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Eutectic dynamics: A host of new states

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We have developed a dynamic code solving the standard phenomenological model for eutectic growth, within the quasistationary approach. This provides us with the capability to follow the dynamic evolution of the liquid-solid interface, starting from arbitrary initial conditions. Moreover, it is possible to directly simulate various experimental protocols. Besides broken-parity states we find oscillatory optical (1λ; λ=periodicity), and vacillating-breathing (2λ) modes. The latter exists not only at off-eutectic compositions, but also at eutectic compositions. This contradicts previous (approximate) analyses. We also show the possibility of having experimental access to a branch of states with indented lamellae that we discovered previously within steady-state computations and which are reachable by the dynamic code. We show the myriad of future dynamic investigations offered by this analysis and constituting major progress in the field of eutectic growth.

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When a liquid whose composition is at or close enough to its eutectic composition is directionally solidified (pulled at a constant speed in an external thermal gradient) in a thin film experiment, the solid phase often exhibits an alternating lamellar organization of the two solid phases. Eutectics constitute a unique nonequilibrium system because they present a wide technological importance (most mixtures show a eutectic point) and they offer at the same time a very rich area of *generic* nonequilibrium manifestations of both static and dynamical nature.

Since the Jackson-Hunt work [1] showing the existence of a continuous family of periodic steady-state solutions, considerable progress has been made. Recent theoretical investigations reported on a myriad of steady-state solutions going from broken-parity traveling solutions, indented steady-states (these are solutions exhibiting large pockets and belonging to branches of higher undercooling) to disorder [2–4]. These calculations are based on steady-state considerations. There are, however, many situations where nonsteady growth (e.g., lamellar width oscillations) is observed. Moreover, steady-state calculations cannot be completely conclusive about stability. Thus it appeared highly desirable to develop a time-dependent analysis. Besides the nonlocal nature of interface dynamics, this problem raises nontrivial questions related to the dynamics of the three-phase junction (triple point). This difficulty has been resolved (see below).

Let us briefly present the list of the main results obtained to date by these considerations. (i) We find, beside broken-parity states, oscillatory modes. These are of two types: (a) those which leave the basic spatial wavelength unaltered; (b) oscillations which lead to a period doubling. (ii) Contrary to the (approximate) linear analysis of Datye and Langer [5] and the random walk algorithm by Karma [6], we discover period-doubling oscillations not only for off-eutectic compositions, but also for a eutectic composition. (iii) Another important discovery is that steady-state solutions corresponding to higher branches obtained by our previous code (the indented solutions), which exhibit a large pocket, are reachable by the dynamical code upon an undercooling jump, as we conjectured previously. At the present state of our investigation, we can ascertain that these states are long transients and therefore reachable experimentally. Many other features which can be investigated by the time-dependent analysis will be briefly described, and they will be the subject of an extended communication.

The minimal model for eutectic growth can be cast into the form of an integral equation, which in the quasistationary case (valid for small Péclet numbers $P=\lambda/l$—see last section of Ref. [5]; note that in standard experiments $P\sim 10^{-2}$) reduces to

$$\int_{\Gamma_{sl}} d\Gamma'\, g(\mathbf{r},\mathbf{r}')\frac{\partial u}{\partial n'}=\int_{\Gamma_{sl}} d\Gamma'\, h(\mathbf{r},\mathbf{r}',\mathbf{n}')[u(\mathbf{r}')-u_\infty], \tag{1}$$

where the integration path Γ_{sl} runs along the liquid-solid interface and where $g(\mathbf{r},\mathbf{r}')$ is a suitable Green's function of the operator $\nabla^2+V(\partial_z+\tan\bar{\phi})\partial_x)$ (note that $\tan\bar{\phi}\partial_x$ originates from the time derivative so that for traveling states we are not using the quasi-steady-state approximation, but the full equation); $\mathbf{r},\mathbf{r}'$ are interface points; h can be calculated from g via normal derivatives [2]. $u=(c-c_e)/\Delta c$ is the normalized concentration field in the liquid (c_e: eutectic concentration; Δc: miscibility gap). Diffusion in the solid is neglected, i.e., our model is one-sided. V is the pulling velocity and $\bar{\phi}$ an appropriate average of the local tilt angles (with respect to the z axis) of the solid-solid interfaces at the triple points.

