New Experimental Findings in Two-Dimensional Dendritic Crystal Growth

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Tip-stable, tip-oscillating, and tip-splitting types of dendrites were observed experimentally in a two-dimensional supersaturated NH_4Cl solution. The relation between the tip velocity V and the tip curvature K were measured for the tip-stable type. It was found that V is proportional to K instead of K^2 which is expected from the marginal-stability hypothesis in a two-dimensional melt-growth system.

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The problems of pattern formation have recently attracted many researchers in connection with nonlinear and nonequilibrium phenomena. The investigated growing patterns are mainly classified into two groups. One of them is diffusion-limited aggregation (DLA); randomly diffusing particles attach to the surface. Its pattern is irregular and fractal. These patterns have been simulated by Witten and Sander[1] and Meakin,[2] and discussed theoretically by Muthukumar,[3] Tokuyama and Kawasaki,[4] and Hentschel.[5] They have theoretically obtained an expression for the fractal dimensions of DLA in d-dimensional Euclidean space. Experimentally, Matsushita *et al.*[6] have realized two-dimensional DLA in the system of zinc metal leaves. Brady and Ball[7] have obtained a three-dimensional metal aggregate and Nittmann, Daccord, and Stanley[8] have obtained the fractal dimension of viscous fingers. Recently Vicsek[9] obtained the characteristic length by the simulation of DLA, taking into account surface effects, and tried to make regular patterns.

The other group is dendritic crystallization, which grows forming regular patterns. The mode selection of the regular structures is one of the most important subjects for the pattern formation of nonlinear nonequilibrium systems. The crucial questions in a real dendritic crystallization are these: (i) What is the mechanism that determines the spacing of side branches? (ii) Why does the moving tip interface take the shape of a paraboloid of revolution? (iii) What is the relation between the tip velocity and the tip curvature?

A first theoretical approach to these complex problems has been taken by Langer and Muller-Krumbhaar.[10] The relation $V \propto K^2$ between the tip velocity V and the tip curvature K derived from the proposed marginal-stability hypothesis has been substantiated experimentally in three-dimensional dendritic crystallization,[11] although the hypothesis itself is as yet the subject of various discussions. Recently these dendritic patterns have been simulated by two models, the boundary-layer model by Ben-Jacob *et al.*[12] and the geometrical model by Brower *et al.*[13] and Kessler, Koplik, and Levine.[14] The boundary-layer model is the model of dendritic solidification mainly from the melt growth with the characteristic decay length of the thermal diffusion field, which is much smaller than the radius of curvature of the interface, and with Gibbs-Thomson's boundary condition including the crystal anisotropy. However, Ben-Jacob *et al.* have not succeeded in obtaining a realistic pattern for a regular growing dendrite. The geometrical model is a phenomenological model in which the interfacial dynamics is determined only by the interfacial curvature, and it does not take into account directly the diffusion field out of the crystal. The results show many types of crystal growth; bulky, tip-splitting, tip-stable, and tip-oscillating types.[15]

We report in this paper the two-dimensional experimental results of dendritic crystal growth. One can observe some interesting types, tip-oscillating, tip-stable, and tip-splitting types, in this system far from the equilibrium state. We pay special attention to the relation between the tip velocity and the tip curvature of the tip-stable type.

We show the experimental system in Fig. 1. The supersaturated NH_4Cl solution, whose concentration is 42.625 wt.% (for water) and corresponds to a saturation temperature of 35.0 °C, is sealed in a cell whose thickness is 5 μm. The surface flatness of the slide glasses is ± 1.5 μm and the thermal diffusivity is of order 10^{-4} cm^2/sec. The sealed cell is set on the stage of a microscope, and the temperature and therefore the supersaturation of this system are regulated within ± 0.04 by the flow of a temperature-controlled N_2 gas. The thermal diffusivity of the solution, $D_T \sim 10^{-2}$ cgs units, is much greater than the mass diffusivity of the

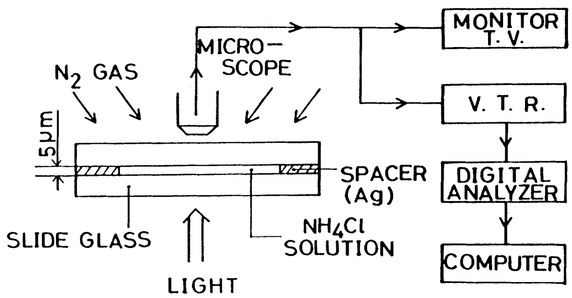

FIG. 1. Experimental system of dendritic crystal growth in a two-dimensional configuration. Dendrites grow in a thin cell of 5-μm thickness and the growth patterns are analyzed by a computer.

solute, $D_c \sim 10^{-5}$ cgs units, and thus this system is limited by mass diffusion. The typical diffusion length of the present work, D_c/v, is of the order 10^3 μm, which is much greater than the system thickness. One can safely assume that the system is two dimensional. The dendritic crystal grows from a spontaneously nucleated seed in the cell. The pictures of the growing dendrites were taken by videotape recording through a microscope, digitized and analyzed by a computer.

