Experimental Observation and Computer Simulations of 3D Triplet Structures in Diffusion Limited Growth of Xenon Crystals

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Changes of growth morphologies are induced by a perturbation of the thermal diffusion field in the surrounding melt of a growing xenon crystal. Apart from the dendritic morphology, seaweed and doublon morphologies and for the first time transitions from dendritic to triplet structures (first predicted by T. Abel, E. Brener, and H. Müller-Krumbhaar [Phys. Rev. E **55**, 7789 (1997)] were observed experimentally. With 3D phase-field simulations it was possible to reproduce the experimental procedure and to verify that triplet structures can grow in a stable way even in the presence of anisotropic surface free energy as found for experimental substances.

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In systems out of thermodynamic equilibrium spatio-temporal structures commonly arise from instabilities of homogeneous states, both in bulk phases and at interfaces. The understanding of pattern formation and morphology selection in diffusion-limited growth is of significance in different fields such as viscous fingering, electrochemical deposition, aggregation, and even in the growth of biological structures (bacteria colonies, coral trees, organs) [1]. Crystal growth has proved to be a particularly well-controlled setting to explore the possible morphologies and to confront theory and experiment.

During growth into undercooled melt, crystals can form various morphologies [2]. Dendrites are the best known shape. In the presence of an anisotropic surface tension a crystal tends to develop dendritic patterns. The morphology and its properties change drastically for vanishing anisotropies. Brener *et al.* [3–6] investigated analytically the influence of the anisotropy of the surface tension and the undercooling on the morphology of the growing crystal in two dimensions and a morphology diagram for these parameters was established. Dendritic structures, defined as the ones having a strong orientational order, are found for sufficiently high anisotropy and moderately low undercoolings. Seaweed patterns—structures without any apparent orientational order—are found for sufficiently low anisotropies and high undercoolings. A special morphology is the *doublon*, which was stated to be the building block of seaweed in two dimensions [3–6]. A doublon consists of two fingers, which grow in the same direction and stabilize each other. In two dimensions there is a narrow channel of liquid along the axis of symmetry between the fingers. Experimentally, Akamatsu *et al.* [7,8] reported the existence of dendritic, doublon and seaweed structures in quasi-two-dimensional thin film directional solidification experiments with an organic alloy (CBr_4-8 mol % C_2Cl_6) in varying the effective interfacial anisotropy, which is dependent on the crystallographic orientation. In bulk samples, Jamgotchian *et al.* [9] used a SCN-0.2wt % acetone solution in a cylindrical setup and found different instability patterns depending on the fluid flow as the driving force.

With the morphology diagram of Brener *et al.* [3–6], substantial progress in understanding the growth behavior of two-dimensional diffusional growth structures could be made analytically. On the other hand the improvement of simulation techniques, especially with the phase-field model [10–12], allows a direct comparison between analytical studies and simulated structures.

In the three-dimensional case much less is known about different morphologies. Analytical studies about 3D dendrites were performed by Brener and Temkin [13,14] and predictions about the contours of dendrites were given, which agree with experimental findings [15,16]. Phase-field simulations of 3D dendrites performed by Plapp and Karma have shown dendrites to grow down to low dimensionless undercoolings of $\Delta \approx 0.05$ [17]. The limitation in simulating 3D structures is the additional spatial dimension, which increases drastically the amount of memory needed to store the domains for temperature and phase-field. The diffusion length, i.e., the distance between the solid-liquid interface and the thermal diffusion front diverges in the limit of low undercoolings. This is a severe numerical problem because it is necessary to keep track of the whole diffusion field in order to simulate the crystal. Therefore, low undercoolings such as the ones found in experiments ($\Delta \leq 10^{-3}$ in dimensionless units for substances like xenon or ice) cannot be simulated up to now. Also, it is not possible to perform computer simulations to support analytical limit calculations for vanishing undercoolings. Therefore, apart from dendrites, very little is known about the behavior of other morphologies in three dimensions [18].

By means of phase-field simulations Singer *et al.* [19] established a morphology diagram for 3D structures. The basic shape of the morphology borders is found to be qualitatively similar to the one predicted by Brener [3–6] in two dimensions, however, shifted in the direction of higher anisotropies. Abel *et al.* [20] performed phase-field simulations with very high undercoolings $\Delta \approx 1$ in a channel. They found stable objects in three dimensions, which seem to have analogous properties as doublons in two dimensions. These triplet patterns or *triplons* consist of three "cooperating fingers." The triplet structures are not imposed by symmetry but are self-organized. Low anisotropies, which do not allow stable growth of dendrites were used. Nestler *et al.* [21] observed triplet structures in a simulation at undercoolings of $0.7 \leq \Delta \leq 0.8$, where—in contrast to Ref. [20]—no boundary conditions of a channel were used. The anisotropy has been set to zero. Triplet structures have also been found in simulations of directional growth by Plapp and Dejmek [22]. Up to now single triplet structures in a "free growth" environment and with a substance with an anisotropy sufficiently large to grow dendrites have not been reported either in experiments or in simulations, as far as we know.

