Cellular states in a boundary-layer model of directional solidification

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We use a boundary-layer model to study the cellular states in directional solidification. Away from threshold a gap develops in the center of the band of allowed states, and the boundaries of the Eckhaus instability move toward longer wavelength.

The problem of pattern formation during crystal growth has received a great deal of theoretical interest recently. In particular, the properties of cellular states formed during the directional solidification of a liquid mixture have been studied extensively. In directional solidification a thin film of a binary alloy is drawn at constant velocity v through a uniform temperature gradient parallel to the direction of motion. The temperature gradient is such that the film starts off in the molten phase and progressively cools as it moves, forming a solidification front perpendicular to the direction of motion.[1] This solidification front exhibits different morphologies as the drawing velocity is increased. We shall use the following terminology to describe these states in order of increasing velocity: planar interface, cellular states (smooth spatially periodic interfaces), cusps (singular spatially periodic interfaces), and dendrites. In the so-called one-sided model, we assume that latent heat at the interface is negligible, that the thermal conductivities are equal in the liquid and solid phases, and that the diffusion of solute in the solid is negligible.

Wollkind and Segel[2] investigated the small-amplitude steady states near the region of neutral stability and demonstrated the existence of stable periodic cellular states for very dilute alloys. Langer and Turski[3] and Langer[4] showed, in the context of the symmetric model of directional solidification, that these states could, in fact, be unstable to long-wavelength perturbations (the Eckhaus instability). Similar results for the one-sided model were derived by Dee and Mathur.[5] What is needed at this point is a probe of the existence and stability of cellular states, away from threshold, outside the region of validity of amplitude equations. This has been done, in part, in the numerical simulations of interface profiles which have been performed by McFadden and Coriell,[6] Ungar and Brown,[7] and Kerszberg.[8] However, these calculations did not provide a complete stability spectrum for the cellular states. It is the purpose of this paper to study these cellular states in the context of a boundary-layer model of directional solidification. The advantages of using local models of interface dynamics in probing the nonlinear behavior of pattern forming systems have been demonstrated recently.[9–13] Here, in the context of directional solidification, we are able to perform by Floquet theory a complete stability analysis of the cellular states far from the threshold of the planar instability. Our preliminary results indicate that sufficiently far from threshold the transition from smooth cellular states to cusp states is associated with the appearance of a gap in the center of the band of stable cellular states. In addition, a portion of the band on each side of the gap becomes amplitude unstable. It is worth pointing out that the model we are studying here can actually be used to describe experiments in a special limit. In the study of dendritic growth it has been shown that for large thermal undercooling the boundary-layer model is a very good approximation to the full diffusion problem. The boundary-layer model of directional solidification that we study here exhibits the same property at large drawing velocities and small solute concentrations. This corresponds physically to a limit where the wavelength of the cellular pattern is much larger than the solute diffusion length. Quantitatively, it can be shown analytically that, in this limit, the stability spectrum of the boundary-layer model, for a planar interface, approaches asymptotically the spectrum for the one-sided model. Detailed calculations will be presented elsewhere. These results indicate that the model presented in this paper should provide a good description of the properties of smooth cellular states in the rapid solidification regime which is, presently, of considerable technological interest.

We turn now to a description of our model; for a review of the topic, see the review article by Langer.[14] Directional solidification is characterized by three lengths. The diffusion length $l=D/v$ determines the range of the solute diffusion field, D being the coefficient of solute diffusivity in the liquid (note that our definition differs by a factor of 2 from other authors). The thermal length $l_T=\beta\Delta C^0/G$ measures the length over which the interface must be displaced to change the equilibrium solute concentration by an amount ΔC^0. Here, ΔC^0 is the concentration gap for a flat interface, β is the slope of the liquidus line, and G is the temperature gradient. The concentration gap is related to the partition coefficient k, which is the fraction of solute remaining in the solid, and the solute concentration at infinity, C^∞, by

$$\Delta C^0=C^\infty\left[\frac{1}{k}-1\right]. \tag{1}$$

Finally, there is the capillary length d_0, which is proportional to the surface tension and acts as a short-wavelength cutoff for interfacial deformations. The control parameters for the one-sided model are then

$$\nu = l_T/l \ , \tag{2a}$$

$$V = d_0/l \ . \tag{2b}$$

We measure all lengths in units of the diffusion length, and time is measured in units of l^2/D.

