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A modified Mullins–Sekerka stability analysis including surface energy effects

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An excess enthalpy correction is proposed to the energy balance condition at the solid-liquid interface used in the morphological stability analysis of a planar interface. The Mullins–Sekerka stability criterion is modified to account for this excess enthalpy. Numerical calculations show that the correction is especially significant at larger growth velocities; larger positive values of excess enthalpy have a stabilizing influence on the interface.

I. INTRODUCTION

When studying the morphological instability of a solid-liquid interface during solidification, it has been found that the classical thermodynamic definition of stability is no longer applicable in determining the morphology of the growing interface; the current state of equilibrium thermodynamics has not furnished a fully acceptable extension either.¹ In order to theoretically analyze morphological stability, heuristic stability criteria have to be used. Perturbation theory has been widely used in morphological stability analyses. This involves perturbing the growing interface morphology in order to determine whether the perturbation will grow with time. The interface is said to be morphologically unstable if the perturbation is amplified as time goes by, and morphologically stable if the perturbation dies off. Excellent reviews of morphological stability analysis are provided in Kurz and Trivedi² and Coriell, McFadden, and Sekerka.³

Mullins and Sekerka^{4,5} were the first to use a perturbation approach to analyze stability in the unidirectional solidification of a binary alloy, by imposing an infinitesimal perturbation to the interface (linear perturbation analysis). Sekerka⁶ established a rigorous criterion for the stability of an initially planar interface subject to an infinitesimal perturbation, which could be any Fourier component of an arbitrary perturbation growth. The now classical Mullins–Sekerka stability criterion was deduced in terms of growth parameters and system characteristics. The analysis assumed the absence of convection effects at the interface; in addition, the thermal diffusivity of both solid and liquid phases was assumed to be far greater than the solute diffusivity. Diffusion of solute in the solid was neglected.

A number of stability analyses have since been reported, that relax some of the assumptions in the Mullins–Sekerka (MS) solution. Delves,⁷ Hurle,⁸ and Coriell, Hurle, and Sekerka⁹ introduced a stagnant-film convection model in their stability analyses. Hurle¹⁰ studied the effect

of Soret diffusion on the morphological stability of a binary alloy crystal and presented a modified MS criterion.

Lemieux and Kotliar¹¹ reexamined the boundary condition of energy conservation at the solid-liquid interface. Similar to the Gibbs–Thomson correction to the temperature of the interface, they proposed a curvature correction to the heat-balance equation at the solid-liquid interface. The influence of this correction term on the microscopic solvability condition was investigated and numerical calculations were presented for a two-dimensional, nonlocal symmetric model of solidification.

Josell¹² also reworked the energy balance equation at an interface (grain boundary or solid-liquid interface) of a pure substance. A new energy balance condition was proposed which includes an extra curvature term proportional to the excess enthalpy of the interface (identical to excess energy if no work is done at the interface during solidification).

In this article we address the interface stability during the solidification of a binary alloy with the inclusion of the excess enthalpy into the interface energy balance equation. We adopt the classical Mullins–Sekerka linear stability analysis approach by a normal mode technique to study the uniform growth of a planar interface into a thermally undercooled liquid. The results are compared with predictions from the MS analysis; a modified stability criterion is proposed to account for the additional curvature (excess enthalpy) term.

II. FORMULATION

We consider the morphological stability of an initially planar interface in a binary alloy that is moving at a constant mean velocity V in the z^* direction. The nomenclature used here is summarized in the Appendix. We assume: (i) There is no solute diffusion in the solid; once the solid is formed, its concentration will not change because of the solute buildup in the liquid; (ii) convection effects are negligible; mass transport in the liquid is only due to diffusion; (iii) the thermal boundary layer is far greater in extent than the solute boundary layer ($D_L \ll D_{th}$); (iv) the solid-

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ification domain (boat) is infinite in extent; (v) the density and specific-heat differences between solid and liquid are negligible ($\rho_S = \rho_L$; $C_S = C_L$).

