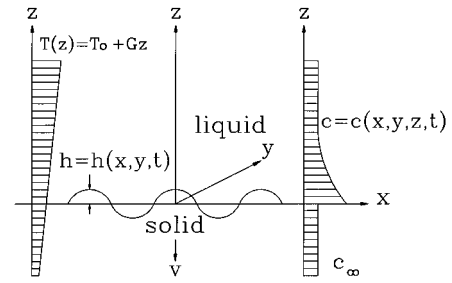


FIG. 1. Physical configuration of the solidification.

and derived amplitude equations which describe relaxation oscillations and the bifurcation structure. Karma and Sarkissian³² studied the oscillatory instability numerically by including the effects of latent heat and the full thermal fields. Huntley and Davis³³ analytically discussed the linear theory of rapid solidification under thermal effects. They found that the thermal effects can dramatically postpone the onset of the oscillatory instability and the critical wave number for the oscillatory instability can be zero or nonzero depending on the material parameters.

In this work, we intend to study the cellular morphologies, both two- and three-dimensional, in the directional solidification by considering the nonequilibrium condition at the solid-liquid interface. The oscillatory mode will not be considered here in this work. We will adopt the FTA, i.e., by neglecting the thermal effects. We have two reasons for adopting the FTA to analyze the cellular morphology. First, when surface energy is sufficiently small in a solidification the cellular mode will occur before the oscillatory mode and according to Huntley and Davis,³³ the cellular mode can only be slightly affected by the latent heat release. Second, by adopting the FTA, we can easily derive an evolution equation for the solidification and make the nonlinear analysis simpler. We will first derive a strongly nonlinear evolution equation by using an integral technique. The one-sided model, although it may produce cusp singularity, will be adopted in this work for the ease of deriving the equation and for that it is actually appropriate for many materials. The technique used in this work, however, may be in future applied to the two-sided model for more general considerations. Three particular evolution equations that this derived equation can recover at their individual long-wave limits then will be shown. Two-dimensional analysis will show that the transition point $M=9/4$ that Riley and Davis¹⁶ have addressed for the bifurcation structures should be modified with the nonequilibrium effect. Finally we analyze the weakly nonlinear instability due to three-dimensional disturbances directly from our equation and show the stability basins in which observable specific morphologies can be predicted.

II. FORMULATION

A. Equations for the system

The physical configuration of directional solidification considered in this work is shown in Fig. 1, where the solidified material is pulled at a given speed V under an imposed constant temperature gradient and is continuously solidified.

To simplify and to make the analysis easier, we consider an infinite one-sided model by neglecting diffusion of solute in the solid.³ We adopt the FTA 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, κ_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 pointing into the melt.

The formulation for the interfacial conditions in nonequilibrium solidification used here is from Merchant and Davis.²⁸ The model of the velocity-dependent segregation coefficient k was proposed by Aziz²⁶ and Jackson *et al.*²⁷ which is given by

$$k(v^*) = c_S^*/c_L^* = \frac{k_E + \gamma_0 v^*}{1 + \gamma_0 v^*}, \quad (2.2)$$

where c_S^* and c_L^* denote the interfacial concentrations of solute in the solid and liquid, respectively, k_E is the equilibrium segregation coefficient [$k_E = k(0)$], and v^* is the interface velocity; $v^* = V$ for a flat interface. The constant γ_0 has dimensions of reciprocal velocity; $1/\gamma_0$ is typically of the size 5 m/s.²⁵ Boettinger and co-workers^{24,25} had derived the appropriate form for the temperature at a planar interface, namely

$$T^*(V, c_L^*) = T_M + m(V)c_L^* - \frac{m_E}{k_E - 1} \frac{V}{V_0}, \quad (2.3)$$

where

$$m(V) = m_E \left\{ 1 - \frac{1}{k_E - 1} [k_E - k[1 - \ln(k/k_E)]] \right\}. \quad (2.4)$$

In Eq. (2.3), T_M represents the melting point of pure material, m is the slope of the liquidus, and $m_E = m(0)$. The parameter V_0 is the upper bound for the rate at which crystallization can occur, and is typically of the order of speed of sound. In metals this can be up to 1000 m/s. If $V_0 = \infty$, the atoms attach infinitely fast, and there is no kinetic undercooling. Relation (2.4) gives the change in liquidus slope due to nonequilibrium segregation.

The formulation for $T^*(V, c_L^*)$ is correct when the interface is flat, say at $z=0$. However, for the analysis to follow, we will suppose the nonequilibrium form of the Gibbs-Thomson relation valid for nonplanar interface, $z = h^*(x, y, t)$, to be

$$T_I^* = T^*(v^*, c_L^*) + T_M \delta_c K, \quad (2.5)$$

where T_I^* is the interfacial temperature, δ_c is the capillarity constant, and K denotes twice the mean curvature of the interface. We will replace V everywhere with its nonplanar form v^* , namely

$$v^* = (V + h_t^*) / (1 + |\nabla h^*|^2)^{1/2}. \quad (2.6)$$

With the above formulations, we then nondimensionalize the system using spatial and temporal scales based on solute diffusion, namely $\delta_L' = D/V$ and $\delta_T' = D/V^2$, respectively. The solute in the liquid is scaled such that

$$c = \frac{c^* - c_\infty / k_E}{(k_E - 1)c_\infty / k_E}, \quad (2.7)$$

where c_∞ is the far-field solute concentration.

The scaled equations governing the solute concentration field c , and the interface deflection $h(x, y, t)$ are as follows: liquid in $z > h(x, y, t)$:

$$\nabla^2 c + c_{zz} + c_z = c_t, \quad (2.8)$$

interface at $z = h(x, y, t)$:

$$c_z - \nabla c \cdot \nabla h = (1 + h_t)[1 + (k_E - 1)c] \frac{k(v) - 1}{k_E - 1}, \quad (2.9)$$

$$\begin{aligned} M^{-1}h - \mu(v - 1) - \frac{\Gamma \nabla^2 h}{(1 + |\nabla h|^2)^{3/2}} - c\overline{m}(v) \\ - \frac{k_E}{(k_E - 1)} \left[\frac{\overline{m}(v)}{k_E} - \frac{\overline{m}(1)}{k} \right] = 0, \end{aligned} \quad (2.10)$$

far-field as $z \rightarrow \infty$:

$$c \rightarrow 1. \quad (2.11)$$

Here, ∇ and ∇^2 represent the two-dimensional gradient and Laplacian operators, respectively, and

$$k(v) = \frac{k_E + \gamma v}{1 + \gamma v}, \quad (2.12)$$

$$\overline{m}(v) = 1 - \frac{1}{k_E - 1} \left\{ k_E - k \left[1 - \ln \left(\frac{k}{k_E} \right) \right] \right\}, \quad (2.13)$$

$$v = \frac{1 + h_t}{(1 + |\nabla h|^2)^{1/2}}, \quad (2.14)$$

$$\overline{k} = k(1) = \frac{k_E + \gamma}{1 + \gamma}. \quad (2.15)$$

The familiar nondimensional parameters appearing in system (2.8)–(2.11) are k_E , the morphological number M ,

$$M = \frac{m_E(k_E - 1)c_\infty V}{k_E D G}, \quad (2.16)$$

and a surface energy parameter Γ ,

$$\Gamma = \frac{T_M \delta_c k_E V}{D m_E (k_E - 1) c_\infty}. \quad (2.17)$$

Two new parameters describe the interface kinetics. They are the attachment-kinetics parameter

$$\mu = V k_E / (k_E - 1)^2 c_\infty V_0, \quad (2.18)$$

and the disequilibrium parameter

$$\gamma = \gamma_0 V. \quad (2.19)$$

When $\mu=0$, there is infinitely rapid interface kinetics and when $\gamma=0$, there is equilibrium segregation.

