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Relationship between snow microstructure and physical and chemical processes

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Abstract

Ice and snow in the environment are important because they not only act as a host to rich chemistry but also provide a matrix for physical exchanges of contaminants within the ecosystem. This review discusses how the structure of snow influences both chemical reactivity and physical processes, which thereby makes snow a unique medium for study. The focus is placed on impacts of the presence of liquid and surface disorder using many experimental studies, simulations, and field observations from the molecular to the micro-scale.

1 Introduction

Ice and snow, as present in Earth's cryosphere, are reactive media (Takenaka et al., 1992; Klán and Holoubek, 2002; Abbatt, 2003), which can result in significant fluxes of trace gases being transferred between them and the atmosphere (Domine and Shepson, 2002). Furthermore, surface snow can efficiently scavenge and accumulate compounds of environmental concern (Wania et al., 1998; Dommergue et al., 2003). At the same time, surface snow is a highly dynamic multi-phase medium, the properties of which and their changes with time, critically affect both physical processes and chemical reactivity (Domine et al., 2008). To better understand underlying processes and their relation to the earth system is of importance to environmental chemistry, atmospheric science, and cryospheric science. This review focuses on chemical and physical snow-pack processes with relevance to polar settings and emphasises the microscopic description of the ice surface and its link with the environment.

1.1 Importance of snow

The release of reactive compounds from the snow-pack to the atmosphere is of importance for the composition and the oxidative capacity of the atmospheric boundary layer in permanently or seasonally snow-covered regions, including the polar regions

(Domine and Shepson, 2002). Strikingly, the depletion of ozone in air masses from the ground up to heights of several kilometres has already been observed in the 1980s at the Arctic coast (Oltmans et al., 1989) and is linked – at least in part – to processes in surface snow and ice (Simpson et al., 2007; Abbatt et al., 2012). Other substantial effects include the emission of nitrogen oxides from snow-packs. For example, in Antarctica NO_x levels typical for urban conditions have been observed (e.g., Davis et al., 2001, 2004; Eisele et al., 2008). In addition some nitrogen oxides and other species have been measured in firn and ice cores (e.g., Fuhrer et al., 1993; Anklin and Bales, 1997; Legrand and Mayewski, 1997; Sommer et al., 2000; Rothlisberger et al., 2001; Frey et al., 2006). Chemical processes have the capacity to significantly modify the amounts of impurities stored within the snow, making the interpretation of concentration profiles impossible without the application of models (Neftel et al., 1995; Wolff, 1995). Snow can act as an important storage and transfer medium for pollutants from the atmosphere to aquatic environments or to the soil. Mercury and persistent organic pollutants are examples of species that may accumulate in surface snow during winter and be released during snowmelt (Wania et al., 1998; Lalonde et al., 2002). However, from a global perspective the overall removal or transfer from the atmosphere to the soil and oceans is likely smaller than the depositional fluxes, because species like nitrogen oxides (Grannas et al., 2007b) and mercury (Durnford and Dastoor, 2011) are partially re-emitted to the atmosphere due to chemical processes in the snow. For other species such as persistent organic pollutants, the transfer to the soil or to the oceans may exceed the initial deposition, as those species may form post-depositionally in surface snow (Grannas et al., 2012). To fully assess the atmosphere-to-soil or -ocean fluxes from a global perspective the post-depositional fate of pollutants and impact of chemistry in snow need to be understood.

1.2 Impurities in snow

How chemical species behave in the snow-pack is largely dependent upon their location in the snow-matrix, where the fate of impurities can be dominated by processes in the bulk, on the surface, or in liquid locations. Figure 1 illustrates this multi-phase system of surface snow, consisting of ice crystals, brine, solid water-insoluble particles, and gas-filled pore space. Adsorbed species react rapidly to changes in the atmospheric environment, while entrapped species experience more solid state like processes. If impurities are concentrated colligative effects result, for example dissolution of impurities may form brine and introduce liquid into the system. Brines are impurity-rich liquid solutions that coexist with the solid ice phase in thermodynamic equilibrium, including solutions with low ionic concentration. Pockets of liquid or liquid in grain boundaries can migrate under the influence of temperature gradients and promote transport of species at faster diffusional rates than within the solid lattice (Hoekstra and Osterkamp, 1965). Such effects have been discussed for sea ice (Harrison, 1965; Weeks and Ackley, 1986), for surface snow (Meyer and Wania, 2008), and glacial ice (Rempel et al., 2001, 2002) where the transport of species is governed by a combination of gravitation forces, diffusion and temperature gradients. Each of these processes – reversible surface adsorption (Grannas et al., 2002), solid-state diffusion (Bales et al., 1995; Barret et al., 2011a), and uptake to the liquid fraction in snow (Herbert et al., 2006a) – has been proposed as the dominant mechanism for trace gas exchange with the overlying air for specific species and conditions.

Considering the dynamic character of the ice matrix, the location of impurities in surface snow is not necessarily reflected by the way they have initially been incorporated. A major source of impurities in surface snow is the atmosphere. Riming leads to the retention of soluble atmospheric trace gases (e.g. SO_2, H_2O_2, NH_3, HNO_3, CH_2O, CHOOH, HCl, Hg(II)) into the ice particles later found in snow samples (Snider and Huang, 1998; Long et al., 2010; Douglas et al., 2011). Thus rimed snow and ice are usually more concentrated with impurities than other types of deposited snow (Mitchell and Lamb, 1989; Poulida et al., 1998). Volatile atmospheric trace gases, such as nitrogen oxides, mercury, volatile organics, and acidic trace gases can also be taken up directly from the gas phase, likely affecting surface snow composition strongly (Abbatt, 2003; Huthwelker et al., 2006; Grannas et al., 2007b; Steffen et al., 2008). Initially, impurities in rimed snow are located in the interior of crystals, adsorbed species are present at the ice surface. However, a recent study showed that about 60 % of the total snow mass can be redistributed during less than a day, when temperature gradients build up in snow (Pinzer and Schneebeli, 2009b). Further, freeze-thaw cycles that are common in maritime mountain regions can also occur in the Arctic (Meyer and Wania, 2008) and lead to further redistribution of impurities (Eichler et al., 2001). How impurities respond to such strong rearrangements of the ice phase may thus be more important for their ultimate fate than their initial mode of incorporation. Consequently, the steady state distribution of impurities that is eventually reached in surface snow is a complicated amalgam of deposition and evolution.

1.3 Structure of snow

Significant progress has been made characterising the multi-phase structure of snow in recent years. However, analysing the composition of snow in-situ is difficult – as snow is physically not very stable and mechanically fragile. For example, it is common to chemically analyse snow by melting samples – the drawback of this approach is that the information on location of the chemical species within the microstructure is lost (Blackford, 2007). Drawing a complete portrait of the complex reactive matrix of snow requires examining its material constituents on a molecular level. Surfaces are a particular area of microstructure, where physical characteristics vary significantly from those of the bulk. In polycrystalline materials, like ice, surfaces can be internal, where multiple crystals meet, or external, where crystals readily interact with the surrounding environment. At surfaces, the symmetric structure of ice is necessarily modified because of the outer layer's missing bonds and subsequent reconstructions and relaxations of the surfacial molecular layers to minimize free energy. This is a well-established phenomenon in surface physics of ice (Frenkel, 1946; Henson and Robinson, 2004; Henson et al., 2005; Hobbs, 2010) and other solid materials such as colloids (Alsayed et al., 2005), ceramics (Clarke, 1987), and metals (Frenken and van der Veen, 1985). Such molecular disorder at the surface is frequently referred to as surface disorder, premelting, a quasi-liquid layer, or a liquid-like layer. The use of these synonyms has provoked some controversy and confusion (Baker and Dash, 1996; Knight, 1996b,a), and in this review we will therefore clearly differentiate between the general disorder at the surfaces and the special cases where specific properties approach those of a super-cooled liquid. Only then will we describe the surface disorder as liquid-like or quasi-liquid and use the term quasi-liquid layer (QLL). In other cases the terms surface disorder or disordered interface (DI) will be used. We feel that this differentiation is of paramount importance in atmospheric and cryospheric science, as it is connected to the key questions addressed by this review; how can the solid, liquid, and disordered fraction of ice surfaces be quantified depending on conditions such as temperature or impurity content? Which chemical processes occur in these specific locations? Under what environmental conditions is the behaviour of disordered ice surfaces similar to that of solid surfaces, similar to a liquid, or a unique interface that is distinct from both? Note that we avoid the use of the term "premelting," even though it is commonly used synonymously with surface disorder in material science, because we believe it invites confusion with the formation of a true melt.

1.4 Scope and aim of review

The goal of this review is to summarize the current state of knowledge on physical processes and chemical reactivity in surface snow and relate this to the microstructure of ice and snow. It addresses topics that have been identified as top-research priorities in several preceding reviews, each focusing on different fields of cryospheric science, such as the uptake of acidic trace gases to ice (Abbatt, 2003; Huthwelker et al., 2006), the snow chemistry (Grannas et al., 2007b), halogen chemistry (Simpson et al., 2007; Abbatt et al., 2012), fate of organics (McNeill et al., 2012), and mercury chemistry in snow (Steffen et al., 2008). Focussing on the microscopic and molecular level previous reviews have revealed that there is much to learn about the local environment that contaminants and impurities experience. In light of the open questions, this review discusses processes of relevance for the polar cryosphere such as sintering, adsorption, diffusion, freezing and chemical reactivity including heterogeneous chemistry, photochemistry, redox chemistry and other bimolecular reactions. This review is made unique by developing a more detailed microscopic picture of surface snow. The review thus also builds heavily on previous reviews that have dealt with physical processes (Huthwelker et al., 2006; Blackford et al., 2007; Domine et al., 2008) and the microstructure of ice (Dash et al., 1995, 2006) and snow (Domine et al., 2008). Here, we focus on those issues that are important to improve and develop our understanding of polar snow cover. This review is therefore comprehensive and discusses findings from laboratory and field studies, molecular dynamics simulations, and selected snow-chemistry box models.

2 The multi-phase structure of snow

Physical and chemical processes in snow take place in a complex, multi-phase structure, the characterisation and analysis of which has made considerable progress in recent years. In this section we consider particularly three features of snow each of which is fundamental to understand processes in snow: (i) how liquid is distributed in surface-snow, (ii) how impurities are allocated in snow and ice, and (iii) how ice interfaces are structured at the molecular level. For an in-depth review on macroscopic structural aspects of surface snow, we refer the reader to the review by Domine et al. (2008).

2.1 The ice phase

Physical processes such as mass transport, sintering, and grain evolution profoundly impact the constant evolution of solid ice. As a result observational tools are extremely useful for monitoring and describing ice samples. X-ray computed microtomography (XMT) is used with the aim of developing and optimizing model descriptions of heat transfer and the physical stability of the surface snow (Blackford, 2007;

Flin and Brzoska, 2008; Pinzer and Schneebeli, 2009a). Laboratory X-ray sources have yielded 3-D images of snow (e.g., Schneebeli and Sokratov, 2004; Heggli et al., 2011) and polar firn (Freitag et al., 2004) at 5–40 µm resolution. Thus, sub-µm scales are no longer reserved to more brilliant synchrotron radiation facilities and can be reached with high-resolution laboratory X-rays. From such images, the surface area of snow samples have been characterized (Kerbrat et al., 2008). Surface area is an important property of the surface snow as it is the interface where adsorption and exchange with the gas phase and overlaying atmosphere occur. The beauty of XMT is its non-destructive nature allowing observations in situ of snow-pack samples (Pinzer and Schneebeli, 2009a). Monitoring of a snow-pack exposed to temperature gradients revealed that most of the ice sublimates and re-condenses within 2–3 days (Sect. 3.1). How impurities respond to the high mass fluxes that result is currently not known, and cannot be analysed using XMT because impurity levels in snow are generally too low.

Grain boundaries, the contact area between two ice crystals, have provoked interest as reservoirs for impurities and as reactive locations (Huthwelker et al., 2006). Typical grain sizes in natural surface snow and ice range from tens of micrometres to a few millimetres, up to a few centimetres in some artificial ice samples, and even larger at the base of polar ice sheets. In snow and ice any thermodynamic potential gradients will result in grain metamorphosis. However, for artificial snow samples in isothermal conditions the grain boundary area, i.e. the total contact area between individual crystals, was found to be stable for 6 months at 233 K and 253 K (Riche et al., 2012). Optical techniques are excellent for observing the length scales of surface snow and in the past, glacial ice analysis primarily relied on optical microscopy for structural characterization (Wilen et al., 2003). Figure 2 shows grains in a thin section of polycrystalline ice, viewed with polarized light, where the different grain colours result from the characteristic anisotropy of ice and show different crystallographic orientations. A limitation of optical microscopy is that it can only be used on 2-D samples which means that the 3-D snow samples need to be cut into sections ≤ 0.5 mm in thickness. Thus, in the case of firn and snow their porous nature largely prevents such analyses and texture measurements remain much more common for harder ice samples. Even so, there are a number of different approaches that have been used to overcome this limitation in order to observe the texture of wet snow using optical microscopy (Blackford, 2007).

2.2 The liquid phase and chemical impurities

Because the presence of liquid water strongly influences the physical and potentially the chemical properties of snow, observing liquid in samples in situ has been a focus of recent studies. It should be pointed out that here we refer to a thermodynamically stable bulk liquid solution, but not to impurities present in a potentially disordered reservoir. XMT has been used to infer the distribution of liquid in porous ice samples. Most of these studies have dealt with sea-ice and are discussed here to show the potential use for snow samples. Using XMT is more difficult when liquid is present, due to the small difference in the liquid–solid absorption contrast. A contrast agent may be added to enhance the brine – ice absorption contrast when studying saline ice grown in the laboratory (Golden et al., 2007), although laboratory ice may differ from natural sea ice. Therefore to image sea ice, samples have been centrifuged to replace brine by air prior to XMT imaging (Maus et al., 2008). While it has been claimed that brine networks have been imaged in sea ice by XMT (Obbard et al., 2009) and in natural marine ice gas hydrate mixtures (Murshed et al., 2008), other investigators have not been able to do so. Hence it seems likely that the features documented by these authors, to a certain degree, are sea salts that have precipitated at their imaging temperature of 263 K. Solid salts are more easily distinguished from ice due to their much higher absorption of X-rays.

There have been a number of studies using low temperature scanning electron microscopy (LTSEM) which have identified solid particles such as dust and salt impurities like sodium chloride and sulphate, in snow and ice (e.g., Mulvaney et al., 1988; Cullen and Baker, 2001; Barnes et al., 2002; Baker et al., 2003; Obbard et al., 2003; Barnes and Wolff, 2004; Lomonaco et al., 2011; Spaulding et al., 2011). State-of-the-art LT-SEM instruments have a resolution of 5 nm. The first direct observation of sulfuric acid, concentrated in triple junctions and to a lesser extent at grain boundaries, in Antarctic ice was made using an electron dispersive (EDS) X-ray detector analysis in LTSEM (Mulvaney et al., 1988). Since this first observation there have been a number of LTSEM studies of polar ice with EDS analysis of impurities indicating that impurities are preferentially located in disconnected regions along the grain boundaries (see Blackford, 2007, for studies prior to 2007). Yet, a statistically sound demonstration of impurities distribution and a clear quantitative analysis is still lacking. More studies characterizing the material structure of ice are needed to be able to interpret the results in an atmospheric context. It is also of note that most studies have focused on glacial ice, which is different from surface snow, making extrapolations of impurity distributions from those findings to snow questionable for a number of reasons: (i) glacial ice is more dense than snow and temperature gradients are reduced, resulting in less sintering and ice mass transport; (ii) glacial ice is much older than surface snow and impurities have had more time to be transported through the ice matrix.

An extensive LTSEM microstructural characterisation of Antarctic firn has been made by Spaulding et al. (2011). They observed distinct impurity patterns and related those to their sources. It has also been claimed that the impurities control the microstructure found at those locations. This finding would be important, if true, as it means that the chemical species in the ice influence the structure, and the chemical reactions themselves are influenced by the structure. It should be cautioned, as the relevant processes during densification and evolution of firn structure and their time scales were not studied, that the observed patterns might also be due simply to different impurity sources.

Soluble impurities are often present as liquids in ice. The liquid nature of sulphuric acid in triple junctions of Antarctic ice has been shown using Raman microscopy by Fukazawa et al. (1998). Liquids in ice have even been observed at temperatures below the eutectic temperature of the bulk NaCl solution (Cho et al., 2002). As discussed in Sect. 3.4.3 kinetic restrictions might cause this observed deviation from thermodynamic predictions. In addition, geometric constraints can stabilize liquids in confined reservoirs, even below the eutectic temperature as theoretically treated by Nye (1991). If inclusions of liquid are small, with radii in the nm range, the Kelvin effect leads to a substantial melting point depression. The Kelvin effect states that the melting point depression (dT) depends on the radius (r) of a particle, or inclusion: $dT \sim 1/r$. Melting point depressions of 15–40 K have been found for water and solutes in nm-sized confinements (Aristov et al., 1997; Christenson, 2001). The theoretical treatment presented by Nye (1991) combines both the Kelvin effect and solution theory and arrives at an expression for the equilibrium size of a triple junction, which was shown to be consistent with the observed temperature dependence of SO_2 uptake into packed ice beds (Huthwelker et al., 2001).

At grain boundaries, liquid can form channels or isolated patches. When the dihedral angle (θ, where a region of liquid intersects two grain boundaries) is $> 60°$ liquid is trapped in isolated pockets at grain boundary triple points; whereas when $\theta < 60°$ liquid wets grains boundaries and can form interconnected channels (Nye, 1973; Waff and Bulau, 1979). The surface energies are highly compound specific (see also Sect. 3.4.3). Recently, Cheng et al. (2010) have shown that the presence of electrolytes can trigger the occurrence of random inclusions at high concentrations, whereas at lower concentrations solutions tend to freeze and thereby form connected channels. Morphology and surface energy in the ice–NaCl system has been studied by LTSEM using ice particles frozen in liquid nitrogen doped with NaCl (Blackford et al., 2007). Figure 3 shows the shape of the ice and the liquid NaCl-rich brine phase (in preparation for the LTSEM the brine is solidified by quenching to retain the equilibrium morphology) after etching of the ice matrix. The brine concentrates in vein structures where three or more grains meet and as inclusions on grain boundaries that appear as small mushroom-like features in the image. These images are rich in detail and provide qualitative structural information, which in itself is useful – as interconnected paths or isolated pockets of second phase liquid can be detected. By fracturing samples and creating planar 2-D surfaces more details of brine at grain boundaries is available (Fig. 4). Quantitative measurements of the dihedral angle can also be made, from which the brine–ice surface energy can be calculated (Blackford et al., 2007). Due to the quenching procedure liquid inclusions in the ice crystals cannot be observed using LTSEM. How ice bound liquid responds to snow metamorphism, and in particular how crystal properties like orientation influence liquid migration remain open questions.

Thus, LTSEM studies indicate that impurities form both connected web-like networks and concentrate in small, local features along the grain boundary network. To achieve a sound understanding of the distribution of impurities in ice more data is needed and LTSEM provides one possible approach for that, as long as the impurities agglomerate macroscopically. It is of note that most studies have dealt with glacial ice, and extrapolation of those results to surface snow is questionable. The solute-containing liquid phases within the ice microstructure can form veins or isolated pockets. The particular morphology of the liquid impurities depends on the relative surface energies of the components and can be derived based on LTSEM measurements. Liquids can also be present well below the eutectic temperature of the bulk solutions in nanometre-sized micro-pockets within bulk ice, that are impossible to observe using LTSEM. LTSEM. Finally, it is noted that in future studies the problems with the ice–brine contrast may be overcome by means of phase-contrast-based XMT (McDonald et al., 2011) enabling the observation of brine and void air simultaneously. This technique, though, has not yet been applied to natural ice.

2.3 The disordered interface

The surface of ice hosts chemical reactions and is the interface at which exchanges with the overlying air take place. Its properties, i.e. the degree and extent of disorder, determine the local environment that impurities are exposed to and thus may significantly impact their fate at a molecular level. Figure 5 compiles measurements and estimates of the thickness of the disordered interface and includes results from thermodynamic calculations, experimental studies, and molecular dynamics simulations. It is important to note that the thickness is not a direct observable in any of these experimental studies and the given values represent average values over the entire probing area. In particular, this explains values below 0.3 nm, which is the diameter of a water molecule and sets the lower limit of a physically meaningful thickness. Additional uncertainties due to translating the observables to layer thicknesses may also partially explain low values.

2.3.1 Thermodynamics of surface disorder

Theoretically, the disorder can be thought of by analogy to wetting behaviour and complete thermodynamic descriptions of the disordered interface have been developed and are best found in dedicated reviews on the topic (Dash et al., 2006; Luo and Chiang, 2008). As in wetting, at each surface or interface disorder is a direct consequence of the particular intermolecular interactions of the system. Here we attempt to qualitatively summarize the relevant aspects of the behaviour.

In equilibrium, a disordered interface will exist on a solid ice surface if it lowers the free energy of the system. That is, if by its existence an intermediate layer of thickness d reduces the total excess surface energy $F_S = (s_{lv} + s_{ls} - s_{sv})f(d) + s_{sv}$ (Israelachvili, 1991; Dash et al., 2006) whose value can vary between the dry and wet surfaces. Here s_{lv}, s_{ls} and s_{sv} are the surface energies of the liquid–vapour, liquid–solid and solid–vapour interface, respectively. Theoretically the functional dependence of the surface energy $f(d)$ comes from knowledge of the intermolecular forces at the interface. In the case of ice and other molecular materials it is typical to use van der Waals forces whose long-range potential across two surfaces falls off quadratically with distance. In systems with impurities or with surface charge, exponentially decaying electrostatic Coulomb interactions can be used to model the interactions between charged particles (Israelachvili, 1991), in addition to the common colligative depression of the melting temperature, which also results in additional liquid (Beaglehole, 1991). Thus the theoretical treatment predicts that the temperature dependence of the layer thickness varies depending on which interactions are dominating (Wettlaufer, 1999; Dash et al., 2006). As a consequence of these predictions in certain cases thickness can behave non-monotonically with respect to temperature and/or impurity level

(Benatov and Wettlaufer, 2004; Thomson, 2010). The resulting thickness versus temperature relations are summarized in Fig. 5 for different ices and compared with experimental results.

