# The enigmatic snowflake

author: Vladimir Radulovič
mentor: prof. dr. Rudi Podgornik
January $1^{st}$, 2009

# Contents

# 1 Abstract

In this seminar the physical mechanisms governing the formation of snow crystals are examined. The main focus is on the dynamics of crystal growth from the vapour phase. The basic physical processes are reviewed, especially the interplay of particle diffusion, heat diffusion and surface attachment kinetics during crystal growth, as well as growth instabilities that have important effects on snow crystal development.

# 2 Introduction

Snow crystals, also called snowflakes, are single crystals of ice that grow from water vapour. They form in copious numbers in the atmosphere and are well known for their elaborate, symmetrical patterns. Because of this symmetry and the rich variety of different patterns that can be observed in natural snowfalls, snowflakes have provided scientists a source of curiosity and scientific study for centuries. Among the great minds who have pondered over the subject we have Johannes Kepler, who in 1611 wrote a short treatise in which he described the possible origins of snow crystal symmetry and René Descartes who in 1637, as a part of his famous treatise on weather phenomena, *Les Météores*, gave a detailed account of the many different forms of natural snow crystals.
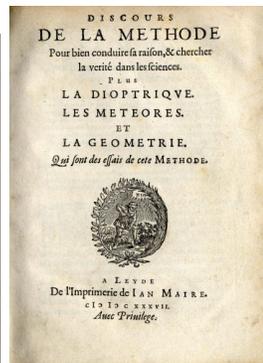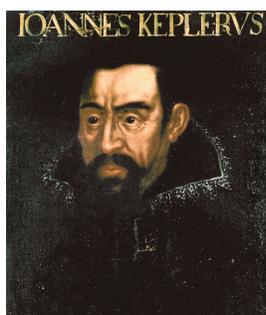


*Left: Johannes Kepler*
*Centre and Right: René Descartes and the front page of his work*
*Discours de la Methode which includes Les Météores*