B. The evolution equation

In this subsection, we will derive the evolution equation for the system (2.8)–(2.11), which can describe the interfacial behavior during the solidification. This equation will appear in the form of a partial differential equation with the interface deflection $h(x, y, t)$ being the dependent variable and x, y , and t are the independent variables.

We derive the evolution equation by using the method of integral approximation which was developed by Kapitza³⁴ in researching thin-film flows, following an idea put forth by von Kármán³⁵ for gaining quantitative information about boundary layers of the flow of a viscous fluid at a high Reynolds number past a flat plate. We are encouraged to use this method because the distribution of the solute concentration near the interface is very similar to the boundary layer of thin-film flow, especially when the interface is deformed in a periodic long-wave type.

Following Hsieh and Hwang,¹⁷ we first look for suitable functions of the distribution of solute concentration which is assumed in the form

$$c' = 1 + P(x, y, t)e^{h-z} + Q(x, y, t)(h-z)e^{h-z} + R(x, y, t)(h-z)^2e^{h-z}, \quad (2.20)$$

and automatically satisfies the far-field condition (2.11). Expression (2.20) also is required to satisfy the interface conditions (2.9) and (2.10), so we find

$$P = -1 + \frac{1}{\overline{m}(v)} \left\{ M^{-1}h - \Gamma \nabla \cdot \left[\frac{\nabla h}{(1+|\nabla h|^2)^{1/2}} \right] + \mu(v-1) - \frac{k_E}{k_E-1} \left[\frac{\overline{m}(v)}{k_E} - \frac{\overline{m}(1)}{k} \right] \right\}, \quad (2.21)$$

$$Q = - \left\{ (1+h_t)[1+(k_E-1)(1+P)] \frac{k-1}{k_E-1} + \nabla P \cdot \nabla h \right\} / (1+|\nabla h|^2) - P. \quad (2.22)$$

The last term of Eq. (2.20), which does not appear in the report of Hsieh and Hwang,¹⁷ is added so that c' is forced to satisfy the governing equation (2.8) at the region very close to the solid-liquid interface. Therefore, the final unknown function $R(x, y, t)$, can be found by putting the assumed concentration Eq. (2.20), together with Eqs. (2.21) and (2.22), into the governing equation (2.8) and letting $z \rightarrow h^+$, then one has

$$2R = \left\{ \left(\frac{\partial}{\partial t} - \nabla^2 \right) P + (P+Q)(h_t - \nabla^2 h) - (P+Q)|\nabla h|^2 - 2\nabla(P+Q) \cdot \nabla h \right\} / (1+|\nabla h|^2) - Q. \quad (2.23)$$

The choice of c' , however, does not satisfy the governing equation as $z > h$. But as one simply substitutes Eqs. (2.20)–(2.23) into Eq. (2.8) and then integrates every term of Eq. (2.8) from $z=h$ to infinite, as shown by the following solute flux conservation equation:

$$\int_h^\infty \left(\nabla^2 + \frac{\partial^2}{\partial z^2} + \frac{\partial}{\partial z} - \frac{\partial}{\partial t} \right) c' dz = 0, \quad (2.24)$$

then one will obtain the evolution equation:

$$Q(1+|\nabla h|^2) + \left(\frac{\partial}{\partial t} - \nabla^2 \right) Q - \left(\frac{\partial}{\partial t} - \nabla^2 \right) P - (h_t - \nabla^2 h)P + P|\nabla h|^2 + 2\nabla P \cdot \nabla h - \left(\frac{\partial}{\partial t} - \nabla^2 \right) 2R = 0, \quad (2.25)$$

where P , Q , and R are expressed in Eqs. (2.21)–(2.23).

Since in deriving the evolution equation, h is assumed to be $O(1)$, the evolution equation (2.25) is strongly nonlinear. If the wave number and the growth rate of the interfacial disturbance are asymptotically small, and terms $\nabla^2 c$ and c_t in Eq. (2.8) in turn are asymptotically small, then the governing equation (2.8) is dominated by c_{zz} and c_z and the choice of approximate solute Eq. (2.20) is straightforward.

Equation (2.25) is in fact very complicated 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 of h . Through the term $(\partial/\partial t - \nabla^2)2R$, and compared with Ref. 17 (where $R=0$, equivalently) if the nonequilibrium effect is excluded, Eq. (2.25) contains more linear and nonlinear terms with high-order temporal and spatial derivatives, leading to more accurate result even if the wave number is only finitely small. Therefore we argue that the chosen c' in the present work is in a better way than in Hsieh and Hwang.¹⁷ Further, if extremely long-wave limits are considered, this equation can also recover simpler evolution equations associated with their limits. What follows are some examples.

If the parameters are chosen as $M^{-1} = k_E/k - \epsilon$, $k_E = \kappa_E \epsilon^2$, $\gamma = \gamma \epsilon^2$, $k = (\kappa_E + \gamma) \epsilon^2 = \kappa \epsilon^2$, with the scalings,

$$\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right) = \epsilon^{1/2} \left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y} \right), \quad \frac{\partial}{\partial t} = \epsilon^2 \frac{\partial}{\partial \tau}, \quad h = \epsilon H,$$

where $|\epsilon| \ll 1$, then our equation will reduce to

$$\kappa_E H + \frac{\kappa_E}{\kappa} H_\tau + \Gamma \nabla^4 H + \nabla^2 H = \frac{\kappa_E}{\kappa} \nabla \cdot (H \nabla H). \quad (2.26)$$

If the parameters and scalings are chosen as $\epsilon = k_E^{-1} - \Gamma$, $\gamma = \gamma \epsilon$, $\mu = \mu \epsilon$, $M^{-1} = M^{-1} \epsilon^2$,

$$\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right) = \epsilon^{1/2} \left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y} \right), \quad \frac{\partial}{\partial t} = \epsilon \frac{\partial}{\partial \tau},$$

then our equation will reduce to

$$\begin{aligned}
& k_E \overline{M}^{-1} h + \left(k_E - \frac{2-k_E}{k_E} \right) \nabla^2 h + \left(1 + \frac{1}{k_E} \right) \nabla^4 h \\
& + (k_E \overline{\mu} - \gamma) h_\tau - \left(2 + \frac{1}{k_E} \right) \nabla^2 h_\tau + h_{\tau\tau} \\
& = -\frac{1}{k_E} \nabla \cdot (\nabla^2 h \nabla h) + \nabla^2 h h_\tau - \frac{1}{2} \overline{\gamma} |\nabla h|^2 + |\nabla h|^2_\tau \\
& - \nabla^2 (|\nabla h|^2) - \frac{1}{2} \nabla \cdot (\nabla h |\nabla h|^2). \quad (2.27)
\end{aligned}$$

If the parameters are chosen as $\epsilon = \Gamma^{-1/2}$, $k_E = \kappa_E \epsilon^2$, $\gamma = \overline{\gamma} \epsilon^2$, $k = (\kappa_E + \overline{\gamma}) \epsilon^2$, and

$$\left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y} \right) = \epsilon \left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y} \right), \quad \frac{\partial}{\partial t} = \epsilon^2 \frac{\partial}{\partial \tau},$$

then our equation will reduce to

$$\begin{aligned}
& M^{-1} h_\tau - \nabla^2 h_\tau + \nabla^4 h + \left(\frac{\kappa_E}{\kappa} - \overline{\kappa} - M^{-1} \right) \nabla^2 h + \overline{\kappa} M^{-1} h \\
& = M^{-1} \nabla \cdot (h \nabla h) - \nabla \cdot (\nabla^2 h \nabla h). \quad (2.28)
\end{aligned}$$

A brief discussion of the above scalings can be found in the Appendix.

When the nonequilibrium effect is not taken account in the analysis, i.e., as $\gamma = \mu = 0$, Eqs. (2.26)–(2.28) will be identical to those Sivashinsky,¹⁴ Brattkus and Davis,¹⁵ and Riley and Davis¹⁶ have obtained. In the last long-wave limit Riley and Davis concluded that the transition point of the two-dimensional bifurcation is at $M^{-1} = 4/9$ (which corresponds to the zero Laudau constant β_1 shown in the next section), while if the nonequilibrium effect is considered, this result should be modified as $M^{-1} = 4k_E/(9k)$, which will be smaller than 4/9.

