11th International Conference on the Physics and Chemistry of Ice (PCI-2006)

Bremerhaven, Germany, 23-28 July 2006

Abstracts

Edited by Frank Wilhelms and Werner F. Kuhs

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Preface

The 11th International Conference on the Physics and Chemistry of Ice (PCI-2006) took place in Bremerhaven, Germany, 23-28 July 2006. It was jointly organized by the *University of Göttingen* and the *Alfred-Wegener-Institute* (*AWI*), the main German institution for polar research. The attendance was higher than ever with 157 scientists from 20 nations highlighting the ever increasing interest in the various frozen forms of water. As the preceding conferences PCI-2006 was organized under the auspices of an International Scientific Committee. This committee was led for many years by John W. Glen and is chaired since 2002 by Stephen H. Kirby. Professor John W. Glen was honoured during PCI-2006 for his seminal contributions to the field of ice physics and his four decades of dedicated leadership of the International Conferences on the Physics and Chemistry of Ice. The members of the International Scientific Committee preparing PCI-2006 were J.Paul Devlin, John W. Glen, Takeo Hondoh, Stephen H. Kirby, Werner F. Kuhs, Norikazu Maeno, Victor F. Petrenko, Patricia L.M. Plummer, and John S. Tse; the final program was the responsibility of Werner F. Kuhs. The oral presentations were given in the premises of the *Deutsches Schiffahrtsmuse*um (*DSM*) a few meters away from the *Alfred-Wegener-Institute*. It was probably the hottest week of summer 2006 in Germany with all ice breaking and melting between participants in the social part of the conference, yet with solid and profound exchange in the cooler, pleasantly air-conditioned lecture hall hosting excellent presentations followed by rich and lively discussions. In the spirit of promoting the exchange between scientists from various fields of ice research no parallel sessions were organized. Thus every participant got a chance to follow the entire program – seemingly a success as indicated by the excellent attendance and expressed also in various feedbacks of participants. Ample room was given to poster presentations resulting in a lively exchange and accompanied by very welcome German beer – it was hot as I mentioned above. The poster prize was shared by Sebastian Schöder und Sergei Skiba – both of them receiving a copy of the book *Physics of Ice* signed by the authors Viktor F. Petrenko and Robert W. Whitworth, members of the prize committee.

Papers were collected during the conference for inclusion in a volume of Proceedings of the Royal Society of London, Series A. This volume presents the abstracts of all presentations. It may be useful here to give a list of the preceding conferences and their proceedings:

Erlenbach (Switzerland) 1962. Proceedings were not published.
Sapporo (Japan) 1966. *Physics of Snow and Ice* (Ed. H.Oura). International Conference on Low Temperature Science, Sapporo, August 14-19, 1966, Hokkaido University, Institute of Low Temperature Science, 1967 (712 pages).
München (Germany) 1968. *Physics of ice* (Eds. N.Riehl, B.Bullemer, H.Engelhardt), Proceedings of the International Symposium on Physics of Ice, Munich, September 9-14, 1968, Plenum Press, New York, 1969 (642 pages).
Ottawa (Canada) 1972. Physics and Chemistry of Ice (Eds. E.Whalley, S.J.Jones, L.W.Gold), Papers presented at the Symposium on the Physics and Chemistry of Ice, Ottawa, August 14-18, 1972, Royal Society of Canada, Ottawa, 1973 (403 pages).
Cambridge (England) 1977. Symposium on the Physics and Chemistry of Ice, Cambridge, September 12-16, 1977. Published in *Journal of Glaciology*, 1977, Vol.21 (714 pages).
Rolla (Missouri, USA) 1982. Sixth International Symposium on the Physics and Chemistry of Ice, Rolla, August 2-6, 1982. Published in *Journal of Physical Chemistry*, 1983, Vol.87(21), pp. 4015-4340.
Grenoble (France) 1986. VIIth Symposium on the Physics and Chemistry of Ice, Grenoble, September 1-5, 1986. Published in *Journal de Physique*, 1987, Vol.48(3), Supplément Colloque N°1, (707 pages).
Sapporo (Japan) 1991. *Physics and Chemistry of Ice* (Eds. N.Maeno, T.Hondoh). Proceedings of the International Symposium on the Physics and Chemistry of Ice, Sapporo, September 1-6, 1991, Hokkaido University Press, Sapporo, Japan, 1992 (516 pages).
Hanover (New Hampshire, USA) 1996. Physics and Chemistry of Ice, Hanover, August 27-31, 1996. Published in *Journal of Physical Chemistry B*, 1997, Vol.101(32), pp. 6079-6312.
St. John’s (Canada) 2002. 10th International Conference on the Physics and Chemistry of Ice, St. John’s, July 14-19, 2002. Published in Canadian Journal of Physics, 2003, Vol.81(1/2), pp.1-544.

A good review of the scope of this series of conferences (prior to 1996) is found in an article by John W.Glen in Journal of Physical Chemistry B 101 (1997) 6079-6081. The richness of topics and disciplines in the wide field of physics and chemistry of ice is reflected therein. PCI-2006 certainly has confirmed this aspect and has reinforced the beneficial presence of biology and snow research. The ever larger and wider audience suggests that this series of ice conferences is as young as 40 years ago. During the meeting in Bremerhaven the International Scientific Committee has agreed on the location of the next conference – it will be organized in Sapporo in 2010 by our Japanese colleagues lead by Takeo Hondoh.

Göttingen and Bremerhaven, December 2006

Werner F. Kuhs and Frank Wilhelms

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Photograph: H. Grobe

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Acknowledgements

The organizers of this conference are very grateful to Ines Ringel (Göttingen) who had to carry the burden of handling the submitted abstracts, papers and referees' comments as well as to deal with numerous requests of the participants, authors and referees. Her professional skill, personal dedication and friendly manner were crucial for the success of this conference.

Crucial financial support was obtained from the Deutsche Forschungsgemeinschaft (DFG) and the City of Bremerhaven, the AWI and the GZG/University of Göttingen with further contributions from the DSM, the Historical Museum of Bremerhaven, RCOM/University of Bremen, bremenports GmbH & Co KG, and the Deutsche Gesellschaft für Polarforschung e.V.

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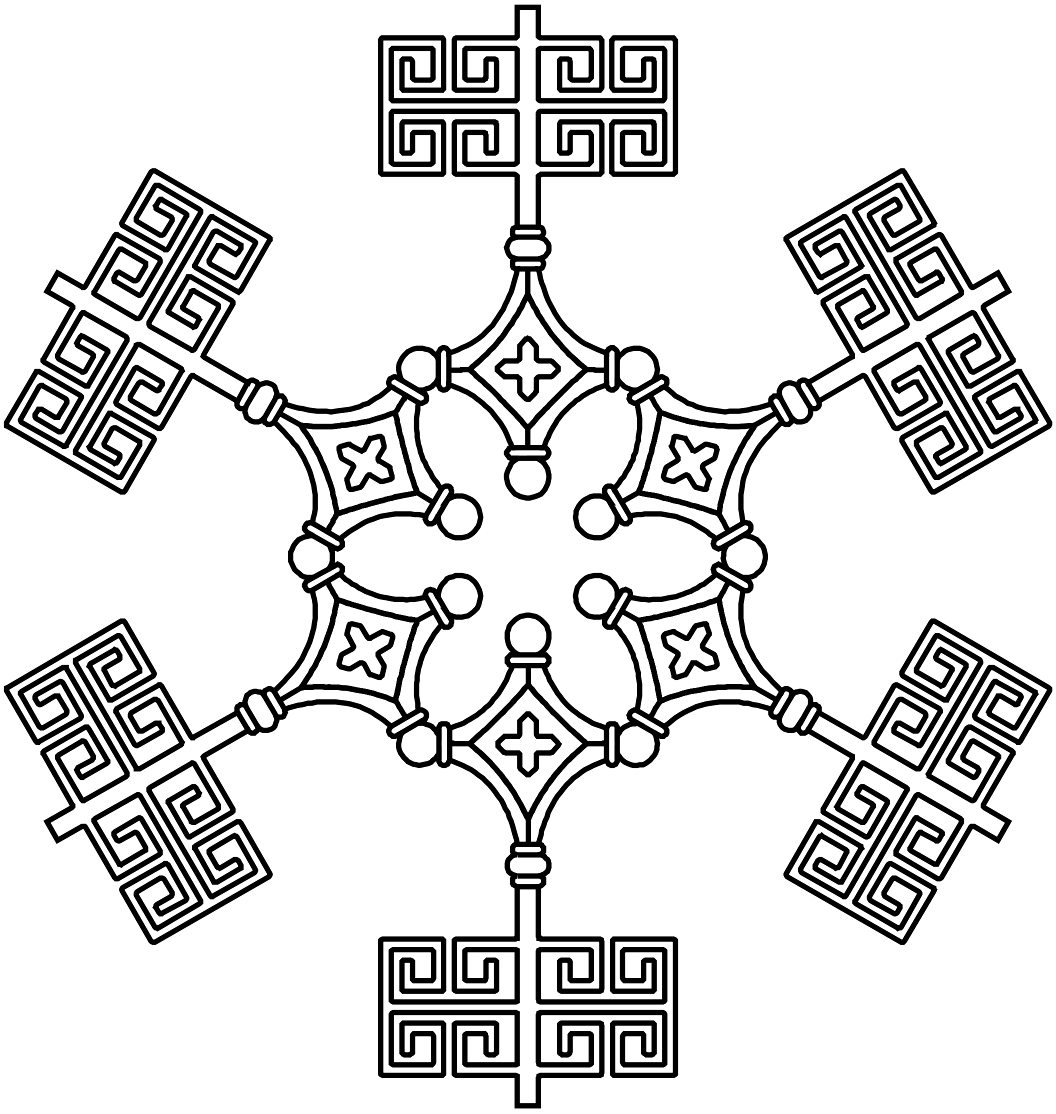
DGP

Ice in biology and transport properties

Chair: T. Hondoh



Monday 09:15 am - 10:00 am **O001 (invited)**

Selection for ´ice resistance´, antifreeze proteins and ice or hydrate inhibition

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Some organisms adapt to winter conditions or polar climates and the consequent threat of cellular damage associated with ice growth by the production of antifreeze proteins (AFPs), which adsorb to the surface of microscopic ice crystals and result in noncolligative freezing point depression. At temperatures close to melting, they also hinder ice recrystallization (IR). As well, AFPs adsorb to hydrates, changing the octahedral morphology and inhibiting growth [1]. AFPs have been isolated and characterized from a variety of species including fish, insects, plants and bacteria, and although these proteins have been known for over 30 years [2], it is remarkable that we still do not fully appreciate their biological role. Some structure-function studies have been hampered by the difficulty of obtaining sufficient active protein from the expression of recombinant versions of cloned AFPs in the bacterium, E. coli. In order to address these problems, we sought microorganisms with the ability to produce active AFPs, either introduced using molecular tools or encoded by endogenous sequences. Previously, expeditions have been launched to polar regions with the express purpose of identifying novel microbes with antifreeze activities, but our research budget was more modest. As a result, we have devised two powerful selective regimes, freeze-thaw resistance and ice affinity, which have enabled us to identify microbes with ice-active molecules from our own "backyard". A novel cryocycler [3] subjected soil cultures to multiple freeze-thaw cycles and although overall microbial population complexity was drastically reduced, selected cultures proved to be more than 1000-fold more freeze-thaw tolerant than the original consortium. One of these inhibited IR. A second selective regime, that of ice-affinity selection, allowed the identification of microbes showing three classes of ice-active properties; IR inhibition, ice nucleation and ice-shaping activities. Some of the ‘ice-resistant’ microbes obtained from the selective regimes appeared to have some affect on a model hydrate, strengthening our contention that molecular properties important for ice adsorption may overlap with those for hydrate inhibition. As well, since these resistant microbes are readily obtainable, the development of this equipment to select for these rare, but most interesting bacterial species offers hope that insights into the overwintering survival of communities may also come from these studies.

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Properties of water around antifreeze proteins from atomistic simulations

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Antifreeze proteins are found in insects[1] and fishes[2] which inhabit cold environments and function by adsorbing to the surface of small ice crystals, thereby preventing further growth. In many cases, the putative ice-binding face(s) have been identified by mutation studies and molecular modeling.

However, in almost all modeling studies, the protein is docked onto a perfect ice surface, whereas it is well-known that the ice-water interface is not clearly defined[3]. Based on results from mutagenesis experiments and simulations, it has previously been suggested that the protein itself assists in the formation of the binding site[4], a hypothesis strengthened by the observation of structural water molecules at the ice-binding surface of the protein in X-ray structures of antifreeze proteins from insects[5].

If this is the case, additional structuring of (liquid) water would be expected around the ice-binding site of the protein in solution.

Using atomistic molecular dynamics simulations of antifreeze proteins in (liquid) water at a range of temperatures and with different water models, we have investigated the structure and dynamics of the water molecules close to the protein. The role of the motion of protein side-chains in the observed dynamics was also assessed. Our results provide insight into the mechanism of protein-ice recognition at the molecular level and complement the existing wealth of experimental data available.

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Monday 10:25 am - 10:50 am **O003**

Diffusion, incorporation, and segregation of antifreeze proteins at the ice/solution interface

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Antifreeze proteins (AFPs) and glycoproteins (AFGPs) are found in nature in many cold weather organisms including fish, amphibians, plants and insects. These proteins suppress the freezing temperature of the blood serum in fish just enough to keep them from freezing in their supercooled environments and inhibit ice recrystallization enough to reduce damage in freeze tolerant organisms, making them essential for survival. A complete description of the AFGP/AFP surface interaction is lacking and is necessary to understand the mechanism. However, it is known that the surface molecules of ice are extremely mobile and that their behavior can change quite dramatically over a small range of temperatures. Here, the temperatures of interests are only a few degrees below the melting point, where ice is known to have an extensive surface melting or quasi-liquid layer (qll), that only augments the difficulty of directly probing an already complex system.

In the present work, we study ice crystal growth in AFGP and AFP solutions with phase contrast and fluorescence microscopy in a 2-d growth apparatus and in free solution growth under various conditions including microgravity. With fluorescence microscopy we have directly visualized the protein dynamics at the interface of a growing ice crystal. Contrary to previous understandings, the proteins become incorporated into brine veins and not directly into the crystal matrix. This indicates that the proteins only weakly adsorb to the interface. Under slower growth conditions no brine veins are present and the protein builds up at the interface of the growing ice crystal and the diffusion of the protein away from the interface can be directly visualized. Free-solution growth experiments show an anisotropic self-oscillatory growth mode of the steps and interface near the freezing temperature. We also confirmed an anisotropic enhancement of the growth rates under certain conditions as observed by Furukawa et al. Similar experiments carried out under the microgravity condition show the importance of heat dissipation from the growing interface. We will further discuss the implications of our results on the AFP/AFGP mechanism.

Monday 11:20 am - 11:45 am O004

Comparative proton activity at the surface and in the interior of ice nanocrystals: Isotopic exchange rates of D_2O isolated in H_2O ice particles

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The overlap within a cold condensation cell, of separate pulses of dilute D_2O and more concentrated H_2O vapors in helium carrier gas, results in the formation of cubic H_2O nanocrystals containing isolated D_2O molecules at substitutional sites. Warming above ~130 K, or doping with a trace of acid near 100 K, results in isotopic exchange with the formation of isolated HDO over a period of minutes to hours [1]. Since the isolated isotopomers have distinct known infrared spectra, the exchange rate, and thus the proton activity within the particles, can be monitored by FTIR spectroscopy. Fortunately for the present study, the absorption bands of the dangling-D molecules at the particle surface also occur at unique frequencies for the D_2O and HDO isotopomers (2725 and 2713 cm-1, respectively [2]). Because of the great surface area of an aerosol of ice nanocrystals, it is, therefore, possible to monitor the rate of isotopic exchange on the ice surface using the intensity of the dangling-D stretch bands. The exchange rate/proton activity at the surface is found to be more than an order of magnitude greater than for the particle interior. Though large, this difference compares well with that deduced using reactive ion scattering from the surface of ice films on a metal substrate [3].

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Monday 11:45 am - 12:10 pm **O005**

On the mechanism of proton transport in hexagonal ice

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Molecular dynamics and material transport in ordinary crystalline ice are known to be intimately related with the occurence of disorder in the proton sub-lattice. Special ice-typical lattice defects, the "Bjerrum defects" and "ionic defects", coexist with other solid-state defects (interstitials or vacancies) and originate from local distortions in the random conformation of the hydrogen bond network. Using deuteron NMR stimulated echo experiments [1] we identify the mechanism of (defect and) proton translational diffusion which turns out to be a concerted two-step process [2]. A localized "fast" molecular reorientation mediated by Bjerrum defects is followed by a "slow" jump process which leads to the long-range diffusion.
The temperature dependence of both processes in combination with literature data of tracer diffusion coefficients reveals that the material transport must originate from interstitial mediated diffusion of intact water molecules. The time scale associated with the slower component of this two-step mechanism contradicts (in parts) the standard interpretation of the dielectric Debye-relaxation.

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Monday 12:10 pm - 12:35 pm **O006**

Fast molecular transport in hydrogen-filled ices by high-pressure high-resolution diamond anvil cell NMR

Okuchi T.[1], **Takigawa M.**[2], **Shu J.**[3], **Mao H.-k.**[3], **Hemley R.J.**[3], **Yagi T.**[2]

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We report NMR spectra and relaxation times of filled-ice II and Ic hydrogen hydrates [1]. These were measured *in situ* at pressures 0.9 to 3.6 GPa using a novel high-resolution diamond anvil cell NMR method which has become available very recently [2]. Guest H_2 gave a narrow resonance indicating their fast transport between ice cavity sites (Fig). The hopping frequency was estimated from their relaxation times, giving a liquid-like diffusion coefficient that was not much sensitive to pressure, because ice framework sustains the space for guest diffusion. The framework H_2O gave a broad resonance due to dipolar interaction (Fig). However, the observed linewidth was smaller than pure ice, indicating some mobility of their protons. Curiously enough, the filled ice II has a fully proton-ordered framework, within which the protons must be immobile. The logical consequence is framework-guest interexchange of protons, revealing chemically very active nature of the filled-ice hydrate.

