Cellular multiplets in directional solidification

Przemek Kopczyński, Wouter-Jan Rappel, and Alain Karma
Department of Physics and Center for Interdisciplinary Research on Complex Systems, Northeastern University, Boston, Massachusetts 02115
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We report the existence of new branches of steady state cellular structures in directional solidification. These structures consist of repeating cellular subunits, or multiplets, each containing a set of distinct cells separated by unequal grooves. A detailed numerical study of the symmetric model of directional solidification reveals that all multiplets bifurcate off the main singlet solution branch in two sets. Two points on the main branch, one corresponding to the onset of the Eckhaus instability at small cell spacing and the other to a fold of this branch at large spacing, are argued to be separate accumulation points for each set of multiplets. The set of structures bifurcating near the fold are morphologically similar to experimentally observed multiplets. In contrast, those bifurcating near the Eckhaus instability do not resemble experimental shapes. Furthermore, they are argued to be generically unstable. [S1063-651X(97)50202-9]

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Directional solidification of alloys or liquid crystals exhibits a variety of interfacial patterns. The most basic pattern is the periodic cellular array that forms when the pulling velocity V exceeds a critical velocity V_c corresponding to the onset of the Mullins-Sekerka instability [1]. Close to onset, this array consists of identical cells with wavelength λ that are separated by grooves of equal depth. This regular array has been investigated extensively, both experimentally [2–6] and theoretically in diffusive growth models of directional solidification [6–10].

Recent experiments have demonstrated the existence of more complex steady state structures in the directional growth of succinonitrile-acetone [5]. These structures, or ''multiplets,'' consist of groups of cells that are repeated every N grooves. For example, the basic cellular array consists of singlets with $N=1$ while a pairwise grouping of cells leads to doublets with $N=2$. Experimentally, these doublets were found to be stable while higher order multiplets were observed to be transient. An example of an experimental doublet from Ref. [5] can be seen in Fig. 1, which shows that the pairwise grouping of cells to doublets leads to asymmetric cell shapes with a broken parity. Similar parity broken cell shapes have been found numerically in dendritic growth in a channel in two [11,12] and three dimensions [13] and in directional solidification [14]. In addition, higher order multiplets were found in a numerical simulation of eutectic growth ($N=2-7$) [15] and in a numerical investigation of the one-dimensional Swift-Hohenberg equation [16].

In this paper, we present a numerical study of multiplets in directional solidification. Aside from the already observed doublet [14], we find two sets of branches of multiplets that bifurcate from the main singlet branch. We find that the existence of these sets can be understood in terms of the stability structure of the main branch using analytical arguments similar to those used previously to interpret the existence of multiplets in the Swift-Hohenberg equation [16]. One set consists of multiplets that are qualitatively similar to the experimentally observed multiplets while the other set exhibits multiplets that have morphologies that are different from the experimentally observed ones.

We have investigated the standard equations for the symmetric model with a nonconstant concentration jump at the interface. The basic equations of this model are given by

$$D\nabla^2 u + V\partial_z u = \partial_t u, \tag{1}$$

$$u_L = 1 - d_0\kappa - \xi/l_T, \tag{2}$$

$$[k+(1-k)u_L]v_n = -D\left[\frac{\partial u}{\partial n}\right]^{\pm}, \tag{3}$$

where $u \equiv (C-C_\infty)/\Delta C$ is the dimensionless concentration field, C is the actual concentration, C_∞ is the nominal alloy concentration, and $\Delta C = C_\infty(1/k-1)$ is the concentration jump of the reference planar interface. The values of u on the liquid and solid sides of the boundary are defined respec-