The concentration and thermal fields in both the liquid and solid are controlled by diffusion of solute in the liquid and by conduction in the liquid and solid. We choose our coordinate system to be moving in the z^* direction at a constant velocity with the origin at $z^* = 0$ (mean position of the interface). The three governing equations are

$$D_L \left(\frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial z^{*2}} \right) \tilde{c} + V \frac{\partial \tilde{c}}{\partial z^*} = \frac{\partial \tilde{c}}{\partial t}, \quad (1a)$$

$$D_{th} \left(\frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial z^{*2}} \right) \tilde{T} + V \frac{\partial \tilde{T}}{\partial z^*} = \frac{\partial \tilde{T}}{\partial t}, \quad (1b)$$

$$D'_{th} \left(\frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial z^{*2}} \right) \tilde{T}' + V \frac{\partial \tilde{T}'}{\partial z^*} = \frac{\partial \tilde{T}'}{\partial t}. \quad (1c)$$

There are three far-field boundary conditions: as $z^* \rightarrow \infty$, $\tilde{c} \rightarrow \tilde{c}_\infty$, $\tilde{T} \rightarrow \tilde{T}_\infty$; and as $z^* \rightarrow -\infty$, $\tilde{T}' \rightarrow \tilde{T}'_{-\infty}$. Four boundary conditions can be identified at the interface:

$$\tilde{T} = \tilde{T}' \quad (2a)$$

$$\tilde{T} = m\tilde{c} + T_M + T_M \Gamma \kappa, \quad (2b)$$

$$k_S \frac{\partial \tilde{T}'}{\partial \tilde{n}} - k_L \frac{\partial \tilde{T}}{\partial \tilde{n}} = L\tilde{v}, \quad (2c)$$

$$\tilde{v}(k-1)\tilde{c} = D_L \frac{\partial \tilde{c}}{\partial \tilde{n}}. \quad (2d)$$

Equation (2a) implies that at the interface, the solid and liquid temperatures are equal. Equation (2b) is dictated by the coupling relation between the interface melting temperature and concentration effects. It takes into account the constitutional undercooling as well as the curvature effect (zero if the interface is planar). Equation (2c) represents the conservation of energy at the interface. The left-hand side of the equation reflects the heat flux at the interface due to conduction in the liquid and solid. The right-hand side is the heat released by the interface during freezing, which is associated with the interfacial free energy at the liquid-solid interface. However, it does not take into account the interfacial excess enthalpy effect which could be non-negligible for some systems when interface curvature is very large. Equation (2d) ensures mass conservation at the interface.

In this article we rewrite the energy balance equation at the interface to account for the interface excess enthalpy. We first introduce essential concepts related to surface energy, surface free energy and interface excess free energy, and excess enthalpy. A good discussion of energy balance between two-phase interfaces can be found in the text by Murr.¹³

A. Energy conservation at the solid-liquid interface: Excess enthalpy effects

A modified energy conservation condition at the solid-liquid interface is derived according to Lemieux and Kotliar,¹¹ Josell,¹² and Cahn.¹⁴

In order to reconsider the liquid-solid interfacial energy conservation we need to clarify the concept of excess properties. Consider the phase energy, volume, and entropy of a single component of material with number of atoms N per unit interface area, which has atomic volume Ω , atomic entropy S_0 , and atomic energy (internal energy) E_0 . The excess values of these properties at the interface can be defined as

$$E_{\text{excess}} = E_{\text{TOT}} - E_0 N, \quad V_{\text{excess}} = V_{\text{TOT}} - \Omega N, \\ S_{\text{excess}} = S_{\text{TOT}} - S_0 N. \quad (3)$$

According to Gibbs' equation for free energy, we define the interfacial excess free energy as

$$\gamma = G_{\text{TOT}} - G_0 N = E_{\text{excess}} - TS_{\text{excess}} + PV_{\text{excess}},$$

assuming T and P are uniform between the two phases at the interface.

During solidification the area of the solid-liquid interface increases as the crystal grows. The total volume of the material changes when an atom escapes from the liquid into the solid; this change consists of volume changes in the solid ($\Delta V_S = \Omega_S$) and in the liquid ($\Delta V_L = \Omega_L$), as well as an excess volume V_{excess} due to the interface curvature. Therefore, the total volume change is

$$\Delta V = \Delta V_L + \Delta V_S + V_{\text{excess}} = \Omega_S - \Omega_L + V_A \Delta_A,$$

where V_A is excess volume per unit area of the interface and Δ_A is the change in interface area, equal to $\Omega_S \kappa$, where κ is the interface curvature. By similar arguments, the total internal energy change in the material will be

