

Diffusion field around a dendrite growing under microgravity

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The Ivantsov diffusion field is tested for a free dendrite growing under microgravity. We made an *in situ* measurement of concentration distribution around the tip of a steady-state dendrite of NH_4Cl growing from an aqueous solution by means of interferometry, where the supersaturation was set by pressure control. The experimental data on the concentration diffusion field can be fitted very well by the Ivantsov solution with two parameters, the diffusion length and the supersaturation. The best fit values for the two show very good agreement with values independently estimated. This means that the tip is approximately at equilibrium, i.e., no sign of a kinetic effect is detected in the concentration at the tip.

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Dendritic crystal growth is one of the recent hot topics in the physics of nonlinear pattern formation [1–3]. The diffusion field around the tip of a free dendrite was given by Ivantsov [4], where the tip was a paraboloid of revolution moving with steady-state velocity v and the surface tension and surface kinetics were neglected. The Ivantsov theory gives a relation between the dimensionless supersaturation (or supercooling) Δ and the Péclet number p as

$$\Delta = pe^p E_1(p). \quad (1)$$

Here, it is defined that $p \equiv \rho v / 2D$ and $E_1(p) \equiv \int_p^\infty (e^{-s}/s) ds$, where ρ is the tip radius and D is the diffusion constant. Equation (1), which we call the Ivantsov equation, is considered to give a relation between v and ρ at a given Δ . Even if the surface tension and/or surface kinetics exist, the Ivantsov equation still approximately holds when their contributions to the concentration at the interface are much smaller than Δ . Although v and ρ are uniquely selected for a given Δ in real systems, an infinite number of combinations are allowed in the Ivantsov equation. Thus the recent central issue in the study of dendritic growth has been to find another relation which uniquely determines v and ρ coupled with the Ivantsov equation.

However, the Ivantsov equation has not yet been firmly established from the experimental point of view. Objections against its validity to a real system have risen from measurements of the concentration field by interferometry: Raz *et al.* [5] and Tanaka and Sano [6] reported that the concentration at the tip of an NH_4Cl dendrite growing from an aqueous solution significantly shifted from the equilibrium to the supersaturated side, which was attributed to the effect of the surface kinetics. This means that the Ivantsov equation does not hold at least for this system. Emsellem and Tabeling [7]

made a similar measurement for the growth of NH_4Br in solutions and in gels. They found a similar discrepancy in the concentration at the tip for growth in solutions, but good agreement with the Ivantsov theory for growth in gels; they strongly suggested the effect of convection for the solution growth. Thus the Ivantsov theory has never been confirmed for growth in liquid through the measurement of the diffusion field.

In this work, we test the validity of the Ivantsov theory for the diffusion field around an NH_4Cl free-dendrite growing from an aqueous solution under microgravity by means of interferometry, where buoyancy-driven convection is expected to be suppressed. For the purpose of quick operation during the short microgravity experiment, we apply our original growth method [8], i.e., the dynamic pressure-control method, where pressure is taken as an operation parameter of supersaturation based on the pressure dependence of the solubility.

Details of our experimental equipment and techniques are given elsewhere [8]. Here we describe important points for the present analysis and discussion. In our method, a specimen is enclosed in an inner cell, which is further enclosed in a pressure cell with optical windows. A space for crystal growth is a rectangular cylinder of 1.02 mm in thickness and $3 \times 7 \text{ mm}^2$ in cross section. A seed crystal glued at the tip of a needle (Pt–5% Au) is held at the center of the growth space. Figure 1 shows the geometry around the seed. The seed is a single crystal with dendritic shape and is so aligned that its cubic $\langle 100 \rangle$ directions are parallel to the rectangular observation frame. The branches of the NH_4Cl dendrite preferentially grow into those directions at low supersaturations. We define the directions z and x to be parallel to the growth directions of dendritic branches as indicated in Fig. 1, and y to be parallel to the optical axis. The exposed length of the

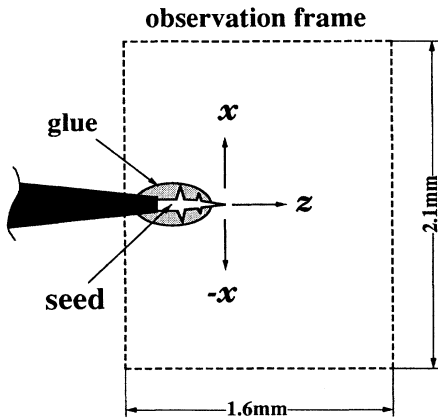


FIG. 1. Geometry around a seed crystal.

seed is about 0.1 mm and the centering accuracy of its tip along the optical axis is within ± 0.1 mm. In the present experiment, the distances from the boundaries of the growth space to the tips of the dendritic arms growing into the z and x directions are larger than the diffusion length, $l \equiv 2D/v$ (less than 0.4 mm, as shown below), which allows the free growth of the tips [5].