Just as in wetting, the formation of the disordered interface can be partial or complete, a difference that depends upon the relative cohesive versus adhesive forces controlling the system. When cohesion of the disordered molecules dominates, droplets will form, creating liquid islands on a solid surface (see Sect. 2.2). Alternatively, when adhesion dominates the liquid will wet the surface. Early experiments on ice surfaces at temperatures just below the melting point showed that liquid water droplets do not completely wet ice surfaces (Knight, 1971; Makkonen, 1997; Ketcham and Hobbs, 2011). It has been calculated, based on the theory of dispersion forces that the wettability of a pure ice surface depends on the thickness of the surface disorder (Elbaum and Schick, 1991). For very thin layers, complete wetting is favourable and thus the thickness of the surface disorder is expected to grow with temperature. At a certain thickness, however, the cohesion of the liquid wins over the adhesion to the ice, leaving individual small droplets sitting on top of a thin disordered layer, which cannot further grow in thickness. This has two consequences, (1) it explains the coherence of water drops on ice surfaces that are covered by a surface disorder and (2) predicts that the increase in thickness of the surface disorder stops at a certain thickness. For clean ice surfaces Elbaum and Schick (1991) calculated maximum thicknesses of a few nm. However in the natural environment, where impurities are ubiquitous, complete melting is thermodynamically always expected.

In summary, the surface disorder can be treated thermodynamically in analogy to wetting theory, and has been successfully applied to model the experimentally determined thickness of a surface disordered region. However, it is important to point out that using the wetting theory assumes that interfacial forces stabilize a homogeneous surface layer. This approximation is in contrast to theoretical predictions and experimental evidence. Furthermore, thermodynamics suggest that the disordered interface of pure ice differs significantly from the disorder in presence of impurities. On pure ice surfaces the thickness of disorder is finite, but when impurities are present the thickness diverges as temperatures increase. This thermodynamic treatment of the disordered interface allows treatment of the disorder and colligative melting in one unified model, so these two important regimes can be treated under environmental temperature and impurity conditions.

2.3.2 Observation of surface disorder

Observation of the thickness and effect of impurities

The disordered interface on ice surfaces has been investigated by many techniques (Li and Somorjai, 2007). These techniques are based either on observations of properties of the ice surface that change with the degree of molecular order or the structure at the surface is probed directly (see Li and Somorjai, 2007, for a complete list of individual studies).

Experimental results for ice–vapour interfaces are summarized in Fig. 5, showing that the measured thicknesses vary widely between different studies. There are several factors contributing to this variability. Different techniques have inherently different probing depths and examine different physical properties of the surface layer. For example, proton channelling is elemental specific and probes atomic positions in the interfacial region, while ellipsometry probes changes of the refractive index and extinction coefficient with the use of an appropriate optical model. The different probing depth is critical in measurements of the disordered interface, because the ice surface is highly anisotropic (Sects. 2.3.3 and 3.3.1). Some techniques also interact with the surface more than others, thereby adding uncertainty to the observations.

In addition to wide variations in observed or predicted thicknesses, the onset temperature at which surface disorder is observed varies between different techniques. Sum Frequency Generation (SFG) probes anisotropic surface vibrational modes of water. Although it is difficult to quantitatively assess the thickness with this technique, it is inherently surface sensitive and observes an onset in surface disorder of the interfacial water molecules near 198 K (Wei et al., 2001). In contrast to these results, proton backscattering observes onsets at 233 K (Golecki and Jaccard, 1978) and ellipsometry at 243 K and 268 K, respectively (Furukawa and Nada, 1997; McNeill et al., 2006).

As seen in Fig. 5, different ice crystal orientations give rise to different thickness results in otherwise identical experiments (Furukawa et al., 1987; Sazaki et al., 2012), consistent with molecular dynamics simulations (see Sect. 2.3.3). Surface disorder is also affected by the presence of impurities, as theoretically predicted (Sects. 2.3.1 and 2.3.3), and experimentally verified by optical reflectance (Elbaum et al., 1993), by ellipsometry (McNeill et al., 2006, 2007), and directly by Auger-yield near-edge X-ray absorption fine structure (NEXAFS) (Bluhm et al., 2002). Observations of impurity amplified or induced disorder at ice surfaces depend on experimental conditions and the method of experimental probing. Using synchrotron based, surface sensitive NEXAFS Starr et al. (2011) found that low concentrations of acetone on the surface of ice did not induce observable disorder at temperatures of 245 K and (Křepelová et al., 2010b) reported the presence of ordered ice surfaces in the presence of low concentrations of nitrate at 230 K. NEXAFS, however, probes the upper few nm of an ice sample, and thus the observation of ordered ice suggests that disorder does not spread throughout the entire upper few nm, but leaves room for disorder on the scale of a few molecular layers. An interesting feature of these types of studies is that the local environment of water molecules and of the impurities can be probed simultaneously. While the spectral features of the ice revealed that the disorder is limited (at maximum) to the upper-most crystal layers, it was shown by probing the nitrate that individual molecules are surrounded by hydration shells just as they would be in liquid water (Křepelová et al., 2010b). This results in some heterogeneity of the disordered interface at low surface coverage of nitrate where pronounced disorder, with liquid like properties, is limited to the vicinity of the impurities. Other potential sources of thickness variability may stem from ice preparation (vapour deposition versus cleavage of a single crystal), different ambient vapour environments (air or some inert gas versus pure water vapour), and differences in water vapour over- or under-saturation that give rise to different condensation and/or evaporation rates. Thus, thickness measurements from identical experimental techniques (e.g. atomic force microscopy (AFM); see Fig. 5) can vary by more than order of magnitude, likely due to some combination of the aforementioned variability as well as in the case of AFM, variation in the AFM tip temperature and composition (Döppenschmidt and Butt, 2000; Pittenger et al., 2001; Goertz et al., 2009).

Observation of properties

Is there a gradual change from the disorder to liquid water, as the melting temperature is approached and crossed? Spectroscopic studies give clear indications that with the onset of melting, the properties at the surface change abruptly and that the disordered interface has structural features that are very different from supercooled water (Lied et al., 1994; Wei et al., 2001). Furthermore, sum frequency generation (SFG) (Wei et al., 2001), proton channelling (Golecki and Jaccard, 1978), and glancing X-ray studies (Lied et al., 1994) show that the disordered interface is not homogeneous perpendicular to the ice–air interface. Rather its properties gradually change with depth. This suggests that simple models that parameterize the disordered interface as a thin, homogenous water-like layer are questionable and contradict AFM measurements, where a sharp border between the disordered interface and the bulk ice has been found (Döppenschmidt and Butt, 2000).

While the thickness variation in the disordered interface has been heavily studied, few observations exist with regard to how the disorder is distributed laterally on a molecular level at the ice – vapour interface. This is a very challenging task from an experimental perspective. Considering a disordered interface that is observed to be ≈ 1 nm thick (≈ 3 monolayers of water, ML), is the thickness varied across the surface with < 3 ML in some spots and >3 ML in others? Could 1 nm of disorder be a combination of ≈ 1 monolayer in equilibrium with nano-sized droplets across the surface, or is the entire surface wetted by ≈ 3 monolayers quasi-liquid water? These questions must be asked with the understanding that under ambient conditions, the lateral distribution of water molecules evolves on short time scales, making their structure difficult to probe. Sazaki et al. (2012) recently reported pioneering observations in this direction. While most surface sensitive techniques detect average thicknesses over large sample areas, they used laser confocal microscopy to monitor the ice surface close to its melting point and observed two types of disordered interfaces with different morphologies and dynamics. Liquid, including droplet movements over the surface and their collision and coalescence were observed in both cases, with a lateral resolution on the order of ≈ 1 mm. Thus, while the molecular level information is not observed in the lateral direction, these interesting results challenge the current understanding of disordered interface observations, from which a homogeneous distribution of the disordered thickness is derived. A further indication of a heterogeneous distribution of surface disorder comes from surface-sensitive studies that probe impurities on ice surfaces (Sect. 2.3.2). The work by Sazaki et al. (2012) further revealed that growing steps on the basal plane of ice crystals can be observed up to the melting point. This shows that surface disorder for a wide temperature range – except within a fraction of a degree from melting – may preserve some long-range order.

To summarize: in view of the uncertainties it is currently impossible to give an exact parameterisation of the thickness versus temperature dependence of the disordered interface on ice. This is a critical issue to work on, as parameterizing the thickness of the disordered interface is a significant difficulty in developing snow-chemistry models face (Sect. 4.3). What is evident from Fig. 5 is that the disordered interface conclusively exists below the bulk melting temperature, and one has to be extremely careful when interpreting and generalizing observations of surface disorder. There are clear indications that the disordered interface is different from a pure liquid phase and thus these observational studies do not justify the use of a catch-all term like quasi-liquid. First, the disordered interface is not homogeneous perpendicular to the surface. Secondly, some studies indicate that its structure does not continuously evolve into the structure of the liquid with increasing temperatures. Impurities induce surface disorder with its extent critically depending on the type of impurity (and temperature). Additionally, there are indications that surface disorder is thicker in vicinity of impurities.

2.3.3 Molecular simulations of surface disorder

Molecular dynamics (MD) and Monte Carlo (MC) simulations provide a useful tool to study the surface disorder of ice with resolution at the atomic level. These simulations are particularly useful for following the development of the surface disorder from initiation to its macroscopic extent, molecule by molecule. They are, however, often limited to a total "sample" thickness of below 10 nm. Only recently, efficient coarse-grained MD-simulations have allowed simulating systems with a thickness of 16 nm (Shepherd et al., 2012). Similar limitations also apply to the lateral dimensions of the sample. To overcome this issue, periodic boundary conditions are typically used and the simulations are, thus, effectively performed for an infinite, flat surface of a single crystal. Simulations of a polycrystalline ice surface involving multiple grain boundaries are yet to be undertaken. Simulations are also time limited, with standard classical MD simulations covering time scales up to several microseconds.

In spite of the prevailing spatial and temporal limitations of molecular simulations, important new results concerning the structure and dynamics of the ice–vapour interface have been obtained during the last decade since the pioneering work summarized in a review by Girardet and Toubin (2001). Critical to any simulation is how well the underlying potentials that are used to parameterize the intra- and inter-molecular interactions capture the physics of the system. Recently, much progress has been made developing and critically evaluating water models, including their ability to adequately describe the general features of water over the entirety of phase space, including fundamental quantities such as the melting point of ice (Vega et al., 2009; Vega and Abascal, 2011). While no model is perfect and universally accepted, their drawbacks are known and can be accounted for. One other approach is the use of MD simulations that do not rely on the assumption of underlying potentials (Mantz et al., 2000, 2001a,b). Such simulations have been used to study molecular-level disorder with and without impurities.

Here we review the primary findings of MD simulation efforts. To account for inter-model differences all temperatures are given relative to the individual model melting point (T_m).

Simulations of disorder on pure ice

Molecular dynamics simulations show that a disordered layer develops spontaneously at the free surface of ice at temperatures below the melting point (Bolton and Pettersson, 2000; Picaud, 2006; Vega et al., 2006; Bishop et al., 2009; Neshyba et al., 2009; Pereyra and Carignano, 2009; Pfalzgraff et al., 2011). This has been observed regardless of the water model and the crystallographic plane exposed to the vapour phase (Fig. 7). The onset temperature of disorder is found to depend on the crystal facet exposed to the vapour phase, for example on the basal plane, the first sign of interfacial disorder occurs about 100 K below the melting point, whereas on the prism plane disorder was observed around T_m-80 K (Conde et al., 2008).

The thickness of the disorder also shows systematic differences between the different crystal facets (Conde et al., 2008; Pfalzgraff et al., 2011) in agreement with experimental observations (Sect. 2.3.2). Simulations reveal that the surface disorder begins with a small fraction of water molecules leaving the outermost crystalline layer of ice and becoming mobile as adsorbed molecules on the crystal lattice (Bishop et al., 2009; Pfalzgraff et al., 2011). With increasing temperature, the number of vacancies in the outermost crystalline layer increases, giving rise to aggregates of (increasingly mobile) adsorbed molecules on top of the crystal and, at the same time, resulting in higher disorder and mobility of molecules within the outermost crystalline layer itself.

While the number of disordered molecules grows steadily with temperature, the disordered interface remains, up to about T_m-10 K, limited to the outermost molecular layer of the ice. Only at higher temperatures does the disorder propagate to additional ice layers and the thickness of the disordered interface increases to about 0.5 nm (Fig. 5). It is important to note that different water models yield practically the same thickness when compared at the same degree of undercooling relative to the model melting points (Vega et al., 2006; Paesani and Voth, 2008; Bishop et al., 2009; Neshyba et al., 2009; Muchová et al., 2011; Pfalzgraff et al., 2011). A recent large-scale, long-time simulation employing the coarse-grained "mW" model of water further corroborated this molecular picture of ice surface (Shepherd et al., 2012). Although, at T_m-1 K their simulations show larger fluctuations of the disordered interface's thickness with increases of its thickness of about 2 nm for periods of about 50 ns than do previous smaller-scale, atomistic simulations. Thus, apart from temperatures very close to T_m, molecular simulations provide a consistent and robust picture of the surface disorder, independent of a specific water model used in the simulation. In addition to the spatial and temporal limitations of current molecular simulations, obtaining reliable results at temperatures just below the melting point is further complicated by the fact that the melting point of the model ice is typically subject to an uncertainty of ±2 K. Large-scale simulations and more accurate estimates of the melting point of models will be needed to increase accuracy within this environmentally relevant temperature region.

Simulation of disorder induced by ionic impurities

MD simulations of ice growth from supercooled salt solutions have revealed that the presence of ions increases the thickness of the interfacial disorder compared to pure ice, both at the free ice surface and at the grain boundaries (Vrbka and Jungwirth, 2005; Carignano et al., 2006, 2007; Bauerecker et al., 2008). The same conclusion has been found for some small organics, we refer the reader to the recent review by McNeill et al. (2012) for an in-depth discussion on organics. Current molecular simulation studies are limited in terms of the size of the systems and, hence, the spatial scale of inhomogeneities that can be investigated. Nevertheless, the existence of a uniform disordered interfacial layer is not likely in the presence of ions. Instead, a pronounced tendency for ion clustering has been seen upon freezing salt solutions, resulting in the coexistence of thick ion-containing disordered regions and regions of pure ice with thin layers of interfacial disorder. This picture agrees with recent observations of impurity-induced disorder using surface sensitive spectroscopy (Sect. 2.3.2). So far, only a few MD studies using selected concentrations of NaCl at defined temperatures have been performed. More simulation work is needed to obtain quantitative results regarding the effects of temperature, salt concentration and ionic composition on the thickness and character of the disordered interface. Uncertainty also remains as to the distribution of various ions within the disordered layer and their propensity for either the ice-liquid or the liquid–vapour interfaces, or for the interior of the unfrozen liquid.

In summary, MD simulations are well suited to investigate the disordered interface on a molecular level. At low temperatures MD simulations show that the disordered interface is limited to the outermost crystal layers, or even to parts of the outermost layer. Only for undercoolings of less than 10 K does the thickness of the disordered interface significantly increase with temperature. There are indications that impurity induced disorder is most pronounced in the immediate vicinity of impurities leading to some heterogeneity of the surface disorder. More MD studies that deal with mobility of water and impurities in the disordered interface are discussed in Sect. 3.3.1.

2.4 Conclusions about the multi-phase structure

The structure of surface snow has since long been a focus of interest. Recently, non-destructive methods have been used to observe in-situ structural changes of snow samples with time in situ and from this the surface area, an important property, can be derived. Such XMT analyses give quantitative 3-D geometrical data, without destroying samples, and allow observations of dynamic structural changes (Sect. 2.1). Observing the liquid water and void air simultaneously in porous samples is delicate and continued developments of phase-contrast XMT are one way to tackle this issue. Although XMT provides no chemical data, complementary SEM studies can assess the chemical composition of agglomerates at particular locations within the microstructure. Such studies have shown that some impurities accumulate along grain boundaries, while others are concentrated in isolated spots. What controls the precise distribution is an area of active investigation.

It is possible to identify morphologically similar features with both XMT and SEM and to infer where the grain boundaries and chemical species are in the full 3-D structure. While a hybridization of these methods shows significant potential to contribute to the understanding of snow, to date many studies have focused on polar or glacial ice. These are motivated by trying to understand the long-term fate of impurities in ice cores that serve as climate-proxies and environmental archives. It may be possible to use knowledge of how the location of chemical species changes from firn to ice and to make "backwards" predictions about how species are transferred between snow and firn. The scale at which these techniques operate may be too coarse to identify particular chemical species and processes, however incorporating microstructure features at these length scales into current frameworks poses a significant challenge to the community.

The surface of ice is increasingly disordered at temperatures approaching the melting point, as this is an intrinsic property of all crystals. Thermodynamic considerations, observations and MD simulations of ice surfaces and interfaces clearly show this continuous increase of interfacial disorder with temperature. Less clear, however, are the onset temperature, the thickness, and the functional dependence of this disordered interface. Here, individual observations differ widely as do simulations and thermodynamic calculations based upon varying initial assumptions.

Perpendicular to the ice surface the disorder does not evolve homogeneously, however, the importance of resolving this micro-scale inhomogeneity for macroscopic modelling is debated (Baker and Dash, 1996; Knight, 1996b,a). Furthermore, the resolution of many experimental techniques that probe the ice surface, provide evidence that the disordered interface is not simply supercooled bulk water. Even at higher temperatures relevant to the snow-pack, the picture of the disordered interface having a character of a (supercooled) liquid is very simplified. Furthermore, there are indications from MD simulations and recent experimental observations that the disorder on the surface might be unevenly distributed, preferentially evolve at surface defects and in the vicinity of impurities. Observing this lateral heterogeneity experimentally is challenging, as most methods average over larger surface areas. One recent study, however, claims to have successfully observed such isolated disordered regions on ice surfaces (Sazaki et al., 2012). This strong impact of impurities on the thickness and structure of the disordered interface makes the discussion on the disorder on pure ice less relevant for environmental systems where impurities are always present.

3 Physical processes

Snow and snow surfaces physically interact with the surrounding environment in a number of important ways. From its very inception snow is continually undergoing metamorphosis, which is changing its density and surface area by mass transport. Here we briefly discuss snow metamorphism, but for more details we refer the reader to earlier comprehensive reviews (Maeno and Ebinuma, 1983; Colbeck, 1997; Blackford, 2007; Domine et al., 2008; Hobbs, 2010). Adsorption and diffusion are two processes where the disordered interface may play a special role and both are known to be important for the fate of atmospheric trace gases in the cryosphere. Freeze and melt cycles occur frequently, often diurnally, in the environment, and the fate of solutes during such cycling is of geophysical importance. Likewise, in the laboratory ice samples are most often frozen from solutions, requiring some understanding of how such samples relate to natural occurring specimens.

3.1 Snow metamorphism

Snow in the air can take many morphological forms: classic six-pointed multi-armed stellar crystals, needles, columns, plates, or fragments that form because of the action of wind induced fracturing (Fierz et al., 2009). There are strong thermodynamic driving forces that change the shape of crystals in snow-packs. In snow, morphological changes are often classified by the underlying temperature conditions, either isothermal or temperature gradient conditions. Isothermal metamorphosis leads to changes in snow form that reduce high angular aspect ratios in favour of more rounded forms, and correspondingly reduce the surface area of the system (Colbeck, 1986; Kaempfer and Schneebeli, 2007; Chen and Baker, 2010). In temperature gradient conditions, for instance when the snow-pack is warmed at its surface during the day from sun or radiatively cooled at night, morphological changes occur quickly. Because isothermal conditions are rare in the natural environment, changes of snow shape due to temperature and vapour gradients are common and respond in complicated, subtle ways to changes in temperature and humidity (Arons and Colbeck, 1995; Schneebeli and Sokratov, 2004). Temperature gradient changes can occur over a range of time scales: from fractions of seconds (Szabo and Schneebeli, 2007), to diurnally and seasonally. Field measurements have shown such alternating temperature gradients in the top 0.2 m of alpine and Arctic snow-packs (Birkeland et al., 1998; Dadic et al., 2008). Pinzer and Schneebeli (2009b,a) studied snow metamorphism under alternating temperature gradients (with 12 h periods) using XMT. They found that up to 60 % of the total ice mass was redistributed during the 12 h cycle. Such high water fluxes mean that ice sublimates and condensates with a characteristic residence time of just 2–3 days (Pinzer et al., 2012). An illustrative video of their experimental observations of the metamorphism indicates that the mass fluxes are much higher than previously thought and what happens to impurities distributed within the snow is not clear (Pinzer et al., 2012). Most laboratory investigations on adsorption, diffusion, and chemical reactivity in ice are done with stable ice phases. Thus whether the temperature gradient metamorphism impacts those processes is discussed for adsorption and diffusion processes (Sects. 3.2 and 3.3).

Morphological changes in snow and ice are altered considerably by the presence of liquid phase material in addition to solid-state processes and vapour phase transport (Meyer and Wania, 2008). In general liquid-rich snow and ice densifies considerably more than dry-sintered material. Portions of the system melt which coarsens the average particle size of the system; densification is aided by capillary forces between ice particles; and the liquid is located at particular places in the microstructure – grain boundaries (Sect. 2.2). The liquid provides another route for material transport; transport in liquids is much faster than in solids – both via diffusion and also advection. Liquid phase sintering of snow has been studied less in comparison with dry sintering; and the influence of other chemical species on liquid phase sintering in snow and ice is not well known. However liquid phase sintering is of considerable industrial importance in materials processing. There exists a significant literature in materials science on this topic – that may give useful insights for snow and ice systems.

3.2 Adsorption

Numerous studies have been conducted to elucidate the nature of the interaction between trace gases in the atmosphere and the surface of ice. These investigations give insight into the role of the solid ice surface, the disordered interface, and the importance of liquid in gas-ice interactions vis-à-vis differences in uptake behaviour by ice surfaces of different morphologies (Diehl et al., 1995; Bartels-Rausch et al., 2004; McNeill et al., 2007; Abbatt et al., 2008) and by pure versus doped ice surfaces (Chu et al., 1993, 2000b; Conklin and Bales, 1993; Journet et al., 2005; Hoog et al., 2007; Kerbrat et al., 2007; Petitjean et al., 2009). How snow metamorphism impacts the adsorption of trace gases is also discussed.