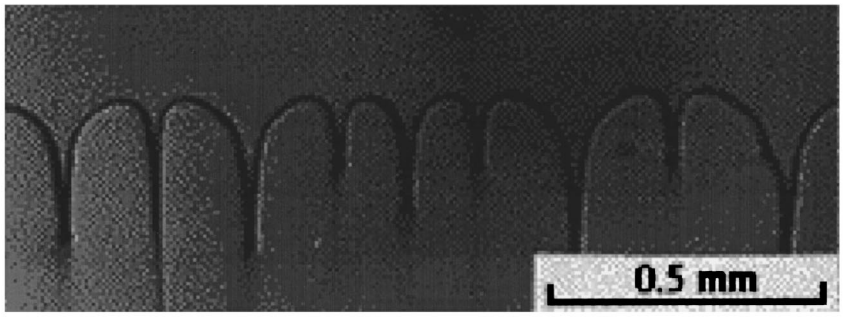

FIG. 1. An example of a doublet found in the experimental system of Ref. [5].

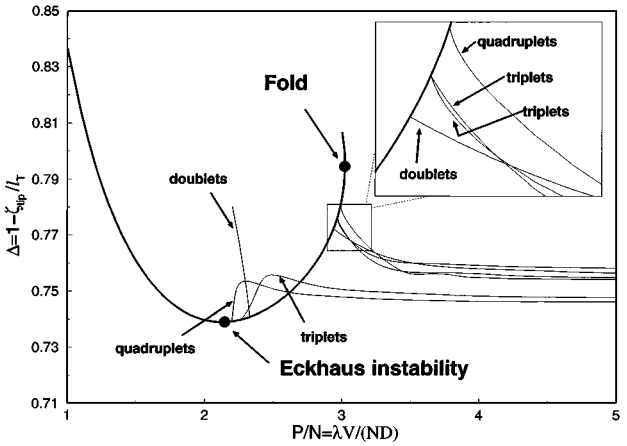

FIG. 2. Plot of cell tip undercooling vs dimensionless spacing showing the main branch (thick solid line) and multiplet branches (thin lines). The solid circles on the main branch indicate the points at which the solution becomes unstable against a perturbation with Bloch wave number $Q=0$. These two points correspond to the Eckhaus instability (low P) and the fold of the singlet steady state branch (high P). The inset shows a magnification of the bifurcation sequence accumulating at the fold for high P.

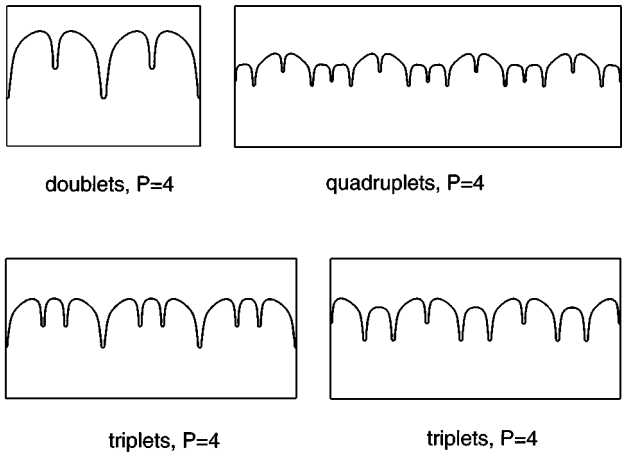

FIG. 3. Typical shapes of the multiplets corresponding to the branches in Fig. 2 that bifurcate from the singlet branch on the high P side near the fold. These shapes closely resemble the experimentally observed ones.

tively by u_L [Eq. (2)] and $u_S=k(u_L-1)$; k is the partition coefficient, $d_0=\Gamma/|m|\Delta C$ is the chemical capillary length where Γ is the Gibbs-Thomson coefficient and m is the liquidus slope, $l_T=|m|\Delta C/g$ is the thermal length where g is the temperature gradient, D is the solute diffusivity taken to be equal in both phases, κ is the interface curvature, ξ is the z coordinate of the interface, v_n is the normal velocity, and $[\partial u/\partial n]^{\pm}$ measures the jump in the normal gradient of u at the boundary.

