Atmospheric Ice Formation Processes

10

Bernd Kärcher

Abstract

This contribution provides a basic introduction to the formation of ice in clouds. Various pathways to ice nucleation and factors controlling ice formation processes are addressed. Challenges in characterizing the atmospheric ice phase and novel approaches to better understanding the fundamental mechanisms involved in ice nucleation are outlined.

10.1 Introduction

Water is the only material that occurs in all three phases in the Earth system. Water vapor is the most effective *greenhouse gas* and has a considerable effect on the *radiation budget*. A fundamental constraint on the abundance of water vapor is the *Clausius-Clapeyron* relationship (Becker 1978) determining the maximum amount of water vapor a given volume of air can hold in *thermodynamic equilibrium*. Saturation denotes the condition in which the vapor pressure of a substance in a condensed phase is equal to its equilibrium *vapor pressure* (see Fig. 10.1 for water). Water vapor in excess of the saturation values is termed *supersaturated* and the excess vapor turns into liquid water or ice. Liquid water is the main component in cloud droplets and most *aerosol* particles, allowing trace species to dissolve, forming aqueous *solution droplets* and initiating chemical reactions. Solid water in the form of *ice crystals* often initiates the formation of *precipitation*

B. Kärcher (✉)
DLR, Institute of Atmospheric Physics (IPA), Münchner Straße 20,
82234 Oberpfaffenhofen, Germany
e-mail: bernd.kaercher@dlr.de

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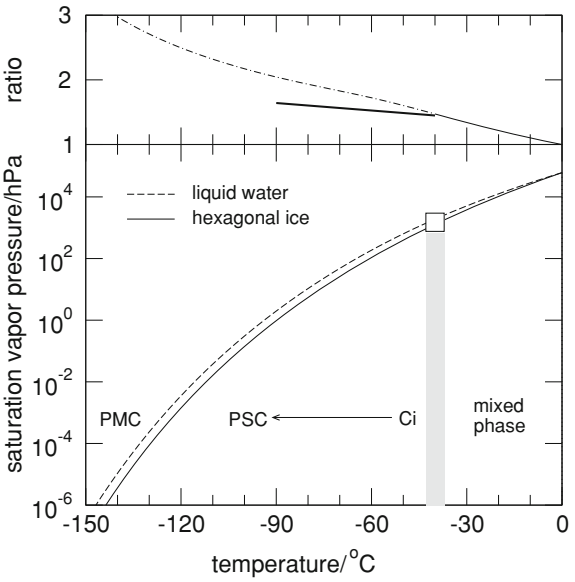

Fig. 10.1 Partial pressures of water molecules in thermodynamic equilibrium with liquid water and hexagonal ice, and their ratio (*top panel*), versus temperature (Murphy and Koop 2005). The spontaneous freezing temperature of supercooled pure water is indicated (*square*), along with the temperature ranges in which the various ice-containing clouds typically form. The water-to-ice pressure ratio, R, is indicated by a solid curve at temperatures where pure liquid water exists. Ice supersaturation (R–1), in mixed-phase clouds reaches a peak value of $\sim$0.47 at –40 °C. The thick solid curve marks the ice supersaturation where supercooled aqueous aerosol droplets freeze homogeneously in cirrus and PSCs (Koop 2004)

in tropospheric clouds and is involved in cloud *electrification*. High altitude clouds composed entirely of ice crystals warm the *climate* by absorbing Earth's *infrared radiation* (*cirrus* and *contrail cirrus* clouds, altitudes $\sim$10 km), are involved in polar *ozone depletion* (*polar stratospheric clouds*, PSCs, $\sim$20 km), and act as sensitive indicators of atmospheric changes (*polar mesospheric clouds*, PMCs, $\sim$85 km). *Ice* is the thermodynamically most stable water phase at subfreezing temperatures.

Ice nucleation plays an important role in diverse areas such as cryobiology and atmospheric cloud formation. In general, nucleation summarizes the processes by which material is transferred from one phase to another. The formation of a new phase, initiated by an external forcing, is driven by a supersaturation of the parent phase (vapor or liquid)—making it more abundant than dictated by thermodynamic equilibrium (i.e., in saturated conditions). The forcing, usually a cooling, is necessary to overcome the energy barrier to nucleation. The parent phase is unstable, exhibiting a tendency to establish saturated (equilibrium) conditions. The new phase has lower bulk energy and is therefore more stable. Once molecular-sized, stable patches of the new phase ('critical clusters') have been created due to

the energy supplied by thermal molecular motion, they grow further, depleting the parent supersaturation. In the case of liquid water/ice particles, this latter growth process is termed condensation/deposition; the reverse processes are *evaporation/sublimation*.

