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Growth mechanisms to explain the primary and secondary habits of snow crystals

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Abstract

By estimating the diffusion field adjacent to growing snow crystals and using a variety of ice crystal growth data, it is shown that most observations of snow crystal habits above -22° C are explained by dislocation-promoted growth at small sizes and low supersaturations, but otherwise layer nucleation controls the growth habits in agreement with the Knight-Frank theory. The formation of capped columns, crown crystals, and hollowed crystals, and the growth rates of needles and dendrites also fit predictions of the theory. The analysis suggests that dendrites at water saturation retain small facets at their growing tips. Below -22° C, the available data together with predicted trends of the edge energy show that spiral steps and layer nucleation can explain why both tabular and columnar forms grow at the same temperature but different supersaturations. Other growth mechanisms that were proposed in the past, such as step speed variations, surface phase transitions and adatom migration across crystal edges are incapable of explaining the wide variety of available habit data.

§1. INTRODUCTION

Growth shapes of faceted crystals are determined by the relative growth rates of their faces and thus controlled by surface kinetics and bulk transport of both material and heat. Hence, growth shapes are much more diverse than equilibrium shapes, which are determined by surface free energies. Of all single-component vapourgrown crystals studied to date, few have shapes (habits) as sensitive to environmental conditions and probably none has been studied as long as the snow crystal. Their variable habits were noted at least as far back as Descartes (Frank 1982) and their usual sixfold symmetry was first recorded around 135 BC (Needham and Gwei-Djen 1961), but how the habit depends on environmental conditions was not found until 1936 (Nakaya and Sekido 1936). Further work by many scientists on how the snow crystal habit depends on temperature and supersaturation in an atmosphere of air is summarized as figure 1. Despite many attempts over their long history of study, a complete, widely accepted theory for their growth habits has not emerged. This paper shows that the interplay between two mechanisms can explain both figure 1 and also how crystal habit depends on the ambient gas pressure.

Snow crystal shape is classified into primary and secondary habits. The primary habit of single crystals depends on their aspect ratio Γ : the ratio of the maximum length 2c along the c axis (0001) to the maximum width 2a along (1120) (figure 2).

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Figure 1. Modified Nakaya diagram of snow crystal growth habits after about 10 min growth at 1 atm at various ambient temperatures and supersaturations (aufm Kampe et al. 1951, Nakaya 1954, Hallett and Mason 1958a, Kobayashi 1961, Wang and Fukuta 1985, Takahashi et al. 1991). The high-supersaturation primary habits (labelled at the top) are less exaggerated at 3.3 min (Yamashita 1974, Ryan et al. 1976). The water saturation curve is the ice supersaturation of liquid water equilibrium. Terms are from Magono and Lee (1966): solid thick plate (C1g), hexagonal plate (P1a), solid column (C1e), hollow column (C1f), elementary sheath (N1c), elementary needle (N1a), crystal with broad branches or sector plate (Plc) and dendritic crystal (P1e). Only Cle and Clg are simple eight-sided polyhedra; all others have lacunae, that is slower-growing regions, on their faces. The dotted curves are boundaries of Ple and N1c growth without air flow; they extend a few per cent lower in supersaturation for free-falling crystals (Takahashi et al. 1991). Polycrystals and trigonal crystals are not shown as their formation depends on the nucleation conditions. The vertical dividing lines separating the high-supersaturation primary habits range between the value of -20° C obtained by aufm Kampe *et al.* to the value of -25° C found by Hallett and Mason for the coldest transition but are more consistent among experiments at the warmer transitions. Because latent heating increases the surface temperature with increasing supersaturation, these dividing lines should tilt towards the ordinate (Rottner and Vali 1974). Low-supersaturation habits usually have Γ (defined in figure 2) between 0.5 and 2.0, although there are many exceptions and conflicting observations owing to variations in defect content, thermal gradients, substrate influences and growth times (Nelson and Knight 1998); hence, they are not shown. Above -20°C and below 0.1% supersaturation, the equilibrium habit is tabular with $\Gamma \approx 0.4$, but well rounded in the basal plane above -10°C (Colbeck 1985), although supersaturation gradients might have affected the measured Γ .

This ranges from tabular ($\Gamma < 1$) through isometric ($\Gamma \approx 1$) to columnar ($\Gamma > 1$). The secondary habit is the finer details of shape, such as the magnitude of Γ , the amount of hollowing, and the number and shape of branches or needles. Except at the lowest supersaturations, the primary habit depends only on temperature in an inert-gas atmosphere, whereas the secondary habit changes with time, temperature, supersaturation, crystal size, vapour mean free path and thermal conductivity of the



Figure 2. (a) Dimensions of a solid prismatic ice crystal and (b) the shape used for calculations of aspect ratio Γ during growth. $\Gamma = c/a$ and the face names are the same for both shapes. z is a general coordinate used for both faces to describe positions on the surface.

air. Both habits are also sensitive to small concentrations of gaseous impurities. For example, Hallett and Mason (1958b) and Nakaya *et al.* (1958) found that 10^{-3} mbar of isobutyl alcohol and 10^{-5} mbar of acetone respectively cause habit changes near -16° C. In contrast, sublimation shapes depend only on the initial crystal shape before sublimating (Nelson 1998). Because snow crystal surfaces are mostly facets, growth is by step formation and motion; therefore, the goal here is to determine the step sources and how they determine the crystal habit. This involves calculating the step generation rate for various growth mechanisms on freely falling crystals, which requires estimates of the surface parameters and comparison of the various processes that affect growth.

The Burton, Cabrera and Frank (BCF) (1951) theory of spiral-step growth and adatom diffusion is used here because it predicts both observations of dislocation outcrops (Gonda et al. 1994) and the relation between the adatom migration distance (Mason et al. 1963) and the step speeds (Kobayashi 1967) even though it is not designed for partly disordered surfaces such as ice and poorly estimates the migration distance and step speeds on the basal face. The diffusing species on ice surfaces could be single molecules, surface vacancies or molecular clusters, and their diffusion constant could be concentration dependent (Zinke-Allmang and Feldman 1988, Myers-Beaghton and Vvedensky 1990). Thus more general surface diffusion models that include adatom-adatom interactions and vacancies might ultimately be needed for ice surfaces, but they contain parameters that are at present difficult to estimate. Furthermore, although stacking faults are common in frost crystals (McKnight and Hallett 1978, Mizuno 1978) and could produce self-propagating regions on prism faces that have easier layer nucleation (van de Waal 1996), their growth mechanism on ice surfaces has not been developed. Hence, even though they might promote tabular growth in some conditions, only spiral step and layer nucleation growth mechanisms are considered here. Finally, except where noted, latent heating of the crystals is not considered.

Accurate prediction of crystal habit in cold cirrus clouds might improve climate modelling because the habit, which is varied and often polycrystalline, affects the optical properties of these clouds (Iaquinta *et al.* 1995, Macke *et al.* 1998). Below -22° C, columnar forms are more common (Heymsfield and Platt 1984, aufm Kampe

et al. 1951), although both primary habits are observed in clouds (Korolev et al. 1999), in experiments (Gonda and Koike 1983) and even side by side (Keller et al. 1980). A better understanding of snow crystal growth mechanisms can clarify the habit diagram in figure 1, which thus has important applications.

§2. PRIMARY HABIT

2.1. Layer nucleation: adatom migration over edges

Extending a suggestion by Hallett (1961), Mason *et al.* (1963) proposed that columnar crystals form when the adatom migration distance x_b on the basal face is less than the adatom migration distance x_p on the prism face, and vice versa for tabular crystals. (The subscripts b and p refer to basal and prism faces respectively.) They argued that a smaller x_b results in a net migration of adatoms from the prism to the basal and consequently more rapid nucleation on the latter face. The opposite was assumed true when x_b is greater than x_p . Mason (1993) used this argument plus data on growth shapes to predict values of x_p , which have not been measured.

There are three problems with their hypothesis. Firstly, it fails unless the basal and prism faces have nearly identical layer nucleation rates far from edges. However, instead, these two faces should have different layer nucleation rates because they probably have different surface energies and hence different edge energies (§2.3). Secondly, assuming that there are equal layer nucleation rates for both faces far from the edge, assuming that there is no additional energy barrier for an adatom to cross the edge and assuming that nucleation occurs at equal distances from the edge for both faces, then the BCF theory instead predicts the opposite primary habits to those that Mason et al. explained. Changing the latter two assumptions can alter this conclusion but that would introduce new unknown surface parameters. Finally, if adatom migration determines the primary habit when crystal sizes are several microns or less, then according to Mason's (1993) equations, the primary habit would be independent of supersaturation, which is contrary to low-supersaturation data (figure 1) and low-temperature data ($\S 2.6$), and the secondary habit would be very sensitive to the initial crystal size, which is contrary to the data given later in figure 9. Thus, adatom migration over edges cannot explain the primary habit, although it might affect the growth rates of small-area faces (§ 3.4).

2.2. Layer nucleation: step speeds

Hobbs and Scott (1965) suggested that nucleation rates increase with increasing speed of isolated steps; therefore, Hallett's (1961) measured step speeds on the basal face could explain the primary habit if certain prism-face step speeds are assumed. However, Kobayashi (1967) and Cho and Hallett (1984) later measured different step speeds that could not explain the primary habit according to this model. Furthermore, as suggested by Lamb and Scott (1972), if the BCF model had been used consistently in their theory, variations in the step speed would not cause variations in the nucleation rates because the step separation would vary in the opposite manner. Thus theory and lack of relevant data make it difficult to explain primary habit in terms of step speeds.

2.3. Layer nucleation: critical supersaturations

Knight (1972, 1996) and Frank (1974) suggested that the primary habit could be explained by the relative rates of layer nucleation on the basal and prism faces.

Because only small increases in supersaturation above a critical value result in large increases in the growth rate, only small relative changes in the critical supersaturations between the basal and prism faces are needed to produce different primary habits.

At low supersaturations, the growth rate R for a face nucleating circular disc embryos at the edge with supersaturation σ_e is proportional to

$$R \propto \exp\left[48\left(1 - \frac{\sigma_{\rm cr}}{\sigma_{\rm e}}\right)\right],$$
 (1)

where σ_{cr} is the critical supersaturation at which one layer per second is nucleated on the surface (appendix A). For a circular disc embryo, this is

$$\sigma_{\rm cr} \equiv \frac{\pi a_0 \kappa^2}{48 (kT)^2},\tag{2}$$

where a_0 is the area of a molecule on the surface, κ is the edge energy, k is Boltzmann's constant and T is the temperature. It follows from equation (1) that a 10% increase in σ_e near σ_{cr} results in a growth rate increase of exp (4.8) \approx 100; from equation (2), the same growth rate change results from a 10% decrease in σ_{cr} , which needs only a 5% decrease in κ . Referring to figure 3, if the critical supersaturation on the basal σ_{cr-b} is less than that on the prism σ_{cr-p} , and both step sources are at the edge with supersaturation σ_e , then almost no growth occurs at supersaturations less than line a; between lines a and b there is only growth on the basal leading to thin columns; however, at supersaturations above line b, both faces grow until at c they grow at equal rates. (This saturation in growth rates is described in appendix A.) Except for the brief initial growth on micron-sized crystals when the surface supersaturation σ_e can be close to the ambient, σ_e is well below line c. Thus over most of the range in which growth occurs, it only occurs on one face leading to very thin or narrow crystals. Therefore, the layer nucleation mechanism requires that $\sigma_{cr-b} > \sigma_{cr-p}$ above -3° C, $\sigma_{cr-b} < \sigma_{cr-p}$ between -9 and -3° C, $\sigma_{cr-b} > \sigma_{cr-p}$ between -22 and -9° C, and $\sigma_{cr-b} < \sigma_{cr-p}$ below -22° C to explain the primary



Figure 3. Growth habit from layer nucleation on both basal and prism faces as a function of surface supersaturation when the basal critical value is the lowest.