3.2.1 Uptake to solid ice surfaces

The adsorption of trace gases onto solid ice surfaces is an important uptake process under a wide range of conditions (Abbatt, 2003; Huthwelker et al., 2006). Therefore the interactions of many trace gases with ice surfaces have been parameterized based purely on surface adsorption (Crowley et al., 2010). However, describing the uptake as only a surface process, may neglect the burial of adsorbates driven by the high evaporation and condensation rates of water onto ice. How this affects the equilibrium partitioning of trace gases to ice remains an open issue (Sect. 3.2.3). Here, we first focus on results from studies at temperatures below ≈ 245 K, where the disordered interface is very thin and where its properties are most crystalline-like (Sect. 2.3.2). Adsorption studies of alcohols (ethanol to hexanol) on thin ice films at temperatures between 213 and 245 K have been conducted (Sokolov and Abbatt, 2002). The authors concluded that the uptake on ice is adequately described by surface adsorption. Furthermore, they argued that the poor correlation between gas–ice and the gas–water (i.e. Henry's Law constant) partitioning equilibrium constants (see McNeill et al., 2012, for a detailed discussion and definitions) at 228 K, indicates that the disordered interface, if present, does not fully dissolve these polar organics and therefore has no significant impact on the uptake of these species. This conclusion was verified experimentally using a combination of surface sensitive X-ray photoemission and near-edge X-ray absorption spectroscopy in a study of ice surface properties pre- and post-acetone adsorption (Starr et al., 2011). The measurements of acetone directly on the surface of ice at temperatures below 245 K, confirmed that the Langmuir model could successfully describe the adsorption. At the same time, spectra of the ice surface revealed that the disordered interface was not thicker than the probing depth of a few nm both before and during adsorption of acetone (see also Sect. 2.3.2). These results agree with findings that the uptake of a larger set of non-polar organics at 266 K are not explained by their dissolution into supercooled water (Roth et al., 2004). Roth et al. show that interfacial disorder of 10–50 nm thickness, can only (partially) explain experimentally observed uptake, and if assumed thicknesses are below 2 nm the impact of dissolution is entirely negligible.

The uptake of weak organic and inorganic acids to ice has been successfully described as Langmuir type surface adsorption in both laboratory investigations and through theoretical calculations. Examples include, formic acid and acetic acid uptake at temperatures as high as 230 K (Compoint et al., 2002; Picaud et al., 2005; Allouche and Bahr, 2006; von Hessberg et al., 2008; Symington et al., 2010) , peroxynitric acid as high as 253 K (Ulrich et al., 2012), nitrous acid < 210 K (Fenter and

Rossi, 1996; Bartels-Rausch et al., 2002; Chu et al., 2000a; Kerbrat et al., 2010b) , and H_2O_2 < 233 K (Clegg and Abbatt, 2001; Pouvesle et al., 2010). The recent experiments by Pouvesle et al. (2010) and Ulrich et al. (2012) are noteworthy. Reversible adsorption of H_2O_2 to ice was found to be much more pronounced than previously found (Pouvesle et al., 2010), which would make this surface process quite significant at environmental conditions. For HNO_4, less adsorption was found in a recent study at lower concentration than was deduced in an earlier study (Ulrich et al., 2012). The Langmuir-type adsorption holds for low concentrations of adsorbates, at higher concentrations adsorbate–adsorbate interaction might lead to a deviation from adsorption behaviour described by Langmuir. Such self-association has been discussed mainly for those chemicals that can form common hydrogen bonds such as formic acid, acetic acid, ethanol, and acetone (Abbatt et al., 2008; von Hessberg et al., 2008; Symington et al., 2010) (see also Sect. 4.2.1).

Adsorption of trace gases to solid surfaces has also been found to accurately describe uptake to polycrystalline ice at temperatures below 223 K. Bartels-Rausch et al. (2004) observed indistinguishable adsorption behaviour of acetone on different types of artificial and natural snow with varying levels of inter-grain contact area, a parameter that has been shown to vary by as much as a factor of 3 in different artificial snow types (Riche et al., 2012).

3.2.2 Uptake to the disordered interface

Pure ice

A number of laboratory experiments have been conducted with the goal of characterizing the effect of surface disorder on the uptake of acids such as HCl , HNO_3, CF_3COOH, HONO, acetic acid, formic acid, H_2O_2, and SO_2 to ice samples (Clapsaddle and Lamb, 1989; Conklin and Bales, 1993; Abbatt, 1997; Chu et al., 2000b; Clegg and Abbatt, 2001; Burkhart et al., 2002; Huthwelker et al., 2004; Ullerstam et al., 2005; McNeill et al., 2007, 2006; Kerbrat et al., 2010b; Symington et al., 2010). The drastically increased uptake of trace gases, such as HCl, HNO_3, volatile and chlorinated organics, to snow in presence of brine lead to the expectation of increased uptake to disordered interfaces, relative to pure ice surfaces (see Sect. 3.2.4). In the experiments discussed here, concentrations were generally low enough to prevent melting, i.e. the existence of brine, based on the bulk phase diagram.

Recently, direct laboratory evidence showed that HCl – ice interactions are highly dependent on the surface state of the ice substrate (McNeill et al., 2006, 2007). Surface disorder on ice exposed to HCl in the gas phase at temperatures as low as 189 K was observed using ellipsometry. Simultaneously HCl uptake profiles were monitored, confirming that the presence of a disordered interface had substantial impact on HCl uptake into the ice. The effect of ice surface disorder on the uptake of HNO_3 on ice has been inferred but not yet directly identified. A recent reanalysis of HNO_3 uptake (Ullerstam et al., 2005) used a kinetic model that included diffusion of the adsorbed species, potentially into a disordered interface, to find a theoretical fit for the measurement data (Cox et al., 2005). This result is consistent with earlier observations and interpretations made for HNO_3 (Abbatt, 1997) and HCl (Huthwelker et al., 2004). Another relatively strong acid, CF_3COOH with a pKa of 0.3 at 298 K, has shown partially reversible uptake (Symington et al., 2010). Due to its low pKa, the authors suggested that the uptake behaviour of CF_3COOH might be comparable to that of strong acids like HCl. Thus they compared their uptake results to the HCl studies conducted by McNeill et al. (2006, 2007) and inferred that CF_3COOH induces surface disorder into which the acid diffuses and where it forms hydrates at temperatures of 200–230 K. Evidence also exists that the influence of surface disorder on uptake is not limited to highly acidic trace gases. Clegg and Abbatt (2001) studied the uptake of SO_2, a weak acid, onto smooth ice films in a coated-wall flow tube from 213–238 K and found a dissociative profile that was enhanced at higher temperatures. The authors suggested that this behaviour might be due to the presence of a disordered interface that facilitates SO_2 to H^+ dissociation and HSO_3^- ions via the formation of hydrates on ice. Interestingly, a number of SO_2 uptake studies on ice spheres showed that the uptake was enhanced at higher temperatures close to the ice melting point, in contrast to the expectations of a classical adsorption process, indicating the presence of the disordered interface (Sommerfeld and Lamb, 1986; Clapsaddle and Lamb, 1989). In the latter study, the observed uptake kinetics was diffusion-like for the course of hours to days, and hence inconsistent with a simple Langmuir type uptake process on the ice surface itself. Moreover, the temperature dependence of the long-lasting uptake kinetics, is consistent with the diffusion into the veins of the highly polycrystalline ice bed (Huthwelker et al., 2006), using the concept and thermodynamic equations as suggested by Nye (1991) and Mader (1992).

In contrast, early experiments on the uptake of H_2O_2 to artificial snow showed increased uptake with decreasing temperature from 270 K to 243 K, inline with adsorption dominating the uptake (Conklin et al., 1993). Further analysis showed that even at temperatures close to the melting point – where the disordered interface is thick and potentially has liquid-like properties – only 20 % of the uptake may be based on dissolution. Due to the long experimental times, the uptake exceeds multi-layer coverage of H_2O_2 on ice in some experiments, which might explain the bulk dissolution observed. Uptake experiments of benzene and acetone performed at temperatures ranging from 214 to 266 K on polycrystalline ice films and artificial snow showed higher saturated surface coverage with increasing temperatures (below temperatures at which full dissolution/multilayer formation occurs), which suggests that the disorder might be enhancing uptake at higher temperatures (Abbatt et al., 2008). In contrast, volatile organic formaldehyde was not observed to undergo increased partitioning to ice at 268 K compared to 258 K or 238 K, even though the thickness of the disordered interface can be expected to increase over this temperature range (Burkhart et al., 2002). This suggests that dissolution into the disordered interface plays only a minor role in formaldehyde partitioning to ice. However, the formaldehyde – water phase diagram and the potential dissolution of formaldehyde into ice was not discussed in that study. The presence of high concentrations of adsorbates has been found to lead to cluster formation, as observed at colder temperatures on ice surfaces. Cluster formation of aromatics on the surface of the disordered interface may impact the absorption spectra and the photochemical reactivity of the adsorbate (Kahan and Donaldson, 2007, 2008, 2010; Kahan et al., 2010a).

Co-adsorption

The presence of some impurities enhances or even induces the formation of the disordered interface (Sects. 2.3.2 and 2.3.3). Here we discuss studies that investigated how impurity-induced changes ice surface properties subsequently modify uptake processes, when multiple trace gases are introduced simultaneously to an ice sample. For example, co-adsorption studies of HCl and CH_3COOH showed a twofold increase in acetic acid uptake when the partial pressure of HCl was increased from 7×10^{-7} Torr (non-disordering) to 2×10^{-6} Torr (disorder-inducing) at 212 K and constant acetic acid partial pressure, 4.2×10^{-6} Torr (McNeill et al., 2006). This was the first study showing that inducing disorder by solutal dosing impacts the trace gas uptake at low temperatures, where disorder without solutes is minimal and its impact on the uptake process is negligible. The fact that the increased uptake induced by co-adsorption critically depends on the experimental conditions might also explain why in other studies the presence of HCl did not significantly change the uptake behaviour of butanol (Sokolov and Abbatt, 2002). Enhancement of acetone uptake at temperatures less than 245 K in the presence of CF_3COOH was observed in co-adsorption studies of CF_3COOH and acetone that also provided additional indirect evidence for the formation of a disordered interface (Symington et al., 2010).

The co-adsorption of two weak acids was recently investigated by Kerbrat et al. (2010) at temperatures up to 243 K. The influence of acetic acid on the uptake of HONO in a packed bed flow tube experiment could be well reproduced by Langmuir's competitive adsorption model. Acidity and surface disorder did not seem to play a role. This interpretation supports results from earlier work on the co-adsorption of formic and acetic acid (von Hessberg et al., 2008) and butanol and acetic acid (Sokolov and Abbatt, 2002). The role of surface disorder also seems less important in the uptake process when two strong acids co-adsorb. For HCl and HNO_3 a competition has been observed, so that for both acids the surface coverage is lowered. HNO_3 seems to bind more strongly than HCl to the ice, allowing HCl to be displaced by HNO_3 (Hynes et al., 2002; Sokolov and Abbatt, 2002; Cox et al., 2005).

3.2.3 Uptake to growing ice

We have so far treated the ice surface as a static interface to which trace gases adsorb and establish a reversible adsorption equilibrium. However, the natural temperature gradients in snow lead to significant water vapour fluxes, resulting in an ever growing or sublimating interface (Sect. 3.1). Even in equilibrium many thousands of monolayers of water exchange per second at the surface (Huthwelker et al., 2006). How adsorbed species respond to these water fluxes and in particular to growing ice conditions, depends on their residence time on the surface. If the residence time is long compared to the arrival time separation of water molecules bombarding the surface growing ice may bury adsorbed molecules (Conklin et al., 1993; Domine and Thibert, 1996; Karcher and Basko, 2004). The surface residence time may be linked to the adsorption enthalpy (Huthwelker et al., 2006; Bartels-Rausch et al., 2005). Thus, available parameterisations of trace gas adsorption obtained from experiments under equilibrium conditions may not adequately describe partitioning to snow under temperature gradient conditions for species with more negative adsorption enthalpies than water on ice. A few studies have addressed this issue for HCl (Domine and Rauzy, 2004), for HNO_3 (Ullerstam and Abbatt, 2005) and for aromatic hydrocarbons (Fries et al., 2007). In general, the results show increased uptake of trace gases in growing ice, when compared to adsorption at equilibrium conditions. However, the interpretation of these experiments has remained difficult because ice growth rates were poorly defined or could not be varied over sufficiently large ranges.

3.2.4 Uptake to brine

The interaction of trace gases with ice and snow changes drastically when the ice begins to melt and a liquid fraction is available. This has significant environmental consequences. Herbert et al. (2006b) investigated the diffusion of some chlorinated organics through a snow-pack at temperatures very close to 273 K. In their field study they found that the surface adsorption constant generally over-predicts the adsorption of these chemicals to the wet snow surface and suggested that the use of the gas–liquid partitioning constant, Henry's constant (Sander, 1999), might be better suited to describe air–snow partitioning.

A drastic change in the adsorption properties once a liquid phase is present has also been seen in well-defined laboratory experiments (Abbatt, 1997; Journet et al., 2005; Kerbrat et al., 2007; Petitjean et al., 2009). In these studies the uptake of volatile organics or HNO_3 on pure ice surfaces and on super-cooled solutions doped with HNO_3 at temperature below 243 K was investigated. The findings indicated that uptake to the solutions is increased enormously relative to the pure ice surface. Other early studies of SO_2 uptake to ice doped with NaCl also found that the observed partitioning can be well described by dissolution into a liquid phase if its volume is estimated using melting point depression (Conklin and Bales, 1993). Similarly, Tasaki and Okada (2009) examined the retention of water-soluble organics in a chromatographic column packed with ice spheres. The ice was doped with NaCl and it was found that the retention largely increased with the formation of liquid brine. At low temperatures, in the absence of brine, adsorption to the surface was the dominant retention mechanism, while at higher temperatures partitioning to the liquid phase became more important.

In summary, there are clearly two regimes of trace gas–ice interaction: at temperatures below approximately 245 K and low trace gas concentration, adsorption and co-adsorption to solid surfaces, i.e. the Langmuir model, describe the uptake to ice surface very well (Crowley et al., 2010). At these temperatures, the presence of grain boundaries does not seem to impact the adsorption of volatile organics (Bartels-Rausch et al., 2004). Noteworthy, due to their atmospheric importance, are two recent remeasurements of the adsorption of H_2O_2 and of HNO_4 to ice (Pouvesle et al., 2010; Ulrich et al., 2012). These new data suggest that the uptake of H_2O_2 to the ice surface is much more significant than previously thought, and might thus be an important process determining the fate of H_2O_2 in the snow-covered environment. HNO_4 on the other hand was found to adsorb much less than previously thought making the surface snow a less important sink of atmospheric HNO_4. This Langmuir-type parameterisation of trace gas adsorption might not be adequate when water condenses to the ice surface under non-equilibrium conditions for those species with a more negative adsorption enthalpy than water on ice. Parameterizing the uptake to growing ice needs future attention. With the formation of brine, due to melting at high temperature or solute concentrations, the uptake of all water-soluble atmospheric trace gases changes significantly. Although the brine can be highly concentrated, Henry's law constants determined using diluted solutions are widely used to describe the equilibrium between the gas phase and the liquid phase present in the snow. While this assumption seems to be supported by current field and laboratory work, it should be verified that the same parameterizations can be used for snow and for diluted solutions. Moreover, interactions between solutes in brine and between solutes and dissolved gases have possible feedback effects on the formation and extent of brine and need to be studied in more detail.

Despite the tremendous amount of research on gas-ice interactions, adsorption in the (intermediate) temperature and solute regime where significant surface disorder is present is still an inadequately understood topic. Many investigators have studied trace gas-ice interactions and invoked quite different interpretations of the uptake process. Interpretations included uptake into a disordered surface layer, a liquid interface, or a confined reservoir such as grain boundaries. Very few studies, however, have direct experimental evidence of surface disordering indicative of interfacial layer presence or its formation under the conditions of the uptake experiments (McNeill et al., 2007; Starr et al., 2011). Integration of ice surface observations with the results of uptake studies under the same conditions can be extremely helpful in accurately interpreting experimental results. Surface-sensitive spectroscopy is an interesting technique in this respect as it allows deriving chemical and structural information of both the ice surface and the adsorbed species in-situ (Sect. 2.3.2). The understanding of the role of surface disorder on the uptake of trace gases continues to be refined. However, it is clear that uptake by ice has been significantly enhanced when optical methods have detected enhanced surface disorder, possibly because chemical reactions – such as hydrate formation – are fostered. Strong acids seem to respond more sensitively to the surface structure than other soluble species. Because adsorption of trace gases can induce ice surface disorder, simultaneous adsorption of different trace gases has been found to lead to a higher uptake in some studies. In other studies, other effects such as acid–base equilibria or competition for adsorption sites may overrule any effects of surface disorder.

3.3 Migration

Migration of trace gases and impurities in snow and ice has important environmental implications (Dash et al., 1995, 2006). Shifts of specific ions and gases in the chronology of ice-core records, widening of concentration peaks of certain tracers in ice cores, impacts on the snow – atmosphere exchange of trace gases, and long-term losses observed in laboratory experiments on the uptake of trace gases to ice have been explained by migration processes. In this chapter we will start by giving an overview on the mobility of water in ice, which gives important information on the micro-properties of ice and its surface. Next, we will elaborate on laboratory experiments that focused on determining the kinetics or thermodynamics of migration processes of solutes in ice. Finally, we will focus on field observations on migration in snow that illustrate the different processes involved and their complexity.

The transport of volatile species through the porous snow-pack is of high importance for the release of trace gases from the surface snow to the atmosphere. In absence of wind-pumping this transport is driven by gas-phase diffusion (Domine et al., 2008). The effective diffusion through porous materials such as a snow-pack can be well described taking into account geometric properties and total gas volume (Schwarzenbach et al., 2003). Uncertainty comes from deriving the geometric properties of the snow-pack. Recent work has further shown, that for adsorbing species the interaction with the snow surface can significantly reduce the diffusivity through the snow-pack leading to longer residence times of the diffusive species in the snow-pack (Herbert et al., 2006b; Seok et al., 2009; Pinzer et al., 2010). This aspect of transport through snow is not further considered here, but we refer to the reviews by Domine et al. (2008) and McNeill et al. (2012).

3.3.1 Diffusion of water in ice

The mobility of water molecules and protons in bulk ice has been studied intensely for more than 50 yr (Petrenko and Whitworth, 1999). Defects play a central role, most prominently vacancies and interstitials as well as orientational and ionic defects (Fig. 6). Molecular mobility of water molecules is important for the uptake of foreign molecular species in bulk ice or in the more disordered surface layers of ice, with the notable exception of very small species like H_2 and He which can diffuse within the perfect ice Ih lattice (Strauss et al., 1994; Satoh et al., 1996; Ikeda-Fukazawa and Kawamura, 2004). Thus it is worthwhile to look at the water molecules' mobilities, both for translational and rotational degrees of freedom.

Experimental work on diffusion of water in ice

To summarize the large body of work in bulk ice the following may be stated: at high temperatures the long-range transport of protons is of interstitial nature and is achieved by the transport of intact water molecules via intrinsic defects that are created by thermal activation (Geil et al., 2005). This jump migration is at the origin of the dominant relaxation process at temperatures above 230–240 K as seen in dielectric spectroscopy

(Kawada, 1978) or deuteron spin alignment measurements (Geil et al., 2005). The water molecules' diffusion coefficients, summarized in Petrenko and Whitworth (1999), decrease from ≈ 2 to $0.22 \times 10^{-15}\,\mathrm{m^2\,s^{-1}}$ between 263 K and 233 K, in good agreement with tracer diffusion work (Blicks et al., 1966; Delibaltas et al., 1966; Ramseier, 1967) and direct observations by synchrotron X-ray topography (Ramseier, 1967). Also molecular dynamic studies support an interstitial mechanism for water self-diffusion (Goto et al., 1986). At lower temperatures of ≈ 150 K spin-alignment relaxations are dominated by a so-called fast process, which is related to extrinsic defects which are promoting re-orientational jumps of water molecules by passing Bjerrum defects (Goto et al., 1986; Geil et al., 2005). Thus the fast process does not lead to a long-range transport of water molecules. Dielectric Bjerrum defects are created by impurities and may be injected into the bulk from the disordered ice surface (Devlin and Buch, 2007) where they are more abundant, in particular at high temperatures (Dosch et al., 1996). Whether water molecules migrate in the bulk below 220 K preferentially via a vacancy mechanism as suggested by Livingston and George (2002) remains an open question. Very little indeed is known about vacancies in hexagonal ice (Petrenko and Whitworth, 1999).

Much less is known about the corresponding water or (connected) proton mobilities on the ice surface, along grain boundaries and other imperfections of the ice lattice. Nuclear magnetic resonance work was done on ice surfaces from which diffusivities were deduced (Mizuno and Hanafusa, 1987). The water molecule self-diffusion coefficient was established for the temperature range from 253 K to the melting point and amounts to $2.2 \times 10^{-13}\,\mathrm{m^2\,s^{-1}}$ at 263 K, i.e. about two orders of magnitude faster than in single crystalline bulk ice and clearly slower than in super-cooled liquid water with a value of $\approx 7 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ (Gillen et al., 1972; Price et al., 1999). Water mobilities in the surface layer of ice situated between those of bulk ice and super-cooled water thus justify the name quasi-liquid-layer (QLL). One should, however, note that in the experiment of Mizuno and Hanafusa (1987) some sintering of the particles may have occurred so that the diffusivities do not represent true surface values. Using the technique of groove formation time (Mullins, 1957) in polycrystalline ice to deduce surface diffusivities values of $3.5 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ and $3 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ at 271 K and 263 K, respectively, were obtained (Nasello et al., 2007); these numbers are quite close to the values of supercooled water, casting further doubts on the surface nature of the results of Mizuno and Hanafusa (1987). For experimental studies of surface diffusivities at temperatures well below 200 K other techniques have been developed and were reviewed more recently (Park et al., 2010). There is evidence that a translational surface mobility in the outer ice layers is preserved down to temperatures of 130 K (Verdaguer et al., 2006; Lee et al., 2007); water molecules in adlayers may even be mobile down to 100 K (Jung et al., 2004).

Interestingly, the water mobility across grain boundaries is two orders of magnitude smaller than the mobility at the ice surface (Nasello et al., 2005) approaching the values of Mizuno and Hanafusa (1987) discussed above; thus it seems that the water molecules' mobilities at the surface and in grain boundaries are quite different, while the latter are still enhanced by more than 3 orders of magnitude over the bulk values (Mullins, 1957; Nasello et al., 2005). The intermediate diffusivity in grain boundaries between that of crystalline ice and water was later confirmed by Lu et al. (2009).