In Figs. 2(a)–2(c), we show distinctive types of growing dendrites in our two-dimensional system. Fig. 2(a) shows a tip-oscillating type. This is observed in a very low supersaturated solution.[16] The tip velocity and the tip curvature oscillate in time and the side-branching mechanism is strongly related to this oscillation. When the tip velocity decreases and the shape of the tip interface becomes less pointed, the protrusions which grow to be the side branches are formed at both sides of the tip. The pattern thus formed is generally very regular.[17]

Morris and Winegard[18] have briefly reported this type of dendrites in three dimensions; however, the mechanism of this type has not been understood yet. The physical mechanism might be considered as the interaction between the interface and the diffusion field out of the crystal. For example, the latent heat may temporarily reduce the supersaturation at the tip and after thermal relaxation the tip may grow again. In the two-dimensional case this viewpoint is not appropriate, because one can sometimes observe side branches of a completely antisymmetric phase, which means that one side of the interface is pulled out and the corresponding position of another side pushed in. If the oscillation is caused by the above interaction, the side branches should always be of a symmetric phase. We think that the origin of the oscillations may be found in the state of the tip interface. For example, the surface diffusion constant or the surface tension might be affected by an impurity in the solution.[16,18]

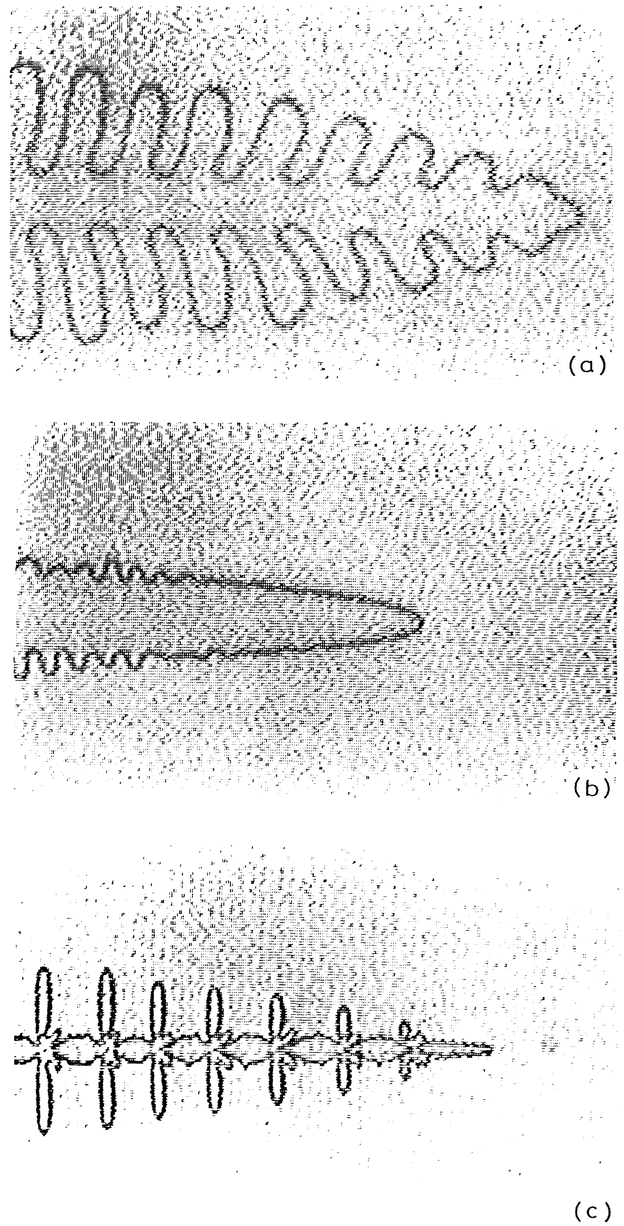

FIG. 2. Photograph of typical two-dimensional growth types taken from videotape recording, as one increases the supersaturation. (a) Tip-oscillating type, whose tip curvature oscillates in time; (b) tip-stable type, whose tip is a parabola and steady in time; (c) tip-splitting type, whose tip splits periodically into ⟨110⟩ direction.

This physical mechanism might correspond to the results of the tip-oscillating model in the two-dimensional simulation of the geometrical model.[13–15]

For a moderate supersaturation regime of the solution, the dendritic crystal becomes a tip-stable type [Fig. 2(b)]. As we will discuss later, the shape of the tip interface is a perfect parabola. Although the tip shape in three dimensions is also a paraboloid of revolution, the differences between them are that (i) the tip velocity in two dimensions is lower than that in three dimensions at the same supersaturation, and (ii) the protrusions from the two sides of interfaces in Fig. 2(b) are not correlated with each other in the two-dimensional case. The reason for (i) is probably the limited flow of solution to the tip in two dimensions. The convection originating from the latent heat at the tip in three dimensions always exists and increases the tip velocity. However, convection in the two-dimensional cell is not allowed because the Rayleigh number in this system is much smaller than the critical value. The reason for (ii) is the following: According to our observation in the three-dimensional dendrite of a NH_4Cl solution, the interfacial instability (Mulins-Sekerka instability[19]) of the paraboloid of revolution is the preliminary instability, which causes successive rings on the paraboloid of revolution. The side branches grow from this ring in the favored crystal direction; therefore, the dendritic side branches grow in several easy axes which are correlated to each other. In contrast, in a two-dimensional system there is no interaction between the two interfaces because they are geometrically separated and cannot influence each other by means of the diffusion field. Furthermore, less solute at the interface compared with the case of three dimensions would soon make a dendritic coarsening. The destabilized interface is consequently irregular.