Figure 4. Measured critical supersaturations σ_{cr-b} and σ_{cr-p} for the basal (■) and prism
 (▲, ▼) faces respectively (Nelson and Knight 1998). The left-hand ordinate is for the hand-drawn shaded curve that fits the adatom migration distance data on the basal face (Mason *et al.* 1963).

habits in figure 1. Nelson and Knight (1998) found that many basal faces and some prism faces were perfect, which allowed direct measurement of σ_{cr-b} and σ_{cr-p} ; the data, reproduced as figure 4, directly supports this mechanism above -16° C. Finally, that layer nucleation probably controls sector and dendritic growth follows from the straightness of their arms (Nelson and Knight 1998) and their near-symmetric growth patterns (Frank 1982). Imperfections, particularly from dislocation outcrops, alters the simple description in this section; however, the formation of lacunae can minimize the influence of imperfections, thus allowing layer nucleation to produce extreme habits on nearly perfect regions of snow crystals (§ 3).

2.4. Spiral-step growth

Spiral steps, probably from surface outcrops of screw dislocations, could affect snow crystal growth: spiral steps have been observed to grow and evaporate ice crystal faces (Furukawa and Kohata 1993, Gonda et al. 1994), substrate-grown crystals in pure vapour often follow the spiral-step prediction of the BCF theory (Lamb and Scott 1972, Beckmann and Lacmann 1982, Sei and Gonda 1989) and, above -20° C, negative crystals grown in ice blocks with many dislocations have the same primary habit as high-supersaturation positive crystals (Knight and Knight 1965, Furukawa and Kohata 1993). X-ray measurements also showed screw and edge dislocations in vapour-grown ice (McKnight and Hallett 1978, Mizuno 1978). However, the dislocation density was highest where the crystals were supported, and some dislocation-free prism faces grew at the same rate as those with dislocations. Also, after observing etch pits on snow crystals, Kuroiwa (1961) suggested that the crystals collected small particles during free fall that produced dislocations. Such dislocations could produce spiral steps during growth but, for collection to be significant, the crystals must be relatively large (§3.5) and, furthermore, etch pits can form without dislocations.

Although cloud supersaturations can exceed 30% (water saturation when $T < -27^{\circ}$ C), surface supersaturations near the crystal σ are small because vapour

exchange with the surface is much faster than vapour diffusion. In this case, the growth rate from a distribution of spiral steps is (BCF)

$$\frac{\mathrm{d}c}{\mathrm{d}t} \propto \beta \varepsilon \sigma^2 \left(\frac{2kTx_{\mathrm{b}}}{19a_0\kappa_{\mathrm{b}}}\right) = \beta \varepsilon \frac{\sigma^2}{\sigma_1},\tag{3}$$

where β is the collisional sticking coefficient of a vapour molecule on the terrace multiplied by a factor that would be less than one if impurities block growth sites and ε is a dimensionless factor that depends on σ and both the positions and signs of the dislocations. At supersaturations above the characteristic supersaturation σ_1 , the right-hand side of equation (3) is multiplied by $\tanh(\sigma_1/\sigma)$, which makes the growth rate independent of σ_1 . Spiral-step growth rates are further reduced by

- (i) coupling between vapour and adatom diffusion fields when the vapour mean free path is less than x_b (Gilmer *et al.* 1971) and
- (ii) the depletion of adatom concentration at the spiral centre by nearby spiral turns (Surek *et al.* 1973).

Effect (i) can be large at low supersaturations, whereas effect (ii) is relatively small but, for simplicity, neither effect is considered here. ε depends on the configuration of dislocations in the initial crystal nucleus and its variability would cause variations in crystal habit under the same conditions (for example Lubetkin and Dunning (1978)), as would the two types of spiral step with different σ_{1b} values measured at -28.5° C (Gonda *et al.* 1994). The most anisotropic growth occurs when the growth-dominating spirals are at the edge (see figure 9 later), which occurs in the unlikely case that each face has many spiral steps with $\varepsilon \approx 1$; the resulting ratio of growth rates is independent of σ :

$$\frac{\mathrm{d}c}{\mathrm{d}a} = \frac{\beta_{\mathrm{b}}}{\beta_{\mathrm{p}}} \frac{x_{\mathrm{b}}/\kappa_{\mathrm{b}}}{x_{\mathrm{p}}/\kappa_{\mathrm{p}}} = \frac{\beta_{\mathrm{b}}}{\beta_{\mathrm{p}}} \frac{\sigma_{\mathrm{1p}}}{\sigma_{\mathrm{1b}}}.$$
(4)

Sei and Gonda (1989) argued that the primary habit is controlled by β_b/β_p , which they measured on ice crystals grown in a pure vapour on a substrate. However, the measured ratios varied from 0.64 to 1.3 and were even closer to one because of temperature gradients in the crystals (Nelson 1993); thus β_b/β_p cannot explain the observed high-supersaturation snow crystal Γ values that typically range from 0.01 to 20. Hereafter β_b and β_p are assumed to be one. Lamb and Scott (1972) instead argued that σ_{1p}/σ_{1b} determines the primary habits, which is consistent with the lowsupersaturation data of Kobayashi (1961) and the negative crystal data, both sets of which also had considerable variation in Γ . Unfortunately, most direct measurements of σ_{1p} and σ_{1b} are unreliable because growth rates are affected by both temperature gradients and layer nucleation between spiral steps (§ 2.7).

Both spiral-step and layer nucleation growth rates increase when κ decreases, although the former also depends on x_b and x_p ; therefore, low-supersaturation primary habits can be the same or different from high-supersaturation habits depending on how much x_b differs from x_p , the latter of which has not been measured. For instance, if x_p is close to $4 \mu m$ (the maximum value of x_b), then equation (4) with $\kappa_b/\kappa_p \approx (\sigma_{cr-b}/\sigma_{cr-p})^{1/2}$ (equation (2)) and the data in figure 4 can explain the nearly isometric tabular crystals observed by Kobayashi (1961) below and above -10° C. However, layer nucleation growth rates increase much more rapidly with

supersaturation than does spiral-step growth, and so growth at moderate to high supersaturations is more probably due to layer nucleation ($\S2.7$).

2.5. Surface phase transitions

Kuroda and Lacmann (KL) (1982) argued that the growth rate of each face is fastest when rough, slower when surface melted and slowest when smooth; furthermore, KL assumed that each of these phases would occur on each face over some temperature range. The theory of Fukuta and Lu (1994) also required rough and surface-melted surfaces. The arguments below indicate serious flaws in both theories.

On rough surfaces, the growth rate is proportional to the surface supersaturation σ , which is non-uniform on a facet in a diffusion field. Hence, rough snow crystal surfaces cannot remain faceted. However, only prism facets have vanished on snow crystals (Keller *et al.* 1980, Yamashita and Asano 1984), but this is rare. Rough surfaces thus cannot explain the primary habit of a snow crystal.

In a uniform melt layer, both the liquid-vapour and the solid-melt interfaces have phase changes. The liquid-vapour interface cannot limit growth as all incident vapour molecules condense. So instead, KL assumed that the solid-melt interface limits growth, but it was shown by Nelson and Knight (1998) that measured critical supersaturations are at least ten times greater than those that would result from such solidification-limited growth. This discrepancy should only worsen if the melt layer is partly ice like (Mizuno and Hanafusa 1987) for the following reason: critical supersaturations for the solid-melt growth should decrease with decreasing edge energy κ (e.g. equation (2)), but κ should decrease as the two phases become more nearly equal. Conversely, if the vapour interface retains ice-like ordering, as the data of Golecki and Jaccard (1978) showed, the vapour interface would limit growth, which is contrary to KL's assumption. Measurements of surface disorder are inconsistent (Petrenko and Whitworth 1999) and theories of surface melt layers are disputed (Knight 1996); nevertheless, growth into a surface melt layer is inconsistent with data.

KL argued that vapour diffusion causes columnar growth at low temperatures but, instead, the diffusion field calculations for spheroids by Ham (1959) and cylinders by Nelson and Baker (1996) show that vapour diffusion favours no particular Γ . The side-by-side column and plate observed by Keller *et al.* (1980) also cannot be explained by their diffusion field argument. A more fundamental problem with the KL theory is that it requires the basal's roughening temperature coincidently to equal the prism's surface-melting transition temperature.

2.6. Primary habits at low temperatures

Below about -22° C, mostly columns grow in clouds (figure 1), but both primary habits occur when supersaturations are low. Thus layer nucleation cannot be the sole growth mechanism. Although information about growth mechanisms at low temperatures is lacking, the previously described trends and theories are extended to lower temperatures to see what they predict.

A striking feature of the basal face critical supersaturations σ_{cr-b} is the resemblance to measured x_b values (figure 4) and basal step speed data (Kobayashi 1967, Cho and Hallet 1984). If σ_{cr-b} continues to follow the x_b trend to lower temperatures by decreasing, and if σ_{cr-p} continues to increase, then layer nucleation should cause a transition to high-supersaturation columnar growth below about -20° C, in agreement with figure 1. (However, σ_{cr-b} cannot decrease as low as the values in the

needle-growth regime because needles are not observed at low temperature even with the higher water saturation.) Based on observed habits at water saturation, Wood *et al.* (2001) also argued that $\sigma_{cr-b} < \sigma_{cr-p}$ below -22° C. Explaining why the σ_{cr-b} and x_b temperature trends are similar is speculative, but these quantities could be correlated through the surface concentration of adatoms. When the adatom concentration is high, the edge energy κ and thus σ_{cr-b} should be low because there are more adatoms in contact with the step (analogous to a two-dimensional solid-melt interface); the increased adatom concentration can also significantly decrease the surface diffusion constant (Zinke-Allmang and Feldman 1988, Myers-Beaghton and Vvedensky 1990), which would decrease x_b if the adatom desorption rate remains relatively constant (BCF).

