

INTERPRETATION OF THE ORIENTATION OF ICE DENDRITES GROWING FROM SUPERCOOLED WATER

By LAURA LEVI

(Consejo Nacional de Investigaciones Científicas y Técnicas, Rivadavia 1917, Buenos Aires, Argentina)

ABSTRACT. An interpretation is proposed of the phenomenon of splitting of ice dendrites growing from supercooled water and of their orientation at an angle α to the basal plane. Both phenomena are related to the instabilities which develop on the dendritic cap when the ratio V_c/V_a of the growth velocities in the direction of the c - and a -axes exceeds a certain limit. The different interface supercoolings, $(\delta T_i)_a$ and $(\delta T_i)_c$, at the tip and at the sides of the dendrite cap are considered. Although V_c/V_a increases with the bath supercooling ΔT it is found that $V_c \ll V_a$ for $(\delta T_i)_c = (\delta T_i)_a$ through the whole range investigated ($0 < \Delta T \leq 18$ deg). The increase of α with the concentration of solutes is also qualitatively explained. Considering the kinetic theory of the molecular growth mechanism, the results obtained for V_c as a function of $(\delta T_i)_c$ would indicate that most of the studied interval must correspond to the transitional regime of growth.

RÉSUMÉ. *Interprétation de l'orientation des dendrites de glace croissantes dans l'eau surfondue.* On propose une interprétation du phénomène de scission des dendrites de glace croissantes dans l'eau surfondue et de son orientation d'un angle α du plan basal. On met ce phénomène en relation avec les instabilités qui se formeraient à l'extrémité de la dendrite, quand la rapport V_c/V_a entre les vitesses de croissance dans la direction des axes c et a dépasse une certaine limite. On considère les différents refroidissements à l'interface $(\delta T_i)_a$ et $(\delta T_i)_c$ existents à l'extrémité et aux côtés de la pointe de la dendrite. On trouve que $V_c \ll V_a$ pour $(\delta T_i)_c = (\delta T_i)_a$ dans tout l'intervalle des températures étudié ($0 < \Delta T \leq 18$ deg), bien que V_c/V_a croisse avec le refroidissement de l'eau, ΔT . On explique aussi, qualitativement, l'observation que α croît avec la concentration d'une solution. En considérant la théorie cinétique du mécanisme moléculaire de solidification, on trouve que la dépendance de V_c de $(\delta T_i)_c$ indique que l'intervalle étudié doit correspondre, dans sa plus grande partie, au régime de croissance de transition.

ZUSAMMENFASSUNG. *Interpretation der Orientierung von in unterkühltem Wasser gewachsenen Eisdendriten.* Es wird eine Interpretation für die Erscheinung der Spaltung von in unterkühltem Wasser gewachsenen Eisdendriten und ihrer Orientierung unter einem Winkel α gegen die Basisfläche vorgeschlagen. Beide Eigenschaften werden in Beziehung zu der Instabilität gebracht, welche am Dendritenkopf entsteht, wenn das Verhältnis V_c/V_a der Wachstumsgeschwindigkeiten in Richtung der c - und a -Achsen einen bestimmten Grenzwert unterschreitet. Die unterschiedlichen Unterkühlungen $(\delta T_i)_a$ und $(\delta T_i)_c$ der Grenzflächen an der Spitze und an den Seiten des Dendritenkopfes werden betrachtet. Obgleich V_c/V_a mit der Unterkühlung ΔT des Bades wächst, wurde über den gesamten untersuchten Bereich ($0 < \Delta T \leq 18$ deg) bei $(\delta T_i)_c = (\delta T_i)_a$ $V_c \ll V_a$ gefunden. Ebenso wird das Wachsen von mit der Lösungskonzentration qualitativ erklärt. Bei Berücksichtigung der kinetischen Theorie des molekularen Wachstumsmechanismus führen die für V_c als Funktion von $(T_i)_c$ erhaltenen Ergebnisse dazu, dass der grösste Teil des untersuchten Intervalls dem Zustand gleichmässigen Wachsens entsprechen muss.

