

## Growth Forms of Snow Crystals

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Snow crystals, i.e. ice crystals grown from the vapour phase show a remarkable variation of growth forms with growth conditions like temperature and supersaturation. In this paper, we shall interpret the habit change and morphological instability of snow crystals on the basis of crystal growth processes.

### INTRODUCTION

It is well known that growth forms of snow crystals, i.e. ice crystals grown from the vapour phase, sensitively depend on growth conditions (Nakaya:1954, Hallett & Mason:1958, Kobayashi:1961). Nakaya called the snow crystals "letter from the sky", since their various forms include the meteorological information from the inside of clouds.

Fig.1 is a schematical diagram representing the relation between growth forms and growth conditions which is based on a Kobayashi's diagram(1961). Firstly it shows that basic habit changes three times with decreasing temperature: at  $-4^{\circ}\text{C}$  from plate to column, at  $-10^{\circ}\text{C}$  from column to plate and at  $-22^{\circ}\text{C}$  from plate to column. Secondly it shows that increasing supersaturation causes transitions from very thick plates to skeletal plates to dendrites, or from solid prismatic columns to hollow prisms to needles. In other words, the surfaces of the polyhedral ice crystals become morphologically unstable by way of preferred growth of edges and corners of the crystals with increasing supersaturation.

In spite of many experimental studies, mechanisms of such remarkable change in growth forms had been theoretically unclarified. However, during the last five years, progress has been made in understanding the surface structure, surface growth kinetics, habit change and morphological instability of snow crystals. In this paper, only essential ideas of the recent theoretical studies are briefly surveyed. For the details, the reader may refer to the papers (Kuroda & Lacmann:1982, Kuroda:1983).

HABIT CHANGE

The basic habit of snow crystals bounded by two basal {0001} and six prism {1010} faces changes with decreasing temperature as shown in Fig.1. When we consider the growth of snow crystals, we should notice that the growth temperature of snow crystals is very high, since it is not far below the melting point 0°C of ice. Therefore, Kuroda and Lacmann(1982) theoretically investigated the dependence on temperature T of the structure of basal and prism surfaces of ice as well as their growth mechanisms, and proposed a new interpretation of habit change of snow crystals.

The results are as follows(Fig.2): The surface is covered with a quasi liquid layer just below 0°C, whose thickness  $\delta$  and coverage  $\mathfrak{J}$  ( $>1$ ) decreases with decreasing temperature and becomes equal to the thickness of the monolayer ( $\mathfrak{J} = 1$ ) at a transition temperature  $T_{I/II}$ . The surface at temperatures  $T < T_{I/II}$  may be rough on a molecular level because of adsorption of water molecules themselves with coverage  $\mathfrak{J} < 1$ . The number of adsorbed molecules decreases with decreasing temperature and becomes very small, e.g.  $\mathfrak{J} < 0.02$  at the next transition temperature  $T_{II/III}$ . The surface at temperatures  $T < T_{II/III}$  is molecularly smooth as assumed in previous theories of crystal growth from vapour [Burton, Cabrera and Frank:1951]. The growth mechanism, i.e. the way how the molecules are incorporated into crystal lattice at the surface, depends on the surface structure. Therefore, three growth mechanisms take place on one surface with decreasing temperature (Fig.2):

- I) Vapour-Quasi liquid-Solid growth mechanism on the surface covered with a quasi liquid layer ( $0^\circ\text{C} > T > T_{I/II}$ ;  $\mathfrak{J} > 1$ ),
- II) Adhesive growth mechanism on the rough surface ( $T_{I/II} > T > T_{II/III}$ ;  $1 > \mathfrak{J} > 0.02$ ) and
- III) Two-dimensional nucleation growth mechanism on the smooth surface ( $T_{II/III} > T$ ;  $0.02 > \mathfrak{J}$ ).