Experimentally, it was shown by Stalder and Bilgram [23] that, apart from dendrites, it is also possible to produce seaweed and doublon structures in 3D. The doublon looks like two interacting dendrites where each finger has three instead of four fins [19,23,24]. The channel between the two fingers is topologically different from the one in 2D as it is possible to transport heat away perpendicular to the main growth direction, whereas in 2D this is not possible. The properties of doublons in three dimensions were studied in Refs. [19,24,25]. It was proposed that in the 3D case doublons should be considered as a separate morphology class.

In our experiments the growth of xenon crystals into undercooled melt is initiated by means of the capillary injection technique. Xenon is a model substance for metals as it forms a simple liquid of spherical atoms, it has a low melting entropy to form rough solid-liquid interfaces at atomic scale and it crystallizes in fcc-structure. Xenon is transparent and therefore allows an *in situ* observation of the growing crystal. The melting temperature of xenon is $T_m = 161.3897$ K. Typical undercoolings that can be obtained in our experiments are $40 \leq \Delta T \leq 220$ mK ($0.6 \times 10^{-3} \leq \Delta \leq 4 \times 10^{-3}$ in dimensionless units). By means of a periscope we image the crystal onto the CCD chip of a digital camera. The optical resolution of the periscope is 1.22 μm. A digital camera with a pixel resolution of 1280×1024 is acquiring 12 bit gray scale images for further analysis. Our experimental setup allows to turn the capillary in order to orient the crystal so that the maximum projection area can be imaged. A detailed description of our experimental setup is given in Ref. [15].

In order to induce a morphology change the growing crystal is perturbed. A perturbation is achieved by shifting the capillary with the growing crystal downwards to a region where the temperature is still very close to the initial undercooling and homogeneously distributed. By this shift the isotherms around the crystal are washed away and the whole surface is exposed to the same thermal conditions and therefore the growth velocity is the same at any point at the surface of the crystal. This leads to a decrease of the curvature of the crystal surface and thus to surface instabilities and eventually to changes in the morphology. During the subsequent growth of the crystal the thermal gradient distribution at the surface is reestablished. Therefore only transient states can be observed [23,24].

For the first time three-tip structures were observed in our experiments of the solidification of xenon. A perturbation of the crystal leads to the development of three tips, which are mutually influencing each other. An image of such a triplon is given in Fig. 1. The three tips grow at the same velocity. From the orientation of the axis of growth and the anisotropy directions (original dendritic fin directions) it is visible that the outer two tips form a doublon oriented in the anisotropy directions and that the middle tip forms a separate tip in the rear of the structure. The triplet structures are not in a stationary environment; therefore, they relax back to dendrites. After a typical time (~30–40 s) one of the tips is taking the lead, leaving the other tips behind. There are two possible explanations why triplets are not stable in our experiments: (i) Convective effects might perturb the tips in such a way that the stability is lost. (ii) The stability of doublons in two dimensions strongly depends on the undercooling. Similarly, it would be conceivable that the undercoolings in our experiments are too low to favor stable triplet structures in 3D.

The observed behavior can be explained as follows: after the initial perturbation, the structure grows much faster than in steady state since the gradients at the solid-liquid interface are close to the ones found at the initial undercooling. This leads to an almost spherical growth shape at the tip. The tip of this structure grows so big that the interface can be assumed to be almost planar on the local length scale. Small perturbations on this quasiflat two-dimensional surface would develop independently according to a Mullins-Sekerka instability. The probability of

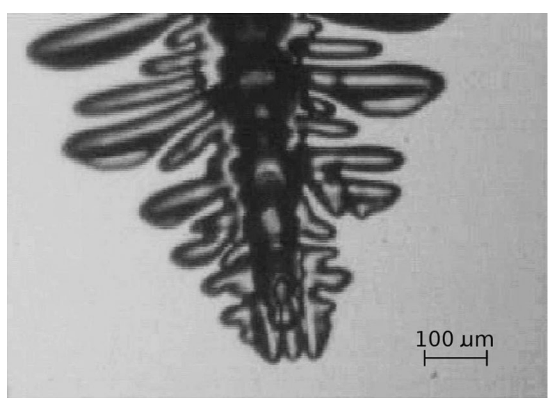

FIG. 1. Experimental observation of a three-tip structure after a perturbation of the crystal. Because of the anisotropy of the surface free energy the triplet structure is not absolutely symmetric, but composed of a doublon and an additional dendrite tip.

developing n identical perturbations or tips, which would influence each other decreases with increasing number of tips. This is the reason why doublon structures are observed more often than triplet or higher order multiplet structures, which have also been grown with our setup.