$$\Delta E = \Delta E_S + \Delta E_L + E_{\text{excess}} \\ = E_S - E_L + E_A \Delta_A = E_S - E_L + E_A \Omega_S \kappa,$$

where E_A is excess energy per unit interfacial area. At the same time, there should be work done, and heat absorbed, by the system ($\Delta Q + \Delta W$), where

$$\Delta Q = \frac{\Omega_S}{\tilde{v}} \left(-k_S \frac{\partial \tilde{T}_S}{\partial \tilde{n}} + k_L \frac{\partial \tilde{T}_L}{\partial \tilde{n}} \right), \quad (4a)$$

$$\Delta W = -P \Delta V = -P(\Omega_S - \Omega_L + V_A \Omega_S \kappa). \quad (4b)$$

Applying the first law of thermodynamics at the interface, we obtain

$$E_A \Omega_S \kappa + E_S - E_L = \frac{\Omega_S}{\tilde{v}} \left(-k_S \frac{\partial \tilde{T}_S}{\partial \tilde{n}} + k_L \frac{\partial \tilde{T}_L}{\partial \tilde{n}} \right) \\ - P(\Omega_S - \Omega_L + V_A \Omega_S \kappa). \quad (5)$$

Thus, in terms of enthalpy,

$$H_A \Omega_S \kappa + (H_S - H_L) = \frac{\Omega_S}{\tilde{v}} \left(-k_S \frac{\partial \tilde{T}_S}{\partial \tilde{n}} + k_L \frac{\partial \tilde{T}_L}{\partial \tilde{n}} \right), \quad (6)$$

where

$$H_S - H_L = (E_S + P\Omega_S) - (E_L + P\Omega_L) = -L\Omega_S. \quad (7)$$

Therefore,

$$k_S \frac{\partial \tilde{T}_S}{\partial \tilde{h}} - k_L \frac{\partial \tilde{T}_L}{\partial \tilde{h}} = L\tilde{v}(1 + p\kappa), \quad (8)$$

where $p = -H_A/L$.

This is the new interface energy balance condition that is used in the stability analysis that follows.

III. SOLUTION PROCEDURE

We nondimensionalize all variables in our analysis using the following factors:¹⁵ length D_L/V ; length scale for interface amplitude $\max|\zeta^*(\tilde{x}, t)|$; temperature T_M ; concentration $c_0^*(0)$ (liquid concentration at planar interface); time D_L/V^2 . Also, we assume that $D_L/D_{th} \ll 1$ (which is true for many alloys) and eliminate terms with this factor in the governing equations and boundary conditions. This leads to

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)c + \frac{\partial c}{\partial z} = \frac{\partial c}{\partial t}, \quad (9a)$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)T = 0, \quad (9b)$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2}\right)T' = 0. \quad (9c)$$

The boundary conditions at the interface $z = \epsilon\zeta(x, t)$, are

$$T = T', \quad (10a)$$

$$T = 1 + M + U\epsilon\zeta_{xx}(1 + \epsilon^2\zeta_x^2)^{-3/2}, \quad (10b)$$

$$\begin{aligned} n \frac{\partial T'}{\partial z} - \frac{\partial T}{\partial z} - \epsilon\zeta_x \left(n \frac{\partial T'}{\partial x} - \frac{\partial T}{\partial x} \right) \\ = l(1 + \epsilon\zeta_x) [1 + pU\epsilon\zeta_{xx}(1 + \epsilon^2\zeta_x^2)^{-3/2}], \end{aligned} \quad (10c)$$

$$\frac{\partial c}{\partial z} - \epsilon\zeta_x \frac{\partial c}{\partial x} = (k-1)c(1 + \epsilon\zeta_x). \quad (10d)$$

The far-field conditions as $|z| \rightarrow \infty$ are

$$c = c_L(\infty), \quad T = T_L(\infty), \quad T' = T_S(-\infty). \quad (11)$$

In order to study the morphological stability of an initially planar interface, we adopt the perturbation approach of Mullins and Sekerka^{5,6} through the following steps: (i) Obtain an analytical steady-state solution for the unperturbed planar interface; (ii) impose an arbitrary infinitesimal perturbation (linear perturbation analysis) on the initially planar interface; (iii) obtain an approximate solution for the case of the perturbed interface, using perturbation theory; (iv) finally, examine the solution and determine whether the interface will grow with time (unstable) or vanish (stable) (we do this in Sec. IV and establish a stability criterion for specific solidification conditions).