Our calculations are based on the standard boundary integral approach [17] that allows us to recast Eqs. (1)–(3) into the single integral equation

$$\frac{(1+k)}{2}u_L=\int ds G[k+(1-k)u_L]v_n+D \times\int ds\frac{\partial G}{\partial n}(1-k)u_L-V \times\int dx G(1-k)u_L, \tag{4}$$

where s is the arclength coordinate along the solid-liquid boundary and G is the Green's function, which corresponds to Eq. (1). The spatially periodic steady states are found numerically using a Newton-Raphson iteration scheme of the time-independent integral. Details of this procedure can be found in [8,9]. For the material parameters we took $k=0.9$ corresponding to liquid crystals [18], and $d_0/l_T=1.14\times10^{-3}$. We examined the cell shapes in the nonlinear regime at the constant dimensionless pulling velocity $Vd_0/D=1.614\times10^{-2}$ corresponding to $6\times V_c$.

The complete branch diagram of steady state structures is presented in Fig. 2 where we plot the cell tip undercooling (defined as $\Delta=1-\xi_{\rm tip}/l_T$) versus the dimensionless spacing, P/N, for that particular velocity. The dimensionless spacing is defined as the dimensionless wavelength, the Peclet number $P=\lambda V/D$, normalized by the number of grooves N in the subunit. Thus, the wavelength of a singlet is equal to its spacing, the wavelength of a doublet is twice its spacing, etc. This definition ensures that the multiplet branches in the diagram bifurcate off the main branch in a continuous fashion although the wavelength changes discontinuously at the bifurcation.

The main solution branch in Fig. 2 is represented by a thick line and corresponds to the basic regular cellular array with wavelength λ and wave number q (i.e., singlets with $N=1$). We have found two sets of multiplets that bifurcate off the main branch. These sets, one for high P and one for low P, are shown as thin lines in Fig. 2. Typical shapes of the multiplets belonging to these sets are shown in Fig. 3 for the high P bifurcation sequence and in Fig. 4 for the low P bifurcation sequence (the x and y scales are equal in Figs. 3 and 4). The inset of Fig. 2 shows a closeup of the high P bifurcation sequence.

The existence of the multiplets can be explained by studying the stability of the main branch. Using the same tech-

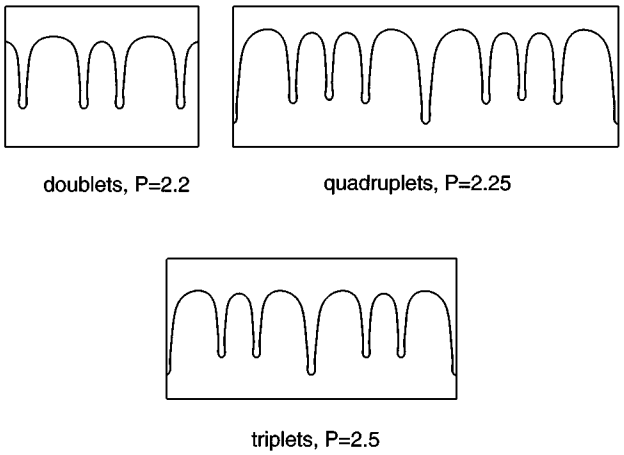

FIG. 4. Typical shapes of the multiplets corresponding to the branches in Fig. 2 that bifurcate from the singlet branch on the low P side near the Eckhaus instability. These shapes do not have any known experimental counterpart.