Molecular Dynamics simulations of diffusion of water in ice

Molecular dynamics simulations can be used to evaluate diffusivities for surface molecules in the disordered interface of ice. At a temperature of T_m-9 K the diffusivity of $\approx 8 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ was obtained with some anisotropy imposed by the underlying water structure (see below). By 59 K below melting this value drops to $1.8 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ (Gladich et al., 2011). These surface diffusion coefficients agree with available experimental data by Nasello et al. (2007) to within quoted precision for the entire temperature range, corroborating thus the experimental finding that the coefficient of self-diffusion on ice is similar to that of supercooled liquid. All these values are orders of magnitude larger than what was established by NMR work on thick water layers on ice (Mizuno and Hanafusa, 1987) which illustrates one of the pertinent problems in work on the disordered interface: the results depend very much on the method used. It is noteworthy that molecular dynamics work supports clear differences in mobility between the outermost and the inner water layers (Bolton and Petterson, 2000; Toubin et al., 2001). Such layer-to-layer differences were already established in the work by Nada and Furukawa (1997) and are, in fact, an ubiquitous feature of ice surfaces over a large range of temperatures (Grecea et al., 2004; Park et al., 2010). Consequently, techniques sensitive to the outermost surface layers will always get higher water mobilities than methods looking at the bulk of the disordered surface layer or at grain boundaries; the differences may well span orders of magnitude.

Further analysis of the MD studies helped to identify diffusion mechanisms on the ice surface and indicated distinct differences of diffusion in super-cooled liquid and in the disordered interface. In an MD study of water self-diffusion on ice surface between 180 and 210 K, Bolton and Petterson (2000) proposed a diffusion mechanism in which molecules in the outermost layers of ice surface move horizontally by repeatedly breaking and forming hydrogen bonds. Subsequent MD investigation by Bishop et al. (2009) showed that the outermost, most weakly-bound water molecules on the vapour exposed basal surface exhibit “extraordinary diffusivity”, being an order of magnitude faster than other surface molecules. Further MD work by Pfalzgraff et al. (2010, 2011); Gladich et al. (2011) confirmed the enhanced mobility of water molecules on free ice surfaces in the temperature range from 230 K to the melting point and provided more details regarding the diffusion mechanism at different temperatures. An Arrhenius analysis of MD-simulated self-diffusion coefficient on ice yielded a positive Arrhenius curvature, implying a change in the mechanism of self-diffusion with an increase in energy of activation from low to high temperature. Since supercooled water is known to exhibit the opposite Arrhenius curvature, i.e. the energy of activation is a decreasing function of temperature, it implies that self-diffusion on the ice surface occurs by significantly different mechanisms compared to bulk self-diffusion in supercooled water. In addition, self-diffusion on ice surface was found to be orientationally dependent at low temperatures, when the disordered layer is thin and the mobile water molecules are strongly influenced by the directional anisotropy of the underlying crystalline terrain. A rather sharp transition to isotropic diffusivity is observed in the temperature range of 240–250 K; self-diffusion at higher temperatures, which occurs within an increasingly thick disordered layer, is instead governed by quasi-3-dimensional liquid-like mechanisms that are isotropic regardless of the geometry of the underlying crystalline ice matrix. In such thick liquid-like layer the ions display free diffusion while in a thin layer the ions are strongly affected by the underlying crystalline ice and move by an ice surface hopping mechanism (Carignano et al., 2007). For the ions to diffuse freely following a Brownian pattern, the interfacial liquid layer has to be at least three full molecular layers thick.

3.3.2 Migration processes of impurities in laboratory studies

Recent laboratory experiments give indications for the occurrence of diffusive processes during the uptake of acidic trace gases to ice surfaces. A long-lasting uptake of highly acidic trace gases to ice surfaces has been observed in some studies (Abbatt, 2003; Huthwelker et al., 2006; Bartels-Rausch et al., 2012). This long-lasting tail of the uptake can be fitted by diffusion equations (Abbatt, 2003; Huthwelker et al., 2006) that might indicate that diffusive processes cause this behaviour. Recently, such long lasting uptake has also been observed for HONO, a weak inorganic acid. Kerbrat et al. (2010b) studied the interactions of HONO with polycrystalline ice in a packed ice bed flow tube at temperatures between 213 and 253 K. Those packed beds have a large volume to surface ratio and are thus more sensitive to bulk processes. Generally, experimental times during those laboratory experiments are short, seldom exceeding hours. Thus, one might expect an even higher importance of diffusive uptake, compared to adsorption, in the field (Kerbrat et al., 2010b). Further, a recent reanalysis of data on the uptake of HNO_3 (Ullerstam et al., 2005) to ice at conditions without evident long-lasting uptake, revealed that diffusion may also significantly contribute to the overall uptake. For this, Cox et al. (2005) were able to obtain best fits to the data with a kinetic model only when diffusion of the adsorbed species was included. We would like to note, however, that no such long-time uptake has been observed for other species such as acetic acid, even in packed bed flow tubes (Kerbrat et al., 2010a). Even more importantly, the locations (bulk solid ice, grain boundaries, etc.) where the species diffuse during the laboratory experiments is unknown, and surface restructuring has also been proposed to explain long-lasting uptake (Huthwelker et al., 2006).

Diffusion of impurities to the solid bulk

Diffusion and solubility of atmospheric trace species in ice are highly important for both atmospheric processes and ice core analyses (Domine et al., 1995). Still, reliable data are scarce, because diffusion and solubility are extremely difficult to measure due to numerous experimental artefacts that can arise. Moreover it is a challenge to isolate and quantitatively measure individual process, such as surface adsorption, diffusion into grain boundaries or the bulk ice crystal lattice. Huthwelker et al. (2006) presented a detailed discussion of such pit-falls and carefully re-analysed existing data thereby more reliably the measurements. Doing so, the scatter of for example HCl diffusion measurements can be reduced from 10 to 2 orders of magnitude (Huthwelker et al., 2006). Thibert and Domine (1997) exposed ice single crystals to a well-controlled atmosphere of diluted trace gases. After exposure for periods of days to weeks, the diffusion profile of the trace gas was obtained by serial sectioning of the ice crystals and subsequent chemical analysis. From these profiles, taken at different temperatures, the thermodynamic solubility in ice and diffusion coefficients could be derived. While this method is limited to species with sufficient solubility in ice they are applicable to species of atmospheric relevance. This method provides diffusion constants at 253 K for HCl, HNO_3, HCHO (Thibert and Domine, 1997, 1998; Barret et al., 2011b) of $\approx 3 \times 10^{-16}$, 7×10^{-15}, and 6×10^{-16} $m^2 s^{-1}$, respectively. These measurements are technically demanding as discussed in the original work and from a broader perspective in Huthwelker et al. (2006). In earlier studies, measurements of water soluble species in ice have been attempted by freezing a liquid solution and measuring the ice–water partitioning (De Micheli and Iribarne, 1963; Gross et al., 1977). These studies showed that the incorporation of trace elements are strongly affected by dynamic processes at the ice–water interface making the determination of the actual thermodynamic partitioning almost impossible (Sect. 3.1).

Ballenegger et al. (2006) estimated the diffusion coefficient of HCHO in ice using molecular dynamics calculations. They obtained a value of $4 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$ at 260 K, orders of magnitude larger than the values derived from measurements. Here, artefacts, such as short circuits or grain boundaries enhance diffusion, causing the experimentally observed diffusion to be faster than the diffusion in a perfect crystal lattice. The overestimation of the modelled diffusion constants might be due to limitations of the model. Such limitations may include an imperfect representation of the ice structure for diffusion processes, and molecular structures that are too rigid to predict sites where HCHO would, in fact, be stabilized and reside longer than computed. Also, hydration of HCHO may take place in bulk ice, which would intuitively slow down diffusion because of increased molecular size. This process was not taken into account in the MD model. One may speculate that due to the finite size typically used in molecular dynamics studies, the model might still not simulate a thermodynamically stable ice lattice, but rather ice in a confided reservoir, where the diffusion is expected to be enhanced, compared to the one in a perfect crystal lattice.

Infrared laser resonant desorption have also been used to study diffusion of HCl in ice (Livingston et al., 2000). The beauty of the technique is that laser ablation resolves sub- µm ice thicknesses, compared to ≈ 20 µm for serial sectioning of macroscopic crystals mechanically. Hence, experiments on shorter timescales seem possible. In the experiments presented by Livingston et al. (2000) HCl dopant concentrations were high enough to form hydrates in the ice, and hence cannot be directly applied to the diffusion of diluted trace gases in the thermodynamic stability domain of ice. This was corroborated by the work of Domine et al. (2001), who used infrared spectroscopy to show that the high concentrations used, considerably perturb the ice structure, rendering it almost amorphous, so that the diffusion coefficients measured are not those of crystalline ice. Indeed, Livingston et al. (2000) report $D_{\mathrm{HCl}} = 5 \times 10^{-14}\,\mathrm{m^2\,s^{-1}}$ at 170 K, an unrealistically high value, compared to values in the range 10^{-16} to $10^{-15}\,\mathrm{m^2\,s^{-1}}$ in the range 238–265 K found by Thibert and Domine (1997). The profiling techniques discussed above are destructive, rendering direct in situ observation of the diffusion process difficult. Here, accelerator based techniques, such as Rutherford backscattering (RBS) or X-ray photon spectroscopy (XPS) might become viable tools. In an RBS experiment, He^{2+} ions are shot into ice and the energy spectrum of the backscattered ions is a direct measure of the depth profile of the impurities in ice. It has been demonstrated that this technique can be used to follow the diffusion of HBr into ice in situ (Huthwelker et al., 2002; Krieger et al., 2002) at HBr vapour pressures in the stability domain of ice. While RBS has a depth resolution of some 100 nm, XPS is well suited for mechanistic studies with a spatial resolution of a few nm.

Diffusion into grain boundaries

Diffusion measurements of trace elements in grain boundaries are virtually non-existent, because it is already very difficult to prove the existence of impurities in these reservoirs. Grain boundaries and other defects in the ice such as dislocations and small-angle boundaries, which are formed by a 2-D network of regrouped dislocations, can act as diffusion short-circuits (Domine et al., 1994; Thibert and Domine, 1997; Barret et al., 2011a). Similarly, the triple junctions are candidates for such diffusion short cuts. One way to asses the impact of grain boundaries on the diffusion through ice is to perform the same experiment using different types of ice. Indeed, there is evidence that polycrystallinity enhances diffusion. For example, Aguzzi et al. (2003) found HCl and HBr to diffuse an order of magnitude faster in polycrystalline ice compared to single crystal ice at 200 K. In contrast, Satoh et al. (1996) measured the diffusion coefficients of He and of Ne by exposing single and polycrystals of ice to the gas of interest and monitoring pressure changes. They found that those gases did not diffuse faster in polycrystalline ice compared to single crystals. Based on its mobility in ice cores, Roberts et al. (2009) evaluated that the diffusion coefficient of methane sulfonic acid in ice was $4.1 \times 10^{-13}\,m^2\,s^{-1}$, orders of magnitude higher than the single-crystal diffusion coefficients that have been measured for HCl, HNO_3, and HCHO, as described above. Such a high value is unlikely for a large molecule, and a more reasonable interpretation is that mobility takes place in grain boundaries or at triple junctions (so called veins). However, the possible presence of brines in veins makes the interpretation of these data in terms of process and medium delicate. This may suggest that the density of grain boundaries must be considered to interpret the results. Domine et al. (1994) asserted that to differentiate diffusion in defects and in bulk ice, an optimal relationship between diffusion coefficient and experimental time must be found. A low polycrystallinity combined with the appropriate duration choice could minimize the net effect of grain boundary diffusion, but that would not necessarily mean that grain boundary would not enhance the net diffusion.

3.3.3 Observation of migration in the field

Peak widening and shifts of peaks in ice cores have been observed for soluble inorganic and organic species (De Angelis and Legrand, 1994; Pasteur and Mulvaney, 2000). De Angelis and Legrand (1994) studied the volcanic signal in Greenland ice cores, and in particular the SO_4^{2-}, F^- and Cl^- signals. They noted that in some layers ascribed to volcanic eruptions, the 3 signals coincided well while in others the F^- peak was shifted relative to the other two. Shifting did not occur when an (alkaline) ash layer fixing the F^- was present. In the absence of ash, F^- was excluded from the volcanic acidic layer. The author proposed that migration took place in the upper part of the firn, by diffusion of HF in the gas phase. Solid-state diffusion of HF is also proposed to account for peak widening over the years. By comparing peak width at 1210 m depth (age 7400 yr) to those of recent eruptions, the authors proposed a diffusion coefficient for HF of $1.9 \times 10^{-12}\,m^2\,s^{-1}$ in ice. This value compares well with the coefficient of HF measured in laboratory ice, $5 \times 10^{-12}\,m^2\,s^{-1}$ (Kopp et al., 1965).

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Interactive Discussion

Pasteur and Mulvaney (2000) observed the migration of methanesulfonate (MSA), a product of the atmospheric oxidation of dimethylsulfide, in firn and ice cores. MSA deposition occurs in summer but at some sites migration to the winter layer is observed after a site-dependent number of years. An interesting observation is that the migration leads to very good coincidence with the dominant Na^+ ions, that deposit mostly in winter. The authors analysed several hypotheses and their favoured mechanism is "the migration of MSA in the snow-pack via an initial diffusion in either the vapour or liquid phase which is halted by precipitation in the winter layer when the MSA forms an insoluble salt with a cation." However, it is not clear why the summer sulfate peak does not migrate with the same mechanism. For sulfate Traversi et al. (2009) postulated that the mobility depends on the presence of other ions forming soluble, and thus very mobile, salts. Rempel et al. (2002) elaborated on that explanation. They suggested that most water-soluble species found in ice cores were, in fact, concentrated in triple junctions (veins) and quadruple points (nodes) between ice crystals, where they formed a concentrated liquid solution (Sect. 2.2). At the specific conditions of this study, there are more impurities in the winter layers, so that liquid in veins and nodes is more abundant. MSA is less concentrated in the winter layers and therefore migrates there through the liquid veins, simply by virtue of the concentration gradient. Since there is more liquid in the winter layers and MSA concentrations are determined from bulk ice samples, eventually more MSA ends up in the winter layers and the MSA peaks essentially superpose with the dominant Na^+ signal. This elegant hypothesis explains the MSA observations, although for the moment, it has not been applied to the SO_4^{2-} signal for further testing. Diffusion here therefore does not take place in crystalline ice, but in liquids. We propose here that HF diffusion observed by De Angelis and Legrand (1994)is indeed in the solid phase because HF solubility in ice is sufficient to accommodate all the HF found in ice cores, while the solubility of large molecules in crystalline ice is extremely low so that MSA is rejected to veins and nodes, as observed also for SO_4^{2-} (Mulvaney et al., 1988). This strongly suggests that the estimation of the diffusion coefficient of MSA in solid ice by Roberts et al. (2009), $D_{MSA} = 4.1 \times 10^{-13}\ m^2\ s^{-1}$, is in fact diffusion in veins and not in ice crystals. Indeed, this value is orders of magnitude higher than the single-crystal diffusion coefficients measured for HCl, HNO_3, and HCHO (Thibert and Domine, 1997, 1998; Barret et al., 2011b) and even higher than the self-diffusion coefficient of water in ice (Sect. 3.3.1), which is extremely unlikely for such a large molecule.

On shorter time scales the exchange of H_2O_2 and of HCHO between the ice and the overlaying atmosphere has been described based on the formation of ice solid solution and of diffusion in ice. The accumulation of H_2O_2 was successfully modelled for long time scales of up to one year at several locations and is discussed in Sect. 3.5. Here, we emphasise a recent study on the HCHO exchange between the atmosphere and surface snow in the Arctic (Barret et al., 2011a). Those authors measured simultaneously HCHO in the snow and the atmosphere and were able to reproduce the variations in HCHO snow concentrations using the thermodynamics of the ice – HCHO solid solution and by modelling diffusion in and out of snow crystals. To our knowledge, this is the only study using a value of the diffusion coefficient of HCHO that has been independently measured in well controlled laboratory experiments by Barret et al. (2011b): $D_{\text{HCHO}} = 6 \times 10^{-16}\,\text{m}^2\,\text{s}^{-1}$. In that study, the authors showed that solid-state diffusion resulted in a four-fold increase in snow HCHO over a 48 h period. We refer to the review by McNeill et al. (2012) for a detailed discussion on this topic. More details on the modelling aspect of this study and earlier simulations of H_2O_2 and HCHO in surface snow (McConnell et al., 1998; Hutterli et al., 2003) are discussed in Sect. 3.5.

The above shows that solid-state diffusion can be important for understanding the composition of environmental ice and snow and its evolution: it can explain observed migration of species in ice cores and also the partitioning of highly soluble species between snow and the atmosphere. The above examples also illustrate the complexity of migration in natural snow and ice, where diffusion into the solid ice crystal or liquid diffusion in grain boundaries can dominate. Further, the large impact of the presence of other impurities is suggested. The precise role of liquid and solid diffusion and of grain boundaries and other defects in the ice-crystal on either process are usually not directly accessible from field studies taken the complexity of the involved systems.

The possible formation of ice solid solutions by small molecules such as CH_3OH and HCOOH deserves investigations. The study of Fries et al. (2007) suggest that small concentrations of large molecules may be incorporated within the ice crystalline lattice, but this may be out-of-equilibrium processes that, for practical purposes, can be considered metastable, given the expected long diffusion times. These out-of-equilibrium processes are poorly understood today.

In summary, observations of the mobility of water on ice reveal that the ice surface has unique properties. Water molecules remain mobile on the surface down to 130 K. At temperatures close to the melting point, where the disordered interface is thick, the self-diffusion of water is essentially the same as that of supercooled water. Molecular dynamics simulations support this conclusion and show a profound orientational dependence of the ice surface. Outer surface layers diffuse much more rapid than inner layers, which makes the ice surface very different from a bulk liquid. Even in thick films covering the surface, diffusion in the layers close to the surface is highly influenced by interactions with the surface molecules. Moreover, an analysis of the activation energy of the diffusion reveals the opposite temperature dependency as has been found in liquid water, and diffusion of ions on thin disordered layers is strongly influenced by the underlying crystal. All of this indicates that the diffusion mechanism is very different in the disordered interface from diffusion in supercooled water. Describing the diffusion of water in the disordered interface as liquid-like might however be a reasonable simplification, MD simulations show a sharp transition of the diffusion mechanism above 240–250 K where the diffusion constant in the upper layer of the disordered interface approaches that of supercooled water at high temperatures.

Deducing the role of diffusion in snow and characterising it in laboratory experiments with ice remains a difficult and essential issue for most species. The main obstacle is that solutes can diffuse in different media: the bulk ice, along grain boundaries, on the surface of ice, and in liquid present in the snow. Laboratory experiments and MD simulations clearly show that these diffusivities differ by orders of magnitude. Direct observation of the diffusion process and of the reservoir into which diffusion occurs are missing and the diffusion routes dominating for individual species or conditions are currently unknown.

Diffusion is important for explaining snow–atmosphere exchange of soluble species, the long-term fate of impurities in ice cores, and also for interpreting laboratory measurements. Field studies and laboratory experiments indicate that diffusion into ice might dominate the air–ice exchange of formaldehyde and HF; MSA diffusion might favourably occur in liquids kept in grain boundaries. Given their high solubility in single crystalline ice, further species that might diffuse significantly into single crystals in the environment are HCl and HNO_3. NH_3 is a particular case with an extremely rapid diffusion in bulk ice even at low temperatures with values 3×10^8 times larger than the self-diffusion of water molecules at 140 K (Livingston and George, 2002). This makes NH_3 a further candidate for uptake into the ice matrix at polar conditions, even though measurements at relevant temperatures are missing.

3.4 Freezing

The presence of liquid significantly changes the characteristics of adsorption (Sect. 3.2), migration (Sect. 3.3), metamorphism (Sect. 3.1), and chemical reactivity (Sect. 4.1). Here, we discuss how well the co-existence of water and ice can be predicted. Further, the distribution of solutes between the forming ice phase and the remaining liquid and where the liquid is situated, i.e. at the air–ice interface, in grain boundaries, or in micro-pockets, is discussed. Freeze – thaw cycles occur frequently in the natural snow-pack, even in the Arctic (Meyer and Wania, 2008) Snow can hold up to 3 % liquid water before liquid starts to drain (Colbeck, 1978). Melt-water can redistribute impurities in firn (Eichler et al., 2001). In laboratory experiments, ice samples are often prepared by freezing liquid water.

3.4.1 Amount and concentration of brine

Sea-salt solutions and well defined NaCl or $(NH_4)_2SO_4$ solutions generally follow the predicted bulk phase behaviour during freezing, but freezing of emulsions, that resemble water droplets in the atmosphere, can be kinetically hindered so that a meta-stable liquid phase exists well below the eutectic temperature (Koop et al., 2000; Bogdan, 2010). Koop et al. (2000) concluded that sea-salt particles remain liquid under environmental relevant temperatures both as aerosol in the boundary layer, as well as deposits on snow. This is mainly due to the presence of some solutes with very low eutectic temperatures. Cho et al. (2002) have confirmed using NMR that the concentration of NaCl in the remaining liquid phase above the eutectic temperature is well described based on the phase diagram. For this, the concentration in the brine was derived at various temperatures while the sample was in thermodynamic equilibrium. They further developed a parameterization to calculate the amount of liquid in freezing systems. This approach was recently expanded by Kuo et al. (2011). They substituted concentrations by activities and included two additional loss processes of solutes from the brine during freezing, the solubility of solutes in the ice crystal and the volatilization to the gas phase. With this approach the total amount and concentration of solution can be predicted during the freezing process of solutions containing salts or inorganic, volatile acids, as long as the freezing follows the thermodynamic equilibrium. These approaches assume that the solutes are completely expelled from the growing ice. Indeed, it is an intrinsic feature of the freezing process that ions are predominantly excluded from growing ice. Early work found partition coefficients between the solid ice and liquid in the 0.1 to 10^{-3} range for freezing of NH_3 and salts of F^- and NH_4^+ (Jaccard and Levi, 1961). These small partitioning coefficients justify neglecting the fraction of solutes that is incorporated into the ice. Molecular dynamics simulations of ice growth from supercooled salt solutions have revealed the microscopic mechanism whereby ions are excluded from growing ice (Vrbka and Jungwirth, 2005; Carignano et al., 2006, 2007; Bauerecker et al., 2008). The rejection of ions from freezing salt solutions occurs due to fluctuations of the ion density in solution. A local reduction of ionic density in the vicinity of the freezing ice front enables the growth of a new ice layer. The dissolved salt thus slows down the freezing process that leads to the formation of an almost pure ice, with the majority of the ions confined to unfrozen brine present as inclusions within ice, at grain boundaries as well as at a free surface of ice. Incorporation of individual ions or ion pairs into the growing ice matrix is, however, possible and has been observed in molecular simulations, albeit as a significantly less likely fate of the ionic impurities during the freezing process. Quantifying the distribution of solutes between the surface and the interior of the growing ice and the fraction of brine that is trapped in the ice is difficult, because the observed incorporation of solutes into the growing ice depends strongly on experimental parameters such as the counter ion, concentration, and freezing rate (Hobbs, 2010). For the entrapment of brine between grains the vertical freezing of sea ice is a natural laboratory. Because solute is transported away from the interface less rapidly than heat, there will be supercooling present near the freezing interface, leading to its breakdown into cells. For saline solutions this transition has been well documented in 2-D growth cells (Körber, 1988; Nagashima and Furukawa, 1997). The process is termed morphological instability and creates the cellular freezing interface by which sea ice grows into seawater and determines its microstructure (Wettlaufer, 1992; Maus, 2007). Note that stirring of the liquid can influence the solute incorporation by affecting the solutal and thermal boundary layers, and thus changing the conditions of cellular breakdown (Weeks and Lofgren, 1966; Kvajić and Brajović, 1970). Regarding the incorporation within the grains ions are more readily incorporated into the ice matrix than non-ionized solutes (Hobbs, 2010). Nevertheless, large organic molecules such as glucose (Halde, 1980), carboxymethyl cellulose (Smith and Pounder, 1960), and alkylbenzenes (Fries et al., 2007) can be incorporated within ice samples during freezing of liquid solutions. Whether solutes end up in brine inclusions, in grain boundaries, at the free ice surface, or within the crystalline lattice during growth is essentially an open, but important, question. The formation of a solid solution, which

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is most likely highly supersaturated, is consistent with the kinetic model of Domine and Thibert (1996).

