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GROWTH OF ICE CRYSTALS FROM THE VAPOUR PHASE.
INTERACTION OF BASAL AND PRISM FACES THROUGH THE DIFFUSION PROCESS
AND THE SURFACE KINETIC PROCESS

E. YOKOYAMA and T. KURODA
The Institute of Low Temperature Sciences, Hokkaido University.
Sapporo 060, Japan

Abstract - The following two processes are relevant to the growth of ice crystals from the vapour phase: i) diffusion process of water molecules, ii) surface kinetic process for incorporating the molecules into crystal lattice. The purpose of the present study is to investigate the interaction of basal and prism faces from various points of view by taking into account both processes self-consistently. The obtained results are as follows: (1) The growth rate of prism face decreases with increasing axial ratio c/b, i.e. increasing area of prism face, under the condition of constant periphery length of a crystal. On the other hand, the growth rate of basal face increases, since both faces scramble for water molecules in air. (2) The interaction of both faces decreases with increasing diffusion constant. (3) The mass growth rate is almost independent of the axial ratio for a constant periphery length of a crystal and for various diffusion constant.

1. Introduction

The following two processes are relevant to the growth of ice crystals from the vapour phase: i) Diffusion process of water molecules towards crystal surface, ii) Surface kinetic process for incorporating the molecules into crystal lattice. The latter process including generation of steps and their lateral motion contributes to retaining flatness of the basal and prism faces which are constituent surfaces of a growing hexagonal prism-shaped ice. The basal and prism faces of a growing ice crystal are expected to interact to each other because of coupling of both processes.

In the most of the previous theoretical studies on vapour growth of ice[1], however, the surface kinetic process was neglected. The purposes of the present study are as follows: (1) to clarify how the basal and prism faces interact to each other by taking into account both the diffusion process and the surface kinetic process self-consistently, (2) to investigate the dependence of growth rates of both faces on
axial ratio $c/b$ and on diffusion constant $D$, (3) to investigate the dependence of mass growth rate on the axial ratio $c/b$ and (4) to pursue the change of axial ratio with time. To simplify the problem, we treated two-dimensional rectangular crystal which consists of a (1210) face limited at its intersections with basal and prism faces (Fig.1). Precisely speaking, transport process of sublimation heat may also concern the interaction of both faces. This process was assumed to be negligible, however, unless the sublimation heat generated at growing interface is too large, i.e. growth rate is too large.

2. Diffusion field

Let us define the supersaturation $\sigma$ as

$$\sigma = \frac{(p - p_e)}{p_e}$$

(1)

where $p$ is the pressure of water vapour and $p_e$ the equilibrium vapour pressure of ice. When a polyhedral crystal grows retaining its macroscopically flat surface, the supersaturation determined by Laplace's equation is not uniform over the crystal surface[2,3]. Using a conformal mapping and Fourier transform[2], it is shown that supersaturation $\sigma_s^b$ at the center of basal face and $\sigma_s^p$ at the center of prism face are given as

$$\sigma_s^b = \sigma_\infty - (b+c)(B_1q^p + B_2q^b)$$
$$\sigma_s^p = \sigma_\infty - (b+c)(P_1q^p + P_2q^b)$$

(2)

where $\sigma_\infty$ is the supersaturation at some distance $L$ apart from the center of crystal, and $q^b = (\partial \sigma / \partial n)_{basal}$ and $q^p = (\partial \sigma / \partial n)_{prism}$ are normal gradients of supersaturation at basal and prism faces which are unknown parameters given as boundary conditions for Laplace's equation and determined later[3]. $P_1$, $P_2$, $B_1$ and $B_2$ are constants which depend on axial ratio $c/b$ and on ratio $L/(b+c)$, and are obtained by numerical integrals. Fig.2 shows the dependence on the axial ratio of $P_1$, $P_2$, $B_1$ and $B_2$ for $L/(b+c)=50$. It should be noted that the values of $q^b$ and $q^p$ correspond to the growth rate $R_d^b$ of basal face and the growth rate $R_d^p$ of prism face determined by diffusion flux towards each surface, i.e.

$$R_d^b = (p_e/kT)v_cDq^b$$
$$R_d^p = (p_e/kT)v_cDq^p$$

(3)

Here $D$ is the diffusion constant of water molecule, $v_c$ the volume of a molecule in crystal, $k$ the Boltzmann constant and $T$ the absolute temperature. It should be noticed that $\sigma_s^p$ at the prism face depends on $q^p$ representing the sink action for water molecules at the prism surface and also on $q^b$ at basal face and vice versa.
3. Surface kinetic process