Low-supersaturation growth can be consistently different from high-supersaturation growth. If dislocations outcrop and make spiral steps on a face, they dominate growth at 6 values below a transition supersaturation that should increase with increasing $\sigma_{\rm cr}/\sigma_1$, which, from equations (2) and (3), increases with $\kappa^* x$. Above -16° C, dislocations dominate growth only at low supersaturations for both faces. On the basal face, $x_{\rm b}$ continues to decrease to the lowest temperature measured $(-30^{\circ}C)$ and thus this transition supersaturation should remain low at low temperatures; however, on the prism face, $\sigma_{\rm cr-p}$ and thus $\kappa_{\rm p}$ seems to increase with decreasing temperature (figure 4), which follows the BCF trend that also predicts that x_p increases; hence, dislocations probably dominate prism-face growth at a greater range of supersaturation at low temperatures. It follows that the lowest supersaturation habits at low temperature should be tabular. Therefore, a hypothesis for the primary habits below -22° C is faster layer nucleation on the basal face near liquid water saturation, leading to columnar growth, but dislocation-aided growth usually leading to tabular forms at lower supersaturations. Because of variations in the activities, densities and positions of dislocations among crystals formed different ways and because of variations in supersaturation, this transition to mostly columnar growth could vary for different observations. This might explain the relatively wide range of reported transition temperatures for the low-temperature primary habit in figure 1.

Other observations agree with this hypothesis. c-axis whisker growth suggests that σ_{cr-p} increases to several per cent at $-40^{\circ}C$ (Kobayashi 1965). These whiskers and the long, thin, solid columnar 'diamond dust' observed by Shimizu (1963) can form at low supersaturations and when relatively few dislocations are present in the crystal because columnar growth needs only one dislocation outcrop on a basal face, whereas tabular growth requires at least one outcrop on each of two adjacent prism faces. (If only one prism face grows, the increasing areas of the adjacent faces will make it vanish.) Finally, crystals in cirriform clouds are usually single or clusters of hollow columns thus indicating higher supersaturation growth (\S 3.2, 5), whereas tabular crystals generally have few lacunæ (aufm Kampe et al. 1951), which indicates lower supersaturations. Also, low-supersaturation low-temperature experiments consistently predict tabular forms; Gonda and Koike (1982) and Gonda (1983) found tabular growth below -30° C; measured slopes of growth hillocks are steeper on the prism than on the basal face at -28.5° C (Gonda *et al.* 1996); finally, most low-temperature measurements of growth rates in negative crystals, in which spiral steps were observed, had faster prism-face growth (Furukawa and Kohata 1993). Although this hypothesis for low-temperature habits is speculative, it links a wide range of observations. The limiting Γ of about 1.4 for snow crystals on a fibre observed by Kobayashi (1961) are difficult to explain by this argument, but influences from the fibre or the mixed growth mechanism described below (§2.7) might explain this limiting Γ .

2.7. Simultaneous spiral-step and layer nucleation growth

The general situation of layer nucleation between spiral steps is hard to analyse accurately because of supersaturation gradients, variations in dislocation outcrops and fluctuations in step spacings. A simplified formula for the ratio of layer nucleation to spiral-step growth rates (Lewis 1980) that fit data on potassium dihydrogen phosphate crystal growth (De Yoreo *et al.* 1994) predicts that the surface supersaturation should be about 30% higher than measured σ_{cr} values for growth to be dominated by layer nucleation. This requires significantly larger ambient supersaturations but can be reached at the higher supersaturations in the atmosphere because critical supersaturations are so small.

§3. SECONDARY HABITS

3.1. Effects of vapour diffusion

Snow crystals grow thinner or narrower and with lacunae as the ambient supersaturation increases (figure 1); but, at a fixed temperature and supersaturation, crystals are more isometric and have fewer lacunae as the vapour diffusivity increases (Gonda 1980, Kobayashi 1958, Isono 1958). These phenomena arise because the gas surrounding the crystals causes supersaturation gradients normal to and along crystal surfaces respectively, as shown in this section.

The vapour supersaturation σ at the surface, averaged over about the vapour mean free path, is determined by vapour diffusion and the normal growth rate (m s⁻¹). The latter depends on σ . For the basal face

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \Omega \frac{v}{4} N_{\mathrm{eq}} \alpha_{\mathrm{b}} \sigma(\mathbf{z}_{\mathrm{b}}), \tag{5}$$

where Ω is the volume per molecule in ice, v is the mean molecular speed in the vapour, N_{eq} is the equilibrium vapour density at the surface temperature (typically less than 1°C above ambient for solid polyhedral crystals (Nelson and Baker 1996)), $\sigma(z)$ is the supersaturation at position z, and α_b is the condensation coefficient where steps form at z_b . The relation for da/dt follows from equation (5) using obvious substitutions. Assuming that the tips of needle crystals are 0.5° C warmer than the ambient, the needle (N1a) growth rates after 10min growth as measured by Takahashi et al. (1991) give $\alpha_b = 1.0 \times 10^{-3}/\sigma$. This $\alpha_b(\sigma)$ relation is compared with that deduced for layer nucleation growth in figure 5. The intersection of the curves at c is near $\alpha = 0.5$ with a surface supersaturation of 0.18%. This is consistent with the argument that only the basal face grows by layer nucleation because the surface supersaturation cannot rise much above the critical value of 0.15%. Conversely, σ must exceed 0.45% to nucleate layers on the adjacent prism faces, which requires a growth rate 4.5 times faster. Hence, the prism face probably grows by spiral steps at a supersaturation near 0.03%, where curves a in figure 5 intersect. At -15.5° C, the dendritic (Ple) growth rate data of Takahashi et al. (1991) yield similar conclusions (figure 6); the estimated supersaturation at the tip is about 0.55%, only slightly higher than the critical value, and $\alpha = 0.8$. Because σ must exceed 2.5% to nucleate steps on the basal face at this temperature, only the



Figure 5. Estimated surface supersaturations on needle (N1a) crystals based on measured c and a data from Takahashi et al. (1991); solid curve c, inferred $\alpha(\sigma)$ at -5.3° C for the basal face; solid curve a, inferred $\alpha(\sigma)$ at -5.3° C for the prism. Physically, α must be less than the dotted line at one. The shaded curves are bounded by the two $\alpha(\sigma)$ functions for layer nucleation (appendix A) fitted to σ_{cr-b} data in figure 4. The intersection of the shaded curves and curve c estimates the surface supersaturation σ_e at the edge. The prism-face σ_p needs to be about 0.0045 for layer nucleation, which is unlikely; hence, it is probably at the intersection of solid curve a with the broken line, which assumes spiral growth with $\sigma_{1p} = 0.8\%$.

prism face grows by layer nucleation. The basal face probably grows by spiral steps with σ near 0.1%, where curves c in figure 6 intersect. Hence, the measured growth rates of P1e and N1a crystals indicate that the outermost tips grow by layer nucleation and grow only in the fast-growth directions. Furthermore, that α is slightly less than one in both cases agrees with the observed small areas of the growing tips (§ 3.3).

Use of equation (5) for both faces shows that the ratio of the basal to prism face growth rates, and hence Γ , depends on surface kinetics via the α values and stepsource positions $(\mathbf{z}_{b}, \mathbf{z}_{p})$. The diffusion field affects Γ indirectly via its influence on the surface supersaturations and hence α and not directly as used by KL to explain columnar growth at low temperatures. Chen and Lamb (1994) calculated Γ by using fixed high-supersaturation values of α_{b} and α_{p} and assumed that the surface supersaturation is proportional to the vapour gradient. However, because each α clearly depends on surface supersaturation, growth habits are calculated here by integrating equation (5) for both faces with the following estimates of the surface supersaturation.

Assuming steady-state vapour diffusion with diffusion constant D, uniform flux across each face, and a crystal larger than the vapour mean free path, the surface supersaturation is

$$\sigma(\mathbf{z}) = \sigma_{\infty} - \alpha_{\rm b} \sigma(\mathbf{z}_{\rm b}) r_{\rm b} h_{\rm b}(\mathbf{z}, \Gamma) - \alpha_{\rm p} \sigma(\mathbf{z}_{\rm p}) r_{\rm p} h_{\rm p}(\mathbf{z}, \Gamma), \tag{6}$$

(appendix B) where $r_b \equiv av/(2^{3/2}D)$ and $r_p \equiv (ac)^{1/2}(v/2D)$ are the mean radii of the total basal face and prism face areas respectively scaled by the vapour mean free path 4D/v; $h_b(\mathbf{z}, \Gamma)$ and $h_p(\mathbf{z}, \Gamma)$ are functions (equations (B9)) that decrease at points \mathbf{z} further from the centre of face b or p because the effect of the vapour density flux to



Figure 6. Estimated surface supersaturations on dendritic (P1e) crystals based on measured c and a data from Takahashi et al. (1991); solid curve a, inferred $\alpha(\sigma)$ at -14.4° C for the prism face; solid curve c, inferred $\alpha(\sigma)$ at -14.4° C for the basal. The shaded curves are the same as those in figure 5 except that they are fitted to σ_{cr-p} data. The intersection of the shaded curves and curve a estimates the surface supersaturation σ_e at the edge. The basal-face σ_b needs to be about 0.026 for layer nucleation, which is unlikely; hence, it is probably at the intersection of solid curve c with the broken line, which assumes spiral growth with $\sigma_{1b} = 2.5\%$.

a face diminishes at points further from the face (see figures B 1 and B 2). Equation (6) is understood by picturing the crystal faces as interacting via their ability to deplete the surrounding air of vapour. The strength of the interaction depends on the shape h_b and h_p , the sizes r_b and r_p of each face and the growth rate of each face (proportional to $\alpha\sigma$). For instance, if both growth rates are zero ($\alpha = 0$), there is no vapour depletion and all surface supersaturations equal the ambient value σ_{∞} . Conversely, if there is only growth on the basal face ($\alpha_p = 0$) then $\sigma(z)$ decreases on the left-hand side of the equation as $\alpha_b r_b h_b(z)$ increases because vapour is depleted by growth on the basal face; furthermore, this decrease is greater for z nearer the basal face because h_b is larger there, as expected and predicted. The analogous equation for diffusion to a sphere has just one flux term with $h = \frac{1}{2}$, which is close to that for h_b and h_p at $\Gamma = 1$ (see figures B 1 and B 2).

To see which growth mechanisms explain the growth habits in Gonda's (1980) experiments, growth rates of each face for various α_b and α_p were calculated using equations (5) and (6). Starting with 4 µm isometric crystals, growth rates were integrated until the crystals fell about 5 cm to the substrate. This distance is small enough that few crystals developed lacunae, thus allowing the finite cylinder to be a good approximation. Libbrecht (1999) did related calculations with a finite cylinder but instead used crystal shapes from Yamashita (1974) to estimate the condensation coefficients. However, because Yamashita's crystals fell 15 m and had lacunae, Libbrecht's calculations probably overestimated the values. Gonda's (1980) data were used because they are more complete, but Isono (1958), Kobayashi (1958) and Beckmann (1982) obtained results consistent with Gonda's data.

