Array of doublets: A branch of cellular solutions in directional solidification

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In directional solidification of alloys, the interface pattern assumes a cellular structure, with a periodic array of cells, when the velocity is increased beyond the threshold of planar interface instability. A detailed experimental study in the succinonitrile-acetone system has revealed a branch of cellular structure in which the interface pattern consists of a periodic array of coupled cells or doublets. This doublet interface evolves with two characteristic length scales at the advancing front: a small intraspacing between the cells in a doublet, whose selection is sharp, and a larger interspacing corresponding to the distance between cells in adjoining doublets, whose selection is weak. The dynamics of the time-dependent evolution of a doublet interface is investigated by statistical analysis of tip spacings, by using a Fourier transform of the interface shape and through the study of the variation of shape parameters with time. These dynamical studies have confirmed the selection of doublet interface as a stable solution of the cellular pattern formation. A range of stable regime for an array with doublets is determined and the key factor that controls the formation of regular cells or doublets in an array is discussed. When doublets are unstable, time dependency may follow due to a source mechanism at grain boundaries, which induces strong spatiotemporal chaos.

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I. INTRODUCTION

During the directional solidification of an alloy, the solid-liquid interface assumes a variety of patterns that are governed by the conditions of growth. For constant composition and temperature gradient, the interface pattern changes from a planar to a cellular to a dendritic interface as the velocity is increased [1,2]. The nonplanar interface morphology for a dendritic growth has now been properly characterized for the dendrite region near the tip, and the tip region of dendrite has been shown to be very close to a paraboloid of revolution in the three-dimensional model. The dendrite tip radius is uniquely selected by the anisotropy in the interfacial energy [3] and the dendrite tip radius is found not to be influenced by the presence of neighboring dendrites in an array [4]. In contrast, the steady-state shape, the nature of the tip radius selection, and the interaction between neighboring cells have not been properly characterized for a cellular array.

Theoretical models of cellular growth are based on an isolated cell that is confined in a channel of width, or diameter, that is equal to the primary spacing. The shape of the cell that gives a steady-state growth has been modeled approximately [3,5–10]. The resulting microstructure is assumed to consist of an array of stable cells in which each cell shape can vary only slightly depending upon the local spacing of the cell. Detailed experimental studies in thin cells have been carried out to examine the process of wavelength selection for a cellular array, and the dynamical process of wavelength selection has been investigated by using the Fourier transform of the pattern [11]. These studies have shown that the distribution of cells in an array, after a long time, has a finite width which indicates a weak selection for the cell spacing.

In contrast to the theoretical models and earlier experimental results, experimental evidence will be presented in this paper that shows the presence of another branch of cellular solutions in which a cellular pattern consists of an array of pairwise groupings of cells which we shall refer to as the doublets. The morphology of cells in a doublet is significantly different from that of an individual cell and a strong coupling exists between the two cells in a doublet. In addition to the formation of doublets, higher-order multiplets (e.g., triplets) have also been observed in the experimental study.

The formation and stability of an array with doublets has been investigated in this study. The dynamical pro-

cesses leading to the reorganization of an unstable planar interface into a periodic array of individual cells or doublets have been analyzed from the instant a planar interface becomes unstable to the development of the final array. In order to observe the process of the selection of doublets over individual cells, experimental studies have been carried out in a transparent model, the succinonitrile-acetone system. In this case, the changes in interface shapes with time can be photographed and the process of wavelength selection can be examined through the fast Fourier transform (FFT) of these patterns. Furthermore, the mechanisms of wavelength selection can also be examined *in situ* so that the mechanism that is predominant in the selection of doublets can be properly identified. In addition, experimental studies on cellular pattern formation have been carried out over a range of velocity so as to characterize the range of velocity over which the doublets are stable. The characteristic features of an interface with an array of doublets, the range of control parameter over which the doublet interface is stable, and the mechanisms in the nonlinear range that lead to the formation of doublets will be discussed in this paper. Besides, it will be shown that, when doublets are not stable, grain boundaries may behave as a source of spatiotemporal chaos.

II. EXPERIMENTAL PROCEDURE

Directional solidification studies have been carried out in succinonitrile-acetone mixtures. The as-received succinonitrile (SCN) was first distilled at 75–90 °C, and the distilled SCN was collected into 6-mm-i.d., 120-cm-long Pyrex tubes under vacuum and sealed with a torch for zone refining. The distilled SCN was then zone refined with 50–70 passes.

The Hele-Shaw cell which contained the sample was made from two pieces of transparent glass slides of dimensions: $2.55\times7.65\times0.2$ cm^3. These two slides were first separated by a predetermined gap size (≈150 μm) by the use of spacers, and two sides were sealed with a low melting point glass powder which was placed at the edges and melted in a furnace at 500 °C. The other two sides were left open in order to fill the cell with the succinonitrile-acetone mixture. A calibrated thermocouple was placed into the cell from one side before the glass slides were sealed.

Since SCN is susceptible to the moisture in the air, the filling of the cell was carried out in an inert atmosphere. For this purpose, a special loading chamber was built, as described by Han and Trivedi [12], which contained a movable copper block whose temperature can be controlled by the flow of hot or cold water through the block. The tube of zone-refined SCN was first placed in the chamber and the Hele-Shaw cell was fixed onto the copper block with a rubber band and the copper block was heated. Initially some zone-refined SCN was melted from the tube under vacuum, and the necessary amount of acetone added into the chamber by using a syringe. Next, the copper block which contained the sample cell was lowered into the mixture to fill the cell by the capillarity action. Once filled, the cell was rapidly cooled by cooling the copper block. Because of the high vapor pressure of acetone, some acetone is lost during the filling procedure so that the accurate concentration of acetone was determined after filling the cell by the ring heater method [13].

The solidification equipment used in this study was similar in principle to that described by Hunt, Jackson, and Brown [14], with several modifications to improve the drive mechanism to obtain a constant velocity and to obtain a better control of the temperature gradient [4].

The directional solidification study was carried out by translating the Hele-Shaw cell at a constant velocity through a temperature gradient stage. The drive mechanism consisted of the cell carriage on the ballscrew and a stepping motor which was controlled by a Commodore 64 computer. The velocity of a desired run was checked by measuring the actual displacement of the sample with linear variable differential transformer as a function of time. The temperature gradient stage consisted of hot and cold chambers which were separated by a small, predetermined, distance to obtain a linear temperature variation in the sample. The hot and cold stages were made of large copper blocks to maintain constant temperatures, and the chambers were maintained at desired temperatures by circulating a constant temperature fluid. The temperature of the hot and the cold baths were maintained constant within ±0.1 °C for the temperature range used in this study. The temperature variation inside the sample was monitored by the calibrated thermocouple that was placed inside the Hele-Shaw cell prior to filling. A thin glass cover slip was placed over the sample across the hot and cold chambers in order to reduce the air convection from the top.