Equation (1) becomes an integral equation for the interface position $\zeta(x,t)$ by inserting the expressions for the diffusion field and its normal derivative in terms of $\zeta(x,t)$, which are the Gibbs-Thomson and the Stefan conditions, respectively. The latter is a continuity equation relating the normal velocity v_n to the concentration gradient at the interface:

$$-\frac{\partial u}{\partial n} \propto v_n, \tag{2}$$

where the exact prefactors are known (see, e.g., [2]) but of no particular interest in this brief exposition. Finally, to complete the model formulation, we have to impose mechanical equilibrium conditions at the points where the three phases meet. For given isotropic surface tensions, these conditions are simply expressed by the requirement that the contact angles $\theta_\alpha, \theta_\beta$ take on definite values: $\theta_\alpha = \vartheta_\alpha$, $\theta_\beta = \vartheta_\beta$.

To translate this into numerics, we employ a discretization procedure reducing the integral equation to a set of algebraic equations:

$$\sum_j G_{ij} q_j = \sum_j H_{ij}[u_j - u_\infty], \tag{3}$$

where the matrix elements G_{ij} and H_{ij} are integrals on discretization intervals given, e.g., in [7], while q_j and u_j are the discretized normal derivatives and field values at the interface. We employ both an intrinsic representation of the interface in the manner of McLean and Saffman [8] and Cartesian coordinates, switching back and forth between them at convenience. Note that each of the quantities appearing in Eq. (1) depends on the interface positions $\mathbf{r}_j = (x_j, \zeta_j)$. Given the interface, the u_j are known from the Gibbs-Thomson condition and G_{ij} as well as H_{ij} are calculable, being determined by geometry alone. The general strategy [9] for a dynamic code based on (1) is then very simple: invert G to obtain the normal derivatives q_j and from these calculate the normal velocities v_{nj} using (1). Step the interface forward in time, e.g., according to

$$\mathbf{r}_j^{(\mathrm{new})} = \mathbf{r}_j^{(\mathrm{old})} + \Delta t v_{nj} \mathbf{n}_j, \tag{4}$$

where Δt is a small time step and $\mathbf{n}_j$ the normal vector to the interface at $\mathbf{r}_j$.

One problem arises, however: at the triple points, the normal derivative has jump discontinuities. This has been resolved but will be discussed in an extended paper. Moreover, the three-phase junction at a triple point was allowed to rotate locally, thus enabling changes of the local tilt angle. We have found it convenient to assign a finite mobility to the triple points, in such a way that the time scale for mechanical equilibrium be faster than all other times of interest (in particular, the time step).

In addition to the normal velocities, we introduced the gauge-field property of the tangential velocities to keep the discretization points at roughly equal distances. Here, we will rather focus on the physical results obtained.

In order to check the code, we first reproduce known results obtained from steady-state considerations. In the neighborhood of the minimum undercooling the dynamics reach steady-state symmetric patterns, identical to those obtained from the steady-state code [2,3]. They are robust against various perturbations. This shows the stability of these structures versus hard-mode fluctuations. Another test consists in taking a symmetric state near the minimum undercooling and to suddenly change a parameter, e.g., the pulling velocity or the wavelength. In particular, we found that on quadrupling the pulling velocity, the pattern normally becomes unstable with respect to parity breaking, and a tilted state arises. An example is shown in Fig. 1. In fact, what we have done this way is to repeat, on the computer, the experiment performed by Faivre and Mergy [10] after our suggestion [3].