3

With the development of photography in the late 19th century, Wilson Bentley catalogued several thousand snow crystal images that he had acquired over several decades. Bentleys images popularised the snow crystal as a winter icon and were largely responsible for the widespread notion that no two snowflakes are alike. Some particularly well-formed symmetrical specimens are shown in the bottom figures.
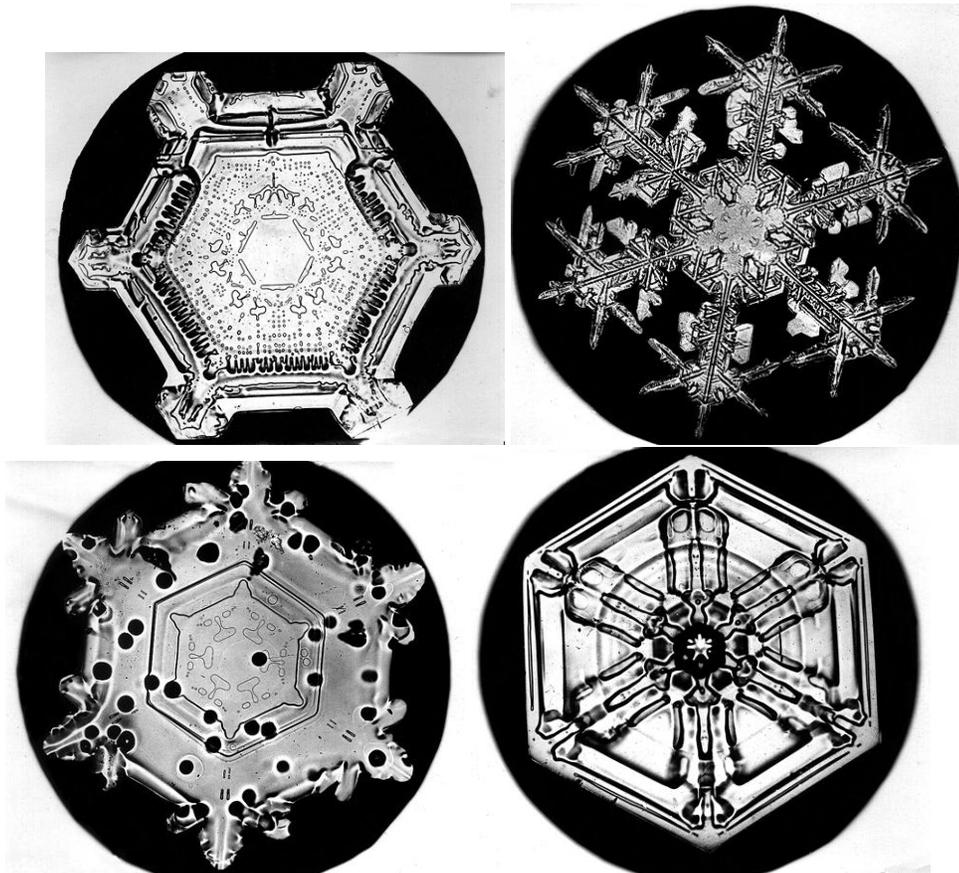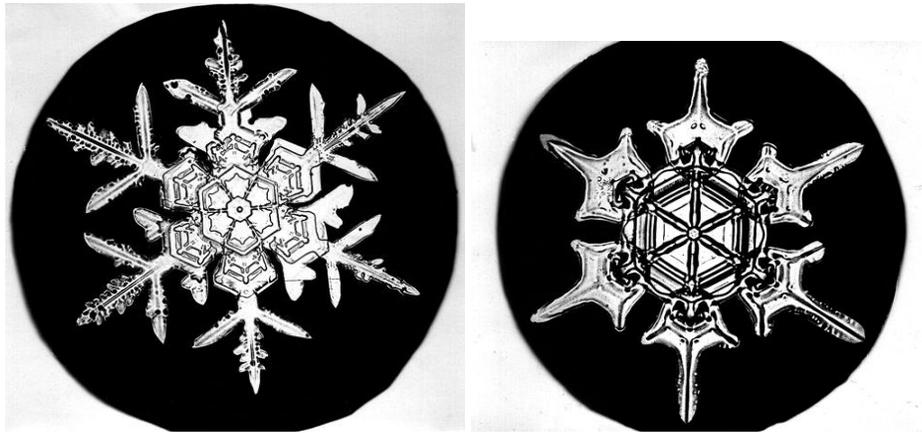
*Top six figures: photographs of particularly well-formed snowflakes*
*taken by Wilson Bentley himself*
*Bottom: Wilson Bentley at work*



Most natural snow crystals, however, are smaller and are generally blockier in appearance, usually without the high degree of symmetry present in well-formed specimens. Polycrystalline forms are also exceedingly common. For an unbiased sample the reader is invited to go outside with a magnifying glass or microscope during a light snowfall.

# 3 The morphology diagram

Wilson Bentley's images prompted the Japanese physicist Ukichiro Nakaya to perform the first snow crystal formation experiments under controlled conditions in the 1930s. He studied the morphology of snow crystals grown at different temperatures and supersaturations at atmospheric pressure and categorized natural snow crystals that appeared in various meteorological conditions. The morphology diagram shown below is the combined result of his observations. Subsequent studies have confirmed its validity [2] [3] [4].
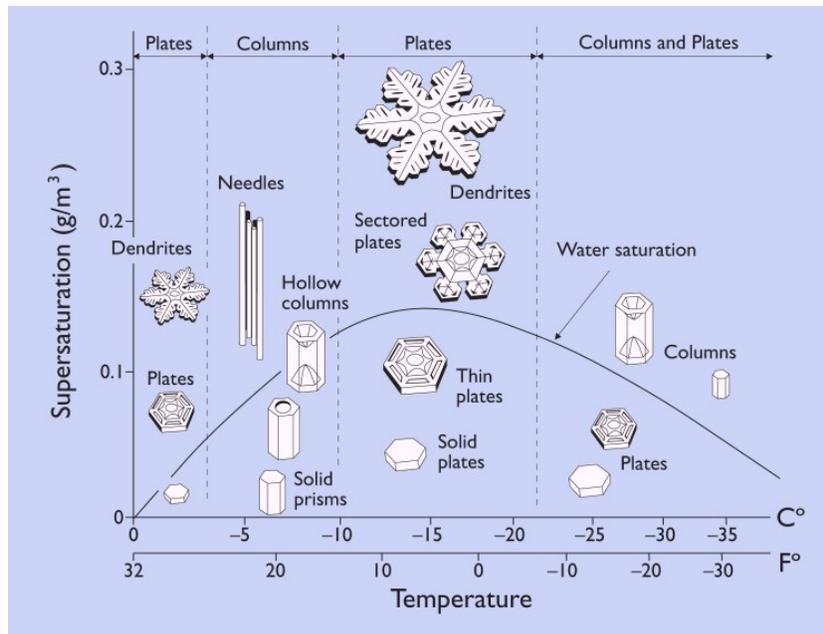