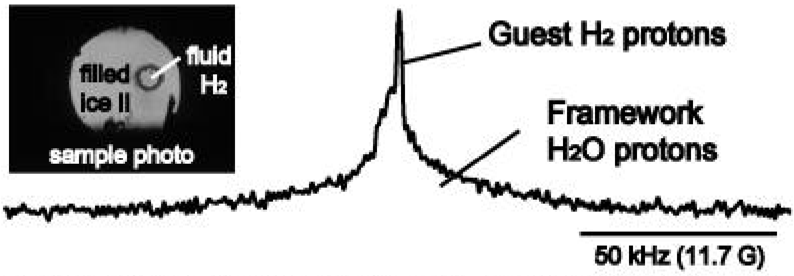

Fig. H_2-filled ice II powder NMR spectrum at 2.1 GPa and room T
[Fig]

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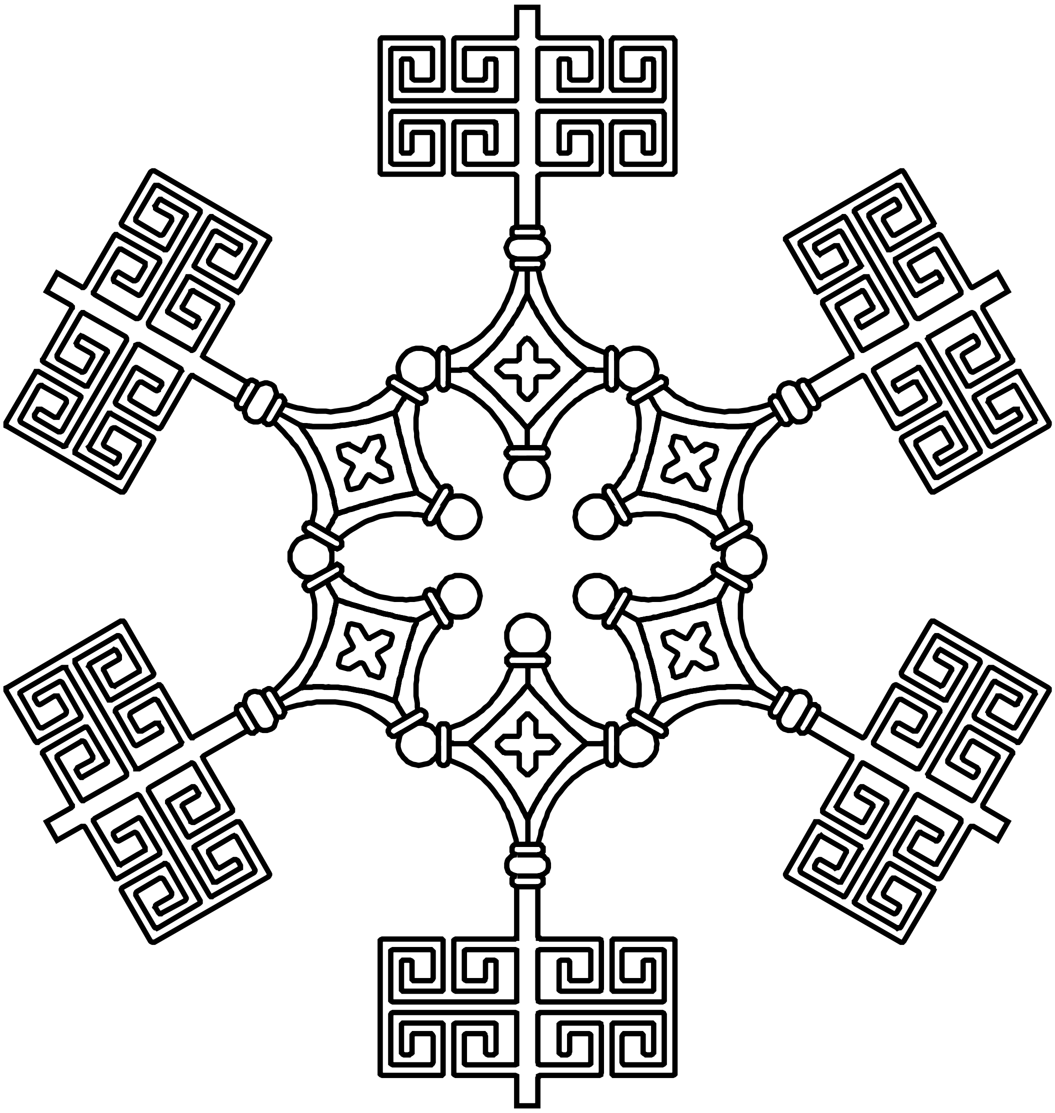
Snow and chemistry of ice

Chair: P. Plummer



Monday 03:15 pm - 04:00 pm **O007 (invited)**

Physical and chemical evolution of dry snowpacks during metamorphism

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The dry snowpack is an air-ice mixture with a high interfacial surface area that is subjected to physical transformations driven mostly by temperature gradients in the snowpack and by curvature gradients at the crystal scale. These gradients generate sublimation-condensation cycles that produce changes in snow crystals sizes and shapes [1,2], causing major modifications in physical variables of the snowpack, such as surface area, thermal conductivity, density, albedo, light transmission, and permeability. All these changes can be grouped under the term "snow metamorphism". Snow also contains chemical impurities in the form of adsorbed and dissolved gases and trapped atmospheric aerosols. They can be released from or taken up by the snowpack during metamorphism, changing the chemical composition of snow. Because snow and its impurities are irradiated by sunlight, they form a complex multiphase photochemical reactor that can produce enough reactive species to dramatically modify the composition of the overlying atmosphere [3]. The efficiency of this reactor depends on its physical properties that determine for example light fluxes and ventilation. Thus snow metamorphism will modify both the physical and chemical properties of the snowpack.

Global warming will reduce the temperature gradient in the snowpack and affect snow metamorphism. The physics and chemistry of the snowpack will therefore be different in a warmer world. The snowpack has a major impact not only on atmospheric composition, but also on climate, on the transfer of chemical species between the atmosphere and terrestrial ecosystems, and on ground temperature, and therefore on soil microbial activity and vegetation growth. Changes in snow metamorphism can then have widespread environmental consequences. To investigate these effects, we have performed laboratory and field studies where physical and chemical changes in snowpacks have been monitored as a function of temperature and temperature gradient. Data showing the effects of both these parameters on the density, specific surface area, permeability, albedo, light transmission, and aldehyde concentrations in the snowpack will be presented. These results allow us to speculate on the possible existence of feedback loops between snow metamorphism and global warming. These speculated mechanisms deserve further investigations to understand fully the impact of global warming at high latitudes.

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The temperature gradient metamorphism of snow: Model and validation using X-ray microtomographic images

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Among the different kinds of metamorphisms that may occur in snow, the temperature gradient (TG) metamorphism is probably the most interesting. Typically occurring by cold and clear night, when the TG between the top and the bottom of the snow layer is high, this metamorphism is characterized by the formation of facets at the bottom of the grains, while upper parts remain rounded [1].

Since the TG metamorphism may be the source of week layer formation in the snow cover, its study has major issues in avalanche studies and is an active research field in snow and ice community. Despite of this interest, the TG metamorphism remains quite poorly understood. In particular, two fundamental questions have not been fully solved. First, what is the driving force of the matter exchange in the ice matrix and what are the associated mechanisms? Second, what determines concretely whether well-rounded or faceted shapes can appear?

These two questions have been addressed and partly solved by Colbeck [2] twenty years ago, but the results where based on 2D observations and very simple approximations on the snow geometry. In our approach, we would like to take advantage of X-ray microtomographic techniques and revisit these questions by using high-resolution 3D images.

A simple physical model describing the temperature gradient metamorphism of snow is presented in this work. This model, based on Kelvin and Langmuir-Knudsen equations, is close to a previously developed model of isothermal metamorphism [3], but takes into account the variation of the saturating vapor pressure with temperature.

It can determine locally whether the ice is condensing or sublimating, just depending on both the temperatures in the snow matrix and the local mean curvatures of the ice/pore interface. This model can also explain the formation of facets that occurs during the metamorphism.

Thanks to X-ray microtomographic images of snow samples obtained under moderate temperature gradient conditions, the validity of this model has been verified. This offers interesting outcomes for the numerical simulation of the temperature gradient metamorphism.

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Monday 04:55 pm - 05:20 pm **O009**

Tomographic characterization of soluble and insoluble impurities and their transport in ice

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Impurities of halogene salts in ice and on its surface are thought to play a key role for the catalytic ozone destruction [1]. Furthermore atmospheric ice particles are well known to transport trace substances from the troposphere into the stratosphere. To understand such processes the loaction and the mobility of trapped impurities in ice has to be known.

With the extended experimental setup at the X04SA Beam Line at the SLS we performed micro computer tomography at temperatures of 230 K with a spatial resolution of 1.4 µm to study the location of impurities and to characterize them. Natural graupel grains as well as ice frozen from NaBr solutions were analyzed. We performed tomographic scans at different times while raising the temperature from 230 to 260 K in several steps to observe changes of the morphology of air- and salt-filled voids. A decrease in curvature of voids occupied by air could be seen in both types of samples. The salt inclusions accumulated in the middle of the ice sphere.

Additionally, the behavior of chlorine and iodine in one single sample was monitored while the temperature increased. Different types of aerosol material were investigated. Samples contained octanol to represent insoluble, but liquid urban aerosols [2]. Bentonite and quartz particles suspended in salt solutions were frozen to simulate ice formation as it occurs on two different types of mineral dust. A strong dependence of the morphology of voids filled by either air or salt on temperature to which they were exposed to for freezing could be deduced based on the geometrical characterization.

This finding was extended by analyzing various samples from a 1 % (wt.) solution of NaBr exposed to temperatures from 200 – 270 K. A strong temperature dependence became evident. The trapped inclusions will become larger, if the exposure temperature is lower. Summarizing all these results we were able to model a cumulative volume distribution of air as well as of the impurity. Therefore we used Fick´s 1st law of diffusion as employed by Carte [3] to describe the impurity concentration of the dissolved impurity at the freezing ice front. For each time step the supersaturation (with respect to formation of pure substance) of the dissolved impurities, was calculated. Once a supersaturation reaches a critical value, nucleation is allowed and solid of gaseous inclusion form.

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Monday 05:20 pm - 05:45 pm **O010**

Vapour deposited H_2O-Ethanol and H_2O-formaldehyde gas mixtures investigated by micro-Raman scattering and X-ray diffraction

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In the atmosphere, ice (or snow) crystals can incorporate gases during their growth by condensation or by collisions with supercooled droplets which subsequently freeze. Both gas trapping mechanisms may induce changes in the ice structure, composition and reactivity, and therefore also affect the gas phase composition. Incorporation of species by condensation is also a dominant process occurring in cold interstellar medium or comets at relatively different temperature and concentration conditions.

Several studies demonstrate the increasing interest for the interaction of small oxygenated organics (e.g. formaldehyde, methanol, ethanol, etc) with ice due to their potential impact on the atmospheric and snowpack chemistry [1,2]. Moreover, formaldehyde present in cometary's ices has been studied intensively in the context of reaction products of multi-component gas condensed ice mixtures [3].

In the present study, we report on the characterization by micro-Raman scattering of vapor deposited gas-H_2O mixtures (formaldehyde, ethanol) of different compositions. We obtain information on the structural nature of the deposited solids from all Raman active vibrations in the 800-3800 cm-1 spectral range. Different hydrate phases are crystallized and identified by X-ray diffraction during annealing of the amorphous deposited solid at different temperatures. The influence of the water/gas ratio and of the water-gas flow during the deposition is examined from the viewpoint of the phase transformation mechanism for the growing crystalline hydrogen-bonded solid. Hydrates formation is observed between ~ 120 K and 140 K i.e., at temperature somewhat lower than the amorphous -> cubic ice Ic transition in pure ice. The ethanol hydrate phase is apparently distinct from that of solid ethanol or from the expected clathtrate hydrate type II usually encountered in frozen aqueous solutions. Deposits with lower ethanol content show the coexistence of ice Ic with an additional hydrate phase crystallizing at higher temperature (~ 170 K). In co-condensed H_2CO:H_2O gas mixtures, a metastable crystalline phase is first obtained at ~ 140 K and transformed at ~150 K in a clathrate phase. A comparison of these results with those obtained on the corresponding frozen aqueous solutions suggests that vapor deposited ice mixtures reflect the existence of clusters of a distinctive structural nature with respect to those encountered in frozen aqueous mixtures.

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Monday 05:45 pm - 06:10 pm **O011**

Uptake processes of nitrous oxide on ice studied with radioactively tracers

<u>Huthwelker T.</u>[1], Kerbat M.[1], Pinzer B.[2], Kaempfer T.[2], Schneebeli M.[2], Ammann M.[1]

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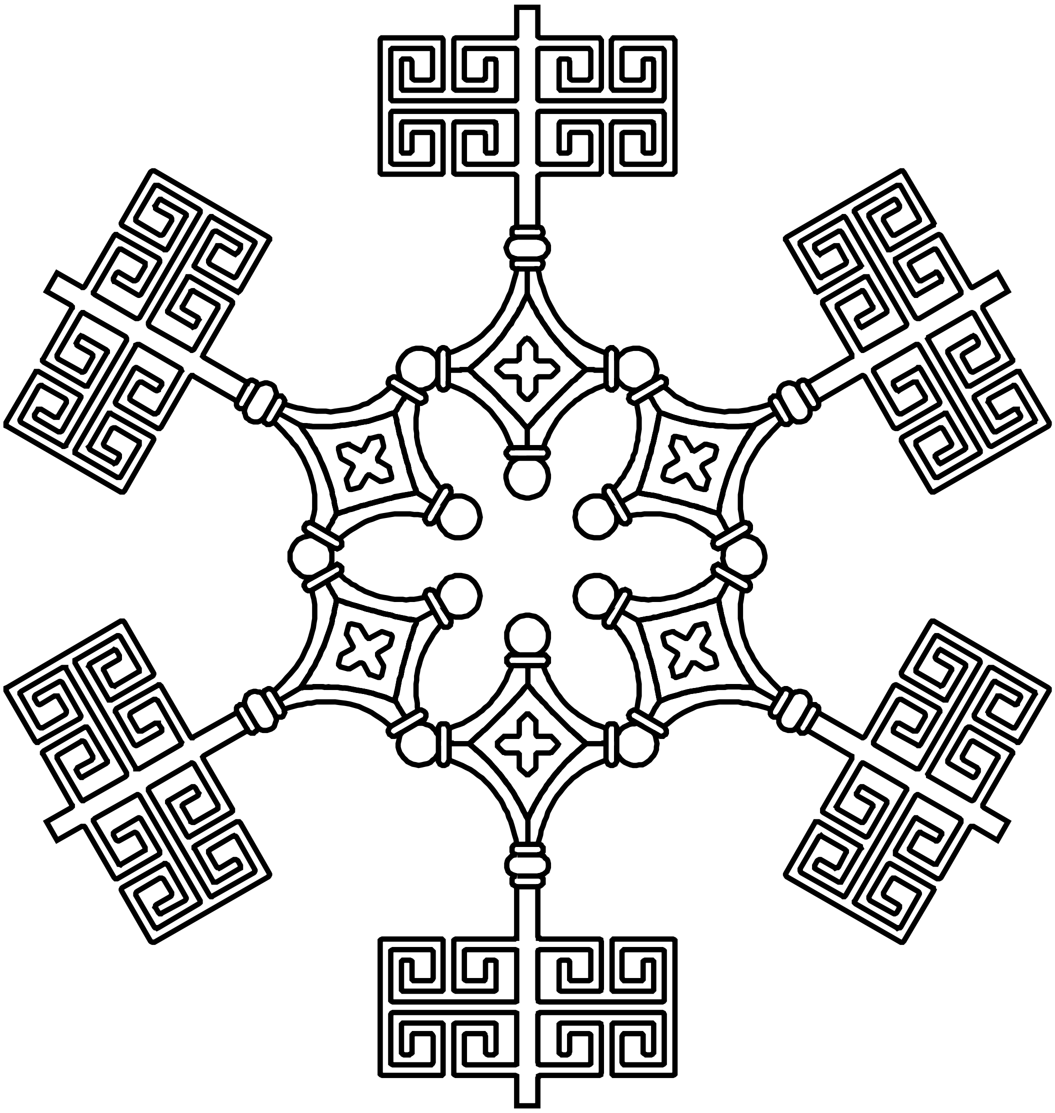
Nitrous acid (HONO) plays an important role in atmospheric chemistry as it easily photodissociates and produce hydroxyl radicals (OH). This powerful oxidant strongly affects the composition of our atmosphere and is involved in the formation of the tropospheric ozone. Ice and snow cover a significant amount of the Earth and may be a major source or sink for HONO, which can adsorb on its surface. Therefore, it is of great importance to know both the equilibrium partioning and the migration kinetics of this compound in snow.

A classical method to study such processes is measuring the breakthrough curve of the trace gas through artificial snow. Short-lives radioactive nitrogen (13N) was produced at the PSI accelerator facility to label HONO. The migration of the labeled HONO through packed ice beds is studied non-destructively and in situ. The kinetics of the HONO migration is compared with a full numerical simulation of the adsorption and diffusion processes. By this method, we obtained information about the equilibrium partitioning and can distinguish between bulk and surface processes.

The artificial snow produced by freezing small ice spheres in liquid nitrogen, and allowing sufficient time for sintering to a packed ice bed. This ice bed is characterized using BET measurements and microtomography.

High pressure and amorphous ices

Chair: J. Ripmeester



Tuesday 09:05 am - 09:50 am **O012 (invited)**

Basic concepts of defects in ice

Buch V.[1]

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Transport and relaxation properties of ice are believed to be dominated by defects. The pertinent macroscopic properties have been a subject of research over many years. The existence of defects has been inferred and some molecular level models were proposed. However defects, being rare, are difficult to observe direcly, and some of the molecular models still in use, such as the Bjerrum D-defects, are grossly outdated. Kinetic models which include potentially crucial role of transport along grain boundaries seem to be needed. The available defect theories and recent advances will be summarized. The open questions will be pointed out.