The dimensionless excess solute concentration in the liquid,

$$u = \frac{C(\mathbf{x},t) - C^\infty}{\Delta C^0} \ , \tag{3}$$

obeys the Gibbs-Thomson boundary condition at the interface,

$$u(\text{interface}) \equiv u_s = 1 - \frac{\xi(s)}{\nu} - V\kappa(s) \ , \tag{4}$$

where we have introduced ξ, the displacement of the interface from its planar position, κ, the curvature of the interface, and s, the arclength along the interface. It is convenient to consider the quantity

$$h = \int_0^\infty u \, d\eta \simeq u_s l_b \ , \tag{5}$$

which is the excess solute per unit length of the interface. The coordinate η measures distance along the normal to the interface; l_b is the decay length of u along the normal to the interface. The approximation (5) is the essence of the boundary-layer model; l_b is regarded as the thickness of a boundary layer of excess solute at the interface, allowing us to replace the two-dimensional diffusion equation governing $u(\mathbf{x},t)$ by a simpler phenomenological equation for h. This approximation is valid whenever the diffusion length is much smaller than the wavelength of the cellular states. For states which contain cusps, this approximation must break down. In this way, a limited form of nonlocality is retained in the model. The boundary condition expressing the conservation of solute is then

$$v_n = -\frac{(\hat{\mathbf{n}}\cdot\nabla u)_{\text{interface}}}{k+(1-k)u_s} \simeq \frac{u_s^2}{h(k+(1-k)u_s)} \ . \tag{6}$$

The dynamical equation for h is a statement of conservation of solute:

$$\left.\frac{\partial h}{\partial t}\right|_n = v_n k(1-u_s) - v_n \kappa h + \frac{\partial}{\partial s}\left[\frac{h}{u_s}\frac{\partial u_s}{\partial s}\right] \ . \tag{7}$$

The notation $\partial h/\partial t\,|_n$ denotes a derivative following the motion of a point on the interface. Thus, s becomes a dynamical variable in this formulation. The exact kinematic equations of the interface are

$$\left.\frac{\partial \kappa}{\partial t}\right|_n = -\left[\kappa^2 + \frac{\partial^2}{\partial s^2}\right] v_n \ , \tag{8a}$$

$$\frac{ds}{dt} = \int_0^s \kappa v_n \, ds' \ . \tag{8b}$$

Together with Eqs. (4)—(7), they constitute the boundary-layer model of directional solidification (BLM).

We now summarize our results. After the planar interface becomes unstable it restabilizes into a periodic cellular state for restricted values of k and v. We have derived for the BLM an amplitude equation describing the cellular states near threshold. We find that for a given value of k, cellular states will exist, at least infinitesimally close to threshold, for values of $V > V_c(k)$, where $V_c(k)$ diverges as k tends toward zero. This result is in good qualitative agreement with the previous results of Wollkind and Segel[2] and Dee and Mathur.[5] Quantitatively, $V_c(k)$ is larger for the BLM than for the one-sided model. This is not surprising since for $V = V_c(k)$, q_c, the critical wave number, is not small and we do not expect exact quantitative agreement in this region (e.g., $k = 0.1$, $q_c = 0.4$, and $V_c = 1.5$).

The results of the amplitude equation are asymptotically exact as $\Delta\nu \to 0$. To investigate the cellular states of the BLM far from threshold, we have found numerically stationary solutions of the equations of motion (7) and (8) and have investigated their stability by Floquet theory. Here, we only give a brief outline of our method. The stationary solutions of the equations of motion are described by a set of four coupled ordinary differential equations with dependent variables (θ, ξ, u, $\partial u/\partial s \equiv \lambda$) and independent variable s. All spatially periodic solutions can be identified by finding the set of values ξ^0, u^0 which generate trajectories, in the (θ,ξ,u,λ) space, which leave $\theta = 0$ at $\xi = \xi^0$, $u = u^0$, and $\lambda = 0$, and intersect $\theta = 0$ again at $\lambda = 0$. To study the stability of a stationary solution of wave number q, we write the dynamical field $\psi(x,t) \equiv [h(x,t), \xi(x,t)]$ as its stationary value $\psi_s(q,x)$ plus a small perturbation

$$\delta\psi_{qq'}(x,t) = e^{iq'x} \sum_{n=-\infty}^{\infty} \delta\psi_n e^{inqx + \omega_n(q,q')t} \ . \tag{9}$$

We then linearize the equations of motion about $\psi_s(q,x)$, expressed in terms of horizontal distance x rather than curvilinear distance s, and solve numerically the resulting eigenvalue problem.