III. THE AMPLITUDE EQUATIONS

The evolution equation (2.25) describes the dynamics of the interface position h . The basic solution of it is obviously the planar interface, i.e., $h = h_0 = 0$. It is the stability of this solution to a particular class of perturbations with which we are concerned in the Segel-Stuart method.³⁶ We assume that, to third-order terms in the amplitude functions $A_1(t)$, $A_2(t)$, and $A_3(t)$, the hexagonal interface satisfies the equation

$$\begin{aligned}
h(x, y, t) = & \{A_1 + a \overline{A_2 A_3} + b A_1^2 \overline{A_1} + d A_1 (|A_2|^2 + |A_3|^2)\} \exp(i \mathbf{u}_1 \cdot \mathbf{r}) + \{A_2 + a \overline{A_3 A_1} + b A_2^2 \overline{A_2} + d A_2 (|A_3|^2 + |A_1|^2)\} \\
& \times \exp(i \mathbf{u}_2 \cdot \mathbf{r}) + \{A_3 + a \overline{A_1 A_2} + b A_3^2 \overline{A_3} + d A_3 (|A_1|^2 + |A_2|^2)\} \exp(i \mathbf{u}_3 \cdot \mathbf{r}) + f \{A_1 \overline{A_2} \exp(i [\mathbf{u}_1 - \mathbf{u}_2] \cdot \mathbf{r}) + A_2 \overline{A_3} \\
& \times \exp(i [\mathbf{u}_2 - \mathbf{u}_3] \cdot \mathbf{r}) + A_3 \overline{A_1} \exp(i [\mathbf{u}_3 - \mathbf{u}_1] \cdot \mathbf{r})\} + e \{A_1^2 \exp(2i \mathbf{u}_1 \cdot \mathbf{r}) + A_2^2 \exp(2i \mathbf{u}_2 \cdot \mathbf{r}) + A_3^2 \exp(2i \mathbf{u}_3 \cdot \mathbf{r})\} \\
& + \frac{1}{2} g \{(|A_1|^2 + |A_2|^2 + |A_3|^2)\} + \text{c.c.}, \quad (3.1)
\end{aligned}$$

where c.c. represents complex conjugate, $\overline{A_i}$ 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 $\mathbf{r} = (x, y)$. Clearly expression (3.1) of the hexagonal structure may recover the bandlike structure if only one amplitude is nonzero. 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 examine Eq. (3.1) and expect that the amplitude functions $A_i(t)$ satisfy the following amplitude equations to third order:

$$\begin{aligned}
dA_1/dt = & \sigma A_1 - \beta \overline{A_2 A_3} - \beta_1 A_1^2 \overline{A_1} - \beta_2 A_1 (|A_2|^2 + |A_3|^2), \\
dA_2/dt = & \sigma A_2 - \beta \overline{A_3 A_1} - \beta_1 A_2^2 \overline{A_2} - \beta_2 A_2 (|A_3|^2 + |A_1|^2), \quad (3.2)
\end{aligned}$$

$$dA_3/dt = \sigma A_3 - \beta \overline{A_1 A_2} - \beta_1 A_3^2 \overline{A_3} - \beta_2 A_3 (|A_1|^2 + |A_2|^2),$$

where σ is the growth rate of the disturbance, and β , β_1 , and β_2 , are solvability constants to be determined. The evolutions of A_i 's then are ensured by Eq. (3.2) 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 predict which morphology can be found in the solidified alloys.

We simply substitute Eq. (3.1), together with Eq. (3.2), into the evolution equation (2.25), then compare the amplitude in every independent periodic mode. Thus, at the first order of A_i , we obtain the dispersion relation which is expressed by

$$\begin{aligned}
& S_1 \sigma^3 + \left[M^{-1} + \Gamma \omega^2 + S_1 + 2S_1 (\overline{k} + \omega^2) + S_0 \frac{1-\gamma}{1+\gamma} \right] \sigma^2 + \left[2\omega^2 (M^{-1} + \Gamma \omega^2) + (1+2\overline{k}) (M^{-1} + \Gamma \omega^2 + S_1 \omega^2) + S_1 \omega^4 + \overline{k} S_1 \right. \\
& \left. - (1+2\omega^2) S_0 \frac{\gamma}{1+\gamma} \right] \sigma + (M^{-1} + \Gamma \omega^2) [\omega^2 + \omega^4 + \overline{k} (1+2\omega^2)] - S_0 \omega^2 (1+\omega^2) = 0, \quad (3.3)
\end{aligned}$$

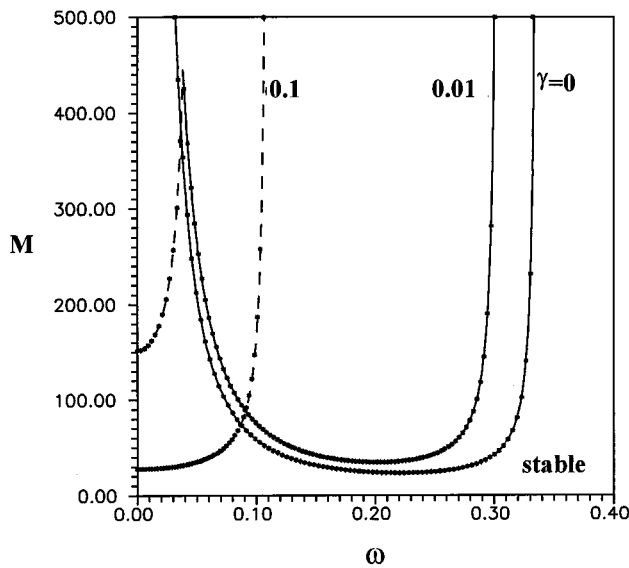


FIG. 2. Neutral stability curves for $k_E=0.2$, $\mu=0$, $\Gamma=3.0$ under $\gamma=0$, 0.01, and 0.1, respectively. The solid lines denote the steady branches, while the broken lines denote the oscillatory branches. The marks are from the present analysis.

where

$$\begin{aligned} S_0 &= \frac{k_E \overline{m}(1)}{k_E + \gamma}, \\ S_1 &= \mu - \frac{\ln(\overline{k}/k_E) \gamma k_E}{(1 + \gamma)(k_E - 1)(k_E + \gamma)}. \end{aligned} \quad (3.4)$$

It is clear to see that the dispersion relation (3.3) admits two types of modes. For $\text{Re}(\sigma)=\text{Im}(\sigma)=0$, the basic state become unstable to steady, cellular disturbances, and the relation (3.3) can be rearranged by

$$M^{-1} = \frac{S_0(\omega^2 + \omega^4)}{\omega^2 + \omega^4 + k(1 + 2\omega^2)} - \Gamma\omega^2. \quad (3.5)$$

For $\text{Re}(\sigma)=0$ with $\text{Im}(\sigma)\neq 0$, the basic state will be unstable to oscillatory disturbances whose most dangerous mode occurs at zero wave number, a pulsatile mode. For $\gamma=0$, only the steady cellular mode can be predicted by this analysis, while the presence of nonequilibrium effects, $\gamma\neq 0$, will destabilize the previous damped oscillatory mode²² and in the same time will stabilize the cellular mode.