In the curves in figure 7, the general trend at high vapour diffusivities is due to the smaller vapour gradients normal to the surface because there is less air to impede vapour transport. Without lacunae, the aspect ratio should approach the ratio of the



Figure 7. Calculated Γ for layer nucleation and spiral step growth compared with Gonda's (1980) measurements (\bullet). In the experiments, small supercooled drops were put in a chamber where a small fraction of them froze, grew and then fell approximately 5 cm on to a glass substrate to be measured. The temperature was -7° C and the gas pressure was varied. Curve 1 represents Γ for a crystal initially with $c = a = 2 \,\mu m$ that grew by spiral steps with $\sigma_{1b} = 4\%$ and $\sigma_{1p} = 8\%$. The crystal for curve 2 had the same initial size but grew at low supersaturations by spiral steps with $\sigma_{1b} = 0.4\%$ and $\sigma_{1p} = 0.8\%$ and by layer nucleation ($\sigma_{cr-b} = 0.17\%$ and $\sigma_{r-p} = 0.3\%$) with equal terrace collection (equation (A 6)) at higher surface supersaturations. Curve 3 used spiral-step growth as for curve 1 except that $\sigma_{1b} = 0.4\%$ and $\sigma_{1p} = 0.8\%$. Curve 4 is like curve 2 except only layer nucleation occurred. The broken curve is identical with curve 1, except that $c = a = 6 \,\mu m$. In this and following figures, the hexagonal crystal sketches are to aid interpretation only; all calculations used cylinders.

sticking coefficients. As σ_{∞} is 7%, values of σ_1 less than this will lead to a saturation of growth step density so that both $\alpha_{\rm b}$ and $\alpha_{\rm n}$ approach the sticking coefficients on each face. Therefore, data at high vapour diffusivities indicate that this ratio is unity. As it is unlikely that both sticking coefficients are equal unless they are both the maximum value of one, Gonda's (1980) data supports previously analysed data (Nelson 1993) that the sticking coefficients are near unity. In curve 1 of figure 7, one of the characteristic supersaturations is greater than the ambient value and so isometric growth does not occur. Because the data show isometric growth at high diffusivities, the actual values of σ_{1b} and σ_{1p} must be smaller than the ambient value of 7%; for instance, curve 3 agrees with the data when $\sigma_{1b} = 0.4\%$ and $\sigma_{1p} = 0.8\%$. If instead, only layer nucleation occurs, the step density saturates too easily at the high surface supersaturations from the larger diffusivities (curve 4); also, growth is too anisotropic at the low supersaturations from small vapour diffusivities unless spiral steps are included (curve 2). The broken curve in figure 7 shows that initially larger isometric crystals cannot develop large Γ values in such a short time. This is because they fall to the substrate sooner and grow more slowly. In conclusion, the habits of small snow crystals at $-7^{\circ}C$ are explained by a spiral-step-like mechanism with σ_{1b} and σ_{1p} near 0.4% and 0.8% respectively.

Gonda's (1980) data near -15° C and 16% ambient supersaturation is similarly analysed in figure 8. Spiral-step growth fits high-vapour diffusivity data when $\sigma_{1b} = 0.5\%$ and $\sigma_{1p} = 2.0\%$, which are close to the directly measured values of 1.1% and 3.1% of Gonda et al. (1994). The discrepancy could indicate coupling of vapour and surface diffusion ($\S2.4$). However, the data at low vapour diffusivities are not fitted by spiral growth, which produces shapes that are too isometric but, unlike the columnar crystals at -7° C, the tabular crystals had lacunae at the lowest diffusivities, and thus probably grew by layer nucleation, which has a greater growth anisotropy than spiral growth. Lacunary growth is also more anisotropic because arms growing from crystal corners have higher surface supersaturations than the centre of the basal face (§3.2). As with columnar growth at -7° C, layer nucleation by itself cannot easily explain the data. In these experiments, the crystal formed by the freezing of droplets, which probably had large stresses from the expansion upon freezing that could produce dislocations. Hence, the comparison of calculation with experiment supports the argument that the growth of small snow crystals can be explained by spiral steps, but layer nucleation is required to explain the greater growth anisotropies with lacunae (Nelson and Knight 1998). Beckmann (1982) argued that the trend towards isometric growth as pressure decreased was due to a lessening of impurity blocking at steps (β in equation (3)), but these calculations showed that such surface effects are not needed to explain the data.

These comparisons with calculation have uncertainties: fall distances, initial crystal sizes, varying ambient supersaturations, adatom migration over the edges during the initial growth, and uncertainties in the condensation coefficients from vapour-surface coupling. Nevertheless, they show that growth at small sizes probably occurs by a defect mechanism similar to or the same as spiral steps with characteristic supersaturations near the measured critical supersaturations, but layer nucleation could influence growth when the crystals become larger.



Figure 8. Gonda's (1980) data for growth at -15° C (\bullet), with conditions and calculated curves as described in figure 7. Curve 1 used spiral steps with $\sigma_{1b} = 2.6\%$ and $\sigma_{1p} = 0.4\%$ and initially $c = a = 2 \,\mu$ m. Curve 2 used $\sigma_{1b} = 2.0\%$ and $\sigma_{1p} = 0.5\%$ but otherwise the same as curve 1. Curve 3 used layer nucleation with equal terrace collection (equation (A 6)) and $\sigma_{cr-b} = 2.6\%$ and $\sigma_{cr-p} = 0.4\%$.

The trend towards extreme aspect ratios as the supersaturation increases or the crystals become larger also fits predictions of spiral step and layer nucleation growth. For instance, near -15° C and 1% supersaturation, near-isometric growth is common (Kobayashi 1961, Rottner and Vali 1974, Wang and Fukuta 1985) but, at 16% supersaturation, $\Gamma \approx 0.01$ (Takahashi *et al.* 1991). Spiral-step growth can dominate over layer nucleation when crystals are small or the supersaturation is low, but otherwise layer nucleation dominates over spiral steps because it occurs wherever the surface supersaturation. Needles and dendrite arms protrude into regions of higher supersaturation; furthermore, they are unlikely to contain spiral steps as X-ray measurements do not indicate the formation of dislocations during growth (McKnight and Hallett 1978, Mizuno 1978). Therefore, extreme growth anisotropy from layer nucleation can also occur on imperfect crystals in air when nearly perfect fast-growing regions of a face extend outwards from slow-growing imperfect regions.

At low ambient supersaturations, σ from equation (6) is initially high if $r_{\rm p}$ and $r_{\rm h}$ are initially about 4 ($c, a \approx 1 \,\mu\text{m}$ at 1 atm) or less but quickly decreases during growth. The adatom supersaturation can be lower still because of nearby molecular sinks from permanent steps ($\S2.7$). Therefore, if the ambient supersaturation is sufficiently low, even if above σ_{cr} , layer nucleation might never dominate growth. For example, when spiral steps in the face centres control growth with $\sigma_{1b} = 2.0\%$ and $\sigma_{1p} = 0.5\%$, and both a and c equal 7 µm, the decrease is still about 15% during growth, which brings the surface supersaturation below that needed to nucleate new layers at 1% and 2% ambient supersaturations. The time evolution of Γ for these cases is shown in figure 9. Although α_b/α_p is 0.25 at the same low σ , instead Γ becomes very nearly 0.8 because σ on the prism face is lower than that on the basal face. The higher supersaturation causes faster initial changes in Γ because of the faster growth rate, but slower changes in Γ later because the crystal is larger. This limiting Γ is slightly larger than that measured by Kobayashi at between -10 and -20° C and less than 3% ambient supersaturation; however, the calculations shown in figure 9 also indicate that Γ is significantly smaller when the step sources are at the edge. Because the spiral steps cannot always be exactly in the face centres, the agreement of calculation with measurement is well within the variations in measured Γ . Therefore spiral steps can explain the low-supersaturation habits, and their various positions on a face can lead to considerable variations in Γ .

At higher supersaturations, the edge area remains above the critical value as the crystal grows so that nucleation should eventually occur there. This leads to lacunae sooner than at lower supersaturations. With lacunae, only a relatively small area on the fast-growing face has an appreciable growth rate. Because decreasing the face area increases the supersaturation on that face (equation (6)), the rate of layer nucleation increases, which further decreases the rim area (§4). An accurate calculation of this phenomenon goes beyond the approximations here but is described qualitatively through the example in figure 10. For this figure, growth occurred only along the outer rim of the prism face to simulate lacunae: r_p in equation (6) was kept a twentieth of the actual size of the face. At -15° C and water saturation (16%), Γ and the crystal size very nearly matched the measured values of Takahashi *et al.* (1991) at -14.4° C and water saturation; after 20 min growth, Γ and the disc radii *a* were 0.009 and 1.6 mm respectively for the calculation, versus 0.01 and 1.4 mm for the measurements. Without the lacunae, the width would have been more than ten times smaller. Also, the calculated σ_e decreased to about 0.58%



Figure 9. Calculated Γ for spiral-step growth at low supersaturations, an ambient temperature of -15° C, air at 1 atm, and comparison with Kobayashi's (1961) measurements under approximately the same conditions. Plotted curves assume $\sigma_{1b} = 2.0\%$ and $\sigma_{1p} = 0.5\%$, face-centred step sources and 14 µm initial widths. For 1% and 2% ambient supersaturations, the widths after 20 min were 50 and 70 µm respectively. If instead the step sources were at the edge, $\Gamma = 0.40$ and 0.35 at 20 min for 1% and 2% supersaturations respectively. The right-hand ordinate is for larger crystals grown at 2% supersaturation. The large open diamonds are the initial (top) and final (bottom) calculated Γ values for initial and final widths of 70 and 200 µm respectively and facecentred step sources. With edge step sources, $\Gamma = 0.51$ at 200 µm. The crosses are measured values for the same sizes and approximately the same growth times. The horizontal dotted line is an average limiting $\Gamma \pm 0.07$ value measured for about nine crystals with initial widths averaging about 90 µm.

after 20 min, in close agreement with the estimated 0.57% measured value in §3.3. The calculated supersaturation at the basal centre was 0.05% at 20 min, which is half that estimated from figure 6. This calculation is unrealistic in detail because it has cylindrical symmetry instead of hexagonal and because the r_p value, which is 20 times smaller, poorly describes lacunary growth; nevertheless, the transition in figure 1 from solid thick plate (C1g) in figure 9 to sector plate (P1c) in figure 10 as the supersaturation increases can thus be explained quantitatively using lacunae. Furthermore, this argument also explains the transition in figure 1 from solid column (C1e) to elementary sheath (N1c) with increasing supersaturation when the columnar functions for α_b and α_p are used. Therefore, lacunae are essential for extreme aspect ratios at higher supersaturations when spiral steps are present. To complete the explanation, it is shown below (§ 3.2) why lacunae form at higher supersaturations and smaller vapour diffusivities.

3.2. Lacuna formation on snow crystals

Supersaturation is known to vary across crystal faces (Humphreys-Owen 1949, Seeger 1953). Thus, higher-supersaturation regions on a face would always grow



Figure 10. Calculated Γ for layer nucleation growth on the edge of the prism. Here $\sigma_{\rm cr-p} = 0.45\%$ and only 5% of the rim area grew, whereas basal growth was by a spiral step in the face centre with $\sigma_{\rm 1b} = 2.0\%$. Initially, $a = 7\,\mu\text{m}$ and $\Gamma = 1$. The ambient temperature was -15°C and the ambient supersaturation was 16% (water saturation). Growth took place in air at 1 atm, but air flow was neglected. The broken curve is from Ple data of Takahashi *et al.* (1991) for the same conditions.

faster than lower-supersaturation regions except that the steps become closer in the latter regions (Chernov 1974, Frank 1974), thus becoming more efficient molecular sinks (i.e. α increases). Monte Carlo calculations of cubic crystals in a diffusion field show that higher-supersaturation edge regions on a face will grow faster than the centre of a face when the crystal exceeds a certain size that decreases with increasing supersaturation (Xiao *et al.* 1991). Calculations of finite cylinders lead to the same conclusion but also show that lacunae should usually form on only the fast-growing face of most snow crystals, except at low supersaturations, which supports the data in figure 1 (Nelson and Baker 1996). Yokoyama and Kuroda (1990) calculated spiral-step growth on two-dimensional crystals numerically and found that six main arms formed at high supersaturations, but their restriction to two dimensions and neglect of layer nucleation make their results unrealistic to explain other details of snow crystals.

