Shallow Cells in Directional Solidification

G. J. Merchant and S. H. Davis
Department of Engineering Sciences and Applied Mathematics, Northwestern University, Evanston, Illinois 60208
(Received 10 April 1989)

We present existing theory on two-dimensional transitions (appropriate to thin parallel-plate geometries) in such a way that one can identify easily conditions for the onset of shallow cells. By doing so we can give conditions under which succinonitrile-acetone mixtures should undergo supercritical bifurcation in *experimentally accessible ranges.* These results suggest a means for the quantitative test of the Mullins and Sekerka model and its weakly nonlinear extensions.

PACS numbers: 81.30.Fb, 47.20.Hw, 47.20.Ky, 81.10.Fq

When a binary mixture is directionally solidified, a rich variety of transitions of pattern and microstructure are revealed.[1] As the pulling speed V is increased from zero, the planar solid-liquid interface becomes unstable to spatially periodic cells, which deepen with V. As V is increased further, there is a dendritic transition, and finally at large V these structures fade away as the speed approaches the "absolute stability limit" where the planar interface regains stability.[2,3]

Presumably, the low-speed transition to cells is associated with a critical speed V_c, and corresponding wavelength λ_c, both of which are determined by linear stability theory.[2] Such a theory and its weakly nonlinear extensions via bifurcation theory[4,5] should be valid when the equilibrium cell amplitude A_e increases smoothly from zero as V passes through V_c; this is the case of *supercritical bifurcation. Subcritical bifurcation* occurs when cells appear through jump transitions at values of V somewhat below V_c.

When supercritical bifurcation occurs, the wavelength λ of the cells near V_c should be close to λ_c. However, in the subcritical case, the jump transitions create cells of wavelengths that may differ substantially from λ_c. This is one possible difficulty in the comparisons between theory and experiment. These comparisons are made more difficult due to the fact that the neutral curve of linear theory, V vs λ, is often very flat near V_c so that wavelength selection is weak;[6] when V is just above V_c, many λ correspond to growing modes of linear theory, and, hence, secondary or even tertiary bifurcations may occur near V_c.

Recently, there has been a great deal of interest in the experimental test of the Mullins and Sekerka model[2] and the associated generalizations of it to weakly nonlinear[4,5] regimes. Experimentalists[7-9] have sought to examine *quantitatively* the accuracy of theoretical models. These tests are difficult because subcritical transitions usually occur at the onset of cellular morphologies near V_c. In such cases de Cheveigné *et al.*[10] show that the λ first seen differs from λ_c by factors of 2–3.

The purpose of this Letter is to present existing theory on two-dimensional transitions (appropriate to thin parallel-plate geometries) in such a way that one can identify easily conditions for supercritical bifurcation. By doing so we can give conditions under which succinonitrile-acetone mixtures (SCN-A), the best-documented transparent binary alloy available,[11] should undergo supercritical bifurcation in *experimentally accessible ranges.* This corresponds to the onset of *shallow cells* whose amplitudes A_e increase smoothly and whose wavelengths vary smoothly from λ_c as V is increased past V_c. The inclusion of latent-heat effects in the model is crucial for these materials since the thermal-conductivity ratio, n, of solid to liquid is near unity. The location of the transition point, which separates subcritical from supercritical behavior, is very sensitive[5] to the presence of latent heat when $n \approx 1$.

The classic mathematical model of the directional solidification process of a dilute binary mixture is due to Mullins and Sekerka,[2] who assume the mixture to be isotropic and the liquid to be free of convection. They perform a linear stability analysis of the planar front and obtain an expression for the critical pulling speed V_c, above which the planar interface is unstable. By further neglecting solute diffusion in the solid and assuming that the thermal diffusivities in both phases are much larger than the solute diffusivity in the melt, they find an expression for V_c which, for low pulling speeds, reduces to a form of the constitutional undercooling condition[12] modified by latent heat L,

$$V_c \sim \frac{2kDG\kappa_L}{\kappa_L m(k-1)(1+n)c_\infty - kDL}. \tag{1}$$

In the above k is the segregation coefficient, m the local slope of the liquidus, n the ratio of thermal conductivities, c_∞ the concentration of solute at infinity, D the solute diffusion in the liquid, κ_L the thermal conductivity in the liquid, and G the temperature gradient in the liquid at the interface. Note that γ, the surface energy, is absent from this expression in the small-velocity limit considered.