*The morphology diagram shows different types of snow crystals that grow in air at atmospheric pressure, as a function of temperature and water vapour supersaturation. The morphology switches from plates at $T \approx -2°\text{C}$ to columns at $T \approx -5°\text{C}$, then back to plates at $T \approx -15°\text{C}$ and then back to columns at $T < -30°\text{C}$. Higher supersaturations produce more complex structures.*

# 4 The formation of a snow crystal

Snow crystal formation begins in a cloud made of liquid water droplets nucleated on minute dust particles. Pure water droplets of microscopic dimensions can be supercooled to temperatures of about $-40°$C before they freeze, which means that the water vapour of a cloud is supersaturated. As the cloud temperature drops to around $-10°$C the water droplets begin to freeze, but not all of them freeze simultaneously. A frozen droplet will begin to accumulate water molecules from its surroundings. The vapour that makes up the cloud will stay supersaturated by virtue of the remaining unfrozen droplets. As the crystal grows facets will form. The resulting shape of a nascent crystal is often a hexagonal prism. Because of reasons, which will be explained later, as the prisms become larger branches start to form. Since the snow crystals fall through the cloud, they experience different temperatures and humidities along their descent, and thus their growth behaviour changes with time. Because all six arms experience the same conditions as they grow, the result is a rather complex growth pattern for each arm of the crystal, with all six arms developing roughly the same pattern. If there are no collisions with other ice or water particles, a snow crystal can grow into a rather elaborate, six-fold symmetric shape. This is how the bulk of the liquid water that makes up a cloud is transformed into ice.

# 5 The physics behind snow crystal formation

The normal form of ice has a hexagonal crystal structure, so the basic ice crystal shape is a hexagonal prism. Other forms of ice, like for instance cubic ice, have different crystal structures and are responsible for the formation of twinned and polycrystalline snow crystals. We will concentrate on hexagonal crystals, so we will ignore the other forms.

For an ice crystal growing from water vapour the **Hertz-Knudsen formula** [5] gives us the growth velocity normal to the surface:

$$v_n = \alpha \frac{c_{sat}}{c_{solid}} \sqrt{\frac{k_B T}{2\pi m}} \sigma_{surf} = \alpha v_{kin} \sigma_{surf} \tag{1}$$

In the above formula $m$ is the mass of a water molecule, $c_{solid} =$

$\rho_{ice}/m$ is the molecule number density of ice, $c_{sat}(T)$ is the equilibrium number density of water molecules above a flat ice surface and $\sigma_{surf} = (c_{surf} - c_{sat})/c_{sat}$ is the supersaturation just above the growing ice crystal surface.

The parameter $\alpha$ is the **condensation coefficient** into which all the physical processes, which determine how water molecules are incorporated into the ice crystal lattice - the **attachment kinetics** - are lumped. The condensation coefficient will therefore depend on a whole range of parameters and properties like temperature, supersaturation, the surface structure and geometry and the surface chemistry, to name a few. If water molecules striking the surface are instantly incorporated into the lattice, then $\alpha = 1$, otherwise $\alpha < 1$. For a molecularly rough or a liquid surface we expect $\alpha \approx 1$ [6]. The general assumption, which may not always be valid, is that the incorporation of water molecules into an ice crystal lattice is a local process. Nonlocal effects, like transport between facets, could make the above assumption invalid. For example: in a plate-like crystal transport from the basal facets to the prism facets would enhance the growth of the prism facets, which implies $\alpha_{prismfacet} > 1$. If this happens one should include the transport effects directly into the problem.