Directional solidification experiments were carried out for succinonitrile-acetone samples with acetone compositions of 0.15 and 0.5 wt. %. The temperatures of the hot and cold baths were kept constant throughout a given set of experiments. For constant temperatures of the baths, small variations in temperature gradients were found with the change in velocity, and these variations in temperature gradient were also measured experimentally. The control parameter of the experiment was mainly the velocity whose value was changed in different experimental runs. Thus, cellular pattern formation was examined as a function of velocity, or as a function of a dimensionless parameter, $\nu=V\Delta T_0/GD$, in which V is the velocity, ΔT_0 the equilibrium freezing range of the alloy, G the temperature gradient at the interface, and D the diffusion coefficient of solute in the liquid. Since $\nu=1$ is the critical velocity for the planar interface instability, experiments were carried out for $\nu>1$.

Before each run, the entire cell was first held in the hot chamber for several hours to ensure thermal and solutal equilibria. The cell was then translated into the thermal gradient field to solidify a small volume fraction of the liquid. The cell was kept stationary for the time necessary to develop a planar interface. Actual directional solidification runs were then made by imposing a desired velocity.

A microscope placed above the sample was used to observe the interface morphologies as a function of time. A

camera on the microscope with automatic exposure and time was also used to record any variation on the interface as a function of time and all quantitative measurements were made from the negatives and their enlargements.

III. DOUBLET INTERFACE

A. Morphological features

During the directional solidification of alloys, two distinctly different forms of cellular arrays were observed under different growth conditions when the solidification process was carried out for a sufficiently long time for the interface to achieve the velocity that was equal to the externally imposed velocity. Figures 1(a) and 1(b) show these two forms of cellular arrays. The cellular array in Fig. 1(a) is the array that is commonly observed and reported in the literature, and it consists of individual cells with some characteristic average spacing and with some range of nearest-neighbor spacings. In contrast, the cellular array shown in Fig. 1(b) has a distinctly different mode of pattern selection, and the entire cellular interface consists of an array of doublets.

The doublet interface has several distinct characteristics. (1) The shape of an individual cell in a doublet is highly asymmetric. (2) The tip spacing at the macroscopic front between the cells in a given doublet, which we shall call *intraspacing* and denote λ_{intra}, is significantly smaller than that between cells in adjoining doublets, λ_{inter}, which we shall call *interspacing*. (3) Concomitantly, the depth of the grooves within the doublets, from here on the *intradepth* d_{intra}, is significantly smaller than the depth of the grooves between neighboring doublets, namely the *interdepth* d_{inter}. (4) The primary spacing in the solidified material, which is given by the distance λ_g between the grooves further behind the interface, does not vary very much over the entire array which includes the grooves inside the doublets and those between the doublets.

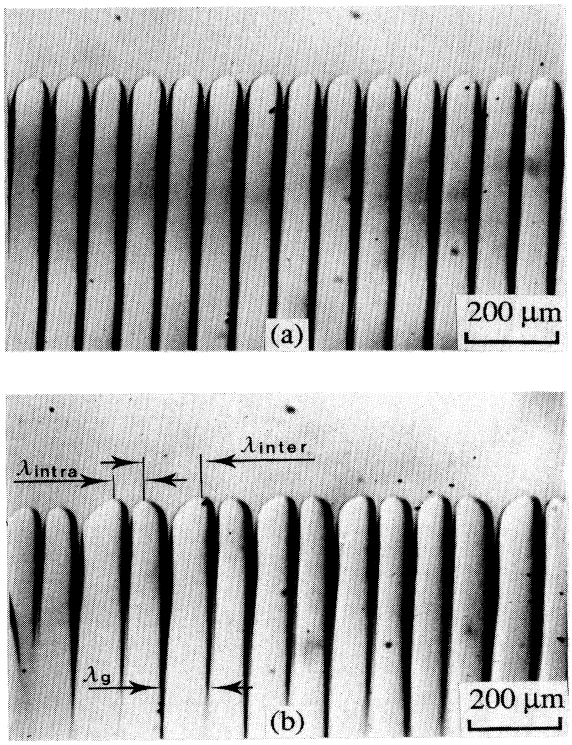

FIG. 1. (a) Regular cellular array. Succinonitrile–0.15 wt. % acetone. $V=5$ μm/s. $G=62$ °C/cm. $\nu=2.4$. (b) Doublet interface. Succinonitrile–0.15 wt. % acetone. $V=4$ μm/s. $G=65$ °C/cm. $\nu=1.8$.

B. Dynamics of planar interface instability

In order to examine the dynamics of the formation and selection of doublets in a cellular interface, *in situ* examination of the interface was carried out as a function of time after the planar interface became unstable. Figure 2 shows the shape of the interface shortly after the interface became unstable. For a sample which contains grain boundaries, the initial perturbations form at grain boundaries (GB), and then they amplify to form two nascent cells on the two sides of the boundary. The basic shape of these perturbations is asymmetric since the growth of each perturbation is favored away from the boundary since the solute field interaction between these perturbations slows down the growth of the interface segment that is towards the grain-boundary groove. While these grain-boundary perturbations amplify with time, morphological instability propagates laterally along the interface in the form of small wave packets.

When the grain boundaries are separated by a large distance, other morphological instabilities progressively initiate within the grain with a certain periodicity. These instabilities nucleate as small depressions whose sides then amplify to give a couple of asymmetric cells that resembles the pattern formed at the grain boundaries. Again, from these new pairs of cells there is a lateral propagation of morphological instability along the interface. The precise location at which the instabilities within a grain form is found to be influenced by the presence of grain boundaries, although one would expect a regular periodicity of these perturbations if the crystal were perfect. Initially, the amplitude of the perturbations at the grain boundary is the largest, and the amplitudes of the coupled cells within the grain decreases with distance away from the grain boundary. This relative amplification rate gives rise to a long-wavelength periodicity of the interface, as seen in Fig. 2.

C. Dynamics of doublet formation

The initial perturbation of the interface and the long-range periodicity of the pattern are found in all experiments whether they give rise to an array of cells or doublets. Thus the selection of a doublet interface occurs through the nonlinear dynamics of pattern selection process. Figure 3 shows the time evolution of a cellular pattern in a regime where an array of doublets is stable. In the nonlinear growth regime, the selection of a larger wavelength occurs through the elimination of certain cells, Fig. 3(a). As a given cell is eliminated [shown as tip elimination (TE) in the figure], the cells that neighbored it

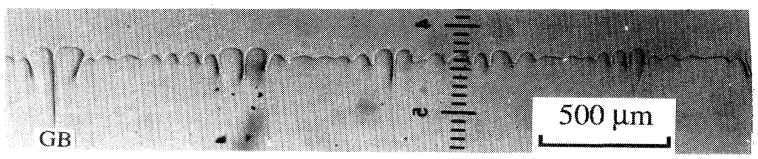

FIG. 2. Progressive initiation of coupled cells within a large grain and lateral propagation of morphological instability in the form of wave packets. Succinonitrile–0.5 wt. % acetone. $V=1\ \mu$m/s. $G=30$ °C/cm. $\nu=3.2$.

bend and envelope the space initially occupied by the eliminated cell, thereby giving rise to a doublet appearance. The doublet structure formed initially through the elimination of a cell is not always stable and it can be eliminated during the further nonlinear growth of the array. The stability of the doublet interface occurs through the latter part of the nonlinear pattern formation. For a stable interface of an array of doublets, the doublet formation occurs along the entire interface, and the doublets become more similar with time, Figs. 3(b) and 3(c). The spacing between the cells within the doublets and the spacing between the neighboring doublets progressively become more uniform. In fact, it is this selection phase that is critical in the formation of an array of doublets, which shows that doublet formation is an integral part of the pattern selection process, that then governs the dynamics of the interface.