Wollkind and Segel[4] consider two-dimensional bifurcation theory neglecting latent heat and obtain an equation for the time evolution of the leading-order distur-

bance amplitude A, namely,

$$dA/dt = a_0 A - a_1 A |A|^2 . \quad (2)$$

As $t \to \infty$, $A \to A_e = (a_0/a_1)^{1/2}$, the steady-state cell amplitude. Here a_0 is the linear-theory growth rate, and a_1 is the Landau coefficient; if $a_1 > 0$, the bifurcation to cells is supercritical while if $a_1 < 0$, the bifurcation is subcritical. We define the point at which $a_1 = 0$ as the *transition point* which separates the two types of bifurcation. Alexander, Wollkind, and Sekerka[5] include the effect of latent heat and in the vicinity of $V = V_c$ obtain a modified Landau coefficient given in the low-pulling-speed limit by

$$a_1 \sim \frac{1 - n + I^{-1}(n+1)}{(1+I^{-1})(1+n)\Gamma} + O\left[\left(\frac{4k}{\Gamma}\right)^{2/3}\right], \quad (3)$$

where

$$I^{-1} = \frac{kLD}{(k-1)(1+n)\kappa_L m c_\infty} \quad (4a)$$

is a latent-heat parameter,

$$\Gamma = \frac{\gamma T_m k V}{Lm(k-1)c_\infty D} \quad (4b)$$

is a scaled surface energy, and T_m is the melting point of the pure solvent.

One can see from formula (3) that if $1-n$ is far from zero, latent-heat effects are not very important. However, if $n \approx 1$, as in SCN-A, then the magnitude and, indeed, the *sign* of a_1 is very sensitive to latent-heat effects. For example, if $n = 1$ and latent heat were neglected, the leading term in Eq. (3) would be zero, yet by adding a realistic amount of latent heat to give $I^{-1} \approx 10^{-3}$, and noticing that at low pulling speeds $\Gamma \approx 10^{-6}$, the leading term now becomes $\approx 10^3$. There is thus a dramatic alteration of the location of the transition point. The transparent organics SCN and tetrabromomethane (CBr_4), favored for use in experiments,[7-9,13,14] have values of n very near unity.

In Fig. 1(a) we show for various temperature gradients G the instability conditions in the (c_∞, V) plane using the linear-theory results of Mullins and Sekerka[2] and the material property values for the SCN-A mixture given by de Cheveigné *et al.*[10] For a given G the planar interface is predicted to be stable to the left of the curve and unstable to the right. The graph includes as well, the two-dimensional bifurcation results;[5] the transition point between subcritical (dashed line) and supercritical (solid line) behavior is located easily. The neutral stability curve can be seen to approach the low-pulling-speed asymptote given by Eq. (1). Figure 1(b) is identical to Fig. 1(a) except that latent heat has been set to zero. The affects of the neglect of latent heat for SCN-A can be seen by comparing Figs. 1(a) and 1(b).

There are two observations worth making. The critical conditions (of linear theory) for the onset of cellular

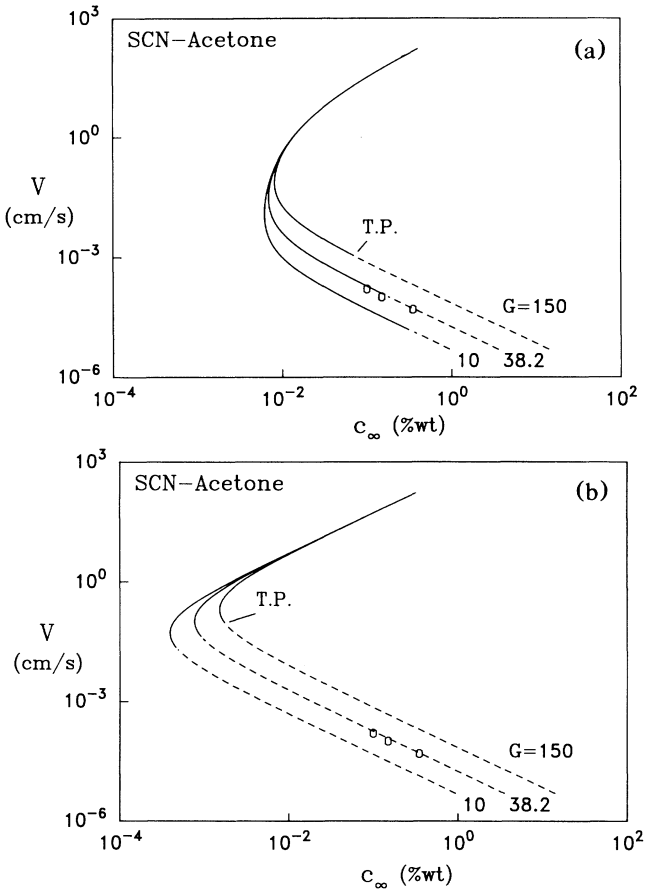

FIG. 1. (a) Neutral stability (Ref. 2) curves in the (c_∞, V) plane for succinotirole-acetone, *including* the effects of latent heat, at several temperature gradients G in units of K/cm. The region inside the curve corresponds to an unstable planar interface. The dashed lines indicate regions of subcritical bifurcation (Ref. 5), the solid lines indicate supercritical bifurcation (Ref. 5), and T.P. denotes the transition point that separates these. The open circles correspond to the experimental results of Eshelman and Trivedi (Ref. 9). (b) Neutral stability (Ref. 2) curves in the (c_∞, V) plane for succinonitrile-acetone, *neglecting* the effects of latent heat, at several temperature gradients G in units of K/cm. The region inside the curve corresponds to an unstable planar interface. The dashed lines indicate regions of subcritical bifurcation (Ref. 5), the solid lines indicate supercritical bifurcation (Ref. 5), and T.P. denotes the transition point that separate these. The open circles correspond to the experimental results of Eshelman and Trivedi (Ref. 9).