Tuesday 09:50 am - 10:15 am **O013**

Two new hydrogen ordered phases of ice: ices XIII and XIV

Salzmann C.G.[1], Radaelli P.G.[2], Hallbrucker A.[3], Mayer E.[3], Finney J.L.[4]

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[3]Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innsbruck, Austria

[4]Department of Physics and Astronomy, University College London, London WCE BT, United Kingdom

Two new hydrogen ordered phases of ice have been prepared by cooling the hydrogen disordered ices V and XII under pressure.
[1] Previous attempts to unlock the geometrical frustration in hydrogen bonded structures have focused on doping with potassium hydroxide and have had success in partially increasing the hydrogen ordering in ice Ih.
[2] By doping with hydrochloric acid we have prepared ice XIII and ice XIV and analyzed their structure by powder neutron diffraction. The space group symmetries are $P2_1/a$ for ice XIII and $P2_12_12_1$ for ice XIV. The two new phases were also characterised by Raman spectroscopy and the spectroscopic differences with their hydrogen disordered counterparts are discussed. The hydrogen order / disorder phase transitions were followed at ambient pressure by neutron diffraction, Raman spectroscopy, and differential scanning calorimetry and tested for reversibility.

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Tuesday 10:15 am - 10:40 am **O014**

Deuteron spin-lattice relaxation in high density amorphous ices

Scheuermann M.[1], **Geil B.**[2], **Fujara F.**[1]

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[2]Universität Dortmund, Experimentelle Physik III, Dortmund, Germany

Temperature dependent deuteron spin-lattice relaxation times T_1 have been obtained from water in its three amorphous states: low density amorphous (LDA), high density amorphous (HDA), and very high density amorphous (VHDA). It is found that in all of these states the magnetization recovery is essentially monoexponential and that T_1 of LDA is significantly different to that of the higher-density forms. Thus, T_1 can be used as a monitor parameter to study the kinetics of the transitions from HDA to LDA and from VHDA to LDA.

HDA and VHDA (D_2O) have been prepared at appropriate pressures and temperatures. Then the samples have been recovered to ambient pressure at liquid nitrogen temperature. T_1-measurements have been performed while increasing the temperature stepwise. At a defined temperature (depending on the state of the initial sample) a discontinuity in T_1 indicates a phase transition. The amorphous ice phases transform to LDA, which in turn crystallizes to cubic ice I_c. The obtained values for the transition temperatures of HDA/LDA, 108 K, and VHDA/LDA, 120 K, agree well with recent neutron scattering experiments, indicating stability of VHDA at temperatures higher than those of HDA.

During the transformation of VHDA to LDA an intermediate state is formed due to annealing on a strongly temperature dependent time scale. Although the two ranges of T_1 of HDA and VHDA are not well seperated, this intermediate state is clearly determined to be HDA-like in terms of its dynamical properties. On the other hand, this transition from VHDA to the HDA-like state occurs at temperatures above the stability limit of native HDA.

These findings strongly question all attempts to consider HDA and VHDA as two distinct thermodynamical phases. The observed high-density states rather belong to the same class of amorphous ice.

Tuesday 10:40 am - 11:05 am **O015**

X-ray absorption spectra and the structure of ordered and disordered high pressure ices

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[1]University of Saskatchewan, Physics and Engineering Physics, Saskatoon, Canada

[2]National Research Council of Canada, Steaice Institute for Molecular Sciences, Ottawa, Canada

[3]University of Ottawa, Department of Chemistry, Ottawa, Canada

A recent report on the interpretation of the x-ray absorption spectrum (XAS) of liquid water has stimulated intense debate on the hydrogen bond network of water in the condensed state [1]. To gain a better understanding and insight on the the XAS of water, in this presentation, new theoretical and experimental results on the oxygen core level absorption spectra of proton-disordered liquid water, ice Ih low density and high density amorphous ies and proton-ordered ice II, ice XI and ice VIII will be presented. Convergence of the calculated spectra with respect to the size of the water clusters and long range electrostatic interactions was examined. The goals of these studies are (i) to explain the nature of the near edge absorption features and their relationship to the local hydrogen bond structure of water and (ii) to utilize the sensitivity of XAS on the local strucuture to investigate the nature of the transformation of high density amorphous (HDA) to low density amorphous (LDA) ice [2].

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Tuesday 11:40 am - 12:05 am **O016**

Four phases of amorphous water: simulations vs experiment

<u>Brovchenko I.</u>[1], Oleinikova A.[1]

[1]University of Dortmund, Physical Chemistry, Dortmund, Germany

Experimental discovery of the phase transition from low-density amorphous ice (LDA) to high-density amorphous ice (HDA) [1] was supported by simulations of a liquid-liquid transition in supercooled water [2]. The discovery of the very-high-density amorphous ice (VHDA) [3] has indicated, although indirectly, a possibility of more then one phase transition between amorphous water phases. Multiple liquid-liquid transitions in supercooled water for the first time were obtained in simulations of ST2 and TIP4P water models [4]. The general character of this phenomena was confirmed by observation of multiple liquid-liquid transitions for fluid with multistep interaction potential [5], TIP5P water model [6], polarizable water model [7], SPCE water model and ST2 water model with reaction field for long-range Coulombic interaction [8].

Recent experiments of Loerting et al.(Phys.Rev.Lett., in press) have proved existence of at least two phase transitions: LDA ↔ HDA and HDA ↔ VHDA. We have compared the simulated phase diagram for various water models with experiment to identify amorphous phases of water, seen in simulations. Phase I, corresponding to LDA, consists mainly of tetrahedrally coordinated water molecules with 4 neighbour in the first coordination shell. Phase II, not seen yet in experiment, is enriched with molecules, which are tetrahedrally ordered, having 4 to 6 nearest neighbours. In phase III, corresponding to HDA, a majority of water molecules are still tetrahedrally coordinated. Transition from phase III to phase IV, corresponding to the VHDA, is characterised by noticeable drop of tetrahedral order and phase IV consists mainly of molecules with isotropic angular distribution of the nearest neighbours. Various characteristics of the local order in four amorphous water phases are analysed and their main structural properties are presented.

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Tuesday 12:05 am - 12:30 am **O017**

Annealed high density amorphous ice and the two-liquid model of water

Nelmes R.[1], Loveday J.[1], Strässle T.[2], Bull C.[1], Guthrie M.[1], Hamel G.[2], Klotz S.[2]

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[2]Université P. et M. Curie, IMPMC, CNRS-UMR 7590, Paris, France

The nature of the transformation between the low- and high-density forms of amorphous ice, LDA and HDA, could hold the key to understanding the anomalous properties of water. HDA is made under pressure, and can be recovered to ambient pressure at low temperature and transformed to LDA by warming. Numerous experiments have been done without reaching a clear consensus as to whether the transformation is discontinuous – which would support a two-liquid model of water – or continuous. We show that strikingly different behaviour is obtained if the HDA is first annealed under pressure in the 0.1-0.4 GPa (1-4 kbar) range: the transition from this annealed HDA to LDA is clearly discontinuous. Taken together with the evidence previously obtained that the in-situ HDA/LDA transition at ~0.2 GPa is also discontinuous [1], this makes a two-liquid model then appear very plausible.

Our results also show that the very high density form, VHDA, exists (meta)stably only at pressures above ~0.8 GPa, and transforms into the annealed HDA at lower pressures.

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On the nature of the amorphous polymorphism of water and its apparent multiple phase transitions.

Koza M.M.[1], Schober H.[1], May R.[1], Hansen T.[1]

[1]Institut Laue Langevin, Grenoble, France

Throughout recent years there has been a growing scientific interest in the phenomenon of amorphous polymorphism, i.e., in the presence of more than one amorphous structure in a single substance. Amorphous ice has been playing a major role in this studies due to the moderate thermodynamic conditions at which the disordered structures can be formed. Despite a remarkable progress comprising the comprehension of properties of this phenomenon the most essential question, namely ´What is the origin of amorphous polymorphism in water?´, could not be answered, yet [1].

Recent experimental, theoretical and simulation work does not give any clear answer to this questions, and rather creates an inconsistent picture of what amorphous polymorphism of water could be. There are papers referring that besides the well established high-density amorphous (HDA; 39 molec./nm^3) and low-density amorphous (LDA; 31 molec./nm^3) phases there is at least one more distinct phase namely the very high-density amorphous (vHDA; 41 molec./nm^3) ice [2], and possibly four distinct liquid states [3]. On the one hand, the transformation between these structures is considered as being of first-order [4]. On the other hand, it is explained as a continuous relaxation process of an amorphous matrix, thus, questioning the entire concept of a multi-phase picture [5].

In addition, it has been also questioned, whether the supposed glass-transition of water (T_g = 135 K) has been correctly established [6], which is, of course, a central argument for linking the disordered ice structures to the supposed liquid states.

When studying phase transition phenomena the essential experimental observable in scattering experiments is the signal in the small-angle scattering regime. Basically, it contains information on the compressibility of the transforming system, on the correlation-lengths of critical fluctuations, and on the cluster size of phase mixtures. Moreover, {it in situ} experiments allow to extract information on the kinetics of the transformation and thus the activation energy of the transition process [7].

We will present extensive data, from {it in situ} small-angle neutron scattering experiments on the transformations of amorphous ice phases. We will critically review the current perceptions of the amorphous polymorphism of water, based on the small-angle scattering data, and discuss some questions raised by other experimental data that require clarification.

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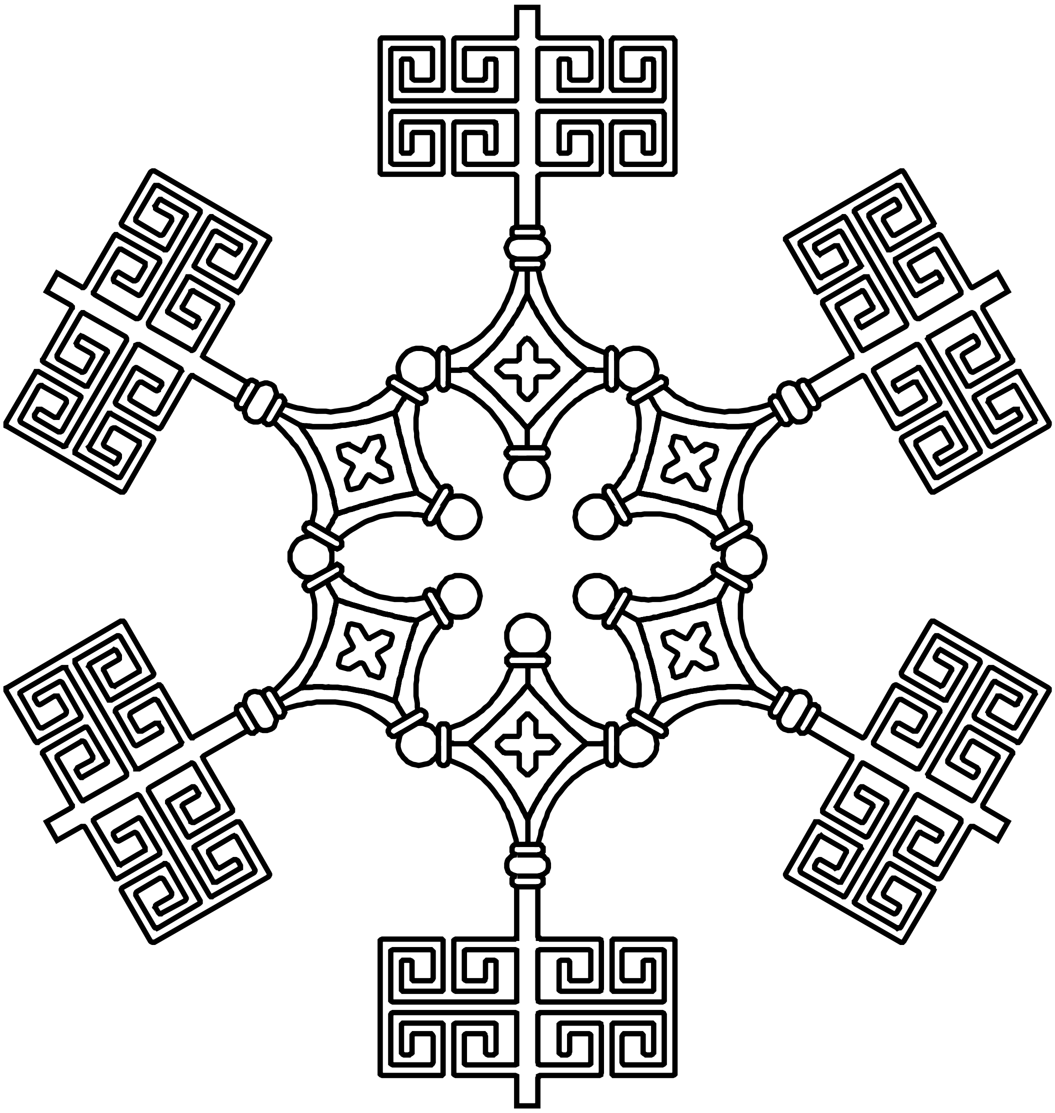
Thermodynamics and Quantum chemistry

Chair: J. Tse



Wednesday 09:05 am - 09:50 am **O019 (invited)**

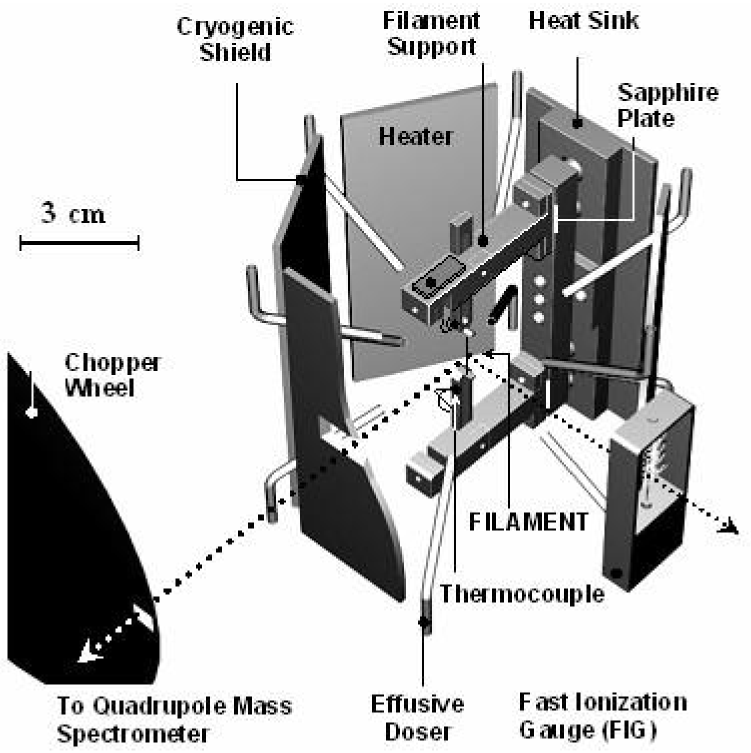
Studies of fundamental physical phenomena in polycrystalline ice near its melting point by fast thermal desorption spectroscopy and microcalorimetry

Sadtchenko V.[1]

[1]The George Washington University, Chemistry, Washington, DC, United States of America

Ice is a volatile molecular solid ubiquitously present in nature. Due to their fundamental and applied significance physical and chemical processes involving ice have been a subject of intense experimental and theoretical scrutiny for the past decades. In particular, reactivity, surface morphology, and transport phenomena in thin ice films have been studied at cryogenic temperatures with standard surface-science techniques under high vacuum conditions. Although this approach has numerous advantages, it has been confined to temperatures below -100 deg. C due to ice volatility. Over the past four years, we have developed an experimental apparatus that made it possible to overcome challenges associated with the introduction of volatile solids into a high vacuum environment [1]. This new experimental employs a unique combination of Fast Thermal Desorption Spectroscopy (FTDS), Microcalorimetry, and Time-of-flight Mass Spectrometry to study physical phenomena in of micrometer thick polycrystalline ice films vapor deposited on a thin (10 micrometer in diameter) filament. We will discuss the details of our approach, and review experiments conducted in our laboratory, which include:

1. Measurements of relaxation dynamics in low density amorphous ice during rapid heating.
2. Studies of water vaporization mechanisms from ice single crystals and from grain boundary grooves at temperatures near ice melting point.
3. Studies of surface morphology of rapidly desorbing polycrystalline ice film.
4. Studies of diffusive transport of various dopants in the bulk of polycrystalline ice at temperatures near 0 deg. C.



[Fast thermal desorption spectroscopy apparatus]

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Wednesday 09:50 am - 10:15 am **O020**

Small and middle-sized water-ice nanoparticles in thermal equilibrium

Bauerecker S.[1], **Schultze M.**[1], **Kessler T.**[1], **Wargenau A.**[1], **Selk Y.**[1], **Grunenberg J.**[2]

[1]Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Braunschweig, Germany

[2]Institut für Organische Chemie, Technische Universität Braunschweig, Braunschweig, Germany

During the last years, we developed a collisional cooling technique with an integrated multiple-reflection White optics [1]. Due to the relatively large optical pathlength of up to 20 m the detection sensibility of the system is high enough to use rapid-scan FTIR spectroscopy for investigation of the formation process of molecular nanoparticles growing by desublimation of supercooled molecules. Intermediate temperatures can be adjusted with an accuracy of better than ± 0.4 K in the temperature range of 4 to 400 K. At temperatures below 20 K high supersaturation and nucleation rates occur which are used for the generation of nanoparticles of around one nanometer in size.

