INITIAL STAGES OF MORPHOLOGICAL INSTABILITY OF VAPOUR GROWN ICE CRYSTALS

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Abstract. Initial stages of the appearance of morphological instability of ice crystals are investigated by means of replica techniques and SEM. The different kinds of instability are classified according to their appearance on different crystal faces as well as to their mode of formation. It is established that crystals with rounded edges can also develop morphological instability. A mechanism is proposed for explanation of this phenomenon. The formation of dendrite instability begins below $-10^\circ$ C while the other kind of instability is observed in the whole temperature interval investigated. The results of this morphological study are considered from the point of view of the theory of morphological instability of crystals with polygonal growth forms.

1. Introduction

Ice is among the most suitable substances for the experimental study of the problem of morphological instability. A great variety is the main reason for its unstable forms. This diversity was first demonstrated in the excellent and detailed investigations of Nakaya$^1$ and his school. His studies greatly contributed to our present knowledge of ice forming processes in the atmosphere.

All geometrical characteristics of the complex shape of the snowflakes can be observed separately only at the early stages of morphological instability. Thus, the initial stages are of the highest significance for comparison of theory with experimental results, as available theories deal with these stages or more specifically with the transition from stable to unstable growth. Hence, in any experiment aimed at a comparison with theory one should investigate precisely the early stages of morphological instability.

A number of isolated experimental studies$^2$-$^4$ of the initial stages of morphological instability of ice have been conducted so far. This paper is an
attempt for a more systematic investigation of the initial stages of growth instability of ice crystals in order to compare theory with experiment.

2. **Experimental**

Ice crystals in free fall were nucleated and grown in a 50-liter fog chamber. A supercooled fog was created by condensation of water vapours. The freezing of the fog droplets was initiated by shock wave produced via breaking a paper membrane by means of a small pump with a piston. In about 5 to 7 seconds numerous free growing ice crystals were observed by light reflections under suitable illumination. After about 10 minutes they began to disappear as a result of evaporation. The technique developed by Schaefer\(^5\) was used to prepare formvar replicas from the freely falling crystals during the first minute of the described procedure. Thus, the initial stages of the development of morphological instability were fixed. The replicas were metallized with Au by vacuum evaporation and observed by SEM JEOL T-200.

The advantage of this method is possibility for simultaneous creation of a large number of ice crystals without using ice forming nuclei or a substrate. The temperature was maintained from \(-3\) to \(-26^\circ C\) with an accuracy of \(\pm 1^\circ C\). The supersaturation was not strictly controlled and was estimated by means of a hygrometer.

3. **Results and Discussion**

In order to investigate the early stages of morphological instability one needs to study the crystals formed just after freezing of the fog. The supersaturation changes rapidly during this period, due to the freezing of the majority of the water drops. Thus, it is impossible to measure precisely the supersaturation when working in a fog chamber.

The smallest observed crystals in our experiments were of the order of water drops (approximately in 10 microns diameter) making up. Crystals under about 20 microns are morphologically stable (Plate 1, Plate 2(a), (c), (e), Plate 3(a), Plate 4(a)). Their initial size was determined by size of the frozen droplets. Hence, the order of the critical size for the appearance of instability was hard to establish. Moreover, in order to see this instability experimentally a sufficient quantity of ice should crystallize from the vapours. Hence, the minimum crystal size for the appearance of instability is somewhat larger than the drop size. For this reason, the size of about 20 microns should be considered as an upper limit. This limit is considerably lower than the expected one according to the theory of instability of polygonal crystals\(^6\)\(^{10}\) as well as that given by Fletcher.\(^10\)

Free falling crystals lay down on the formvar layer with the most
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Plate 3.
developed face. As a result plate-like crystals were replicated as hexagons (Plate 3(a)) and column-like crystals as rectangles (Plate 4(a)).

The observed crystal habit changes with temperature according to the four regions of the Nakaya-Kobayashi diagram\(^1\) which is seen on the corresponding Plates.\(^1\)\(^-\)\(^4\) The transition temperatures between the different regions in the diagram were found to be 1 to 2°C higher than those established in literature. This deviation gives the accuracy of the temperature measurement in our experiments and probably is due to the slight vertical temperature gradient in our chamber. Possibly for this reason crystals falling on the formvar are formed at a slightly higher temperature.