In order to study the nonlinear dynamics of the formation of an array with doublets, the time evolution of the spacing was studied. The time evolution of two characteristic spacings was considered: the tip spacing λ_t between the cells in an array and the groove spacing λ_g, which in a transient should be measured along the macroscopic interface. The histograms of these spacings for patterns formed after 2400, 5000, and 8400 s are shown in Fig. 4. The tip spacing initially shows a somewhat symmetric distribution which becomes skewed with time. Finally, the histogram for the tip spacing can be visualized as consisting of two peaks: a sharp peak at small spacing value, which corresponds to the intraspacing, and a diffuse peak, which corresponds to the interspacing. The diffuse peak is very similar to the spacing distribution one obtains for an array of single cells. The new feature for the doublet formation is the presence of a sharp peak at a small spacing value which indicates a specific selection of an array of doublets. In contrast to the tip spacing, the distribution curves for the groove spacing show a quite different behavior. The histogram for groove spacing is initially broad but, as it is usually observed [15], it narrows with time with a single peak. Thus, the groove spacing moves towards a uniform spacing, eventually equivalent to the classical primary spacing, whereas the

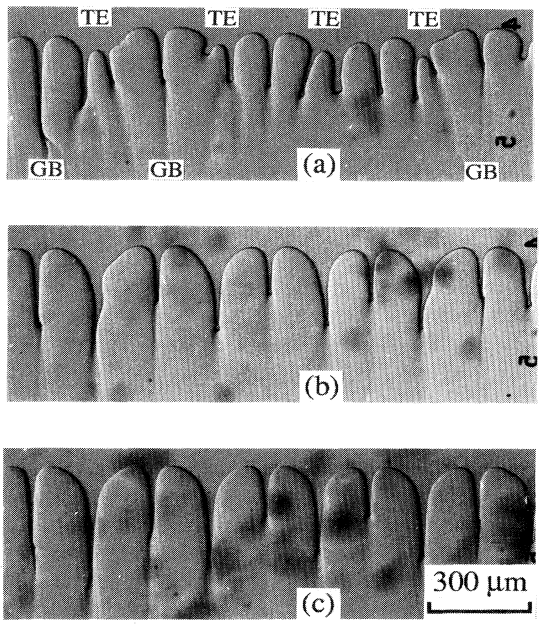

FIG. 3. Formation of a stable array of cellular doublets. Patterns formed after (a) 2400 s, (b) 5000 s, and (c) 8400 s of growth. Succinonitrile–0.5 wt. % acetone. $V=0.75\ \mu$m/s. $G=43$ °C/cm. $\nu=1.7$.

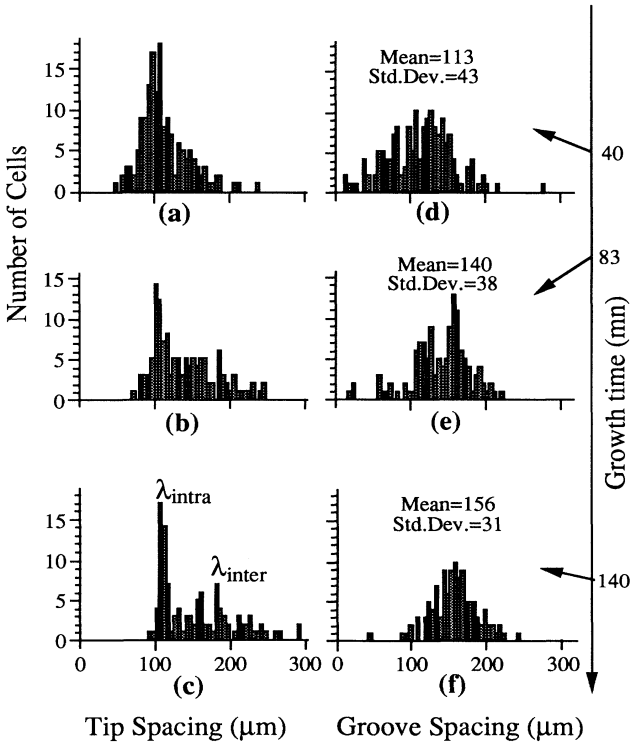

FIG. 4. Time evolution of (a)–(c) the histogram of the tip spacing and (d)–(f) the histogram of the groove spacing. Succinonitrile–0.5 wt. % acetone. $V=0.75\ \mu$m/s. $G=43$ °C/cm. $\nu=1.7$.

tip spacing splits into two characteristic spacings. The time evolution of the groove depth is very similar to that of the tip spacing, with again the building of two peaks in the histogram: a sharp peak at small value for the depth of the grooves inside the doublets d_{intra} and a diffuse peak for the depth of the grooves between the doublets d_{inter}. Such a behavior is a distinct characteristic of the interface selecting a new solution of a cellular interface which consists of an array of doublets.

It follows from a plot in the (velocity, wave number) diagram (Fig. 5) that the four characteristic spacings for a steady doublet interface all fall within the unstable band given by the linear analysis of morphological instability, far below the most linearly unstable mode (dashed line).

The building of two characteristic tip spacings has been clearly established from both direct observation and analysis of the evolution of the spacing distribution. The detailed dynamics of doublet formation can also be visualized by examining the Fourier transform of the interface pattern as a function of time, as shown in Fig. 6 for the arrays partially displayed in Fig. 3. Initially, one observes a finite number of peaks indicating the selection of specific wavelengths. A peak at low wave number ($\omega \approx 0.01$ μm^{-1}) shows the characteristic long-wavelength instability of the pattern that develops initially, and this peak disappears with time as this wavelength becomes unstable. This long-wavelength modulation of the cellular front is clearly seen in Fig. 3(a). Such long-wavelength perturbations are also evident in previous studies of cellular microstructures carried out in the succinonitrile-acetone [16] and pivalic acid–ethanol [17] systems, which up to now have yet never attracted specific attention. With increasing time, the selection of two specific wave numbers is evident. The peak centered at $\omega \approx 0.02$ μm^{-1} ($\lambda = 314$ μm) is for the periodicity of the doublet spacing, whereas the peak centered at $\omega \approx 0.04$ μm^{-1} ($\lambda = 157$ μm) is for the periodicity that corresponds to the groove spacing, namely λ_g. Note that

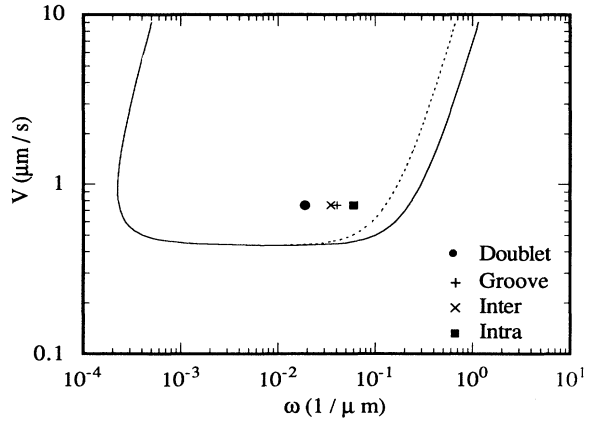

FIG. 5. Plot of the four characteristic spacings of the steady doublet interface of Fig. 3(c) in the (velocity, wave number) diagram. The full line corresponds to the limit of morphological instability given by the linear analysis and the dashed line to the most linearly unstable mode. These lines are computed for succinonitrile–0.5 wt. % acetone alloys solidified at $G = 43$ °C/cm.