A water phase is *ice-supersaturated* at a certain temperature if the concentration of water molecules exceeds the ice-saturated value. In Earth's *atmosphere*, ice forms in ice-supersaturated conditions mainly within liquid water or aqueous aerosol droplets, or on the solid surfaces of a subset of aerosol particles known as heterogeneous *ice nuclei* (IN). Ice crystals formed this way acquire sizes ranging between a millionth of a centimeter (0.01 μm) and several millimeters (1 000 μm) and can develop into precipitation particles (*snow*, *graupel*, *hail*) in low-altitude clouds. It has long been known that the geometrical forms of snowflakes bear evidence of the hexagonal crystal lattice of water molecules that are tied together by a *hydrogen-bonding* network.[1] Three geometrical arrangements of ice exist in the atmosphere: *hexagonal*, *cubic*, and *amorphous* (noncrystalline) (Hobbs 1974). The two latter form at low temperatures and transform into the more stable, hexagonal, arrangement upon warming. Water ice has also been discovered on other planets in our *solar system*, on some of their moons, in the rings of Saturn, and on asteroidal surfaces.

Hexagonal or cubic ice does not nucleate from the vapor phase alone in the atmosphere. Therefore, aerosol particles must serve as the precursors of ice crystals. This chapter provides a brief overview of aerosol-mediated pathways to ice formation in clouds (nucleation modes) and addresses dynamical controls of cloud ice formation with special emphasis on cirrus.

10.2 Aerosol-Mediated Modes of Ice Nucleation

Cloud particles form by nucleation (i.e., nonequilibrium) processes (Houze Jr. 1993). At *temperatures* below the equilibrium melting point (0 °C or 273.15 K) cloud particles may be composed of either *supercooled water* or ice. Ice crystals may form either homogeneously in cloud water droplets, in water condensed on aerosol particles, or heterogeneously involving water with solid impurities. The exact temperature at which ice forms depends on the nucleation process. The presence of IN in supercooled liquid water droplets has been shown to be necessary for the formation of ice-containing clouds at temperatures above about –30 °C. Incomplete understanding of ice initiation—the first appearance of the ice phase—is a large obstacle for the detailed numerical modeling of ice processes in clouds.

[1] Water is a highly ordered liquid with water molecules conjoined by hydrogen atoms. The exact number of hydrogen bonds formed by a molecule of liquid water (up to four because the oxygen atom of one water molecule has two lone pairs of electrons) depends on the temperature. In crystalline ice, hydrogen bonding creates a lattice structure exhibiting long range order. Amorphous water lacks this long range order yet it is still more 'solid-like' than liquid water.

10.2.1 Homogeneous Ice Nucleation

Small samples of liquid water can be supercooled to a temperature of about –40 °C (≈235 K), the spontaneous (or homogeneous) freezing temperature. *Homogeneous freezing* occurs at a range of temperatures depending on the sample volume (droplet size), the rate of cooling, the degree of purity of the water substance, and on other factors (Pruppacher and Klett 1978). The temperature regime in which supercooled liquid water droplets and ice crystals can coexist in the atmosphere defines the existence region of mixed-phase clouds (Fig. 10.1). Below the spontaneous freezing temperature, ice nucleates in aqueous droplets in a very short time (relative to meteorological time scales), quickly solidifying the entire droplet volume. In such cold conditions, water droplets can no longer exist. Cirrus and contrail cirrus are pure ice clouds occurring across a wide range of temperatures.

Aqueous aerosol particles containing soluble matter (*solutes*) at high humidity are sometimes called '*haze*' droplets. A common solute in atmospheric (particularly stratospheric) aerosol particles is *sulfuric acid*, but organic species are taken up by them as well. *Hygroscopic* material dissolved in aerosol particles attracts water molecules and thereby decreases the freezing temperature of pure water. In this way, ice nucleation can be suppressed to very low temperatures. Enhanced uptake of *nitric acid* in aqueous sulfuric acid particles causes the formation of liquid PSC particles in the winter polar lower stratosphere. These particles freeze homogeneously around –90 °C (≈185 K), forming ice-phase clouds.[2] PSCs are largely responsible for the formation of the '*ozone hole*' (Solomon 1999).

Solutes may precipitate in aqueous solution particles when the solute concentration becomes too high, forming crystalline inclusions (e.g., in *sea salt* particles containing *sodium chloride* as solute). With increasing humidity hygroscopic solution particles absorb more water molecules and those precipitates can melt away. This solid-to-liquid phase transition is termed deliquescence. Often *deliquescence* occurs before freezing. Homogeneous freezing temperatures of fully liquid, aqueous solution droplets have been measured below −40 °C for a wide array of solutes and solute concentrations (Koop 2004). It has been found that homogeneous ice nucleation in aerosols commences very suddenly within a narrow range of high ice supersaturations and is determined by the temperature and *water activity*—a thermodynamic property of the solution droplets equal to the ratio between the water vapor pressures of the solution and of pure water under the same conditions—and not by the chemical nature of the aerosol particles. The rate of freezing is proportional to the droplets' volume owing to the stochastic nature of the homogeneous nucleation process, and also depends on the rate of cooling.

[2] These are known as 'type-2' PSCs, in contrast to type-1 PSCs that form at slightly warmer temperatures and contain nitric acid, either dissolved in the liquid phase or present as solid nitric acid trihydrate (NAT) crystals.

