Parity Breaking in Eutectic Growth

K. Kassner and C. Misbah[a]
Institut für Festkörperforschung des Forschungszentrums Jülich, D-5170 Jülich, Federal Republic of Germany
(Received 26 April 1990)

Using the boundary-integral formulation we show that the fully isotropic model of eutectic growth in directional solidification supports solutions with a broken parity symmetry. These correspond to the tilted "waves" observed recently by Faivre *et al.* Our results are in good agreement with these experiments. For a fixed wavelength λ we predict a collapse to zero of the tilt angle ϕ at a critical velocity $V=V_c$ which scales as $V_c \sim \lambda^{-2}$. For not too small V we find that $\phi \simeq$const along the line $\lambda^2 V=$const. We make predictions which call for new experimental investigations.

PACS numbers: 61.50.Cj, 05.70.Fh, 68.35.Ja, 81.30.Fb

Recently, Faivre *et al.*[1] reported experiments on the evolution of the liquid-solid interface during directional solidification of the transparent CBr_4-C_2Cl_6 lamellar eutectic alloy. They observed, under some conditions, the birth of small domains of tilted lamellae moving transversely along the growth front. The tilt angle ϕ is a well-defined finite quantity ($25° \pm 3°$). Such "solitary modes" were previously discovered by Simon, Bechhofer, and Libchaber[2] during the growth of a nematic liquid crystal.

An essential step was made by Coullet, Goldstein, and Gunaratne[3] who suggested that these traveling domains are localized inclusions of a new antisymmetric state. In their phenomenological picture such a state should emerge from a secondary bifurcation of the symmetric basic state. This would mean, in particular, that there should exist in the extended system stationary periodic solutions with a broken parity symmetry.

More recently, Brattkus *et al.*[4] made an analytical attempt to investigate tilted solutions in eutectic growth. They showed that if tilted solutions are to exist, they can occur in general only for isolated values of the tilt angle. However, their analysis indicates that, for large thermal gradients where their approximation is expected to be valid, the only solution that exists is the symmetric one. We will return to this point later.

In this Letter we present a powerful numerical method, based on the boundary-integral formulation, to investigate front morphologies during directional solidification of eutectics. We find that generically a discrete set of tilted solutions coexist with untilted ones within a wide range of the growth velocity. In particular, we have not found, so far, a lower velocity threshold for the existence of tilted solutions. Here we focus attention on the experimental setup of Faivre *et al.*[1] We obtain good agreement with the experimental findings and make predictions which can be tested experimentally.

The well-known model can be found in Refs. 5 and 6. We do not make use here of the quasistationary approximation. It is by now standard to convert the basic equations into a closed integral equation for the interface profile $\zeta(x,t)$, describing one-dimensional deformations. Tilted solutions move in the laboratory frame at a constant speed transversely to the growth front. In the rest frame of the pattern the integral equation reads

$$\int d\Gamma\, g(\mathbf{r},\mathbf{r}')\frac{\partial w(\mathbf{r})}{\partial n}=\int d\Gamma\, w(\mathbf{r})\left[\frac{\partial}{\partial n}g(\mathbf{r},\mathbf{r}')-\frac{1}{2l}(n_z+n_x\tan\phi)g(\mathbf{r},\mathbf{r}')-\frac{\delta(\mathbf{r}-\mathbf{r}')}{2}\right],$$