As the starting solution, 99.8% pure NH_4Cl (Merck, Suprapur) is dissolved into pure water which has been filtered through a $0.22 \mu\text{m}$ membrane filter after distillation and deionization. The concentration is set to be 27.98 wt % so as to be undersaturated at atmospheric pressure and our experimental temperature (26.2 ± 0.1 °C). Pressure is jumped up to 71.5 ± 0.1 MPa, which makes the solution supersaturated (the solubility of NH_4Cl in water decreases with pressure [9]). After a transient period of a few seconds, a condition of uniform supersaturation is established. Our microgravity experiment was performed in the small rocket TR-1A [10], where a microgravity level less than $10^{-4}G$ was obtained for 6 min.

In our experiment, the observation of crystal morphology and interferometry (wavelength, $\lambda = 680$ nm) of the solution are switched at 3-s intervals and recorded by a VCR. In this interferometer, fringes are formed for a phase difference of $\lambda/2$. Details of the optical configuration are reported in [8,11]. The direction of the fringes is set to be approximately perpendicular to the z direction in Fig. 1. Contour lines of integrated concentration (integrated through the thickness of the solution) for every $\lambda/2$ phase shift are obtained as moiré fringes by superimposing a reference fringe pattern over the fringe pattern concerned. Figure 2 shows an example of extracted moiré fringes for the growth under microgravity, which gives us an intuitive picture of the symmetry of the concentration distribution. For the purpose of quantitative analysis of the concentration profile, however, we directly measure shifts of interference fringes from their reference positions on digitized images (640×480 pixels, $3.39 \mu\text{m}/\text{pixel}$) of original interferograms. In the following analysis, we neglect the latent heat of crystallization and consider chemical-diffusion-limited growth at constant temperature based on much faster thermal diffusion than chemical diffusion [3].

In our method we can observe growth of three $\langle 100 \rangle$ main

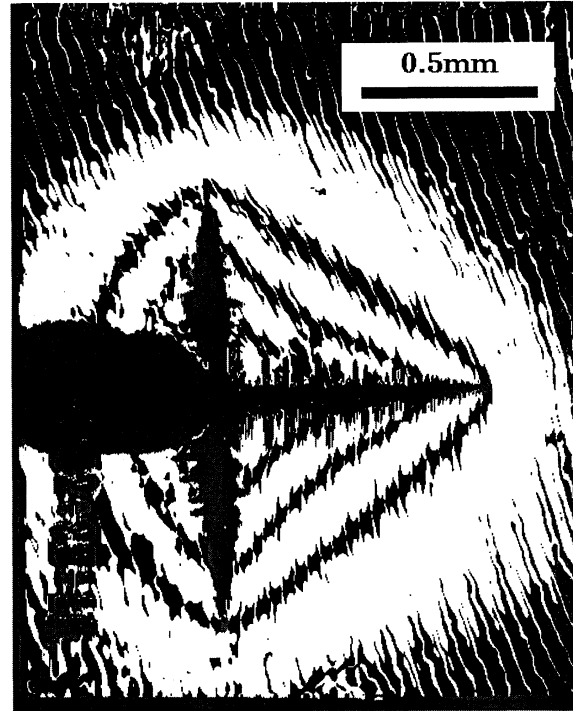


FIG. 2. A contour map for the integrated concentration around a dendrite growing under microgravity. The phase shift between neighboring contour lines is $\lambda/2$. The longitudinal streaks are vestiges of the original interferograms.

arms directed to z , x , and $-x$ as indicated in Fig. 1. Under microgravity these three arms grow approximately the same length, where the steady-state growth velocities of the tips coincide within $\pm 2\%$ difference, and the concentration distribution shows high symmetry, as seen in Fig. 2. On the other hand, a terrestrial experiment done under similar conditions shows remarkable differences: tip velocities highly depend on growth directions relative to the gravity vector and the concentration distribution is markedly deformed due to buoyancy-driven convection, which will be reported elsewhere.