A. Steady-state solution for planar interface

Following the above procedure, we first consider the steady-state solution for Eq. (9), and its boundary conditions, Eqs. (10) and (11), assuming the interface to be planar. Equation (9) now becomes³

$$\frac{d^2c}{dz^2} + \frac{dc}{dz} = 0, \quad (12a)$$

$$\frac{d^2T}{dz^2} = 0, \quad (12b)$$

$$\frac{d^2T'}{dz^2} = 0. \quad (12c)$$

The corresponding steady-state planar solution is

$$c(z) = c_L(z) = 1 + (k-1)(1 - e^{-z}), \quad (13a)$$

$$T(z) = T_L(z) = 1 + M + Gz, \quad (13b)$$

$$T'(z) = T_S(z) = 1 + M + G'z = 1 + M + [(G+l)/n]z. \quad (13c)$$

B. Perturbing the interface

We impose the perturbation $z = \epsilon\zeta(x, t)$ on our initially planar interface, $z = 0$. The amplitude function $\zeta(x, t)$ can be written in an infinite series in terms of ϵ (note that $\max|\zeta(x, t)| = 1$):

$$z = \epsilon\zeta(x, t) = \sum_{n=1}^{\infty} \epsilon^n \zeta_n(x, t). \quad (14)$$

Since the perturbation imposed is considered to have an infinitesimal amplitude, we neglect all higher-order terms in ϵ , and retain only the first-order term; according to Fourier theory, this kind of perturbation can be built up as a superposition of sinusoidal waves with an arbitrary frequency ω in terms of x :

$$z = \epsilon\zeta_1(x, t) = \zeta_{11} e^{a_0 t} \cos \omega x, \quad (15)$$

where ζ_{11} is a constant, and a_0 is the growth rate with time according to

$$\frac{1}{\epsilon\zeta_1} \frac{\partial(\epsilon\zeta_1)}{\partial t} = a_0. \quad (16)$$

If $a_0 > 0$, $\lim_{t \rightarrow \infty} \epsilon\zeta_1(x, t) = \infty$, and the interface is unstable, while for $a_0 < 0$, $\lim_{t \rightarrow \infty} \epsilon\zeta_1(x, t) = 0$, and the interface is stable.

C. Linear perturbation analysis

The approximate solutions for the concentration and temperature fields should have forms similar to the perturbation at the interface:

$$c(x, z, t; \epsilon) = c_L(z) + \epsilon c_{11}(z) e^{a_0 t} \cos \omega x, \quad (17a)$$

$$T(x, z, t; \epsilon) = T_L(z) + \epsilon T_{11}(z) e^{a_0 t} \cos \omega x, \quad (17b)$$

$$T'(x, z, t; \epsilon) = T'_S(z) + \epsilon T'_{11}(z) e^{a_0 t} \cos \omega x. \quad (17c)$$

We substitute the above expressions into the governing equations and the corresponding boundary conditions at the interface, and use Taylor expansions about $z=0$ to expand the boundary conditions at the interface. Retaining only the terms of the first order in ϵ and neglecting all higher-order terms, we have

$$\left(\frac{d^2}{dz^2}-\omega^2+\frac{d}{dz}-a_0\right)c_{11}(z)=0, \quad (18a)$$

$$\left(\frac{d^2}{dz^2}-\omega^2\right)T_{11}(z)=0, \quad (18b)$$

$$\left(\frac{d^2}{dz^2}-\omega^2\right)T'_{11}(z)=0. \quad (18c)$$

The boundary conditions at $z=0$ are

$$T_{11}(0)-Mc_{11}(0)+\xi_{11}[G+U\omega^2-M(k-1)]=0, \quad (19a)$$

$$T_{11}(0)-T'_{11}(0)+\xi_{11}\left(\frac{G(n-1)-l}{n}\right)=0, \quad (19b)$$

$$DT_{11}(0)-nDT'_{11}(0)+\xi_{11}l(a_0-pU\omega^2)=0, \quad (19c)$$

$$Dc_{11}(0)-(k-1)c_{11}(0)+(1-k)(k+a_0)\xi_{11}=0, \quad (19d)$$

where $D \equiv d/dz$. We consider the alloy undergoing solidification in an infinitely long boat, which implies that the perturbation at the interface will not affect the far-field concentration and temperature values. Thus,