1. INTRODUCTION

The growth process of ice dendrites from supercooled water has been studied for many years, because it was considered by metallurgists as a typical case of dendritic growth, and useful comparisons could be made with the features observed in other substances. Furthermore, the interest in ice dendrites has increased recently, due to their importance in problems of atmospheric physics. Several works have been published on their growth modes and velocity (Lindenmeyer, unpublished; Lindenmeyer and Chalmers, 1966; Hallett, 1964; Macklin and Ryan, 1965, 1966, 1968; Pruppacher, 1967[a], [b]).

Special characteristics of these dendrites are their development as planar dendrites and their splitting and changes of orientation, which occur with increasing supercooling. According to Lindenmeyer (unpublished) and Macklin and Ryan (1968), the direction of the dendrite axis should coincide with that of the resultant of the growth velocities V_a and V_c in the direction of the a - and c -axis respectively. This would be the direction of maximum growth velocity, given by:

$$V = V_a \cos \alpha + V_c \sin \alpha. \quad (1)$$

where α represents the inclination of the dendrites with respect to the basal plane. The

increase of the angle α with the supercooling would then indicate an increase of the velocity ratio V_c/V_a .

This interpretation is not, however, directly supported by the theory of dendritic growth (Bolling and Tiller, 1961). Actually, according to this theory, dendrites should have their axis in the direction of maximum growth velocity which simultaneously satisfies a condition of symmetry at the tip of the dendrite with respect to the crystalline structure. Then, as long as $V_a > V_c$, the axis of the dendrites should coincide with the a -axis and the increase of V_c/V_a should only result in an increase in the dendrite thickness with respect to an ideal dendrite grown at the same supercooling.

In the present paper a mechanism is proposed to explain the splitting and inclination of ice dendrites which takes into account the hypothesis of Lindenmeyer and of Macklin and Ryan and also the theory of Bolling and Tiller.

For clarity, the experimental observations of the phenomenon and some points of the theory will be summarized below.

2. EXPERIMENTAL EVIDENCE

(a) *Growth velocity in the direction of the a -axis.* This velocity has been studied by several authors as a function of the bath supercooling ΔT , and slightly different results have been obtained (Lindenmeyer, unpublished; Lindenmeyer and Chalmers, 1966; Hallett, 1964; Macklin and Ryan, 1966, 1968; Pruppacher, 1967[b]). Following Pruppacher, V_a can be expressed as

$$V_a = 0.035(\Delta T)^{2.22}. \quad (2)$$

The curve of $V_a(\Delta T)$ has been compared by Pruppacher to the corresponding theoretical curve, calculated by Bolling and Tiller (1961). He shows that both curves might coincide if an interface supercooling $(\delta T_i)_a$ is supposed to exist at the tip of the dendrite, and he concludes that, in the range of temperatures investigated (0° to -18°C), two intervals may be considered, so that

$$V_a = 1.38(\delta T_i)_a^2 \quad 0 < \Delta T \leq 9 \text{ deg}, \quad (3)$$

$$V_a = 2.50(\delta T_i)_a \quad 9 \text{ deg} \leq \Delta T. \quad (4)$$

In terms of the molecular mechanism of growth, the first interval should correspond to growth by lateral spreading of steps and the second to the continuous growth regime.

(b) *Orientation of dendrites with respect to the basal plane.* According to the measurements of several different authors (Lindenmeyer, unpublished; Macklin and Ryan, 1965, 1966, 1968; Pruppacher, 1967[a]), the dendrites split, for $\Delta T > 1-2^\circ\text{C}$, in symmetrical branches, forming between them an angle 2α , which increases with ΔT and which tends to a limiting value $2\alpha = 45^\circ$ for $\Delta T > 9 \text{ deg}$. This was shown specially clearly by Pruppacher, who extended his measurements down to $\Delta T = 14 \text{ deg}$. For larger supercoolings direct measurements of 2α were not possible.

However in one case Hallett (1964) was able to measure the growth velocity of dendrites in the direction of the c and a axes at $\Delta T = 16 \text{ deg}$ and deduced $\alpha = 38^\circ$ at this supercooling. Furthermore there is indirect evidence that 2α should increase for $\Delta T > 14 \text{ deg}$. It has been shown by Levi and Aufdermaur (1969) that, when ice structures formed by accretion and freezing of supercooled droplets are obtained with a surface temperature $< 0^\circ\text{C}$, the crystal c -axes tend to be oriented in the direction of growth, when the temperature of the air and of the arriving droplets are in the range $0 > t_a > -8^\circ\text{C}$. At colder temperatures ($-8 > t_a > -15^\circ\text{C}$) the c -axes form with this direction an angle $10^\circ < \phi < 30^\circ$, while they form an angle $\phi = 45^\circ$ for $t_a = -18$ or -22°C .