At present the highest temperature region I (Plate 1) in the diagram remains insufficiently investigated in our experiments because of difficulties in replica preparation near the melting point. The preliminary results obtained at the highest temperatures showed a considerable rounding of the edges of the plate-like crystals admixed with column-like ones (Plate 1). This fact is in agreement with our previous optical microscope investigations\(^2\) on the progressive rounding on ice grown in vacuum, as well as with the results of Keller et al.\(^3\) The appearance of rounded (nonsingular) surfaces in case of ice near the melting point has been considered by us as an effect of surface roughening.

The main type of morphological instability which is observed in both sharp or rounded edge crystals is manifested as a retardation in the advancement of the central part of the crystal face during growth (Plate 2(b), (d), Plate 3(b), (d)). In region II (Plate 2) and III (Plate 3) of the Nakaya-Kobayashi diagram (region I is insufficiently investigated) the initial stage of the appearance of instability can be seen on the faster growing face\(^4\) (the prismatic face in the case of plate-like crystals (Plate 3(b), (d)) and the basal one in the case of column-like ones (Plate 2(b), (d), (f)).

In the low temperature region IV (Plate 4) in our experiments such distinctions could not be made. In this case the crystals are often replicated either with a disturbed morphological stability on both faces—prismatic and basal (Plate 4(f)) or separately (Plate 4(c), (d)) without any order. An appearance of instability of the faster growing face in this region (at \(-30°C\) was described by Gonda and Koike.\(^5\)

One can divide this type of instability into two cases depending on whether it appears on initially sharp or rounded edge crystals. The basis for this distinction is the assumption for a possible difference in the mechanisms of development of instability. The instability of polygonal crystals with sharp edges has been repeatedly discussed in literature from a theoretical point of view. However, the case of polygonal crystals with strongly rounded edges has not yet been investigated theoretically. It is clear that one can hardly speak about inhomogeneity of the supersaturation at the surface of such small crystals with rounded edges. It is difficult to imagine that the rounded edge
becomes a source of steps as well. From a morphological point of view such a distinction should be understood conditionally, since the rounding of the edges of isometric crystals with increasing temperature is changed gradually as was shown in our previous investigations.\textsuperscript{12} The morphological data do not support the assumption for two different mechanisms disturbing the morphological stability in both cases.

At lower temperatures below $-10^\circ$C (regions III and IV) another type of instability appears. It consists of thin dendrite branches formed out of the sharpened corners of the crystals (Plate 3(c), (e), Plate 4(h)). This type of instability can be observed both combined with the previous one or independently. In our experiments transition forms between these two kinds of instability were not observed. For this reason we suppose that a different mechanism can be responsible for this type of instability. The morphological difference between both kinds is a growth retardation in the middle of the face in the first case and a preferential growth of a narrow region around the corners at the second one. The second kind instability is quite analogous to that characteristic for the whisker formation. Similar morphological picture was observed in the case of whisker formation on the corners of urotropine crystals grown from hexadecane solution.\textsuperscript{15} In the case of ice both kinds of instability coexist below $-10^\circ$C. Thus the different supersaturation can be a possible reason for the appearance of the first or the second one. Unfortunately, in our experiments the supersaturation could not be controlled.

A possible explanation of the observed instability of crystals with rounded regions (Plate 2) can be proposed. Kuroda \textit{et al.}\textsuperscript{8,9} introduced in the theory of instability of polygonal crystals the surface diffusion as an additional stabilizing factor equilizing the inhomogeneity of supersaturation above a flat face. Independently, the surface diffusion flow of a slow growing neighbour face can lead to the preferential growth of the region around the edge provided the initial stage of instability is manifested on the faster growing face. Thus, it is clear that surface diffusion on the slow growing neighbour face can play the role of a destabilizing factor. The material transport to the edge is analogous to that in the case of whisker formation investigated by Dittmar and Neumann.\textsuperscript{14} Due to the lower growth rate of some faces the molecules from the vapour phase are transported along the surface instead of being incorporated. The rounded surface of the region between slow and fast growing faces serves as a drain for the molecular flow. In cases when this flow can not be disturbed homogeneously on the fast growing face it causes the preferential growth around the rounded edge. Thus, the surface diffusion on the slow growing face is a destabilizing factor.

The detailed investigation on the later stages of crystal growth instabilities shows a complicated morphology (Plate 3(f), Plate 5) which is very interesting from the point of development of instabilities. We hope to continue this line of investigations in a subsequent paper.
Plate 5.
REFERENCES