Due to relation (3.3), we show neutral stability curves in Fig. 2, for the parameters $k_E=0.2$, $\mu=0$, $\Gamma=3.0$ under $\gamma=0$, 0.01, and 0.1, respectively. The result is compared with previous linear analysis^{28,29} and is found to be very accurate. For $\gamma=0$, no oscillatory mode is found and the most dangerous mode is steady. For $\gamma=0.01$, the oscillatory branch is found and the steady branch is somewhat lifted higher and to the left, but the cellular instability still would occur first (at lower M). As γ increases, the cellular instability will occur first until it reaches some particular value, say $\bar{\gamma}$. When $\gamma > \bar{\gamma}$, the oscillatory mode will turn out to occur first, and as γ increases more to make $\Gamma > \Gamma_s$, where

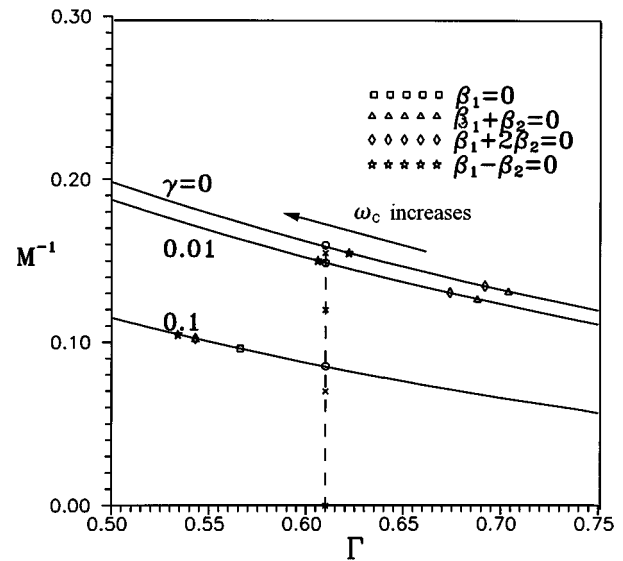


FIG. 3. Marginal stability curves in the (Γ, M^{-1}) plane for $k_E=0.47$, $\mu=0$. The cross marks represent the operating points at $\Gamma=0.61$ and $M^{-1}=0.155$, 0.12 , and 0.07 , respectively. The circle marks denote the corresponding critical conditions $M_c^{-1}=0.159$, $\omega_c^2=0.319$ for $\gamma=0$, $M_c^{-1}=0.149$, $\omega_c^2=0.310$ for $\gamma=0.01$, $M_c^{-1}=0.085$, $\omega_c^2=0.236$ for $\gamma=0.1$, respectively. On each curve, basin (5) is on the left-hand side of star mark, basin (4) is between the star and diamond marks, basin (3) is between the diamond and triangle marks, basin (2) is between the triangle and square marks, and basin (1) is on the right-hand side of the square marks.

$$\Gamma_S = k_E \left[\frac{1 - k_E + (k_E + \gamma) \ln(\overline{k/k_E})}{(1 - k_F)(\gamma + k)^2} \right], \quad (3.6)$$

then the steady branch will disappear. In Fig. 2 we see that for $\gamma=0.1$, no steady branch is found since then Γ is already far beyond Γ_S .

As the pulling speed is not so high to lead the oscillatory instability to occur first, i.e., when $\gamma < \bar{\gamma}$, the cellular morphology will be observed even the disequilibrium effect is considered. So in this paper we will consider the steady branch only. Furthermore, as can be seen in Eq. (3.5), the attachment-kinetics parameter μ will not affect the steady branch, so in the computation of this paper, we will simply choose $\mu=0$. For given Γ , k_E , γ , and μ , M^{-1} varies with ω^2 , then the critical wave number can be determined by letting $dM^{-1}/d\omega^2=0$, and we will find the relation

$$\Gamma = \frac{S_0 k [1 + 2(\omega_c^2 + \overline{\omega_c^4})]}{[\omega_c^2 + \overline{\omega_c^4} + k(1 + 2\overline{\omega_c^2})]^2}, \quad (3.7)$$

where ω_c is the critical wave number. After ω_c being obtained, the critical value M_c in turn can be evaluated from Eq. (3.5). Alternatively, for given k_E , γ , and μ , one can also determine the critical values M_c and Γ_c by Eqs. (3.5) and (3.7), respectively, at each particular ω_c . With this, we show in Fig. 3 marginal stability curves for $k_E=0.47$ and $\mu=0$

under $\gamma=0, 0.01$, and 0.1 , respectively. Again, this figure shows the stabilizing effect of γ on the steady cellular disturbance. Note that if a point (Γ, M^{-1}) does not locate on the marginal stability curve, with the other parameters fixed,

then it stands for that the critical condition is exceeded or deferred.

When going forward to the second order of A_i 's, one finds, if the critical condition is only slightly exceeded,

$$e = e(\sigma \rightarrow 0) = \{-2\omega^2(M^{-1} + \Gamma\omega^2) + 4(M^{-1} + \Gamma\omega^2)\omega^4[(k_E - 1)/(1 + \gamma) + 2\bar{k}] + S_0\omega^2(\gamma/2 - 4\omega^2)/(1 + \gamma) + S_2\omega^2[-\bar{k}/2 - 2(1 + 2\bar{k})\omega^2 + 8\omega^4]\}/\{(M^{-1} + 4\Gamma\omega^2)[\bar{k} + (1 + 2\bar{k})(4\omega^2 + 16\omega^4)] - 4\omega^2(1 + 4\omega^2)S_0\}, \quad (3.8)$$

$$f = f(\sigma \rightarrow 0) = \{-3\omega^2(M^{-1} + \Gamma\omega^2) + 3(M^{-1} + \Gamma\omega^2)\omega^4[(k_E - 1)/(1 + \gamma) + 2\bar{k}] + S_0\omega^2(\gamma/2 - 3\omega^2)/(1 + \gamma) + S_2\omega^2[-\bar{k} - 3(1 + 2\bar{k})\omega^2 + 9\omega^4]/2\}/\{(M^{-1} + 3\Gamma\omega^2)[\bar{k} + (1 + 2\bar{k})(3\omega^2 + 9\omega^4)] - 3\omega^2(1 + 3\omega^2)S_0\}, \quad (3.9)$$

$$g = g(\sigma \rightarrow 0) = 0, \quad (3.10)$$

and

$$\beta - \sigma a = r(\sigma), \quad (3.11)$$

where

$$\begin{aligned} r(\sigma) = & \left\{ -8S_4\sigma^4 + \sigma^3 \left[-\frac{2S_0}{(1+\gamma)} \left(1 + \frac{4\gamma}{(1+\gamma)} \right) - 4S_1 \frac{(1-k_E)(1-\gamma)}{(1+\gamma)^2} - 8S_3 - 4S_4[(1+2\bar{k}) + 2\omega^2] \right] + \sigma^2 \right. \\ & \left[-4 \frac{(1-k_E)(1-\gamma)}{(1+\gamma)^2} (M^{-1} + \Gamma\omega^2) - \frac{S_0}{(1+\gamma)} \left(\frac{2\gamma}{(1+\gamma)} + \omega^2 + \frac{4\gamma\omega^2}{(1+\gamma)} \right) + 2S_1\omega^2 \left(2 - \frac{(1-k_E)(1-\gamma)}{(1+\gamma)^2} \right) \right. \\ & \left. + 2S_1 \frac{[k_E + \gamma(2+\gamma)]}{(1+\gamma)^2} - 2S_2\omega^2 - 4S_3[1 + 2\bar{k} + 2\omega^2] - 2S_4[\bar{k} + (1 + 2\bar{k})\omega^2 + \omega^4] \right] \\ & + \sigma \left[2 \frac{[k_E + \gamma(2+\gamma)]}{(1+\gamma)^2} (M^{-1} + \Gamma\omega^2) + 2\omega^2 \left(2 - \frac{(1-k_E)(1-\gamma)}{(1+\gamma)^2} \right) (M^{-1} + \Gamma\omega^2) - \frac{2S_0\omega^2}{(1+\gamma)} + S_1\omega^2(1 + 2\omega^2) \right. \\ & \left. - 2\bar{k}S_3(M^{-1} + \Gamma\omega^2) - S_2[(1 + 2\bar{k})\omega^2 + 2\omega^4] - 2S_3[(1 + 2\bar{k})\omega^2 + \omega^4] \right] + (1 + 2\omega^2)\omega^2(M^{-1} + \Gamma\omega^2) \\ & + \frac{S_0\omega^2}{(1+\gamma)} \left(\frac{\gamma}{2} - \omega^2 \right) - \frac{S_2\omega^2}{2} [\bar{k} + (1 + 2\bar{k})\omega^2 + \omega^4] \left. \right\} / \left\{ 7\sigma^2S_1 + 3\sigma \left(M^{-1} + \Gamma\omega^2 + S_1 + 2S_1(\bar{k} + \omega^2) + S_0 \frac{1-\gamma}{1+\gamma} \right) \right. \\ & \left. + \left[2\omega^2(M^{-1} + \Gamma\omega^2) + (1 + 2\bar{k})(M^{-1} + \Gamma\omega^2 + S_1\omega^2) + S_1\omega^4 + \bar{k}S_1 - (1 + 2\omega^2)S_0 \frac{\gamma}{1+\gamma} \right] \right\}. \quad (3.12) \end{aligned}$$