If spiral growth occurs with the aid of a screw dislocation emerging at center of the surface, the growth rate \( R_k(\sigma_s) \) determined by the surface growth kinetics is a function of supersaturation \( \sigma_s \) at center of the referred surface. The growth rate \( R_k \) is expressed by Hertz-Knudsen equation

\[
R_k = a(\sigma_s)\sqrt{\frac{p_0\sigma_s}{2\pi mkT}}
\]

with a so-called sublimation coefficient \( a(\sigma_s) \) (or condensation coefficient )

\[
a(\sigma_s) = a_1(\sigma_s/\sigma_1)\tanh(\sigma_1/\sigma_s)
\]

\[
a(\sigma_s) = \begin{cases} 
    a_1 \sigma_s/\sigma_1 & (\sigma_s << \sigma_1) \\
    a_1 & (\sigma_s >> \sigma_1)
\end{cases}
\]

where

\[
a_1 = \frac{9.5}{\sigma_1 kT}
\]

In eq.(4) \( m \) is the mass of a water molecule. In eqs.(5) and (5)', \( a_1 \) is the sticking coefficient, i.e. the ratio of molecules which stick on the surface at the instance when they have impinged on it, \( f_0 \) the surface area occupied by a water molecule, \( \kappa \) the edge free energy per unit length in a step and \( x_s \) the mean diffusion distance of an admolecule on a surface. We must discriminate between values of \( \sigma_1 \) at basal and prism faces because of the difference of \( \kappa \) at both faces.

\[
\sigma_1 b = 9.5 f_0 k \kappa / kT x_s \quad \sigma_1 P = 9.5 f_0 k \kappa \kappa P / kT x_s
\]

It is to be noted that \( a(\sigma_s) \) which represents the activity of the surface for incorporating water molecules into ice crystal depends on \( \sigma_s \), since the density of steps being sink of molecules is controlled by \( \sigma_s \).

From eqs.(2) and (4), it is clear that the growth rate \( R_k b \) of basal face depends not only on \( q^b \) but also \( q^p \) through the supersaturation \( \sigma_s b \) and \( R_k P \) also depends both on \( q^p \) and \( q^b \). Namely, both faces interact to each other through the diffusion process and the surface kinetic process.

4. Determination of Unknown parameters \( q^b \) and \( q^p \)

Unknown parameters \( q^b \) and \( q^p \), and consequently the growth rates \( R^b \) and \( R^p \), are determined by mass balance equations at both surfaces; the growth rate \( R^b d \) (eq.3) of basal face determined by volume diffusion is equal to the growth rate \( R^b k \) (eq.4) determined by the surface kinetics, i.e.

\[
R^b d(q^b) = R^b k(\sigma_s b(q^p q^b)) = R^b
\]

The same equation holds also for the prism face, i.e.

\[
R^p d(q^p) = R^p k(\sigma_s P(q^p q^b)) = R^p
\]

Eqs.(9) and (10) are simultaneous equations for \( q^b \) and \( q^p \).

5. Results

In this section we investigate the interaction of basal and prism faces from various points of view. In order to show it clearly, we compare the two cases; (I) The screw dislocations emerge both at centers of basal and prism faces. (II) The screw dislocation emerges only at center of prism face, while basal face does not grow. The values of the following quantities are kept constant in this study:
\[ \alpha_1 = 0.1[5,6], \alpha_2 = 15\%, \sigma_1 = 2.9\%, \sigma_2 = 2.5\%, T = 253.15 K, p_e = 0.776 \text{Torr}, V_c = 3.25 \times 10^{-23} \text{cm}^3, m = 3.0 \times 10^{-23} \text{g}, 2(b+c) = 0.1 \text{cm (constant)} \text{ and } L = 2.5 \text{cm}. \] The values of axial ratio \( c/b \) and diffusion constant \( D \) are changed.

5.1 An example for interaction of both faces

Table 1 shows a result obtained for \( D = 0.22 \text{cm}^2/\text{sec} \) (corresponding to 1 atm of air pressure), and \( c/b = 0.2 \). The growth rate \( R_2^p \) of prism face in the case (II) is nearly twice the growth rate \( R_1^p \) in the case (I), since \( \sigma_s^p \) in the case (II) is larger than that in the case (I) because of no diffusion flow towards the basal face in the case (II). It clearly shows that the growth rate of a surface is strongly influenced by that of the other surface through the diffusion process and the surface kinetic process.