It was shown that two transition temperatures  $T_{I/II}$  and  $T_{II/III}$  were lower for prism {1010} faces than for basal {0001} faces respectively. If we assign  $T_{I/II}$  (0001) = -4°C,  $T_{I/II}$  (1010) = -10°C,  $T_{II/III}$  (0001) = -10°C and  $T_{II/III}$  (1010) = -20°C, we can divide the temperature range into four parts according to the combination of growth mechanisms of {0001} and {1010} faces (Fig.2). The complicated habit change is caused mainly by this change in combination of growth mechanisms with temperature.

After this proposal, ellipsometric study of the quasi liquid layer on ice basal and prism faces has

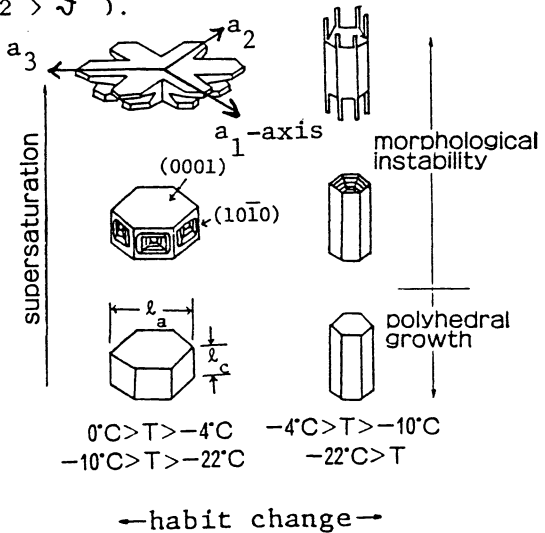


Fig.1 Growth forms depending on temperature and supersaturation.

been carried out (Yamamoto et al:1984, Furukawa et al:1985). By ellipsometry, we can determine the values of refractive index and the thickness of a transition layer on a crystal surface (Azzam and Bashara:1977). It was found that the transition layer appeared at temperatures not far below 0°C as temperature approached 0°C. The measured refractive indices of the transition layers on basal and prism faces were 1.330 being very close to the value 1.3327 of bulk water at 0°C, while the refractive index of ice is 1.307. It means that the transition layers on ice surfaces can be regarded as quasi liquid layer. The temperature dependence of the thickness of the quasi liquid layer showed the difference between basal and prism faces. The results are qualitatively in a good agreement with the theoretical predictions by Kuroda and Lacmann (1982). The details will be discussed elsewhere.

MORPHOLOGICAL INSTABILITY

Polyhedral snow crystals can grow in a stable way retaining their habit, plate or column, at low supersaturations. With increasing supersaturation, however, the morphological instability of the polyhedral crystals occurs by way of the preferred growth of edges and corners.

In order to pursue this morphological instability, we must self-consistently solve three-dimensional diffusion field surrounding a polyhedral crystal and growth kinetics at the surface over which the supersaturation is not uniform: it is largest at the corners and smallest at the center of the surface (Seeger:1953, Chernov:1974, Kuroda et al:1977). From the standpoint of the surface growth kinetics, the excess supersaturation at corners is the destabilizing factor of the polyhedral morphology of the crystals. On the other hand, the stabilizing factor is the variation of the local kinetic coefficient, i.e. growth rate per unit supersaturation, by adjustment of the step distribution (Chernov: 1974).

Frank (1974; 1982) qualitatively discussed the formation mechanism of the three-dimensional external shape of snow crystals by propagation of the steps nucleated at crystal corners towards the facet centre. Kuroda, Irisawa and Ookawa (1977) quantitatively investigated the stability limit of cube crystal growing from the solution as a function of supersaturation at infi-

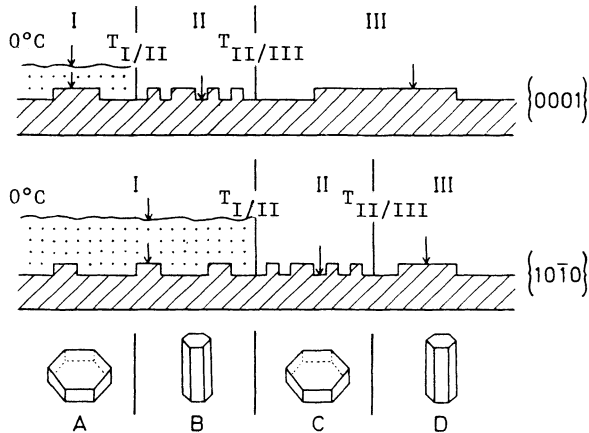


Fig. 2. Schematic representation of the combination of growth kinetics of {0001} and {10 $\bar{1}$ 0} faces depending on temperature. (after Kuroda and Lacmann:1982).