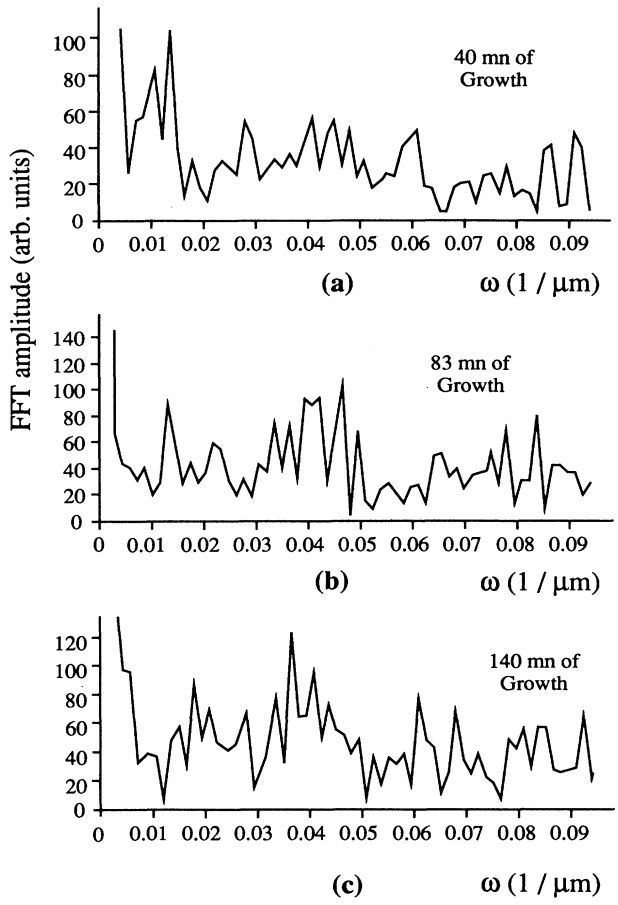

FIG. 6. Analysis of the building of the characteristic wave numbers of a doublet interface by using the fast Fourier transforms of the interface shapes shown in Fig. 3.

the peaks at larger wave numbers (e.g., at $\omega \approx 0.06$ μm^{-1} or $\lambda = 105$ μm) correspond to the higher harmonics since the shape of the cell in a doublet is not symmetric. By varying the total number of points and/or shifting the starting point, no significant change is induced in the spectra, from which it follows that the sensitivity of the FFT's with respect to the discrete sampling of the shape

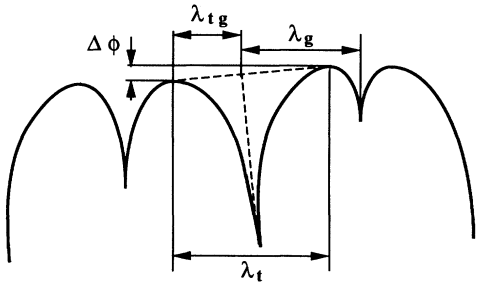

FIG. 7. Schematic representation of a pair of doublets, which defines the tip to groove distance λ_{tg} and the shift between adjacent cell tips $\Delta\phi$, which is associated with the long-wavelength component in the shape of the solidification front and the dynamical selection of the microstructure.

of the doublet interface is rather weak.

The Fourier transform analysis shows the selection of different wavelengths during the nonlinear pattern propagation. The final shapes of the cells in a doublet are also characteristics of the nonlinear selection process, and the selection of these shapes can be examined by analyzing the changes in the cell shape with time. Figure 7 is a schematic diagram of a pair of doublets, and it defines specific distances which alter with time. These distances are the nearest-neighbor groove spacing λ_g, the distance between the tips of adjacent cells λ_t and the tip to groove distance λ_{tg}. During the transient time, due to the long-wavelength component in the shape of the solidification front and the dynamical selection of the microstructure, the tips of the adjacent cells are not at the same temperature so that their relative positions can be characterized by the shift $\Delta\phi$. Figure 8 shows the relationship between $\Delta\phi$ and λ_{tg}/λ_t. A simple linear relationship is obtained for these variables. Initially, the points show a wider spread in the values of $\Delta\phi$ or λ_{tg}/λ_t. However, with time, the spread becomes narrower, and finally all points cluster abut the value $\Delta\phi=0$, i.e., to $\lambda_{tg}/\lambda_t=0.5$, which means that the symmetry with respect to the grooves is preserved in a doublet array.

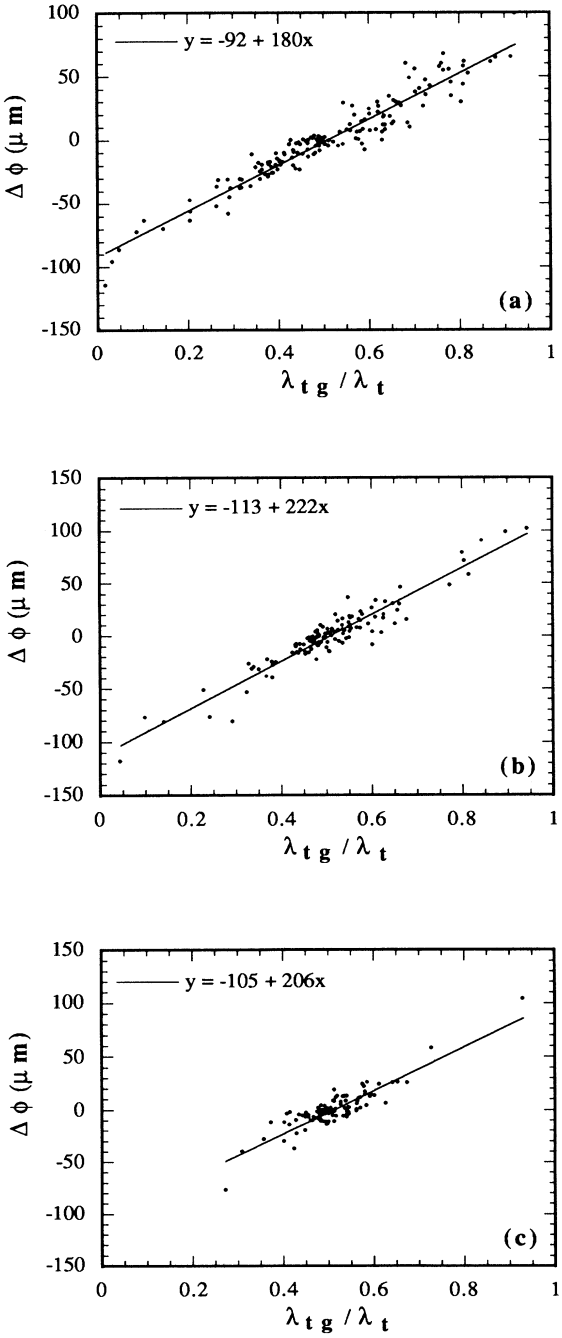

FIG. 8. Relationship between $\Delta\phi$ and λ_{tg}/λ_t for the interface patterns shown in Fig. 3, i.e., after (a) 2400 s, (b) 5000 s, and (c) 8400 s of growth.