It has been established observationally that soluble *organics* hinder homogeneous freezing (Cziczo et al. 2004) and can reduce the uptake of water molecules, causing organic-rich liquid particles to preferentially remain unfrozen (Kärcher and Koop 2005). A remarkable feature of some *supercooled*, organic-rich aqueous solutions is that they form glasses—highly viscous, amorphous substances behaving like solids—at low temperatures (Murray 2008). The extremely high viscosity of the liquid vitrifying at a transition temperature characteristic to the solution droplets (Koop et al. 2011) impedes molecular motion and therefore homogeneous ice nucleation. *Glassy* aerosol particles may explain the high supersaturations observed at the tropical *tropopause*, although there is an ongoing debate as to the accuracy of humidity measurements at low temperatures and pressures. Below –70 °C cubic ice nucleates in preference to hexagonal ice, thereby enhancing the *dehydration* (*'freeze-drying'*) caused by cold cirrus clouds and PSCs (Murphy 2003). Cubic ice transforms into hexagonal ice within minutes to days, depending on temperature. At warmer temperatures, cubic ice transforms so rapidly into hexagonal ice that the cubic ice is not observed.

Solution droplets containing substances dissolved in the water phase are ubiquitous and abundant in the *troposphere* and *lower stratosphere*. Therefore, the availability of such particles acting as *precursors* for ice crystal formation is not a limiting factor for cirrus and PSC formation. In the temperature range between 0 °C and about –40 °C cloud ice must form by a heterogeneous process since *homogeneous freezing* does not occur.

10.2.2 Heterogeneous Ice Nucleation

Heterogeneous pathways (modes) to ice formation are catalyzed by aerosol particles providing solid surfaces upon which nucleation can take place. It is thought that favorable tropospheric IN should possess one or more of the following properties (Pruppacher and Klett 1978): they should be highly water-insoluble and larger than a ten-thousandth of a millimeter (0.1 μm), have a lattice structure similar to crystalline ice, and contain active sites—distinct surface features that facilitate the attachment and clustering of water molecules into an ice-like arrangement. Other factors must play a role as well, since particles with the same set of these properties may still exhibit different ice-nucleating behavior. Among those factors is the ability of chemical groups at particle surfaces to accept and donate hydrogen bonds.

Perfect IN would exhibit very small energy barriers to nucleation and therefore form ice crystals slightly above ice saturation (contrary to homogeneous freezing of supercooled liquid water or solution droplets), but such particles are hardly found in the atmospheric aerosol. As opposed to the homogeneous case, heterogeneous ice nucleation behavior may vary strongly between individual particles in a sample and can proceed over a wide range of supersaturations or temperatures. This renders the interpretation of experimental data and modeling of this process difficult. Observed

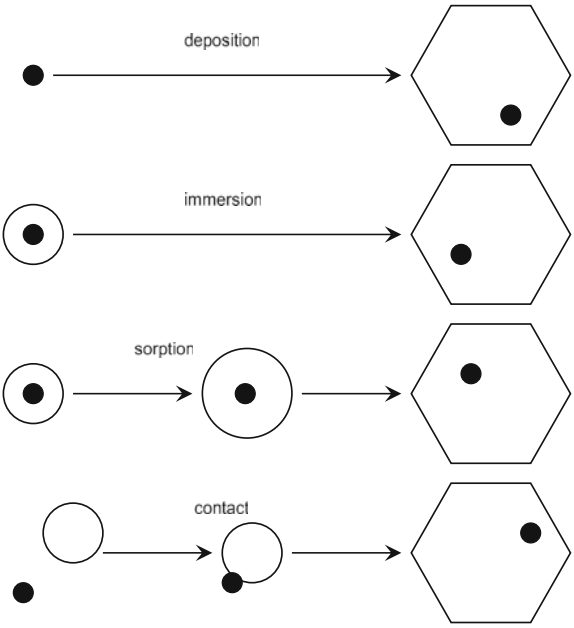

Fig. 10.2 Schematic showing the principal modes of primary heterogeneous ice initiation in clouds. Filled circles indicate IN, open circles are supercooled water droplets or aqueous aerosol particles, and hexagons symbolize ice crystals containing the IN upon which they have formed as inclusions. Terminology follows (Vali 1985). Other modes exist (see text), changing the conditions of the IN and their physical interaction with the droplets

IN constitute only a small subset by number of all tropospheric aerosol particles. Most IN appear to be present or active in the largest aerosol particles and under the most favorable conditions 1 particle out of 1 000 of the total aerosol population can serve as IN (DeMott et al. 2011). While free tropospheric IN concentrations are comparatively low (up to about 10 IN per liter of air), short-term increases in IN concentrations exceeding average values by orders of magnitude ('IN-storms') have been observed. In such cases, IN may control cloud formation and development, particularly mixed-phase clouds (Sassen et al. 2003).