There are two branches of the eigenvalue spectrum $\omega_n(q,q')$ with $n = 1$. The translational branch satisfies

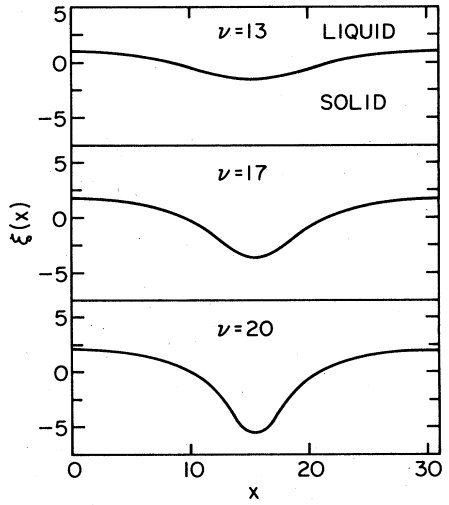

FIG. 1. Cellular interfaces on a one-to-one scale for $k = 0.1$, $V = 5$, and $\nu = 13$, 17, and 20. Lengths are measured in units of the diffusion length.

$\omega_1(q,q'=0)=0$, and the sign of its curvature at $q'=0$ gives the boundaries of the Eckhaus instability. The second branch $\omega_1(q,q')$ determines the stability of the cellular interface against amplitude perturbations.

We have chosen $k=0.1$ and $V=5$ and studied the cellular states as ν is increased above its threshold value $\nu_c=11.65$. We show in Fig. 1 a series of interface profiles which exhibit a front-back asymmetry which increases with ν.

To quantify the interface profiles we have found it convenient to calculate the root-mean-square amplitude (rms) up to the fifth harmonic:

$$\langle A(q)\rangle=\left[\frac{1}{6}\sum_{m=0}^{5}A_m^2(q)\right]^{1/2}, \tag{10a}$$

$$A_m(q)=\frac{1}{\lambda}\int_{-\lambda/2}^{\lambda/2}\cos(mqx)\xi_s(q,x)dx\ . \tag{10b}$$

We found that the higher harmonics were insignificant.

We have plotted in Fig. 2 this rms amplitude versus wave vector for three different values of ν, and we have also indicated the various regions of stability and instability.

At $\nu=13$ the results are qualitatively similar to amplitude-equation results and we find a family of cellular states, dominated by their fundamental harmonic, which covers the entire range of unstable wave vectors. Only a small portion of this family of cellular states is Eckhaus stable. We have found that the boundaries of the Eckhaus instability calculated numerically occurred at smaller wave numbers than the boundaries as calculated from the amplitude equation. This trend persists at higher values of ν.

As ν increases beyond a nonzero critical value, the second harmonic becomes more important and unstable states with $q<q_c$ terminate for sufficiently small rms amplitude. The disappearance of these states is associated with the emergence of an unstable branch of long-wavelength cellular states. This is shown in Fig. 2 for $\nu=20$ and 21. A feature of greater importance is shown in Fig. 2 for $\nu=21$. In this situation an additional gap appears in the center of the band where stationary states no longer exist. Associated with this gap opening, we find an extreme sensitivity of the cellular states towards amplitude fluctuations. We have plotted in Fig. 3(a) $\omega_1(q,q'=0)$ versus wave numbers in the center of the band for $\nu=20$. The states which correspond to the largest interface deformation are weakly stable to amplitude fluctuations at $\nu=20$. At $\nu=21$ the cellular states become unstable against amplitude fluctuations, on either side of the central band gap, as the cells become deeper. This feature is shown in Fig. 3(b), where we have plotted $\omega_1(q,q'=0)$ versus the coordinate of the bottom of the cell as one moves along the (A,B) trajectory indicated in Fig. 2.

The appearance of a central band gap and the simultaneous appearance of amplitude unstable cellular states are connected. This connection follows from straightforward considerations of bifurcation theory. Consider the two special points which define the edge of the central band gap, where $\partial\langle A(q)\rangle/\partial q=\infty$. For $\nu=21$, they occur at $q_{\min}=0.85$ and $q_{\max}=1.07$. As q approaches $q_{\min}$ from the left ($q\to q_{\min}^-$), there exist two stationary states with the same wave number, such that their difference tends toward zero. Consequently, one can construct from the difference of these two states an eigenvector of the linearized operator [obtained by linearizing the equa-