A recent spectroscopic investigation showed that the amount of solutes in brine at the ice – air interface could be quite different from the fraction that is trapped within inclusions in the ice crystal. Wren and Donaldson (2011) reported only a minor increase in nitrate concentration at the ice surface during freezing and suggested that nitrate might be favourably incorporated into pockets or grain boundaries inside bulk ice at 258–268 K. A similar tendency of nitrite to be captured in liquid reservoirs inside the growing ice was suggested earlier (Takenaka et al., 1996). In contrast, using surface sensitive spectroscopy Křepelová et al. (2010a) showed that frozen solutions of NaCl above the eutectic exhibited a composition on the ice surface consistent with the phase diagram of the bulk solution. This is in agreement with earlier work by Döppenschmidt and Butt (2000) where solid NaCl crystals were identified at the ice surface at temperatures below the eutectic using AFM. One reason for the discrepancy seen in the experiments by Křepelová et al. (2010a) and Wren and Donaldson (2011) might be that the preference to be trapped in pockets is a compound specific effect (see also Sect. 2.3.2), as also suggested by Wren and Donaldson (2011).

The salinity of the remaining liquid adjusts to temperature to maintain thermodynamic phase equilibrium during the freezing process. The total amount of liquid in a freezing system, as given by the total amount of solutes that is not incorporated into the growing ice, might vary significantly based on experimental parameters. Further there is experimental evidence that the distribution of the remaining liquids between the supersaturated solid solution, micro-pockets, grain boundaries and the free ice surface shows some variability among different solutes.

At cold temperatures, the solubility limits of major components can be reached (Thomas and Dieckmann, 2009). For example, from the six major ions present in seawater, sulfate and sodium start to precipitate in the form of mirabilite ($Na_2SO_4 \cdot 10H_2O$) at 266, sodium chloride precipitates 250 K and carbonate at 271 K. The above processes reduce the total amount of dissolved ions and thus the volume of liquid and its pH. If liquid brine and solid precipitates are separated, the distribution of ions in bulk snow or sea ice will also change. Some observations however remain puzzling. For example, sea ice that has never experienced temperatures below 265 K has been found to be depleted in sulfate (Lewis and Thompson, 1950). In a very recent study with young sea ice, Maus et al. (2011) concluded that differential diffusion rather than eutectic precipitation leads to significant ion depletion of sulfate and potassium in brine and enrichment of sulfate in surface ice and snow. In that study it was proposed that this process acts together with convection due to gravity drainage, which is the main mechanism of desalination of sea ice (Untersteiner, 1968; Niedrauer and Martin, 1979; Weeks and Ackley, 1986; Hunke et al., 2011). The term gravity drainage summarises all processes that lead to replacement of interstitial brine by sea water. During the freezing season, the driving force for this drainage is the concentration gradient in the brine, heavier brine lying above lighter seawater. During the melting season flushing driven by surface melt water is dominant.

Noteworthy environmental signatures and feedbacks of ion fractionation and impurity redistribution in the microstructure of sea ice and snow are (i) the carbon budget and (ii) ozone depletion events. (i) Precipitation of calcite is accompanied by degassing of CO_2. If brine convection transfers the CO_2 to deeper oceanic layers, while the salt crystals remain in the ice, then seasonal sea ice growth can contribute significantly to the global carbon budget (Jones and Coote, 1981; Rysgaard et al., 2007). If the precipitates remain in the ice, or if calcium precipitates as ikaite ($CaCO_3 \cdot 6H_2O$), as supported by recent observations, this effect is not expected (Dieckmann et al., 2008; Morin et al., 2008). Determinations of calcium range from an enrichment (Tsurikov, 1974; Weeks and Ackley, 1986; Granskog et al., 2004), to slight (Anderson and Jones, 1985) and strong depletion of calcium in old natural sea ice (Addison, 1977). Such differences have sometimes been attributed to the method of analysis, for example a lack of redissolution of calcium carbonate upon melting (Anderson and Jones, 1985). The problem has also been addressed indirectly by alkalinity and CO_2 determinations (Lyakhin, 1970; Killawee et al., 1998; Tison et al., 2002; Papadimitriou et al., 2003; Dellille et al., 2007; Rysgaard et al., 2007) , but due to the importance of the saturation index and biological activity an interpretation in terms of sea ice physics and ion precipitation remains speculative. A possible role of the microstructure of sea ice in mediating air–sea gas exchange has been noted (Gosink et al., 1976; Semiletov et al., 2004) but not clarified due to a lack in microstructural data. (ii) The role of bromine as a catalyst for the destruction of tropospheric ozone, outlined in recent years (Simpson et al., 2007; Abbatt et al., 2012), is a consequence of its precipitation at much lower temperatures than chlorine. It may be enhanced (bromine explosion) by a reduced buffering capacity of sea ice brine due to calcite precipitation (Sander and Burrows, 2006). In case of precipitation of calcium as ikaite ($CaCO_3 \cdot 6H_2O$), supported by recent observations, this effect is not expected (Dieckmann et al., 2008; Morin et al., 2008). The process furthermore depends on the ability of liquid brine to migrate to the surface, and hence on the detailed microstructure and permeability of sea ice.

3.4.2 Freezing potential

The selective incorporation of ions into the ice matrix can lead to the generation of a charge imbalance at the freezing front (Workman and Reynolds, 1950). This freezing potential can cause redox reactions or when neutralized by the flow of the H^+/OH^- acid–base changes of the remaining solution (Sect. 4.1). These may cause a hydrolysis or (de)protonation of other compounds present in it. Organic chromophores' spectra for example may be therefore strongly red-shifted and consequently photo-degraded by sun irradiation much faster than they would be in the liquid of original pH.

The charge imbalance creates a large electrical potential, when the product of the growth rate and electrolyte concentration at the freezing front exceeds a critical value that depends on pH (Bronshteyn and Chernov, 1991; Sola and Corti, 1993). Workman and Reynolds (1950) found that the potential is larger for diluted solutions and reports potentials of up to 200 V, for solutions of 10^{-5} M. The potential is a function of the time, freezing rate, concentration of salt(s) as well as other solutes and crystal orientation. In follow up studies (Lodge et al., 1956; Cobb and Gross, 1969; Murphy, 1970), the magnitudes of the freezing potentials of identical solutions were scattered because these factors were not kept constant. Measuring freezing potentials across the interface between single crystals and electrolyte solutions significantly improved reproducibility (Wilson and Haymet, 2008). The magnitude of the freezing potential varies over time – it grows very rapidly after the freezing and then gradually decays. Its maximum value depends strongly on the freezing rate. The maximum values were found for 25 µm s^{-1} in one study (Wilson and Haymet, 2008, 2010). Usually, the highest freezing potentials are measured when the concentration of the salt ranges from 10^{-5} M to 10^{-3} M. When the concentration is higher (over ≈ 10^{-2} M) or lower (below 10^{-6} M) the freezing potential becomes negligible or vanishes. A model, developed by Bronshteyn and Chernov (1991), was applied to successfully explain these observations. It takes into the account the composition of the freezing front – the concentration of cations and anions, protons and hydroxyl anions and their diffusion and distribution coefficients between the solution and the ice. It does not consider precipitation of individual components other than ice. Decrease of the freezing potential with high rate of cooling was explained by formation of parallel finger-like crystals perpendicular to the crystallization front, which strongly increases the interface area and also the H^+/OH^- interfacial flows, thus making the freezing potential absent or at least not measurable. A similar mechanism is suggested for high salt concentrations. At low concentrations the signal is too weak to be measurable. As the model calculates individual species' concentrations in the unfrozen solution it also predicts its pH change under certain conditions. pH changes of the remaining brine during freezing have later been confirmed and found to qualitatively follow the predictions based on the reported differential incorporation by UV–VIS spectroscopy of cresol red (Heger et al., 2006) and by NMR study of 3-fluorobenzoic acid (Robinson et al., 2006). Nonionic solutes, such as DMSO, glycerol or sucrose, significantly reduces the freezing potential (Rastogi and Tripathi, 1985; Sola and Corti, 1993) , these observations are not yet explained and need future investigation.

Even though the absolute values of freezing potentials are poorly reproduced due to the technical difficulties, the phenomenon uncovers important microstructural behaviour during freezing with not yet well scrutinized physical-chemical consequences. A handful of suggested examples is given here where we think the freezing potential is important and should be considered during the process of freezing in the environment. A freezing potential originates from unequal distribution coefficients between the solution and the ice. Thus its measurement may be one of the few options how to access, at least relatively, the amount of ions incorporated into the ice lattice. Overall, the effects of freezing potential may be of importance whenever the distribution coefficients of cations and anions are not equal, which is expectably the most common case for freezing of environmental solutions.

3.4.3 Fate of solutes in the disordered interface

Once the temperature falls enough to completely freeze ice, the question arises as to how solutes interact with the ice surface. It has been suggested, that the impurities are solvated in the disordered interface (Smith and Pounder, 1960; Wang, 1961, 1964; Gross et al., 1987; Dash et al., 1995; Cohen et al., 1996; Finnegan and Pitter, 1997; Petrenko and Whitworth, 1999; Giannelli et al., 2001; Cho et al., 2002; Heger et al., 2005; Vrbka and Jungwirth, 2005). Solvation of small acids and bases has been observed spectroscopically at ice surfaces at temperatures above 240 K (Kahan et al., 2007; Wren and Donaldson, 2011). Molecular dynamics simulations and spectroscopic measurements suggest that larger, less hydrophylic species such as aromatic hydrocarbons are less well-solvated in the disordered interface than in aqueous solutions or supercooled water (Ardura et al., 2009; Kahan et al., 2010c).

The properties of solutes below the eutectic point have been the focus of much research, but current studies give no conclusive picture. Using surface sensitive, synchrotron based X-ray spectroscopy, Křepelová et al. (2010a) found no evidence for a liquid on the surface of frozen solutions of NaCl below the eutectic, in line with expectations from the phase diagram. This technique probes the local, chemical environment of the chloride anions and does not rely on bulk properties. In contrast, NMR investigations have revealed the existence of liquid solutions well below the eutectic (Cho et al., 2002; Guzmán et al., 2006; Robinson et al., 2006). Because the amount of liquid closely followed temperature during warming periods toward the eutectic temperature in the study by Cho et al. (2002), the authors argued that kinetics could not explain the existence of liquid. One difference between the two studies is that, Křepelová et al. (2010a) probed the upper surface, while Cho et al. (2002) also probed the bulk ice. During the freezing process, brine may have been trapped in micro-pockets within the bulk ice. The size of those micro-pockets is not known, but if these are in the nm range, a substantial Kelvin effect lowering the freezing point would be the consequence, as detailed in Sect. 2.2. We propose here that geometric constraints to the liquid volume kept in the micro-pockets might explain the observed freezing point depression. Results may thus not be general, but depend on the specific freezing conditions. Additionally, compound specific effects may alter the freezing behaviour. In an earlier NMR study the liquid fraction of natural sea ice with a more complex chemical composition was well described based on the eutectic concentrations of salts (Richardson, 1976).

In summary, the concentration of solutes in the brine liquid that results from freezing is unambiguously given by thermodynamics and detailed parameterisations are available (Kuo et al., 2011). Solubility limits of common environmental solutes in snow are often reached as surface snow cools, which lowers the amount of solutes in solution significantly and may change the chemical composition and pH of the remaining brine. Due to its environmental importance (Simpson et al., 2007; Abbatt et al., 2012), this process should be included in parameterization approaches. An open question is how solutes distribute. They might be included into the ice crystal, in liquid inclusions within bulk ice, or remain at ice surfaces or in grain boundaries. The solubility in the ice crystal is generally low, however the incorporation is solute dependent which might create electrical potentials during the freezing process. Further studies related to the freezing of solutes are needed. The fate of solutes below the eutectic also needs further investigation. Some studies have revealed the existence of a liquid phase well below eutectic temperatures. One reason for this might be the melting point depression in very small pockets that host those solutes within the ice. Surface-sensitive studies indicate that the solutes precipitate as predicted by the phase diagram. Very little is also known about the contaminants on the surface when a disordered interface is present.

3.5 Physical processes in models

Detailed snow-pack models taking into account some of the above-described physical processes were developed for species like H_2O_2 and HCHO. Hutterli et al. (2003) presented atmosphere–snow models for these two species based on 1-D models previously developed by McConnell et al. (1998) and Hutterli et al. (1999). Motivation came from the knowledge that hydrogen peroxide is the only major atmospheric oxidant that is conserved in snow. The reconstruction of its atmospheric concentration from the ice core record can deliver crucial information to constrain photochemical modelling of the past atmosphere (Thompson, 1995; Frey et al., 2005; Lamarque et al., 2011) and has attracted great interest (e.g. Neftel et al., 1995; Anklin and Bales, 1997; McConnell et al., 1997; Frey et al., 2006). Similar reasons have led to the examination of formaldehyde in ice cores, since the oxidation of methane by hydroxyl radicals is the major source of atmospheric formaldehyde. Thus, reconstructed atmospheric formaldehyde concentrations would constitute a strong constraint on photochemical modelling of past methane and hydroxyl radical concentrations (Staffelbach et al., 1991).

Snow-pack modeling of H_2O_2 and HCHO was applied to conditions at Summit, Greenland to simulate concentration profiles in surface snow for a 6 yrs period (Hutterli et al., 2003). Transport of H_2O_2 and HCHO in the interstitial air, the exchange between snow grains and the adjacent interstitial air, and snow metamorphism were treated in the model. Snow temperatures were calculated using observed air temperatures (annual mean temperature 241 K) and the heat conductivity of the snow. The conductivity was determined using the snow density based on a measured profile. The same density profile was used to calculate the specific surface area, which was subsequently used to estimate an average radius of the snow grains. The transport in the interstitial air took into account molecular diffusivities, which were corrected according to the snow temperature and the firn density. Fresh snow was regularly added throughout the year corresponding to a total accumulation of 23 $\mathrm{g\,cm^{-2}\,yr^{-1}}$. As a result, older snow was transferred into deeper layers causing an increase of the snow density according to the employed density–depth relationship, a decrease in the specific surface area and a corresponding increase of the average grain radius. Therefore, the metamorphism of the snow is represented in the model in a simplified way.

Concentrations in the atmospheric boundary layer were used as an upper limit of interstitial air concentrations. These concentrations were derived by off-line calculations using a box model with a comprehensive atmospheric chemistry mechanism. The obtained annual cycles for H_2O_2 and HCHO boundary layer concentrations were scaled to agree with concentrations observed at Summit. The atmospheric concentrations were used together with meteorological observations, such as temperature and humidity, to determine H_2O_2 and HCHO concentrations in fresh snow. Diffusional growth of snow at cloud level is thought to not introduce any fractionation between water and H_2O_2, thus the co-condensation model is applied, to calculate the fresh snow concentrations, as described in Sigg et al. (1992). The HCHO concentrations in the fresh snow were further scaled in order to reproduce observed firn concentrations at greater depths. The co-condensation mechanism caused a super-saturation of the fresh snow in HCHO and H_2O_2 and only about 50 % of the HCHO and H_2O_2 initially present is preserved in the snow-pack and firn. Previous simulations for H_2O_2 demonstrated that at the snow surface H_2O_2 in the ice phase was always out-of-phase with the gas phase due to fast changes in the atmospheric conditions and the snow properties resulting also in a non-uniform distribution of H_2O_2 inside the grains of the older snow (McConnell et al., 1998). Sensitivity studies further revealed that only the HCHO concentrations were significantly affected by the transport in the interstitial air and the accumulation rates, while the effect on H_2O_2 concentrations remained small for typical Greenland conditions (Hutterli et al., 2003). Tripling Summit accumulation rates of 0.23 $\mathrm{g\,cm^{-2}\,yr^{-1}}$ did not have a large impact on H_2O_2 preservation. However lower snowfall rates, like those in Antarctica (0.07 to 0.3 $\mathrm{g\,cm^{-2}\,yr^{-1}}$) demonstrate a large impact of accumulation rate on H_2O_2 (Frey et al., 2006), suggesting that if surface snow is quickly buried the resulting concentrations can be far away from equilibrium. The modelling study by Hutterli et al. (2003) thus showed that for H_2O_2 and HCHO physical cycling dominates in determining concentrations although both compounds undergo photochemical reactions in the snow.

The physical cycling – the exchange of impurities between the snow grains and the adjacent interstitial air – was calculated based on empirical correlations from field and laboratory experiments (Conklin et al., 1993; McConnell et al., 1997; Hutterli et al., 1999; Burkhart et al., 2002). In the case of HCHO, the concentrations in the condensed phase were simulated according to a bulk approach assuming that HCHO is mostly absorbed at the surface of the grains. In contrast, for H_2O_2 it was assumed that it is contained in the bulk solid of the snow grains and not adsorbed at the surface (McConnell et al., 1998). Therefore, a temperature-dependent air–snow partitioning coefficient was employed to determine the equilibrium between firn air concentrations and the concentrations in the outermost layer of the assumed spherical snow grains. Inside the grains, the transport of H_2O_2 was simulated using ten spherical layers and a temperature-dependent diffusion coefficient. In the case of H_2O_2 the empirical equilibrium constant was considerably lower than the extrapolated Henry's law constant. Moreover, the constant decreased strongly from 228 K to approximately 261 K, before it slightly increase at higher temperatures (Conklin et al., 1993). These different temperature dependences of the equilibrium may reflect the adsorption processes at very low temperatures and the uptake in the liquid fraction at higher temperatures.

Since recent studies have resulted in independent and more detailed description of the equilibria of H_2O_2 and HCHO between the gas phase and the snow taking into account the adsorption at the surface and the dissolution in the bulk ice phase (Pouvesle et al., 2010; Barret et al., 2011b) new modelling studies using such data are warranted. The application of such upgraded models to the same data sets as in the previous studies based on empirical relationships may be used to investigate if the laboratory data are sufficient to reconstruct the observed H_2O_2 and HCHO profiles in the snow and in the firn cores and to determine the dominant uptake process for both species.

3.6 Conclusions about physical processes

Physical processes in snow and ice play an important role in the fate of contaminants in snow and the exchange with the air. For example, a strong influence of sorption and snow metamorphism on the flux of H_2O_2 and VOC from the snow to the atmosphere has been found (Meyer et al., 2006; Grannas et al., 2007b). Migration in ice can explain observed shifts of concentration profiles of some solutes in ice cores and also air–snow exchanges for some soluble species such as formaldehyde (McConnell et al., 1998; Barret et al., 2011a,b). These examples illustrate that several processes can operate simultaneously and it remains a challenging task to identify those that dominate the migration of specific species or specific observations. Diffusion can take place into the solid ice matrix, along grain boundaries, on the surface, and in the liquid phase embedded in surface snow. The presence of impurities can significantly influence diffusion rates and solubility by preferentially trapping certain species. For example, F^- was observed to be trapped in ice cores by alkaline dust (De Angelis and Legrand, 1994). Laboratory experiments on bulk diffusion show Na^+ is trapped by HCl at cold temperatures (Livingston and George, 2002). Moreover, diffusion into the solid ice matrix can proceed via different mechanisms, either by breaking bonds in the water network of the crystal or by interstitial diffusion. Each of these processes has designated diffusivity rates and currently there are no direct field observations of the diffusion mechanism or reservoirs to which species diffuse. As a result indirect arguments are used to explain observed shifts ice core signals, that occur over long time periods. More direct observations of the diffusion are urgently recommended. Molecular dynamics simulations have suggested a bond breaking mechanism for the diffusion of formaldehyde in snow (Ballenegger et al., 2006) that is different than the interstitial mechanism of water migration and potentially explains the observed fast diffusivity. It is unlikely that surface disorder along grain boundaries or on crystal surfaces can significantly impact bulk diffusion on the long time scales operating in ice cores. Yet, defects might be injected from the disordered interface into the solid (Devlin and Buch, 2007), where their presence would enhance diffusion rates of water and of impurities.

On shorter time-scales, typical for air–ice exchange, sorption processes usually dominate. These occur by two mechanisms with very different thermodynamic properties, either by adsorption to the ice surface, or by dissolution into liquid fraction of the surface snow. Adsorption dominates at temperatures below ≈ 245 K and uptake of most trace gases can be parameterized by Langmuir adsorption. This holds for many experiments where two trace gases are dosed to the ice simultaneously, a situation that might be closer to settings found in nature. In the presence of liquid, Henry partitioning seems better suited to describe sorption to snow. Less is known about the role of the disordered interface on sorption processes. The presence of surface disorder has been shown to fundamentally change the uptake behaviour of acidic trace gases leading to a long-term, almost continuous uptake on the experimental time scales (McNeill et al., 2006, 2007). In other experiments it was argued that the uptake of volatile organics is significantly enhanced at higher temperatures where a disordered interface might have been present (Abbatt et al., 2008). An inherent characteristic of the long-term uptake is that it can be described by diffusion laws. Huthwelker et al. (2006) have argued that both surface restructuring and bulk-diffusion may cause this uptake. They argue that the reservoir presented by the disordered interface is too small to explain long-lasting uptake and thus the trace gases must diffuse into grain-boundaries. Yet, as Huthwelker et al. (2006) notes, the experimental results are not conclusive and this remains essentially an open question. What is important is that diffusion thus seems to be dominating already at short time scales of typical laboratory experiments.