At 167 K ± 0.4 K we found a sharp transition in the formation process of solid water nanoparticles: the particle size almost doubles from 450 to 800 nm and the formation time triples from about 2 to 6 s. In the present contribution several possible formation mechanisms are discussed to explain this striking behavior. As a basis of analysis the exact size determination of the particles during the formation process is crucial. For that purpose, we use the Discrete Dipole Approximation (DDA) method [2] for calculation of scattering and absorption parts of the extinction spectra. Only varying one single model parameter – the particle size – the accordance with the experimental data is excellent for spherical shape of the particles.

Infrared spectra of smaller water particles covered by nitrogen molecules in the size range of 20 to 100 water molecules per particle are compared with ab-initio calculated nanocomposite spectra. Here, the B3LYP method and the 6-311++G(3df,3dp) basis set were used for geometry optimization and frequency calculations of several clusters up to the $(H2O)_{20}(N2)_6$ cluster. As a starting geometry of the water core of the nanocomposites we used minimum energy structures of water clusters [3]. Both main effects of the nitrogen mantle on the infrared spectra, a redshift of about 20 cm^{-1} and a considerable increase in strength of the free O-H band, are in accordance with the experiment.

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Quantum mechanical calculations of $L(H_2O)_{20}$ clusters ($L=H_2O$, CH_4, CH_3OH, H_3O^+

Xantheas S.[1]

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We present the results of first principles electronic structure calculations (DFT and MP2) for the structure and stability of $L(H_2O)_{20}$ clusters ($L=H_2O$, CH_4, CH_3OH, H_3O^+). The host dodecahedron 5^{12} $(H_2O)_{20}$ cluster presents a challenge in assessing the relative order of the low-lying structures (1) which need to be screened as potential candidates for the most energetically stable configurations of the systems resembling clathrate formation. The structures and relative stabilities for several guest molecules such as H_2O, CH_4, CH_3OH and H_3O^+ embedded in the 19 most energetically stable networks of the host dodecahedron cluster were investigated. The first principles results are compared with the ones obtained from classical interaction potentials.

(1) M. Kirov, G. S. Fanourgakis and S. S. Xantheas, J. Chem. Phys. (submitted)

Topological transitions between ice phases

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Ice has a famously complex phase diagram, where thermal and statistical physics [1] have served well in the elucidation of the features of the phase diagram. In this study instead we consider the structural and stability properties of ice by the use of the gradient vector field of the charge density using the theory of atoms in molecules (AIM). The analysis of the charge density is also relevant for experimental techniques (e.g. X-ray diffraction) which yield a real space charge density distribution. We explore a method to determine the routes between known phases for future studies extended to less certain ones. For instance it is possible to understand when a bond is close to rupturing [2,3] or in which direction the electrons and hence atoms prefer to move [4]. In this novel study we follow the bonding topology of ice ih, ice II and ice IX as examples to demonstrate how the bonding changes and gives possible route by which one phase might evolve from another. The phases where chosen since they are share common phase boundaries and two of the phases contain hexagonal rings, (ice Ih and ice II).

References

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Wednesday 11:35 am - 12:00 pm **O023**

New techniques and results for hydrogen bond order/disorder transitions in ice: understanding known phases and predicting new phases

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Considerable debate in the literature has surrounded the existence of an ice Ih/XI hydrogen bond ordering transition, the nature of the ice III/IX transition, and possible transitions to hydrogen bond ordered forms of ice V and VI. We have developed a technique for treating hydrogen bond order/disorder in ice phases that combines periodic density functional theory with an analytic approach that allows a full statistical mechanical treatment of hydrogen bond fluctuations.

The theoretical methods used to predict these phase transitions have been validated by comparing their prediction to the well-characterized ice VII/VIII proton ordering transition[1]. Then results are presented confirming the Ih/XI transition, shedding new light on pre- and post-transitional order for III/IX transition, and predicting a new low-temperature hydrogen bond ordered forms of ices V and VI[2]. Applications are made to the dielectric properties of ice. The theory provides insight into the interaction between defects in ice with the H-bond topology of the surrounding lattice, and the role of defects in the mechanism of order/disorder phase transitions.

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Wednesday 12:00 pm - 12:25 pm **O024**

Observation of the local structure of protons in ices and water using Neutron Compton Scattering

Reiter G.[1], Burnham C.[2], Reichert H.[3], Kolesnikov A.[4], Mayers J.[5], Dosch H.[3]

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[2]University of Houston, Houston, United States of America

[3]Max Planck Institute, Stuttgart, Germany

[4]Argonne National Laboratory, Argonne, United States of America

[5]ISIS, Rutherford-Appleton Laboratory, Chiton, United Kingdom

Measurements of the momentum distribution of protons in ices and water using Neutron Compton Scattering are directly sensitive to the Born-Oppenheimer potential experienced by the proton[1,2]. Measurements have been made of the 3-D momentum distribution in crystalline ice Ih and the spherically averaged momentum distribution in polycrystalline ice VI and high density amorphous ice. These reveal that empirical potentials that describe the isolated water molecule must be modified to describe the change in the covalent bond as the distance to the acceptor oxygen in the hydrogen bond changes. The change in the covalent bond for ice Ih compared to the free molecule is large on the scale of differences that can be measured, and can be accounted for by introducing anharmonicity into the intramolecular potential. The variation of stretch mode frequency with O-O bond length can then be used to infer the distribution of bond lengths in water from the momentum distribution.

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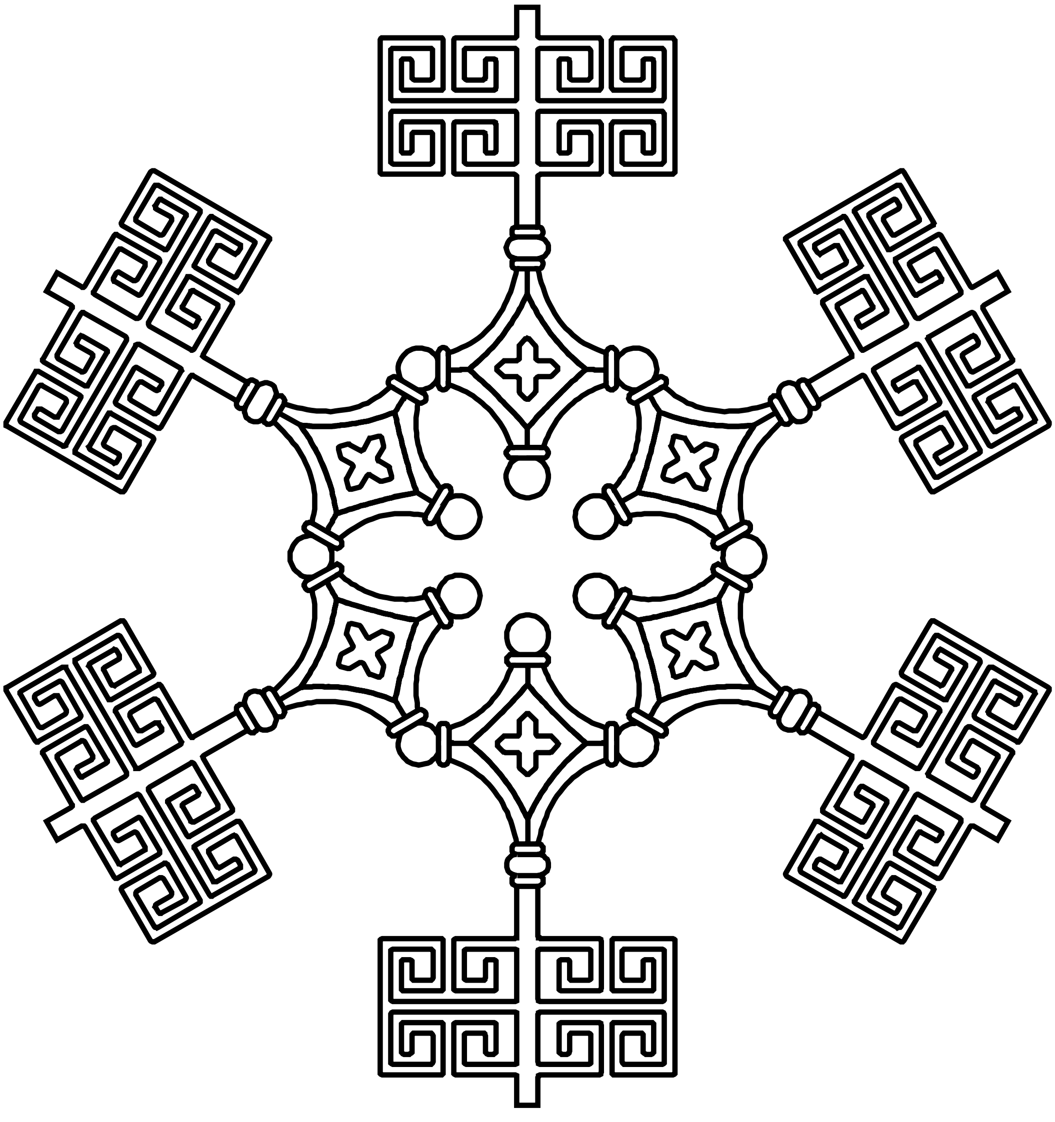
Defective ice and ice defects

Chair: P. Devlin



Wednesday 02:00 pm - 02:45 pm **O025 (invited)**

Molecular simulations of ice and gas hydrate nucleation

Radhakrishnan R.[1], Anderson B.J.[2], Borghi G.P.[3], Tester J.W.[4], Trout B.L.[4]

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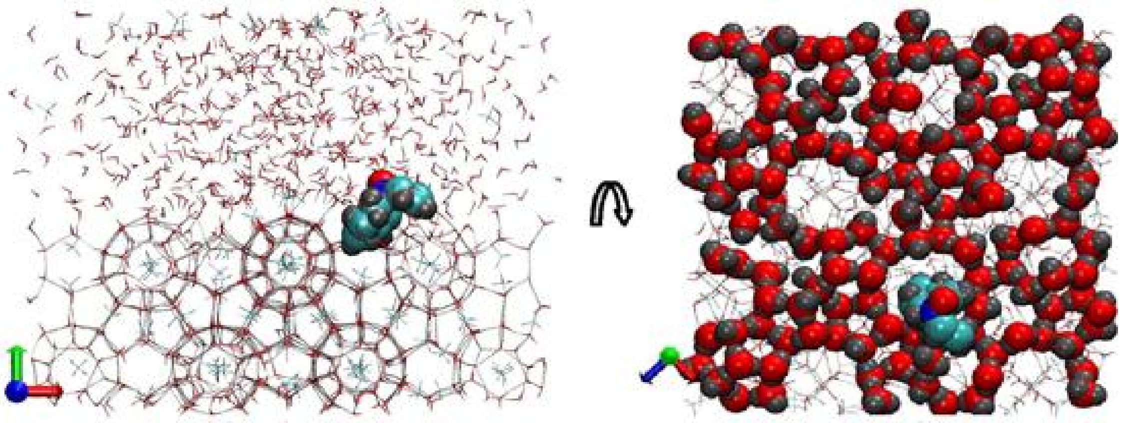
[2]University of West Virginia, Department of Chemical Engineering, Morgantown, WV, United States of America

[3]EniTecnologie S.p.A., Center for Upstream Oil & Gas Technologies, Milan, Italy

[4]Massachusetts Insitute of Technology, Department of Chemical Engineering, Cambridge, MA, United States of America

We present an overview of cutting edge molecular simulation methods applied to understanding the nucleation of ice and gas hydrates. These methods allow us to probe the molecular details of these complex processes, quantify their kinetics, and engineer new ways of changing the kinetics. Specifically, we first select order parameters, mathematical functions that can describe the nucleation process. We use these order parameters within Monte Carlo and molecular dynamics simulations in order to explore the parts of the free energy surfaces related to nucleation. Along the way, we also test the order parameters for their ability to describe the nucleation process and determine the molecular mechanism for nucleation. We also describe how we have used molecular dynamics simulations to understand the inhibition of clathrate-hydrate formation, of tremendous interest to oil and gas companies, and use that understanding to design new kinetic inhibitors.



side view top view

[Inhibition of a SII clathrate-hydrate]

References

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Wednesday 02:45 pm - 03:10 pm **O026**

Ice nucleation on alpha-Al_2O_3 surfaces

Thayer G.E.[1], Ewing G.E.[2], Richardson H.H.[3]

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[2]Indiana University, Department of Chemistry, Bloomington, Indiana, United States of America

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Over 50 years ago, Bernard Vonnegut searched the crystallographic literature for substrates that might be effective heterogeneous ice nucleation (IN) agents. He identified AgI whose crystal lattice matched that of Ih ice to within 2% [1]. A smoke of AgI was found to be effective in IN and is still used in cloud seeding. In subsequent years a number of investigations have shown that not only lattice spacing, but surface defect density and the hydrophobic nature of surfaces contribute to the capability of substrates to nucleate ice [2-6]. However the mechanisms that determine ice-nucleating effectiveness of inorganic substrates are still un-decided. To explore the mechanism of heterogeneous IN, it is important to work with well-defined surfaces. Consequently, we have chosen alpha-Al_2O_3 as a model substrate since its surfaces have been extensively studied and they can be prepared in a variety of morphologies. Moreover Al_2O_3 has been demonstrated to be an effective IN substrate [2, 4, 7].

The effect of morphology in previous work on IN substrates (recent experiments performed on BaF2 [5], as well as early experiments on AgI [3]), presents evidence of the significant role of substrate geometry in the heterogeneous IN process. Further support is given by a model developed by N.H. Fletcher [6], which sets a foundation for understanding the effectiveness of nanoscale pits as surface nucleation sites. Since Fletcher's theory favors nucleation on substrates that wet ice, the hydroxylated surface of Al_2O_3, prepared with controlled surface morphology, is an excellent substrate for continued study of IN.

We report here IN temperatures on three distinct Al_2O_3 surfaces. 1) atomically flat, ultrasmooth Al_2O_3 (0001); 2) nanopitted Al_2O_3 (0001); and 3) Al_2O_3 nanospheres. We find a range of IN temperatures from -30° to -5° C by monitoring the temperature that supercooled water freezes during a temperature cycle under conditions where the cooling rate is held constant [4, 8].

We offer a theoretical model to account for the observed IN temperatures based on specific surface morphologies, as determined from AFM measurements, and from equilibrium contact angle measurements.

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Laboratory studies of the formation of cubic ice in aqueous droplets

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The homogeneous freezing of aqueous solution droplets in the Earth's atmosphere is thought to be an important mechanism in ice cloud formation. This process has generally been assumed to result in ice particles with the stable hexagonal crystal structure (ice Ih). However, we have found that metastable cubic ice (ice Ic) can form under conditions relevant to the Earth´s upper troposphere (~10-20 km altitude). In an experimental study we froze micrometer-sized aqueous droplets, which were suspended in an oil emulsion, by cooling them at a modest rate (10 K / min) and measuring their crystalline structure with X-ray diffraction. Cubic ice was found to be a significant product when pure water droplets homogeneously froze between 237.5 K and 230.4 K. Our results show that as the size of the water droplets decreased from 17.0 µm to 5.6 µm, the formation of cubic ice was favoured. This is a particularly exciting result since ice Ic has only been produced in the past through very rapid cooling at low temperatures or from the decomposition of other ice phases and hydrates. The formation of ice Ic in these droplets is consistent with the previous suggestion that cubic ice is the crystalline phase that nucleates when pure water droplets freeze homogeneously at 235 K. We also investigated the ice Ic to ice Ih phase transition kinetics and found that cubic ice can persist for many hours below ~240 K – much longer than has been found in many previous studies. It seems likely that we measured the solid-to-solid ice Ic to ice Ih phase transition, whereas others have measured this in addition to a gas-phase mass transport ice Ic to ice Ih mechanism. When concentrated solution droplets of $(NH_4)_2(SO_4)$, $(NH_4)_3H(SO_4)_2$, HNO_3 and NaCl homogeneously freeze below 190 K, they do so exclusively to ice Ic with some stacking faults. The amount of ice Ic that forms when solution droplets freeze at temperatures above 200 K is strongly solute-type and solute-concentration dependent. *A priori*, one might expect the amount of ice Ic to simply increase with lower freezing temperatures. However, this is not always the case. For example, in contrast to pure water droplets, 5 wt% HNO_3 solution droplets freeze exclusively to ice Ih. In contrast, droplets of $(NH_4)_3H(SO_4)_2$ that freeze at a similar temperature do so to a mixture of ice Ic and ice Ih, much like pure water droplets. These results will be discussed.

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Wednesday 03:35 pm - 04:00 pm **O028**

Modelling ice Ic of different origin and stacking-faulted hexagonal ice using neutron powder diffraction data

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Ice Ic, known as a second solid crystalline phase at ambient pressure since 1943 [1] can be obtained from high-pressure polymorphs of ice (e.g., II, V, XII, IX and HDA) [2] upon warming at ambient pressure or by condensation of water vapor at temperatures from 130 to 150 K [3]. None of the obtained phases show a diffraction pattern of well-crystallized cubic ice. Moreover, the deviations from this idealized structure are different for different starting materials. The appearance of broad reflections in neutron diffraction experiments with intensities not in agreement with a simple cubic structure was first explained by anisotropic particle size effects [4]. A closer peak shape investigation of the main cubic reflections and the appearance of broad peaks at Bragg angles typical for ice Ih lead to the assignment of the underlying defects as deformation stacking faults [5].

Above 150 K ice Ic is unstable with respect to hexagonal ice Ih. The transition takes place over a large temperature range, slowly at 150 K, faster at 190 and 210 K, depending, again, on the way, the cubic ice was produced. Even at these temperatures, the transition is not complete but leaves a stacking faulted hexagonal ice, which transforms further to pure ice Ih above 240 K as shown by an in situ neutron powder diffraction study [6].

Moreover, ice Ic and defective ice Ih is formed at temperatures well above 200 K upon decomposition of gas hydrates as observed in time-resolved neutron diffraction experiments [6]. To quantify the amount of the resulting ice phase from our diffraction data a proper description of these defective ices is needed. Here we present a way to fit the diffraction peak profiles with different models of stacking disorder [7]. This allows us to distinguish different samples with different histories in terms of their stacking distributions. An adapted range of sufficiently large unit cells with different, non-random stacking sequences is created for each sample and a linear combination of these replicas fits the measured neutron diffraction data. In this way a quantitative determination of the total amount of ice present can be obtained.