where the integration is performed along the $(L\text{-}\alpha)+(L\text{-}\beta)$ boundaries. g is the Green's function, which corresponds to the stationary propagator in the frame where tilted states are steady, and $w(\mathbf{r})$ is defined as $w(\mathbf{r})=[c_L(\mathbf{r})-c_\infty]/\Delta c$, where c_L is the concentration of the β component in the liquid, c_∞ its value at infinity, and $\Delta c=c_{e,\beta}-c_{e,\alpha}$ the miscibility gap. Since both $w(\mathbf{r})$ and $\partial w/\partial n$ are known on the boundary from the Gibbs-Thomson and continuity equations, the integral equation actually constitutes a functional equation for the boundary contour. The diffusion and thermal lengths are denoted by l and l_T^μ, respectively, for the μ phase, $\mu=\alpha,\beta$. ϕ is the tilt angle which may be positive or negative. It goes without saying that if a tilted state with an angle ϕ solves the full set of equations, so does a state with angle $-\phi$. The integral equation should be supplemented by the mechanical equilibrium conditions at the triple points. As an example we give the mechanical condition at (x_1,ζ_1): $\vartheta_\beta+\phi=\frac{3}{2}\vartheta_1-\frac{1}{2}\vartheta_2$ (see Fig. 1), where the (β phase) pinning angle ϑ_β is obtained by equating the interface tension components parallel and perpendicular to the solid-solid interface. This condition follows from a second-order accurate extrapolation. We seek periodic solutions. As in Ref. 7, we have constructed a stationary code that solves the integral equation subject to mechanical boundary conditions. The method of discretization is due to Saito, Goldbeck-Wood, and Müller-Krumbhaar.[8]

The discretization elements are indicated in Fig. 1. As in previous work,[7] we find it convenient to use, instead of Cartesian coordinates, an intrinsic representation of the

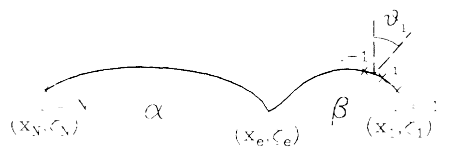

FIG. 1. Schematic illustration of the discretization procedure and the variables ϑ_i and x_e,ζ_e as used in the numerical code.

curve by the angle ϑ between the growth axis and the normal to the interface, as a function of the arclength. The interface position is then fixed by the coordinates (x_e,ζ_e) (Fig. 1) of one eutectic point. Choosing $N = N_\alpha + N_\beta$ discretization points (which delimit equal arclength intervals) we have $N_\alpha - 1 + N_\beta - 1 = N - 2$ angle variables plus the coordinates x_e,ζ_e; i.e., the number of unknowns is N. We impose the integral equation everywhere except at the end points where the two phases meet. There we require mechanical equilibrium of the surface tensions instead. The curvatures are evaluated at these points by means of a third-order accurate extrapolation.

By simple counting of equations we see that there are $N-4$ equations from the integral equation, two equilibrium conditions at (x_e,ζ_e), and one each at (x_1,ζ_1) and (x_N,ζ_N), totaling up to N equations.

Hitherto, we have made no assumption whatsoever on the value of the tilt angle, so that the N equations can *a priori* be solved for each value of ϕ. We are seeking periodic solutions, but for an arbitrary value of the tilt angle the interface will exhibit a discontinuity at the end points of the interval $[0,\lambda]$. We must therefore require $\zeta_1(\phi) - \zeta_N(\phi) = 0$, which constitutes a "quantization condition" for the tilt angle and leads to the selection of a discrete set of possible ϕ values. As previously,[7] our discretized nonlinear algebraic equations are solved by a Newton-Raphson method.

We have found that the "microscopic" model of eutectic growth admits solutions with isolated values of the tilt angle as expected from the aforementioned quantization conditions. We have made a systematic investigation of these solutions for the experimental setup of Faivre *et al.*[1] A typical set of parameters used in these calculations is given in Table I. We should mention that the diffusion coefficient is not accurately known for this system. This means that we can convert our diffusion length into a physical velocity only within an order of magnitude. In what follows we will assume that $D \simeq 10^{-5}\ \mathrm{cm^2 s^{-1}}$. Also the pinning angles are not well known. We find that although a variation of these angles by 10% to 30% does not alter our conclusions, it may induce quantitative changes by almost the same percentage. In what follows l_T^β ($\simeq l_T^\alpha$) is taken as the unit of length. The diffusion length is typically on the order of the thermal length. We should signal that, for $V<12$, the actual λ is smaller than the $\lambda_{\min}$ of Jackson and Hunt[5] for axisymmetric growth (more details will given elsewhere). Figure 2 shows a tilted solution for $V=2.8$ which corresponds to a tilt angle of 22°. For the same parameters we have found another tilted solution with a smaller angle (about 10°). So far we have seen only two branches for the present set of parameters. These solutions coexist with the completely symmetric one. Figure

TABLE I. The values of the parameters used in this calculation.