$$z \rightarrow \infty, \quad c_{11}(z) \rightarrow 0, \quad T_{11}(z) \rightarrow 0, \quad (20a)$$

$$z \rightarrow -\infty, \quad T'_{11}(z) \rightarrow 0. \quad (20b)$$

The problem now reduces to the solution of a system of homogeneous ordinary differential equations with homogeneous boundary conditions. In order to solve this, we first assume the solution to be of the following form:

$$c_{11}(z)=A_{11} \exp(-\omega^*z), \quad (21a)$$

$$T_{11}(z)=B_{11} \exp(-\omega_1z), \quad (21b)$$

$$T'_{11}(z)=E_{11} \exp(-\omega_2z). \quad (21c)$$

We further denote $\xi_{11}=D_{11}$. Notice that these solutions automatically satisfy the boundary conditions as $|z| \rightarrow \infty$. Inserting these solutions into Eq. (18), we obtain

$$\omega^*=\frac{1}{2}+\sqrt{\frac{1}{4}+\omega^2+a_0}, \quad (22a)$$

$$\omega_1=\omega, \quad (22b)$$

$$\omega_2=-\omega. \quad (22c)$$

Using a similar procedure, the boundary conditions at $z=0$ can be shown to be

$$\begin{bmatrix} M & -1 & 0 & M(k-1)-\omega^2U-G \\ 0 & 1 & -1 & \frac{G(n-1)-l}{n} \\ 0 & 1 & n & -\frac{la_0}{\omega}+lpU\omega \\ \omega^*+k-1 & 0 & 0 & (k-1)(k+a_0) \end{bmatrix} \begin{bmatrix} A_{11} \\ B_{11} \\ E_{11} \\ D_{11} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \quad (23)$$

In order to find nontrivial roots ($A_{11}, B_{11}, E_{11}, D_{11}$ not all zero) for this system of linear homogeneous equations, the determinant of the coefficient matrix should be zero. That is,

$$a_0+k-(\omega^*+k-1)\left(1-\frac{\omega^2U}{M(k-1)}-\frac{2G}{M(k-1)(n+1)}-\frac{l[1+(a_0/\omega)-pU\omega]}{M(k-1)(n+1)}\right)=0. \quad (24)$$

Let

$$g=\frac{2G+l}{M(k-1)(n+1)}, \quad \frac{A}{k}=\frac{U}{M(k-1)}, \quad (25)$$

$$I^{-1}=\frac{l}{M(k-1)(n+1)}, \quad R=\omega^*-\frac{1}{2}.$$

Then,

$$a_0=\frac{\omega[-g-(A/k)\omega^2+pU\omega/I+(R-\frac{1}{2})/(R-\frac{1}{2}+k)]}{(1/I)+\omega/(R-\frac{1}{2}+k)}. \quad (26)$$

For $p=0$, this equation is identical to Eq. (14) of Coriell and co-workers.³ Once a_0 is determined, we can solve Eq. (23) to obtain

$$A_{11}=(1-k)\left[1-\frac{A}{k}\omega^2-g-\left(\frac{a_0}{\omega}-pU\omega\right)I^{-1}\right]D_{11}, \quad (27a)$$

$$B_{11}=\frac{l[a_0-pU\omega^2(1+M)]}{\omega(n+1)}D_{11}-\frac{G(n-1)-l}{(n+1)}D_{11}, \quad (27b)$$

$$E_{11}=\frac{l[a_0-pU\omega^2(1+M)]}{\omega(n+1)}D_{11}+\frac{G(n-1)-l}{n(n+1)}D_{11}. \quad (27c)$$

Finally, the solution to the governing equations (18) with the boundary conditions (19) becomes

$$c_{11}(z)=(1-k)\left[1-\frac{A}{k}\omega^2-g-\left(\frac{a_0}{\omega}-pU\omega\right)I^{-1}\right]D_{11}e^{-\omega^*z}, \quad (28a)$$

$$T_{11}(z)=\left(\frac{l[a_0-pU\omega^2(1+M)]}{\omega(n+1)}-\frac{G(n-1)-l}{(n+1)}\right)D_{11}e^{-\omega z}, \quad (28b)$$

$$T'_{11}(z)=\left(\frac{l[a_0-pU\omega^2(1+M)]}{\omega(n+1)}+\frac{G(n-1)-l}{n(n+1)}\right)D_{11}e^{\omega z}. \quad (28c)$$