Here

$$\begin{aligned} S_2 &= \mu + \frac{\ln(\bar{k}/k_E)\gamma k_E}{(1+\gamma)(k_E-1)(k_E+\gamma)}, \\ S_3 &= \frac{\ln(\bar{k}/k_E)\gamma}{m(1)(1+\gamma)^2}, \\ S_4 &= S_3 \left\{ \mu + \frac{k_E}{(k_E+\gamma)} \frac{\gamma m(1)}{(k_E-1)} \left[1 - \frac{\ln(\bar{k}/k_E)}{m(1)(1+\gamma)} \right] \right\}. \quad (3.13) \end{aligned}$$

According to the analysis of Sriranganathan, Wollkind, and Oulton,¹⁰ we should take

$$\begin{aligned} \beta = \lim_{\sigma \rightarrow 0} r(\sigma) = & \left\{ (1 + 2\omega^2)\omega^2(M^{-1} + \Gamma\omega^2) + \frac{S_0\omega^2}{(1+\gamma)} \left(\frac{\gamma}{2} - \omega^2 \right) - \frac{S_2\omega^2}{2} [\bar{k} + (1 + 2\bar{k})\omega^2 + \omega^4] \right\} / \left\{ 2\omega^2(M^{-1} + \Gamma\omega^2) \right. \\ & \left. + (1 + 2\bar{k})(M^{-1} + \Gamma\omega^2 + S_1\omega^2) + S_1\omega^4 + \bar{k}S_1 - (1 + 2\omega^2)S_0 \frac{\gamma}{1+\gamma} \right\}, \quad (3.14) \end{aligned}$$

and

$$a = \lim_{\sigma \rightarrow 0} \frac{\beta - r(\sigma)}{\sigma} = - \frac{dr(0)}{d\sigma}. \quad (3.15)$$

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

$$\beta_1 - 2\sigma b = r_1(\sigma), \quad (3.16)$$

and

$$\beta_2 - 2\sigma d = r_2(\sigma). \quad (3.17)$$

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

$$\begin{aligned} \beta_1 = r_1(\sigma \rightarrow 0) = & \left\{ (M^{-1} - 2\Gamma\omega^2)\omega^2 e + M^{-1}\omega^2 g + 2S_0 \frac{\gamma}{(1+\gamma)} \omega^2 e - 2\overline{k}S_2\omega^2 e - 4S_0\omega^4 e + \frac{(1-k_E)}{(1+\gamma)} M^{-1}\omega^4(g+5e) \right. \\ & + 8 \frac{(1-k_E)}{(1+\gamma)} \omega^6 e \Gamma + 8\overline{k}M^{-1}\omega^4 e + 20\overline{k}\Gamma\omega^6 e + 4S_0 \frac{\gamma}{(1+\gamma)} \omega^4 e - 2(1+2\overline{k})S_2\omega^4 e - 2S_2\omega^6 e \\ & - k \left[\frac{3}{2} \Gamma\omega^4 + \frac{1}{2} S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right] - \frac{3}{2} S_2\omega^4 + \frac{1}{2} S_0 \frac{\gamma}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 \\ & - \omega^2 \left[(1+2\overline{k}) \left(\frac{3}{2} \Gamma\omega^4 + \frac{1}{2} S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right) - S_0 \frac{\gamma}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 - 2S_2\omega^4 + \frac{(k_E-1)}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 \right. \\ & + \left. \left(\frac{3}{2} \Gamma\omega^4 + \frac{1}{2} S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right) \omega^2 + \frac{5}{2} S_0 \frac{\gamma}{(1+\gamma)} \omega^4 - \frac{5}{2} \frac{k_E-1}{(1+\gamma)} S_2\omega^4 + 6(M^{-1}\omega^4 \right. \\ & \left. \left. + \Gamma\omega^6 - S_0\omega^4) \right] \right\} / \left\{ 2\omega^2(M^{-1} + \Gamma\omega^2) + (1+2\overline{k})(M^{-1} + \Gamma\omega^2 + S_1\omega^2) + S_1\omega^4 + \overline{k}S_1 - (1+2\omega^2)S_0 \frac{\gamma}{1+\gamma} \right\}, \quad (3.18) \end{aligned}$$

$$\begin{aligned} \beta_2 = r_2(\sigma \rightarrow 0) = & \left\{ (M^{-1} + \Gamma\omega^2)\omega^2 a + M^{-1}\omega^2(f+g) - \frac{3}{2} S_1\omega^2\beta - \frac{[k_E + \gamma(2+\gamma)]}{(1+\gamma)^2} (M^{-1} + \Gamma\omega^2)\beta \right. \\ & + \frac{1}{2} S_0 \frac{\gamma}{(1+\gamma)} \omega^2(3f+a) - \frac{1}{2} \overline{k}S_2\omega^2(3f+a) - \overline{k}S_3(M^{-1} + \Gamma\omega^2)\beta + S_0\omega^4 \frac{1}{1+\gamma} \beta - S_0\omega^4(3f+a) \\ & + S_0\omega^2\beta + \frac{(1-k_E)(1-\gamma)}{(1+\gamma)^2} (M^{-1} + \Gamma\omega^2)\omega^2\beta - 2 \frac{(1-k_E)}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2\beta \\ & + \frac{(1-k_E)}{(1+\gamma)} M^{-1}\omega^4[g+4(f+a)] + 6 \frac{(1-k_E)}{(1+\gamma)} \Gamma\omega^6(f+a) - \frac{(1-k_E)}{(1+\gamma)} S_1\omega^4\beta \\ & + 2\overline{k}M^{-1}[S_0\omega^4(3f+a) - S_0\omega^2\beta] + 2\overline{k}\Gamma[S_0\omega^6(6f+a) - S_0\omega^4\beta] + \overline{k}S_1\omega^4\beta + S_0\omega^4 \frac{\gamma}{1+\gamma} (3f+a) \\ & - S_0\omega^2 \frac{\gamma}{1+\gamma} \beta - S_0\omega^4 \frac{1}{1+\gamma} \beta - (1+2\overline{k})\omega^2 \left[\frac{1}{2} S_2\omega^2(3f+a) - S_3(M^{-1} + \Gamma\omega^2)\beta \right] + \frac{1}{2} (1+2\overline{k})S_2\omega^2\beta \\ & - k \left[\frac{3}{2} \Gamma\omega^4 + S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right] - \frac{3}{2} S_2\omega^4 + S_0 \frac{\gamma}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 \\ & - \omega^2 \left[(1+2\overline{k}) \left(\frac{3}{2} \Gamma\omega^4 + S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right) - 2S_0 \frac{\gamma}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 - S_2\omega^4 \right. \\ & + 2 \frac{(k_E-1)}{(1+\gamma)} (M^{-1} + \Gamma\omega^2)\omega^2 + \left. \left(\frac{3}{2} \Gamma\omega^4 + S_3(M^{-1} + \Gamma\omega^2)\omega^2 \right) \omega^2 + 2S_0 \frac{\gamma}{(1+\gamma)} \omega^4 - 2 \frac{k_E-1}{(1+\gamma)} S_2\omega^4 \right. \\ & \left. + 8(M^{-1}\omega^4 + \Gamma\omega^6 - S_0\omega^4) \right] + \beta^2 \left[M^{-1} + \Gamma\omega^2 + S_1 + 2S_1(\overline{k} + \omega^2) \right. \\ & \left. + S_0 \frac{1-\gamma}{1+\gamma} \right] \right\} / \left\{ 2\omega^2(M^{-1} + \Gamma\omega^2) + (1+2\overline{k})(M^{-1} + \Gamma\omega^2 + S_1\omega^2) + S_1\omega^4 + \overline{k}S_1 - (1+2\omega^2)S_0 \frac{\gamma}{1+\gamma} \right\} - \beta a. \quad (3.19) \end{aligned}$$

It should be mentioned here that, some of the parameters appearing in Eqs. (3.8)–(3.19) should be the critical values and we have dropped out of them the subscript symbol c .