Since supercooled water droplets do not freeze easily at temperatures in the mixed-phase cloud regime, the presence of IN is vital in order to turn liquid water clouds at least partially into ice clouds ('glaciation'). Another mechanism inducing glaciation is the seeding of liquid water-phase clouds by falling ice crystals forming in cirrus clouds at higher altitudes. In the early stages of glaciation, the ice crystals grow quickly by water vapor deposition since the ice supersaturation is large (Fig. 10.1 top, thin solid curve). Thus, glaciation may proceed within tens of minutes in originally purely liquid water-phase clouds, producing a colloidally unstable mixed-phase cloud. The water substance is transferred from the droplets to the ice crystals either by evaporation and diffusion of water vapor through the air or by collection and rapid freezing (riming) of droplets with sufficiently large ice crystals. The glaciation time scale is largely controlled by the temperature and the number and physical properties of the ice crystals. In honor of its discoverers, the cloud glaciation mechanism is termed the Wegener-Bergeron-Findeisen

process. Completely glaciated, purely ice-phase clouds are found at temperatures up to about –10 °C; at higher temperatures cloud particles usually stay liquid.

Figure 10.2 depicts the principal conceptual heterogeneous ice initiation modes. During deposition nucleation, water vapor is transported onto the surface of an IN, taking on a crystalline form and bypassing the formation of liquid water. Immersion nuclei are droplet inclusions initiating the freezing of the particle in which they reside. Sorption nucleation refers to the condensation of water vapor onto a nucleus followed by freezing and is therefore also referred to as condensation freezing. Contact nucleation occurs when IN and droplets come mechanically into contact by collisions. The latter mode is only efficient in the presence of cloud droplets (i.e., in mixed-phase clouds) since they offer a much larger area for collision than the smaller aerosol droplets. Immersion and condensation freezing are not easily distinguishable in measurements. The sets of supersaturations and temperatures at which each of these modes become active are generally different even for the same type of IN.

10.2.3 Other Ice Nucleation Modes

A number of further primary ice nucleation mechanisms are known, often identified in laboratory experiments. Their atmospheric relevance is not well established. Some are related to partially soluble organic and inorganic aerosol phases. Ammonium sulfate crystals may precipitate in aqueous solutions and act as IN before deliquescence occurs. A significant IN activity has been found for oxalic acid when present as a hydrated crystal in aqueous solution droplets. Glassy aerosols impeding homogeneous freezing can actually nucleate ice heterogeneously (Murray et al. 2010). These mechanisms require quite low tropospheric temperatures so that mainly cirrus formation would be affected. Other primary ice formation processes include freezing of evaporating supercooled water droplets and contact freezing ‘inside-out’ (immersed IN collide with the water droplet surface). The presence of electrical charges may also increase the efficiency of nucleation by reducing the nucleation energy barrier and may enhance the contact nucleation process (electro-scavenging).

The ice activity in IN samples usually increases with decreasing temperature and increasing supersaturation. Several mechanisms have been identified modifying this picture. The activity of some IN can be deactivated (damped) by liquid—particularly organic—surface coatings. On the other hand, water droplets covered by certain long-chain alcohols can nucleate ice already at –1 °C. Even without the action of such species, it has been argued that surface crystallization of supercooled water may rival volume-dependent homogeneous freezing. There is a pending discussion on memory effects, meaning that the retention of ice or ice-like liquid layers of water molecules at the surfaces of ice crystal residues—the particles that remain when ice crystals sublimate completely—facilitates ice formation in a subsequent nucleation event (pre-activation).

The temperatures at which the first ice crystals form in liquid water-phase clouds are usually lower than about –10 °C and vary with locale and time. Measurements in mixed-phase clouds reveal that the number of ice crystals sometimes dramatically exceeds the number of available IN. Their ratio can exceed 1 000 around –10 °C and typically decreases with temperature and towards the cloud tops. Such large ratios likely result from secondary ice production processes, such as the fragmentation of large cloud droplets during freezing, the mechanical fracturing of evaporating crystals, and the production of ice splinters during riming. The latter mechanism—referred to as the Hallett-Mossop process—takes place in a narrow temperature window between –3 °C and –8 °C in the presence of cloud droplets larger than a few thousandth of a centimeter (10 μm). It is the only secondary ice formation process active in clouds that has been confirmed experimentally. Ice splinters are collected by cloud droplets that in turn freeze, acting as riming centers to produce new splinters. Hence, this process, also referred to as ice multiplication, is particularly effective as a secondary source of cloud ice.

10.2.4 Ice Nucleation in Clouds

Cloud particle concentrations vary substantially. The formation and development of tropospheric ice clouds are complicated by the many modes of ice nucleation mediated by aerosol particles and supercooled water droplets (Cantrell and Heymsfield 2005), but also depend on the dynamical environment supporting ice nucleation. Only when particles are in close proximity may they physically interact with each other.