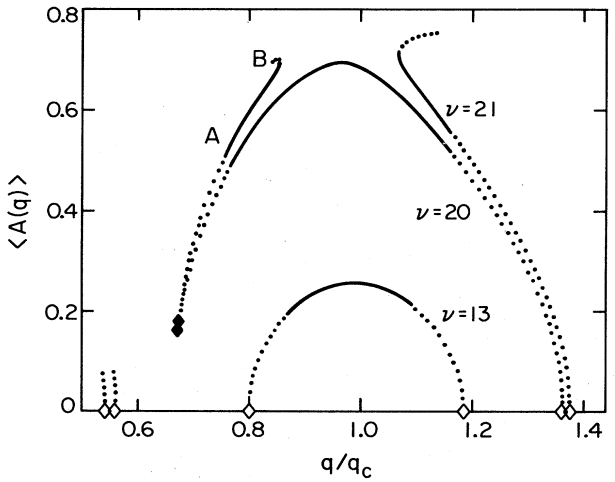

FIG. 2. rms amplitude vs q/q_c for $k=0.1$, $V=5$, and $\nu=13$, 20, and 21. q_c is the wave number at which the planar interface first becomes unstable. The bifurcation points are indicated by ◆, and the terminations of the band of cellular states at $\nu=20$ and 21 are indicated by ◇. The stable states and the unstable states are indicated by a solid line and a dotted line, respectively.

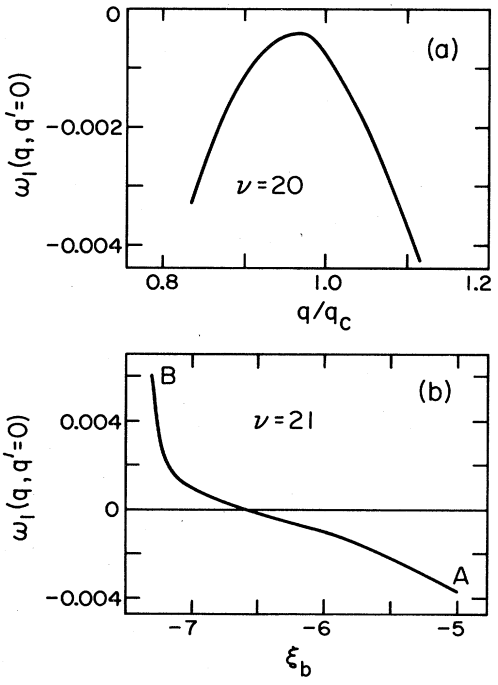

FIG. 3. (a) $\omega_1(q,q'=0)$ vs q/q_c for $\nu=20$; (b) $\omega_1(q,q'=0)$ vs the depth of the cells measured from the planar interface, along the (A,B) trajectory indicated in Fig. 2.

tions of motion about $\psi_s(q_{\min},x)$], with zero eigenvalue and which corresponds to an amplitude perturbation of $\psi_s(q_{\min},x)$. The same argument holds as $q \rightarrow q^+_{\max}$ and, consequently, the two edges of the central band gap are points of marginal stability with respect to amplitude perturbations.

It is customary to enclose by a line in the (ν,q) plane the region where stable cellular states exist (e.g., Busse balloon in hydrodynamics). We have not been able to scan all values of ν, but our results indicate that the region of stability lies within a balloon with two horns on either side of the center of the band of allowed states.

Now we address the question of how the interface can evolve from different initial conditions into a grooved state. When the planar interface is perturbed from random initial conditions, it will grow at a wave number very close to the fastest growing mode. At $\nu=21$ this wave number is inside the central gap where no stationary states exist, and the interface evolves directly into a more grooved structure. The band of stationary states on either side of the gap in Fig. 2 for $\nu=21$ is inaccessible starting from a perturbed planar interface. Nevertheless, it can be reached by preparing the interface at the desired wavelength at higher or lower velocity (higher or lower values of V and ν), and then suddenly quenching the system to $V=5$ and $\nu=21$. In this situation, the interface will either remain stable or evolve toward a more grooved structure via an amplitude instability. This evolution, however, may be very slow on the timescale of the experiment since the unstable states are only weakly unstable [$\omega_1(q,q'=0)$ is slightly greater than zero; see Fig. 3(b)].

In conclusion, we have shown within the context of a local model of directional solidification that the cellular-to-cusp transition can be associated either with the appearance of a gap in the center of the band of allowed states or an amplitude instability of a subset of these states. We have also shown that the boundaries of the Eckhaus instability differ from amplitude-equation results away from threshold and move toward longer wavelengths.

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