IV. THE STEADY-STATE SOLUTIONS AND THEIR STABILITIES

In the directional solidification of a dilute binary alloy, we often observe three types of the morphological structures. They are the planar interface, the two-dimensional bandlike cell and the three-dimensional hexagonal cell or node. Here we should look for the steady-state solutions for these morphologies and discuss their stabilities after the corresponding constants can be estimated from the expressions in the above section. For the analysis of regular patterns, we can assume $A_1 = A_1 = A/2$ and $A_2 = A_2 = A_3 = A_3 = B/4$, then the amplitude equations (3.2) will reduce to

$$\begin{aligned} dA/dt &= \sigma A - \frac{1}{8} \beta B^2 - \frac{1}{4} \beta_1 A^3 - \frac{1}{8} \beta_2 A B^2 = F(A, B), \\ dB/dt &= \sigma B - \frac{1}{2} \beta A B - \frac{1}{4} \beta_2 A^2 B - \frac{1}{16} (\beta_1 + \beta_2) B^3 \\ &= G(A, B). \end{aligned} \quad (4.1)$$

In particular the equilibrium points (A_0, B_0) of Eq. (4.1), which are those points such that $F(A_0, B_0) = G(A_0, B_0) = 0$, can be catalogued as follows:³⁰

$$\begin{aligned} \alpha_1 : A_0 &= B_0 = 0; \\ \alpha_2 : A_0 &= \pm 2 \sqrt{\sigma / \beta_1}, \quad B_0 = 0; \\ \alpha_{3-1} : A_0 &= [-\beta \pm \sqrt{\beta^2 + 4\sigma(\beta_1 + 2\beta_2)}] / (\beta_1 + 2\beta_2), \\ B_0 &= 2A_0; \\ \alpha_{3-2} : A_0 &= [-\beta \pm \sqrt{\beta^2 + 4\sigma(\beta_1 + 2\beta_2)}] / (\beta_1 + 2\beta_2), \\ B_0 &= -2A_0; \\ \alpha_4 : A_0 &= -2\beta / (\beta_2 - \beta_1), \\ B_0 &= \pm 4 \sqrt{[\sigma - \beta^2 \beta_1 (\beta_2 - \beta_1)^{-2}] / (\beta_1 + \beta_2)}. \end{aligned} \quad (4.2)$$

The equilibrium points of α_1 correspond to a planar interface while the equilibrium solutions of α_2 represent equivalent observable two-dimensional bandlike cells. 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} , which will be seen later, will depend on B_0^2 and thus will reveal identical result, we therefore will only discuss the steady-state solutions of α_{3-1} . For alloys having $k_E < 1$, hexagonal structures with $A_0 > 0$ correspond to cells with dome-shaped centers projecting into the melt 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. The equilibrium points α_4 represent cells bounded by some closed nonhexagonal con-

tour, 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 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 Eq. (4.1) be in the form

$$A(t) = A_0 + \epsilon X \exp(\rho t) + O(\epsilon^2), \quad (4.3)$$

$$B(t) = B_0 + \epsilon Y \exp(\rho t) + O(\epsilon^2), \quad (4.4)$$

where $|\epsilon| \ll 1$. A somewhat limited nature of following stability analysis should be mentioned here because no spatial dependence is performed in Eqs. (4.1). Aside from this, anyway, the analysis that is about to be undertaken is useful for the present situation. Substituting these solutions into Eq. (4.1), 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

$$\rho^2 + p\rho + q = 0, \quad (4.5)$$

where

$$p = -2\sigma + \frac{1}{2}\beta A_0 + \frac{1}{4}(3\beta_1 + \beta_2)A_0^2 + \frac{1}{16}(3\beta_1 + 5\beta_2)B_0^2, \quad (4.6)$$

$$\begin{aligned} q &= (\sigma - \frac{3}{4}\beta_1 A_0^2 - \frac{1}{8}\beta_2 B_0^2) [\sigma - \frac{1}{2}\beta A_0 - \frac{1}{4}\beta_2 A_0^2 \\ &\quad - \frac{3}{16}(\beta_1 + \beta_2)B_0^2] - \frac{1}{8}B_0^2(\beta + \beta_2 A_0)^2. \end{aligned} \quad (4.7)$$

That is, the stability of the steady-state solution depends on the constants p and q . 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

$$p > 0 \quad \text{and} \quad q > 0. \quad (4.8)$$

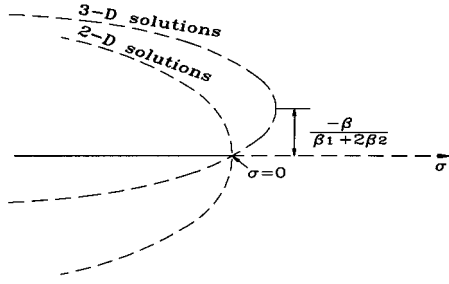
So far we should keep in mind that the equilibrium point (A_0, B_0) and the constant p and q are determined by the constants σ , β , β_1 , and β_2 . The constants β , β_1 , and β_2 in turn are determined by critical values of the parameters such as M , Γ , k_E , ω , γ , and μ . As to the parameter σ , when the critical condition is slightly exceeded, it can be evaluated by the dispersion relation (3.3). If one chooses M as the bifurcation parameter such that

$$M^{-1} = M_c^{-1} - \delta, \quad (4.9)$$

then one has

$$\begin{aligned} \delta &= \sigma [2\omega_c^2 (M_c^{-1} + \Gamma \omega_c^2) + (1 + 2\bar{k}) (M_c^{-1} + \Gamma \omega_c^2 + S_1 \omega_c^2) \\ &\quad + S_1 \omega_c^4 + S_1 \bar{k} - (1 + 2\omega_c^2) S_0 \gamma / (1 + \gamma)] / [\omega_c^2 + \omega_c^4 \\ &\quad + \bar{k} (1 + 2\omega_c^2)] + O(\sigma^2), \end{aligned} \quad (4.10)$$

for given Γ , k_E , γ , and μ .

FIG. 4. Bifurcation diagrams for $\beta_2 < \beta_1 < 0$.

V. RESULTS AND DISCUSSION

In this section, we shall study the stabilities of the equilibrium points of α_1 , α_2 , and α_{3-1} , respectively, and predict the observable morphologies. It should be kept in mind that the stability analysis to the equilibrium solution is due to three-dimensional disturbances; see Eqs. (4.3) and (4.4).