For a quantitative test of the Ivantsov diffusion field, we analyze the concentration distribution ahead of the tip of the z arm for the growth under microgravity. We take the z axis as the central axis of the z arm, and fix the coordinate system to the cell. Figure 3 shows changes in positions of the tip and of forward fringes on the z axis, where the origin of time is taken at the instant of the pressure jump. The slope of the graph for the tip position gives its growth velocity, which reaches a steady-state value ($v = 12.62 \pm 0.10 \mu\text{m/s}$) in 30 s. The slower growth at the early stage must be caused by interaction with other arms of the dendrite. Shifts of fringes along the z axis, δz , give the integrated concentration, $I(z) \equiv \int_{-d/2}^{d/2} [u(\mathbf{r}) - \Delta]_{x=0} dy$, as

$$I(z) = -(\lambda/2a)(\delta z/w). \quad (2)$$

Here the definitions of the symbols are as follows: d is the thickness of the solution, 1.02 mm; $u(\mathbf{r}) \equiv [c(\mathbf{r}) - c_{\text{eq}}]/[c_s - c_{\text{eq}}]$, where $c(\mathbf{r})$ is the concentration measured by the

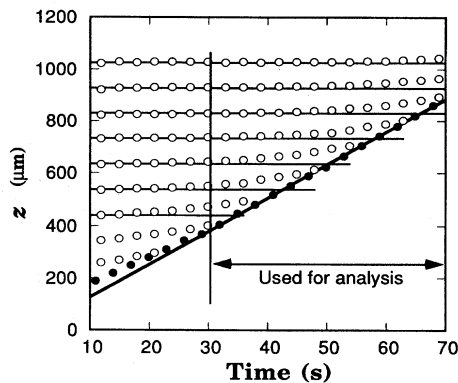


FIG. 3. Positions of interference fringes on the z axis (open circles) and the tip position (closed circles). Error bars are smaller than the symbols. The horizontal lines represent reference positions of fringes.

mass of solute per unit volume, c_{eq} is its equilibrium value, and c_s is the density of the crystal; $a \equiv \partial n / \partial u$ where n is the refractive index of solution; and w is the spacing of reference fringes. Using Eq. (2), we can calculate $I(z)$'s for the data between 30 and 70 s in Fig. 3. After converting z into the distance from the tip, \tilde{z} , we plot $I(\tilde{z})$'s in Fig. 4. Here we use $a = 0.219$ measured at 25 °C and atmospheric pressure, which is the same value as in [5]. If we assume the sensitivity of the interferometer is 0.1 fringes, the sensitivity in terms of the integrated concentration is $\Delta I = 0.16 \mu\text{m}$. In Fig. 4 the different symbols show different times, so that it is confirmed that the concentration profile, as well as the tip velocity, is independent of time, i.e., a steady-state growth is established.

According to the Ivantsov theory, the integrated concentration along the z axis is given as

$$I(\tilde{z}) = -b \int_{-d/2}^{d/2} E_1 \left(\frac{\sqrt{y^2 + \tilde{z}^2} + \tilde{z}}{l} \right) dy, \quad (3)$$

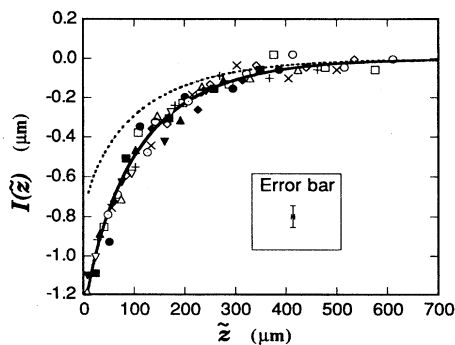


FIG. 4. Integrated concentration along the z axis obtained from the data in Fig. 3. Here \tilde{z} denotes the forward distance from the tip. The different symbols show different times. The error bars originate from ± 1 pixel error in digitized images. The solid line is the best fit of the Ivantsov solution, Eq. (3). The broken line shows concentration for the case that the tip deviates 500 μm from the center of the cell toward the y direction.