D. Accommodation of grain size

The dynamics of cellular pattern formation are influenced by the presence of grain boundaries since instability always initiates at these boundaries. Initial perturbations at the grain boundary give rise to coupled cells which may form nuclei for the doublet formation. When the stable array consists of doublets, the initially coupled cells adjust to conform to the pattern formed in the entire array. Experimental studies were therefore carried out to examine how the patterns formed at the grain boundaries influence the doublet formation in an entire array.

Three specific observations were made regarding the dynamics of doublet formation in the presence of grain boundaries. The first observation (Fig. 9) shows the normal situation for doublets, with the grain boundary attached to the groove inside the doublet, together with a grain boundary attached to the groove between adjoining doublets (shown by an arrow in the figure), which indicates the ability of the initial coupled cells formed at the boundary to reverse their shape in order to conform to the stable solution of the array. Next, we examined the effect of the width of the grain on the development of a doublet array. In principle, this width would influence the doublet formation since a regular array of doublets may not be accommodated within this finite interface segment. In order to obtain a stable array, a lateral motion

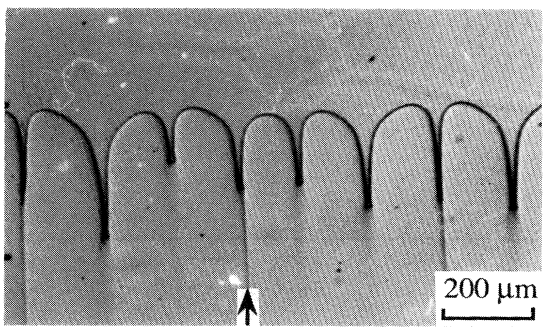

FIG. 9. Normal accommodation of doublets at grain boundaries, together with a grain boundary attached to a groove in between doublets (arrow), which indicates the local reversal of initial coupled cells. Succinonitrile–0.5 wt. % acetone. $V=0.75\ \mu$m/s. $G=43\,^{\circ}$C/cm. $\nu=1.7$.

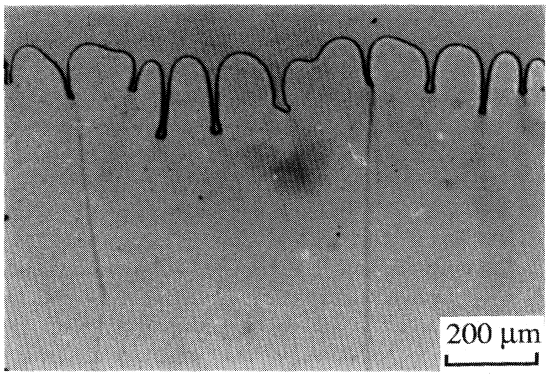

FIG. 10. Lateral motion of grain boundaries when the width of the grain is not compatible with the fitting of a stable doublet array. Succinonitrile–0.5 wt. % acetone. $V=0.75$ μm/s. $G=43°$ C/cm. $\nu=1.7$.

of grain boundary was observed so as to increase or decrease the width of the grain, as shown in Fig. 10. Alternately, or concomitantly, to grain-boundary shift, additional cells can be incorporated within some doublets, thus forming multiplets, or individual cells can occasionally develop between doublets, which will be considered as defects. Obviously, the smaller the mobility of the grain boundaries the more favored the latter mechanism.

E. Range of stability

The dynamical studies discussed above show that the dynamics of the selection process leads to the stable array of doublets with characteristic spacings and characteristic shapes of cells. These studies confirm that the interface pattern with an array of doublets is a stable solution of the nonlinear pattern formation and it represents a new branch in the stability of the periodic array of cells.

The range of stability of doublet formation is found to be very narrow, and the velocity regime for a stable array of doublets is shown schematically in Fig. 11. The formation of doublets occurs in the regime where finite-amplitude cells transform to deep cells. Indeed, considering that cells have finite depth when the groove depth d is less than or of the order of the spacing λ, Fig. 3(c) gives

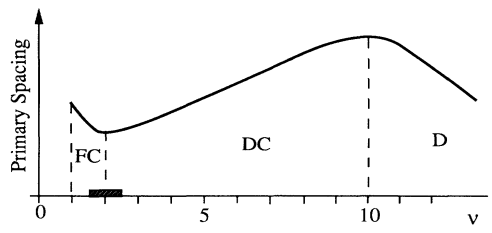

FIG. 11. Experimental range of stability of a doublet interface (dashed segment). The full line gives the schematic variation of the primary spacing with the level of morphological instability ν, as observed for succinonitrile-acetone alloys. FC, finite amplitude cells; DC, deep cells; D, dendrites.

an example of cellular doublets with finite depth [$d=O(\lambda)$] and Fig. 1(b) corresponds to deep cellular doublets ($d>\lambda$). Experimental observations show that whether an interface with a doublet formation is stable or not depends upon the competition between the formation of doublets and the tip-splitting phenomenon. An array of doublets form when the tip splitting is suppressed. Below the lower limit of doublet formation, the finite-amplitude cells, which are in the limit $d<\lambda$, are characterized by a very low curvature of the tip region so that the cell front is nearly planar which can readily become unstable with respect to tip splitting. Similarly, the tip-splitting phenomenon becomes easier when the velocity is above the stable regime of an array of doublet formation, as discussed in the next section.

Besides, there is a further argument against the extension of the doublet range far above the threshold of morphological instability of the planar solid-liquid interface. Indeed, recent analysis of regular cells in the succinonitrile-acetone system [9] have shown that cells form in an attempt to suppress the source of instability, i.e., constitutional supercooling, by protruding into the bulk liquid. Then, due to this protrusion mechanism, a cell in a doublet, which can be seen as formed by the association of a large and deep half-cell with a narrow and shallow one, would rapidly become less affected by the difference between the intra- and intergroove depths as the amplitude of the interface microstructure is increased. Consequently, the concomitant asymmetry of the cap, characterized by the difference between the intra- and intertip spacings, would also tend to vanish, which means that doublets would become no longer distinguishable from classical deep cells.

