VAPOR GROWTH MECHANISM OF A CRYSTAL SURFACE COVERED WITH A QUASI-LIQUID LAYER – EFFECT OF SELF-DIFFUSION COEFFICIENT OF THE QUASI-LIQUID LAYER ON THE GROWTH RATE

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For several years, progress has been made in understanding surface melting as well as surface roughening of various crystals such as ice, lead, rare gases etc. A so-called quasi-liquid layer (QLL), caused by surface melting, is expected to influence the vapor growth mechanism of crystals at temperatures not far below their melting points. The effect of the self-diffusion coefficient \( D \) of a QLL on the growth rate is investigated in this study. It is shown that the condensation coefficient \( \alpha_{\text{QLL}} \) involved in the Hertz–Knudsen equation decreases with a decrease in \( D \) because of difficulty of rearrangement of molecules from QLL to crystal and this effect appears more clearly for crystals with larger equilibrium vapor pressure. The expression for the rate of spiral growth of the surface covered with QLL is also derived as a function of supersaturation.

1. Introduction

Three mechanisms of crystals growth from the vapor are well known [1], i.e. (1) two-dimensional nucleation growth mechanism and (2) spiral growth mechanism with the aid of screw dislocations at temperatures below roughening temperature \( T_r \), and (3) adhesive growth mechanism above \( T_r \). Growth led by the first or the second mechanism is called lateral growth.

On the other hand, it has recently been confirmed for various crystals, e.g. ice by ellipsometry [2], lead by proton back scattering [3,4], rare gases by molecular dynamics [5,6] and by observation of morphology [7], that surface melting occurs at temperatures not far below the melting point \( T_m \).

A so-called quasi-liquid layer (QLL) caused by the surface melting is expected to provide a new growth mechanism from the vapor at high temperatures near \( T_m \), which is different from those mentioned above. Lacmann and Stranski [8] proposed the so-called vapor–quasi-liquid–solid (VQLS) mechanism for the first time. Then, Chernov [9] also discussed the growth mechanism using the concept of disjoining pressure for QLL. Beckmann and Lacmann [10] measured the growth rates of ice crystals from the vapor at temperatures of \(-7 \) to \(-15^\circ \text{C} \) and interpreted the results by two-dimensional nucleation growth for the surface covered with QLL. Recently, Sei and Gonda [11] argued from their measurement of growth rates that the \{0001\} and \{10\overline{1}0\} faces of ice crystals grow by VQLS mechanism at temperatures \( 0 \) to \(-2^\circ \text{C} \).

From the viewpoint of anisotropy of surface melting and roughening, i.e. different transition temperatures for \{0001\} and \{10\overline{1}0\} faces of ice crystals, Kuroda and Lacmann [12] proposed a new interpretation for habit changes of growing snow crystals occurring three times with decreasing temperature.

They pointed out that the value of edge energy of a two-dimensional nucleus at the QLL/ice interface is much smaller than that at a vapor/ice interface without QLL, and consequently QLL promotes the growth of ice crystals from the vapor phase. On the other hand, Mizuno and Hanafusa [13] reported recently that the value of the self-diffusion coefficient of a QLL on ice measured by NMR was smaller than that of bulk water by four orders of magnitude and larger than that of ice single crystal by two orders. If it so difficult for water molecules in the QLL to move, the rearrangement process from QLL to crystal lattice may become the rate determining process of vapor growth. There is a possibility, therefore, that the
existence of a QLL inhibits growth. Therefore, the effect of the self-diffusion coefficient of a QLL on the rate of vapor growth has been investigated quantitatively in this study. The dependence on supersaturation of spiral growth of a surface covered with a QLL is also investigated.

2. Vapor growth mechanism of a crystal surface covered with QLL – VQLS mechanism

The growth of a crystal surface covered with a QLL occurs by two processes, i.e. (a) condensation of water vapor into the QLL and (b) crystallization at the QLL/crystal interface [8,9,12].

If the actual vapor pressure \( p \) is larger than the equilibrium vapor pressure \( p(\delta) \) of the QLL with a thickness \( \delta \), vapor is condensed into the QLL and consequently the thickness \( \delta \) increases. The condensation rate \( R_a \) is expressed by the Hertz–Knudsen equation, i.e.

\[
R_a = v_m \frac{p(p(\delta))}{\sqrt{2\pi m kT}},
\]

where \( m \) and \( v_m \) are the mass and volume of a growth unit respectively, \( k \) the Boltzmann constant and \( T \) the absolute temperature. Since \( p(\delta) \) is an increasing function of \( \delta \), \( R_a \) decreases with increasing \( \delta \) [12].