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nity from the crystal and the side length of the cube crystal. Then, Kuroda(1983) discussed the factors other than supersaturation and crystal size that effect the morphological instability of polyhedral crystals, e.g. diffusion constant, thermal diffusivity and so on.

It should be noticed that the morphological instability of the polyhedral crystals bounded by smooth surface in the case of vapour or solution growth from the Mullins-Sekerka instability (Langer:1980) for rough crystal/melt interface.

In the latter problem, the destabilizing factor is supercooling in the melt, while the stabilizing factor is decrease in melting temperature associated with interfacial tension and interface curvature. For an example, Fig.3 shows the morphological instability of an ice crystal growing from the slightly supercooled water (Arakawa and Higuchi:1952). The external shape of the snow dendrite growing from vapour (Fig.1) is similar to that of ice dendrites growing from the melt (Fig.3) in the sense that the primary branches of the dendrites grow along a-axes in both cases. However, the reason for the definite orientation of the former dendrites is quite different from that of the latter dendrites. The primary branches of the snow dendrites are necessarily oriented to the directions which bisect an angle between neighbouring prism faces, i.e. a-axis, since the morphological instability of the hexagonal prism shaped crystal is caused by an excess supersaturation along edges where the neighbouring prism faces intersect. On the other hand, the orientation of the ice dendrites growing from the supercooled water is attributable to the anisotropy of the interfacial tension between ice and water (Kuroda:1986).

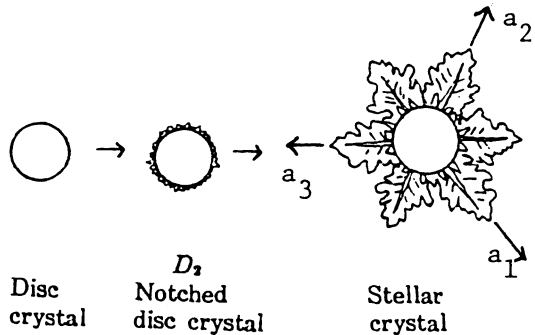


Fig.3 Morphological instability of an ice crystals growing from supercooled water (after Arakawa and Higuchi:1951).

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2-1

Q: What is the difference between "quasi-liquid" and "liquid"?  
(J. Beddow)

A: If the thickness of the quasi-liquid layer is very large, it is the same as the bulk liquid. However, the structure or the properties of very thin quasi-liquid layer would be different from that of bulk liquid because of the influence of ice substrate. Therefore, the layer on crystal surface is called quasi-liquid layer.

Q: Can you measure the density of the quasi-liquid phase? Is it higher than that of ice?  
(M. Toda)

A: We have not directly measured the density of the quasi-liquid layer. However, we found by ellipsometry that the refractive indices of the quasi-liquid layer on basal and prism faces

were 1.330 very close to that of bulk water (1.332 at 0 C). On the other hand, the refractive index of ice is 1.307. This relation means that the density of the quasi-liquid layer is larger than that of ice.

Direct measurement may be possible by means of X-ray diffraction.

Q: Is the quasi-liquid layer a special effect on the ice crystals? Can you see the same effect for the other crystals near the melting point? (M. Matsushita)

A: Yes, for an example, the quasi-liquid layer promotes the growth of ice crystals from the vapour, because the edge energy of a two-dimensional nucleus at the quasi-liquid / ice interface is much smaller than that on the surface without quasi-liquid layer. Since the surface melting can occur also for other crystals, the same effect is expected for them.