These different orientations of the crystal c -axes have been related to the different crystallographic orientations of the dendrites grown during the initial freezing of supercooled droplets.

Then the value $\phi = 45^\circ$ obtained for the lowest temperatures would indicate that α also reaches the same value for a temperature in the interval indicated above.

3. GENERAL THEORY OF DENDRITIC GROWTH

It is known (Bolling and Tiller, 1961) that, for an ideal dendrite, the dendrite cap would be limited by an isothermal surface with the shape of a paraboloid of revolution. The conditions of optimization of the growth velocity V indicate that the radius of curvature of the tip, $\rho/2$, must satisfy the equation

$$\frac{\rho}{2} = \frac{2\gamma_0}{\Delta S(\Delta T - (\delta T_i)_0)} \quad (5)$$

where ΔT and $(\delta T_i)_0$ are the bath and the interface supercooling respectively, ΔS is the entropy of fusion for unit volume and γ_0 is the surface free energy. Since the product $V\rho$ is approximately constant for a given supercooling, if ρ increases according to Equation (5), then the velocity V decreases.

It may be seen from Equation (5) that, for the maximization of V , the preferred direction with respect to the crystalline structure will be that which minimizes $(\delta T_i)_0$. On the other hand, if V_ϕ is the growth velocity in a direction forming an angle ϕ to the dendrite axis, it may be easily seen that, for the conservation of the tip shape, V_ϕ must be given by

$$V_\phi = V_0 \cos \phi \quad (6)$$

where V_0 is the axial velocity.

Using $V = \mu(\delta T_i)$ as the general law for the solidification mechanism, where μ is a coefficient which may depend on the temperature, Equation (6) may be written

$$\mu_\phi(\delta T_i)_\phi = \mu_0(\delta T_i)_0 \cos \phi \quad (7)$$

where $(\delta T_i)_0$ and $(\delta T_i)_\phi$ are the interface supercoolings in the axial direction and in a direction forming the angle ϕ with this axis. These supercoolings are related by the expression

$$(\delta T_i)_\phi = (\delta T_i)_0 + \frac{\gamma_0}{\Delta S} \left(\frac{2}{\rho} - \frac{\gamma_\phi/\gamma_0}{R} \right) \quad (8)$$

where γ_0 and γ_ϕ are the surface free energies in the axial direction and at an angle ϕ to the axis and R is the radius of curvature of the region of the surface characterized by the angle ϕ .

For an isothermal dendrite the radius of curvature R has the expression

$$\frac{1}{R} = \frac{\cos \phi (1 + \cos^2 \phi)}{\rho} \quad (9)$$

Since according to Equations (8) and (9) $R > \rho/2$ and $(\delta T_i)_\phi \geq (\delta T_i)_0$, it also follows from Equation (7) that, for an isothermal dendrite, $\mu_\phi \leq \mu_0 \cos \phi$. When this condition is not satisfied, the surface of an isothermal dendrite becomes unstable. Then, the radius of curvature at the tip should increase above the limit given by Equation (5). The dendrite would get thicker and the growth velocity lower.

4. INTERPRETATION OF ICE DENDRITE CHARACTERISTICS

(a) *Mechanism of splitting and irrational orientation of the dendrites.* We will consider an ice dendrite growing initially in the direction of the a -axis. It has been assumed by Bolling and Tiller that the tip of a dendrite should usually tend to be limited by low index planes. In the case of ice, these planes are $\{10\bar{1}0\}$ and $\{0001\}$, the latter containing the dendrite axis. Then two sides of the dendrite tip will be limited by two $\{10\bar{1}0\}$ planes ($\phi = 60^\circ$), but the other sides, normal to the first ones, should be formed by higher index surfaces, each of them tending to a $\{0001\}$ plane ($\phi = 90^\circ$) at some distance from the tip.