We first note that for equilibrium point α_1

$$p = -2\sigma \quad \text{and} \quad q = \sigma^2. \quad (5.1)$$

Hence the planar interface is locally stable if $\sigma < 0$. For equilibrium point α_2 , we rearrange relations (4.6) and (4.7) and find

$$p = \frac{1}{4}A_0[(\beta_1 + \beta_2)A_0 + 2\beta] \\ q = \frac{1}{8}\beta_1 A_0^3[2\beta - (\beta_1 - \beta_2)A_0]. \quad (5.2)$$

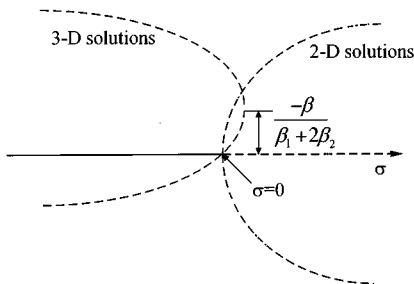
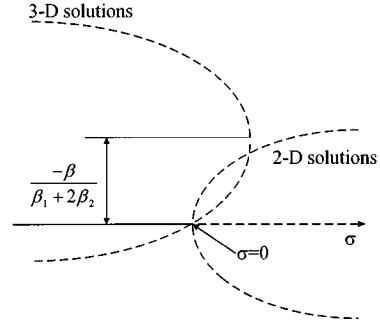
For equilibrium point α_{3-1} , we in turn have

$$p = \frac{1}{2}A_0[(2\beta_1 + \beta_2)A_0 - \beta], \\ q = \frac{1}{4}A_0^2[(\beta_1 + 2\beta_2)A_0 - \beta][(\beta_1 - \beta_2)A_0 - 2\beta]. \quad (5.3)$$

Examining Eqs. (5.2) and (5.3), we conclude that the stabilities of equilibrium points of α_2 and α_{3-1} are determined by which sense the constants β_1 , $\beta_1 + \beta_2$, $\beta_1 + 2\beta_2$, and $\beta_1 - \beta_2$ are. We thus consider the following five basins of bifurcation.

(1) $\beta_2 < \beta_1 < 0$: We find that for equilibrium points of α_2 , Eq. (4.1) becomes a Landau equation subject to a subcritical bifurcation and both two-dimensional solutions $A_0^{(1)}$ and $A_0^{(2)}$ are unstable. The three-dimensional structures $A_0^{(1)}$ and $A_0^{(2)}$ of α_{3-1} are unstable, too. See Fig. 4 for the bifurcation diagrams.

(2) $\beta_2 < 0 < \beta_1$, and $\beta_1 + \beta_2 < 0$: The Landau equation for the equilibrium points of α_2 is subject to a supercritical bi-

FIG. 5. Bifurcation diagrams for $\beta_2 < 0 < \beta_1$ and $\beta_1 + \beta_2 < 0$.FIG. 6. Bifurcation diagrams for $\beta_2 < 0 < \beta_1$, $\beta_1 + \beta_2 > 0$, and $\beta_1 + 2\beta_2 < 0$.

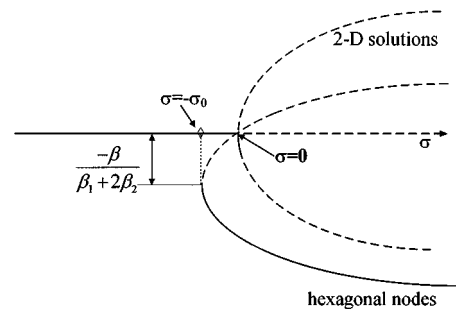
furcation but the two-dimensional solution $A_0^{(2)}$ is unstable and $A_0^{(1)}$ is stable only if $A_0^{(1)} < -2\beta/(\beta_1 + \beta_2)$, mathematically. Physically, since the two-dimensional cells $A_0^{(1)}$ and $A_0^{(2)}$ are equivalent structures, however, the bandlike cell cannot be observed. The three-dimensional solutions $A_0^{(1)}$ and $A_0^{(2)}$ of α_{3-1} are unstable. See Fig. 5 for the physical bifurcation diagrams.

(3) $\beta_2 < 0 < \beta_1$, $\beta_1 + \beta_2 > 0$, and $\beta_1 + 2\beta_2 < 0$: The Landau equation for the two-dimensional solutions $A_0^{(1)}$ and $A_0^{(2)}$ is subject to a supercritical bifurcation, and although $A_0^{(1)}$ can be stable if $A_0^{(1)} < 2\beta/(\beta_1 - \beta_2)$ the bandlike cell still is not observable because $A_0^{(2)}$ is unstable. The three-dimensional solutions $A_0^{(1)}$ and $A_0^{(2)}$ of α_{3-1} are unstable. See Fig. 6 for the physical bifurcation diagrams.

(4) $\beta_1 > 0$, $\beta_1 > \beta_2$, and $\beta_1 + 2\beta_2 > 0$: We find that two-dimensional solution $A_0^{(2)}$ is unstable and $A_0^{(1)}$ is stable if $A_0^{(1)} < 2\beta/(\beta_1 - \beta_2)$, while the three-dimensional solution $A_0^{(1)}$ is unstable and $A_0^{(2)}$ is locally stable for $\sigma > -\sigma_0$, where $\sigma_0 = \beta^2/4(\beta_1 + 2\beta_2)$, which is a positive constant. Since three-dimensional $A_0^{(1)}$ corresponds to dome-shaped cells and $A_0^{(2)}$ represents nodes, so in this case we conclude that the three-dimensional nodes can be observable. The bifurcation diagrams can be found in Fig. 7.

(5) $0 < \beta_1 < \beta_2$: We find that the two-dimensional solution $A_0^{(1)}$ is stable and $A_0^{(2)}$ is stable only if $A_0^{(2)} > 2\beta/(\beta_1 - \beta_2)$ or, from (4.2), for $\sigma > \sigma_1$, where $\sigma_1 = \beta^2\beta_1/(\beta_1 - \beta_2)^2$. Thus in this basin, the two-dimensional cell can be seen as $\sigma > \sigma_1$. The three-dimensional solution $A_0^{(1)}$ is unstable and $A_0^{(2)}$ is stable if $-\beta/(\beta_1 + 2\beta_2) > A_0^{(2)} > 2\beta/(\beta_1 - \beta_2)$, or alternatively, for $-\sigma_0 < \sigma < \sigma_2$, where $\sigma_2 = \beta^2(2\beta_1 + \beta_2)/(\beta_1 - \beta_2)^2$. See Fig. 8 for the bifurcation diagrams.

Before showing the result, we should see when the ampli-

FIG. 7. Bifurcation diagrams for $\beta_1 > 0$, $\beta_1 > \beta_2$, and $\beta_1 + 2\beta_2 > 0$.

$M_c^{-1}=0.149$ and $\omega_c^2=0.310$ for $\gamma=0.01$, and $M_c^{-1}=0.085$ and $\omega_c^2=0.236$ for $\gamma=0.1$. Now, we have clearly seen that in Figs. 3 and 11 the upper critical point is located in basin (5), for $\gamma=0$, the middle critical point is located in basin (4), for $\gamma=0.01$, and the lower critical point, basin (1) for $\gamma=0.1$. For the same Γ , the disequilibrium effects can change the location of the critical point in the basins of bifurcation and make the critical wave number smaller, as well. From Figs. 3 and 11 we also find that for the upper operating point the morphology for $\gamma=0$ is three-dimensional nodes, while for $\gamma=0.01$ and 0.1 the planar interface will be found; for the middle operating point the morphology for $\gamma=0$ and $\gamma=0.01$ is three-dimensional nodes and for $\gamma=0.1$, is planar interface, and for the lower operating point the morphology for $\gamma=0$ and $\gamma=0.01$ is nodes, while for $\gamma=0.1$ the equilibrium solutions are unstable. These interesting phenomena are due to the disequilibrium effect which can lower down the marginal stability curve and the curves of $\sigma=\sigma_1$ and $\sigma=\sigma_2$.

