Theoretical Study of Growth Patterns of Snow Crystals

Etsuro YOKOYAMA* and Toshio KURODA

*Institute of Low Temperature Science, Hokkaido University,
Sapporo 060, Japan*

Abstract. When a crystal grows under a given growth conditions, its external form changes with time and a pattern is formed as a whole. As is well known, many beautiful patterns are formed in response to various growth conditions. We propose a model of pattern formation in the growth of snow crystals, that takes into account the surface kinetic process, for incorporation of water molecules into a crystal and the diffusion process, and produce various patterns such as circular patterns, hexagonal patterns and dendritic patterns starting from an initial circular crystal. We finally obtain a phase diagram showing a relation between growth patterns of snow crystals and growth conditions given by the dimensionless crystal size L relative to the mean free path of a water molecule in air and the supersaturation σ_∞ at $-15°C$.

1. Introduction

Growth forms of snow crystals remarkably depend on the growth conditions such as supersaturation and temperature. One should note furthermore, that each crystal changes its external form during growth under definite environmental conditions, namely pattern is formed. A spherical single ice crystal of the order of $1–10$ μm in radius is formed by freezing of a supercooled water droplet in cloud, then it grows into a hexagonal prism bounded by two basal $\{0001\}$- and six prism $\{10\bar{1}0\}$-faces by adsorbing supersaturated water vapor. The hexagonal prism develops further into various patterns, e.g., plate, column, dendrite, needle etc.,

---

* Present address: Department of Physics, Carnegie Mellon University, Pittsburg, PA 15213-3890, U.S.A.

according to the growth conditions in the cloud (Nakaya, 1954; Kobayashi, 1961; Kobayashi and Kuroda, 1987) as shown in Fig. 1.

    The purposes of this paper are to simulate the pattern formation in growth of snow crystals, controlled by a diffusion process for supplying the water molecules in air, toward the crystal surface and a surface kinetic process for incorporating them into crystal lattice, and to understand how these processes play roles in the pattern formation.

    We treat the formation of various patterns starting from a circular single ice crystal, perpendicular to c-axis at –15°C, which is a typical temperature for the development of dendritic pattern crystal. For the details of the simulation and the analysis of the produced patterns, reader may refer to the paper (Yokoyama and Kuroda, 1990).

    On the other hand, basic habit of snow crystals bounded by two basal and six prism faces changes with decreasing temperature: plates to columns at –4°C, columns to plates at –10°C and plates to columns at –22°C (Fig. 1). Kuroda and Lacmann (1982) proposed a new interpretation of the habit change based on a viewpoint of surface melting and surface roughening which are expected to occur on basal and prism faces of ice crystals at different temperatures respectively. After
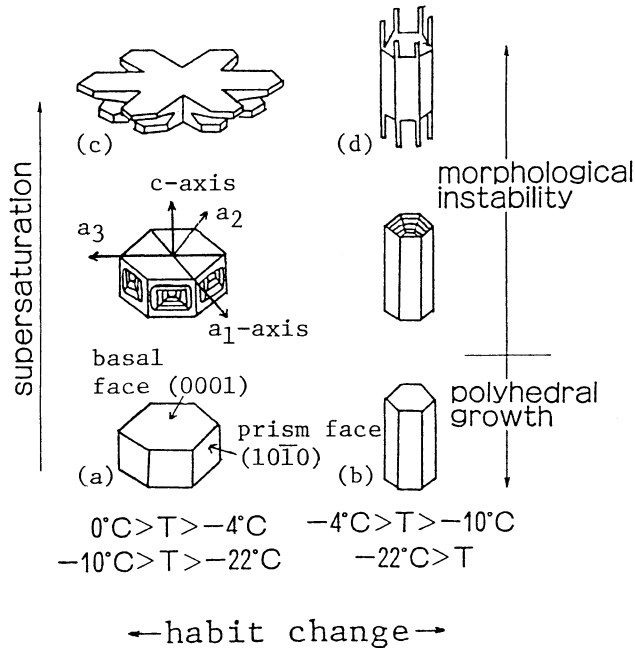

Fig. 1. Schematic representation of variation of growth patterns of snow crystals with growth conditions.

the proposal, ellipsometric study of the surface structure of ice has been carried out by Furukawa *et al.* (1987), and it was found that surface melting occurs at −2°C on basal face and at −4°C on prism face. The measured temperature dependences of the thickness of quasi-liquid layer for each surface which was produced by surface melting are qualitatively in good agreement with theoretical predictions by Kuroda and Lacmann (1982). However, the measured transition temperatures of surface melting are higher than those assigned for interpretation of the habit change. Thus, the habit change of snow crystals should be theoretically pursued further.