We see from Equation (9) that the radius of curvature R will tend to ∞ ($1/R \rightarrow 0$) for $\phi \rightarrow 90^\circ$ and Equation (8) may be simplified to

$$(\delta T_i)_{90} \approx (\delta T_i)_0 + \frac{\gamma_0}{\Delta S} \frac{2}{\rho}. \quad (10)$$

Using Equation (5) this may also be written

$$(\delta T_i)_{90} \approx \frac{1}{2}(\Delta T + (\delta T_i)_0). \quad (10')$$

From Equation (10'), $(\delta T_i)_{90}$ is obtained easily, since the value of $(\delta T_i)_0$ corresponding to a given ΔT may be calculated by applying Pruppacher's results (1967[b]) represented by Equations (3) or (4) and by the experimental curve of V as a function of ΔT (represented by Equation (2) for $\Delta T < 9^\circ\text{C}$). Some values of these supercoolings are given in the last columns of Table I. Here $(\delta T_i)_0$ and $(\delta T_i)_{90}$ have been represented by $(\delta T_i)_a$ and $(\delta T_i)_c$ respectively, to indicate the corresponding crystallographic direction. The table shows that $(\delta T_i)_c \approx 3(\delta T_i)_a$ and that the ratio of these supercoolings varies very slowly with the temperature.

TABLE I. GROWTH VELOCITIES AND INTERFACE SUPERCOOLINGS PARALLEL TO a - AND c -AXES

ΔT deg	α	V_a cm/s	V_c cm/s	$(\delta T_i)_a$ deg	$(\delta T_i)_c$ deg
2	$4^\circ 36'$	0.15	0.014	0.3	1.1
4	$9^\circ 18'$	0.9	0.14	0.8	2.4
6	$13^\circ 48'$	2.0	0.5	1.2	3.6
8	$18^\circ 24'$	4.0	1.3	1.7	4.9
18	45°	10.0	10.0	4.0	11.0

On the other hand, it may be observed from Equations (8) and (9) that the variation of $(\delta T_i)_\phi$ with the angle ϕ must be more pronounced for $\phi > 45^\circ$ than in the vicinity of the tip. Actually, for $\phi < 45^\circ$, $\cos \phi$ decreases slowly and γ_ϕ probably increases because the index of the surface increases; on the contrary, for $\phi > 45^\circ$, the variation of $\cos \phi$ is faster and γ_ϕ should decrease, tending to a minimum value for $\phi = 90^\circ$. Then, in the region of large ϕ , where $(\delta T_i)_\phi$ increases rapidly, the approximately paraboloidal cap of the dendrite would become unstable, and for V_c/V_a larger than a given limit, a protuberance could be formed on the surface.

Now, since the radius of curvature at the tip of the protuberance will be smaller than that of the original dendrite, its growth velocity will be higher and the protuberance will overtake the dendritic tip. Then, if we start with an initially basal dendrite, two symmetrical instabilities will be formed at both sides of the tip and the phenomenon will determine the splitting of the dendrite.

After the splitting, the thermal interaction between the two symmetrical branches will hinder the splitting phenomenon on the inside surfaces and the instability effect will operate periodically only on the outside surfaces, determining the inclination of the dendrites. However, with the increase of the distance between the two advancing tips, the interaction will decrease and new splittings will take place, the more frequently the larger the value of α .

According to this interpretation, the growth direction of a dendrite would be the resultant of the advance of the dendrite tip in the direction of the a -axis and of its shifting in the direction of the c -axis because of the formation of lateral layers. Accordingly, Equation (1) would be maintained and, for a given bath supercooling ΔT , the velocity V_c could be obtained from V_a (as indicated by Macklin and Ryan (1968)), by means of the expression

$$V_c = V_a \tan \alpha \quad (11)$$

though the values of V_c and V_a would correspond to different interface supercoolings.

(b) *Effect of the temperature on the ratio V_c/V_a .* In Table I V_a and V_c have been calculated for several values of ΔT . Because of the uncertainty of the results in the range $9 \leq \Delta T \leq 14$

deg (Pruppacher, 1967[b]), the calculated points are taken in the interval $0 < \Delta T < 9$ deg, with the exception of the last point, at $\Delta T \approx 18$ deg.