The most efficient deposition or immersion nuclei might have already caused ice formation in low-altitude clouds and precipitated before reaching cirrus altitudes (Wiaczek et al. 2010). It is therefore conceivable that IN play only a minor role in cirrus development, except perhaps when they are directly emitted at high altitude (e.g., by aircraft), are rapidly lofted from their source regions in the boundary layer (e.g., by convection), or when cirrus form in slow updrafts. In cold and strongly ice-supersaturated conditions, nitric acid may be taken up in liquid aerosol particles, enhancing the freezing droplet volume and therefore promoting the formation of haze droplets and thin (often invisible) cirrus clouds (Kärcher and Solomon 1999). The water droplets in exhaust contrails, generated by particles emitted from aircraft jet engines, freeze homogeneously within about one wingspan behind airplanes cruising at altitudes where contrail formation is prevalent (Kärcher 1999). It is not necessary to ascribe any particular heterogeneous ice-nucleating property to aircraft-produced particles to explain initial properties of such contrails below the spontaneous freezing temperature.

Very low temperatures are necessary to form PSCs and PMCs owing to the extreme dryness of their atmospheric environment with only few water molecules per million air molecules. These extremely tenuous clouds are susceptible to even small changes in air temperature, in the abundance of water vapor, or in the

radiative characteristics of the atmosphere. The ice clouds in the winter polar stratosphere nucleate homogeneously on supercooled liquid droplets that are a ten-thousandth of a millimeter (0.1 μm) large and constitute the majority of the stratospheric aerosol. Other routes to stratospheric ice cloud formation involving solid hydrates of nitric acid also exist (Peter 1997). The ice clouds in the high-latitude summer mesosphere are thought to form primarily by deposition nucleation on meteoric smoke particles with sizes of only a millionth of a millimeter (0.001 μm). Other candidates for mesospheric ice formation include charged molecular clusters (atmospheric ions) that are abundant at mesospheric altitudes. It has also been proposed that amorphous solid water nucleates homogeneously from the vapor phase if the number of nucleating smoke particles is limited (Murray and Jensen 2010). Observational evidence is insufficient for deciding which nucleation pathway dominates. Water-containing particles in PMCs cause strong radar signals known as polar mesosphere summer echoes. Larger ice crystals at the cloud base give rise to the night-shining (noctilucent) clouds observable during twilight. They are the coldest clouds on Earth, forming at the edge of space below –125 °C ($\approx$150 K) (Rapp and Thomas 2006).

10.2.5 Sources of Ice Nuclei

Heterogeneous ice nuclei originate from natural and man-made sources, predominantly deriving from Earth's surface. *Mineral dust* is perhaps the best documented IN present in the atmosphere. The majority of dust emissions are natural, mostly from the Sahara and Gobi deserts. About one-third of the mineral dust emissions arise from human activities such as land use and desertification. Dust particles are complex mixtures composed of metal oxides or carbonates and come in many chemical variations and sizes, each with different IN behavior. The clay minerals montmorillionite and kaolinite—common weathering products containing sodium, calcium, magnesium, aluminum, and silicon—have been used as surrogates for real mineral dust particles from different source regions in modeling studies examining the alteration of mixed-phase clouds by IN.

A large number of natural and *anthropogenic* incomplete *combustion* processes involving hydrocarbons produce impure *black carbon* (*soot*) particles, a form of amorphous carbon. These particles are associated with various organic and inorganic emissions present as surface *coatings*. Details of the particle surface *morphology*, size, and chemistry may explain the wide variety of ice-nucleating behavior of atmospheric soot samples. The available laboratory and field information regarding the efficiency of these particles for ice formation is not entirely conclusive but suggests that soot particles, while highly variable as a source, are not implicated as primary ice-forming agents in the troposphere. Further anthropogenic IN (e.g., produced by steel and copper smelters) are far less abundant than soot.

High molecular weight organic compounds—such as long-chain alcohols—are produced by open *biomass burning*, i.e., the burning of vegetation over vast areas

including wildfires and deforestation, and can act as IN in such areas. Maritime air masses are thought to be deficient in IN, although marine *biogenic* particles (e.g., phytoplankton) can function as immersion nuclei when present within sea salt droplets. Pollen, leaf litter, fungal spores, strains of bacteria, and even viruses are known to be good ice-nucleating agents and they may affect the precipitation development in clouds near their source regions. *Volcanic ash* particles have rather moderate effects on tropospheric ice formation, although some of them (containing silicate) can become quite ice-active at low temperatures. Silver iodide particles—frequently used in cloud seeding experiments—possess a crystallographic structure similar to ice and are therefore efficient IN, triggering ice formation already at –6 °C. Finally, ablated *meteorite* material represents an extraterrestrial source of deposition nuclei in the upper atmosphere. The experimental characterization of IN types in different locales and seasons is an active area of research.