where $b \equiv \Delta / E_1(p)$. Strictly speaking, the origin of the coordinate system should be at the center of the curvature of the tip, but we can safely neglect the difference of ρ , the tip radius, as confirmed below. We fit the plotted data in Fig. 4 with Eq. (3) and obtain the best fit values for b and the diffusion length l as $b_{\text{fit}} = (2.08 \pm 0.17) \times 10^{-3}$ and $l_{\text{fit}} = 355 \pm 23 \mu\text{m}$, and, in addition, the supersaturation and the Péclet number are given from b_{fit} using the definition of b and Eq. (1) as $\Delta_{\text{fit}} = (1.17 \pm 0.08) \times 10^{-2}$ and $p_{\text{fit}} = (2.08 \pm 0.17) \times 10^{-3}$. Here the uncertainties represent 90% confidence levels due to statistical errors. In Fig. 4, the best fit line is shown by a solid line, which confirms that the measured concentration profile is qualitatively described by the Ivantsov diffusion field. Now we can make quantitative checks for l_{fit} and Δ_{fit} . The linear extrapolation of reported values [12] for the diffusion constant at 25 °C under atmospheric pressure gives $D = 2.28 \times 10^3 \mu\text{m}^2/\text{s}$ for our concentration. The pressure dependence of the diffusion constant has not been measured. But the dependence is not considered to be significant because the viscosity of water almost stays constant up to 100 MPa at room temperature [13]. For the tip growth velocity of the present experiment, this results in $l = 361 \mu\text{m}$, which agrees with l_{fit} very well.

It should be possible to evaluate the supersaturation from accurate solubility data. The available solubility data under pressure, however, are not accurate enough to evaluate such a small supersaturation as the present case. We therefore estimate it from our experiment itself. At the late stage of the crystal growth, the concentration around the base of the dendritic main arms reaches the equilibrium value independent of y . The fringe shift in this case is given by Eq. (2) with $I = -d\Delta$ as $(\delta z/w)_{\text{eq}} = 2ad\Delta/\lambda$. Since we got $(\delta z/w)_{\text{eq}} = 7.2 \pm 0.5$ in our experiment, the estimated value for Δ is $(1.10 \pm 0.08) \times 10^{-2}$, which also shows good agreement with the best fit value Δ_{fit} . This means that the Ivantsov equation approximately holds, at least, under our experimental condition. With l_{fit} and p_{fit} , we get a self-consistent tip radius $\rho = l_{\text{fit}} p_{\text{fit}} = 0.74 \mu\text{m}$, which is well below the spatial resolution limit of the present experiment. This justifies the above-mentioned neglect of ρ in the choice of the origin of the coordinate system.

The application of the Ivantsov theory to our experimental data has given consistent results. This means that the shape of the three-dimensional dendrite can be effectively regarded as a paraboloid of revolution, although its real shape seems to be largely deviating from it. Therefore the self-consistent tip radius might be different from the actual tip radius, which cannot be measured in the present experiment due to the limit of spatial resolution. This should be a crucial point in a more complete test of the theory.

The previous works [5,6] do not show consistent results with the Ivantsov theory. There seem to be two possible causes for the disagreement between them and this work other than convection. One is the difference in regimes of the supersaturation, Δ . Although values of Δ are not explicitly given in [5,6], they are comparable to and larger than our Δ , judging from their tip velocities. The kinetic effect should become relatively stronger at larger Δ . The other is the centering error of tip positions. If the actual tip position deviates from the center of the cell toward the y direction, the integrated concentration changes. It is possible to estimate the

effect of the centering error, Δy , by shifting the limits of integration in Eq. (3). In Fig. 4, we show a profile of the integrated concentration by a broken line for $\Delta y = 500 \mu\text{m}$, where b_{fit} and l_{fit} are used in the calculation. This condition corresponds to the case that the tip is near the bottom of the cell. The profile looks as if the concentration around the tip increased. This effect is negligible in our experiment ($\Delta y < 100 \mu\text{m}$), but can be significant in terrestrial experiments when crystals freely lie on the bottom.