As observed by previous authors (Hallett, 1964; Macklin and Ryan, 1966), the results show that, if only the bath supercooling is considered, V_c increases rapidly with respect to V_a with increasing ΔT , reaching approximately the same value when ΔT approaches 18 deg. It could now be of interest to compare pairs of values of V_a and V_c corresponding to the same interface supercooling. This may be done if we observe that, in Table I, $(\delta T_i)_c$ for $\Delta T = 2$ deg approximately coincides with $(\delta T_i)_a$ corresponding to $\Delta T = 6$ deg and similarly that $(\delta T_i)_c$ for $\Delta T = 8$ deg may be compared with $(\delta T_i)_a$ for $\Delta T \approx 18$ deg. Therefore

$$V_c/V_a \approx 7 \times 10^{-3} \quad \text{for} \quad (\delta T_i) \approx 1 \text{ deg}, \quad (12)$$

$$V_c/V_a \approx 1.3 \times 10^{-1} \quad \text{for} \quad (\delta T_i) \approx 4 \text{ deg}, \quad (12')$$

and we see that, if the same interface supercooling is considered, then, through the whole studied range, $V_c \ll V_a$, though the ratio of these velocities evidently decreases with increasing (δT_i) .

It should be noted that the values of α and V_c in the last line of the table have been indicated as approximate; this, as mentioned before, is because of the uncertainty of the accretion experiments, and also because, if the present interpretation is correct, the value $\alpha = 45^\circ$ would not correspond to a single value of ΔT but should remain constant over a certain temperature interval and possibly represent a limiting value. In fact, it is easy to see that $\alpha > 45^\circ$ could take place only when $V_c > V_a$ for $(\delta T_i)_c \leq (\delta T_i)_a$, i.e. when the c - and a -axes interchange their role in the growth of dendrites. Then there would be an interval of temperatures where an increase of the ratio V_c/V_a could only determine an increase of the dendrite thickness with respect to the theoretical thickness of isothermal dendrites at the same supercooling.

Experimentally it has been found in accretion experiments, that the orientation of the c -axis of crystals to the growth direction reached 45° at an air temperature of -18°C and remained at this orientation down to the lowest temperature of the experiments, -22°C in similar injection conditions. This result is in agreement with the above observation, though it must be noted that this interval of air temperature, of only 4 deg, may not be considered as a definitive proof of the effect under discussion.

(c) *Dendrite width and thickness.* According to the mechanism of splitting and inclination of ice dendrites proposed here, the dendrite tip should always point with its region of maximum curvature in the direction of the a -axis. This is in agreement with the schematic representation proposed initially by Macklin and Ryan (1965). However, later on (Macklin and Ryan, 1966), the same authors assumed the dendrite tip was oriented as the main body of the dendrite. It may be noted that the latter hypothesis encounters some difficulty if the thickness of the dendrites is considered. In fact, since in this case, on increasing ΔT , V_c would approach V_a for the same interface supercooling, the growth velocity should become of the same order of magnitude in all directions and the dendrites should increase in thickness, independently of their orientation (non-isothermal dendrites). On the other hand it is known (Pruppacher, 1967[a]) that the ice dendrites become very thin on increasing the supercooling. Their thickness has not been studied in detail, but some measurements exist of their width in the basal plane (Hallett, 1964), which may be used for comparison.

In the first column of Table II the width of the dendrites (secondary branches), obtained from Hallett's curves, is given for a few temperatures. From these values, the radius of curvature at the tip, $\frac{1}{2}\rho$, has been obtained considering in the calculations the dendrite cap as a paraboloid of revolution and supposing that the width ($= 2R$) was measured at about 1 mm from the tip (as may be deduced from Hallett's figures). The results are represented in the third column of the table ($\frac{1}{2}\rho$ exp.). Finally the theoretical values of $\frac{1}{2}\rho$, shown in the fourth column, were obtained by Bolling and Tiller (1961), as an application of the theory of

non-isothermal dendrites. The comparison of the figures in the third and the fourth column shows that the development of the ice dendrites in the basal plane is in approximate agreement with the theoretical results.