On the other hand, the chemical potential \( \Delta \mu(\delta) \) of the QLL becomes positive when its thickness \( \delta \) exceeds the equilibrium thickness \( \delta_{eq} \) because of the condensation of vapor into the QLL. Therefore, crystallization occurs at the QLL/crystal interface, so that \( \delta \) decreases. The freezing rate \( R_b(\Delta \mu(\delta)) \) increases as \( \Delta \mu(\delta) \) increases, i.e. it increases with increasing \( \delta \). The expression for \( R_b \) as a function of \( \Delta \mu(\delta) \) depends on the structure of the QLL/crystal interface. There are three cases in general.

2.1. Rough interface

Since a rough QLL/crystal interface can advance continuously normal to itself without recourse to a lateral motion of the steps, i.e. so-called adhesive growth occurs, \( R_b^{ad} \) may be given by

\[
R_b^{ad} = D \frac{\Delta \mu(\delta)}{akT},
\]

from the analogy of the growth from the bulk melt [14]. In eq. (2), \( a \) is the radius of a growth unit and \( D \) the self-diffusion coefficient of QLL. Using the relation between \( \Delta \mu(\delta) \), \( p(\delta) \) and equilibrium vapor pressure vapor pressure \( p_c^e \) of a crystal, i.e. \( \Delta \mu(\delta) = kT \ln[p(\delta)/p_c^e] \), eq. (2) can be expressed as

\[
R_b^{ad} = D \frac{p(\delta) - p_c^e}{p_c^e},
\]

if \( [p(\delta) - p_c^e]/p_c^e \ll 1 \).

2.2. Smooth interface where screw dislocations emerge

Spiral growth is possible with the aid of screw dislocations [14] and the freezing rate \( R_b^{sp} \) is given by

\[
R_b^{sp} = \frac{D \sqrt{\Delta \mu(\delta)^2}}{4\pi \kappa_{QLL} a^2 kT},
\]

\[
R_b^{sp} = \frac{kT D}{4\pi \kappa_{QLL} a^2} \left( \frac{p(\delta) - p_c^e}{p_c^e} \right)^2,
\]

where \( \kappa_{QLL} \) is the step energy.

2.3. Smooth interface where no screw dislocation emerges [12]

The rate \( R_b^{nu} \) is determined by two-dimensional multi-nucleation as follows:

\[
R_b^{nu} = C \exp(-\Delta G^*/3kT),
\]

with \( \Delta G^* = \kappa_{QLL} f_0/\Delta \mu(\delta) \) and \( C = a^{-1} (\sqrt{\pi} / 3)^{1/3} \left[ \Delta \mu(\delta)/kT \right]^{5/6} D. \Delta G^* \) is the formation free energy of a two-dimensional critical nucleus and \( f_0 \) the occupied area by a growth unit on the surface. \( R_b \) increases with \( \Delta \mu(\delta) \) at a constant temperature in all the above cases. \( R_b(\delta_{eq}) = 0 \), since the quasi-liquid layer exists in equilibrium with ice \( (\Delta \mu(\delta_{eq}) = 0) \), and \( R_b(\infty) \) agrees with the crystallization rate from the melt.
At steady state both \( R_a \) and \( R_b \) must be equal
\[
R_a(\delta_a(T), \Delta p) = R_b(\delta_b(T)) = R_{\text{QLL}}(T, \Delta p). \tag{5}
\]

From this balance equation, we can evaluate the growth rate \( R_{\text{QLL}}(T, \Delta p) \) and the thickness \( \delta_a(T, \Delta p) \) of the QLL under steady state conditions as a function of temperature \( T \) and absolute supersaturation \( \Delta p = p - p^e \) in each case. It should be noticed that \( R_{\text{QLL}} \) is independent of the relation of the equilibrium vapor pressure \( p(\delta) \) of the quasi-liquid layer, because both \( R_a \) and \( R_b \) depend on \( \delta \) only through \( p(\delta) \). On the other hand, \( \delta_a \) depends on it.

3. The rate of growth produced by the VQLS mechanism and dependence of condensation coefficient \( \alpha_{\text{QLL}} \) on the self-diffusion constant \( D \) and supersaturation \( \sigma \)

The rate \( R_{\text{QLL}} \) of growth produced by the VQLS mechanism can be expressed in the form of a Hertz–Knudsen equation with condensation coefficient \( \alpha_{\text{QLL}} \):
\[
R_{\text{QLL}} = \alpha_{\text{QLL}} \frac{v_m(p-p^e)}{\sqrt{2\pi mkT}}, \tag{6}
\]
where the behavior of \( \alpha_{\text{QLL}} \) depends on the structure of the QLL/crystal interface through expressions from \( R_b \) (eqs. (2), (3) and (4)).