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Wednesday 04:00 pm - 04:25 pm **O029**

First principles computational studies of hydrogen bonds in ice Ih

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It is the hydrogen bond that is responsible for most, if not all, of the unique properties of water ice. This bond is strong enough to cause water ice to exhibit more stable solid structures than any other material but weak enough to be easily broken at ambient temperatures or pressures. The difficulty of dealing with this intermediate strength interaction has lead most theoretical studies to consider the hydrogen bond as purely electrostatic, sometimes including polarization from surrounding media, and the water molecule as a rigid body. However, this oversimplification has lead to an ever-increasing number of empirical interaction potentials, nearly as many as there are properties to be studied. The increase in the sensitivity of a variety of experimental methods to examine the molecular environment of the water molecule in a condensed phase, including probing the hydrogen bond, requires a corresponding increase in sophistication in the theoretical treatment of hydrogen bonding.

The report continues our use of quantum mechanical calculations to study the details of the water-water interaction in Ice Ih. Large clusters of water molecules are used to examine, for example,

1) the energetics of defect formation caused by proton migration,
2) defect migration and annihilation,
3) disruption of the lattice by interstitials, and
4) absorption and/or reaction on an ice surface.

We also examine the changes in molecular orbital populations of the H-bonded molecules as the local environments change.

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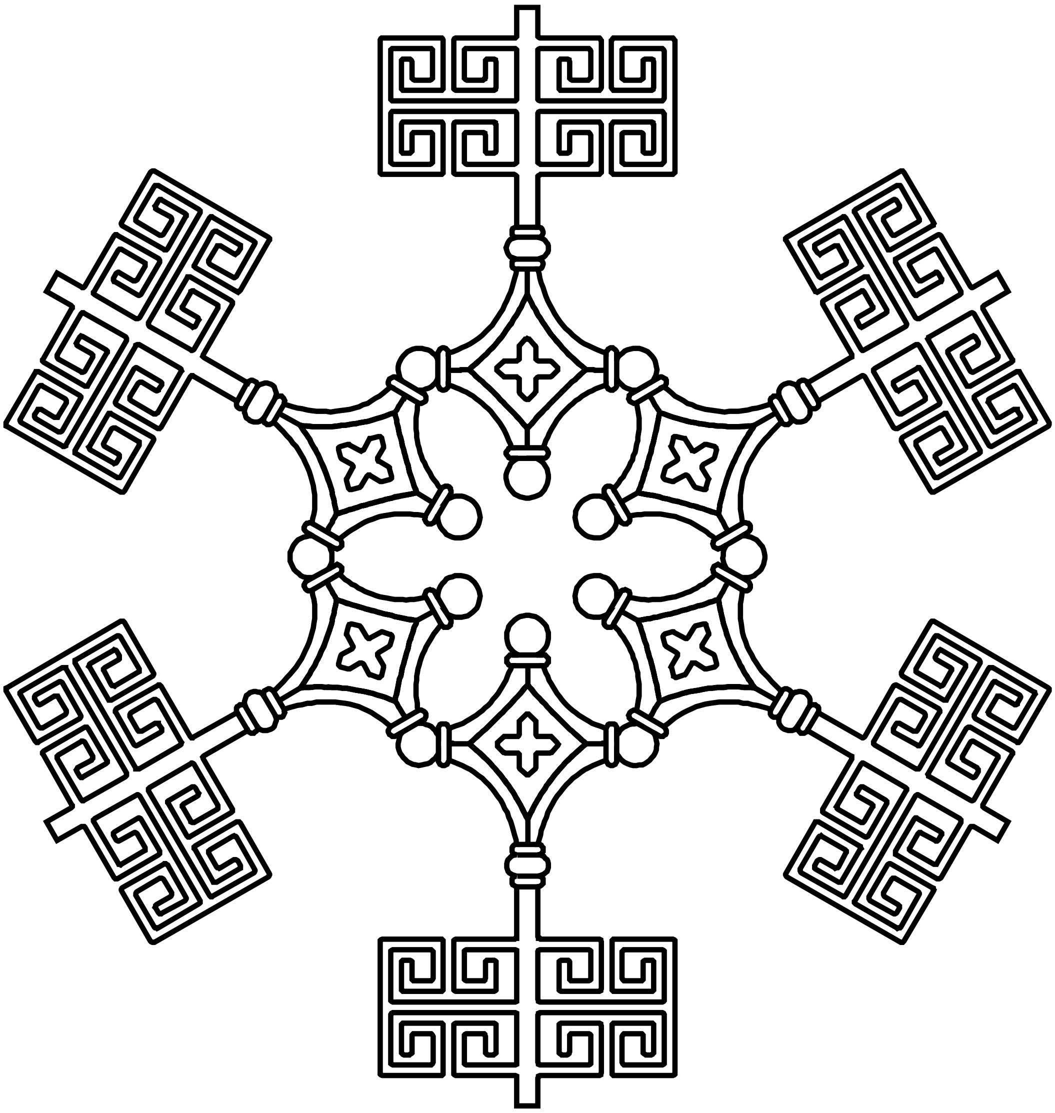
Gas hydrates

Chair: S. Kirby



Thursday 09:05 am - 09:50 am **O030 (invited)**

Improving our understanding of gas hydrate formation processes – the application of molecular-scale techniques

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Natural gas hydrates continue to evoke a lot of interest for a variety of reasons. Their large gas storage capacity is of great interest as the trapped natural gas is seen as a potential global energy resource as well as a possible agent of climate change. Also, hydrates have been proposed as media for gas storage and transport, and, more traditionally, hydrates in pipelines continue to be a major problem for the gas and oil industry by forming plugs. Although hydrates are crystalline materials, they are non-stoichiometric and form from components that have very low mutual solubility. Thus, the understanding of hydrate formation and decomposition is a multifaceted research problem involving structure, composition, guest distribution over the different lattice sites, phase equilibria, and kinetics, including nucleation, mass and heat transfer. Traditionally, bulk methods have been used to obtain a variety of parameters important in the understanding of hydrate processes, but there is general agreement among hydrate researchers that molecular-scale information is needed to build better mechanistic models. Techniques such as diffraction and NMR spectroscopy are especially powerful allies in that they give complementary information on the long range and local order in hydrate systems. When such structural probes can be combined with time and space resolution, one can start to unravel some of the complex processes that occur during hydrate formation. In this contribution a number of insights into hydrate processes will be presented which will impact the development of mechanistic models.

Fundamental studies for a new H_2 separation method using gas hydrates

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H_2 has become the object of attention as a clean and promising energy resource. The steam reforming of hydrocarbons is a well-known technique in the H_2 production processes. The gas mixture including CO, CO_2 and H_2 is generated by the steam reforming. H_2 cannot be stabilized in any hydrate cages except for an extremely high-pressure region [1]. On the other hand, CO_2 generates structure-I (s-I) hydrate easily in moderate conditions [2]. In the present study, we have proposed that gas hydrates are available as a medium of H_2 separation from such gas mixtures. As a fundamental study, we have investigated the isothermal phase equilibria (pressure - composition relations) for the H_2, CO_2 and water ternary system in the presence of gas hydrate phase. The experimental results suggest that gas hydrates formed from the H_2 + CO_2 gas mixture are pure CO_2 hydrates and H_2 behaves as if it is only like a diluent gas [3].

Tetrahydrofuran (hereafter, THF) generates structure-II (s-II) hydrate with empty S-cages at atmospheric pressure and temperature over the ice point [4]. The chemical formula of THF hydrate is $C_4H_8O \cdot 17H_2O$ (stoichiometric mole fraction of THF: 5.6 mol%). THF has been used widely as an additive that reduces the equilibrium pressure for other gas hydrate systems (for example, CH_4 and N_2 hydrates) [5]. Then, we have investigated the isothermal phase equilibria (pressure - composition relations) for the H_2, CO_2, THF and water quaternary system in the presence of the gas hydrate phase. The experimental results reveal that the addition of THF induces the large pressure reduction from the equilibrium pressure without THF. The largest pressure reduction is given by the stoichiometric THF solution of 5.6 mol%. However, the obtained phase diagram indicates that H_2 occupies the hydrate cage, as a result, a mixed gas hydrate including THF, CO_2 and H_2 comes into existence. That is, the advantage of THF addition depends on the operating condition for the H_2 separation process and the composition of mixed gas.

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Clathrate hydrate formation and growth: new experimental results versus modelled data

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[2]GeoForschungsZentrum Potsdam, Section 5.1, Potsdam, Germany

In 1987 Englezos and Bishnoi [1] developed the first model regarding the growth of gas hydrates from a liquid bulk. They assume that the dissolved gas molecule diffuses from liquid bulk through boundary layer around the hydrate particles, before a reaction at hydrate interface encase the gas molecule into a hydrate lattice. Regarding the nucleation of gas hydrates, Christiansen and Sloan [2] suggested that water molecules form labile clusters around the dissolved guest molecules which than agglomerate. Both hypotheses have in common that the gas (guest) molecule has to be dissolved in the liquid water phase. This leads to the conclusion that the solubility of the gas is one factor which affects incorporation of the gas molecules in the hydrate lattice. Other researchers, such as Rodger and Kvamme [3,4] supposed, that the gas molecules adsorb at the water surface before water molecules encase the adsorbed gas molecules and transform into a hydrate lattice. For this model the solubility of the gas is negligible.

In this work we studied the incorporation of different gases in the hydrate lattices depending on their properties (solubility, molecular weight, dimension, etc.) For this purpose investigations on gas hydrates which have been synthesized from gas mixtures and water or ice have been performed. The gas mixtures contain besides of methane the isomers of butane (n-butane; iso-butane) and pentane (iso-pentane, 2,2-dimethylpropane), respectively. Preliminary results lead to the conclusion that the solubility of the individual gas is negligible. It turns out that the gas composition in the hydrate phase is similar to the composition of the gas phase and not to the ratio of the dissolved gases in the water phase. These results have been compared to measurements on systems containing methane, carbon dioxide, hydrogen sulphide and nitrogen, where a similar trend could be observed. Additionally, systems with and without a free gas phase have been investigated. The experimental results are interpreted using common models of hydrate nucleation and growth.

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Rates and mechanisms of conversion of ice nanocrystals to ether clathrate hydrates: Guest-molecule catalytic effects at ~120K

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An FTIR investigation of the rates and energetics of conversion of ice nanocrystals within 3-D arrays to ether clathrate-hydrate (CH) particles at ~120K is reported. After an induction period, apparently necessitated by relatively slow nucleation of the CH phase, the well-established shrinking-core model of particle-adsorbate reaction [1] applies to these conversions in the presence of an abundance of adsorbed ether. This implies that the transport of the ether adsorbate through the product crust encasing a reacting particle core (a necessary aspect of a particle reaction mechanism) is the rate controlling factor. Diffusion moves adsorbed reactant molecules to the reaction zone at the interface of the ice core with the product (CH) crust. The results indicate that ether-hydrate formation rates near 120K resemble rates for gas hydrates measured near 260K [2]; implying rates greater by many orders of magnitude for comparable temperatures. A surprising secondary enhancement of ether CH-formation rates by the simultaneous incorporation of simple small gas molecules (N_2, CO_2, CH_4, CO and N_2O) has also been quantified in this study. The rapid CH formation at low temperatures is conjectured to derive from defect-facilitated transport of reactants to an interfacial reaction zone, with the defect populations enhanced through transient H-bonding of guest-ether proton-acceptor groups with O-H groups of the hydrate cage walls [3,4].

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Clathrate hydrates of argon, methane and acetone synthesized at 0.5-0.8 GPa. Structures, composition, thermal expansion and self-preservation

Manakov A.[1], **Ogienko A.**[2], **Kurnosov A.**[2], **Komarov V.**[2], **Ancharov A.**[3], **Voronin V.**[4], **Berger I.**[4], **Nesterov A.**[5], **Sheromov M.**[6]

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For the first time the quenched samples of high-pressure argon, methane and acetone clathrate hydrates has been recovered. The studied samples of the gas hydrates were prepared under high-pressure conditions and quenched at 77 K. The compositions of argon and methane high-pressure gas hydrates have been determined by direct measurement of gas volume emitted in the cource of hydrate decomposition. The composition of the argon hydrate (structure H, stable at 460-770 MPa) was found to be $Ar\cdot(3.27\pm0.17)H_2O$. This result shows a good agreement with the refinement of the argon hydrate structure using neutron powder diffraction data and helps to rationalize the evolution of hydrate structures in the Ar-H_2O system at high pressures. The quenched argon hydrate was found to dissociate in two steps. The first step (170-190 K) corresponds to a partial dissociation of the hydrate and the self-preservation of a residual part of the hydrate with an ice cover. Presumably, significant amounts of ice Ic form at this stage. The second step (210-230 K) corresponds to the dissociation of the residual part of the hydrate. Some aspects of the mechanism of self-preservation of clathrate hydrates was discussed on the basis of these data. The composition of the methane hydrate (cubic structure I, stable up to 620 MPa) was found to be $CH_4\cdot5.76H_2O$. Temperature dependence of the unit cell parameters for both hydrates has been also studied. Calculated from these results, the thermal expansivities for the structure H argon hydrate are α_a=76.6 K^{-1}, α_c=77.4 K^{-1} (in the 100-250 K temperature range) and for the cubic structure I methane hydrate are α_a=32.2 K^{-1}, α_a=53.0 K^{-1}, α_a=73.5 K^{-1} at 100, 150 and 200 K, respectively. The structure of the acetone clathrate hydrate has been determined by powder X-ray diffraction method and appeared to be very similar to the structure of high-pressure tetrahydrofuran hydrate recently determined in [1]. The distinctive feature of this structure is the only type of polyhedral cavity existing in the hydrate framework. The shape of corresponding polyhedron was not known earlier.

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Thursday 12:00 pm - 12:25 pm **O035**

Metastable ice VII at ambient pressure: New insights from neutron, Raman, and DSC measurements

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[3]University of Oxford, Inorganic Chemisty Laboratory, Oxford, United Kingdom

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When ice VI is compressed at low temperatures it transforms to metastable ice VII which can be recovered to ambient pressure at these temperatures [1,2]. We have shown previously [2] that macroscopic amounts of ice D_2O VII at 1 bar can be produced using the Paris-Edinburgh press to study its structural and transformation properties using neutron diffraction. Here we present new ambient pressure data of H_2O ice VII on its lattice dynamics using incoherent inelastic neutron scattering (IINS) carried out at 20 K at the TOSCA spectrometer of the ISIS facility [3]. We compare these IINS spectra as well as Raman spectra in the range 100-3500 cm-1 with corresponding data of its fully ordered form, H_2O ice VIII. The transformation behaviour on heating was studied by DSC, both for ice VII and ice VIII. These comparative studies give some insight into the effect of disorder in the dominant high pressure ice phases VII et VIII. Our study also allows excluding the existence of two types of hydrogen bonds, as previously suggested [4].

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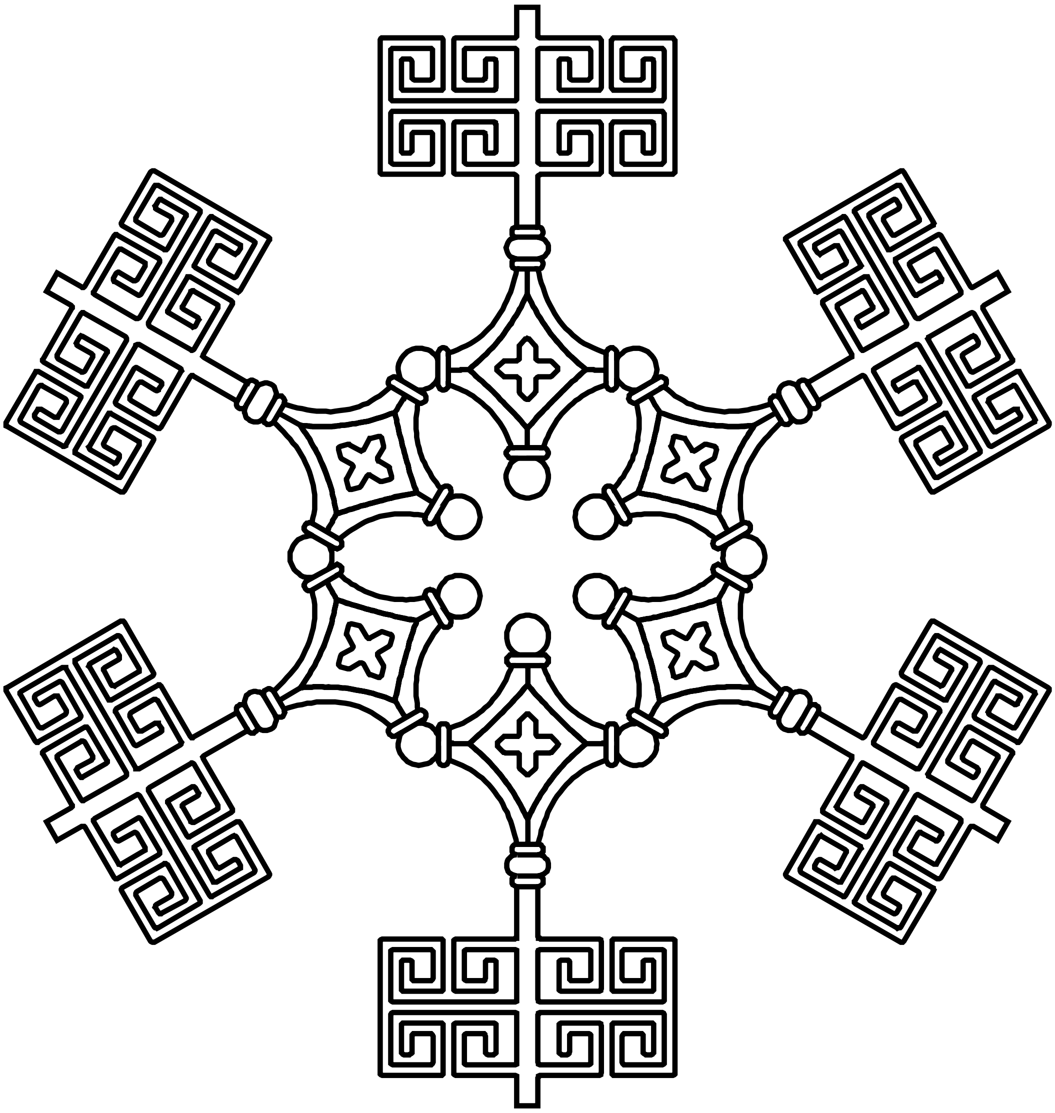
Ice mechanics

Chair: J. Glen



Thursday 02:00 pm - 02:45 pm **O036 (invited)**

Ice microphysics and ice deformation

Faria S.H.[1]

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No other material than ice has been so intimately related to the more than five thousand years history of mankind´s fascination for crystals. From the Greeks´ krystallos and Han Ying´s Moral Discourses up to Kepler´s Strena and Dalton´s atom, ice has been a motive power for the establishment of materials science and crystallography as new branches of modern science. Most alluring is the fact that, in spite of so many centuries of inquiry, ice remains in the spotlight of contemporary scientific arena, by continually challenging us with new phenomena and puzzling behavior. In this keynote we review the role of ice microphysics in the history of science and survey the past and modern research on ice microstructure and deformation around the world. Special emphasis is given on the anisotropic creep and recrystallization of cold glaciers and ice sheets, the role of growth, recovery, and heterogeneous deformation of ice grains, as well as some curious microstructural features recently observed in the EPICA Dronning Maud Land ice core.