TABLE II. RADIUS OF CURVATURE AT THE TIP OF DENDRITES IN THE BASAL PLANE

ΔT deg	Width μm	$\frac{1}{2}\rho$ <i>exp.</i> μm	$\frac{1}{2}\rho$ <i>theor.</i> μm
1.6	42	0.45	0.50
3.7	26	0.17	0.13
4.8	20	0.10	0.11

Since these dendrites are, over the whole range studied, much thinner than they are wide, it follows that the theory of non-isothermal dendrites should not be applied to calculate their thickness and so $V_c \ll V_a$ for the same interface supercooling, in agreement with the present interpretation.

(d) *Modification of the angle α for ice dendrites growing in aqueous solutions.* The growth velocity and the angle 2α have been measured in aqueous solutions of several electrolytes by Lindenmeyer (unpublished) and by Pruppacher (1967[a]) and in solutions of sucrose by Macklin and Ryan (1966, 1968). The results are very similar. They show that the presence of a solute in water decreases the growth velocity and increases the angle 2α . The effect is nearly independent of the solute substance.

So, for electrolyte solutions of a concentration 10^{-1}N , the limiting value of 2α (similar to the limit $2\alpha = 45^\circ$ for pure water) is shifted to $2\alpha = 60^\circ$. This is reached for instance at $\Delta T = 4$ deg and at $\Delta T = 6$ deg for Na salts and for NH_3 salts respectively. Macklin and Ryan (1968) do not give the angle 2α directly, but they plot the growth velocities V_a and V_c as a function of ΔT . By comparing the curves the angle 2α may be calculated and the limit value is obtained again at $2\alpha \approx 60^\circ$ for a 10^{-1}N sucrose solution (reached at $\Delta T \approx 4$ deg).

Macklin and Ryan also indicate that the initial temperature of splitting ΔT_0 is increased for solutions as compared with pure water, being for instance $\Delta T_0 = 1.2$ deg for a 10^{-1}N and $\Delta T_0 = 0.2$ deg for a $2 \times 10^{-1}\text{N}$ sucrose solution (the same authors give $\Delta T_0 = 2.7$ deg for pure water).

It is known that the inhibition of the growth velocity caused by the presence of a solute is related to the concentrated layer formed at the interface of the advancing tip (Bolling and Tiller, 1961) which reduces the melting point and consequently the effective interface supercooling with respect to the bath supercooling. Now, according to the interpretation of the splitting and inclination of dendrites proposed here, the concentration gradient existing near the dendrite tip could also be the cause of the increase of α . Actually, since the lateral growth is much slower than the advance of the tip, the concentration layer may get diluted along the dendrite body. Supposing this part of the dendrite can be considered as approximately isothermal, the interface supercooling should increase at some distance from the tip and consequently the effects of the lateral instabilities considered above should also increase.

This interpretation would explain why the effect depends very little on the particular substance used as a solute. It would also eliminate the contradiction observed by Pruppacher (1967[a]) with the results obtained for ice growing in capillaries*, according to which the growth velocity of ice in the direction of the c -axis, measured in other experiments, would be slightly inhibited by the presence of small concentrations of some electrolyte. In fact, this would be a minor effect compared with the change of the interface concentration along the dendrite body.

* This contradiction has been observed by Pruppacher (1967[a]), who also cites Farrar (unpublished) and Sperry (unpublished). For the present article, these two items could not be consulted.

On the other hand, this kind of explanation could not be applied if the interpretation of the irrational growth of ice dendrites given by Macklin and Ryan (1966) is accepted, because in this case the phenomenon would not be related to the different supercoolings existing at different points of the dendrite cap.

CONCLUSIONS

The results discussed above may now be used to obtain the law of the growth velocity of ice in the direction of the c -axis as a function of $(\delta T_i)_c$.

In the interval of bath supercoolings $2 \text{ deg} \leq \Delta T \leq 8 \text{ deg}$,

$$V_c = 0.01 (\delta T_i)_c^3. \quad (13)$$

The average exponent n of $(\delta T_i)_c$ is slightly smaller in the last interval of Table I, $8 \text{ deg} < \Delta T < 18 \text{ deg}$, where it is $n \approx 2.5$.