In order to validate our growth model and the shape of the observed triplet structure, we have performed phase-field simulations with the Karma-Rappel model [12]. The temporal evolution of the phase-field parameter $\phi(x, y, z)$ and the temperature field $\theta(x, y, z)$ is described by a set of dimensionless PDEs

$$\tau \frac{\partial \phi}{\partial t} = W^2 \nabla(\eta^2 \nabla \phi) + (\phi - \lambda \theta(1 - \phi^2))(1 - \phi^2) + W^2 \sum_{d=1}^{3} \frac{\partial}{\partial x_d}\left(|\nabla \phi|^2 \eta \frac{\partial \eta}{\partial(\partial \phi / \partial x_d)} \right), \quad (1)$$

$$\frac{\partial \theta}{\partial t} = \nabla^2 \theta + \frac{1}{2} \frac{\partial \phi}{\partial t}, \quad (2)$$

where $\eta = \eta(\varepsilon_4, \mathbf{n})$ and $\tau = \tau(\varepsilon_4, \mathbf{n})$ are the anisotropic surface tension and the kinetic coefficient, respectively, ε_4 is the strength of the anisotropy, $\mathbf{n}$ is the outwards normal vector of the interface and λ specifies the ratio between the interface width W and the capillary length. The phase-field parameter takes on constant values in the liquid (−1.0) and the solid (1.0) and changes smoothly over the thin diffuse interface. The phase-field equations were solved with the Finite Difference method on a uniform $400 \times 400 \times 400$ grid with the following parameters: $\Delta = 0.4, 0.5, 0.6$, $\varepsilon_4 = 0.025$, $\lambda = 5$, $\Delta x = 0.8$, $\Delta t = 0.05$. In order to reduce computational cost, the phase-field and the temperature field were repeatedly shifted downwards and fresh undercooled liquid was supplied on the top of the computational domain. This allowed us to observe the development of a solidifying structure and at the same time to avoid the influence of the domain boundaries on the diffusion field.

A morphology produced by the phase-field method is strongly influenced by the initial conditions. In our study [19] we have found that with a small spherical seed as the initial conditions it is not possible to produce either doublon nor triplet structures. Only the use of two spherical seeds placed at a certain distance from each other or a distorted rugby ball shape as initial conditions allowed us to observe structures, which looked qualitatively similar to the doublons found in our experiments. Similarly, the triplons could be produced with three initial seeds.

In the present study we have performed the following procedure to reproduce the experimental conditions: First, the growth of a single dendrite was simulated until it reached steady state. Then the temperature field around the dendrite was assigned the value of the initial undercooling, that is the isotherms were washed away as in the experiment, where the dendrite is shifted downwards into the colder regions of the liquid. In order to speed up the computations, random noise with normal distribution has been added to the solid-liquid interface at the dendrite tip to simulate the effect of the thermal fluctuations. As a result of this washing procedure, the dendrite tip thickens significantly in the cold liquid and, at the same time, develops instabilities. Depending on the strength and distribution of the imposed noise one or several bumps develop at the interface. Consequently, as the thermal field stabilizes around the tip, it continues its growth either as a single tip or splits up into doublon, triplet, or even quadruplet structures. After a while each of the growing tips tries to develop the four fins along the anisotropy directions. As they feel their mutual influence not all fins can grow further.

A three-dimensional steady-state dendrite tip for $\Delta = 0.5$, shown in Fig. 2, is the starting point for the simulation of a triplet structure. The high temperature gradients and imposed noise on the tip lead to three perturbations which grow independently and start influencing each other [Fig. 3(a)]. In Fig. 3(b) a later stage stable triplet structure in shown. It can be seen that due to the strong orientation along the anisotropy directions two of the tips form a slightly perturbed doublon whereas the third grows as a dendrite where one of the fins reaches into the doublon structure. This morphology is coherent with our experimental observation. Between the different undercoolings used for the simulations we have not found any qualitative differences.