nique as in Ref. [19], we perturb the steady states with wave number q, $\mathbf{r}_q^0(s)$, with a shift along the normal direction of the general form

$$\mathbf{r}_q = \mathbf{r}_q^0(s) + \mathbf{n}_q^0(s)\,\delta_{q,Q}(s)\exp[iQ\lambda s/s_q^0 + \omega(Q;q)t],$$

where $Q \in [-\pi/\lambda, \pi/\lambda]$ is the Bloch wave vector, $\mathbf{n}_q^0(s)$ is the normal unit vector, and s_q^0 is the total arclength of the cell over a complete period. The Floquet-Bloch theorem implies that $\delta_{q,Q}(s)$ is a function that has the same periodicity as the underlying steady states: $\delta_{q,Q}(s+s_q^0) = \delta_{q,Q}(s)$. By solving the resulting eigenvalue problem we examined the stability of an infinite cellular array against perturbations of all possible wavelengths. We have found that the main branch is unstable against a perturbation with the wave number $Q=0$ at two distinct values of P. Those two points are shown in Fig. 2 as solid circles and correspond to, respectively, the long wavelength Eckhaus instability at small P and the fold of the main branch at high P. Thus, the main branch is stable against $Q=0$ perturbations for P values that are in between these two points, which are argued below to be accumulation points for the bifurcation sequences of multiplet branches.

In the region between these points, on both the low and high P sides, the main branch loses its stability to modes with finite wave number Q that are within the first Brillouin zone. The first unstable mode we encounter when we approach either accumulation point is at the edge of the first Brillouin zone, i.e., $Q/q=0.5$. As we move along the singlet branch towards either of the two accumulation points, from the stable side, we find a continuum of growth modes that cross zero at decreasing values of Q/q and become positive. Every zero crossing of a growth mode with wave number Q corresponds to a bifurcation off the singlet branch of a new solution branch with wave number Q. For example, for $Q/q=1/2$, the wavelength of the new structure is twice that of the main branch. Thus, the new solution corresponds to a doublet ($N=2$). Similarly, $Q/q=1/3$ corresponds to the bifurcation point of triplets ($N=3$) and $Q/q=1/4$ to the bifurcation point of quadruplets ($N=4$), etc. To illustrate the bifurcation sequence further we have plotted in Fig. 5 the Floquet stability spectrum showing the growth rate of the perturbation as a function of the perturbation wave number. The diagram is drawn for a solution on the main branch with a Peclet number that is slightly higher than the Peclet number corresponding to the Eckhaus instability. This point is stable against perturbations with $Q=0$ but already unstable against perturbations with a wave number greater than a marginal stable wave number, Q_c, denoted by a solid circle in Fig. 5. Since the growth rate with wave number Q_c is crossing zero, a new branch corresponding to a multiplet with wavenumber Q_c will bifurcate off the main branch at this P value. As we approach the Eckhaus point or the fold from the stable side with respect to $Q=0$, Q_c approaches zero and multiplets with monotonically increasing values of N will bifurcate off the main branch until we reach the accumulation points for which $N=\infty$. In other words, the points on the singlet branch that are unstable against perturbations with Bloch wave number $Q=0$ are accumulation points of multiplets. Furthermore, the multiplets, except the doublet, should bifurcate in *pairs* due to the $x \to -x$ symmetry in the problem.

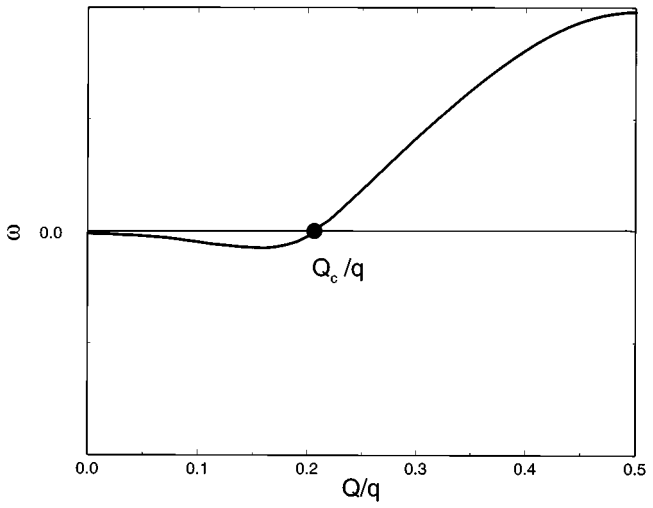

FIG. 5. Floquet spectrum of a main branch solution that is Eckhaus stable. This solution is marginally stable for $Q=Q_c$ and is unstable for $Q>Q_c$. As we approach the Eckhaus instability, Q approaches $Q=0$ and multiplets with smaller and smaller wave numbers bifurcate off the main branch.