3.1. Rough QLL/crystal interface

The condensation coefficient \( \alpha_{\text{QLL}}^{\text{ad}} \) for a rough QLL/crystal interface is obtained by substituting eqs. (1) and (2’) in eq. (5),
\[
\alpha_{\text{QLL}}^{\text{ad}} = 1 - \left(1 + \frac{D\sqrt{2\pi mkT}}{av_m p^e} \right)^{-1}. \tag{7}
\]

The growth rate \( R_{\text{QLL}}^{\text{ad}} \) with condensation coefficient \( \alpha_{\text{QLL}}^{\text{ad}} \) for a rough QLL/crystals interface linearly increases with supersaturation \( \sigma = (p - p^e)/p^e \). The slope of the growth rate \( R_{\text{QLL}}^{\text{ad}} \) versus \( \sigma \) is determined by \( \alpha_{\text{QLL}}^{\text{ad}} \) which depends on the self-diffusion coefficient \( D \) of QLL.

Fig. 1. The dependence of the condensation coefficient \( \alpha_{\text{QLL}}^{\text{ad}} \) for a rough QLL/crystal interface on the self-diffusion coefficient \( D \) of QLL. Solid line: ice crystal at \(-3^\circ\text{C}\); broken line: Xe crystal at 156.4K.

While the values of \( D \) for bulk liquids are of the order of \( 10^{-5} \)–\( 10^{-6}\) cm\(^2\)/s, the values of \( D \) for a thin QLL might be smaller and \( D \) for the molecules adjacent to a QLL/crystal interface may be smallest, since the underlying crystal influences the movement of the molecules in the QLL.

The diffusion coefficient, \( D \), appears in eqs. (2), (3) and (4) through the activation process for rearrangement of the molecules adjacent to the QLL/crystal interface. Thus, the effect of \( D \) for the QLL on \( \alpha_{\text{QLL}}^{\text{ad}} \) is of interest. The \( \alpha_{\text{QLL}}^{\text{ad}} \) behaves as follows for extreme values of \( D \):
\[
\alpha_{\text{QLL}}^{\text{ad}} = 1, \quad \text{for } D \gg D_c, \tag{8}
\]
\[
\alpha_{\text{QLL}}^{\text{ad}} = D\sqrt{2\pi mkT}/av_m p^e, \quad \text{for } D \ll D_c, \tag{8’}
\]
\[
D_c = av_m p^e/\sqrt{2\pi mkT}. \tag{9}
\]

The dependence on \( D \) of \( \alpha_{\text{QLL}}^{\text{ad}} \) for an ice crystal at \(-3^\circ\text{C}\) is shown in fig. 1 by the solid line. Note that \( \alpha_{\text{QLL}}^{\text{ad}} \) becomes much smaller than unity (eq. (8’)) because of the difficulty of rearrangement from QLL to the crystal lattice, if \( D \) is much smaller than the critical value \( D_c \) given by eq. (9). According to the experimental results using NMR (Mizuno and Hanafusa [13]), the values of \( D \) for the QLL of ice crystals are very small, i.e.
(1.4–3.1) × 10^{-9} \text{cm}^2/\text{s} at temperatures of −20 to −1.5°C. However, the corresponding values of \( \alpha_{\text{QLL}}^{\text{ad}} \) estimated by eq. (7) are 0.3–0.5 (fig. 1). Thus, the inhibiting effect of \( D \) for the QLL on the vapor growth rate is not so large for the ice crystal, because \( D_c = 2 \times 10^{-9} \text{cm}^2/\text{s} \) for ice at −3°C. On the other hand, this effect is expected to appear more clearly for crystals with larger vapor pressure \( p_c^e \), since the critical value \( D_c \) increases with \( p_c^e \) (eq. (9)). For example, the \( p_c^e \) of Xe and Kr are larger than the \( p_c^e \) (≈ 10^2 Pa at −20°C) of ice by two orders near melting point.

Maruyama [15] recently found that the condensation coefficients of Xe and Kr crystals at temperatures within 5 K below \( T_m (= 161.4 \text{ K (Xe)}, 115.8 \text{ K (Kr)}) \) were extremely small, i.e. of the order of 10^{-3}. He interpreted the results in terms of a VQLS growth mechanism and estimated the values of \( D \) of QLL on Xe and Kr crystals to be of the order of 10^{-9} \text{cm}^2/\text{s} using eq. (7) (see the broken line in fig. 1).

However, it has recently been reported that \( D \) for a top layer of QLL is larger than \( D \) for a bulk liquid, even though \( D \) decreases from the top layer to the QLL/crystal interface [4–6]. The problem as to which value should be used for \( D \) in eqs. (2), (3) and (4) for various crystals forms the subject for a future investigation.