2. Model and Simulation of Pattern Formation by Means of Boundary Element Method (Yokoyama and Kuroda, 1988, 1990)

The growth rate V_k determined by a surface kinetic process in the direction normal to the surface is given by

$$V_k = \beta(\theta, \sigma_s)\sigma_s,$$ (1)

where σ_s is the surface supersaturation and $\beta(\theta, \sigma_s)$ is the kinetic coefficient depending on a rotation angle θ around c-axis of hexagonal ice crystal and σ_s. The kinetic coefficient $\beta(\theta, \sigma_s)$ has six minima at $0°$, $\pm60°$, $\pm120°$, $180°$ corresponding to six prism faces, i.e., singular surfaces. If the minima are deep enough, anisotropy of growth rate is so strong that prism facets develop their area during growth. We consider only the spiral growth occurs with the aid of screw dislocations. Furthermore, the steps are supplied from screw dislocations emerging at the center of six prism faces until a circular crystal develops into a perfect hexagon, and they are generated at its corners where the supersaturation is largest, once a perfect hexagon has been developed.

It is to be noted that anisotropy of $\beta(\theta, \sigma_s)$ is weakened and the area of facets decreases with increasing σ_s which is controlled by the diffusion process and the surface kinetic process.

On the other hand, the growth rate V_k determined by the surface kinetic process should be equal to the growth rate V_d determined by the volume diffusion process under steady state conditions (Seeger, 1953; Kuroda *et al.*, 1977).

The supersaturation σ in the region surrounding a crystal is governed by the diffusion equation

$$\Delta\sigma = 0$$ (2)

subject to the boundary conditions: the supersaturation is specified by

$$\sigma = \sigma_\infty$$ (3)

on the boundary Γ_1 which is far from the crystal, and the mass conservation conditions mentioned above, i.e.

$$V_k = V_d \tag{4}$$

is required on the boundary Γ_2 representing the crystal surface.

We solve the problem by the boundary element method as follows. At first, we obtain the boundary integral equation from Eq. (2). Using Green's theorem and boundary conditions:

$$\sigma_{si} / 2 + \int_{\text{along}\Gamma_2} \left[q^* + \sigma^* \frac{kT\beta(\theta, \sigma_s)}{v_c p_e D} \right] \sigma_s d\Gamma = \int_{\text{along}\Gamma_1} \left(q_\infty \sigma^* - \sigma_\infty q^* \right) d\Gamma, \tag{5}$$

where σ_{si} is the supersaturation at a point i on Γ_2, q_∞ the normal gradient of supersaturation on Γ_1, σ^* satisfies $\Delta\sigma^* + \delta_i = 0$ (δ_i: the Dirac delta function at a point i), q^* is $\partial\sigma^*/\partial n$, D the diffusion coefficient of water vapor, v_c the volume of a molecule in crystal and p_e the saturated vapor pressure of crystal. Then, we change the Eq. (5) to the algebraic equations with respect to σ_s under the assumption that Γ_1 is far from Γ_2. By solving the algebraic equations, we obtain σ_s, consequently the growth rate $V (= V_k = V_d)$ at each position on the surface at a certain moment and then determine a shape of the growing surface after Δt second.

3. Results

The important numerical values used for the simulation are as follows: T = 258. 15 K (= −15°C), step energy $\kappa = 2.0 \times 10^{-6}$ erg/cm, mean surface diffusion distance $x_s = 400\,d$, step height or lattice constant $d = 4.5 \times 10^{-8}$ cm and radius of initial crystal $r_{co} = 5 \times 10^{-3}$ cm.

Figure 2 shows an example for small value of diffusion coefficient $D = 0.2$ cm^2/s of water molecule in air (corresponding to 1 atm, i.e., 1.01325×10^5 Pa) and low supersaturation $\sigma_\infty = 8.5\%$ at the position far from the crystal. An initial circular crystal becomes a perfect hexagon at 1200 s, since anisotropy of kinetic coefficient $\beta(\theta, \sigma_s)$ is large because of small supersaturation σ_s at the crystal surface for given D and σ_∞. The supersaturation along the hexagon is not uniform, i.e., $\sigma_s = 0.7\%$ at its corners and $\sigma_s = 0.6\%$ at the center of each flat surface at 1200 s. In spite of the non-uniformity, the crystal can continue to grow retaining its polygonal shape by following compensation mechanism (Chernov, 1974): The steps nucleated at corners slow down as they approach the center of the surface because of a decrease in local supersaturation and consequently the step density increases near the center. Since an increase in the density of the steps at which the molecules are incorporated into the crystal causes a larger kinetic coefficient $\beta(\theta, \sigma_s)$, the growth
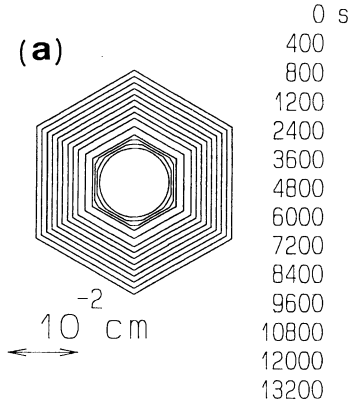
(a)

