CRYSTAL GROWTH: 2-D or Not 2-D?

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1. INTRODUCTION

The evolution of the ice phase in atmospheric clouds starts with the nucleation of primary ice particles and their subsequent growth by the deposition of water vapor under supersaturated conditions. Vapor deposition is an important process to understand because it establishes the initial shapes, masses and fallspeeds of the ice particles that subsequently interact collisionally with other cloud particles and contribute to precipitation via the so-called "cold-rain" mechanism (Young 1993, p. 7). Precisely how vapor molecules contribute to the growth of these ice particles is still unknown, posing a limitation to the development of realistic cloud models.

Ice crystal growth is complicated because of the wide variety of shapes found in nature (Bentley 1901; Weickmann 1945). Non-spherical forms arise from variations across the surface in the probability with which water molecules are able to build into the crystal. A commonly used descriptor of growth efficiency is the deposition coefficient $\alpha$, the fraction of molecules striking the surface that successfully incorporate into the ice lattice and contribute to growth of the particle. By virtue of the crystallographic nature of ice Ih (Petrenko and Whitworth 1999, Chapt. 2), vapor-grown ice crystals are typically bounded by two basal faces and six prism faces, the growths of which are kinetically limited. The primary habit of a crystal (whether it is a plate or a column) is thus determined by the relative magnitudes of the deposition coefficients characterizing the basal and prism faces. Plates evolve, for instance, when $\alpha_{\text{prism}} > \alpha_{\text{basal}}$, whereas columns develop when $\alpha_{\text{basal}} > \alpha_{\text{prism}}$. At high supersaturations, gradients of vapor density across the faces lead to "hollowing" (Nelson and Baker 1996) and to more complicated forms (Yokoyama 1993).

The mechanism of molecular incorporation, although still highly uncertain in detail, is generally thought to involve steps or ledges on otherwise flat surfaces (Hudson 1992, p. 4; Nelson and Baker 1996). The steps are likely to contain numerous "kink" sites, where adsorbed molecules of water find facile incorporation into the lattice (Frenkel 1945; Gilmer et al. 1971). Controversy exists mainly over the origins of the steps, whether they result from two-dimensional (2-D) nucleation or from the emergence of screw dislocations onto the growing surfaces (see Frank 1949, 1982; McKnight and Hallett 1978; Nelson and Knight 1998). Each mechanism of step origin yields a different dependence of the deposition coefficient on supersaturation, which should be reflected in the linear growth rates of the various crystal faces.

This paper explores the inter-relationships between these alternative mechanisms and how the presence of a non-condensable medium (air) influences the overall dependence of growth on ambient supersaturation. The traditional concern about whether 2-D nucleation is the relevant mechanism or not may be mute if the effects of volume diffusion dominate the surface kinetics.

2. THEORETICAL RELATIONSHIPS

The effect of each mechanism of step origin on the growth of a particular crystal face can be expressed in quantitative terms through the use of appropriate theory. For instance, Burton et al. (1951) developed an elaborate theory of growth based on the emergence of one or more screw dislocations on a crystal face exposed to a supersaturation of specified magnitude. The spiral-step mechanism helped resolve the conceptual difficulty of reconciling observed growth rates at low supersaturations with predictions from theory based on the need for steps to be generated by nucleation of new layers on defect-free surfaces (Becker and Döring 1935; Frank 1949). The linear growth rate of a given crystallographic face (i.e., a basal or prism face) can be calculated once certain parameters
The relationship between the edge energy of a face and the transition supersaturation \( s_t \) that characterizes the efficiency of growth on that face can be established through consideration of the thermodynamics of "island" formation. If the island is circular and of monomolecular height \( \alpha \), then the critical radius is given by

\[
 r^* = \frac{\alpha^2 \varepsilon}{\Delta \mu},
\]

where \( \Delta \mu = kT \ln(s+1) \) is the chemical potential difference of molecules in the vapor and condensed phases (Hudson 1992, p. 301). Islands of this size are in unstable equilibrium with the adsorbed molecules in the surface layer. The important point to note is that such critical islands play central roles in both theories of step origin (Hudson 1992, p. 307). On faces with emergent screw dislocations, the spiral steps exhibit local radii of curvature that depend on the distance away from the dislocation. The minimum radius of curvature is equal to the critical value given by Eq. (1). The transition supersaturation for spiral growth is shown through classical theory to be

\[
 s_t = \frac{2\pi r^*}{x_s}, \quad \varepsilon = \frac{2\pi \alpha^2 \varepsilon}{kT x_s},
\]

where \( x_s \) is the mean distance of molecular diffusion on the surface (Burton et al. 1951). Note that \( s_t \) depends directly on \( r^* \) (and hence \( \varepsilon \)) and on \( x_s \). Such a simple relationship between \( s_t \) and \( r^* \) has yet to be demonstrated for 2-D nucleation. Nevertheless, once a critical-size island forms on a defect-free surface, a new layer is able to form and propagate rapidly across the surface, causing the face to advance.