3.2. Smooth QLL/crystal interface where screw dislocations emerge

The condensation coefficient \( \alpha_{\text{QLL}}^{\text{sp}} \) for a smooth surface where screw dislocations emerge is obtained in the same way as \( \alpha_{\text{QLL}}^{\text{ad}} \).

\[
\alpha_{\text{QLL}}^{\text{sp}} = 1 - \left[ 1 + \left( \frac{a}{\lambda} \right)_{\text{st}} \frac{D \sqrt{2 \pi mkT}}{v_m p_c^e \sigma} \right]^{-1},
\]

with

\[
\left( \frac{a}{\lambda} \right)_{\text{st}} = \frac{v_m p_c^e \sigma}{2 \sqrt{2 \pi mkT D}} \left[ 1 + \frac{kT D \sqrt{2 \pi mkT \sigma}}{\pi \kappa_{\text{QLL}} p_c^e \sigma v_m} \right]^{1/2} - 1.
\]

Here \( (a/\lambda)_{\text{st}} \) is the ratio of step height \( a \) and step distance \( \lambda \), i.e. the slope of the spiral hillock at the QLL/crystal interface, under steady state conditions, and \( \sigma = (p - p_c^e)/p_c^e \) is the supersaturation of vapor. It increases with \( \sigma \), and \( \alpha_{\text{QLL}}^{\text{sp}} \) becomes equal to \( \alpha_{\text{QLL}}^{\text{ad}} \) when \( (a/\lambda)_{\text{st}} \) reaches the maximum value \( (a/\lambda)_{\text{max}} = 1 \) (compare eq. (10) with eq. (7)).

Fig. 2 shows the dependence on supersaturation \( \sigma \) of the growth rates \( R \) of ice crystals. Thick lines: spiral growth of the surfaces covered with QLL; thin line: spiral growth of the surface without QLL; broken line: maximum growth rate.

Fig. 2. The dependence on supersaturation \( \sigma \) of the growth rates \( R \) of ice crystals. Thick lines: spiral growth of the surfaces covered with QLL; thin line: spiral growth of the surface without QLL; broken line: maximum growth rate.
broken line is the maximum growth rate from the vapor given by the Hertz–Knudsen equation with the condensation coefficient of unity.

The growth rate $R_{QLL}^{sp}$ for $D = 10^{-5}$ cm$^2$/s is larger than $R^p$ at supersaturations lower than 6% because of the lower value of $\kappa_{QLL}$ at the QLL/ice interface. On the other hand, $R_{QLL}^{sp}$ becomes lower than $R^p$ at supersaturations larger than 6%, since the rearrangement of molecules from QLL to crystal becomes the rate determining process. However, $R_{QLL}^{sp}$ reaches $R^p$ as the supersaturation increases further, since $\alpha_{QLL}^{sp}$ approaches $\alpha_{QLL}^{ad}$ with increasing $\sigma$ [eqs. (7), (10) and (11)].

3.3. Smooth QLL/crystal interface where no screw dislocation emerges

The growth rate $R_{QLL}^{su}$ as well as the coefficient $\alpha_{QLL}^{su}$ in this case cannot be obtained analytically, but only numerically [12]. For a smooth surface of a perfect crystal without QLL, we meet the nucleation difficulty for supersaturations less than the critical one $\sigma_c$. However, if the surface is covered with a QLL, it can grow by two-dimensional nucleation at the QLL/crystal interface even at smaller supersaturations, since the edge free energy $\kappa_{QLL}$ of the nucleus at the QLL/crystal interface is smaller than that on the smooth surface without QLL. The QLL promotes the vapor growth at smaller $\sigma$ because of a decrease in $\kappa_{QLL}$. On the other hand, $R_{QLL}^{su}$ approaches $R_{QLL}^{ad}$ with increasing $\sigma$. Therefore, QLL can inhibit the growth at larger $\sigma$ if $D$ is extremely small.

The growth rates $R_{QLL}^{sp}$ and $R_{QLL}^{su}$ show anisotropy, since the edge energy $\kappa_{QLL}$ depends on the crystallographic orientation of the surfaces, and consequently the facets with larger $\kappa_{QLL}$ develop themselves. The shape of a negative crystal of ice, i.e. a hole in ice, changes from a hexagonal prism bounded by \{0001\} and \{10\overline{1}0\} faces to a sphere which is truncated by small \{0001\} faces at $-2^\circ$C. This change was interpreted as the roughening transition of the QLL/\{10\overline{1}0\} ice interface at $-2^\circ$C by Furukawa et al. [2].

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