Families of asymmetric cells, referred to as "tusks," have been computed by Bennett and Brown [18]. The tusk shapes result from the interaction between several wavelengths, which causes a bifurcation from cells with reflective symmetry. Although the computation is restricted to small collections of shallow cells near the onset of morphological instability, these tusk shapes might be related to the branch of cellular doublets. Indeed, (i) the shape of "inside tusks" [see Fig. 6(d) in Ref. [18]] is qualitatively very similar to the shape of cellular doublets and (ii) tusks and doublets are found to be stable above a critical level of morphological instability.

IV. DISCUSSION

This section is divided into two parts: first, the unstable case with the failure of doublet growth that results in spatiotemporal chaos, and then the dynamics of multiplets and "defects" in an array with doublets will be examined.

A. Spatiotemporal chaos

In order to emphasize the selection process of a doublet interface, it is appropriate to examine the case in which the initial doublet formation is unstable and the nonlinear dynamics give rise to an array of cells. Figure 12 shows the time evolution of a cellular pattern for growth condition of $\nu=3.2$, i.e., above the upper limit of

doublet formation. Note that in this case the initial perturbations also occur with pairwise instabilities at the grain boundaries and at certain locations within the grain, Fig. 12(a). In the nonlinear growth regime, the wavelength selection process begins with cell elimination, Fig. 12(b). This cell elimination causes the neighboring cells to enlarge. However, instead of forming a doublet, these coupled cells undergo the tip-splitting process, which causes the local spacing to decrease slightly. This perturbation in local spacing then is propagated laterally along the array, which provokes cell elimination in the pattern, Fig. 12(c). These nonlinear processes causing tip elimination and tip splitting continue giving rise to a spatiotemporal chaos in the pattern, Fig. 12(d), for the time examined in this experiment.

Experimental observations in the unstable range show that one of the principal sources of chaos is locked on the grain boundaries. Indeed, the tip splitting of the coupled cells attached to a grain boundary occurs at the time these cells become too large. This tip splitting is a discontinuous phenomenon that, in a first approximation, results in the halving of the local spacing. This halving enables the cells on both sides of the grain boundary to attempt to recommence there the building of a doublet which, as before, is doomed to failure. As such a sequence is self-sustained in places where there are grain boundaries, it follows that no steady state can actually be achieved within the entire grains, only if because the tip-splitting phases at grain boundaries repeatedly inject new cells, whose accommodation then induces the rearrangement of the rest of the cellular arrays in the adjacent grains. Moreover, the observations in the unstable case led us to the conclusion that time dependence in cellular growth, which promotes spatiotemporal chaos in the pattern and thus increases array disorder, may be a major cause of the large dispersion of the primary spacing that is usually noticed for deep cells, e.g., in the CBr_4-Br_2 system [19].

B. Multiplets and defects

In Sec. III D, the formation of multiplets, by the incorporation of additional cells within some doublets, and the occasional inclusion of single cells between doublets were recognized as a mean to adapt the interface microstructure to the finite grain size. Figure 13, in which the inter-

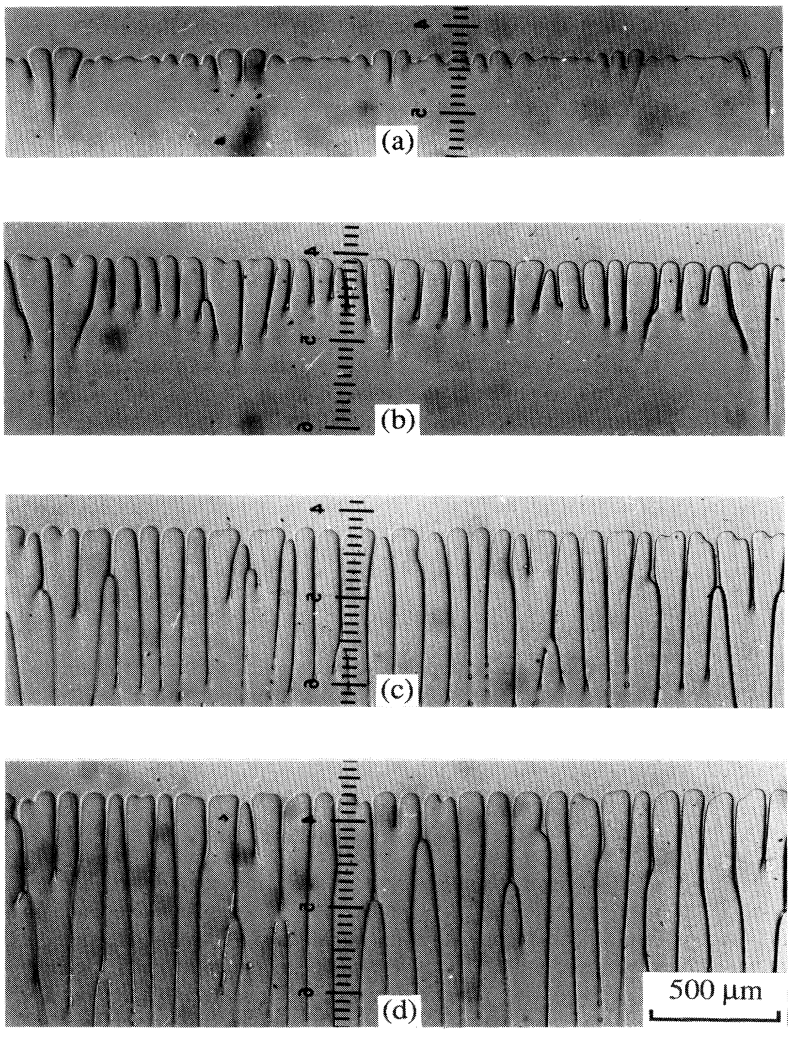

FIG. 12. Failure of the formation of a doublet interface due to the tip splitting of the initial coupled cells. Patterns formed after (a) 2000 s, (b) 2700 s, (c) 3600 s, and (d) 4500 s of growth. Succinonitrile–0.5 wt. % acetone. $V=1\ \mu m/s$. $G=30\,°C/cm$. $\nu=3.2$.

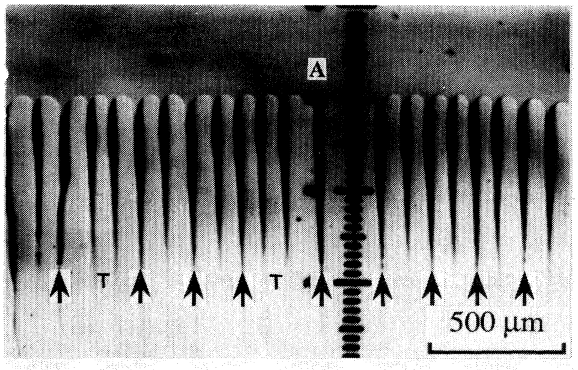

FIG. 13. Coexistence of doublets with triplets (the arrows indicate the intergrooves). Succinonitrile–0.15 wt. % acetone. $V=4\ \mu m/s$. $G=65\,°C/cm$. $\nu=1.8$.

grooves are indicated by arrows, shows the coexistence of doublets with triplets (T). It should be stressed that the multiplets in the central part and on the left-hand side of the picture may be somewhat difficult to individualize for nonexercised eyes, especially when looking only at the tip region. Although it is relatively weak, the slight difference between the intra- and interdepths becomes critical in such situations. It should be mentioned that more triplets and quadruplets were observed in the transition zone between the arrays of doublets and deep cells, which suggests that the increase of disorder in the doublet interface may help the transition to stable single cells.