## 6   Three main processes in snow crystal growth

The growth of a snow crystal depends mainly on attachment kinetics and two transport effects: particle diffusion, which carries water molecules to the growing crystal and heat diffusion, which removes the latent heat generated by solidification. It is the combined effect of these processes, which is responsible for the vast diversity of snow crystal morphologies, so for us to have a grasp on growing snow crystals we must understand these three main processes, and their effect on snow crystal growth. The two transport effects are understood at a fundamental level, the attachment kinetics, however, are not yet understood in detail, so much experimental work has been devoted to exploring the molecular dynamics that occur on a growing ice surface. In order to be able to do so, one must disentangle the different mechanisms that determine crystal growth.

# 7 Particle transport

Particle transport is described by the diffusion equation:

$$\frac{dc}{dt} = D\nabla^2 c, \tag{2}$$

where $c = c(x)$ is the water molecule number density surrounding the crystal and D is the diffusion constant. The characteristic time in which a significant change in $c$ occurs is $\tau_{diffusion} = R^2/D$, where $R$ is the characteristic crystal size. The growth time in terms of $R$ is $2R/v_n$, where $v_n$ is the growth velocity normal to the surface discussed earlier. We define the **Peclet number** as the ratio of these two times:

$$p = \frac{\tau_{diffusion}}{\tau_{growth}} = \frac{Rv_n}{2D} \tag{3}$$

For typical growth rates of snow crystals the Peclet number is of the order of $10^{-5}$, which means that diffusion adjusts the water molecule density around the crystal much faster than its shape can change. This is the reason why the diffusion equation can be reduced to Laplace's equation:

$$\nabla^2 c = 0, \tag{4}$$

which must be solved with appropriate boundary conditions. The continuity equation at the interface gives:

$$v_n = \frac{D}{c_{solid}} \left(\vec{n} \cdot \nabla\right)_{surf} = D\frac{c_{sat}}{c_{solid}} \left(\vec{n} \cdot \nabla\sigma\right), \tag{5}$$

where $\sigma(x) = (c(x) - c_{sat})/c_{sat}$ and $c_{sat}$ is independent of position because to begin with the isothermal case is assumed.

# 8 Spherical crystal growth

Consider the growth of a spherical crystal. The diffusion equation reduces to one dimension and can be solved analytically. We assume the attachment kinetics are the same as those on a flat surface, with an arbitrary $\alpha$, which is constant around the sphere. We consider this problem in three cases of increasing difficulty [7].

## 8.1 Case One: $\alpha < 1$, no heating

Without heating the temperature remains constant and independent of position. The solution of the diffusion equation is:

$$v_n = \frac{\alpha \alpha_{diff}}{\alpha + \alpha_{diff}} v_{kin} \sigma_\infty = \frac{\alpha}{\alpha \alpha_{diff}} \frac{c_{sat}}{c_{solid}} \frac{D\sigma_\infty}{R}, \qquad (6)$$

where $\sigma_\infty$ is the supersaturation far away from the growing crystal and R is the sphere radius. If $\alpha_{diff} \ll \alpha$, the growth velocity becomes independent of $\alpha$:

$$v_n = \frac{c_{sat}}{c_{solid}} \frac{D\sigma_\infty}{R}. \qquad (7)$$

This is purely diffusion-limited growth so attachment kinetics can be neglected. If on the other hand $\alpha \gg \alpha_{diff}$, then the growth velocity reduces to:

$$v_n = \alpha v_{kin} \sigma_\infty. \qquad (8)$$

## 8.2 Case two: $\alpha_{diff} \ll \alpha$, with heating

This case is more complicated than case one since it involves solving a double diffusion problem, it can however be solved analytically. The solution is:

$$v_n = \frac{D}{R} \frac{c_{sat}}{c_{solid}} \frac{\sigma_\infty}{1 + \chi_0}, \qquad (9)$$

where

$$\chi_0 = \frac{\eta D \lambda \rho_{ice}}{\kappa} \frac{c_{sat}}{c_{solid}}, \qquad (10)$$

and where $\lambda$ is the latent heat for the vapour / solid transition, $\kappa$ is the thermal conductivity of the solvent gas, and $\eta$ is defined as $d(\log c_{sat})/dT$. The main effect of heating on the growth is scaling the growth velocity by a factor of $(1 + \chi_0)^{-1}$. In near vacuum conditions we have $\chi_0 \gg 1$ because the diffusion constant is large, and the growth velocity is limited mainly by heating. The expression is:

$$v_n \approx \frac{\kappa}{\lambda \rho \eta} \frac{\sigma_\infty}{R}. \qquad (11)$$