10.3 Dynamical Controls of Cloud Ice Formation

10.3.1 Generation of Supersaturation

Clouds appear in conjunction with a large number of atmospheric motion systems. The supersaturation required to induce cloud formation is created by dynamical effects, mostly by cooling of pockets of air ('parcels') that are lifted due to vertical air motions. The most common ways to force air parcels to ascend are wind convergence, topographic lifting, and *buoyancy* (recalling Archimedes' principle). The parcels may mix with air from their surroundings by *turbulence* or stay isolated (*adiabatic*). Transport of humid air and subsequent mixing moistens the *air parcels* before or during cooling. The water vapor in the rising parcels is deposited on the nucleated ice crystals in ice-supersaturated conditions, producing cloud ice water. The lifting and associated cooling can be quite vigorous (as in convective, towering clouds with updrafts exceeding several meters per second) or rather gentle (as in stratiform, layered clouds, with updraft speeds of up to tens of centimeters per second). While low- and mid-level clouds usually block the sunlight owing to their large water content and exhibit sharp boundaries because cloud droplets quickly evaporate, high altitude *cirrus* are largely transparent and take the form of fibrous wisps since their water content is low and ice crystals do not readily disappear upon leaving the cloud.

In high-reaching (deep) *cumulus clouds*, ice may initially form in the *mixed-phase* temperature regime and is transported aloft and detrained in the form of *anvils* away from the convective core (convective outflow). In anvil cirrus, further ice nucleation may occur after much of the ice mass has been removed by *sedimentation*. The causes of observed onset of *glaciation* in some low-altitude (shallow) cumulus clouds at temperatures above –10 °C are not well understood. Contrary to most natural clouds, hot and moist *jet aircraft* exhaust plumes cool at constant pressure by mixing with cold environmental air, leading to the formation

of contrails. Similar to anvil cirrus, *contrail cirrus* clouds spread by *wind shear*, increasing their horizontal area and are often assembled in clusters clearly visible in satellite imagery. PSCs and PMCs contain up to 10 000 times less ice water than cirrus. They are visible from the ground only under special conditions. In the *Arctic*, the formation of PSCs preferentially occurs over mountain ridges causing rapid vertical wind perturbations and therefore adiabatic cooling of air. Less is known about the small-scale dynamical environment in which PMCs form.

10.3.2 Cirrus Formation by Homogeneous Freezing

As an illustrative example of how cloud ice particles form, the homogeneous ice formation process within an adiabatic air parcel that is subject to steady cooling and free of supercooled water droplets (containing only liquid aerosol particles) is described below. This simplified scenario replicates common cirrus formation conditions. The *relative humidity* over ice (RHI) is equivalent to the (fractional) ice supersaturation. When cooling starts (e.g., at ice saturation, RHI = 100 %), RHI begins to increase. The amount of supersaturated water vapor condensing onto the haze particles acts to reduce RHI, but this amount is very small. Therefore, in the absence of cloud ice particles, RHI increases with time in proportion to the rate of cooling. Homogeneous ice nucleation in the supercooled aerosol will not commence until high ice supersaturation (RHI $\approx$150 %) is reached (Fig. 10.1 top, thick solid curve). Once ice crystals form, they begin to grow by depositing water vapor, reducing RHI towards ice saturation on a time scale that is inversely proportional to the number concentration of nucleated ice crystals. The nucleated ice crystal number scales approximately with the cooling rate (or the equivalent updraft speed) and is determined by the balance between cooling and depositional growth around the point where RHI reaches its peak value. Peak RHI values are only slightly larger than those characterizing the onset of homogeneous freezing unless the cooling rates become much lower than typically observed. The lower the temperature, the slower the ice growth and water vapor depletion, the longer RHI stays around its peak value, and the more crystals form.

A theoretical analysis of this problem is not straightforward, because nucleation and growth of ice crystals may occur simultaneously. Figure 10.3 shows results of a theory describing this scenario (Kärcher and Lohmann 2002). In many places in the upper troposphere, cloud-scale *cooling rates* lie within 1–10 degrees per hour; nucleated ice crystal *concentrations* should therefore mostly range between 100 and 1 000 particles per liter of air. Atmospheric variability in temperature and other variables as well as further cloud development typically produce a broad spectrum of cirrus ice crystal numbers. These *number concentrations* are often larger than those of IN (DeMott et al. 2003), suggesting that on average IN modify, rather than control, cirrus formation processes. A paucity of IN in the upper troposphere (number concentrations below 10–30 per liter of air) implies a