According to equation (5), across the face of a uniformly-growing crystal

$$\alpha \sigma =$$
uniform. (7)

At the step sources α_b and α_p depend upon the local supersaturation, the step formation mechanism, and surface properties but, everywhere else, α depends on how easily molecules reach steps, which depends primarily on the step separation y divided by the migration distance $x: \alpha \to \alpha(y/x)$ (BCF). If steps form at the edge of the prism face with condensation coefficient α_p , equation (7) applied to the edge and centre of the face becomes

$$\alpha_{\rm p}\sigma_{\rm e} = \alpha(y/x_{\rm p})\sigma_{\rm p} \leqslant \sigma_{\rm p},\tag{8}$$

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where the subscripts e and p indicate prism face edge and centre respectively. The last inequality is because condensation coefficients cannot exceed one. However, as a crystal grows or the supersaturation increases, the growth rate at the edge (lefthand side) exceeds that in the centre (right-hand side) when

$$\alpha_{\rm p} \frac{\sigma_{\rm e}}{\sigma_{\rm p}} \ge 1. \tag{9}$$

This is the condition for lacunae to form; thus the left-hand side is called the prismface lacuna parameter. Fluxes to the crystal faces and vapour diffusion determine $\sigma(z)$ across each face, whereas flux uniformity on each face determines how $\alpha(y/x_p)$ varies across each face. This $\alpha(y/x_p)$ is larger where $\sigma(z)$ is smaller (figure 11), but, because α must be less than one, this can only occur if $\alpha_p \sigma_e$ is below the minimum in $\sigma(z)$ as is line i in figure 11. When the supersaturation rises, thus causing $\alpha_{\rm p}\sigma_{\rm e}$ to rise to the level ii, then the step spacing must decrease to zero near the arrows because $\alpha = 1$ there, and growth is slower between the points owing to the smaller σ . This first occurs when the equality in equation (9) holds. Because a single number used for α cannot exactly describe the details of molecular incorporation in steps, the righthand side of equation (9) is probably not exactly one; however, the conclusions here are insensitive to its value. Equations (5), (6) and (9) predict that increases in ambient supersaturation and crystal size can lead to lacunary growth as is commonly observed (for example Kobayashi (1961) and Gonda and Koike (1982)) but, in some cases, an increase in crystal size will prevent lacunae from forming because the surface supersaturation drops during growth.

The lacuna parameter factors α_p and σ_e/σ_p depend differently on Γ , crystal size and ambient supersaturation, and their dependences differ between the fast- and slow-growing faces. On the fast-growing face, the first factor α_p generally decreases during growth as the crystal collects more molecules and lowers the local super-



Figure 11. Formation of lacunae due to $\sigma(\mathbf{z})$ gradients on a prism face. The dotted lines i and ii indicate two possible values of $\alpha_p \sigma_e$ that must equal $\alpha \sigma(\mathbf{z})$ across the face for uniform growth. If line i is $\alpha_p \sigma_e$, the face grows uniformly because the steps in the centre capture molecules with less than 100% efficiency ($\alpha < 1$). For line ii, uniform growth requires an impossible $\alpha > 1$ between the arrows; therefore this central region between the arrows instead grows more slowly than the outer rim and thus approximates the initial boundary of the lacunae.

saturation, whereas the second factor σ_e/σ_p usually increases during growth because the edge and centre of the face are further apart. So the lacuna parameter can increase or decrease during growth at constant ambient supersaturation depending on how rapidly α_p changes with the surface supersaturation. However, when the ambient supersaturation increases, both factors increase and lead to lacunary growth. This prediction agrees with the studies of Chernov (1974), Yokoyama and Kuroda (1990) and Xiao *et al.* (1991) but contrasts with the work of Mason (1993) in which lacunary growth depends only on crystal size.

As an example, consider the case where the prism face is growing from the edge by layer nucleation without influence from spiral steps, and the basal face grows from a spiral in the centre. Except for very small crystals, the formation of lacunae mostly depends on the ratios of the ambient supersaturation to the characteristic supersaturations for each face as indicated by figure 12. In that figure, the lacuna parameter is plotted for three crystal sizes as a function of supersaturation. For example, when the crystal size is 100 times the vapour mean free path (about 11 µm at 1 atm), the lacuna parameter increases slowly with supersaturation from very small values and then abruptly exceeds one above 2.3% ambient supersaturation. This abrupt rise follows from equation (6); any increase in $\alpha_p \sigma_e$ is amplified by its product with $r_{\rm p}h_{\rm p}$ (35 in this case), which forces $\sigma_{\rm p}$ to decrease rapidly to zero, thus causing the lacuna parameter to increase at 2.3%. The more rapid rise in the lacuna parameter at larger r_p shown in figure 12 is thus understood. This example also shows that larger crystals growing solely by layer nucleation are less likely to form lacunae at a given ambient supersaturation. Hence, if a crystal is initially lacunae free, it might not develop lacunae as it grows larger or, if this crystal does initially have lacunae, the face might become complete as the crystal grows, thus



Figure 12. Formation of lacunae on a prism face when the prism face grows by layer nucleation at the edge (equations (A 3) and (A 4)) with $\sigma_{cr-p} = 0.45\%$ and basal growth by a spiral step with $\sigma_1 = 2.5\%$ calculated prism-face lacuna parameter for $\Gamma = 1$ and crystal sizes with $r_p = 10,100$ and 1000. Lacunae should form as the curves exceed one.

forming interior air voids as observed on substrate-grown crystals (Gonda and Koike 1982, 1983). That increasing size is usually found to produce lacunae on snow crystals at higher temperatures (Kobayashi 1961) is thus further evidence that the fast-growing, complete face usually does not grow solely by layer nucleation. Calculating the formation of lacunae when spiral steps and layer nucleation occur simultaneously requires more surface growth parameters than are available from experiment; however, in such a case, α should be approximately proportional to σ^n , where n is between that for pure spiral growth $(n \approx 1-2)$ and that for pure layer nucleation ($n \approx 10-100$). To show how a less supersaturation-sensitive condensation coefficient would affect the formation of lacunae, the prism-face lacuna parameter versus crystal size for $\alpha_p \propto \sigma_e^5$ is plotted in figure 13. For example, when $\Gamma = 1$ the lacuna parameter first decreases with growth but, when the crystal size exceeds about 400 times the vapour mean free path (45 μ m at 1 atm), lacunae should form. This is comparable with the value of 75 µm found by Kobayashi (1961) for growth between -5 and -10° C but, when $\alpha_{p} \propto \sigma^{10}$, the lacuna parameter decreased during growth as it did for pure nucleation growth (figure 12); that is a fast rate of increase in step formation with increasing surface supersaturation leads to an increased likelihood that the facet remains complete as it grows because α_p decreases more rapidly with increasing size.

Because the fast-growing face can be the largest total vapour sink, the vapour density can be more depleted there and thus cause the surface supersaturation to be largest in the centre of the slow-growing face. Therefore, this slow face is much less likely to develop lacunae than the fast-growing face; equivalently, the lacuna parameter of the slow face decreases rapidly as the fast-growing face becomes larger if the fast-growing face is lacuna free (figure 14). However, when the fast-growing face develops lacunae, thus reducing its vapour sink, the slow faces can then develop lacunae in their centres. The latter is probably more common when growth is nearly



Figure 13. Formation of lacunae on a prism face that has an edge step source on the prism with $\alpha_p = (\sigma_e/0.0048)^5$ and face-centred spiral step growth on the basal face with $\alpha_b = \sigma_b/0.025$: calculated lacuna parameter at 1% ambient supersaturation as a function of Γ and crystal size. Lacunae should form as the curves exceed one.



Figure 14. Uniform facet growth on the basal face during tabular growth: basal-face lacuna parameters for increasing crystal sizes with $\sigma_{\infty} = 5\%$ when the prism grows by a step source at the edge as $\alpha_{\rm p} = (\sigma_{\rm e}/0.0045)^5$, but the basal face step source is either at the edge or the face centre, whichever has the greater supersaturation, with $\alpha_{\rm b} = (\sigma/0.025)^5$. Curve a shows that the basal face cannot form lacunae when $\Gamma = 1$. The highest supersaturation is the centre of the basal face, and the prism face lacuna parameter exceeded one. For curve b, $\Gamma = 1$ and the prism face grows only along the rim with $r_{\rm p} = (ac)^{1/2}v/20D$, that is a tenth of its effective radius. The basal face can form lacunae only at small sizes. The break in the curve near 30, and at larger sizes for curves c and d, arises because the region of highest supersaturation moves to the centre of the basal face. Curve c is the same as curve a except that $\Gamma = 0.01$. The lacuna parameter of the prism face exceeded one on this thin tabular crystal. For curve d, $\Gamma = 0.01$ and $r_{\rm p} = (ac)^{1/2}v/20D$. Figures 13 and 14 show that one face can grow uniformly as the other face forms lacunae.

isometric (e.g. see photographs of crystals grown near -9 and -21° C in the paper by Takahashi *et al.* (1991) and the crystal at -7.7° C in the paper by Yamashita (1974)).

In summary, calculations of step motion on a finite cylinder in a diffusion field with measured σ_{cr} values and reasonable spiral-step characteristic supersaturations σ_1 predict sizes and supersaturations at which lacunae first form, in approximate agreement with observations.

3.3. Dendritic growth

For most people, the term snow crystal means dendritic crystal (P1e) even though the latter occurs only in a small range of temperatures and supersaturations (figure 1). One reason is that dendritic crystals grow larger than those grown in other cloud conditions (Takahashi *et al.* 1991) and thus more easily fall to the ground without completely evaporating or melting. Another reason is aesthetics; as Nittman and Stanley (1986) wrote '... every child can distinguish a [snow crystal] from other growth forms'. They proposed a model for dendrite growth that ignores facetting but modelled the overall pattern reasonably well. Instead, the focus here is on just the tip of the dendrite and the equations used are based on layer nucleation and step motion consistent with that in \S 3.2.

Near -15° C and at ambient supersaturations below water saturation (16%), branches have large obvious facets (P1b). At higher supersaturations, the prism facet area near the tip decreases (P1c) and apparently vanishes near 18% ambient supersaturation (P1e). However, the facets might remain during growth but be unnoticed because, firstly, of the difficulty observing small facets on a rapidly growing interface and, secondly, before reaching the ground, snow crystals generally fall through undersaturated air that causes rounding. Differences in facet size can also be seen on different branches on the same crystal. Figure 15 shows such a dendrite: the outermost tips appears fully rounded and had grown in a region of higher surface supersaturation compared with branch tips closer to the centre that have obvious prism facets.