0 s
400
800
1200
2400
3600
4800
6000
7200
8400
9600
10800
12000
13200

10^{-2} cm

Fig. 2. Development of prism faces, i.e., hexagonal pattern for $D = 0.2$ cm^2/s(corresponding to 1 atm) and $\sigma_\infty = 8.5\%$ (after Yokoyama and Kuroda, 1990.)

rate V_k can be constant over the whole surface. Namely, the stabilizing factor of a polygonal crystal is the variation of the local kinetic coefficient by adjustment of step distribution, while the destabilizing factor is the non-uniformity in super-saturation over the surface which is caused by the diffusion processes.

Figures 3 and 4 represent examples of dendritic pattern for larger supersatu-rations σ_∞ and the same small D as the Fig. 2. When an initial circular crystal has become a perfect hexagon in Fig. 3, the growth rate at the corners is larger than that at the center of the surface, because of too large non-uniformity in surface supersaturation ($\sigma_s = 2.9\%$ at the corner and $\sigma_s = 2.0\%$ at the center), which cannot be compensated by step adjustment, and consequently preferred growth at the corners begins. This is onset of transition from a hexagonal to a dendritic pattern. Furthermore, the dendritic pattern becomes more remarkable for much larger $\sigma_\infty =$
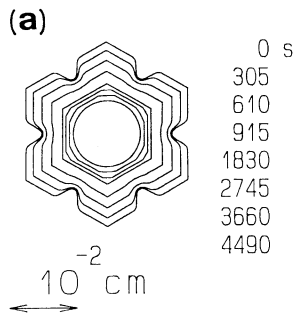
(a)

0 s
305
610
915
1830
2745
3660
4490

10^{-2} cm

Fig. 3. Dendritic pattern for $D = 0.2$ cm^2/s and $\sigma_\infty = 17\%$ (after Yokoyama and Kuroda, 1990).

10^{-2} cm

	0 s
	760
	1520
	2280
	3040
	3800
	4560
	5320
	6080
	6840
	7600
	8360
	9120
	9880
	10640
	11400
	12160
	12920
	13680

(a)
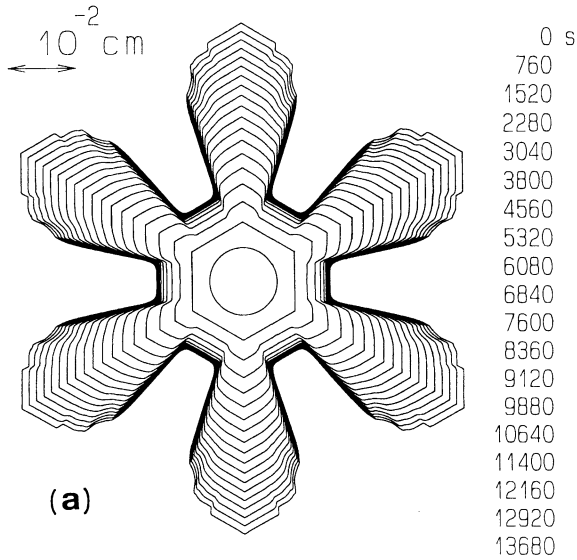
Fig. 4. Dendritic pattern for $D = 0.2$ cm^2/s and $\sigma_\infty = 34\%$ (after Yokoyama and Kuroda, 1990).

(a)

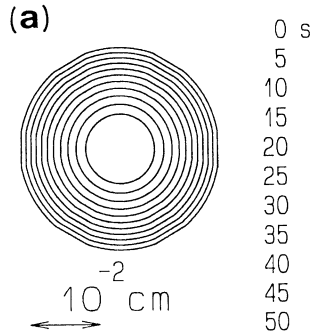|	0 s
	5
	10
	15
	20
	25
	30
	35
	40
	45
	50

10^{-2} cm

Fig. 5. Circular pattern due to kinetic roughening for $D = 40$ cm^2/s (corresponding to 500 Pa of air pressure) and $\sigma_\infty = 17\%$ (after Yokoyama and Kuroda, 1990).

34% as shown in Fig. 4. It should be noticed that six primary branches have periodic structure at the tips which is caused by bunching of monomolecular steps. Such bunches may play a role in the formation of secondary branches, because super-saturation has local maximum at the bunches.