states in the low-pulling-speed region are hardly affected by the neglect of L; this fact is well known.[10] However, the position of the transition point is greatly affected and it is this property that motivates this Letter. For the SCN-A mixture the two-dimensional bifurcations would be subcritical if $L = 0$ but with the proper value of L included, supercritical bifurcations become *experimentally*

accessible. For example, for Fig. 1(a) at $G=38.2$ K/cm, supercritical bifurcation, and thus shallow cells, should appear if c_∞ lies in the wt.% range 0.01 to 0.15, in contrast to the very narrow range shown in Fig. 1(b). The range of supercritical bifurcation increases in size with G.

The only experiments on SCN-A that we have found in the literature in the range we are discussing are those of Eshelman and Trivedi.[9] Their experiment involves concentration profiles that have not settled down to the characteristic exponential as is assumed in the theory. They make a correction for the unsteady profile and their suggested results are shown in Fig. 1 as open circles. They find all three cases to be experimentally subcritical. Our calculations predict that the experiment performed at $c_\infty=0.1$ wt.% should be supercritical. The discrepancies may be attributed to the unsteady nature of the experiment or to uncertainties in the values of the measured material properties used by us.[10]

The main conclusion of this Letter is thus highlighted by Fig. 1. By including latent heat in the analysis the transition point for the transparent-organic mixture succinonitrile-acetone is shifted significantly compared to that for $L=0$. This large shift brings regions of *supercritical bifurcation* into *experimentally accessible parameter ranges,* thus allowing for a complete test of the Mullins and Sekerka model.[2] This shift in the transition point is present in SCN-A, a material with very well-characterized properties and one extremely well suited to experiments.[15] For example, if SCN with 0.1 wt.% acetone is directionally solidified with an imposed temperature gradient of 10 K/cm, one would expect to observe the slow evolution of shallow cells of wavelength λ_c at a pulling speed V_c of approximately 1 μm/s. This Letter is a call for such careful experiments on shallow cells.

The authors wish to thank Professor P. W. Voorhees for useful discussions on aspects of the work. This work was supported by a grant from the National Aeronautics and Space Administration Program on Microgravity Science and Applications.

[1]J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980).

[2]W. W. Mullins and R. F. Sekerka, J. Appl. Phys. **35**, 444 (1964).

[3]W. J. Boettinger, D. Shechtman, R. J. Schaefer, and F. S. Biancaniello, Metall. Trans. A **15**, 55 (1984).

[4]D. J. Wollkind and L. A. Segel, Philos. Trans. Roy. Soc. London **268**, 351 (1970).

[5]J. I. D. Alexander, D. J. Wollkind, and R. F. Sekerka, J. Cryst. Growth **79**, 849 (1986).

[6]M. J. Bennett and R. A. Brown, Phys. Rev. B **39**, 11705 (1988).

[7]S. de Cheveigné, C. Guthmann, and M. M. Lebrun, J. Cryst. Growth **73**, 242 (1985).

[8]S. de Cheveigné, C. Guthmann, and M. M. Lebrun, J. Phys. (Paris) **47**, 2095 (1986).

[9]M. A. Eshelman and R. Trivedi, Acta Metall. **35**, 2443 (1987).

[10]S. de Cheveigné, C. Guthmann, P. Kurowski, E. Vicente and H. Biloni, J. Cryst. Growth **92**, 616 (1988).

[11]M. A. Chopra, Ph.D. thesis, Rensselaer Polytechnic Institute, 1983 (unpublished); M. A. Chopra, M. E. Glilcksman, and N. B. Singh, Metall. Trans. A **19**, 3087 (1988).

[12]W. A. Tiller, J. W. Rutter, K. A. Jackson, and B. Chalmers, Acta Metall. **1**, 428 (1953).

[13]M. A. Eshelman, V. Seetharaman, and R. Trivedi, Acta Metall. **36**, 1165 (1988).

[14]V. Seetharaman, M. A. Eshelman, and R. Trivedi, Acta Metall. **36**, 1175 (1988).

[15]M. E. Glicksman, R. J. Schaefer, and J. D. Ayers, Metall. Trans. A **7**, 1747 (1976).