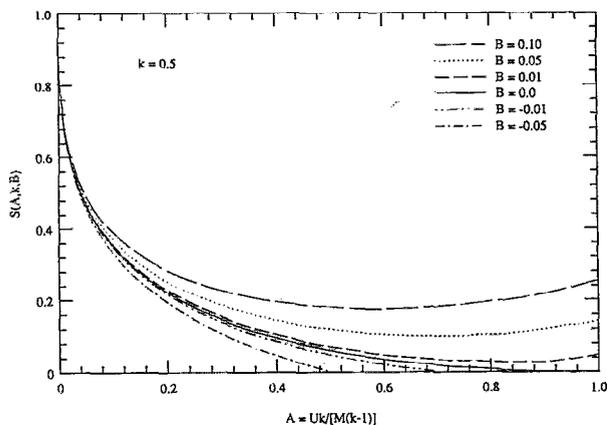


FIG. 1. Influence of the excess enthalpy factor on the stability function at constant $k=0.5$; the region above the curve corresponds to a stable planar interface.

For a linear analysis, stability depends on the sign of the real part of a_0 . We assume that the onset of instability occurs when the real part of the growth rate $\text{Re}(a_0)=0$, from the principle of exchange of stabilities. If the boundary conditions [Eq. (19)] include nonequilibrium effects at the interface, the imaginary part of a_0 could be nonzero at the onset of instability, resulting in the onset of instability being oscillatory in time.³ The denominator of Eq. (26) is positive. Thus, the sign of the numerator determines the stability of the interface. When $a_0=0$, the zeros of the numerator give the value for the critical frequency ω_c , which is the frequency where the interface first starts to break down. We set the numerator equal to zero and rewrite it in terms of $\omega^0 = \sqrt{\frac{1}{4} + \omega^2} - \frac{1}{2}$ to obtain

$$F(\omega^0) = -g - \frac{A}{k} [(\omega^0)^2 + \omega^0] + \frac{\omega^0}{\omega^0 + k} + pU \sqrt{(\omega^0)^2 + \omega^0} I^{-1} = 0. \quad (29)$$

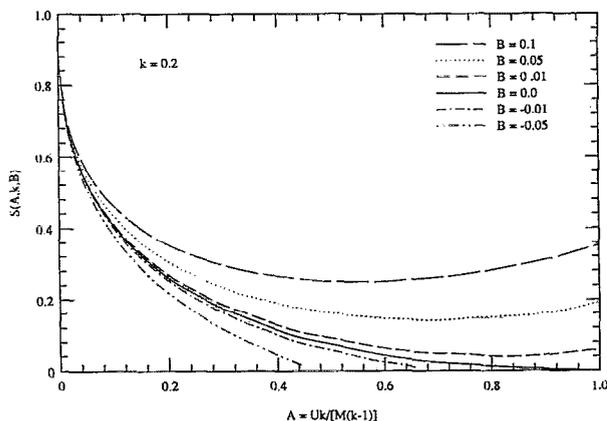


FIG. 2. Influence of the excess enthalpy factor on the stability function at constant $k=0.2$; the region above the curve corresponds to a stable planar interface.

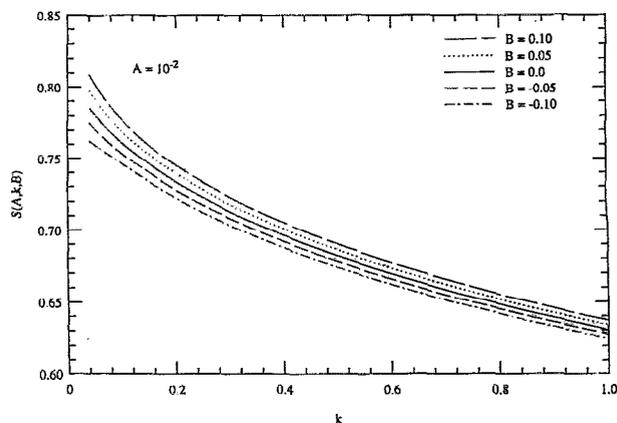


FIG. 3. Influence of the excess enthalpy factor on the variation of the stability function with segregation factor ($A=10^{-2}$); the region above the curve corresponds to a stable planar interface.