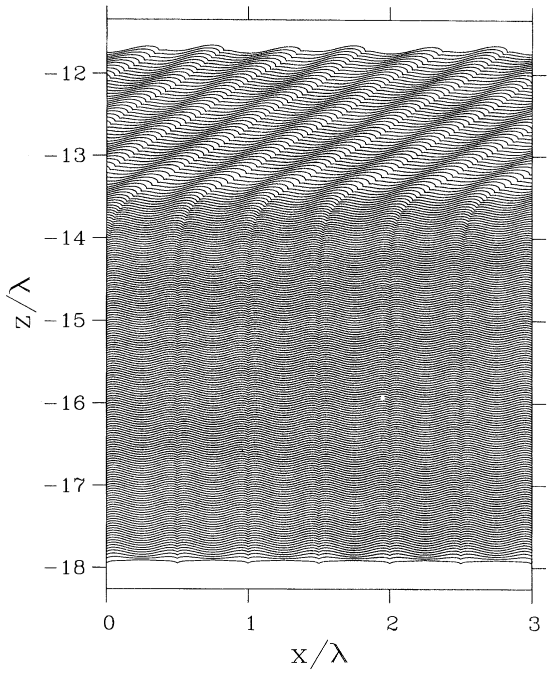

FIG. 1. Appearance of a tilted state upon a velocity jump by a factor of 4. $P = 0.14$.

We took this encouraging result as motivation to try and simulate other experiments on the computer that have *not yet* been performed in reality, although we suggested they might allow interesting observations [11].

The first outcome of our analysis is the detection of higher undercooling (excitedlike) branches corresponding to indented states. This is achieved by taking an initial ordinary stable steady state with $\lambda > \lambda_{\min}$. We then have applied a sudden jump in the *undercooling*. A striking result is that those branches (found by steady-state considerations), and which could—illegitimately—be suspected to be unreachable dynamically, are captured by the dynamical code. We could indeed observe indented states as is demonstrated by Fig. 2. In a real experiment, such a result could be produced by a simultaneous velocity jump to increase the effective wavelength. Inspection of the figure shows that, while indentations of the interface build up, they never come to rest, and the state does not really become stationary; this is presumably a consequence of its instability. Note that the real time corresponding to Fig. 2 is on the order of seconds, i.e., well within the range of experimental observability. Thus we have effectively demonstrated that, other than in hydrodynamics where instability of a state ordinarily precludes its observation, the time scales in eutectic growth are slow enough so that certain unstable states become indeed observable. This in turn allows a thorough experimental exploration of the bifurcation diagram. We believe these experiments would be really worth the effort.

Our next concern is the search for unsteady patterns. Of particular interest are oscillatory modes. In what follows, we

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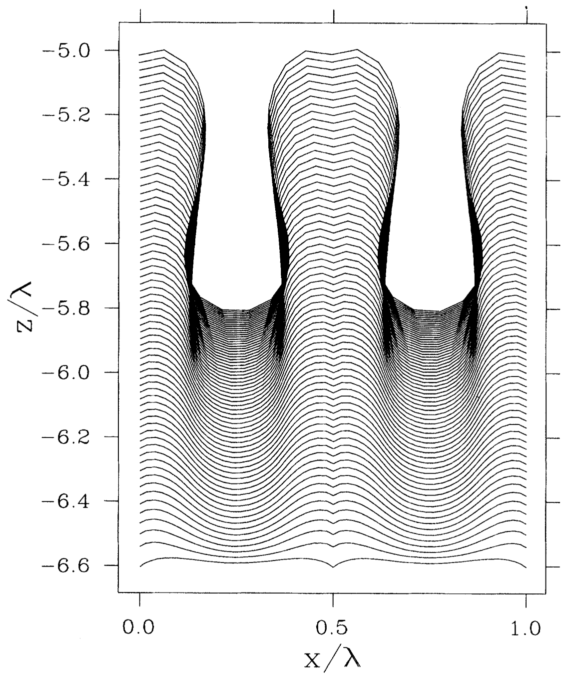

FIG. 2. An indented state. $P=0.25$.

will describe the three most conspicuous oscillatory modes that we have observed so far.