Dislocation patterns in deformed ice and rate-controlling processes in the creep of single crystals and polycrystals

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The observation of “slip bands” in deformed ice single crystals [1]indicates the simultaneous and correlated motion of many dislocations. Acoustic emission analysis revealed the scale-free intermittent motion of dislocations through dislocation avalanches [2]. This spatio-temporel heterogeneity of slip implies long-range internal stresses and a relatively low lattice friction. Ice single crystals were deformed under torsion with the c-axis along the torsion axis and the dislocation patterning was analyzed by synchrotron X-ray topography at the European Synchrotron Radiation Facility. Analysis of topographs reveals a scale invariant character of dislocation arrangement with long-range correlations [3]. Internal stresses then appear of major impact when considering rate-controlling processes. The deformation of the ice sample was simulated by using the Dynamics of Discrete Dislocations model developed by Verdier et al. [4]. Cross-slip of dislocations on prismatic planes induced by the interaction between basal dislocations is shown to be an efficient process for the multiplication of dislocations and a plausible mechanism to explain the stress exponent equal to 2 for single crystals. Comparison between the deformation of monocrystals and polycrystals will be discussed in the context of the behavior of ice at low stresses.

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Physical properties of ice sheets - implications for, and findings from deep ice core drilling

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[2]Universität Göttingen, GZG - Abt. Kristallographie, Göttingen, Germany

[3]University of Technology, Department of Mechanical Engineering, Nagaoka, Japan

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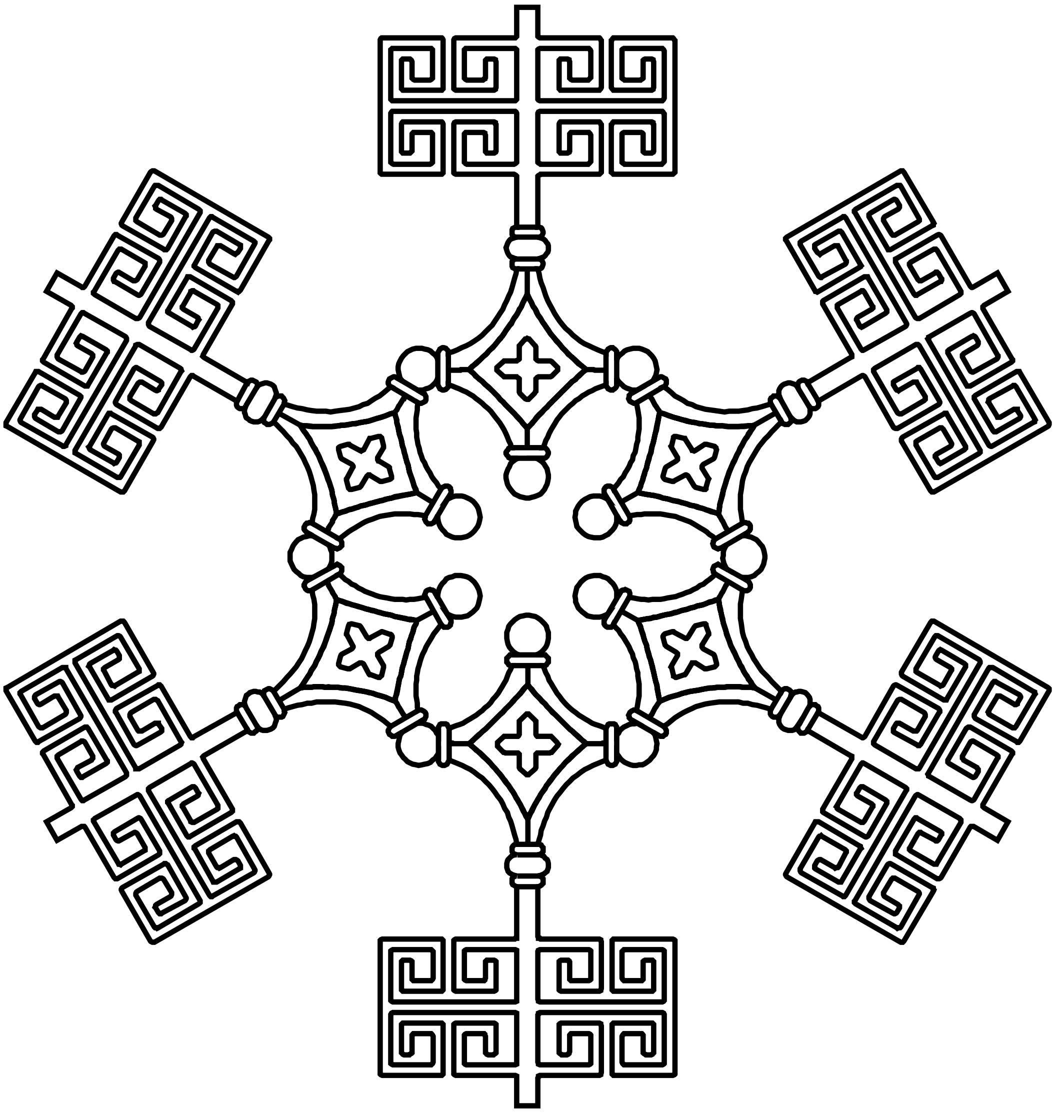
The cutting and flow properties of ice depend strongly on its physical properties, as e.g. crystallite size, shape and fabrics. As the crystallites properties depend on the geochemical impurity and dust load, as well as the ice flow, and thus vary with depth, the cutting behaviour when drilling an ice core will change with depth. We are at the beginning of systematic tests and we will present first qualitative observations and links between cutting size, core production, and ice properties.

The EPICA (European Project for Ice Coring in Antarctica) borehole in DML (Dronning Maud Land, Antarctica) was under-balanced by about three bars its bottom over two years. We found that the borehole closure strongly correlates with the crystallite size record as observed in the ice core. We will discuss this as an illustrative example and suggest to leave bore holes slightly under-balanced for a while to determine the flow properties of ice sheet directly from borehole closure.

Ice surfaces and interfaces

Chair: N. Maeno



Friday 09:05 am - 09:50 am **O039 (invited)**

Ice adhesion and friction: Fundamental aspects and applications

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Two physical properties of ice, its strong adhesion and its low dynamic friction, have driven the interest in ice research for decades. Since both properties are ice/solid-interface phenomena, significant attention was paid to the structure and properties of the ice-solid interfaces. This talk addresses fundamentals and some recent applications of ice adhesion and ice friction.

Ice adhesion in particular brings dangerous and costly problems. There have been numerous attempts to reduce ice adhesion by developing a durable ice-phobic coating. All of the attempts failed to decrease ice adhesion to a level, when ice can be easily removed from the coating. There are three major physical mechanisms of ice adhesion: electrostatic interactions, hydrogen bonding, and Van der Waals interactions. While the first two can be significantly reduces or even totally eliminated, the third one is strong enough to keep ice in place and cannot be cancelled.

A wide variety of deicing methods have been suggested in the past. The methods can be organized into three groups: mechanical ice removers, chemical methods, thermal ice melters. Of those three, only the thermal melters could clean protected structures well without damaging either the structure or polluting an environment.

The main limitation of the thermal deicing is its high energy requirement. Even in still air it typically takes 2 MJ/m2 or more to deice a surface. So much energy is needed, because an ice-structure interface is thermally connected to the ice bulk and to the structure. Thus heating the interface one should heat those large heat masses as well. When air-convection is involved, even more energy is needed. Thus, a large airplane can use up to 25% of fuel to keep its wings ice-free.

A recently invented Pulse Electro Thermal Deicer (PETD) [1], successfully overcomes that high-energy requirement limitation by effectively isolating an ice-solid interface from the environment. When optimized, a pulse deicer requires only 1% of the energy conventionally used in thermal deicing and can deice surfaces in less then one second. The technology was applied to deice airplanes, bridges, car windshields, to release ice from icemakers, and to defrost refrigeration coils.

It was also found that a similar to PETD technique applied to an ice-slider interface, can increase static and low-velocity ice friction up to one hundred times [2]. The method was tested on cross-country skis, non-slip shoes, and car tires.

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Friday 09:50 am - 10:15 am **O040**

Structure of thin film water and ice on α-Al_2O_3(0001)

Thomas A.C.[1], **Richardson H.H.**[1], **Chen L.**[1]

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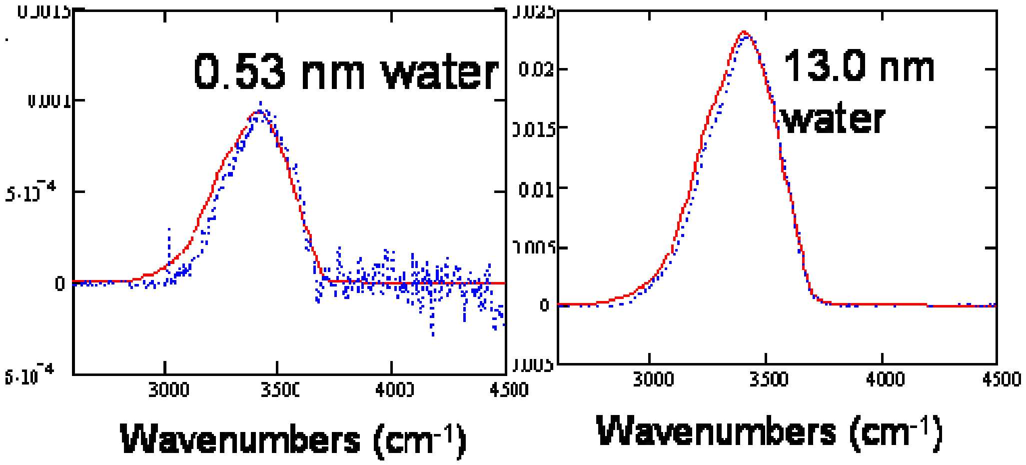
The spectral characteristics of adsorbed thin film water and ice on α-Al_2O_3(0001) were investigated using attenuated total reflection infrared spectroscopy. Thin film water was characterized by collecting extinction spectra as the water vapor was changed for a controlled temperature [1]. Isotherms for water were generated for different temperatures and the heat and entropy of adsorption determined for different coverages. The extinction spectra (shown in figure 1) were compared to calculated spectra using the bulk optical constants for water. A BET and thermodynamic analysis of the isotherms revealed that the structural characteristics of thin film water can be grouped into three distinct regions: molecular (coverages that approach a monolayer), intermediate (coverages between 1 and 15 water layers), and bulk-like (coverages greater than 15 water layers). Thin films of ice on BaF2(111) are not stable even though there is a near perfect lattice match between the (111) face lattice constants and the basal face of Ih ice [2]. In contrast to BaF2(111) thin films of ice are stable on Ge substrates [3-4]. In this paper we will contrast the stability and structure of ice and water on an ultra-smooth surface of α-Al_2O_3(0001).



[figure 1]

Figure 1. Extinction spectra of water at a thickness of 0.53 nm and 13.0 nm. The solid line is the calculated spectrum using bulk optical constants for water.

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Molecular dynamics simulations of brine rejection from freezing salt solutions

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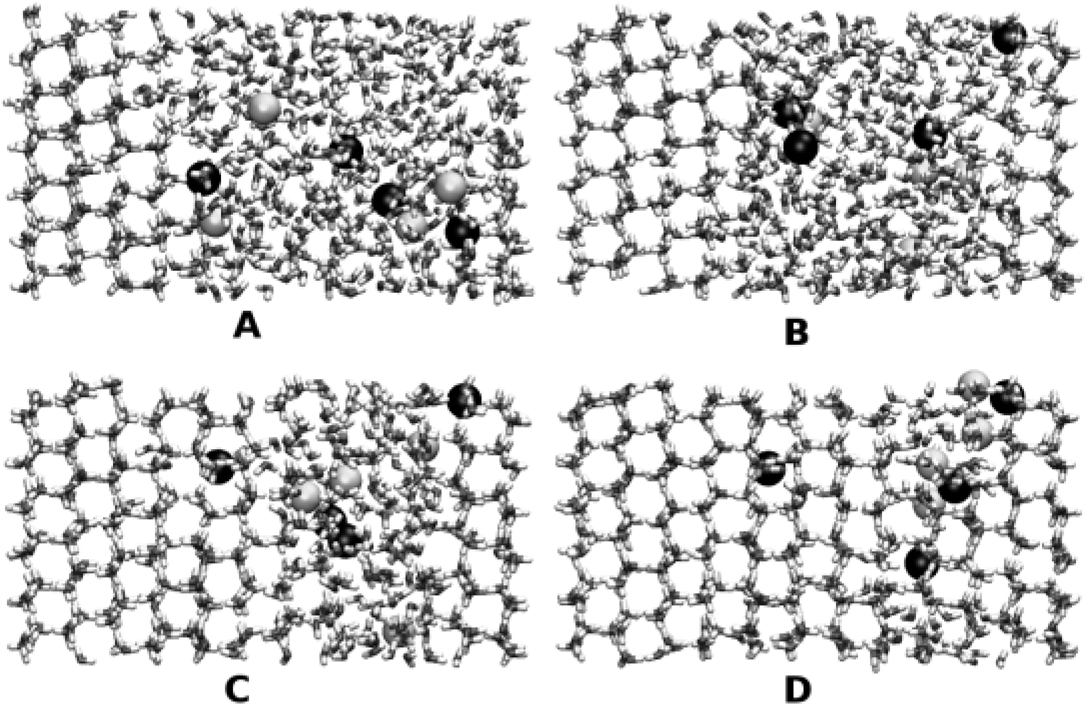
Extensive molecular dynamics (MD) simulations were used to study the atmospherically and technologically very important process of brine rejection from freezing salt solutions.

We focused on obtaining a microscopic picture of freezing of neat water and water containing salt (NaCl) in contact with a patch of ice. After establishing a robust simulation protocol we gained a tool allowing us to monitor the freezing process, following the motion of each water molecule and salt ion. Based on our results we propose a microscopic mechanism of brine rejection, in which a fluctuation (reduction) of the ion density in the vicinity of the ice front is followed by the growth of a new ice layer. This leads to formation of an ice crystal in contact with disordered unfrozen brine layer (see Figure). The freezing process is slowed down in the presence of salt. The freezing rates were also found to be dependent on salt concentration. The anti-freeze effect of NaCl was thus demonstrated at a molecular level.



[Snapshots from the salt water freezing simulation]

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Segregation of salt ions at ice surfaces (amorphous solid water)

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Amorphous solid water (ASW) films, deposited at 115K on Au, exposed to CsI and NaI on one side and CsF [1] vapour on the other side, were studied with metastable impact electron spectroscopy (MIES), UPS(HeI) and TPD between 120K and 200K. Surface segregation of iodide is observed, but not of fluoride, or cesium. The same surface ionic behavior is also derived from molecular dynamics (MD) simulations [2;3] of the analogous aqueous salt solutions. These results give a strong support to the suggested surface propensity of heavier halides (iodide, bromide) in liquid water, and confirm the structural similarity between the amorphous solid and the corresponding liquid. In contrast, no appreciable surface segregation of ions is observed in methanol, neither in the experiment (solid) nor in the simulation (liquid), which points to the remarkable surface properties of water among polar solvents. The propensity of heavier halides for the air/solution interface has important implications for heterogeneous chemical processes, particularly in the atmosphere at ice particles.

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Proton transfer at the surface of low temperature (90-140 K) ice

Kang H.[1]

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Proton transfer at ice surfaces was examined by monitoring the proton concentration and H/D exchange of water molecules at the ice surfaces. Thin ice films were prepared on a Ru(0001) substrate by depositing H_2O and D_2O in various layered structures at 90 -140 K, and protons were supplied from HCl. The progress of H/D exchange and proton migration was monitored by Cs^+ reactive ion scattering technique. The H/D exchange was confined within the first bilayer of the surface at $T < 100$ K. Vertical propagation of the H/D exchange to the interior region was both slow and shallow. Protons buried underneath a thin ice overlayer migrated to the surface slowly, but with a speed appreciably faster than that of water self-diffusion. The observation suggests that protons are mobile near the ice surface, in contrast to some previous reports of proton immobility, and that protons transfer via a different mechanism from water molecular diffusion.