## 8.3 Case three: $\alpha < 1$, with heating

This is the most general case. The final result is:

$$v_n \approx \frac{\alpha}{\alpha(1 + \chi_0) + \alpha_{diff}} \frac{c_{sat}}{c_{solid}} \frac{D\sigma_\infty}{R},$$ (12)

which can be rewritten as:

$$v_n \approx \frac{\alpha^*}{\alpha^* + \alpha_{diff}} \frac{c_{sat}}{c_{solid}} \frac{D\sigma_\infty^*}{R},$$ (13)

where $\alpha^* = \alpha(1 + \chi_0)$ and $\sigma_{infty}^* = \sigma_{infty}/(1 + \chi_0)$. The above expression is remarkably similar to the solution of case one.

The above results are very useful for determining the relative importance of diffusion and attachment kinetics and especially useful when designing or interpreting experiments aimed at measuring $\alpha$. Indeed ice growth experiments are beginning to produce data of sufficient accuracy to shed light on the microphysics that underlies the snow crystal morphology diagram.

# 9  Prism crystal growth - numerical solutions

Real ice crystals are almost certainly nonspherical. That is why in case of a hexagonal prism crystal, a more realistic scenario altogether, we use computer simulations to obtain numerical solutions of the diffusion equation. Much is to be gained, however, by approximating the hexagonal prism crystal with a cylindrical one. Instead of the six prism facets we have one curved surface and instead of the two basal facets we have two circles. In this approximation the double diffusion problem is simpler to solve and easier to visualize. An example of a numerical solution of the diffusion equation for a growing crystal is shown below [8].
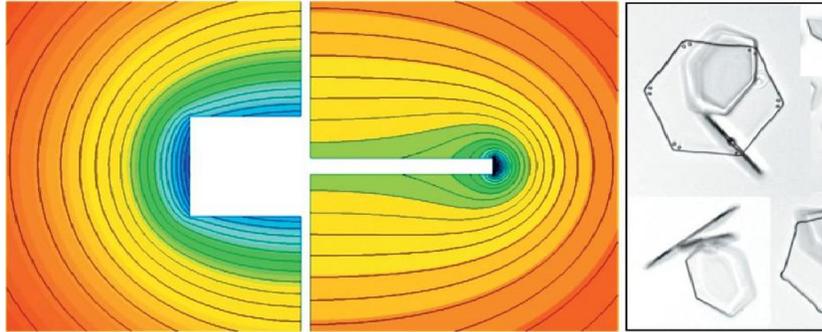
*Diffusion calculations around two growing ice prisms. The contours represent lines of constant supersaturation in the air around the crystal.*
*Left: cross-section of a growing (cylindrical) plate with a diameter / thickness ratio of 2 and $v_{prism}/v_{basal} = 2$. The supersaturation is highest at the corners, which implies that all facets are concave.*
*Centre: same as above, only with a diameter / thickness ratio of 20, and $v_{prism}/v_{basal} = 40$. This time the supersaturation is highest at the centres of the basal facets, which indicates they are convex.*
*Right: thin plates grown in air (scale bar = $50\mu m$)*

Because the prism morphology does not change appreciably during growth, velocity boundary conditions were used. In the first case we have roughly isometric crystals, or crystals for which the growth rates of the basal and prism facets are comparable. As we can see from the simulation (leftmost picture), $\sigma_{surf}$ varies considerably across the growing surface and is maximal at the edges. Since the growth velocity is constant, then the Hertz - Knudsen formula requires $\alpha\sigma_{surf}$ to be constant as well, which implies that $\alpha$ is largest at the centre of the facet.

The fact that $\sigma_{surf}$ is largest at the edges also implies that at a molecular level, rather than being flat, the facets are concave to some degree. The crystal surface grows in a step-like fashion. Steps are generated at the facet edges and propagate inwards as the crystal grows. The step density is highest at the centre, which results in $\alpha$ being maximal at the centre. For larger crystals we have larger variations of $\sigma_{surf}$ across a facet. This, as we shall see later, is what causes the formation of branches.