Kinetic roughening and vapour-liquid-solid (VLS) growth cannot round the tips during growth by the following argument. The former occurs when the Gibbs free energy of the critical embryo decreases to kT (Elwenspoek and van der Eerden 1987). Because the free energy is inversely proportional to the surface supersaturation σ_e , kinetic roughening occurs above a certain supersaturation. From equations (A 1) and (A 2) (appendix A) and measured σ_{cr-p} values, this is about 19%. Instead, VLS growth requires σ_e near liquid water saturation or 16%. The observed growth rate of dendrites and equation (5) allow estimates of the surface supersaturation at the tip:



Figure 15. A dendrite (Ple) collected at ground level. (Photograph courtesy of Charles Knight.)

$$\sigma_{\rm e} = \frac{{\rm d}a/{\rm d}t}{4.5 \times 10^{-27} N_{\rm ea}(T_{\rm e})\alpha_{\rm p}},\tag{10}$$

where T_e is the crystal temperature at the tip. According to the P1e crystal growth measurements of Takahashi *et al.* (1991), $da/dt = 1.2 \,\mu\text{m s}^{-1}$ after growth for 10 min at -14.4°C. Assuming that the tip is completely rounded so that $\alpha_p \approx 1$ and neglecting both the Gibbs–Thompson effect and the temperature rise from latent heating, the surface supersaturation from equation (10) is only 0.52%, far below the values estimated for kinetic roughening and VLS growth. (Including Gibbs–Thompson and latent heating only worsen this discrepancy.) Therefore, on either side of the tip, small facets probably exist, which grow at 30° to the tip direction. Putting the cosine of this angle in the numerator and $T_e = 13.9$ °C (latent heating) in the denominator gives $\alpha_p \sigma_e = 0.0044$. The layer nucleation formula (equations (A 4) and (A 5)) with $\sigma_{cr} = 0.45\%$ predicts $\sigma_e = 0.0057$ and $\alpha_p = 0.78$, the latter value of which implies that the step spacing y is slightly less than x_p (BCF). If $x_p \approx x_b$ from figure 4 and several steps were on the facet, then the facet tip was at least 4 μ m across during growth.

The tips of sector plates (P1b) after 10 min growth had a smaller growth rate, 0.26 μ m s⁻¹ (Takahashi *et al.* 1991), resulting in $\alpha_p \sigma_e = 0.0008$ with the same assumptions as for the Ple dendrite. Instead of an abrupt transition from faceted to rough growth at the tip as supersaturation increases, a continually decreasing facet area is possible (figure 16). The long and short arrows in figure 16(a) show the highest and lowest supersaturation positions on the facet respectively, and the supersaturation using the layer nucleation condensation coefficient described above is plotted on the right. Assuming that the edge of the facet defines the point where $\alpha(y/x_p) = 1$, then a relatively large difference in supersaturation across the facet indicates a relatively large facet area. Increasing the ambient supersaturation (figure 16(b) can decrease the facet area because the higher supersaturation at the tip raises $\alpha_{\rm p}$ and thus the $\alpha = 1$ point on the facet is closer to the tip, and also because the supersaturation gradient near the surface probably increases as the tip sticks out further from the bulk of the crystal. The trend continues in figure 16(c) to further decrease the facet area. Frank (1974) also argued for a decreasing area of facet with increasing supersaturation owing to the lacunary phenomenon but suggested instead that prism faces vanish at the tip during dendritic growth. Tiller (1991) and Nelson and Knight (1998) suggested that the facets, however small, on either side of the tip ensure that the arm strictly grows along $\langle 1\bar{2}10 \rangle$. This direction is also preferred by the rough growth of the tip and branches of ice dendrites in the melt, but adherence to this direction is not as strict (Koo et al. 1991). The electrically enhanced dendritic growth with growth rates greater than $3.5 \,\mu m \, s^{-1}$ is consistent with rough tips (Libbrecht and Tanusheva 1998) but does not apply to atmospheric conditions.

The region of dendritic and needle growth occurs where the growth rate anisotropy from layer nucleation is largest, as indicated by the ratio of basal to prism critical supersaturations (although it is not yet clear whether or not a maximum exists at -16° C). This agrees with the prediction in § 3.2; a large difference in critical supersaturations more easily leads to lacunae and faster growth rates on the face with the lower critical supersaturation.

3.4. Adatom migration between faces

Mason et al. (1963) and Frank (1982) argued that a fast-growing face draws adatoms from an adjoining face, thus reducing the latter's layer nucleation rate near



Figure 16. Sketch of the changing tip shape of an initially broad-branch (P1b) crystal as the ambient supersaturation increases to become a dendrite (P1e). (a) The tip of a P1b crystal. Surface supersaturations at the arrows are estimated in plots on the right and are explained in the text. (b), (c) At higher ambient supersaturations, the facet area at the tip decreases in (b) a P1c crystal and (c) a P1e crystal. Qualitatively, the same transition occurs at a fixed ambient supersaturation as the crystal grows (Takahashi et al. 1991).

the edge and lowering its growth rate. This effect can be large if the slow-growing face is about one surface migration distance across or less but, on larger faces, layers can nucleate a mean migration distance or more from the edge where the surface supersaturation is nearly that at the edge. KL argued that adatom migration from the basal to the thin prism faces of dendrites increases their growth rate, whereas Mason (1993) included both effects to estimate Γ on small crystals. Hallett (1961) has evidence for adatom migration from the basal to prism face of thin ice plates.

Migration between faces will speed up growth of the face that receives net molecules from the adjoining faces. For example, assume a tabular P1e crystal, $x_b = x_p$, no additional energy barrier for migration between faces and that one step always exists on the prism but none on the adjoining basal faces. The growth rate of the prism face is thus the step height *h* divided by the time for the step to cross the face. With collection of adatoms from both upper and lower terraces, the latter time is the face thickness 2*c* divided by the step velocity for an isolated step. Thus

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{x_{\mathrm{b}}}{c} \Omega N_{\mathrm{eq}} \sigma_{\mathrm{e}} \frac{v}{4},\tag{11}$$

which agrees with the work of Sears (1956) but is much less than that estimated by KL. Migration between faces thus increases the growth rate by the factor x_b/c over the maximum ($\alpha_p = 1$) growth rate in equation (5), but by a smaller amount if additional steps are on or within x_b of the prism face. If $x_b \approx 1-5 \,\mu m$ (Mason *et al.* 1963, Gonda *et al.* 1996), then migration between faces has a significant effect only when c or a is less than about $5 \,\mu m$. This is close to the thickness at which Keller *et al.* (1980) observed a transition from rounded discs to faceted plates. The latter workers proposed face-face migration as an explanation for this transition, which is supported by equation (11). Similarly, the non-faceted growth on 'fern-like' crystals observed by Yamashita and Asano (1984) was observed on only the thinner crystals that had $c \approx 5 \,\mu m$.

Comparison of equation (11) with equation (5) shows that x_b/c can substitute for α in the growth rate equation; in particular, it can substitute for the α plotted in figure 6 that was used to estimate σ_e at the tip of a dendrite growing at water saturation. To nucleate new layers, σ_e must be larger than about 0.005; yet, at σ_e above about 0.007, layer nucleation is too fast to explain dendritic growth rates. Because layers must nucleate even when face-face migration affects growth rates, this migration could only have a small effect on dendritic growth rates if $0.005 < \sigma_e < 0.007$; hence, face-face migration can have only a limited effect on dendrites at water saturation or below.

Face-face migration can also occur between prism faces. If x_b is replaced by x_p and if c is replaced by the width w of a narrow prism face between wider prism faces, then equation (11) predicts that, when $w \approx x_p$ or smaller, w could decrease to zero even when other prism faces grow much larger than x_p . This decrease is because of the 120° angle between adjacent prism facets; a prism face that grows at least twice as fast as the neighbouring facets will vanish. Hence, this migration might explain why trigonal, rhombic and pentagonal ice crystals required very small nuclei (Yamashita 1973) but does not explain the prevalence of trigonal shapes. The latter could be due to asymmetric vapour diffusion contours across prism-prism edges on crystals without perfect hexagonal symmetry.

3.5. Air flow

Air flow around free-falling snow crystals affects their shape: dendrites (P1e) grow at lower supersaturations with air flow (figure 1), and double-plate crystals are much smaller on the downwind plate (Iwai 1983); also, frost growth is faster and has more lacunae with air flow (Alena *et al.* 1990) because vapour-rich air is brought closer to the crystal surface, particularly near the edges (Pitter *et al.* 1974, Ji and Wang 1990, 1991). Larger free-falling crystals are more likely to be affected by air flow because the time to establish a steady-state diffusion field increases as the crystal

size squared (Mason 1953). Thus, at a certain size, the crystal falls through the surrounding vapour diffusion region before this region becomes depleted of vapour. Growth rate measurements indicate that this size is about 250 µm (Takahashi et al. 1991). Snow crystals of this size have already established their primary habit and generally have lacunae; therefore, according to $\S3.1$ and 3.3, they should be growing primarily by layer nucleation near the basal-prism edges. Such crystals fall broadside to the air flow on average; hence, the air flow passes closest to the basal-prism edges on tabular crystals and closest to the prism-prism edges on columnar shapes (figure 17). This is supported both by numerical calculations (Ji and Wang 1990, 1991) and by observed riming, the latter of which is primarily at the basal-prism edges of tabular crystals but uniform along the prism faces of columnar crystals (Knight and Knight 1973). Therefore, air flow probably causes the greatest increase in surface supersaturation where the prism-face steps are nucleated on tabular crystals and causes a more uniform increase in surface supersaturation on columnar crystals. This should increase the growth rate anisotropy for all crystals, but much more for the tabular crystals because the face that nucleates steps can rapidly increase its nucleation rate, whereas the adjoining face can remain below its critical value (§3.5). In



Figure 17. Differences in the vapour flow around (a) tabular and (b) columnar crystals.

support of this, Takahashi *et al.* (1991) found that air flow increased the growth rate of tabular crystals but not columnar crystals. In addition, the larger supersaturation gradient from air flow can make the arms thinner and affect the relative sizes of branches on a dendrite (Hallett and Knight 1994).

§4. GROWTH FORMS UNDER CHANGING CONDITIONS

Snow crystals with both tabular and columnar features such as capped columns, scroll crystals and crown crystals regularly form in the atmosphere. Nakaya (1954) showed that combinations, such as the capped column–crown crystal in figure 18, form when a growing crystal transfers between different primary habit temperatures. Mason *et al.* (1963) argued that these occur when adatoms migrate from the slow-growing face to the region within one mean migration distance of the edge on the fast-growing face. However, this implies that they would also form at any super-saturation which they do not; crystals maintain their solid form as they gradually change to the new primary habit at very low supersaturations (Kobayashi 1961).