The onset of instability occurs when there is a real positive double root for $F(\omega^0)$, that is, when $F(\omega^0)=0=\partial F(\omega^0)/\partial \omega^0$. The frequency at which this occurs is $\omega=\omega_c$; then $\omega_c^0 = \sqrt{\frac{1}{4} + \omega_c^2} - \frac{1}{2}$. This will introduce a relationship between g , A , k , and B , where $B=pl/(n+1)$ is a dimensionless excess enthalpy parameter. Using the theory developed by Sekerka,⁶ we write the stability function as a function of A , k , and B :

$$g = S(A, k, B) = 1 + \frac{A}{4k} - \frac{3\sqrt{A}}{2} r - \frac{A(1-2k)}{4k} r^2 + \left(\frac{A}{k}\right) B \left(\frac{2\omega^2 + (\omega^0 + k)(2\omega^0 + 1)}{2\omega}\right), \quad (30)$$

where $r^4 = 1 + 4\omega^2$, and r is the positive root of the equation,

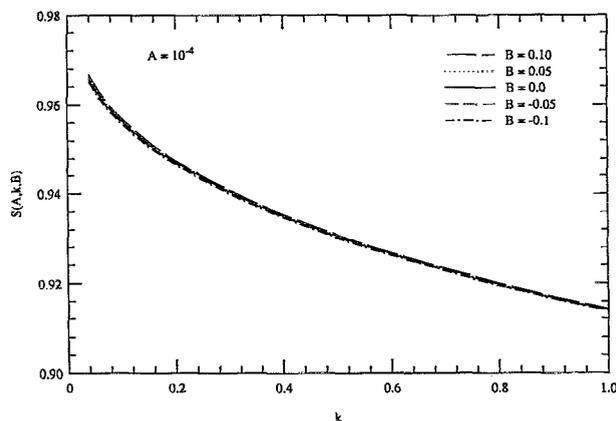


FIG. 4. Influence of the excess enthalpy factor on the variation of the stability function with segregation factor ($A=10^{-4}$); the region above the curve corresponds to a stable planar interface.

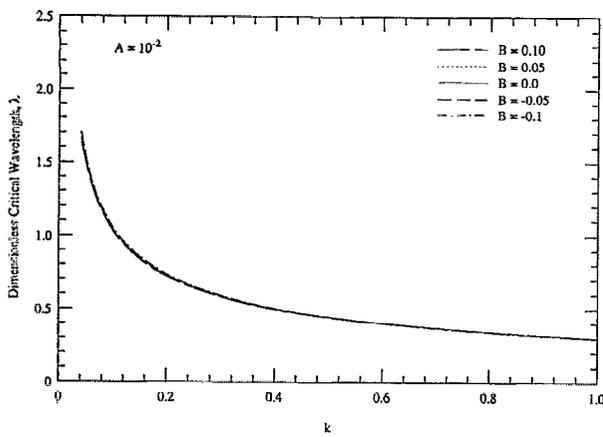


FIG. 5. Influence of the excess enthalpy factor on the critical wavelength of perturbation ($A=10^{-2}$).

$$\frac{A}{k} r^2 \left(\frac{1}{2} r^2 - \frac{1}{2} + k \right)^2 \left(1 - \frac{B}{\sqrt{r^4 - 1}} \right) - k = 0. \quad (31)$$

Notice that when $B=0$ (neglecting the excess enthalpy effect), Eq. (31) reduces to the results of the Mullins–Sekerka stability analysis.

IV. RESULTS AND DISCUSSION

A stability function $S(A, k, B)$ was introduced in the above analysis which, unlike the Mullins–Sekerka analysis, accounts for the excess enthalpy at the interface. When the imposed average temperature gradient is greater than $S(A, k, B)$, the linear analysis predicts stability at the interface. Our modified MS stability criterion is thus

$$g \gg S(A, k, B). \quad (32)$$

The interface is unstable when this inequality is reversed. The variables affecting the stability function include material transport properties, phase diagram variables, solidification velocity, and excess enthalpy. We further examine the stability function in this section.

The effect of excess enthalpy on the interface stability (with fixed k) is investigated in Figs. 1 and 2, by plotting S vs A at different values of B . The MS results are obtained when $B=0$. It is seen from the figures that as B increases, the stability function $S(A, k, B)$ also increases; this implies an increased difficulty in stabilizing the interface. Thus, a larger value of B has a stronger destabilizing effect on the interface. Since B is proportional to p , positive values of excess enthalpy H_A increase the stability of the interface, while negative H_A decreases the stability of interface, compared with the MS results wherein H_A was not considered.