In the second case (centre picture) we have a thin, plate-like crystal. The result of the simulation is exactly the opposite of the

first case. The supersaturation ($\sigma_{surf}$) is largest at the centre of the basal facet, so $\alpha$ is smallest there. Steps are generated near the facet centre and propagate outward, so at a molecular level the basal facet is convex. The dividing line between the concave and the convex cases for prism crystals is seen to occur at diameter / thickness ratios of about 10. There is a third case, which is not shown in the above figure: thin columnar growth, with diameter / thickness ratios much smaller than 1. The solution of the diffusion equation in this case implies convex prism facet. This type of crystals does not readily appear naturally because branching tends to happen before convex prism facets develop

## 10 Attachment kinetics in brief

Since attachment kinetics are too broad a field to be presented in detail in this seminar, we will focus merely on the basics and mention what likely applies to snow crystal growth. As mentioned earlier, for a molecularly rough surface, for which the density of kink sites (kinks = imperfections like bumps, steps, etc.) is the largest possible, we assume that $\alpha \approx 1$ [5].

### 10.1 Nucleation limited growth

While the molecules that attach to a molecularly rough surface are indistinguishable from those forming the surface itself, in case of a molecularly flat surface, the admolecules, in absence of suitable attachment sites tend to evaporate before becoming part of the surface. Growth then only occurs when the admolecule density is high enough for two-dimensional islands to form on the surface: once such an island is formed, its edges provide steps and kinks for the attachment of other molecules. The growth of the crystal then depends on the nucleation rate (the rate of formation of islands) and the island growth rate. If the nucleation rate is low, then each island grows out completely, resulting in layer-by-layer growth; this regime however, is of little relevance for snow crystals. If the nucleation rate is high, there can be islands growing on top of other islands. Various models [5] typically yield the condensation coefficient as:

$$\alpha(T, \sigma_{surf}) \approx A(T, \sigma_{surf}) \exp\left(-\frac{\sigma_{crit}}{\sigma_{surf}}\right), \qquad (14)$$

where

$$\sigma_{crit} = \frac{\pi \beta^2 \Omega_2}{3(k_B T)^2}, \qquad (15)$$

$\beta$ is the free energy for a growth island that is one molecule thick and $\Omega_2$ is the area taken by one molecule on the surface.

## 10.2  Growth mediated by step sources

Anything that provides imperfections at a molecular level can influence the growth of faceted crystals. Examples include impurities, intersections of surfaces with other objects, crystal imperfections, etc. This growth mechanism is important in the case of ice prisms at low supersaturations.

## 10.3  Surface structure

Since attachment kinetics derive from the molecular dynamics at a crystal surface, they are strongly linked to the molecular structure of the surface. The surface of an ice crystal is a very lively place: it is quite complex and exhibits strong temperature dependence near the melting point. That is why it is generally accepted that changes in surface structure must be responsible for the dramatic changes in growth behaviour with temperature. On the surface various forms of reconstitution take place to lower the surface energy, so the crystal structure there is not the same as inside. To make matters worse, near the melting point the kinetic velocity ($v_{kin}$) of water molecules on the surface is large, so imaging techniques like scanning probe microscopy are of no help to us at all for determining the surface structure. This is why we do not yet understand the crystal surface and thus cannot explain the morphology diagram. We can, however, mention two temperature dependent effects, which occur on a crystal surface:

### 10.3.1 Surface roughening

The surface free energy is given by: $F = E - TS$, where $E$ is the binding energy, which favours a smooth surface, and $S$ is the surface entropy, which favours a rough surface. The equilibrium surface structure is determined by the temperature: the lower it is, the closer the structure is to being molecularly flat and the higher it is, the rougher it becomes [5]. If there is a roughening temperature, $T_R$, above which the surface is completely rough, then we have a **roughening transition**. In case of a crystal for which the surface cannot be directly determined we exploit two likely indicators of surface roughening:

1. above $T_R$ the condensation coefficient $\alpha$ is $\approx 1$ and

2. crystal growth is not faceted even at low supersaturations.