Instead, ideas in §3.2 about the formation of lacunae can explain these habits. For example, consider a solid column growing at -8° C (figure 19) that suddenly transfers to -15° C. The prism face is initially completely flat because α_{p} is small; hence, it can be represented by line i in figure 11. When the temperature changes to -15° C, α_{p} rapidly increases and α_{b} decreases; thus line i moves up above the level needed to form lacunae, represented as line ii. Dropping the α_{b} term in equation (6) gives

$$\sigma_{\rm p} \approx \sigma_{\infty} - \alpha_{\rm p} \sigma_{\rm e} r_{\rm p} h_{\rm p}(0, \Gamma). \tag{12}$$

So, the supersaturation at the centre of the prism face σ_p drops rapidly as α_p increases. Thus, as line i moves up to line ii, the bottom of the supersaturation curve drops to a much lower value ensuring that the points at which $\alpha \approx 1$, indicated



1 mm

Figure 18. A capped column with crown features. Because of temperature changes, growth was first columnar, then tabular and finally columnar. (Photograph courtesy of Charles Knight.)



Figure 19. Formation of a capped column. The curves indicate the fractional area of lacunae on the prism face that grows more slowly than the rim; for example 0.8 means a rim area of width 10% of the crystal length 2c grows more rapidly than the centre of the face. $r_b = 140$, $\alpha_b = (\sigma_e/0.025)^5$, $\alpha_p = (\sigma_e/0.0045)^5$ and $\Gamma = 20$ (----) or $\Gamma = 1$ (---). To estimate the area of the rim, the supersaturation was calculated at the centre and edge of the prism face (appendix B) and assumed to vary quadratically across the face.

by arrows in figure 11, move close to the face edge. Therefore, soon after the temperature change, growth will be faster at the edge region outside the arrows. Once this region grows out from the central column, a cap forms and grows more rapidly because its area is smaller and thus does not deplete the surrounding vapour as much as a larger face. After this cap has grown away from the original column, the central column region becomes shielded from the ambient vapour just as one arm on a double plate shields its neighbour (Frank 1982). For these reasons, the thin caps grow outward as tabular crystals. Using the expression for the supersaturation on a face and assuming that the supersaturation varies quadratically across the face, the positions at which the lacunae initially form can be estimated as described for figure 11. The resulting shapes of the crystals are shown in figure 19 for an abrupt transition from a columnar to tabular growth regime. An instantaneous transition should result in thin tabular caps even at fairly low supersaturations if the initial column is large.

The secondary habit also depends on supersaturation changes during growth. For instance, if the supersaturation starts high with growth occurring only along the outer rim of a face and later is lowered significantly, then the facet can spread inward to cover the entire face, thus producing the interior air voids that are observed (Bentley 1924). (However, at low ambient supersaturations, the surface supersaturation decrease caused by the increasing crystal size can also cause these air voids (Gonda and Koike 1983).) If dendrites experience a decrease in supersaturation, their ends develop larger facets and, because of the relatively large sensitivity of layer nucleation rates to supersaturation, natural variations in ambient supersaturation might be the main reason that P1e shapes have such a wide variety that there are 'no two alike' (Bentley 1901).

§ 5. POLYCRYSTALS

Observed polycrystalline habits generally support the previously described growth mechanisms, particularly the mechanism for the different low-temperature primary habits at high and low supersaturations (§2.6). Polycrystals form when drops freeze in either the initial nucleation or during riming (Hallett 1964, Higuchi and Yoshida 1967, Uyeda and Kikuchi 1976), probably because a supercooled meltsolid interface can nucleate new crystal orientations (Knight 1971). The probability of polycrystal formation should thus increase with increasing supercooling and, because the interface area is larger, should also increase with increasing droplet size. This agrees with experiment (Pitter and Pruppacher 1973). Because rapid melt growth and large stresses during drop freezing can generate dislocations and other defects (Tiller 1991), polycrystals are more likely than single crystals to have defects. Hence, both layer nucleation and spiral-step growth can occur. Above -22° C, polycrystals are usually built of branched tabular crystals, which are the most common single-crystal habits at those temperatures. Below -22° C, polycrystals at low supersaturations are built of tabular crystals that are mostly lacunae free (Furukawa and Kobayashi 1978), but at high supersaturations they are built of columns that are usually hollow (Heymsfield and Platt 1984, Gow 1965); this agrees with the supersaturation dependence of single-crystal habits.

§6. Effects from temperature gradients

Temperature gradients in snow crystals were neglected because they increase the complexity of the calculations and should not change the conclusions about the dominant growth mechanisms. Experimentally, however, decreasing the air's thermal conductivity decreases the likelihood of lacunae and makes growth more isometric (Gonda 1980). This can be explained by a larger temperature difference between the centres of the slow- and fast-growing faces; the surface supersaturation on the fast-growing face is reduced by latent heating more than that on the slow-growing face. The formation of lacunae also depends on temperature gradients along the fast-growing faces, but an estimate of this effect, to be reported separately, showed that this effect is small.

§7. CONCLUSIONS

Explaining the known variety of snow crystal habits requires both spiral-step and layer nucleation growth, as had been argued earlier by Frank (1974). Adatom migration between faces, which had been proposed previously as a cause of primary habits, probably influences only a limited number of habits such as thin disc crystals and trigonal crystals. Spiral steps are needed to account for both the low supersaturation and high vapour diffusivity growth shapes, whereas layer nucleation dominates growth at high supersaturations and explains the extreme aspect ratios of dendrites and needles, as first stated by Knight (1972). These two step formation mechanisms together with calculations of vapour diffusion to approximate shapes of snow crystals also explain the observed conditions for lacunae. On imperfect crystals, lacunae are needed for layer nucleation to produce the most anisotropic growth shapes such as needles and dendrites; furthermore, estimates of the supersaturation at the tips of dendrites growing at water saturation indicate that they retain small facets. At temperatures below -22° C, the variety of crystal habits suggests that the prevalence of tabular forms and occasional long solid prisms (N1e) at low supersaturation require either dislocation outcrops or stacking faults, whereas the more common hollow columns at high supersaturation probably arise from relatively fast layer nucleation on the basal faces. Experiments have not yet identified the causes of impurity-induced habit changes (§ 1) but, because the layer nucleation mechanism is very sensitive to changes in edge free energy that can be caused by very low impurity concentrations, impurity-induced habit changes are more probably caused by changes in the layer nucleation rates than by changes in the defect properties or step speeds.

Many observations have been explained by vapour and adatom diffusion on a finite cylinder with layer nucleation and spiral steps; however, further progress can be made, particularly below -16° C where critical supersaturations have not been measured. More experiments are needed to determine shape evolution more accurately, to obtain finer details of the dependence of the condensation coefficients on supersaturation, and to determine the characteristics of spiral or possible stacking-fault step sources on real snow crystals. Recent theoretical work using similar analysis as in §3, but applied to a solid hexagonal prism has a more precise description of the formation of lacunae (Wood et al. 2001). When their model is extended to a hexagonal prism with lacunae, and an accurate model of surface diffusion on icevapour interfaces with competing step sources is determined, predictions of snow crystal growth habits will become more quantitative. However, this paper makes it clear which step formation mechanisms are needed, and what their approximate parameters are. Understanding snow crystal habits at a deeper level will require more knowledge of the surface properties of ice and, because the basal face seems to have more rapidly changing properties with temperature than the prism, knowledge of the microscopic properties of the basal surface might be the most important.

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APPENDIX A

LAYER NUCLEATION AT A CRYSTAL EDGE

Layer nucleation on snow crystals is different from most treatments that assume uniform supersaturation (for example Hillig (1966), Lewis (1980) and Arima and Irisawa (1990)) because vapour diffusion produces supersaturation gradients along snow crystal surfaces. The following treatment is based on the work of Frank (1982) and formulated to use measured critical supersaturations. It is assumed that the edge has the highest supersaturation so that new layers nucleate there, and that the surface supersaturation equals the adatom supersaturation far from a step (BCF). The nucleation rate J per area for disc-shaped embryos at low supersaturations is roughly

$$J = 2\pi r_{\rm c} \nu n_0^2 \exp\left(-\frac{\pi a_0 \kappa^2}{(kT)^2 \sigma(\mathbf{z})}\right),\tag{A1}$$

(Lewis 1980) where r_c , the radius of the critical embryo, equals $a_0 \kappa/kT\sigma_e$; ν is the hopping rate times the jump distance for adatoms of concentration n_0 , κ is the edge energy per length and a_0 is the area occupied by an adatom on the surface (approximately equal to $0.85 \times 10^{-19} \text{ m}^2$). The exponent in equation (A 1) is the Gibbs free energy of a critical embryo divided by kT. With K as the pre-factor in equation (A 1),

$$J = K \exp\left(-\ln\left(KA\right) \frac{\sigma_{\rm cr}}{\sigma(\mathbf{z})}\right),\tag{A 2}$$

where A is the area for nucleation and $\sigma_{\rm cr} = \pi a_0 \kappa^2 / [\ln (KA) (kT)^2]$ is the critical supersaturation defined experimentally as the value of σ when one layer nucleates per second. The terms in the exponent and pre-factor are poorly known but, if $\sigma_{\rm e} \approx 0.01$, a reasonable lower bound for K is $6 \times 10^{29} \,{\rm m}^{-2}$ s. Assuming that $A \approx 10^{-9} \,{\rm m}^2$, $\ln (KA) = 48$. If A is instead only $0.1 \,{\rm \mu m}^{-2}$ (i.e. 10^4 times smaller), $\sigma_{\rm cr}$ as defined above increases by only 20%. Thus, the dependence of $\sigma_{\rm cr}$ on the nucleation area can generally be neglected.

Because σ changes with position on the surface, the growth rate R_n from nucleation is the layer height h multiplied by the integral of J over the area containing only one critical embryo. This area lies between the previously nucleated step and the edge, that is the face perimeter multiplied by the distance y that a step moves towards the centre before the next step nucleates. However, y must be determined self-consistently as it depends on growth rate, and this depends on how a step collects adatoms.

Steps collect adatoms from both lower and upper terraces, but generally with greater collection efficiency from the lower terrace (for example Ehrlich and Hudda (1966), Sears (1955)). The step motion experiments (for example Hallett (1961)) indicate some upper-terrace collection; hence ice step collection should lie between equal collection and only lower terrace collection. In the latter case, the uppermost terrace at the edge is not depleted of adatoms; assuming that this terrace is much smaller than the crystal face, J is relatively uniform in this nucleation region. Hence, the integral of J is just J at the edge multiplied by the area, which depends on σ_e and step spacing y as

$$R_{\rm n} = 6 \times 10^{29} h \exp\left(-48 \frac{\sigma_{\rm cr}}{\sigma_{\rm e}}\right) 2\pi a y. \tag{A3}$$

Requiring self-consistency, equation (A 3) is equated to the growth rate R_s from steps separated by y (BCF) near the crystal edge and, with adatom migration distance x,

$$R_{\rm s} = \Omega \sigma_{\rm e} N_{\rm eq} \frac{v x}{4 y} \tanh\left(\frac{y}{x}\right)$$
$$\equiv \Omega \sigma_{\rm e} N_{\rm eq} \frac{v}{4} \alpha_{\rm no}, \qquad (A4)$$



Figure A1. Condensation coefficients for layer nucleation from an edge with only lowerterrace adatom collection (equations (A 4) and (A 5)) and the exact result using equations (A 3) and (A 4) (....). The rightmost solid curve assumes equal collection from lower and upper terraces (equation (A 6)). The actual curve for ice is unknown but should lie between these two cases.

where $\Omega = ha_0$ and α_{no} is the condensation coefficient for layer nucleation with only lower-terrace collection. At a fixed σ_e , R_s decreases and R_n increases with increasing y such that they are equal at the value that determines the growth rate. Both R_s and R_n , and thus the growth rate, increase with increasing σ_e ; however, as R_n increases much more rapidly than R_s , the step spacing y decreases with increasing σ_e . An accurate approximate solution to equations (A 3) and (A 4) is derived by replacing $\tanh(y/x)$ by y/(x + y):

$$\frac{y}{x} = \left(\frac{48 \times 10^{27} ax \exp\left(-48\sigma_{\rm cr}/\sigma_{\rm e}\right)}{a_0 N v \sigma_{\rm e}^2} + \frac{1}{4}\right)^{1/2} - \frac{1}{2},\tag{A 5}$$

which is very sensitive to σ_e , but insensitive to x. α_{no} is plotted with the exact solution in figure A 1; both increase rapidly, even near one, because the nucleation rate is insensitive to the crystal area.