The stability function is also plotted as a function of k for different values of B at fixed A (10^{-2} , 10^{-4}) in Figs. 3 and 4; the two values of A represent large and small growth velocities, respectively. For the smaller values of A , $S(A, k, B)$ does not vary significantly with B , which means that the excess enthalpy effect does not influence interface stability when A is small. As the growth velocity increases, however, the excess enthalpy correction B becomes in-

creasingly significant in determining stability. As in Figs. 1 and 2, a larger H_A has a stabilizing effect on the interface.

The critical wavelength is plotted as a function of k in Fig. 5 for different values of B at a fixed A (10^{-2}). We find that the critical wavelength, which is the perturbation wavelength at which the interface first starts to break down, is almost entirely unaffected by the excess enthalpy correction for all values of k .

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APPENDIX

We here summarize the nomenclature used in this article: A is the dimensionless parameter affecting stability, $Uk/M(k-1)$; B the dimensionless excess enthalpy parameter, $pl/(n+1)$; a_0 the growth rate of perturbation; $\tilde{c}(\tilde{x}, t, z^*)$ the concentration of solute in liquid (wt %); $c(x, t, z)$ the dimensionless concentration of solute in liquid; $c_0^*(z^*)$ the steady-state liquid concentration field for a planar interface (wt %); $c_L(z)$ the dimensionless concentration field for a planar interface; $C_L(C_S)$ the specific heat per unit volume of liquid (solid); D_L the diffusion coefficient of solute in liquid (m^2/s); $D_{th}(D'_{th})$ the thermal diffusivity of liquid (solid) (m^2/s); $G^*(G'^*)$ the temperature gradient of liquid (solid) at the interface, (dT/dz^*) (dT'/dz^*) (K/m); $G(G')$ the dimensionless temperature gradient of liquid (solid) at the interface, (dT/dz) (dT'/dz); g the weighted temperature gradient, $(2G+l)/[M(k-1)(n+1)]$; H_A the excess enthalpy (J/m^2); I^{-1} the dimensionless latent-heat parameter, $l/[M(k-1)(n+1)]$; k the equilibrium segregation factor; $k_L(k_S)$ the thermal conductivity of the liquid (solid) (W/mK); L the latent heat of fusion per unit volume (J/m^3); l the dimensionless latent heat of fusion, $D_L L/k_L T_M$; m the liquidus slope $d\tilde{T}/d\tilde{c}$ (K/wt %); M the dimensionless undercooling, $[mc_0^*(z^*=0)]/T_M$; n the thermal conductivity ratio k_S/k_L ; P the pressure (N/m^2); p the dimensionless excess enthalpy $-H_A/L$; S the dimensionless stability function; $\tilde{T}(\tilde{T}')(\tilde{x}, z^*, t)$ the liquid (solid) temperature (K); $T(T')(x, z, t)$ the dimensionless liquid (solid) temperature; T_M the melting temperature of pure substance (K); $T_L(z)[T_S(z)]$ the dimensionless steady-state temperature solution for liquid (solid) for a planar interface; t the time (s); t the dimensionless time; U the dimensionless capillarity factor, $\Gamma/(D_L/V)$; V the mean interface velocity (m/s); $\tilde{v}(\tilde{x}, t)$ the local interface velocity (m/s); $v(x, t)$ the dimensionless local interface velocity; $\tilde{x}(x)$ the coordinate (dimensionless) along the planar interface (m); $z^*(z)$ the normal (dimensionless) coordinate moving with velocity V , with origin at the mean interface position (m); ϵ the ratio of interface perturbation amplitude to characteristic length of diffusion boundary layer, $\max|\xi^*(\tilde{x}, t)|/(D_L/V)$; $\xi(x, t)$ the dimensionless perturbation amplitude factor, $\xi^*/\max|\xi^*(\tilde{x}, t)|$; $\xi^*(\tilde{x}, t)$ the in-

terface perturbation amplitude (m); γ the interfacial excess free energy (N m); κ the curvature of surface (m^{-1}); ω the dimensionless perturbation frequency; Γ the capillarity constant (m); and λ the dimensionless perturbation wavelength.

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