The open circles in Fig. 3 correspond to the real interfaces of a typical tip-stable type whose picture is taken by a digital analyzer from videotape recording. A solid line in this figure is a parabola calculated with a best-fit parameter. The tip interface is therefore identified as a perfect parabola extending for about ten tip radii as is the case in the three-dimensional system.[11] However, this parabolic formation as a stable interface of growing dendrite has not been proved theoretically.

Figure 4 shows the relation between the tip velocity V and the tip curvature K obtained by the method described above. The Langer–Muller-Krumbhaar theory predicts that V should be proportional to K^2 in two dimensions as well as in three dimensions.[10] The relation in three dimensions is substantiated experimentally.[11] However, in two dimensions V is proportional to K and there exists a critical curvature K_c. Our experimental result is not in accordance with the theoretical prediction.[20] The existence of K_c corresponds to the observation that at very low supersaturation the tip growth almost stops and the parabolic interface is gradually deformed to be a spherical shape. The relation between V and K may be consequently written as $VR^{d-1} \propto \text{const} \times d$, where R is the tip radius of curvature and d is the Euclidean dimension. Generally speaking, the crystallizing quantity per unit time ϕ at the local interface might seem to increase with increasing σ. This new finding, however, means that ϕ at the tip is constant independent of the nonequilibrium parameter, if we assume the tip interface as a semisphere and a semicircle. Therefore, the tip of a growing dendrite plays a special role. The total ϕ increases with the decrease of the spacing of side branches. We suspect that the relation $VR^{d-1} \propto \text{const}$ may be connected to the formation of a parabolic in-

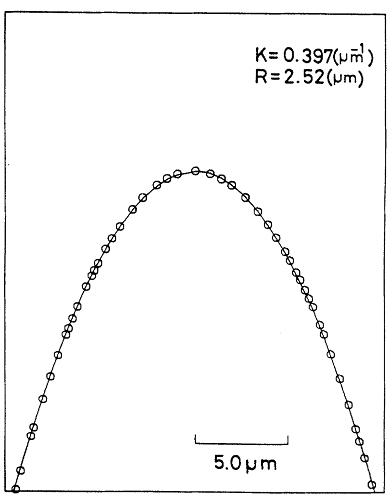

FIG. 3. The tip interface of the tip-stable type is a parabola which extends about 10 radii. The open circles are experimentally observed points, and the solid line is the best-fit parabola curve with the radius of curvature $R = 2.52$ μm. $K = 1/R$.

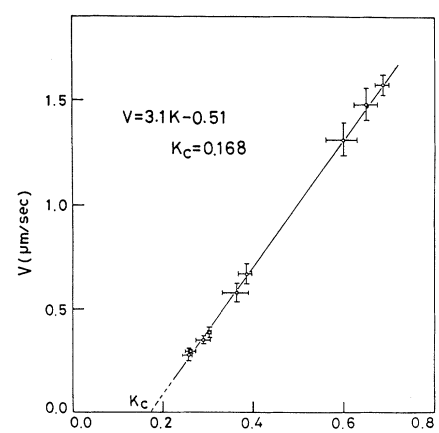

FIG. 4. The tip velocity of the tip-stable type increases linearly with the tip curvature. The temperature of the system was varied from 18.5 °C to 22.7 °C for this measurement, and the saturation temperature of the solution is 35.0 °C.

terface, independent of *d*, and this connection is hoped to be clarified in future.

In Fig. 2(c), we show a tip-splitting type. This type is observed in the case of much higher supersaturation than that in the case of Fig. 2(b) and in the transitional parameter region of the most preferred orientation from the ⟨100⟩ direction to the ⟨110⟩ direction in the system of NH_4Cl. This type is clearly caused by the interaction between the tip interface and the diffusion field out of the crystal. The protrusions from the ⟨100⟩ directional stem are growing to the ⟨110⟩ direction as side branches. However, because there is not enough supersaturation at the tip for both the stem and the side branches to grow together, the side branches stop growing in the ⟨110⟩ direction. The stem velocity is decelerated in this case and then it is gradually recovered. The tip splitting happens again after some time interval which depends on supersaturation. Eventually, a mode of a long wavelength among the side-branching mode of a short wavelength appears, and forms a regular pattern [Fig. 2(c)]. One can also observe various irregular tip-splitting modes at a further high supersaturation, which may be investigated systematically as a chaotic behavior on a dendritic crystal growth.

In summary, three distinctive types of two-dimensionally grown dendritic crystals were observed for the NH_4Cl solution system, as the supersaturation was increased. The tip velocity for the tip-stable type was found to increase linearly with the tip curvature, not in accord with the existing theory.

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