Physical processes thus critically depend on the microstructure of snow. Clearly, snow is not static, but the grain boundaries, porosity, and surface area change with time. The rate of sintering depends on temperature, which can change on scale of seconds or less in snow (Szabo and Schneebeli, 2007). Freezing and melting processes are also important, as the presence of liquid changes the rate of sintering, sorption, and diffusion. Detailed modelling to derive the brine concentrations during the freezing process, based on the thermodynamic phase diagram, but also taking losses by release of volatile species from the brine to the gas phase and non-ideality in the brine solution into account, has recently been presented (Kuo et al., 2011). The total amount of solutes that gets expelled from the ice during the freezing process is highly uncertain and also whether the brine ends up at the air–ice interface, in grain boundaries, or trapped in micro-pockets in the bulk ice. MD simulations have revealed that solutes are expelled from the growing ice, because their density fluctuates in solution and the ice preferentially grows when solutes are absent at the ice water front. However, early experimental work has shown that during freezing morphological instabilities might arise caused by constitutional supercooling during freezing, as there are different diffusive boundary layers for heat and salt (Mullins and Sekerka, 1964), which explains the large scatter in data on the freezing process. A sound understanding of freezing processes is further needed to analyse laboratory experiments, as often the sample matrix is frozen from solutions and freezing conditions might vary widely between different experiments and compared to the field.

Previous models to simulate the physical exchange of species like H_2O_2 and HCHO used empirical parameterizations to describe the equilibria between gas phase and condensed phase. These parameterizations were developed using field observations at different polar sites and reflect the overall exchange processes between the snow and the firn air. Using new experimental results and new parameterizations these exchange processes may be better specified in upgraded models and compared to available long-term observation as in the previous modelling studies. Such simulation may help to better characterize driving processes for the exchange of reactive species between the snow and the atmosphere.

4 Chemical processes

In recent decades numerous field and laboratory studies have established that ice and snow hosts a significant and often unique chemistry (Klán and Holoubek, 2002;

Grannas et al., 2007b; Simpson et al., 2007; Steffen et al., 2008). Domine and Shepson (2002); Grannas et al. (2007b); Abbatt et al. (2012); McNeill et al. (2012) provide excellent overviews of atmospherically relevant reactions that occur in snow and ice and of the large-scale effects of these reactions on air quality, climate change, and on biochemical cycles of the Earth system, especially with respect to chemistry that affects the oxidative capacity of the atmosphere, such as bromine explosions (Abbatt et al., 2012) and the photo-production of hydroxyl radicals (Grannas et al., 2007b). Here we focus on recent laboratory studies that offer insights into the specific physico-chemical properties and the molecular-level interactions of molecules that are responsible for their chemical reactivity in snow and ice. As for the exchange between the atmosphere and the condensed phase of the snow-pack, a number of chemically distinct compartments, such as bulk ice, grain boundaries, the ice surface, liquid brine, and solid precipitates (Sect. 2) including the disordered interface (Sect. 2.3) must be considered. The chemistry in such a multi-phase system can be very complex; the question arises which processes dominate the overall chemical activity in snow and ice. The situation where bulk and surface reaction might occur is very similar to other heterogeneous systems of atmospheric relevance, such as aerosols, where strategies have been developed to differentiate between the importance of heterogeneous vs. bulk reactivity (Kolb et al., 2010; Shiraiwa et al., 2010).

4.1 Reactions during the freezing process

Chemistry occurring during the freezing process has been the focus of many early studies in the field of food chemistry, organic synthesis, and biochemistry (Takenaka et al., 2003). Generally, apparent reaction rates are significantly increased during the freezing process, as concentrations of the solutes increase in the shrinking volume of liquid remaining on the ice surface (Sect. 2.2). For most systems studied until the late 1960s, the observed reaction rates can be well described by aqueous phase kinetics when concentrations in the remaining brine are derived either from the phase diagram or the melting point depression of specific salts (Pincock, 1969).

Pioneering in the field of atmospheric chemistry is the early work by Takenaka et al. (1992) who observed acceleration by a factor of 10^5 in the oxidation rate of nitrite by oxygen during freezing. This implies that a reaction that is usually slow and thus negligible in the liquid phase – such as the conversion of nitrite to nitrate by oxygen – becomes important enough to modify the composition of the sample during freezing. Takenaka et al. (1992) excluded the possibility that this acceleration is driven by catalytic properties of the ice surface. Later it was confirmed that the observed rates could be fully explained by the increase in concentration as the volume of liquid brine is reduced during freezing (Finnegan, 2001; Takenaka and Bandow, 2007). This conclusion holds for soluble species and bimolecular (or higher order) reactions, and has been confirmed with environmentally relevant systems (Grannas et al., 2007a; Wren et al., 2010). One important consequence of this freeze-concentration for environmental chemistry is that faster reaction rates in ice compared to in unfrozen samples can lead to new products and reaction pathways. Sodeau and co-workers have recently identified new reaction pathways for the release of nitric oxide and halogens species to the atmosphere from the freezing of ionic sea-salt solutions, often via trihalide ions (O'Concubhair et al., 2012; O'Driscoll et al., 2008; O'Concubhair and Sodeau, 2012; O'Sullivan and Sodeau, 2010). These studies highlighted the formation of products that are not usually observed under the same conditions in unfrozen solution. Of high relevance for the cryospheric community are this group's recent findings that dissolved elemental mercury is oxidized to Hg^{2+} when frozen in the presence of oxidants such as hydrogen peroxide, nitrous acid, or sulfuric acid and oxygen (O'Concubhair et al., 2012). The apparent rate of chemical reactions during the freezing process is further influenced by other factors, such as changes in pH (O'Sullivan and Sodeau, 2010). A recent study suggests that the reactivity is significantly impacted when solubility limits are reached for one reactant, resulting in physical separation of the reactants during freezing (Gao and Abbatt, 2011). In this study the reactivity of OH, produced from precursors dosed to the unfrozen solution, was lowered toward succinic acid in ice compared to aqueous solution, while reactivity toward malonic acid was not significantly suppressed – in keeping with the solubility limits of these two organics.

Once the temperature drops below the eutectic temperature the phases in the system change drastically as the bulk liquid solidifies. With this phase change, the observed chemical reactivity changes significantly. For example, the chemical reactivity during the freezing process ceases once the sample completely solidifies, as described in the early work by (Takenaka et al., 1996). Directly comparing the reactivity in frozen systems to reactivity in the liquid phase has been the focus of some recent studies related to environmental research (Grannas et al., 2007a; Kahan et al., 2010a; Gao and Abbatt, 2011). Photolytically driven bimolecular reactions of water-soluble organics were found to proceed faster in the liquid phase than in frozen systems (Gao and Abbatt, 2011) or faster in mixtures of ice and brine compared to completely frozen systems (Grannas et al., 2007a). In the latter study NaCl was added to the sample to vary the amount of brine at a given temperature. The study by Grannas et al. (2007a) revealed that the comparison of the rates above and below the eutectic point for a given system strongly depends on concentration: at low salt concentrations, lifetimes of water soluble organics increased when the temperature was lowered below the eutectic, at higher concentrations the observed lifetimes were longer at temperatures above the eutectic. In contrast, water insoluble organic aromatics were found to photolyze faster on ice surfaces in absence of brine (Kahan et al., 2010a). Varying the amount of brine systematically, the chemistry could be tuned from that observed at a pure ice surface (fast) to that observed in aqueous solution (slow) (Kahan et al., 2010a). The different reactivity in the presence of brine compared to ice has implications for the interpretation of reaction rates measured in ice in the laboratory and in the field. At high salt concentrations, where brine is present, aqueous phase kinetics will describe the reaction, but at low salt concentrations, kinetics specific to the ice will need to be invoked. The possibilities that chemistry in partially frozen samples may differ from chemistry in solid ice samples and that chemistry in brine might be more important than reactivity in completely frozen samples complicates the analysis of experiments. This becomes clear when reactions are monitored continuously during the freezing process and in the completely frozen sample. For example, Kim and Choi (2011) described an enhanced reduction of chromate and arsenite in frozen ice. As samples were prepared from liquid solutions, it is proposed here that the major part of the observed chemistry occurred during the freezing process, in agreement with the freeze-concentration effects discussed above and with their observed time dependence (Kim and Choi, 2011). This might also explain why many studies on the chemistry in ice have focused on photolytic or heterogeneous studies, where the starting point of the chemistry can be easily defined, i.e. when the ice is completely frozen.

From the above it is clear that chemistry in the highly concentrated brine that forms during the freezing process can in some cases dominate reactivity in the frozen sample by orders of magnitude. We therefore propose to use the term freeze-concentration effect exclusively to describe second- and higher order chemistry during the freezing process. This implies that the presence of small amounts of liquid in the ice samples can significantly impact the observed rates. Taken that liquid can prevail at temperatures up to approximately 20 K below the bulk eutectic point in nanometre sized inclusions within the bulk ice (Sect. 2.2), aqueous phase reactions need to be considered when interpreting results from high temperature experiments.

4.2 Reactions after the freezing process

Solid ice hosts a unique chemistry that has been the focus of many studies. Both photochemical and other reactions of inorganics and organics have been investigated. Despite the large number of studies, a unified picture of the reactivity in ice still cannot be given. In particular, detailed kinetic studies are rare and thus the following discussion is mostly based on observed rates of product formation or the decay of the starting compound. In that sense, some reactions have been found to be accelerated compared to the unfrozen, liquid sample – with the same amount of reactants – at room temperature. In those experiments an enhanced apparent rate of typically by a factor of approximately 10 has been described (Grannas et al., 2007a; Kahan and Donaldson, 2008; Weber et al., 2009; Kahan and Donaldson, 2010). For other chemical systems similar apparent reaction rates in frozen and in liquid samples were found (Dubowski and Hoffmann, 2000; Klánová et al., 2003a,b; Ružička et al., 2005; Matykiewiczová et al., 2007a; Anastasio and Chu, 2009; Ram and Anastasio, 2009; Galbavy et al., 2010; Kahan et al., 2010c; Beine and Anastasio, 2011; Gao and Abbatt, 2011), while other systems showed a slower reaction in ice with an order of magnitude reduced apparent reaction rates than observed in liquid samples with the same total concentration of reactants (Klánová et al., 2003a; Ružička et al., 2005; Matykiewiczová et al., 2007a; Anastasio and Chu, 2009; Bartels-Rausch et al., 2011; Beine and Anastasio, 2011; Gao and Abbatt, 2011). We are far from a detailed, quantitative understanding of the chemistry in ice, but in recent years important factors have been identified that can explain the observed differences in reactivity. In this emerging picture the observed rates in ice are a consequence of the combination of increased concentration that prevail after freezing alongside electric potential changes that can change reaction mechanisms, the temperature dependency of the reaction, the local chemical environment and the location of the reactants, or a combination of above factors.

4.2.1 Local concentration

One particular study has shown that local concentrations were enhanced by more than 6 orders of magnitude in frozen samples upon slow freezing (Heger et al., 2005). Such enhanced concentration can significantly accelerate bimolecular (or higher order) reaction steps. Examples are the photolytically driven reaction between *p*-nitroanisol and pyridine (Grannas et al., 2007a) and the photolytic reduction of ferric ions in ice by organics (Kim et al., 2010). The iron forms complexes with organic electron donors due to the freeze-concentration effect while the investigated samples are frozen. Upon photolysis the newly formed ligand–metal bond absorbs the photon that initiates the intramolecular redox-process (Kim et al., 2010). Intermolecular redox-reactions promoted by a more efficient electron transfer at the higher concentration could also contribute to enhanced rates. A quantitative description of the reaction rates is often hampered because the local concentrations of reactants are unknown. For example, solubility limits that have been shown to drive the chemistry during the freezing process might be of even higher importance once the samples are completely frozen.

Enhanced local concentrations of aromatics account for faster apparent photolysis rates in ice and at ice surfaces in some cases. Examples of this are benzene and naphthalene (Kahan and Donaldson, 2010; Kahan et al., 2010c). This is an important finding, as unimolecular reactions are not per se concentration dependent: in such cases rather the absorption spectrum changes. In aqueous solutions, as well as in the gas phase, benzene does not absorb light at wavelengths longer than ≈ 290 nm reaching the Earth's surface, and naphthalene absorbs only weakly. On ice, however, the absorption spectra are significantly red-shifted compared to those in dilute solutions, due to self-association of benzene and of naphthalene molecules. Such shifts in the absorption maxima have been utilized in evaluating the nature and magnitude of the intermolecular interactions in ice at 253 and 77 K (Heger and Klán, 2007). Both the presence of water in a close vicinity of the probe molecules and the inter-probe interactions within the self-assembled molecular aggregations were believed to be responsible for the observed changes in the absorption spectra. Enhanced ice–solute or solute–solute interactions have recently been visualized as a cage effect in which the boundaries of the cage are defined by the walls of the micro-pocket or vein that the reagents are trapped in. In the confined space of the cage, reagents and intermediates are unable to diffuse away from one another, and so reactivity is enhanced (Ružička et al., 2005). For a detailed discussion on the photochemistry of organics in ice and on the cage-effect we refer the reader to McNeill et al. (2012).

4.2.2 Mechanism

Klán and co-workers have reported a dramatic alteration of the course of a photoreaction of various halogenated aromatic compounds in frozen aqueous solutions. Instead of photosolvolysis, which is typical in aqueous media, the compounds underwent predominately dehalogenation and bimolecular (radical coupling) reactions below approximately 266 K (Klán et al., 2000; Klán et al., 2001; Klán and Holoubek, 2002; Klánová et al., 2003a,b; Ružička et al., 2005; Matykiewiczová et al., 2007a,b). This is of direct environmental importance, because those degradation products uniquely formed in ice might have a higher toxicity than those formed in water or even as the original starting material. The authors concluded that the change in the dominant reaction pathway was ultimately due to significant increased local concentrations in the frozen samples, or to the inability of water to act as a nucleophile in ice. Interestingly, this change in reaction mechanism seems to alter the apparent reaction rates, as has been suggested by Klánová et al. (2003a). Thus most of these degradations do not show an apparent enhanced rate in ice despite the high local concentrations. A drawback to most of these studies is that they have been performed at higher concentrations than typically present in the environment; these high concentrations might contribute to the unique chemistry observed. Recently, the photochemical degradation of persistent organic compounds at environmentally relevant concentrations has been reported (Matykiewiczová et al., 2007a). Results at these low concentrations showed that different products were formed from those observed at higher concentrations as discussed above. However, most importantly it was confirmed that solvolysis does not occur for this type of substance in ice. To observe such changes in the relative importance of individual reaction pathways upon freezing, a complete mass balance of the products needs to be achieved. This requirement hampers any comparison to other studies, where similar decay pathways in ice and in water have been reported. For example, unidentified products after photolysis of nitrophenol in ice has been found, which suggests that polymerization reactions might have occurred (Dubowski and Hoffmann, 2000).

Reactions that are concentration-independent, such as unimolecular decomposition, are often found to proceed with similar efficiencies in aqueous solution and in ice. For example, the production of hydroxyl radicals from the photolysis of precursors such H_2O_2 (Chu and Anastasio, 2005; Jacobi et al., 2006), NO_3^- (Dubowski et al., 2002; Chu and Anastasio, 2003; Jacobi et al., 2006; Matykiewiczová et al., 2007b) and NO_2^-

(Jacobi et al., 2006; Chu and Anastasio, 2007; Matykiewiczová et al., 2007b) are generally reported to have similar absorption spectra, mechanisms and quantum yields in ice and in aqueous solution, accounting for the temperature dependence of the reactions. While the initial photolysis of these reactions is clearly a unimolecular step, subsequent reactions such as the self-reaction of HO_2 to produce H_2O_2 might add to the complexity. If such back-reactions are favoured, the overall product formation might be significantly decreased (Dubowski et al., 2002; Beine and Anastasio, 2011). Such shifts in the relative importance of individual reaction pathways has also been used to explain the observed decrease of the two-step reduction of Hg(II) in presence of organic electron donors in ice compared to water (Bartels-Rausch et al., 2011).

4.2.3 Chemical environments

Ice and snow in the environment contain complex mixtures of chemicals, each of which can participate and alter chemical reactions (Grannas et al., 2007b). For example, organic chromophores can enhance photochemistry by acting as photosensitizers (Bartels-Rausch et al., 2010, 2011) and by undergoing photolysis to produce reactive species such as OH (Grannas et al., 2007b). They can also suppress photochemistry by acting as a photon filter and by scavenging reactive species (Grannas et al., 2007b). For a detailed discussion on the environmental importance of organics in ice, we refer the reader to a recent review (McNeill et al., 2012). The impact of these and other organic and inorganic constituents of snow on specific reactions has consequently been the focus of many studies. Some of the most interesting are the ones that provide quantitative measures of the nature of the interaction between guest and water-ice host. For example, an indication of the degree to which organic compounds can interact with ice surfaces has been published (Holmes and Sodeau, 1999). A series of halogenocarbons were deposited onto water-ice and, using FT-IR spectroscopy, it was shown that the controlling features of the interaction, the charge density and the molecular polarizability, are predictable from simple measurements of the spectral shift in the ice OH dangling bond.

Abida and Osthoff (2011) recently reported that organic co-solutes ranging from formate to phenol inhibited the release of gas-phase NO_2 from nitrate photolysis in ice, likely due to scavenging of OH. However, halogenated phenols enhanced NO_2 production. This was suggested to be due to acidification of the ice surface due to the formation of acids such as HCl upon oxidation of the halogenated phenol. A suppression of mercury photoreduction was observed in ice that has been doped with halogens and organic chromophores (Bartels-Rausch et al., 2011). This was attributed to the formation of oxidizing halogen species (Jammoul et al., 2009) that promote the reverse reaction. Further, calculations indicate that Hg(II) is complexed by 4 Cl^- in concentrated brine solutions upon freezing, which might limit its reactivity (Bartels-Rausch et al., 2011). Organic co-solutes can also act as hydrogen donors upon photolysis of organic chromophores in ice (Matykiewiczová et al., 2007b). Further, in the presence of several, different types of chromophores the apparent rate of direct photolysis might be surpassed by bimolecular reactions involving photolytical produced radicals. Anthracene and naphthalene are both photolyzed at ice surfaces. It has been found that the observed photolytic degradation was not enhanced in the presence of nitrate or H_2O_2 indicating that the indirect, bimolecular degradation is slower (Kahan and Donaldson, 2008). The competition of primary photochemical processes and hydroxylation in the presence of H_2O_2 by product analysis and apparent formation rate determination have also been reported (Klánová et al., 2003a).

Local pH can be significantly altered during freezing, and can affect acid–base equilibria as well as reactivity of the solutes. For example, the presence of organic acids can result in a 10^2–10^4 increased protonation of cresol red relative to liquid solutions, which is attributed to the higher local concentration of acids at the grain boundaries due to the freeze-concentration effect during sample preparation (Heger et al., 2006). Such pH changes can significantly alter the chemistry during the freezing process, promoting pathways that do not occur in the unfrozen liquid (O'Sullivan and Sodeau, 2010). This change in local pH has been suggested to drive the chemistry even after the sample is completely frozen: a slight increase in apparent photolysis rate of NO_3^- was

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observed with increasing pH (Chu and Anastasio, 2003), while the production of gas-phase NO_2 from this reaction was observed to increase with decreasing pH Abida and Osthoff (2011) , and additional gas-phase products including HONO, $HONO_2$, HO_2NO, and HO_2NO_2 were detected at $pH < 4.5$ Abida and Osthoff (2011). The potential importance of this latter species to ice chemistry has been noted in a number of publications (Riordan et al., 2005; Hellebust et al., 2007, 2010). The photolysis of HONO in ice has been determined to yield approximately eight times more NO and OH than the photolysis of H_2ONO^+ in ice (Chu and Anastasio, 2007). Faster photoreduction of Fe_3^+ and Cr(VI) in ice compared to in aqueous solution has been suggested to occur due to lower pH at ice grain boundary layers because of the exclusion of protons during freezing (Kim et al., 2010). The release of HONO from the photolysis of NO_2 in ice in the presence of humic acid follows the expected pH dependence if freeze-induced pH changes are accounted for (Bartels-Rausch et al., 2010). The apparent photolysis rate of H_2O_2, NO_3^-, and NO_2^- in bulk ice samples has been demonstrated to be independent of pH (Chu and Anastasio, 2003, 2007). Further, reaction efficiencies and product yields of halogen chemistry in ice are influenced by local pH as discussed in great detail in (Abbatt et al., 2012). It is of final note here that ammonium nitrate on ice can be photolysed to release N_2O, a process that is quite different from that found for the photolysis of nitric acid on ice (Koch et al., 1996).

4.2.4 Physical environment and reactivity at the ice surface

The incorporation of solutes in the ice lattice, the capture in micro-pockets within the bulk ice, and the exclusion to the ice surface or to grain boundaries critically depends on conditions such as freezing rate (Sect. 3.4) or the history of gas-phase deposited species (Sect. 3.2). Besides the differences in the local concentration and local chemical environment, both of which may affect chemical mechanisms, the location where reactions occur will affect the fate of the reaction products and thus apparent rates and product distributions. This type of behaviour was discussed recently to explain the observation of a reduced reactivity of approximately a factor of 2 for H_2O_2 photolysis in flash-frozen samples compared to aqueous solutions or slowly frozen samples (Beine and Anastasio, 2011). Dubowski et al. (2001) determined that NO_2 produced from NO_3^- in the uppermost region of the spray-frozen ice samples was able to escape to the gas phase, while that produced at greater depths was photolyzed to NO. Subsequent studies also concluded that the detection of NO_2^- is only possible after the initial photofragments (i.e. NO_2^- and O) escape the ice cage surrounding them (Chu and Anastasio, 2003, 2007; Anastasio et al., 2007). Kahan et al. (2010a,c) recently demonstrated that unimolecular and bimolecular reactions proceed at similar apparent rates in large ice cubes and in aqueous solution, but that the apparent reaction rates are significantly altered when the ice cubes are crushed into ice granules with much greater surface area-to-volume ratios. In these samples, measured reaction rates were the same as those measured in situ at ice surfaces (Kahan et al., 2010a,c). A conclusion from these studies is that in large ice samples the reagents are located primarily in the bulk ice, and reactions measured in melted samples will reflect that. In high surface area samples, reagents are primarily located at the surface, and so surface processes will dominate offline measurements (Kahan et al., 2010a,c). This is supported by studies that reported similar reactivity for species doped to artificial snow from the gas phase and by freezing from solution (Ružička et al., 2005; Kurková et al., 2011). The high surface area-to-volume ratio of artificial snow results in the majority of reagents being associated with the surface, regardless of the sample preparation method.