Besides, Fig. 13 bears strong similarities with Fig. 6(a) in the recent paper by de Cheveigné and Guthmann [20]. Indeed, considering only the upper half of Fig. 13, the cells marked with A then at first sight may appear isolated in an array of deep cells. These cells can be characterized as abnormally wide and flattened on the side facing the other, which is just the definition de Cheveigné and Guthmann introduced for "anomalous" cells. It follows from the present study that such pairs of cells, which are locked on grain boundaries and belong to different multiplets in the range where a doublet interface is stable, merely result from the reversal of the shape of the initial perturbations formed at the grain boundaries in order to fit the cellular microstructure to the width of the grains. As the origin of these cells and their role in pattern selection is now clarified, we rather consider that their presence in the array should be considered as "normal" in a polycrystalline material.

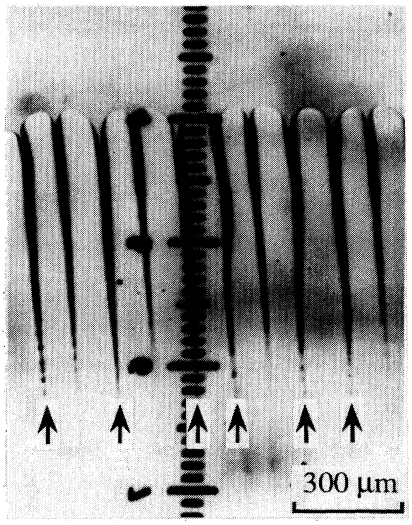

FIG. 14. Two individual cells in an array of doublets, with meandering of the intergrooves (arrows). Succinonitrile–0.15 wt. % acetone. $V=4\ \mu m/s$. $G=59\,°C/cm$. $\nu=2$.

Two individual cells in an array of doublets are shown in Fig. 14. When doublets are stable, individual cells can be considered as defects. Very interestingly, the dynamics of the array frequently gives rise to a meandering behavior of the intergrooves (arrows) whereas the intragrooves remain straight. This observation once more emphasizes the fact that the intragrooves are intrinsic shape characteristics, which are not really flexible. Accordingly, the cells in multiplets, which share a common future, should be considered as a whole and the dynamics of the formation and selection of the microstructure of the solid-liquid interface has to be treated as that of an array of doublets, with other multiplets and defects.

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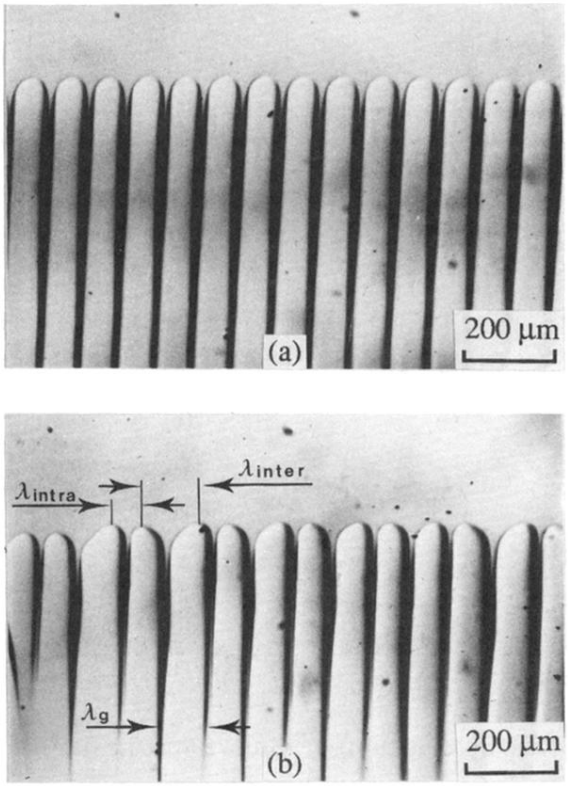

FIG. 1. (a) Regular cellular array. Succinonitrile–0.15 wt. % acetone. $V=5$ μm/s. $G=62$ °C/cm. $\nu=2.4$. (b) Doublet interface. Succinonitrile–0.15 wt. % acetone. $V=4$ μm/s. $G=65$ °C/cm. $\nu=1.8$.

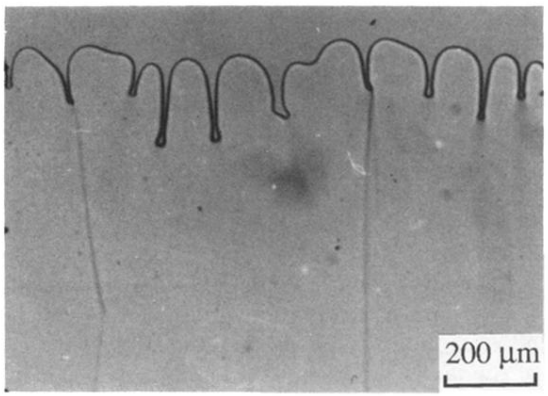

FIG. 10. Lateral motion of grain boundaries when the width of the grain is not compatible with the fitting of a stable doublet array. Succinonitrile–0.5 wt. % acetone. $V=0.75$ μm/s. $G=43^\circ$ C/cm. $\nu=1.7$.