Finally, if for an alloy the parameters γ and Γ can be fixed, i.e., if V and c_∞ are fixed in the realistic operation, in the basin (5) and M^{-1} , or the G in the operation, is tuned from above to below the corresponding M_c^{-1} , then the morphology which can be found will be, in order, the planar interface, the nodes, and the two-dimensional cells. This trend is the same as reported by Takahashi, Kamio, and Trung³⁷ in studying the solidified aluminum alloys under normal pulling speed which is so slow that the disequilibrium effects can be neglected. Indeed, the present result, however, should be further verified by experiments in which the solidification should undergo higher pulling speeds.

VI. CONCLUSION

In this paper we have considered the disequilibrium effects in the directional solidification of a dilute binary alloy. We have used the model proposed by Aziz²⁶ and Jackson *et al.*²⁷ for the velocity-dependent segregation coefficient and considered the velocity dependence of the modified Gibbs-Thomson condition derived by Boettinger and co-workers.^{24,25} The oscillatory mode due to the disequilibrium condition is ignored, since if the surface energy is small and the pulling speed is not high enough then the Mullins and Sekerka cellular mode is preferred. Meanwhile, since the latent heat release can only slightly affect the cellular instability, we therefore ignored the thermal effects and adopted the FTA.

We first derived an evolution equation by an integral technique, then the amplitude equations were determined directly from it. From the amplitude equations, the equilibrium solutions which are catalogued as planar, two-dimensional, and three-dimensional structures were obtained. The stability analysis of these equilibrium solutions to three-dimensional disturbances has also been undertaken. The result of the analysis shows that the marginal stability curve can be divided into five basins of bifurcation structures, for both the two- and three-dimensional equilibrium solutions. The possible morphology to be found depends on the location of the chosen critical condition and how far the system parameters are exceeded from this critical condition. The result shows that if the critical point is located on area (4), where $\beta_1 > 0 > \beta_2$ and $\beta_1 + 2\beta_2 > 0$, when $\sigma > 0$, then three-

dimensional nodes are observable, while if the critical point is located on area (5), where $0 < \beta_1 < \beta_2$, then two-dimensional bandlike cells, when $\sigma > \sigma_1$, and three-dimensional nodes, when $0 < \sigma < \sigma_2$, can be predicted.

From the discussion in the above section, we see that the disequilibrium effect can stabilize the cellular mode, change the location of the critical point in the basin of bifurcation, and most importantly can make the wave number smaller and cause the evolution equation to be more applicable.

ACKNOWLEDGMENT

The authors wish to acknowledge with appreciation the financial support (Grant No. NSC 84-2212-E033-002) provided by the National Science Council of the Republic of China.

APPENDIX

The dispersion relation of the system considered in the present work is expressed by

$$\left[\frac{1}{2} - \frac{1}{2} (1 + 4\sigma + 4\omega^2)^{1/2} - k \right] \times \left\{ \sigma \left(\mu - \frac{k_E \gamma \ln(\bar{k}/k_E)}{(k_E + \gamma)(k_E - 1)(1 + \gamma)} \right) + \Gamma \omega^2 - M^{-1} - \frac{k_E \bar{m}(1)}{k_E + \gamma} \right\} - \frac{k_E \bar{m}(1)}{1 + \gamma} \left(1 + \frac{\sigma}{k_E + \gamma} \right) = 0, \quad (A1)$$

where σ is the growth rate and ω is the wave number of the disturbance to the planar solid-liquid interface. Since the principle of exchange of stability holds, by vanishing σ and treating M^{-1} as the bifurcation parameter, with the others as control parameters, we then have the neutral stability curve which is given by

$$M^{-1} = \left[\frac{1}{2} - \frac{1}{2} (1 + 4\omega^2)^{1/2} - k \right]^{-1} \frac{k_E \bar{m}(1)}{1 + \gamma} + \frac{k_E \bar{m}(1)}{k_E + \gamma} - \Gamma \omega^2. \quad (A2)$$

For given control parameters, the critical wave number ω_c is determined, from $dM^{-1}/d\omega^2=0$, by the relation

$$\Gamma = \left[\frac{1}{2} - \frac{1}{2} (1 + 4\omega^2)^{1/2} - k \right]^{-2} (1 + 4\omega^2)^{-1/2} \frac{k_E \bar{m}(1)}{1 + \gamma}. \quad (A3)$$

Thus, a marginal stability surface in the parameter space is constructed by Eqs. (A2) and (A3). On the marginal stability surface, if we designate the critical wave number ω_c to be asymptotically small and denote it by a positive number δ [which should not be confused with the same symbol appearing in Eqs. (4.10) and (4.11)], then we have the long-wave region which is given by

$$\begin{aligned}
M^{-1} &\sim -(\overline{k} + \delta^2)^{-1} \frac{k_E \overline{m}(1)}{1 + \gamma} + \frac{k_E \overline{m}(1)}{k_E + \gamma} \\
&\quad - (\overline{k} + \delta^2)^{-2} (1 - 2\delta^2) \frac{k_E \overline{m}(1) \delta^2}{1 + \gamma} \Gamma \\
&\sim (\overline{k} + \delta^2)^{-2} (1 - 2\delta^2) \frac{k_E \overline{m}(1)}{1 + \gamma}. \quad (A4)
\end{aligned}$$

So, the scalings of the long-wave limits mentioned in Sec. II can now be discussed briefly.

The first limit to be considered is motivated from the work of Sivashinsky,¹⁴ in which the segregation coefficient k_E is assumed to be $k_E = \kappa_E \delta^4$, much smaller than the wave number. In the present work, the parameter γ is assumed to be $\gamma = \overline{\gamma} \delta^4$, then consequently $\overline{m}(1) \sim 1$ and from Eq. (A4) we have

$$\begin{aligned}
\Gamma &\sim \kappa_E, \\
M^{-1} &\sim \frac{\kappa_E}{\kappa} - 2\kappa_E \delta^2, \quad (A5)
\end{aligned}$$

where $\overline{\kappa} = \kappa_E + \overline{\gamma}$. The magnitude of σ should be meaningfully assumed to be at the same order of k_E , i.e., $\sigma = O(\delta^4)$, from the dispersion relation (A1). Due to these, in Sec. II we have further assumed another number $\epsilon = 2\kappa_E \delta^2$ and have the scaling shown in the section which leads to the evolution equation (2.26).

The second long-wave limit that we consider is the absolute stability limit.¹⁵ In this limit, we set $\gamma = \overline{\gamma} \delta^2$ and $k_E = O(1)$, then consequently from Eq. (A4) we have

$$\Gamma \sim k_E^{-1} - k_E^{-1} \left\{ \frac{2[\overline{\gamma}(1 - k_E) + 1]}{k_E} + 2 + \overline{\gamma} \right\} \delta^2, \quad (A6)$$

$$M^{-1} \sim O(\delta^4).$$

Thus, a number $\epsilon = k_E^{-1} \{2[\overline{\gamma}(1 - k_E) + 1]/k_E + 2 + \overline{\gamma}\} \delta^2$ and the growth rate $\sigma = O(\omega_c^2)$ are assumed in the section for the scaling.

The final long-wave limit is according to Riley and Davis,¹⁶ which comes out from the absolute stability limit but emphasizes the requirement of small segregation coefficient and large surface energy. Here we require $k_E = \kappa_E \delta^2$ and assume $\gamma = \overline{\gamma} \delta^2$, then from Eq. (A4) we have

$$\Gamma \sim \kappa_E (\kappa_E + \overline{\gamma} + 1)^{-2} \delta^{-2}, \quad (A7)$$

$$M^{-1} \sim \kappa_E (\kappa_E + \overline{\gamma})^{-1} - \kappa_E (\kappa_E + \overline{\gamma} + 2) (\kappa_E + \overline{\gamma} + 1)^{-2}.$$

In this section we have made a number $\epsilon = (\kappa_E + \overline{\gamma} + 1) \kappa_E^{-1/2} \delta$ and then assumed σ to be at the same order of ω_c^2 , i.e., $\sigma = O(\epsilon^2)$.

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