$d^{\alpha,\beta}$	$5\times10^{-2}\ \mu$m
λ	30 μm
G	60 K cm^{-1}
Δc	15 wt%
c_∞	1 wt%
m_α^L, m_β^L	-1.48,2.16 K/wt%
m_α^S, m_β^S	-1.48,2.07 K/wt%
$c_e^\beta - c_e^\alpha$	11.13 wt%
$\vartheta_\alpha,\vartheta_\beta$	35°,60°

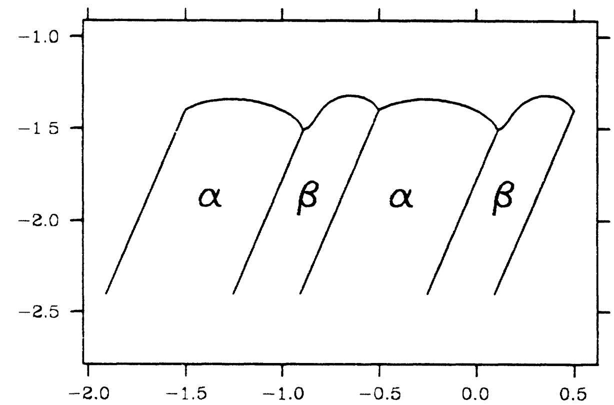

FIG. 2. Tilted solution for $V=2.8$. Other parameters are given in Table I. Lengths are reduced by λ.

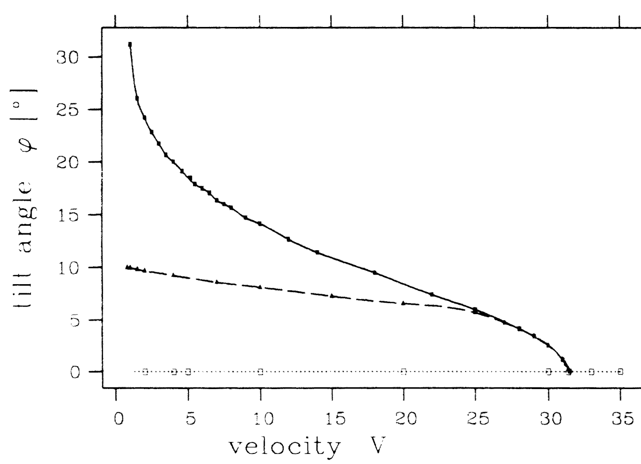

FIG. 3. Tilt angles vs pulling velocity. Three branches can be clearly distinguished.

3 shows the evolution of the tilt angle for both branches, hereafter referred to as the ϕ_1 and the ϕ_2 branch for the smaller and the bigger angles, respectively, as a function of the growth velocity. It is obvious, in view of the above-mentioned uncertainties on the material parameters, that we can only approximately narrow the experimental range down to lie between, say, $V=1$ and $V=5$ in Fig. 3. Three remarks are in order. (i) Tilted solutions exist for very small velocities. So far we have found no indications for a lower velocity threshold. (ii) At higher velocities both branches (ϕ_1 and ϕ_2) collapse to zero roughly as $(V_c-V)^{1/2}$ near a critical velocity V_c. We have investigated the dependence of V_c on λ. We find that V_c scales as $V_c \sim \lambda^{-2}$. This means, if such scaling is always valid, that for a given velocity there should exist a maximum wavelength $\lambda_{\max}$ above which tilted solutions cease to exist. For $V=2.8$, $\lambda_{\max} \simeq 9$ μm. This is much larger than the wavelengths which are seen in experiments. Close to V_c the α phase exhibits a slightly negative curvature, as a precursor of a tip-splitting mode. In reality, if V continues to increase, the splitting becomes more and more pronounced, thus favoring creation of an extra lamella. We should mention that close to V_c it becomes very difficult to discriminate between the two branches. Since it is not yet clear whether such a regime can be achieved in standard experiments, we have not felt it worthwhile here to put this region under close scrutiny. (iii) In a variational picture—with the proviso that this notion has a meaning[9]—the associated potential would possess three extrema at $\phi=0,\phi_1,\phi_2$ (not counting negative ϕ's). Since the untilted solutions are stable (at least in the experimental range), it is appealing to speculate that the ϕ_1 branch is unstable[10] while the ϕ_2 one is stable. This would imply that there exists a metastability domain where the untilted solution coexists with the tilted one with the larger angle ϕ_2. In the experiment of Faivre *et al.*,[1] the creation of a tilted structure requires a finite fluctuation achieved by a sudden jump of the velocity. The tilted solutions then appear as localized domains, which eventually spread out to cover a finite region. It is clear that these observations support our ideas.