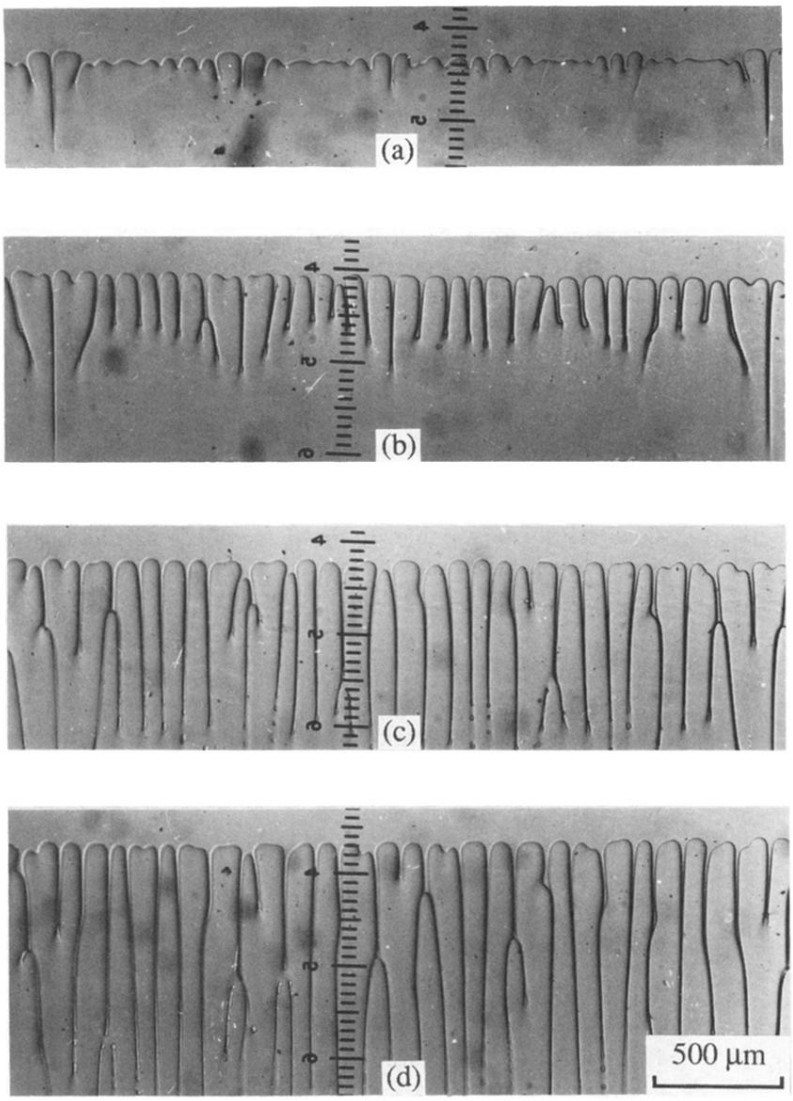

FIG. 12. Failure of the formation of a doublet interface due to the tip splitting of the initial coupled cells. Patterns formed after (a) 2000 s, (b) 2700 s, (c) 3600 s, and (d) 4500 s of growth. Succinonitrile–0.5 wt. % acetone. $V=1\ \mu m/s$. $G=30\,^{\circ}C/cm$. $\nu=3.2$.

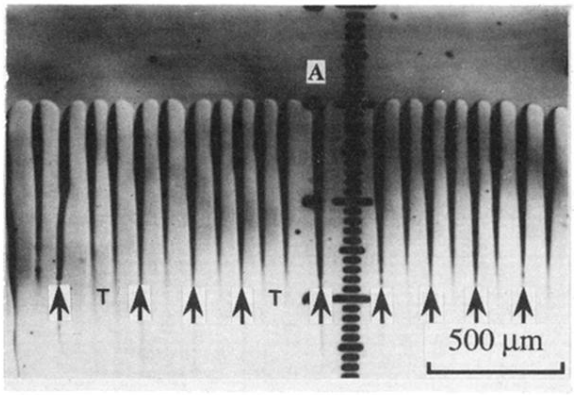

FIG. 13. Coexistence of doublets with triplets (the arrows indicate the intergrooves). Succinonitrile–0.15 wt. % acetone. $V = 4\ \mu$m/s. $G = 65\,^{\circ}$C/cm. $\nu = 1.8$.

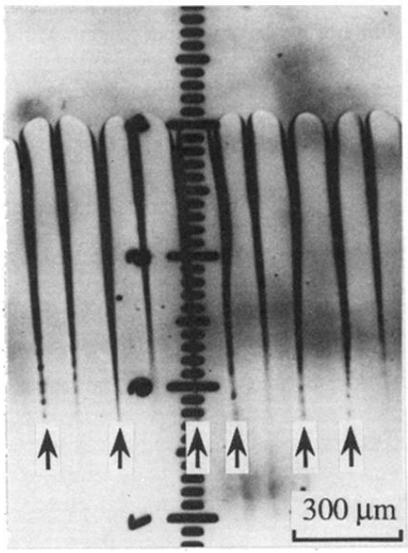

FIG. 14. Two individual cells in an array of doublets, with meandering of the intergrooves (arrows). Succinonitrile–0.15 wt. % acetone. $V = 4\ \mu m/s$. $G = 59\ ^{\circ}C/cm$. $\nu = 2$.

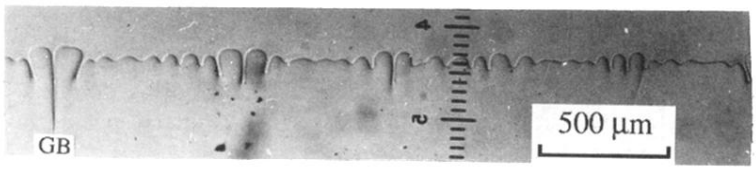

FIG. 2. Progressive initiation of coupled cells within a large grain and lateral propagation of morphological instability in the form of wave packets. Succinonitrile–0.5 wt.% acetone. $V=1\ \mu$m/s. $G=30$°C/cm. $\nu=3.2$.

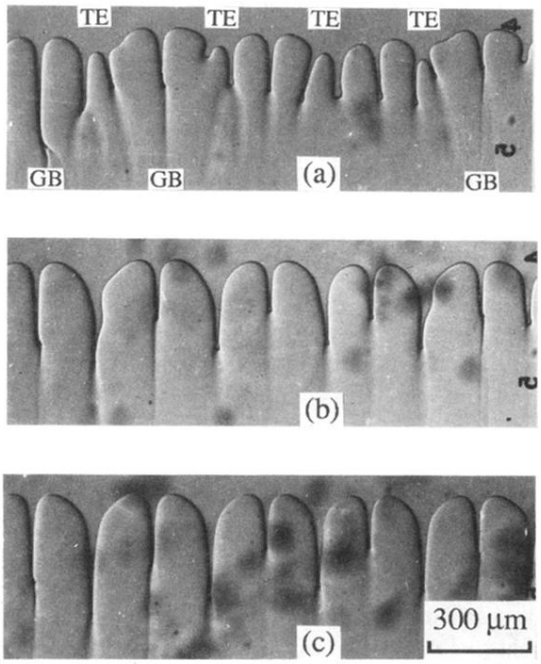

FIG. 3. Formation of a stable array of cellular doublets. Patterns formed after (a) 2400 s, (b) 5000 s, and (c) 8400 s of growth. Succinonitrile–0.5 wt. % acetone. $V=0.75$ μm/s. $G=43$ °C/cm. $\nu=1.7$.

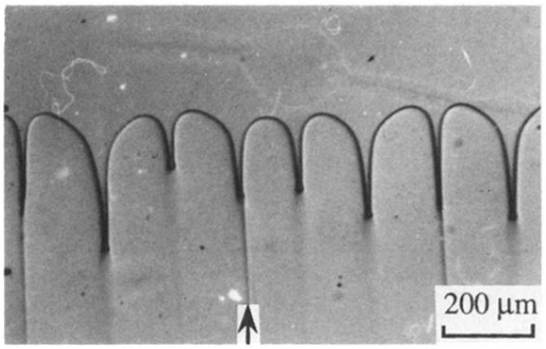

FIG. 9. Normal accommodation of doublets at grain boundaries, together with a grain boundary attached to a groove in between doublets (arrow), which indicates the local reversal of initial coupled cells. Succinonitrile–0.5 wt. % acetone. $V = 0.75\ \mu m/s$. $G = 43\ °C/cm$. $\nu = 1.7$.