Figure 2 shows that both sets of multiplets near the two accumulation points exhibit the correct bifurcation sequence: first a doublet branches off, followed by a triplet, which in turn is followed by a quadruplet. Furthermore, we have verified that the high P triplet comes as a pair (see inset). Due to computational constraints we have not searched for higher order multiplets nor for any other secondary branches.

In Ref. [16] a similar bifurcation sequence was demonstrated to exist in the one-dimensional Swift-Hohenberg model. As in our case, this sequence was connected with a long wavelength Eckhaus instability of the main branch of solutions. It is worth pointing out two minor differences between the sequence in [16] and the sequence in Fig. 2. First of all, unlike in the Swift-Hohenberg equation, both sequences in our model approach the accumulation point from the stable side of the $Q=0$ instability. Secondly, in the Swift-Hohenberg equation the doublets were found to bifurcate in pairs as well [20].

The doublet branch for high P corresponds to the asymmetric cell shapes found in [14], albeit with larger amplitude, and is qualitatively similar to the experimentally observed one. As it branches off the main branch, the cells become asymmetric and every other groove becomes shallower. The doublet for low P on the other hand is connected to a cell elimination mode [19]. This can be clearly seen in Fig. 4 (doublets), where every other cell becomes smaller while the groove depth for every cell remains identical. Both triplet branches for high P (Fig. 3) have a morphology that resemble closely that of experimentally observed triplets [5] while the lower P triplet branch is qualitatively distinct. This suggests that the branches that are experimentally relevant are the ones that are bifurcating for high P. This conclusion is also consistent with Ref. [16] in which it was argued that the sequence of multiplet branches that accumulate at the Eckhaus instability in one-dimensional systems, as in eutec-

tic growth [15], should be generically unstable. Indeed, it was found in [16] that in the one-dimensional Swift-Hohenberg equation the multiplets generated by the Eckhaus instability were unstable. Of course, to determine unambiguously which branch is relevant for directional solidification we have to perform a stability analysis of all the branches. Unfortunately, this is presently outside the range of our computational resources.

Finally, it is worth noting that the inclusion of surface tension anisotropy does not change qualitatively the branch structure. The anisotropy was introduced by replacing d_0 by $d_0[1-15\epsilon\cos(4\theta)]$. We have carefully examined the case for $\epsilon=0.01$ corresponding to 1% anisotropy, for which there exists also two points on the main branch for which the solution is marginally stable with respect to perturbations with $Q=0$. Again, this leads to the sequence of multiplets bifurcation from the main branch and these two points are the accumulation points of these sequences.

In conclusion, we have found a family of new multiplet steady state solutions that originate on the main singlet branch of cells at small and large spacing. These new solutions are characterized by nonequal grooves and asymmetric shapes. The bifurcation points of the branches of multiplets coincide with zero crossings of real eigenvalues of the stability spectrum of cells from the singlet branch. The shapes of doublets and triplets belonging to the high P set are consistent with experimental observations. The multiplets bifurcating near the Eckhaus instability (low P) on the other hand do not resemble experimentally observed multiplets and have been argued here to be unstable. This suggests that only the high P multiplets are experimentally relevant. What remains to be investigated is the stability of the high P multiplets. A recently developed computationally efficient phase field method promises to be quite useful for such a study [21]. It allows one to simulate growth in the absence of kinetics, as is typically the case in low velocity directional solidification experiments. This computational approach can be used to explore the stability of these new structures and, more importantly, to establish which, if any, of the multiplet branches are selected dynamically. It would be also interesting to examine possible secondary branches forking off the multiplet branches.

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