From an atmospheric perspective, reactions at the ice surface–air interface are of high importance, because products from those reactions can easily escape the ice phase. Many studies have thus focused on surface reactions. Here we highlight recent results that indicate that the chemistry on the ice surface is distinctly different from that observed in ice and also on water surfaces. Scientists often use indirect methods of probing reactions at ice surfaces, for example by probing the gas phase above an ice sample or by doping reagents to ice surfaces from the gas phase. We refer the reader to Huthwelker et al. (2006) for a detailed discussion on experimental methods. In those experiments probing surface reactions is usually achieved by using ice samples with a high surface to volume ratio (e. g. Abbatt et al., 1992; McNeill et al., 2007; Bartels-Rausch et al., 2010; Kurková et al., 2011). However, these studies give no direct evidence for the surface reactions, as discussed in Bartels-Rausch et al. (2011). Monitoring reactions at the ice surface requires in situ analysis, which has been done in a limited number of spectroscopic experiments in the IR (e.g. Hellebust et al., 2007) and UV/VIS (e.g. Kahan et al., 2007). The advantage of the UV/VIS spectroscopy approach is that it can be operated at the relatively high temperatures typical for environmental snow-packs.

At the ice surface high local reagent concentrations may be found, due to the formation of clusters or islands of reagents (Sect. 3.2). This localized concentration enhancement is not necessarily due to a freeze-concentration effect, but has also been observed when reactants were dosed from the gas phase (Kahan and Donaldson, 2007, 2008). The effects on reaction mechanisms and kinetics may be similar: the ozonation of phenanthrene and 1,1-diphenylethylene doped from the gas phase was reported to be accelerated at ice and artificial snow grain surfaces compared to liquid water surfaces (Kahan and Donaldson, 2008; Ray et al., 2011). Ozonation of solid films of aromatic compounds also proceeds much more quickly than ozonation of the monomer at the surface of water (Styler et al., 2011), which suggests that the acceleration observed on ice may be due to enhanced local concentrations. These reactions can generally be well described by classical heterogeneous surface chemistry reactions. Other examples are the halogen emissions from frozen sea ice solutions upon reaction with ozone or OH and the heterogeneous reaction of hypohalogenic with halogeneous acids as recently discussed in detail (Abbatt et al., 2012). The heterogeneous photolysis of inorganic species such as NO_2 has been investigated in the presence of humic substances and proxies for these species. These reactions are likely due to energy transfer from the humic substance to the reagent on the ice surface (Bartels-Rausch et al., 2010). In that study it was found that at low total concentrations of organics in the ice sample, the observed rate scaled linearly with concentration of organics and extrapolation of observed rates to experiments on pure organic films showed good agreement, indicating that the reactivity in ice was very similar to that on pure films. At intermediate concentrations of humic acids in the ice film this linear correlation broke, which was explained by agglomeration effects that reduced the amount of organics accessible to the gas phase NO_2. Some differences in heterogeneous reaction rates at ice and water surfaces are not easily described by known reaction mechanisms. For example, hydroxyl radicals were reported to react less efficiently with aromatic compounds at ice surfaces compared to at liquid water surfaces or bulk ice (Kahan et al., 2010b).

While increased photolysis efficiencies of aromatic compounds such as benzene and naphthalene may be due to red-shifts in the absorption spectra of their dimers at ice surfaces (Kahan and Donaldson, 2007, 2008), accelerated photolysis kinetics of other aromatic compounds at ice surfaces such as anthracene and harmine cannot be explained by this (Kahan and Donaldson, 2007; Kahan et al., 2010a). Although these compounds aggregate at ice surfaces, the absorption spectra are not significantly red-shifted on ice compared to in aqueous solution (Kahan and Donaldson, 2007; Kahan et al., 2010a). Under the same experimental conditions, anthracene photolysis in bulk ice proceeded at the same apparent rate as in aqueous solution (Kahan et al., 2010c). The observed rates were independent of temperature between 274 and 297 K in aqueous solution, and between 271 and 257 K on the ice surface (Kahan and Donaldson, 2007). This suggests that a simple temperature dependence or concentration effect cannot explain different reactivity observed at the surface compared to in aqueous solution, and that faster photolysis at ice surfaces is due to different physicochemical properties of the ice surface compared to liquid water. Similarly, the absorption spectra of inorganic acids have been found to be different on ice, compared to in aqueous solution, making the adsorbed species more susceptible to photodissociation, as discussed in Abbatt et al. (2012).

4.2.5 Reactivity at disordered interfaces

The presence of brine significantly accelerates observed reaction efficiencies. The question arises as to whether the rates are also influenced by the surface disorder. McNeill et al. (2006, 2007) found that the apparent reaction rate of HCl with $ClONO_2$ was greatly enhanced when the system was operated at conditions where surface disordering was observed relative to conditions for which no disordering was detected by ellipsometry. Doping with HCl has induced an increased surface disorder at temperatures as low as 200 K. Kahan and Donaldson (2007) did not observe different apparent photolysis rates of anthracene in the temperature range of 271 to 257 K on the ice surface. As the disorder increases significantly over that temperature range (Sect. 2.3), this result implies that the disordered interface has little influence on the photolysis of such insoluble species. For other species, it was argued that liquid-like properties of the disordered interface promote or facilitate heterogeneous reactions. An example is the reaction of SO_2 with H_2O_2 where it was shown that the reaction proceeded via hydrolysis of SO_2 on the ice surface (Clegg and Abbatt, 2001).

4.3 Chemical processes in models

Models that include a description of the complex snow-pack chemistry have recently been developed. Despite progress this is still an emerging topic of research in which rapid developments are likely to occur. Specifically, recently models have been developed with the goal to simulate the impact of chemistry in snow on the chemical composition of the boundary layer air (Michalowski et al., 2000; Boxe and Saiz-Lopez, 2008; Thomas et al., 2011). Central to these models is that all chemical reactions are parameterized to occur in a liquid environment that is in contact with air. For example, measured liquid rate constants and Henry's law constants are applied to a liquid fraction of the snow volume and used to approximate the behaviour of the snow-pack. Such an approach allowed using knowledge from liquid aerosol models to develop snow-chemistry models. It was further motivated by early laboratory work that showed the behaviour of some chemicals in frozen samples may be approximated by treating them analogue to solvated species (Sect. 4.2.2). An example is nitrate photolysis (Dubowski et al., 2002; Chu and Anastasio, 2003; Jacobi et al., 2006; Matykiewiczová et al., 2007b). Often, the existence of the surface disorder with liquid-like properties is used to justify and generalize this approach. This assumption is certainly an over-simplification at temperatures below the freezing point (Sects. 2.3 and 3.3.1). Clearly, the majority of chemical systems studied so far in ice samples show a distinctly different behaviour than that seen in liquid probes so that a general use of aqueous phase chemistry may be questioned (Sect. 4.2). However, it is also clear that liquid might be present in surface snow at environmental conditions (Sect. 3.4) and for those instances chemical transformations might be well captured by this model approach.

The main aim of this chapter is thus to show how well these models including liquid phase mechanisms can capture observed fluxes and/or concentrations of trace gases measured above the snow-pack. These models can thus be used to evaluate if snow-pack chemistry alone can produce elevated concentrations of, for example, bromine monoxide. Treatment of photochemistry in surface snow and ice has focused on halogens and nitrate due to the laboratory and field studies that clearly show that both reactive halogens and nitrogen oxides are emitted from irradiated snow and ice.

The first study integrating simplified chemistry in a 1-D snow model was presented by Liao and Tan (2008) and aimed to simulate the formation of HONO in the snow during a 6-day period at South Pole using prescribed and constant concentrations of nitrate and nitrite. The chemical reactions included the photolysis of NO_3^- assumed to form directly HONO and the photolysis of HONO as its only sink. Subsequently, photolysis rates were calculated based on the simulated spectral actinic fluxes within the porous snow-pack. Due to the fast photolysis of HONO in the surface layers this region did not contribute to a net production of HONO in the snow. Only with the increased vertical transport due to wind-pumping the HONO produced in the deeper layers could efficiently be transported to the surface and into the atmosphere. Overall, the photolysis of nitrate remained smaller than the HONO loss to the atmosphere. Obviously, the simplified parameterization of snow chemistry as done in this model is not adequately describing the observations. For example, an additional source of HONO would be needed to close the reactive nitrogen budget. However, the simulation is based only on a few, selected reactions and model results have not been constrained by observations, which hampers deriving firm conclusions. The results were highly sensitive regarding the pH, the volume of the liquid fraction, and the initial NO_2^- concentration.

Earlier work using a multi-phase box model focused on halogen activation and ozone depletion events in the coastal Arctic (Michalowski et al., 2000). The boundary layer was modelled using aerosol and gas phase chemistry including 16 reactions related to the activation of reactive bromine and chlorine species. Snow and aerosol chemistry included 16 reactions related to the activation of reactive bromine and chlorine species. The free troposphere was treated as an ozone reservoir, with downward mixing of ozone to the boundary layer. The four model components (liquid fraction in snow, boundary layer gas phase, aerosols, and free troposphere) were in contact using transfer coefficients. For the exchange between the boundary layer and the liquid fraction in the snow, transfer functions for HOBr, HOCl, HBr, HCl, and O_3 were chosen in the range of dry deposition velocities to the snow surface. The release of volatile species from the liquid fraction of the snow back to the boundary layer occurred via two steps from the liquid to the interstitial air and from there to the boundary layer. First order rate coefficients for transfer of molecular halogen species (Br_2, Cl_2, and BrCl) from the interstitial air to the boundary layer were also chosen similar to the dry deposition velocities. Using the boundary layer height and the snow-pack depth along with the transfer coefficients, the rate of mixing between the interstitial air and boundary layer gas phase volume was determined. This model showed for the first time emissions of halogens from the surface snow could induce a complete ozone depletion event. The predicted ozone depletion event was five days after model initialization. The study indicated the important role of atmospheric particles in contributing to ozone depletion, because removing particles delayed the onset of the ozone depletion event by two days. The model further showed that without the influence of the snow-pack, no ozone depletion was predicted. In particular this work demonstrated that the concept to restrict chemistry in the snow-pack to a liquid fraction, given that all ions were concentrated in this volume, gave reasonable results for typical coastal Arctic conditions. The sensitivity of model results to the volume of the liquid fraction showed that increasing the volume decreases concentrations and slows the release of halogens. Choosing an appropriate volume of the liquid fraction that represents natural snow reasonably is an obstacle in models and often the choice is based on thicknesses of the disordered interface observed at the relevant temperatures. This is problematic, also because measurements do not give a consistent picture yet (Sect. 2.3.2) and this parameter needs thus to be assumed so that simulation results match observations. At temperatures close to the melting point, melting point depression by impurities and geometric constrains might be used. At lower temperatures, models often use the thickness of the disordered interface, which by itself is not well known (Sect. 2.3.2). Interestingly, a recent re-run of a specific nitrate snow-chemistry model where the liquid fraction was reduced by a factor of up to 100 showed that the overall results were surprisingly robust and only slightly sensitive to the assumed volume of the liquid fraction, when other parameters – such as solubility limits – were accounted for and concentrations adjusted (Bock and Jacobi, 2010; Jacobi, 2011).

Using an approach similar to Michalowski et al. (2000), Boxe and Saiz-Lopez (2008) used a 0-D multi-phase model to study NO_x emissions to the boundary layer resulting from photolysis of nitrate (NO_3) and nitrite (NO_2) impurities in snow. In order to calculate volume fluxes (a surface flux distributed throughout the boundary layer) the model also utilized a volumetric factor (1.22×10^3) which they described as a reaction rate enhancement factor. The calculated fluxes from the 0-D model were then used in a 1-D model to predict the NO and NO_2 vertical profiles as a function of height above the snow-pack. While this study did not include a description of snow physics, the volume fluxes predicted from the model are in good agreement with prior work in Antarctic (Jones et al., 2011) and provided an initial step towards understanding the feasibility of predicting the measured fluxes using a model.

The first full 1-D model of air–snow interactions was presented by Thomas et al. (2011, 2012). While simple in the representation of snow physics (no accumulation or physical transformations in the snow-pack were taken into account during the three day period) this model included the most chemically sophisticated and physically reasonable model of air–snow interactions involving NO_x to date. The model was used to understand both NO and BrO measurements at Summit, Greenland during a three-day focus period with consistent meteorological conditions during summer 2008. For the purposes of their study, Thomas et al. (2011) used primarily aqueous phase chemistry to describe the liquid layer and varied the initial HNO_3 concentrations in the liquid volume so that the model results matched measured NO concentrations in the boundary layer. The remaining fraction of nitrate was treated as unavailable for photochemistry. This was motivated, in part, by an observed fractionation of nitrate between the ice surface and interior reservoirs in a recent laboratory study (Wren and Donaldson, 2011). If nitrate, in fact, is more concentrated in the liquid layer, then it is possible that nitrate reacts via different pathways in environmental snow, for example with precipitates or with organics. For halogens, this study included all of the measured halide ions in melted surface snow (Br and Cl) in the reactive liquid volume. HCHO and H_2O_2 were initialized according to their aqueous Henry's law equilibrium concentrations. Mass transfer was treated according to Schwartz (1986), therefore including diffusion limited Henry's law equilibrium to the liquid fraction and the interstitial air. Photochemistry in the atmosphere was treated using a 4-stream radiative transfer code, in the snow-pack photolysis rates varied with depth according to measured e-folding depth for nitrate at Summit. This study showed that reactions in the liquid layer followed by transfer to the interstitial air and venting of the snow-pack (by wind pumping and diffusion) can explain the levels of NO and BrO measured at Summit. However, it required the assumption that all of the nitrate is not available for photolysis in order to match observations. This indicates that either chemical rates in the snow are indeed different from chemistry in the liquid, or that nitrate preferentially does not accumulate in the liquid fraction of snow. Other possibilities are the use of other aqueous phase parameters, such as Henry law's constant and acid–base equilibrium, or the location of the reactive liquid. Further work on appropriate parameterizations and representation of snow chemistry in models is clearly needed to clarify the uncertainty associated with how these processes are represented.

4.4 Conclusions about of chemistry

Chemistry in ice and at ice surfaces under conditions relevant to the troposphere is a relatively new area of study. The experiments discussed above reflect the complexity of ice and snow as host for chemical reactions. Nevertheless, important insight into the chemical fate of atmospheric species in frozen aqueous media can be summarized as follows.

1. A very important factor affecting the apparent rate of chemical reaction in environmental ices is the presence of liquid water. Many chemical reactions investigated so far proceed more efficiently in the presence of a liquid phase as compared to the totally frozen ice matrix. In particular, the freeze-concentration effect results in significant acceleration of observed rates. This is of importance for a number of reactive systems because reactions that are negligible in the liquid phase may become important in ice systems due to increased concentrations and, on occasion, freeze-potential effects. Aqueous kinetics describe the concentration-dependent chemistry well. This has been shown for heterogeneous reactions such as bromide ozonation, as well as for reactions that occur within bulk regions of ice such as microveins and pockets. Variables such as temperature and total solute concentration will determine the liquid content of the ice and the reagent concentrations, and thus the observed reaction rates. This underlines the importance of identifying the presence of liquid or brine in laboratory ice samples and in ice in environmental settings.

2. Some reactions were found to be moderately accelerated in completely frozen samples compared to in unfrozen samples. By analogy with the

freeze-concentration effect, the higher apparent rates can be understood as a consequence of high local reagent concentrations. Other types of reactions have been found to proceed with similar or even reduced apparent rates in ice compared to the liquid phase. This shows that factors other than local concentration can influence the observed reactivity. Changes in mechanism, local chemical environment, and the local physical environment have been discussed, but more studies are needed to develop a quantitative understanding of chemistry in ice.

3. Unimolecular reactions such as direct photolysis show similar quantum yields and reaction rates in ice as in aqueous solution. Parameterizing these reactions based on aqueous phase reaction rates might thus be justified.
4. Chemistry at the ice surface has been found to be uniquely different from that in the bulk phase. At ice surfaces, the photolysis rates of some species are enhanced compared to in aqueous solution or bulk ice. In these instances, parameterization based on aqueous-phase chemistry is not appropriate. First-order heterogeneous rate coefficients specific to ice surfaces should be used. Unfortunately, only a few rate coefficients for reactions at ice surfaces have been measured: this is an area of research in need of attention. How the surface disorder that occurs naturally on ice crystals or that can be induced by impurities affects chemistry is an important outstanding issue.

As is the case for many areas of environmental study, the measurement of reaction kinetics and products at environmentally-relevant reagent concentrations is technically challenging. As analytical techniques gain sensitivity, revisiting important reactions at environmentally-relevant reagent concentrations will provide links between laboratory experiments and field observations. Despite the challenges involved, these advances are essential for developing correct descriptions of environmental processes used in models. All existing models including reactive chemistry strongly simplify the snow physics. The snow-pack is represented by static conditions and snow density, temperature, and specific surface area are held constant. Reactive species are localized in a liquid environment with a constant volume that takes concentration enhancements due to the reduced volume of this liquid fraction into account. A similar approach has been used to reproduce laboratory experiments investigating the photolysis of nitrate in snow (Honrath et al., 2000; Dubowski et al., 2002; Jacobi and Hilker, 2007; Bock and Jacobi, 2010; Jacobi, 2011). Over time the applied chemical mechanisms have been upgraded from very simplified mechanisms as presented Liao and Tan (2008) to the most advanced model to date presented by Thomas et al. (2011) who extended an existing atmospheric 1-D chemistry model including gas phase, aqueous phase, and heterogeneous chemistry using additional layers to represent chemical processes in the snow. Nevertheless, a full representation of the distinct compartments (bulk ice, grain boundaries, ice surface, liquid brine, solid precipitates, disordered interface) and the different physico-chemical processes has yet not been attempted, in part due to the difficulty in treating the non-equilibrium chemical processes in these complex environments. Significant developments in modelling these processes will be needed in the future, but will require continued close cooperation between laboratory scientists, measurement campaigns, and a corresponding development of an inter-disciplinary model community capable of including these complex physical-chemical processes in models.

5 Synthesis

Snow and ice are of great interest in a number of scientific disciplines ranging from fundamental materials science to applied environmental science (Bartels-Rausch et al., 2012). In this review, we focus on atmospheric and cryospheric sciences of the polar regions, where chemistry and physical processes in snow and ice have a far ranging environmental impact (Grannas et al., 2012). The focus was placed on studies characterizing the snow and ice structure down to a molecular level and which describe physical processes and chemical reactivity. It was demonstrated that for the description of the chemical and physical processes snow-pack properties like structure and microphysical properties are crucial.

On a macroscopic scale density, grain shape and structure are important parameters for the description of chemical reactivity and physical processes. In many models, these physical properties have been assumed to be constant and were based on observations. Such an approach is reasonable if the simulations are restricted to shorter periods like several days and excluding fresh snow. However, even on this time scale the snow temperature undergoes variations linked to diurnal cycles in radiation or rapid changes in air temperatures. Recent advances in X-ray computed micro tomography have enabled us to observe the changes in the structure of a snow sample in situ under such temperature gradients. These studies have revealed huge water mass fluxes on time scales of days. An explicit description of the evolution of the temperature will be needed in future simulations on longer time scales (weeks to multi-annual cycles) and changes in the snow-pack properties due to metamorphism and compaction need to be considered.

Understanding and modelling chemistry in snow will remain difficult since our current knowledge of many crucial components is still very limited. For example, most of the described models including chemical reactions assume that these reactions take place in a liquid environment in the snow matrix (Michalowski et al., 2000; Boxe and Saiz-Lopez, 2008; Thomas et al., 2012). This approach seems well justified when liquid brine is present, as already small amounts of liquid can dominate the chemical reactivity, sintering, exchange of trace gases, and distribution of impurities. Temperature induced thaw-freeze cycles occur frequently in the Arctic environment. Furthermore, ionic and non-soluble organic impurities that are always present in natural snow in variable amounts tend to be excluded from the solid matrix forming brine also present at the crystal surfaces or junctions. Some experiments indicated that the volume of and the concentrations in such a brine fraction can be deduced assuming a simple thermodynamic equilibrium approach using ideal behaviour of the solutes (Cho et al., 2002). Therefore, such an approach has been used by Boxe and Saiz-Lopez (2008) and during further studies based on laboratory experiments (Jacobi and Hilker, 2007; Bock and Jacobi, 2010; Jacobi, 2011) to define a liquid fraction and initial concentrations of the reactants. A recent study refined this approach taking into account the non-ideal behaviour of the solutes in the highly concentrated brine (Kuo et al., 2011) leading to a better agreement with previous laboratory experiments. While thermodynamics predict the concentration of brine for a given amount of impurities in a snow sample, uncertainties with this approach stem from unpredictable fractionation of impurities between the brine and bulk ice phase. For example, Thomas et al. (2012) found best agreement between simulations and observations if a fraction of only 6 % of the measured nitrate in the snow was present at the surface of the snow crystals. However, it remains unclear if a similar fractionation of nitrate can also be applied to a snow-pack with different nitrate or sea salt concentrations or at different temperatures. During freezing impurities can be expelled from the growing ice and from brine at the crystal surface or be captured by micro-pockets in the growing bulk of the ice. In the laboratory, freezing processes have recently been well controlled in some experiments leading to very reproducible fractionation, however uncertainties due to impurity specific effects and uncontrolled freezing conditions remain.

In the field, dynamic redistributions of the liquid phase add to the uncertainty. The partitioning also needs to be considered if concentrations in the liquid fraction are deduced from snow concentrations in melted samples because the observations include the impurities present in all compartments of the condensed phase including a potentially important fraction absorbed at the surface of the snow grains or dissolved in the bulk solid of the snow crystals. So, potentially, only a small fraction of the total impurity content is in contact with the gas phase. Further, reaction rates and pathways have been found to differ between those locations. It is thus of high priority to determine the amount of liquid in surface snow under environmental conditions. Currently it is not possible to observe liquid within the porous snow-pack, but new developments in micro-tomography might facilitate this in future.