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Geometric and electronic structure effects on stimulated reactions on low-temperature ice surfaces

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Radiation induced surface desorption from low temperature water ice plays a crucial role in the astrochemistry of icy planetary surfaces, comets and ice-covered interstellar grains. Excitations from low energy electrons (5-100 eV) or VUV photons (118 nm) can hop between the coupled hydrogen bonding network and migrate until they encounter a surface or a defect where they localize and induce dissociation. Ices deposited at very low temperatures, such as those in interstellar space, exhibit a relatively low density and have a highly porous amorphous structure. These pores enclose discreet volumes of vacuum and give rise to an enormous internal surface area. The electronic structure of water at the interface of these pores should resemble that of the outer surface vacuum interface. The effects of surface termination and the porosity and morphology of amorphous and crystalline D_2O ices on electron and VUV stimulated reactions on/within ice have been studied. In particular, we focus on the generation and trapping of D_2 and O_2[1,2]. These product yields increase from crystalline ice to amorphous ice to highly porous amorphous ice. This is attributed to the increased number of defects, traps and pores in amorphous ice. Molecular deuterium is released in the temperature range from 55 – 105 K for each sample, with two notable bursts at 115 and 132 K for porous amorphous ice. Molecular oxygen is retained within ice until much higher temperatures (> 140 K). The release at this temperature is attributed to sintering and diffusion along grain boundaries in crystalline ice. Amorphous ice releases a surge of trapped O_2 at the 160 K amorphous to crystalline phase transition, which is consistent with codeposition experiments. We have also used electron-stimulated desorption (ESD) to probe reactions and energy exchange on and within low-temperature water ice films. Specifically, we have examined the ESD of H^+, H_2^+, and $H^+(H_2O)_{n=1-8}$ from pristine [3] and HCl dosed ice [4]. The cluster yields and size distributions indicate hole-hole screening distances of 1- 2 nm and facile autoionization of HCl at temperatures as low as 85 K. Studies of water adsorbed onto Xe buffer layers on graphite support the contention that cluster production and desorption requires hole localization and terminal defect sites.

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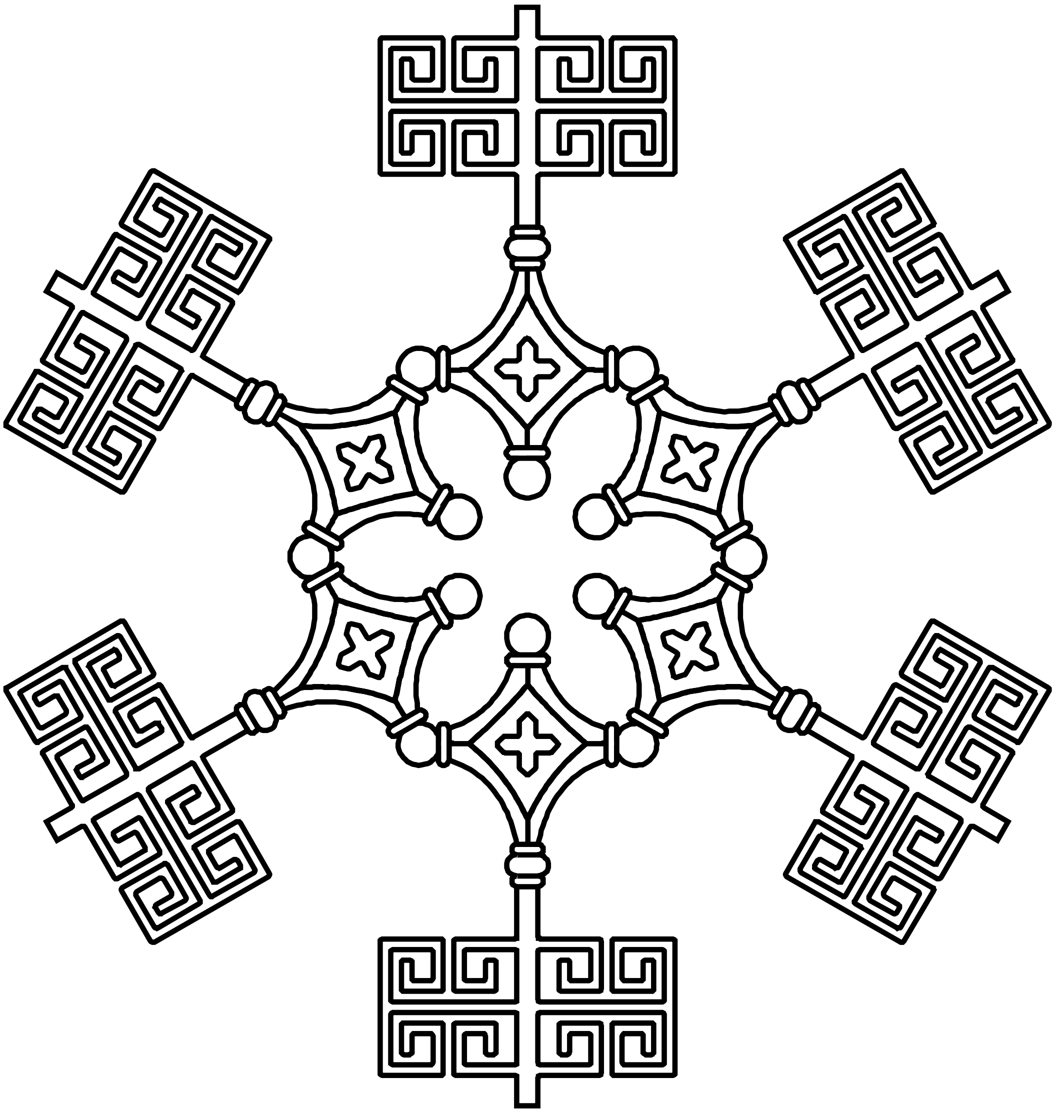
Ice and minerals

Chair: V. Petrenko



Friday 03:15 pm - 04:00 pm **O045 (invited)**

Extraterrestrial ice with emphasis on aggregation/interaction with organic matter

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Recent planetary explorations found a lot of icy bodies in the solar system and many glacial structures on the planetary surfaces. It is proposed by the theoretical studies and astronomical observations that the materials that construct the solar system bodies came from molecular clouds. In the molecular cloud, we can observe water ice and other ices, which are solid of highly volatile molecules: e.g. CO, CH_4, CO_2 etc., and organic matters are also believed to exist [1]. These ices are formed to be sub-micron sized dusts. These sub-micron dusts are supposed to aggregate each other to grow icy bodies in the evolution of the molecular cloud toward the solar nebula [2]. The aggregation of the dusts in the nebula occurs by collision, so that the physical condition of the collisional growth on the dusts and the aggregates are important to clarify the formation process of icy bodies.

Comets are fossils of the material in the primitive solar nebula evolved from the molecular cloud, so that there are a lot of observations finding highly volatile molecules and organic molecules in the comets [1,2]. Recent observations by planetary explorations revealed the densities and the surface structures of the comet nucleus. Thus, we recognize that it is a highly porous body having a surface layer composed of dusts and aggregates [3]. These properties are the same as that of icy planetesimals. Therefore, we can imagine that the comet-like bodies collided each other to become larger icy bodies in the solar nebula.

Impact experiments on the icy materials have been conducted to clarify the accumulation condition of the icy bodies and the formation process of icy satellites [4,5]. The impact strength of ice aggregates with the various porosities was obtained as a result of laboratory experiments: the strength of pure ice aggregates increases with the increase of the porosity from 0 to 40%. However, the impact strength of porous ice-rock mixture has the opposite dependence on the porosity compared to pure ice aggregates: the strength of the mixture decreases with increasing the porosity. According to the theoretical consideration based on the above results, we can obtain the accumulation condition of porous icy bodies and discuss the effect of rock contents on the formation of icy satellites.

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Interfacial melting of ice at SiO_2 interfaces

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The physical behavior of condensed matter can be drastically altered in the presence of interfaces. Using a high-energy X-ray transmission-reflection scheme, we have studied ice-SiO_2 model interfaces. We observed the formation of a quasiliquid layer below the bulk melting temperature and determined its thickness and density as a function of temperature. The quasiliquid layer displays a large density close to 1.17 g/cm^3.

In addition we studied the influence of microscopic interfacial roughness onto the premelting of ice in contact with amorphous SiO_2. We found that the onset of premelting and the initial logarithmic growth of the liquid layer do not depend on the substrate roughness. Beyond a critical thickness of L=1.8nm the molten layer exhibits a strongly enhanced growth following a power law with an exponent 1/3 at the rough interface. The reported anomalous high density of the liquid layer is independent of the roughness, but appears to approach the bulk value as the layer grows.

References

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Friday 04:55 pm - 05:20 pm **O047**

X-ray photon correlation spectroscopy study of ice premelting in powders

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Due to interfacial premelting, unfrozen water can persist in a frozen porous medium to temperatures far below water's bulk melting temperature. The same intermolecular forces that produce the premelted film also result in fluid flow towards colder regions when a temperature gradient is present. This flow is responsible for the frost heave that damages structures when soil freezes and the destruction of biological samples and foods during cryogenic preservation. While current theory can accurately describe the driving force behind this flow, a detailed specification of the hydraulic permeability is required to make quantitative predictions. This permeability depends upon the amount of ice present, which is a function of the local temperature, and the porosity of the medium, which can change as the medium freezes. In order to determine these two quantities, we have performed x-ray photon correlation spectroscopy (XPCS) on frozen mixtures of water and monodisperse silica microspheres. XPCS uses coherent x-rays to determine the dynamic properties of a sample through temporal correlations in the scattered x-rays' interference pattern. Static scattering data, which describes the structure of the sample, can also be obtained during XPCS. We present XPCS-derived effective particle diffusion coefficients and static scattering results for isothermal samples in the temperature range -25°C to 2°C.

Friday 05:20 pm - 05:45 pm **O048**

Experimental geoscience in a freezer: Ice and icy compounds as useful educational analogues for earth and planetary rocks and minerals

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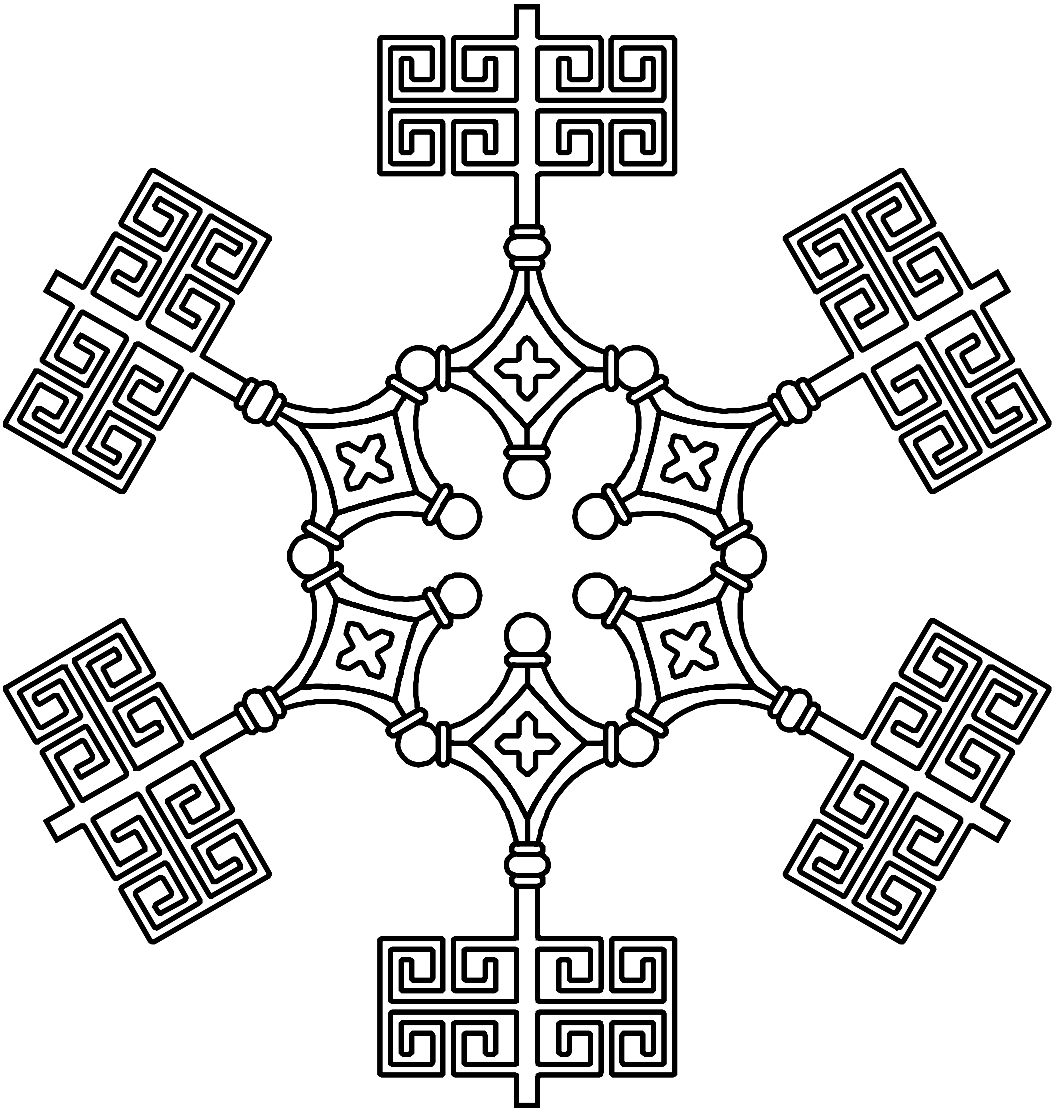
The purpose of this presentation is to stimulate interactive discussion on how to exploit what we have learned in the PCI realm by developing teaching curricula for inexpensive and safe laboratory experiments on ices. The behavior of terrestrial glacial ice (plastic flow, brittle behavior, development of crystallographic preferred orientations and property anisotropy, etc.) has long been recognized by our community as instructive to students of Earth´s interior and the icy planets and moons. Education for science students is most effective when it uses a balance of classroom instruction, personal reading, and laboratory experience. In the geosciences, lab experience of beginning students is usually limited to field trips and classroom identification of rocks and minerals. What is typically lacking is lab experience using experiments on mineral systems in which the fundamental material properties and governing processes are investigated. To do such experiments on silicate mineral systems, particularly at the high-school or undergraduate level, is often impractical, given the high-temperatures required to investigate thermally-activated processes and melting and the high pressures that are often necessary to investigate metamorphic reactions. Not only do ice and icy compounds and mineral systems occur on Earth, in polar planetary regions, and in the moons of the outer solar systems, they are excellent analogues for silicate mineral systems. Many of the processes that occur in Earth´s interior also are thought to in these planetary ices. The hydrogen and van-der-Waals bonding in their structures confer a number of useful properties, including low melting temperatures, high rates of thermally-activated processes at low temperatures, low pressures required for polymorphic reactions, usually relatively low ductile strengths, and low fracture surface energies. These materials are also typically optically transparent and their internal structures may be investigated by sectioning and transmission optical microscopic techniques. Our collaborative group at U.S. Geological Survey and Lawrence Livermore National Lab in California has done basic research on these planetary materials since 1982. This experience indicates that direct experience in measuring a whole suite of physical properties and processes is attainable at freezer temperatures and low applied stresses and pressure.

Poster Session I



Ordering effects on bonding interactions in ice phases

Jenkins S.[1], Kirk S.[2], Ayers P.[3]

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[3]McMaster University, Department of Chemistry, Hamilton, Canada

Ice VIII consists of two interpenetrating tetrahedrally coordinated hydrogen bonded anti-parallel sublattices. Each of the sublattices is highly ordered with all of the water molecules molecular dipoles aligned. The zone-centre modes of ice VIII [1,2] (with symmetry coordinates nTzA1g and nTxEg) exhibit motion that only distorts the inter-sublattice O—O interactions [3] where hydrogen bonding networks are not distorted. Comparisons then can be readily made with the O—O interactions in the less ordered phase ice VII. The effects that differences in the molecular dipole moments of the sublattices of ice VII and ice VIII have on the bonding are quantified by a detailed analysis of the differences of derived bond properties in the O—O interactions where marked differences in bond rigidity, for instance are quantified. In additional we perform similar analysis on ice VI, which possesses two hydrogen bonded sub-lattices as well as ice IX and ice II which do not. The hydrogen bonds in this study have a mixed character; as the total energy density H(r) is negative (except for ice VIII) indicating H(r) indicates of the covalent character of a bond[3], a larger negative value indicates a larger degree of covalency, again the converse being true for positive H(r).

The existence of the large numbers of phases of ice is explainable in terms of the competing effects of covalency and cooperative polarization.

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Monday 01:30 pm - 03:00 pm **005-P002**

Structural and chemical character of ice X and higher pressure ice phases

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The high-pressure phase (cuprite structure) labeled as ice X has been determined experimentally above 40 GPa [1]. This phase has a symmetric hydrogen-bonded structure and oxygen atoms take the body-centred cubic (bcc) arrangement. In relation to this, it was proposed that at very high pressure the oxygen sublattice becomes the denser face-centred cubic (fcc) form and the phase X is transformed into the anti-fluorite structure and after this a pressure-induced insulator-metal transition occurs [2] and that in [3] it was indicated that the evolution of the ice structure under compression to be in order; bcc, hcp (d-hcp), fcc, with the fcc (antifluorite structure) becoming metallic at 1.76 TPa.
In this work we explore using only properties derived from the gradient vector field of the charge density, using the theory of atoms in molecules (AIM), a variety of very high pressure ice phases. In this way we demonstrate the usefulness of the charge density to understand such properties as metallicity [4] when ice is in such extreme conditions (> 100 Gpa, since above this pressure the tunneling effect of the proton ceases).

References

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Monday 01:30 pm - 03:00 pm **008-P003**

Real-space study of mechanical instability in ice XI on a 'bond-by-bond' basis

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The effects of pressure on the structure of ice XI—an ordered form of the phase of ice Ih, which is known to amorphize under pressure—have been previously investigated theoretically using density-functional theory [1]. It was found that pressure induces a mechanical instability, which is initiated by the softening of an acoustic phonon occurring at an incommensurate wavelength. In this work we undertake a parallel theoretical study again using DFT as a starting point, and the theory of atoms in molecules (AIM). The mechanical instability of ice XI can be directly assessed in real space using the changes in the chemical character of the bonding and structural stability [2-4] which may be quantified at the separation between a bond critical point and its nearest ring critical point Dbr. The variation of Dbr that occur as a result of the structural distortion is quantified.