If the wavelength is taken large enough, in the example of Fig. 3 about 30% above $\lambda_{\rm min}$, the oscillation becomes self-sustained. In experiments, such an increased wavelength may be expected in the vicinity of grain boundaries, and oscillatory patterns are indeed often observed to originate there.

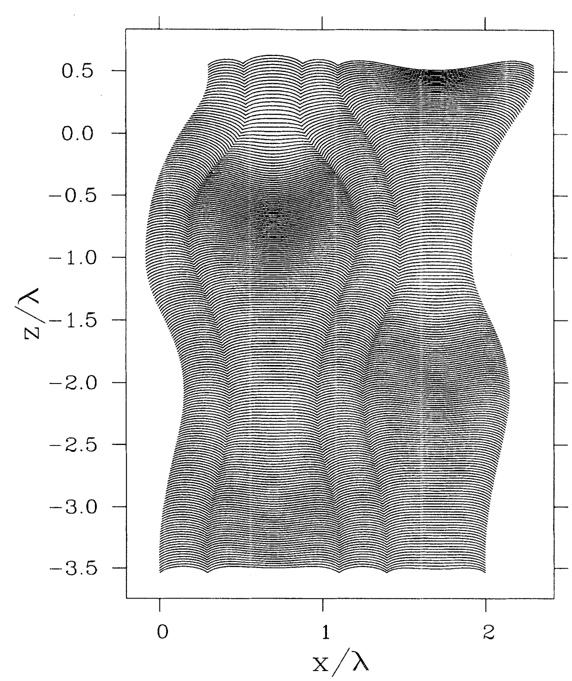

FIG. 3. The VB (2λ) mode at an off-eutectic composition. $P=0.2$.

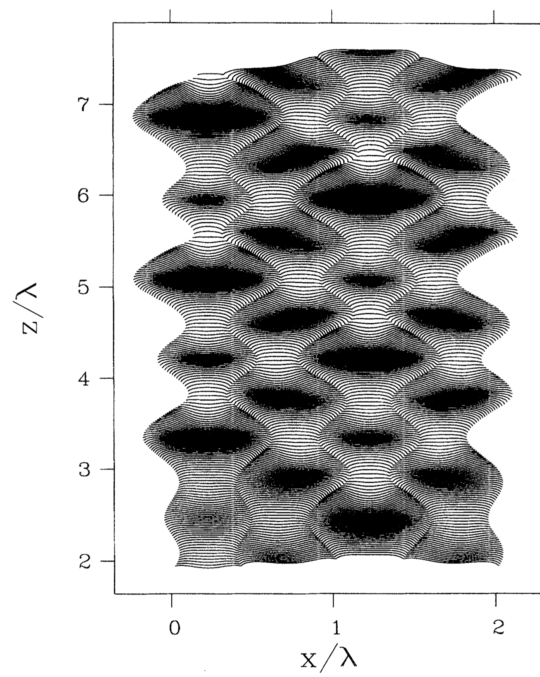

FIG. 4. A complex oscillatory (2λ) mode at the eutectic composition. $P=0.25$.

Figure 3 represents a relatively pure vacillating-breathing (VB) mode; its characteristic is that one of the two phases—the one with the thinner lamellae—is essentially "slaved" by the other. It vacillates left and right without much changing its width, whereas neighboring lamellae of the majority phase get thicker and thinner in phase opposition, representing the "breathing" aspect of the motion. Here we have an off-eutectic composition $(u_\infty=0.2)$.