According to the general theory of the molecular mechanism of growth, Equation (13) should correspond well enough in the interval of temperatures where the transitional growth regime prevails ($n > 2$ according to Cahn and others (1964)). This regime represents the transition between the growth by lateral spreading of steps ($n = 2$) and the continuous regime ($n = 1$).

As observed by Hallett (1964) and by Pruppacher (1967[a]), previous results on the growth of ice in capillaries in the direction of the c -axis, for $\Delta T \leq 1 \text{ deg}$, indicate that in these conditions the growth velocity increases much more slowly than predicted by Equation (13). Though the present and previous results are not strictly comparable because of the different growth methods used, this difference seems to indicate that the transition supercooling $(\delta T_i)_c^*$ between the growth by lateral spreading of steps and the transitional regime must be found near the low limit of Table I ($(\delta T_i)_c^* \leq 1 \text{ deg}$). According to Pruppacher a similar transition in the direction of the a -axis should take place at $(\delta T_i)_a^* = 0.58 \text{ deg}$. Then, if we do not discuss here the difference between the laws represented by Equations (3) and (13), and we admit that both of them may represent the transitional regime, in spite of the different exponent of (δT_i) , we should conclude that the transition temperatures depend very little on the growth direction. Consequently, since (Cahn and others, 1964)

$$(\delta T_i)_a^* = g\gamma v_s T_m / aL$$

where v_s , the molecular volume of the solid, T_m , the melting point, a , the step height, L , the latent heat of fusion and γ are all constants, the parameter g , which is a measure of the diffuseness of the surface, should be approximately the same ($g \approx 10^{-2}$ according to Pruppacher (1967[b]), and the ice surface in contact with the liquid should be rather diffuse, irrespective of its orientation.

ACKNOWLEDGEMENTS

The author is grateful to D. Fainstein for helpful discussions and to E. Achaval for reading the text.

MS. received 15 February 1969 and in revised form 29 July 1969

REFERENCES

- Bolling, G. F., and Tiller, W. A. 1961. Growth from the melt. III. Dendritic growth. *Journal of Applied Physics*, Vol. 32, No. 12, p. 2587-605.
 Cahn, J. W., and others. 1964. The molecular mechanism of solidification, by J. W. Cahn, W. B. Hillig and G. W. Sears. *Acta Metallurgica*, Vol. 12, No. 12, p. 1421-39.
 Hallett, J. 1964. Experimental studies of the crystallization of supercooled water. *Journal of the Atmospheric Sciences*, Vol. 21, No. 6, p. 671-82.

- Levi, L., and Aufdermaur, A. N. 1969. Orientation of ice crystals grown by accretion of supercooled droplets. (In Riehl, N., and others, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9-14, 1968*. Edited by N. Riehl, B. Bullemer, H. Engelhardt. New York, Plenum Press, p. 620-30.)
- Lindenmeyer, C. S. Unpublished. The solidification of supercooled aqueous solutions. [Ph.D. thesis, Harvard University, 1959.]
- Lindenmeyer, C. S., and Chalmers, B. 1966. Growth rate of ice dendrites in aqueous solutions. *Journal of Chemical Physics*, Vol. 45, No. 8, p. 2807-08.
- Macklin, W. C., and Ryan, B. F. 1965. The structure of ice grown in bulk supercooled water. *Journal of the Atmospheric Sciences*, Vol. 22, No. 4, p. 452-59.
- Macklin, W. C., and Ryan, B. F. 1966. Habits of ice grown in supercooled water and aqueous solutions. *Philosophical Magazine*, Eighth Ser., Vol. 14, No. 130, p. 847-60.
- Macklin, W. C., and Ryan, B. F. 1968. Growth velocities of ice in supercooled water and aqueous sucrose solutions. *Philosophical Magazine*, Eighth Ser., Vol. 17, No. 145, p. 83-87.
- Pruppacher, H. R. 1967[a]. Growth modes of ice crystals in supercooled water and aqueous solutions. *Journal of Glaciology*, Vol. 6, No. 47, p. 651-62.
- Pruppacher, H. R. 1967[b]. Interpretation of experimentally determined growth rates of ice crystals in supercooled water. *Journal of Chemical Physics*, Vol. 47, No. 5, p. 1807-13.