Equal collection efficiency is slower because a step travelling from the edge collects molecules from the upper terrace, thus reducing the adatom supersaturation in the nucleation zone. This non-uniform depletion makes the nucleation rate integral intractable. Approximating $\sigma(\mathbf{z})$ by its average over the upper terrace allowed J to be brought out of the integrand, then numerical root finding was used; the result is plotted as the rightmost curve in figure A 1. An approximate fit to the condensation coefficient α_{ne} for equal step capture is

$$\alpha_{\rm ne}(\sigma) \approx \frac{\ln\left[1 + 1000\alpha_{\rm no}(\sigma)\left(1 - \sigma_{\rm cr}/\sigma\right)^2\right]}{\ln\left(1000\right)}.\tag{A6}$$

The growth rate is smaller than that for only lower-terrace collection because the exponent in J has a larger negative value owing to the depleted adatom supersaturation, but it is slightly larger than the multinucleation model for uniform supersatura-

tion calculated by Arima and Irisawa (1990). Both equation (A 4) and equation (A 6) assume many steps on a face, and thus these equations might not be accurate on very small crystal faces.

APPENDIX B

SURFACE SUPERSATURATIONS ON A CYLINDER

Surface vapour supersaturation $\sigma(\mathbf{z})$ on a face controls the step generation rate and the step spacing, thus affecting growth rates, aspect ratios and formation of lacunae on crystals. In general, $\sigma(\mathbf{z})$ at any position \mathbf{z} external to the crystal or on its surface depends on the ambient supersaturation σ_{∞} and dimensionless vapour exchange fluxes F:

$$F_{\rm b} = \alpha_{\rm b} \left(\sigma(\mathbf{z}_{\rm b}) \right) \sigma(\mathbf{z}_{\rm b}) r_{\rm b},$$

$$F_{\rm p} = \alpha_{\rm p} \left(\sigma(\mathbf{z}_{\rm p}) \right) \sigma(\mathbf{z}_{\rm p}) r_{\rm p}.$$
(B1)

(To obtain the vapour fluxes in molecules per second per square metre, drop the r_b and r_p and multiply by $N_{eq}\nu/4$.) These fluxes F also equal the corresponding vapour diffusive fluxes, which are boundary conditions for the steady-state diffusion equation external to the crystal. This boundary-value problem predicts that (Nelson 1994)

$$\sigma(\mathbf{z}) = \sigma_{\infty} - F_{\rm b} h_{\rm b} \left(\mathbf{z}, \Gamma \right) - F_{\rm p} h_{\rm p} \left(\mathbf{z}, \Gamma \right), \tag{B2}$$

where h_b and h_p are positive functions given below for a finite cylinder (figure 2). The step sources will probably be close to face centres or the edge because only these regions can have the greatest supersaturation in a uniform environment. Therefore, only points in the centre of the basal face, the edge or centre of the prism are considered and these are labelled by subscripts b, e and p respectively. To avoid bulky expressions, the dependence of the *h* functions on z and Γ are assumed as is the dependence of α on the supersaturation. For instance, h_{bp} represents $h_b(\mathbf{z}, \Gamma)$ when z is in the centre of the prism face and α_b represents $\alpha_b(\sigma(\mathbf{z}_b))$. Putting equations (B 1) into equation (B 2) gives the surface supersaturation in terms of σ_{∞} , α_b , α_p and facet areas divided by the vapour mean free path. For example, if the edge has the step sources, then $\sigma(\mathbf{z}_b) = \sigma(\mathbf{z}_p) = \sigma_e$; so

$$F_{\rm b} = \frac{\sigma_{\infty} - \sigma_{\rm e} \left(1 + \alpha_{\rm p} r_{\rm p} h_{\rm pe}\right)}{h_{\rm bo}},\tag{B3}$$

$$F_{\rm b} = \alpha_{\rm b} \sigma_{\rm c} r_{\rm b}.\tag{B4}$$

Equation (B 3) shows how the vapour diffusive flux responds to the surface supersaturation at the edge. As σ_e increases, the vapour gradient between the surface and ambient decreases; so this flux decreases. With $\alpha_p > 0$, the basal flux decreases with increasing size of the prism face as expected. Equation (B 4) is the vapour exchange flux; it increases rapidly with increasing σ_e for layer nucleation, but gradually for a spiral step. Setting them equal gives σ_e and thus F_b :

$$\sigma_{\rm e} = \frac{\sigma_{\infty}}{1 + \alpha_{\rm b} r_{\rm b} h_{\rm be} + \alpha_{\rm p} r_{\rm p} h_{\rm pe}},\tag{B5}$$

which must be solved numerically because α_b and α_p are nonlinear functions of σ_e . Putting this into equations (B4) and (B2) gives F_b and σ respectively in the face centres. The latter are J. Nelson

$$\sigma_{\{\mathbf{b},\mathbf{p}\}} = \sigma_{\mathbf{e}}[1 + \alpha_{\mathbf{b}}r_{\mathbf{b}}(h_{\mathbf{b}\mathbf{e}} - h_{\mathbf{b}\{\mathbf{b},\mathbf{p}\}}) + \alpha_{\mathbf{p}}r_{\mathbf{p}}(h_{\mathbf{p}\mathbf{e}} - h_{\mathbf{p}\{\mathbf{b},\mathbf{p}\}})]. \tag{B6}$$

For $\sigma_{\rm b}$, the second term on the right, $h_{\rm be} - h_{\rm bb}$, is negative and the third term is positive so that a large vapour sink on the basal face greatly reduces the vapour density in the centre of the face, but a large sink on the prism has the opposite effect. The converse holds for $\sigma_{\rm p}$. Consistent with the experiments of Humphreys-Owen (1949), the highest surface supersaturation is $\sigma_{\rm b}$ if the prism face grows much faster than the basal face but is $\sigma_{\rm p}$ if the opposite holds. Between these limiting cases, $\sigma_{\rm e}$ is the highest surface supersaturation.

When the supersaturation is greatest in the basal centre, the dominant step sources should also be there and, assuming that prism growth is by layer nucleation, then the edge will be the step source for the prism face. In this case, it can be shown that moving the step source on the basal face to the centre increases the basal growth rate and decreases the prism rate. This effect, and the converse when the prism face centre has the highest supersaturation, tends to reduce growth rate anisotropies unless lacunae form. The solution to equations (B 1) and (B 2) for this case is

$$\sigma_{\rm e} = \frac{\sigma_{\infty}[1 + \alpha_{\rm b}r_{\rm b}(h_{\rm bb} - h_{\rm be})]}{1 + \alpha_{\rm b}r_{\rm b}h_{\rm bb} + \alpha_{\rm p}r_{\rm p}h_{\rm pe} + \alpha_{\rm b}r_{\rm b}\alpha_{\rm p}r_{\rm p}(h_{\rm bb}h_{\rm pe} - h_{\rm be}h_{\rm pb})},\tag{B7}$$

$$\sigma_{\rm b} = \frac{\sigma_{\infty} [1 + \alpha_{\rm p} r_{\rm p} (h_{\rm pe} - h_{\rm pb})]}{1 + \alpha_{\rm b} r_{\rm b} h_{\rm bb} + \alpha_{\rm p} r_{\rm p} h_{\rm pe} + \alpha_{\rm b} r_{\rm b} \alpha_{\rm p} r_{\rm p} (h_{\rm bb} h_{\rm pe} - h_{\rm bc} h_{\rm pb})}.$$
 (B8)

When the step source for the basal is the edge and the centre for the prism, the resulting supersaturations can be obtained from equations (B7) and (B8) by substituting the subscripts on h which indicate the position from e to p and from b to e.



Figure B.1. Functions that describe how growth on the basal face affects supersaturation h_{bb} in the centre of the basal face (----, curve b), supersaturation h_{bp} in the centre of the prism face (-----, curve p) and supersaturation h_{be} at the edge (-----, curve e). The larger the magnitude, the larger is the reduction in supersaturation for a given basal-face growth rate.

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Figure B.2. Similar to figure B1t functions that describe how growth on the prism face affects supersaturation h_{pp} in the centre of the prism face (----, curve p), supersaturation h_{pb} in the centre of the basal face (...., curve b) and supersaturation h_{pe} at the edge (---, curve e).

Similarly, for step sources in the centre of both faces, the supersaturations follow from equations (B7) and (B8) by replacing e with p.

The values of $h_{\rm b}(\mathbf{z}, \Gamma)$ and $h_{\rm p}(\mathbf{z}, \Gamma)$ are products of large matrices with elements containing Bessel and hyperbolic functions (Nelson 1994). Because they are too bulky as such, the following functions that are plotted in figures B1 and B2 are used; these functions fit within about 1% the calculated values for Γ between 0.01 and 20:

$$\begin{aligned} h_{\rm be} &= 0.7071 \times 10^{-0.1315 \, \tanh\{0.8060[\log(\Gamma)+0.1854]-0.0639 \, [\log(\Gamma)]^2\}-0.3314,} \\ h_{\rm bp} &= h_{\rm be}\{0.5019 - 0.499 \, \tanh\left[\log\left(\Gamma^{1.043}\right) - 0.089 \, 82 + 0.048 \, 07 \, [\log\left(\Gamma\right)]^2]\}, \\ h_{\rm bb} &= h_{\rm be}(1.955 + 0.387 \, \tanh\left\{0.819[\log\left(\Gamma\right)+0.215]\}\right), \\ h_{\rm pe} &= 0.3451\Gamma^{[1.932+0.4976 \, \log\left(\Gamma\right)+0.1058 \, [\log(\Gamma)]^2]^{-1}-0.5}, \\ h_{\rm pp} &= h_{\rm pe}(1.583 + 0.2919 \, \tanh\left\{0.7847 \, [\log\left(\Gamma\right)-0.054 \, 85]\right\}), \\ h_{\rm pb} &= h_{\rm pe} - \Gamma^{-0.5}(0.0616 \, \tanh\left\{1.028[\log\left(\Gamma\right)+0.4846]\right\} + 0.0636). \end{aligned}$$

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