What happens at the eutectic concentration where the volume fractions of both phases become equal (on average) can be seen in Fig. 4. This spatiotemporal pattern was started in a very similar way as that of Fig. 3 and initially looked like a VB mode, too. However, the lamellae of the second phase are not narrow now; they are more susceptible to developing their own dynamics. This is not an optical mode (such as the one shown in Fig. 5) but a period-doubling oscillator with a relatively complex spatiotemporal signature. Note that the average undercooling of both the VB mode and the complex oscillation is very close to that of the original steady state.

Furthermore, we found an optical mode; each lamellar width oscillates in phase opposition with that of its neighbors, while the basic spatial periodicity is preserved. This mode was observed as the final state after velocity or undercooling jumps that lead only to transient tilted or other intermediate states. Surprising is the fact that these states were also found at wavelengths between $\lambda_{\rm min}$ and $2\lambda_{\rm min}$, never at a wavelength below $\lambda_{\rm min}$, where they were reportedly seen in experiments [12]. This discrepancy is unresolved so far.

To conclude, we have found a variety of interesting dynamic states by numerical solution of the basic model equation in the quasistationary approximation. Two of the oscillatory states had been known before from experiment; these are the VB and the optical modes. The more complex oscillatory mode has yet to be discovered. To achieve this, a

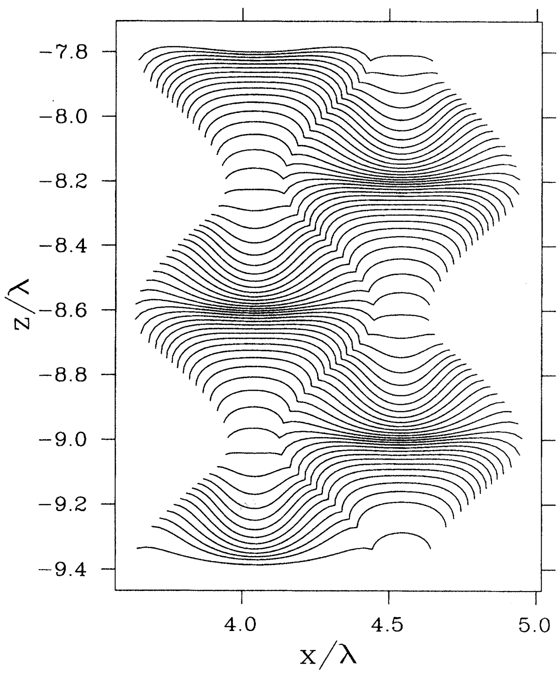

FIG. 5. Optical mode at the eutectic composition. $P=0.16$.

system should be looked at with essentially equal volume fractions of the solid phases (and as symmetric a phase diagram as possible). In any case, we have demonstrated explicitly that neither identical properties of the two phases nor being at the eutectic composition preclude period-doubling oscillations. This contrasts both with the approximate linear stability analysis of Datye and Langer [5] and a random walker algorithm by Karma [6]. The lack of these states in Datye-Langer and Karma's analyses may be symptomatic of a deficiency in their underlying assumptions.

Let us finally briefly enumerate the new prospects that the present analysis offers. (i) We can now study possible transitions to chaos as we discovered in liquid crystal systems, where we demonstrated that an interplay between VB and broken-parity modes leads to chaos [13]. (ii) For extended systems we can study the evolution of a localized tilted domain and its implication on wavelength selection. (iii) The intriguing results on irrational and disordered patterns we recently reported on from steady-state considerations naturally lead one to ask whether these states are reached dynamically [4]. This will settle important questions as to whether the system chooses a solution like a crystal, quasicrystal, or an amorphous substance. (iv) For large enough off-eutectic compositions, one usually observes coexistence of dendrites with lamellar eutectics (coupled zone). The question which deals with the nature and the precise circumstances for the appearance of a coupled-zone growth mode is fascinating. Although this list is far from being exhaustive, it is clear that the present analysis opens various new lines of inquiries with both technological and fundamental importance.

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