There is experimental evidence to support a roughening transition in ice at a temperature of about $-2°$C, and only for the prism facets [9]. Snow crystals in these conditions sometimes occur as very thin plates with almost no prism facets at all, which supports this conclusion.

### 10.3.2 Surface melting

Surface melting is essentially a more developed form of surface roughening. Since the molecules near the surface of a crystal are not so strongly bound as the molecules in the interior, a thin quasi-liquid layer forms on the surface slightly below the melting point. There is ample evidence to support surface melting in ice crystals at temperatures above $-15°$C [10] [11]. Surface melting has a profound effect on the surface structure of ice, and thus on attachment kinetics and it may very well be, that much of the temperature variation seen in the morphology diagram is just down to this phenomenon. What supports this conclusion is that surface melting is known to depend strongly on temperature exactly over the range where snow crystal growth exhibits large variations. Unfortunately the effect of surface melting on crystal growth in general is not yet known. Models of ice crystal growth in presence of surface melting have not yet given results in agreement with experiments.

# 11   Dendritic growth

Hexagonal prism ice crystals appear when the growth is not so strongly limited by particle diffusion, or, in other words, when the supersaturation is low, the crystal size is small, or the background gas pressure is low. Crystal growth is then largely dependent on attachment kinetics. If the above parameters increase sufficiently, diffusion becomes the dominant force in crystal growth dynamics. In this case branches and side branches grow from the surface of the crystals and the growth is known as dendritic (which literally means tree-like). As indicated in the morphology diagram the overall complexity of the dendritic pattern increases with increasing supersaturation as well as with increasing crystal size and background gas density. The dendritic structure often exhibits some self-similar, fractal characteristics. For ice dendrites the smallest structures typically occur on scales of about $1 - 10\mu m$.
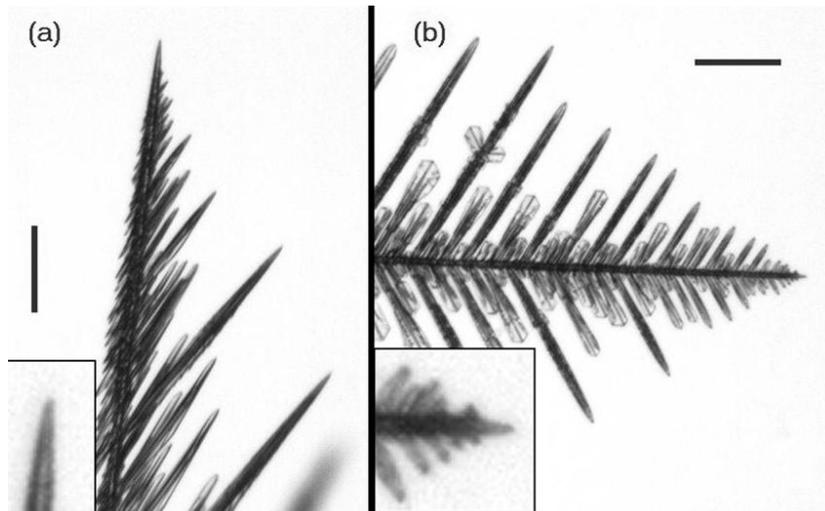


*Left: ice dendrite growing at $T = -5°$C, showing the charachteristic "fishbone" pattern.*
*Right: a "fern-like" dendrite growing at $T = -15°$C.*
*Both structures are planar, both scale bars are $100\mu m$ long and the inserts are $4X$ magnified views of the growing tips.*