<table>
<thead>
<tr>
<th>( \sigma_s^p % )</th>
<th>( R_{cm}^p/\text{sec} )</th>
<th>( \sigma_s^b % )</th>
<th>( R_{cm}^b/\text{sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CASE} (I) )</td>
<td>0.33</td>
<td>5.9 \times 10^{-7}</td>
<td>0.23</td>
</tr>
<tr>
<td>( \text{CASE} (II) )</td>
<td>0.54</td>
<td>1.5 \times 10^{-6}</td>
<td>4.3</td>
</tr>
</tbody>
</table>

5.2 Dependence on axial ratio

Fig. 3 shows the dependence on axial ratio \( c/b \) of the supersaturation at the centers of the prism and basal faces in the above two cases. Fig. 4 represents the dependence on \( c/b \) of the growth rates of both faces corresponding to Fig. 3. The supersaturation \( \sigma_s^p \) on prism face decreases with increasing axial ratio \( c/b \) in the cases (I) and (II), since the supply of water molecules to the prism face becomes insufficient because of increase in the area of prism face acting as sink of molecules. Therefore, the growth rate \( R^p \) of prism face decreases with increasing
axial ratio c/b (Eqs. 4 and 5). On the other hand, the growth rate $R_1^b$ of basal face in the case (I) necessarily increases with increasing c/b since both faces scramble for water molecules in the air.

It is also shown in Fig.4 that the difference between $R_2^P$ and $R_1^P$ decreases with increasing axial ratio c/b. The result is interpreted as follows. Since the area of basal face decreases with increasing c/b, the flux of water molecules incorporated into crystal at the basal face in the case (I) decreases with increasing c/b. Therefore, as c/b increases, the difference between the case (I) and the case (II) in which no water molecules are incorporated at the basal face decreases.

5.3 Dependence on diffusion constant

Fig.5 shows the supersaturation on both faces versus axial ratio for higher diffusion constant $D=447 \text{cm}^2/\text{sec}$ (corresponding to 0.3Torr of air pressure). The supersaturation on both faces does not drop largely from the supersaturation $\sigma_\infty$ and hardly change for various axial ratio c/b in the cases (I) and (II). This is due to easier supply of water molecules by diffusion to the surfaces under the conditions of higher diffusion constant D. Therefore, the growth rate of both faces is almost independent of c/b (Fig.6). Namely, the interaction of both faces decreases with increasing D.

5.4 Mass growth rate

It is of interest to investigate the dependence on axial ratio c/b of the mass growth rate $\frac{dM}{dt}$ which is determined by the total flux of water molecules incorporated into an ice crystal at basal and prism faces. As shown in Fig.7 with thick lines, $\frac{dM}{dt}$ in the case (I) is almost independent of c/b for a constant periphery length of crystal and for various D. Since the growing basal and prism faces scramble for the water molecules which are supplied by diffusion with finite rate, the growth rate of each surface strongly depends on the axial ratio, i.e. the ratio of areas of both faces, while the total mass flux incorporated into a crystal through both faces do not depend on the axial ratio. On the other hand, $\frac{dM}{dt}$ in the case (II) slightly decreases with decreasing c/b (see dashed lines in Fig.7), since the area of basal face which does not grow at all increases with decreasing c/b.

5.5 Change of axial ratio with time

The growth rates of basal and prism faces are self-consistently determined for a given axial ratio c/b according to the method described in section 2, 3 and 4. Then an increase of the lengths of individual axes c and b for a time interval $\Delta t$ is evaluated by the growth rates of basal and prism faces. Therefore, we can pursue the change of axial ratio i.e. the change of crystal shape, with time as shown in Fig.8. The details will be discussed elsewhere shortly.
\[ (b+c) = 0.1 \text{ cm} \]
\[ D = 447 \text{ cm}^2 / \text{sec} \]

Fig. 5. \( \sigma_s \) of both faces versus c/b.

Fig. 6. \( R \) of basal and prism faces corresponding to Fig. 5.

Fig. 7. \( \frac{dM}{dt} \) versus c/b.

Fig. 8. Change of crystal shape with time for a time interval \( \Delta t = 665 \text{ sec} \). Initial size \( 2(c+b) = 0.1 \text{ cm} \), initial axial ratio \( c_0/b_0 = 0.3 \) and \( D = 0.22 \text{ cm}^2 / \text{sec} \).

References
COMMENTS

N. FUKUTA

Your treatment is based on screw dislocation mechanism. Screw dislocation is known to be difficult to nucleate. Hallett and his colleagues failed to detect screw dislocation on natural snow crystals by X-ray analysis. Your treatment, therefore, may be based on non-existing screw dislocation. What is your response to this point?

Answer:

Yes, they reported that snow crystals were dislocation free in most cases. In my opinion, it is not always the case, of course, we can easily apply this treatment to two dimensional nucleation growth of perfect snow crystals and similarly investigate the interaction between basal and prism faces.

K. ROESSLER

Does the kind end quality of the surface play a role in your equations, or, where would you introduce it.

Answer:

As to basal and prism faces, influence of roughening with increasing temperature can be taken into account through the decrease in step free energy which controls the step density. On the other hand, adhesive growth occurs on the other surfaces corresponding to high value of Miller-indices. However, such surfaces quickly disappear because of their very fast growth in comparison with lateral growth.