In principle, this thermodynamic approach holds only down to the temperature of the eutectic point, at which all components form a solid phase. Nevertheless, a concentrated liquid fraction has been observed well below the eutectic temperature of a bulk ice sample (Cho et al., 2002). Surface sensitive spectroscopy, on the other hand, gave no indication of liquid below the eutectic (Křepelová et al., 2010a). Possibly, the liquid observed in the bulk sample was located in nm-sized micropoktes. Just as in small aerosol droplets, freezing might be inhibited by steric reasons in such small confinements. Precise knowledge of the location of impurities is thus important and a unifying theory describing the liquid fraction of ice covering the range of temperatures and impurity concentrations observed in natural snow still needs to be developed. Below the freezing temperature of the system, such an approach is based on the existence of a disordered interface on ice with properties similar to liquid water. This very simplified picture to describe the disordered interface has been used successfully in thermodynamic frameworks, and is somehow supported by water diffusion measurements on ice surfaces. Also MD simulations indicate that in a very thick disordered interface the upper part has structural features approaching those of a supercooled liquid. However, describing the surface disorder as a homogeneous liquid-like phase contradicts direct observations showing distinct structural differences between the disordered interface and a liquid phase. Further, the properties of such a layer such as thickness and volume and their dependence on temperature remain ill defined. However most studies on pure ice indicate that the disordered interface remains rather thin with structural features highly influenced by the underlying solid crystal. This, and the high concentration of impurities in the field make this disordered interface less relevant for understanding snow chemistry in polar regions. It is clear that impurities increase the thickness of the disordered layer. Recent simulations and direct observations however show a more complex picture, where impurities can induce formation of a hydration shell in their vicinity. This means that the impurity experiences an environment similar to an aqueous solution even when the disorder interface is very thin and that the molecular structure at the ice surface may be very very heterogeneous. Further studies are needed for a larger set of impurities and with different methods. How the local disorder induced by some impurities influence the uptake, distribution and chemistry of other impurities is an essential open issue. Approaching the melting point, the lack of knowledge of the surface disorder even increases, as the number of studies investigating the surface disorder and its effects just below the melting point are limited.

It is generally assumed that no reactions take place in the solid phase of the snow grains due to the reduced mobility of the products or because these reactions are too slow. Nevertheless, this portion can constitute an important reservoir for reactive species like H_2O_2 and possibly also for nitrate. In these cases, adsorption, desorption and solid state diffusion need to be considered for the successful modelling of concentration profiles in snow, firn, and ice on longer time (Hutterli et al., 2003).

6 Outlook

Previous modelling attempts in snow chemistry have addressed specific questions such as the conservation of H_2O_2 and HCHO in snow, firn, and ice or the release of reactive species from the snow-pack to the atmosphere. The objectives of the respective studies have determined the degree of the complexity of the physical and chemical parts of the snow models: simulation of snow and firn profiles of H_2O_2 and HCHO have emphasized the role of long-term physical and meteorological processes (e.g. accumulation, compaction, exchange between the gas phase and the bulk solid), while the studies of the nitrate photolysis concentrated on a sophisticated representation of fast chemical processes and the transport in the firn air. So far neither of the models has included fully coupled snow physics and chemistry in which the physical properties of the snow-pack and its changes over time were fully simulated to deliver a consistent frame for the modelling of the chemical processes in the snow-pack.

Nevertheless, it is obvious that for the description of the chemical processes including photochemical reactions, adsorption and desorption on the grain surfaces, diffusion inside the grains, and transport in the interstitial air physical snow properties like temperature, density, grain shape and structure are crucial. In many models, the physical properties have been assumed to be constant and were based on observations. Such an approach is reasonable for the structural parameters like density and grain shape if the simulations are restricted to shorter periods like several days and excluding fresh snow. However, even on this time scale the snow temperature undergoes variations linked to diurnal cycles in radiation or rapid changes in the air temperatures, so that an explicit description of the evolution of the temperature will be needed. For observations on longer time scales (weeks to multi-annual cycles), changes in the snow-pack properties due to metamorphism and compaction need to be considered. Moreover, the accumulation, its rate and timing become important factors determining the direct input and the release of volatile impurities to the snow in the case of H_2O_2 and HCHO (Hutterli et al., 2003). Furthermore, even in polar regions fresh snow can undergo rapid changes contributing to an enhancement of the release of incorporated, but volatile species like HCHO (Jacobi et al., 2002). Snow physics models with varying complexities exists and a model like SNTHERM or the firn air model (Schwander, 1989) was used in previous studies to deliver the snow temperature profiles (McConnell et al., 1998) or the firn air diffusivities (Hutterli et al., 1999). The most complex 1-D snow models existing today incorporate major physical processes in the snow including metamorphism schemes to reproduce the development of snow properties (Brun et al., 1989; Bartelt and Lehning, 2002; Lehning et al., 2002). Although these models were developed to contribute to the forecasting of avalanches in the Alps, further studies have shown their general applicability also to other snow-pack types (e.g. Lejeune et al., 2007; Jacobi et al., 2010) and even to the simulation of snow-pack properties on the top of the large ice sheets (Genthon et al., 2001; Brun et al., 2011). Further parameters, normally not included in snow physics models, but important for the modelling of chemical process like the specific surface area have recently been implemented and validated (Jacobi et al., 2010). The physical snow models are driven by meteorological data either from observations or from other model results. Although the existing snow physics models still contain simplified parameterization of important processes (e.g.

Etchevers et al., 2004) and need to be developed further, such models can constitute a useful physical frame for the simulation of chemical processes in the snow in a 1-D model on different time scales.

This most sophisticated representation of chemical process in a model was based on the use of an atmospheric chemistry model including equilibria between the gas phase and the condensed phase, chemical reactions in the aqueous phase and heterogeneous reactions as typical for aerosols. The adjustment to the specific conditions in the snow-pack was limited to an estimate of the volume of the liquid fraction as reactive compartment for the aqueous phase chemical reactions together with the corresponding enhancement of the concentrations and a fraction of nitrate between the bulk solid and the liquid fraction. However, a full representation of the distinct compartments in the condensed phase is still missing. Although the now available measurements and parameterization presented in this review may help to design a chemistry module to capture important chemical processes, the most crucial point in the near future probably remains the simulation of the liquid fraction in the snow and the distribution of the reactive species between the different compartments like bulk solid, liquid, and ice surface.

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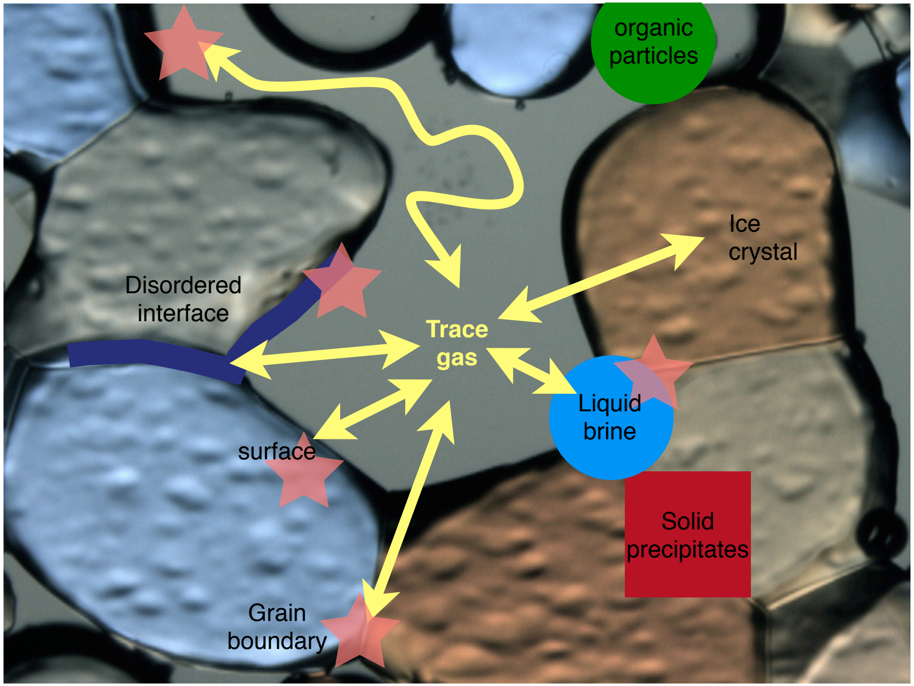


Fig. 1. Illustration of the multi-phase structure of snow. The background image shows an approximately 1mm wide picture of a thin section of alpine snow as seen under a polarized microscope (courtesy of F. Riche and M. Schneebeli, copyright by WSL SLF Davos). The yellow arrows illustrate processes such as adsorption and diffusion through which trace gases may interact with the individual structural features of snow. Pink stars indicate location where reactions might occur. Organic particles are present in snow, but are not further considered in this review.

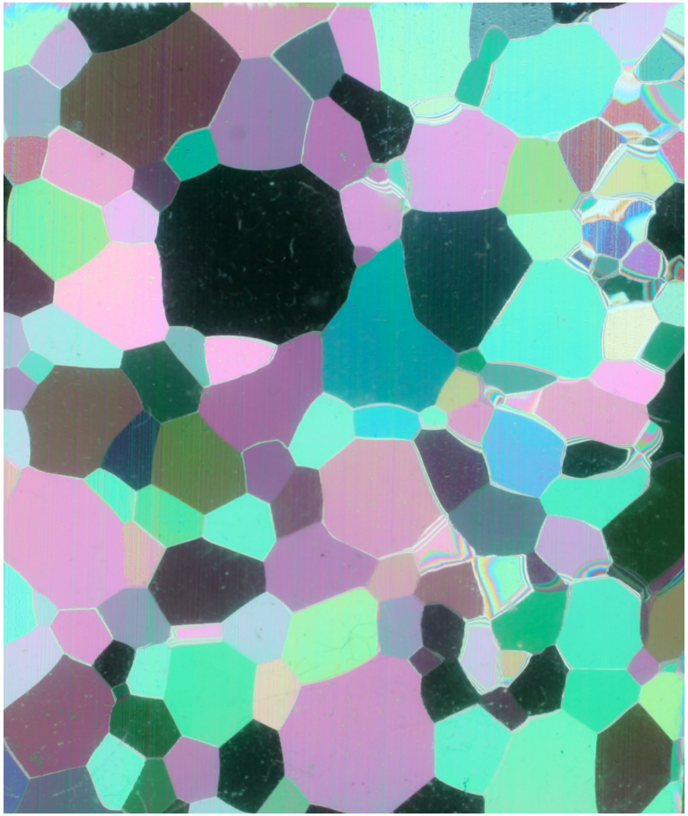


Fig. 2. Microscope image displaying individual ice grains. This optical image was taken from a thin section of ice viewed under polarized light. The individual grains are visible due to their different optical orientation (from Blackford, 2007).

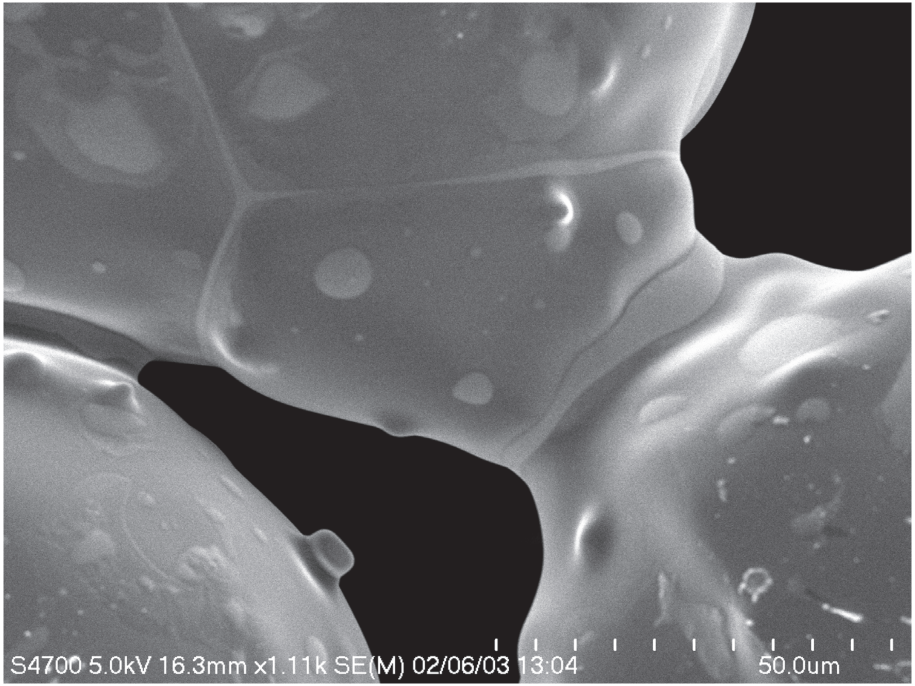


Fig. 3. Low temperature scanning electron microscopy image of ice particles containing salt. The lighter grey regions along grain boundaries and as isolated patches are NaCl $2H_2O$. The darker grey areas show ice (Blackford et al., 2007).

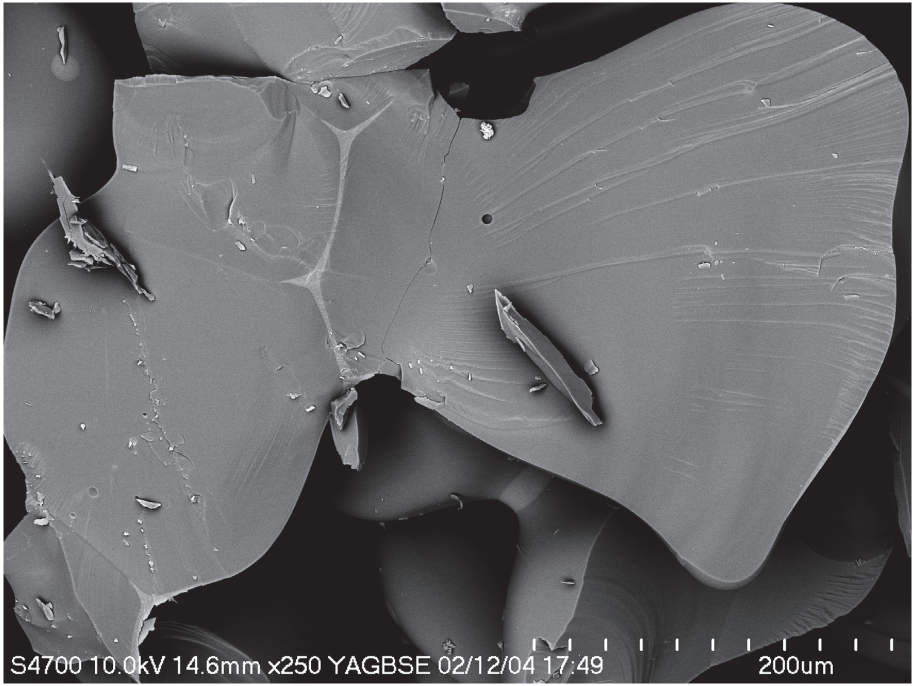


Fig. 4. Low temperature scanning electron microscopy image of fractured ice particles containing salt. Dihedral angle in ice (dark grey) containing salt (light grey) are clearly visible (Blackford et al., 2007).

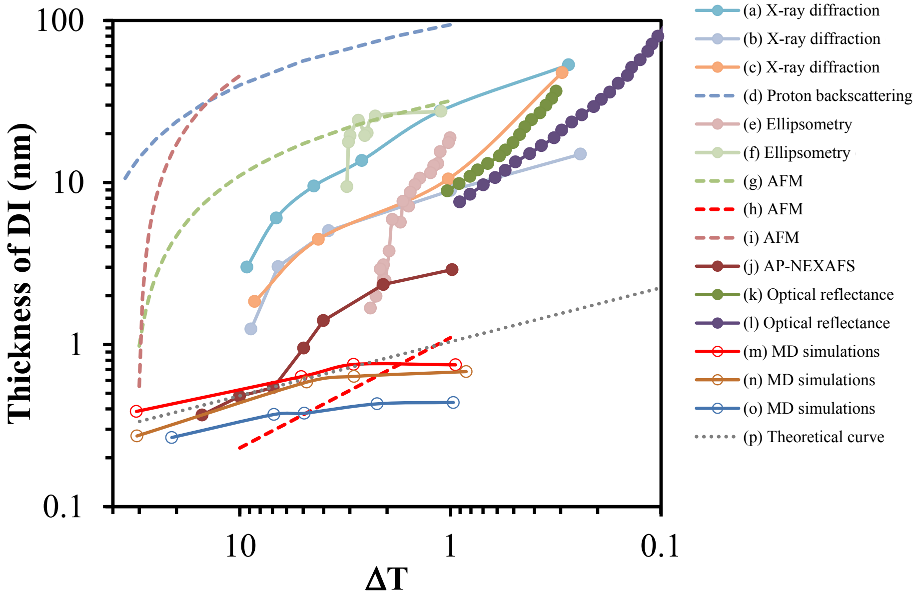
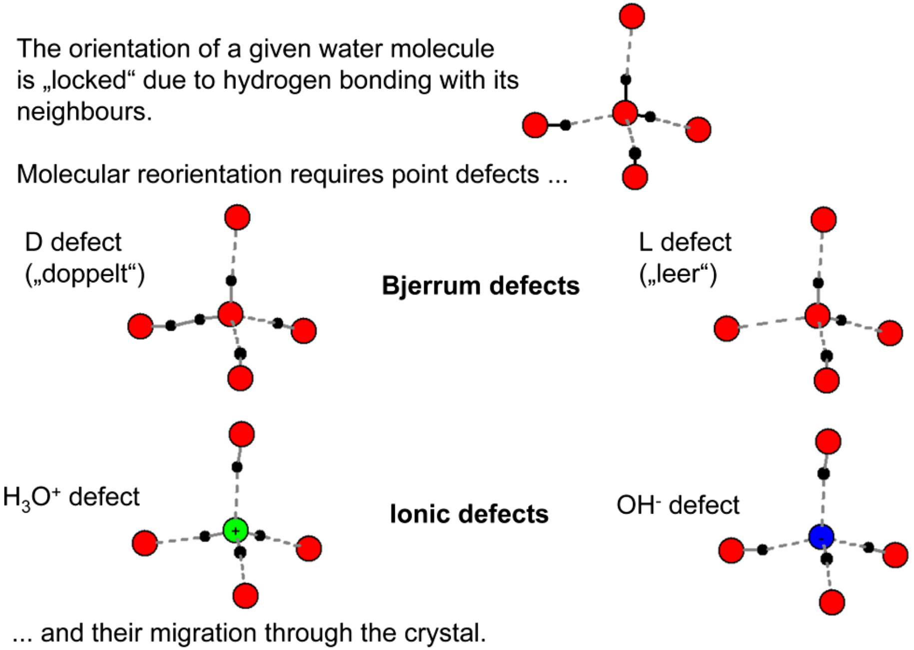


Fig. 5. Comparison of different methods to derive the thickness of the disordered interface (DI) at the free ice surface versus $\Delta T = T_\mathrm{m} - T$. Solid circles are measured data, while dashed lines are results from reported equations fit to experimental data. Molecular dynamics (MD) simulations are represented by open circles. Glancing angle X-ray diffraction (Dosch et al., 1995) on (a) basal and (b, c) prismatic crystal surfaces, (d) proton backscattering (Golecki and Jaccard, 1978) on basal ice, ellipsometry (Furukawa and Nada, 1997) on (e) basal and (f) prismatic, (g) atomic force microscopy (AFM) (Döppenschmidt and Butt, 2000) on a 100 ml frozen droplet and vapour deposited on mica, (h) AFM (Pittenger et al., 2001) for vapour deposited ice on metal, (i) AFM (Goertz et al., 2009) for ice frozen on a metal substrate, (j) ambient pressure near-edge X-ray absorption fine structure (Bluhm et al., 2002) for vapour deposited ice on metal, HeNe laser optical reflectance (Elbaum et al., 1993) on basal crystals in the presence of (k) water vapour and (l) 30 Torr air, TIP4P/Ice MD simulations (Conde et al., 2008) on (m) basal and (n, o) prismatic crystals, (p) general thermodynamic solution (Dash et al., 2006).



The orientation of a given water molecule is „locked“ due to hydrogen bonding with its neighbours.

Molecular reorientation requires point defects ...

... and their migration through the crystal.

Fig. 6. Sketch of possible point defects in ice (Bartels-Rausch et al., 2012).

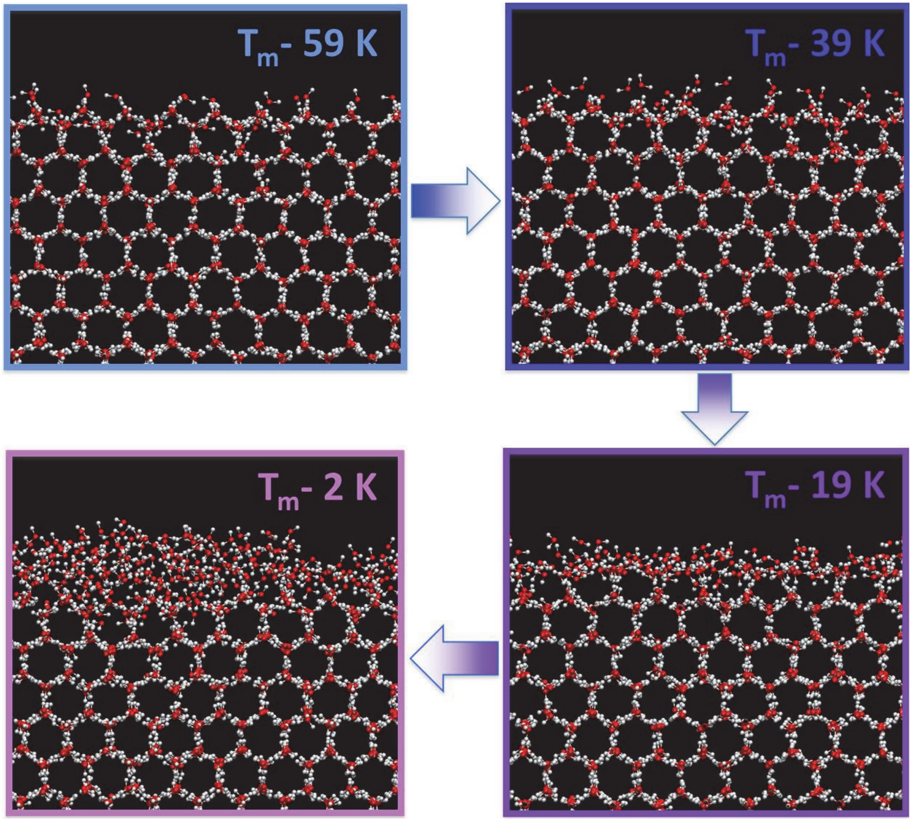


Fig. 7. Snapshots of the prismatic ice/vapour interface for selected simulations. These simulation temperatures correspond to undercooling of −59 K through −2 K relative to the melting point of the water model (NE6, T_m = 289 K) adapted from Gladich et al. (2011).