Our findings indicate that the tilted solution, once created at a certain velocity V_1 when the presumed[1] "metastability barrier" is overcome, should survive within a rather large velocity domain below V_1 when V is again decreased. Recent experiments[11] seem to favor this idea: The tilted wave survives down to $V \simeq 0.8V_1$. We hope that systematic experimental investigations can be carried out in the near future.

For a fixed wavelength, ϕ decreases as V increases before it collapses at V_c. However, it is known experimentally[1,12] that the selected wavelength scales approximately as $\lambda \sim V^{-1/2}$. The same scaling holds at the minimum undercooling point.[5,6] We have studied here the evolution of ϕ for different values of λ and V. From our investigation, we conclude that, for not too small V ($V>4$), ϕ is a function of the combination $\lambda^2 V$ only, $\phi(\lambda,V) = \phi(\lambda^2 V)$, meaning that the tilt angle remains constant along the line $\lambda^2 V=$ const. This result agrees with the experiment of Faivre *et al.*[1] where no noticeable variation of the tilt angle has been detected. It would be interesting to see whether a similar scaling holds when the thermal gradient is allowed to vary.[10] Our scaling result may suggest that the full eutectic problem can be formulated as a nonlinear eigenvalue problem, as in the case of dendrites,[13] for example, where the relevant parameter would be $\lambda^2 V$.

A seemingly common feature[1,2] related to the parity breaking is that the asymmetric state has a larger wavelength λ_a than the corresponding symmetric one λ_s. In eutectic growth it is found experimentally that $\lambda_a/\lambda_s \simeq 2$. We discovered here that the parity breaking is associated with a recession of the growth front. It is interesting to see whether a wavelength increase of the tilted interface may result from a compromise of the coexistence at the same average undercooling Δ of both states.[14] For a few values of V, lying in the experimental range, we have found that at the same Δ, $\lambda_a/\lambda_s \simeq 1.6$. Note that the experimental precision of the ratio λ_a/λ_s is only about 80%. Since the Jackson-Hunt theory[5] predicts that the curve Δ as a function of λ takes on a minimum, there should exist, according to them, a second λ_s ($>\lambda_{\min}$) which provides the same Δ. We have found that the interface (mainly the α phase) exhibits a tip-splitting mode far before (40%) the sought Δ is reached. In reality, this will favor the creation of extra lamellae which leads to a wavelength reduction.

In view of the above results it is tempting to conjecture that the comparison of the average undercooling of the symmetric and asymmetric fronts constitutes a physical criterion for the wavelength selection of tilted waves. We will report on systematic investigations along this line in the near future.