It was not possible to reproduce the results of Abel *et al.* [20] of an absolutely threefold symmetric triplon for parameters where an initial spherical seed would form a dendrite. Apparently the existence of strong enough anisotropy such as the one for our experimental substance xenon (∼1.5%–2.2%) prevents the formation of absolutely symmetric triplons in 3D simulations and experiments. A

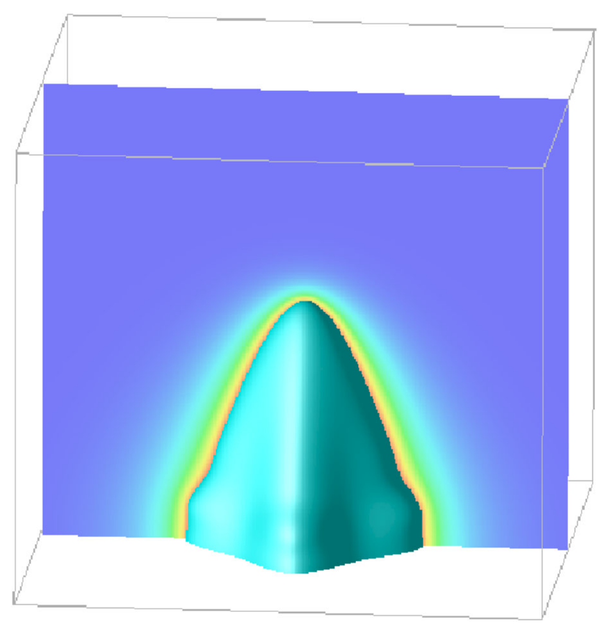

FIG. 2 (color online). Initial phase-field dendrite tip in steady state with temperature field plotted in the liquid for $\Delta = 0.5$. The size of the superimposed box is $400 \times 400 \times 350$ grid nodes.

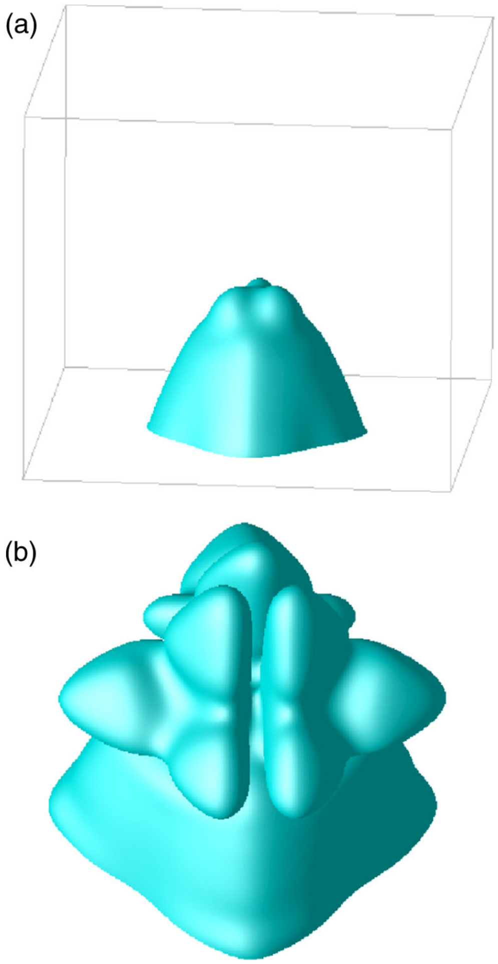

FIG. 3 (color online). (a) After a while the noise perturbation at the tip develops three independently growing small tips. The superimposed box has the same size as in Fig. 2 but is shifted by 60 grid nodes upwards. (b) Later stage of the triplet structure. Because of the presence of an anisotropic surface tension it is composed of a doublon and additional dendritic tip.

quadruplet structure would however be absolutely symmetric, but due to the way the multiplet structures are created, its occurrence is less probable. In the phase-field simulations the found triplet structures with nonvanishing anisotropy of surface tension were growing in a stable way for all investigated undercoolings. The undercoolings used in the simulations were significantly higher than the ones used in the experiments. It might be possible that at lower undercoolings the stability disappears similarly to the results found in our experiments. Undercoolings in the range of the experiments, however, were not possible to simulate.

Multiplet structures were produced experimentally and in phase-field simulations by perturbing the thermal diffusion field around the crystal. The subsequent growth of quasi 2D Mullins-Sekerka instabilities lead to competitive growth between different perturbations, which eventually stabilize to doublon, triplet, or higher order multiplet structures. While stable growth of multiplet structures in experiments could not be observed for longer periods of time, phase-field simulations showed that stable growth can be achieved with one to four tips, where a smaller number of tips is more likely to occur.

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