## 11.1 Branching

Whenever crystal growth is limited by diffusion, the growth of smooth facets is unstable. If we start with a flat crystal surface and add a small bump, the bump will effectively stick out further into the supersaturated medium above the surface. Particle diffusion will bring material to the top of the bump at a faster rate then to the surface. With a greater supply of material, the bump grows larger, which increases the supply even more. Much of the structure in snow crystals derives from this positive feedback effect, which is often called the **Mullins-Sekerka instability**. When we couple the above with attachment kinetics, the picture becomes more complex. We find that faceted crystals can grow stably, but only for so long. The figure below shows the growth of a faceted plate-like crystal.
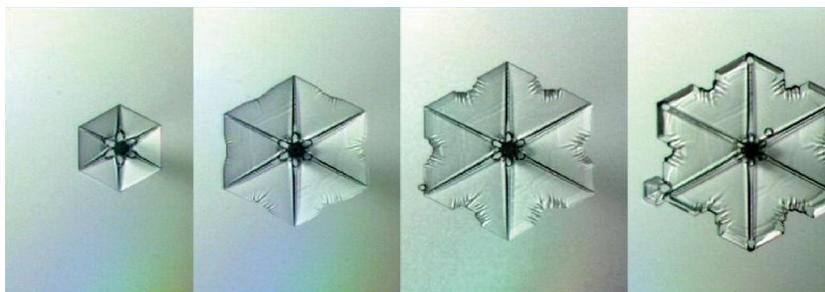


*Series of photographs showing the transition from faceted growth to branched growth. The final crystal size is approximately 1mm. Note the small water droplet in the third picture from the left and how it gives birth to a secondary structure seen in the fourth picture.*

If a facet is to grow stably, then $v(x)$, the perpendicular growth velocity along the surface, must remain constant. Recall that $v = \alpha v_{kin} \sigma_{surf}$ (Equation 1) and that the diffusion equation solutions yield a varying $\sigma_{surf}$ with its minimum value at the facet centres. Thus, as long as the prism structure persists, $\alpha$ must also vary along the surface, reaching its maximum value at the facet centres. Since the diffusion lengths are small compared to the crystal size, the prism facets are slightly concave and their curvature increases as the crystal grows. With time the step density reaches its maximum value at the facet centres, which means that the surface at the centres becomes rough on a molecular level. This, in turn means, that at

the facet centres $\alpha \approx 1$, while $\sigma_{surf}$ continues to decline. The growth velocity is now no longer constant along the surface, which means we have branching. Near temperatures of $-15°$C this instability leads to the familiar six-fold symmetric branching and near $-5°$C to clusters of needle crystals. Convex facets do not exhibit branching, so the growth at temperatures near $-15°$C still remains plate-like.

## 12 References

1. Libbrecht K G 2005 The physics of snow crystals *Rep. Prog. Phys.* **68** 855-895

2. Kobayashi T and Kuroda T 1987 Snow crystals *Morphology of Crystals - Part B* ed I Sunagawa (Tokyo: Terra Scientific) pp 645-743

3. Kobayashi T 1966 On the variation of ice crystal habit with temperature *Conf. on Physics of Snow and Ice (Sapporo, Japan)* pp 95-104

4. Kobayashi T 1961 The growth of snow crystals at low supersaturations *Phil. Mag.* **6** 1363-70

5. Saito Y 1996 *Statistical Physics of Crystal Growth* (Singapore: World Scientific)

6. Hirth J P and Pound G M 1963 *Condensation and Evaporation* (Oxford: Pergamon)

7. Libbrecht K G 2003 Growth Rates of the principle facets of ice between $-10°$C and $-40°$C *J. Cryst. Growth* **247** 530-40

8. Libbrecht K G 2003 Explaining the growth of thin ice crystal plates with structure-dependent attachment kinetics *J. Cryst. Growth* **258** 168-75

9. Elbaum M 1991 Roughening transition observed on the prism facet of ice *Phys. Rev. Lett.* **67** 2982-5

10. Petrenko V F and Whitworth R W 1999 *Physics of Ice* (Oxford: Oxford University Press)

11. Dash J G, Fu H and Wettlaufer J S 1995 The premelting of ice and its environmental consequences *Rep. Prog. Phys.* **58** 115-67

## 13  Images

- www.phys.uu.nl - portrait of Johannes Kepler (page 3)

- faculty.uml.edu - portrait of René Descartes (page 3)

- www.leeds.ac.uk - title page of Descartes's work *Discours de la Methode* (page 3)

- www.its.caltech.edu - Wilson Bentley at work (page 5)

- www.snowflakebentley.com - selected photographs of snowflakes (pages 4-5)

- Libbrecht K G 2005 The physics of snow crystals *Rep. Prog. Phys.* **68** 855-895

  - morphology diagram (page 6)

  - diffusion calculations (page 12)

  - ice dendrites (page 16)

  - transition from faceted to branched growth (page 17)