It has been proposed that the so-called stability parameter, $\sigma \equiv 2Dd_0/v\rho^2$, plays an important role in the selection rule which uniquely determines v and ρ coupled with the Ivantsov equation. Here d_0 is the average capillary length over orientation. It is worthwhile to evaluate σ on the basis of the present result. Using the best fit parameters, it is given $\sigma/d_0 = 1/(l_{\text{fit}} p_{\text{fit}}^2) = 651 \mu\text{m}^{-1}$. We made a preliminary estimation of d_0 after [14] where the radius of a slowly shrinking small crystal was measured. As a result, we got $d_0 \approx 6.5 \times 10^{-5} \mu\text{m}$ and, therefore, $\sigma \approx 0.042$. According to [1], experimentally obtained values of σ for several materials are distributed from 0.017 to 0.081 (for $\text{NH}_4\text{Br-H}_2\text{O}$ [14]). Our value for σ sits in this regime. On the other hand, d_0 for $\text{NH}_4\text{Cl-H}_2\text{O}$ is also given in [6] as $1.59 \times 10^{-3} \mu\text{m}$, which is more than an order of magnitude larger than our value. This yields an extraordinary value for σ of 1.04. Measurements of d_0 might be sensitively affected by experimental

conditions. Additional, careful measurements of d_0 are required.

In conclusion, we made a free dendritic growth of NH_4Cl from an aqueous solution under microgravity, where the tip growth velocity and the concentration diffusion field were measured. We confirmed that the concentration profile in the solution ahead of the tip is well described by the Ivantsov diffusion field, and that the Ivantsov equation between the supersaturation and the Péclet number approximately holds. This means that the tip concentration is approximately equal to the equilibrium value, i.e., no sign of the kinetic effect is detected in the concentration at the tip.

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- [1] M. E. Glicksman and S. P. Marsh, in *Handbook of Crystal Growth*, edited by D. J. T. Hurle (Elsevier Science, Amsterdam, 1993), Vol. 1, Pt. b, p. 1077.
- [2] D. A. Kessler, J. Koplik, and H. Levine, *Adv. Phys.* **37**, 255 (1988).
- [3] J. S. Langer, *Rev. Mod. Phys.* **52**, 1 (1980).
- [4] G. P. Ivantsov, *Dokl. Akad. Nauk SSSR* **58**, 567 (1947).
- [5] E. Raz, S. G. Lipson, and E. Polturak, *Phys. Rev. A* **40**, 1088 (1989).
- [6] A. Tanaka and M. Sano, *J. Cryst. Growth* **125**, 59 (1992).
- [7] V. Emsellem and P. Tabeling, *Europhys. Lett.* **25**, 277 (1994).
- [8] T. Sawada *et al.*, *J. Cryst. Growth* (to be published).
- [9] S. Sawamura *et al.*, *High Pressure Res.* **11**, 347 (1994).
- [10] S. Yoda and H. Takei, *J. Jpn. Soc. Microgravity Appl.* **10**, 2 (1993).
- [11] K. Tsukamoto *et al.*, *J. Jpn. Soc. Microgravity Appl.* **11**, 58 (1994).
- [12] D. E. Gray, *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972).
- [13] K. E. Bett and J. B. Cappi, *Nature (London)* **207**, 620 (1965).
- [14] A. Dougherty and J. P. Gollub, *Phys. Rev. A* **38**, 3043 (1988).

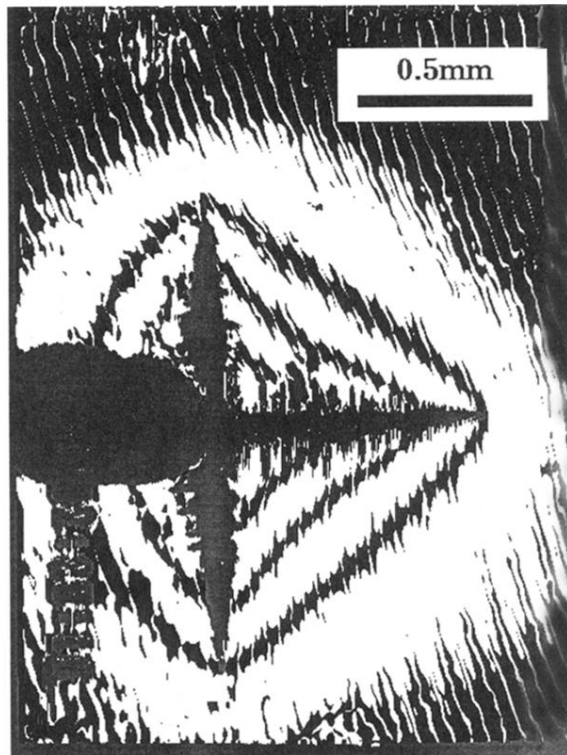


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