On the other hand, an initial circular crystal cannot develop into a hexagon for

large $D = 40$ cm²/s (corresponding to 500 Pa of air pressure, i.e., about 5×10^{-3} atm) and large $\sigma_\infty = 17\%$ (Fig. 5). The surface supersaturation does not drop largely ($\sigma_s = 14\%$ at 0 s) from σ_∞ because of easy supply of molecules at larger D, so that
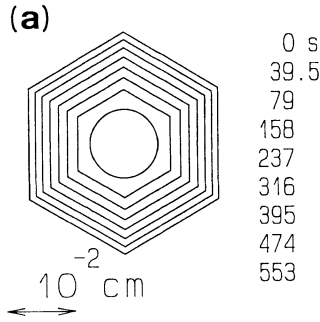
(a)

```
0 s
39.5
79
158
237
316
395
474
553
```

10^{-2} cm

Fig. 6. Hexagonal pattern for $D = 40$ cm²/s and $\sigma_\infty = 3.5\%$ (after Yokoyama and Kuroda, 1990).
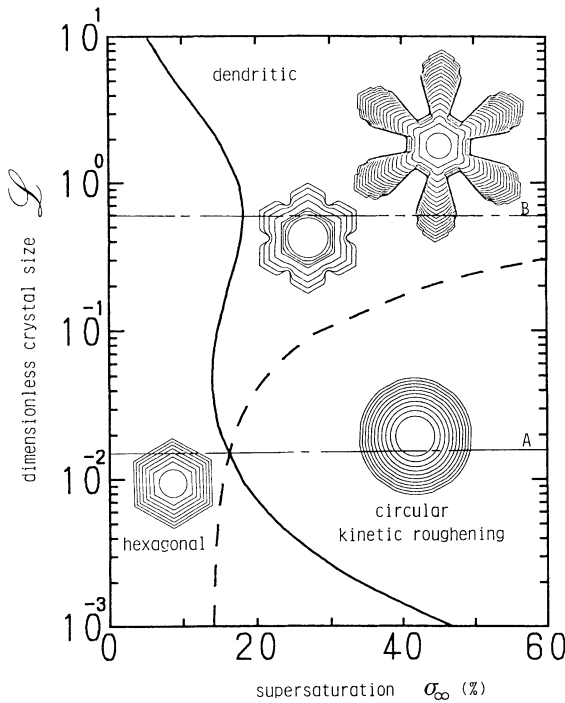
Fig. 7. Diagram showing the relation between the patterns and growth conditions (σ_∞, L) (after Yokoyama and Kuroda, 1990).

anisotropy of the kinetic coefficient vanishes. We call a vanishment of growth rate anisotropy due to such kinetic reason the kinetic roughening (Yokoyama and Kuroda, 1988, 1990). If supersaturation σ_∞ is very small (e.g. 3.5%), however, the anisotropy is so large even at larger D, that an initial circular crystal becomes a perfect hexagon within 79 s, and then the crystal grows retaining its flat surface (Fig. 6).

We analyzed the patterns produced by the simulation i.e., circular pattern, hexagonal pattern and dendritic pattern, and found for the first that the dimensionless crystal size $\mathcal{L}$ relative to the mean free path of a water molecule in air plays an important role in the pattern formation of growing snow crystals (Yokoyama and Kuroda, 1990). Figure 7 is the phase diagram showing a relation between growth patterns of snow crystals and growth conditions given by σ_∞ and $\mathcal{L}$ at $-15°C$.

REFERENCES

Chernov, A. A. (1974), Stability of faceted shapes, J. Cryst. Growth, **24/25**, 11–31.

Furukawa, Y., Yamamoto, M., and Kuroda, T. (1987), Ellipsometric study of the transition layer at the surface of an ice crystal, J. Crystal Growth, **82**, 665–677.

Kobayashi, T. (1961), The growth of snow crystals at low supersaturation, Phil. Mag., **6**, 1363–1370.

Kobayashi, T. and Kuroda, T. (1987), Snow crystals, Morphology of Crystals Part B, edited by I. Sunagawa, p. 645–743 (Terra Sci. Pub. Co.).

Kuroda, T., Irisawa, T., and Ookawa, A. (1977), Growth of polyhedral crystal from solution and its morphological stability, J. Cryst. Growth, **42**, 41–46.

Nakaya, U. (1954), Snow Crystals-Natural and Artificial (Harvard Univ. Pr.).

Seeger, A. (1953), Diffusion problems associated with the growth of crystals from dilute solution, Phil. Mag., **44**, 1–13.

Yokoyama, E. and Kuroda, T. (1988), Pattern formation of snow crystals—Development of facets by means of boundary element method, Dynamics of Ordering Processes in Condensed Matter, edited by S. Komura and H. Furukawa, p. 95–100 (Plenum Publ. Corp.).

Yokoyama, E. and Kuroda, T. (1990), Pattern formation in growth of snow crystals occuring in the surface kinetic process and the diffusion process, Phys. Rev., **A41**, 2038–2049.