Before we conclude, we would like to briefly comment on the large-thermal-gradient results of Brattkus *et al.*[4] Their analysis predicts that no tilted solution exists for $l_T/l \ll 1$. How small this parameter should be has remained unclear. In the present work, we find that tilted solutions exist for values of this parameter down to at least 10^{-2}, with a tilt angle of about 10°. Their treatment in terms of "boundary layers" is legitimate only if the meniscus contribution is localized near the pinning points. We find that this is not accurate for the β phase except for extremely large thermal gradients, in which case only the untilted solution survives,[15] in agreement with their result. We think that a semianalytical analysis using the basic idea of Brattkus *et al.*[4] would constitute a promising tool for further theoretical analysis.

In summary, we have presented a powerful numerical method which allows us to investigate the existence of solutions with a broken parity symmetry. Such solutions drift at a well-defined speed in the laboratory frame. We have found that these solutions do not require crystalline anisotropy, but are intrinsic to the fully isotropic model. Our results agree well with the experimental findings. We have emphasized the importance of measuring accurately some parameters, in particular, the mass diffusion coefficient, the ignorance of which constitutes a major handicap for more precise comparisons with experiments.

We have predicted a collapse, at fixed wavelength, of the discrete set of tilted solutions at a critical velocity V_c. Such velocities are not easily reachable in experiments. One reason is that the Mullins-Sekerka[16] instability intervenes, before V_c is attained, to deform the interface on a larger scale. A simple argument based on the evaluation of the diffusion layer that forms ahead of the front indicates that such an instability should take place at very high V. It is likely that "parasitic" impurities lead prematurely to the Mullins-Sekerka[16] instability. We believe that a highly purified eutectic should give access to the collapse regime by quenching the sample at high speeds. We expect there, in particular, a widening of the wall between the symmetric and asymmetric states, as a precursor to the collapse.

Our analysis predicts that tilted states exist also for small values of V. For the moment little is known experimentally on the extent of the hysteresis. It is likely that this extent is practically infinite.

It is a pleasure to acknowledge stimulating discussions and collaboration with H. Müller-Krumbhaar and A. Ghazali, One of us (C.M.) is grateful to B. Caroli, C. Caroli, and B. Roulett for fruitful discussions and for providing us with their results prior to publication, and to S. de Cheveigné, G. Faivre, C. Guthmann, P. Kurowski, and J. Mergy for enlightening him on many experimental aspects and for informing us about preliminary results. C.M. expresses his gratitude for hospitality and financial support to the Forschungszentrum at Jülich.

[a]Permanent address: Groupe de Physique des Solides, Université Paris VII, associé au CNRS, Place Jussieu, 75005 Paris, France.

[1]G. Faivre, S. de Cheveigné, C. Guthmann, and P. Kurowski, Europhys. Lett. **9**, 779 (1989).

[2]A. J. Simon, J. Bechhofer, and A. Libchaber, Phys. Rev. Lett. **61**, 2574 (1988).

[3]P. Coullet, R. E. Goldstein, and G. H. Gunaratne, Phys. Rev. Lett. **63**, 1954 (1989).

[4]K. Brattkus, B. Caroli, C. Caroli, and B. Roulet, Groupe de Physique des Solides Report No. GPS 90-008 (to be published).

[5]K. A. Jackson and J. D. Hunt, Trans. Metall. Soc. AIME **236**, 1129 (1966).

[6]V. Datye and J. S. Langer, Phys. Rev. B **24**, 4155 (1981).

[7]K. Brattkus and C. Misbah, Phys. Rev. Lett. **64**, 1935 (1990).

[8]Y. Saito, G. Goldbeck-Wood, and H. Müller-Krumbhaar, Phys. Rev. A **38**, 2148 (1988).

[9]Close to a critical point this is the case to lowest order in a Ginzburg-Landau expansion.

[10]This is currently under investigation.

[11]G. Faivre (private communication).

[12]V. Seetharaman and R. Trivedi, Metall. Trans. **19A**, 2955 (1988).

[13]J. S. Langer, in *Chance and Matter,* Proceedings of the Les Houches Summer School, Session XIVI, edited by J. Souletie, J. Vannimenus, and R. Stora (Elsevier, Amsterdam, 1987).

[14]This has been suggested to us by G. Faivre.

[15]More details will be given elsewhere.

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