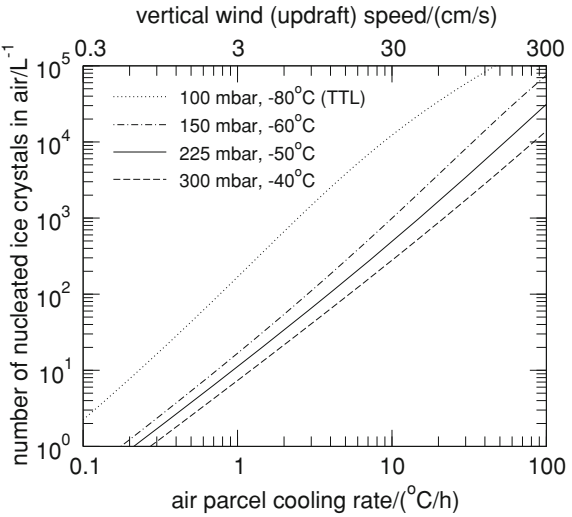

Fig. 10.3 Ice formation from supercooled aerosol particles in an air parcel that is lifted at a constant updraft speed for representative combinations of air pressure and temperature in cirrus conditions. A special case for very cold cirrus clouds forming in the uppermost tropical troposphere (tropical tropopause layer, 'TTL') is included

predominance of homogeneous freezing in cirrus clouds, consistent with the observed high ice supersaturations necessary for homogeneous freezing of haze droplets, at least in extratropical regions (Haag et al. 2003). The theory also predicts that the dependence of nucleated ice crystal number on the size of the freezing aerosol particles is weak. Airborne measurements of ice crystal concentrations can be understood in the way described by this theory, except for the class of cirrus present in the cold upper tropical troposphere, for which significantly smaller ice crystal concentrations have been measured than those shown in Fig. 10.3 at the prevailing cooling rates (Jensen et al. 2010). This may suggest either that ice nucleation processes other than homogeneous freezing are more prevalent in those clouds, or that other mechanisms, such as turbulent mixing with drier air, act towards reducing nucleated ice crystal concentrations.

10.3.3 Role of IN in Cirrus Formation

Having emphasized the importance of homogeneous aerosol freezing for cirrus formation, it is important to note that nucleation on even few IN (1–10 per liter of air) can affect the initial ice crystal number in cirrus clouds and perhaps their further development. The idealized theory has been extended to include effects of IN on the ice formation process. The main effect of efficient IN is to reduce the RHI where ice starts to form. The *deposition* of water vapor on ice crystals nucleating early on the IN slows the subsequent increase in RHI in a cooling event and thereby reduces the number of homogeneously nucleated ice crystals that would have formed in the absence of IN. It may even lead to a complete inhibition of homogeneous freezing. The occurrence and magnitude of this effect depends on the cooling rate as well as on the IN concentration and the temperature and

supersaturation at which the IN nucleate ice. The effect is strong for high (although limited as noted above) IN number concentrations and low cooling rates. On the other hand, sedimentation of ice crystals forming on IN can lead to a removal of those crystals from the nucleation region and thus make homogeneous freezing more likely. The sedimentation effect becomes important for slow cooling causing long nucleation time scales. Although direct ice nucleation from atmospheric aerosols is not the primary determinant for the ice content in anvil and contrail cirrus, ice nucleation may contribute to the ice budgets at some point during their life cycle.

10.3.4 Challenges to Representing Ice Formation in Large-Scale Models

This idealized model framework exemplifies the use of cloud physics theory to describe the interaction of processes in nonconvective lift that eventually lead to the formation of ice in cirrus clouds. The underlying theory has been employed to develop a *parameterization* framework potentially suitable for large-scale models that are not capable of resolving the small spatial and temporal scales pertinent to the atmospheric ice nucleation process in cirrus (Kärcher and Burkhardt 2008). When applying such a parameterization, the challenge is to properly represent the dynamical forcing (cooling rates), the number (ice-active fractions) and nucleation behavior of IN (Hendricks et al. 2011), and the interaction between cirrus and mixed-phase clouds. The forcings driving ice nucleation are not resolved by large-scale models, and the lack of a fundamental understanding of heterogeneous ice nucleation does not allow the prediction of the ice-active fraction of atmospheric IN populations from first principles. Hence, besides the nucleation process, dynamical forcing and ice-active fractions must be parameterized as well (DeMott et al. 2011).

Gravity waves inducing a wide range of cooling rates constitute an important element for the formation of cirrus (Hoyle et al. 2005), Arctic PSCs (Carslaw et al. 1998), and PMCs (Jensen and Thomas 1994). In view of the marked nonlinearity of ice nucleation processes, wave-driven forcing may modify the general picture derived from simple conceptual models of cloud ice formation that are mostly based on the assumption that cooling rates do not vary within the time ice nucleation occurs. Characterizing the cooling rate and resulting supersaturation variability at the spatial scale of clouds probably opens up a novel field of research (Kärcher 2012). Vertical air motion variability that is to a significant degree driven by the release of latent heat during cloud formation is also crucial for the formation of ice in convective clouds. Besides being able to exert a significant effect on the dynamics of mixed-phase clouds, ice particles can also act as seeds for frozen precipitation particles. Therefore, application of cloud physics theory to describe ice formation in low-altitude clouds is arguably more difficult than in the case of cirrus.

Table 10.1 Summary of ice-containing cloud types and selected characteristics related to the ice formation process as discussed in this chapter

Ice cloud type	Altitude (km)	Principal ice-forming agents	Ice supersaturation[a]
Mixed phase	<7	IN, supercooled water droplets	≤0.5[b]
Cirrus[c]	>7	Supercooled liquid aerosol droplets	0.5–0.7[d]
PSC[e]	~20	Ternary solution droplets	0.5–0.7
PMC[f]	~85	Meteoric smoke particles, ions	?