Nelson and Baker (1996) have suggested that the deposition coefficient may be related to the transition supersaturation in a general way for all mechanisms of step generation:

\[
 \alpha = \left( \frac{S}{s_t} \right)^m \tanh \left[ \left( \frac{s_t}{S} \right)^m \right],
\]

where \( m \) is a parameter used to distinguish the different mechanisms. The dependencies of \( \alpha \) on \( s \) shown in Fig. 1, for instance, are based on Eq. (3) with \( m = 1 \) for screw dislocations and with \( m = 30 \) to represent the effect of 2-D nucleation. Variations in the edge energy with temperature or with crystallographic orientation would manifest themselves as variations in \( s_t \) (Eqs. 1 and 2), thus affecting each mechanism of step origin in qualitatively similar ways.
3. PRACTICAL APPLICATIONS

Given the fact that the two main mechanisms of crystal growth are each influenced by a common property of a crystal face, one should be able to apply theory toward some practical ends. Extrapolations of laboratory data of crystal growth to an atmospheric context, for instance, may be facilitated by appropriate reasoning. Nelson and Knight (1996, 1998) have recently measured the critical supersaturations needed to initiate growth on the basal and prism faces of laboratory ice crystals thought to be free of defects. However, ice grown on substrates (e.g., Lamb and Scott 1972) is likely to be defective because of the artificial contact, whereas ice crystals of atmospheric origin may or may not contain dislocations (McKnight and Hallett 1978; Keller et al. 1980; Frank 1982). It is tempting to think that growth rates derived from defective crystals, even if atmospheric crystals prove to be defect free, could be interpreted in terms of a transition or critical supersaturation that would find general application to atmospheric ice.

The presence of a non-condensable gas like air imposes practical limitations that need to be understood. Active growth of a crystal in air necessarily lowers the excess vapor density in the immediate vicinities of the growing faces, leading to gradients of vapor and temperature that impact the overall (measurable) growth of the crystal (Nelson and Baker 1996). The dependence of growth rate on supersaturation derived from classical theory (as depicted in Fig. 1) is appropriate only if the supersaturation is that immediately over the surface. This "local" supersaturation cannot, however, be measured during active growth in air. Crystals grown in a pure-vapor environment could be used, but one still faces the challenge of "taking" those findings to the atmosphere.

Lamb and Chen (1995) considered the impact of air on growth controlled by screw dislocations and showed that the mathematical form of the function \( \alpha(s/s_i) \) changes markedly when using the ambient, rather than the local supersaturation. Instead of an initially linear dependence of \( \alpha \) on \( s/s_i \) (as shown in Fig. 1), the function becomes parabolic, as can be seen in Fig. 2 (solid curve).

A similar analysis has now been performed for the case of growth dominated by 2-D nucleation using the parameterization of the surface physics given by Eq. (3), with \( m = 30 \). Simultaneous consideration of the inherent growth efficiency (dashed curve in Fig. 1) and mass continuity of vapor leads to a general relationship of the form

\[
\alpha = \left( \frac{x}{1 + K\alpha} \right)^m \tanh \left( \frac{(1 + K\alpha)^m}{x} \right),
\]

where \( x = s_{\text{ambient}}/s_i \) and \( K\alpha \) is the ratio of the transport resistances due to volume diffusion and surface kinetics. Equation (4) is an implicit transcendental equation that is typically solved by iteration. The dashed curve in Fig. 2 shows the result for \( K = 10 \), a value characteristic of growth under atmospheric conditions (Lamb and Chen 1995). Note in particular how growth in air (Fig. 2, dashed curve) causes the apparent dependence of \( \alpha \) on \( s \) to be much gentler than in its absence (Fig. 1). In effect, air not only restricts the overall flux of water vapor to the crystal, but it also greatly broadens the range of ambient supersaturations over which moderate growth occurs, even when layers form by 2-D nucleation.

4. CONCLUSIONS

Whereas controversy over the origin of steps responsible for the growth of ice crystals has emphasized the differences arising from 2-D nucleation and screw dislocations, these two mechanisms exhibit a number of similarities that are often overlooked. Both types of steps depend
in concept on the existence of islands of water molecules clustered together on the surface in unstable equilibrium with the population of adsorbed water molecules. The size of these critical islands is the same in both cases, being dependent on the surface free energy, as manifested along the periphery of the critical islands. This edge energy, a material property of each crystal surface, is common to both mechanisms of step origin, so any changes in its magnitude, such as arise from changes in temperature, will affect the growth of the face in the same way, regardless which mechanism is operative.

The presence of air further diminishes the distinction between the effects of 2-D nucleation and spiral steps on the growth of ice. Diffusion of water vapor through the air surrounding a growing crystal clearly restricts the vapor flux, but more importantly, the implied gradients of vapor density cause the local supersaturation immediately over each face to respond simultaneously to the environmental conditions and to the inherent growth efficiency of that face. The nonlinear interactions that arise from this coupling of mass transport in the vapor phase and surface physics cause the deposition coefficients of each mechanism to depend on the ambient supersaturation in fundamentally similar ways. More detailed analyses of this problem in the future may well demonstrate that the evolution of ice by vapor deposition in atmospheric clouds is only weakly dependent upon which model of growth is actually used.

5. ACKNOWLEDGMENTS

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6. REFERENCES