[a] Approximate values at which ice nucleation commences, see also Fig. 10.1
[b] Ice forms at or below liquid water saturation above –40 °C, depending on the ice nucleation mode (Fig. 10.2)
[c] Pure ice clouds may also exist at lower altitudes
[d] Exact value depends on the temperature. Ice nucleation mechanisms in the tropical tropopause region are not well understood
[e] Type-2 polar stratospheric clouds. Supercooled solution particles from the background stratospheric aerosol layer are mainly composed of water and sulfuric acid and take up nitric acid at low temperatures prior to PSC formation. The role of meteoric smoke contributions in ice formation in PSCs is not clear
[f] Sources and ice nucleation behavior of PMC particles, and therefore the supersaturation at which they form, are highly uncertain

10.4 Concluding Remarks

This contribution has been written for a wide readership and therefore provides only a basic introduction to atmospheric ice formation processes. Readers interested in specific details or in-depth discussions might wish to consult the references provided here. Table 10.1 summarizes key features of ice-containing clouds in the atmosphere.

We conclude with a few thoughts on general aspects and future developments. The temperature regime above –20 °C is key to the generation of precipitation often involving the ice phase. Because the corresponding altitudes (a few kilometers) are quite easily accessible, much emphasis was historically put on measuring ice formation processes in situ in this regime. Such measurements have been conducted more frequently at the colder temperatures of the upper troposphere and lowermost stratosphere with the advent of high altitude *research aircraft*, while the mesosphere is studied using remote sensing methods or via rocket-borne sampling. No existing measuring device could probe all the cloud ice formation processes discussed here. Airborne sampling and analysis alter the ice-nucleating properties of the aerosol (e.g., by particle heating) and the mechanical impact of ice at the inlets of particle probes can affect quantitative estimates of crystal number and sizes (e.g., by ice crystal shattering). Furthermore, the fact that small-scale meteorological processes are capable of masking aerosol influences on clouds (Kärcher and Ström 2003) complicates measurements and

their interpretation, the modeling of aerosol-cloud interactions, and the understanding of the behavior of clouds in a changing climate, all of which are topics of present research (Heintzenberg and Charlson 2009).

A theory describing molecular-level nucleation processes in terms of macroscopic quantities developed almost a century ago (Becker and Döring 1935) is often applied to explore general features of the ice nucleation process. Since many of its underlying assumptions cannot be rigorously justified, we should have little confidence in the quantitative predictions of this so-called classical nucleation theory (Hegg and Baker 2009). Nevertheless, it is favorable to have this theory as a framework for first physically-based exploration and discussion, the more so as it seems very unlikely that—in view of the complexity of the problem at hand—a microscopic theory covering the multitude of factors controlling ice nucleation could ever be devised.

The research area of atmospheric ice formation processes has been, and remains, important for the DLR Institute of Atmospheric Physics since a thorough understanding of natural cloud formation is a necessary prerequisite for assessments of atmospheric change caused by human activity. A prime example of such work recently conducted in this institute is the formation of contrail cirrus and the associated alteration of natural cirrus cloudiness (Burkhardt and Kärcher 2011), which has been identified as an important step in better quantifying the overall impact of *aviation* on climate and in developing strategies to mitigate this impact (Boucher 2011). As a technological application, the sudden freezing of supercooled water droplets coming into contact with aircraft surfaces (*aircraft icing*) is relevant to many DLR activities. Adverse effects of aircraft icing in flight—including airfoil and engine stalling—can threaten passenger safety and reduce airplane performance. Measures must be taken to alleviate severe aircraft icing problems by making use of findings regarding atmospheric ice formation, such as estimations of the degree of glaciation in mixed-phase clouds.

Much research remains to better understand the dependencies of ice formation processes on atmospheric conditions. It is of vital importance to untangle the interactions between ice-nucleating aerosols, clouds, and precipitation in the appropriate dynamical environment to provide more reliable simulations of weather and climate. Ice nucleation is only one of many components contributing to atmospheric cloud formation. Nonetheless, a fundamental understanding of molecular processes—in particular those occurring at particle surfaces—would lead to further progress in representing ice formation processes in atmospheric models.

Cloud ice formation processes are closely related to *physical chemistry* and molecular physics as well as *thermodynamics* and statistical physics, reinforcing the notion that *atmospheric physics* is a central subject of the physical sciences. In this way, future research into ice formation will benefit from experimental and theoretical methods established in other areas of physics. Recent examples include the *laser* microscopy of ice crystal surfaces (Sazaki et al. 2010) and first principles calculations of the heterogeneous ice nucleation process (Hu and Michaelides 2007). In conjunction with further advances in the experimental characterization of

the physical and chemical properties as well as the atmospheric variability and abundance of IN, these examples offer promising possibilities to explore open issues regarding the atmospheric ice phase.

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