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Monday 01:30 pm - 03:00 pm **011-P004**

Structure, translational and orientational order of the amorphous ices

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[5]Università degli Studi di Messina, Dipartimento di Fisica, Messina, Italy

In this work we study through computer simulations the three known forms of amorphous ice, namely the low-density (LDA), the high-density (HDA), and the very-high density (VHDA) amorphous ices at various pressures and temperatures. Adopting the TIP4P model we are able to reproduce these three forms by following experiment-like procedures. Those systems are characterized from thermodynamic and structural points of view, in particular through an insightful analysis of the behavior of the second-shell neighbors in the various stages of the simulations. The distance-ranked neighbors are found to be the relevant markers of the differentiation mechanisms of the three forms, since their response to pressure induces specific distortions of the orientational correlations[1]. We show that LDA, HDA, and VHDA are disordered forms whose local structures tend to a single tetrahedral network, to an ice-VII-like arrangement[2], and to a random-close-packed (rcp) simple-liquid-like structure[3], respectively. Despite the major structural deformations induced by pressure, the hydrogen bonds are still present in each of those forms, even though deformations of the tetrahedral angles are necessary to adapt to the denser structures.
Finally, a new approach in terms of the translational and orientational contributions to the two-body entropy, successfully adopted to investigate the low and high-density forms of liquid water[4], is used to provide a new description of the three amorphous forms.

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Molecular mechanisms behind solid-liquid phase transition in ice micro-crystals. A molecular dynamics simulation study

Egorov A.[1], **Brodskaya E.**[2], **Laaksonen A.**[3]

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[2]St.Petersburg University, Department of Chemistry, St.Petersburg, Russian Federation

[3]Stockholm University, Division of Physical Chemistry, Stockholm, Sweden

The phase state of ice micro-crystals of varying sizes, from 20 to 125 molecules, has been studied by classical Molecular Dynamics computer simulations with some model potentials. The simulations have been carried out over a wide temperature range from 0 to 250 K in order to investigate the phase behaviour of small ice aggregates in respect to various characteristics, such as the system size and composition, an initial ice structure, the presence of an ion, its charge, size, etc. Attention was paid both to the shift of melting point related to the bulk phase and structural transformation processes in the clusters during the heating. Possible molecular mechanisms of phase-transition into the ice-clusters have been discussed.

The effect of an inserted particle on the ice-microcrystal melting has appeared to be a complicated process which depends simultaneously on a variety of factors, such as the particle initial position inside the cluster, its charge, size, etc. Moreover, the efficiency of these factors has varied. The details of structure transformation processes during the heating depend mainly on the type of hydration, surface or interior, which is preferable to the ion inserted, and the initial structure of an ice-cage.

This work has been supported by the grants of The Russian Foundation for Basic Research (04-03-32639-a) and The Swedish Science Research Council.

Clusters which occur at interfaces of water and ice

Ziemczonek L.[1]

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We have studied neutral clusters of water which contained hydrogen chloride and methanol. Number of water molecules in this clusters increases from one to six. We have calculated stabilization energies (the differences between the energy of the cluster and the energy of the individual molecules) for these structures. For clusters with hydrogen chloride they are from 4,64 to 37,83 kcal/mol and for those with methanol they are from 22,42 to 59,25 kcal/mol. Configurations of clusters have been calculated by Hartree-Fock ab-initio method with 6-311 G** molecular basis set. Structure and total energies of these clusters are also discussed.

We also apply in our investigations the group-theoretical method. Symmetry of the ice crystal determines kind of molecules which can be adsorbed at the surface of ice. The symmetry group of the adsorbed molecules must be the subgroup of the symmetry group of the ice crystal. These molecules are more likely to be adsorbed at the surface.

Molecular dynamics simulations of organic compounds adsorbed on ice

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It has been recently suggested that heterogeneous chemical processes could be invoked to explain the budgets of partially oxidized volatile organic compounds (VOCs) in the troposphere, because this region of the atmosphere is also characterized by the frequent presence of ice particles in cirrus clouds, which can provide surfaces for heterogeneous chemistry. Besides this influence of heterogeneous processes in the atmospheric chemistry, there still remain fundamental questions concerning how trace gases interact with ice surface. Up to now, a large number of studies have been devoted to nitrated and halogenated molecules indicating that strong interactions take place on the ice surface, leading, for instance, to the dissociation of the HNO_3 and HCl acids. By contrast, the few papers reporting on the adsorption of VOCs on ice all conclude that their uptakes are not as substantial as those of strong acids on ice for tropospheric temperatures between 200 and 240 K. Moreover, some experimental differences have been observed concerning the comparative behavior of these POVOCs on ice, depending on their chemical composition [1].
In this work, we have used molecular dynamics simulations to investigate the adsorption of small VOCs on ice at tropospheric temperatures [193 – 223 K]. The simulations have been done as a function of the adsorbate coverage, up to the completion of one monolayer above the ice surface. The results of these simulatons are compared with available experimental data, especially in terms of adsorption energy and saturation coverage and show a fair agreement for the different molecules considered in the present study [2-5]. Moreover, the simulations show that the interaction between these organic compounds and the ice surface is mainly governed by the formation of hydrogen bonds within the adsorbate and between the adsorbate and the water molecules of the ice surface.
The present study shows that molecular dynamics simulations are an accurate and useful tool for studying interactions between VOCs and ice, under tropospheric conditions.

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Diffusion of formaldehyde and methanol in ice: A molecular dynamics study

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Over the past decade, the role of organic compounds in heterogeneous processes at atmospheric ice interfaces has received much attention. Among the molecules of interest, formaldehyde (HCHO) and methanol (CH_3OH), as a HCHO precursor, are potential sources of HOx and their chemistry and dynamics at the ice or snow surfaces has thus significant implications in the ozone, HOx and NOx cycles [1,2]. The processes involved are adsorption, desorption, diffusion and incorporation at the gas/ice interface. Although the adsorption of both molecules on ice was compared in a previous theoretical study [3], a full understanding of these processes at a molecular level is still far from being complete. In particular, the incorporation, diffusion and release mechanisms of these two organic molecules at the ice surface have not been characterized yet, at least from a theoretical point of view. In the present study, we focus more specially on the diffusion mechanisms of methanol and formaldehyde molecules in bulk ice by means of molecular dynamics simulations, in the temperature range 220-270 K. The influence of the potential models, the ice structure and the nature of the pollutant is discussed, and possible implications to atmospheric chemistry is also addressed.

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Solvation of nitrate ion and hydroxyl radical at the air/water and air/ice interface

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Nitrate ion (NO_3^-) is a ubiquitous trace compound in the troposphere, both in the aqueous atmospheric aerosols and cloud droplets as well as in snow and ice. Photolysis of nitrate solvated in water or ice is one of the key reactions in the atmosphere, however, the reaction mechanism is still not fully understood.
We use a combination of ab initio quantum chemical calculations and classical molecular dynamics techniques to study the solvation properties of NO_3^- and one of its photoproducts, the OH radical. Examples will be given that provide insight into the microsolvation of NO_3^- and OH in small water clusters and their interaction with water both in the liquid and solid phases. The preference of the two species in terms of surface or bulk solvation will also be discussed.[1],[2] Knowing whether a particular species prefers to be fully solvated in the bulk water (ice) or rather partially solvated at the interface is essential for elucidating the mechanism not only of the nitrate photolysis, but of a variety of other heterogeneous reactions taking place in the atmosphere.[3]

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Hydrogen bond topology, new interpretations of order/disorder transitions in ice, and the behavior of defects in a disordered ice lattice

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Among the various phases of ice, certain transitions involve ordering or disordering of H-bonds: Ih/XI, III/IX, and VII/VIII, for example. The mechanism of these phase transitions is intimately linked to defects in ice because there is an interplay between defects and the hydrogen bond order/disorder of the water molecules that surround them. For instance, ice Ih transforms to ice XI only when doped with hydroxide ions, but many questions linger about the mechanism, since experiments suggest that ionic defects are not mobile near the transition temperature.

In this talk, theoretical methods are introduced which are capable of treating H-bond order/disorder in various ice phases, and the interaction of the H-bond topology with defects. The theory uses input from periodic electronic density functional calculations for small unit cells to parameterize interactions in terms of the H-bond topology. With the parameterization, statistical mechanical calculations can be done for large simulation cells.

We are able to describe the small energy differences among the innumerable H-bond configurations possible in a large simulation cell, either to describe phase transitions in pure water or to elucidate the interaction between defects and the topology of the surrounding ice lattice. Results are presented for ionic and Bjerrum defects in ice Ih, and for the phase transitions listed above. Particular emphasis will be given to the ice III/IX transition, and the behavior of hydroxide in ice Ih. We also present predictions of proton ordering phase transitions for ice V and VI.

Computer simulations of the 13 crystalline phase of ice

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We performed by isothermal-isobaric (Parrinello-Rahman) Monte Carlo simulations for the 13 known crystalline phases of water. Testing several non-polarizable models of water we found that none of them was satisfactory. The major shortcomings of the models were in the overestimation by a factor of two (~4-6 kJ/mol) of the internal energy difference between the high-pressure ice phases and the hexagonal phase. This discrepancy is caused by the parameterization to reproduce the density of liquid water at ambient conditions. In water and the low pressure ice phases each molecule has four neighbors, in the high pressure phases, however, there are eight contact neighbors.

We also studied the so-called cis/trans isomerism of ice polymorphs. Two water molecules connected by hydrogen bond in hexagonal ice can have four possible configurations. These configurations are distinguished by the relative orientation of the two molecules and termed for obvious reasons as c-cis, h-cis, c-trans, and h-trans. The occurrence of symmetry permitted dimer orientations is a characteristic feature of each ice phase. In the proton-ordered structures the occurrence of orientations is strictly determined, while in the proton-disordered structures it can vary within certain limits. We performed Monte Carlo simulations using the so-called TIP5P-EW interaction model to study this isomerism for the polymorphs of ice. We found the variation of energy with the frequency of different dimer orientations in the proton-disordered phases is large enough to influence the results of phase stability studies.

Monday 01:30 pm - 03:00 pm **043-P013**

A combined micro-Raman and theoretical study of formaldehyde ice mixtures

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In the atmosphere, formaldehyde (H_2CO) is an important intermediate in the photochemical oxidation of atmospheric hydrocarbons and is closely linked to the production of HOx radicals that control photochemical cycles involving ozone budget in the atmosphere. The interaction of trace gases (such as for e.g. formaldehyde) with ice (from ice clouds or ice in snowpack) can perturb this chemistry [1,2]. The incorporation of gaseous species during ice formation can occur by condensation or by collision with super-cooled liquid droplets. Both mechanisms can affect the ice structure and modify the nature and composition of the incorporated species. In this context, we performed both a micro-Raman spectroscopic study and theoretical calculations on the effects of freezing on formaldehyde-ice binary mixtures. Two kinds of samples were investigated at different concentrations: formaldehyde aqueous solutions [3] composed of oligomers and co-condensed H_2CO:H_2O gas mixtures [4]. Crystallization of various phases was observed experimentally upon temperature increase. From a theoretical point of view, a preliminary study concerns more especially the frozen aqueous solutions. Ab initio calculations are performed to quantify the competitive interactions between oligomers and water molecules. The frequency shifts calculated for small aggregates reproduce the experimental shifts characteristic of the formation of intermolecular H-bonds either between oligomers or between oligomers and water molecules [5]. These first principles calculations serve also to construct a realistic and simple potential model tractable for molecular dynamics simulations. From these latter calculations, the thermal evolution of the system is modelled and compared with the experimental results. For the CH_2O:H_2O gas mixtures, the potential model being validated, classical molecular dynamics are directly carried out mimicking the experimental conditions.

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HX photodissociation on ice : a quantum wave packets study

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In connection with ozone depletion, there has been a widespread interest in characterizing hydrogen halides (HX, X= Cl, Br, F…) adsorption at the ice surface, the acid ionization at the interface representing a key step in the heterogeneous chemical reactions involved in the ozone destruction cycle. A number of experimental and theoretical studies have been carried out to understand the acid/ice interaction. Special attention is now paid to the chemical reactions activated by the UV light. Indeed, radiations initiate chemical processes which transform adsorbed or gas phase molecules into highly reactive radicals. Until now, very few theoretical studies have been reported concerning the photolysis at the ice surface [1], the treatment of such complex processes being rather complex.

The work we present here, concerns the photodissociation of a molecule, HCl and HF, adsorbed at the ice surface. To describe this process, we use a quantum wave packet approach, notably the MCTDH method [2]. As a preliminary study, we have considered HX adsorbed on a frozen surface at 0K and described the dynamics of the H photofragment by 2 degrees of freedom. Results show that part of the wave packet describing the dynamics of the hydrogen is trapped into the ice cavity [3]. The majority of the wave packet is reflected by the surface and presents interferences structures. By contrast, the structures observed in the 2D photodissociation cross section vanish when the H motion is described by 3 degrees of freedom. Secondly, we address a comparison between HF and HCl regarding the adsorbate orientation and the potential energy. Finally, in order to take into account temperature effects, a similar study is carried out on disordered ice surfaces using configurations extracted from MD simulations at atmospherically relevant temperatures.

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Monday 01:30 pm - 03:00 pm **049-P015**

Theoretical study on gases in ice Ih investigated by the molecular orbital method

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Solubility of gases in ice is necessary to understand the behavior of gases in ice sheets but the experimental data of solubility were obtained only for few gases. To investigate the solubility of gas molecules in ice, we conducted molecular orbital calculations for the ice crystal containing a gas molecule using a semiempirical molecular orbital calculation program (MOPAC2000[1]). The calculations were conducted for the model structures of ice which were composed of 96, 288, and 360 water molecules in the unit cell to check the unit cell size dependence of the results. The ice structures of different unit cell sizes containing a gas molecule were optimized under the periodic boundary condition. As for air molecules, O_2 is more stable in ice than N_2. This was in line with our previous results that the migration energy of O_2 in ice was lower than that of N_2. [2] The details of the calculations for air molecules and other gas molecules will be presented. The energetically favored paths of the diffusion of gases in ice lattice will be also presented.

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The bend angle of water in ice Ih: The significance of implementing the non-linear monomer Dipole Moment Surface in classical interaction potentials

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The implementation of the physically accurate non-linear dipole moment surface of the water monomer in the context of the Thole-type interaction potential for water (TTM2-F) results in the only classical potential, which reproduces the experimentally observed increase of the monomer bend angle in ice Ih from its value in the gas phase. This is in contrast to all other classical potentials, which predict a decrease of the monomer bend angle in ice Ih from the gas phase value. The potential also reproduces the increase of the bend angle in small water clusters n=2-21 suggested by first principles electronic structure calculations [MP2 and CCSD(T)], whereas all other classical potentials predict a decrease of the bend angle in the clusters. The far-reaching consequences of this result on the condensed phase properties of liquid water and ice due to its effect on the electrostatic properties through the changes in the molecular dipole and quadrupole moments are discussed.

Optical study of heat generation and melting for gold NPs embedded into ice matrix

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We investigate the system of optically-excited gold NPs in an ice matrix aiming to understand heat generation and melting processes at the nanoscale level. Nanoparticles of CdSe and Au of various sizes embedded in ice are studied with Raman and emission spectroscopy. After several recrystallization cycles the particles are channeled into the grain boundaries of ice where the optical and thermal properties of the nanoparticles are probed with Raman imaging. Strong emission from CdSe particles is observed. The emission spectrum is relatively broad (30 nm FWHM) and peaked at 590 nm. A large percentage of the particles are found at the grain boundaries with a smaller number of particles still embedded in the ice crystals. The emission spectrum suggests that there is aggregation of the CdSe particles. The gold particles (5 nm) after several recrystallization cycles emit strongly around 600 nm. The “yellow emission” is believed to be from plasmon emission of aggregates. The aggregates also relax nonradiatively melting ice at the grain boundaries. Theoretical calculations and experimental data are combined to make a quantitative measure of the amount of heat generated by a single optically-excited gold nanoparticle.

Crystal orientations in quietly frozen ice sheets from fresh and brackish water

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Ice sheets from quietly frozen freshwater bodies are known to build up dominant crystal orientations. The interesting fact is that the dominant orientation can be c-axis horizontal or c-axis vertical. The literature on the driving factors for the geometric selection of quietly frozen freshwater bodies gives different reasons for the build up of a dominant c-axis orientation.

We present results of an experiment the aim of which is to clarify these driving factors. The focus of this study lies on two theories.

One is brought forward by Gow, who states that the dominant crystal orientation is determined by the characteristics of the initial ice skim [1]. In other words, a non-seeded ice skim will result in a c-axis vertical dominant ice sheet and a seeded ice skim will result in c-axis horizontal dominant ice sheet.

The other theory was filed by Shumskii. He states that the dominant crystal orientation is determined by the characteristics of the underlying water body [2]. A water body with a positive temperature gradient from the ice-water interface downwards and the interface at the freezing point isotherm will result in c-axis vertical crystals being dominant. A layer of water at the freezing point or slightly supercooled directly below the ice water interface will result in c-axis horizontal crystals being dominant.

Our experimental setup allows us a high level of control over the temperature gradient in the water column. We used a temperature probe with a high spacial, temporal and temperature resolution. We used crushed ice as seeds. We repeated the experiment at freezing temperatures >-5°C and at temperatures <-10°C to in order to observe whether the air-water temperature difference during initial freezing and the freezing velocity make a difference in the development of dominant crystal orientations.

In further experiments we plan to investigate the freezing of brakish water under the same conditions as above in order to find the salinity above which the behavior becomes similar to that observed in sea water.

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Monday 01:30 pm - 03:00 pm **066-P020**

Relationship between equilibrium and growth or melt shapes of disk crystals

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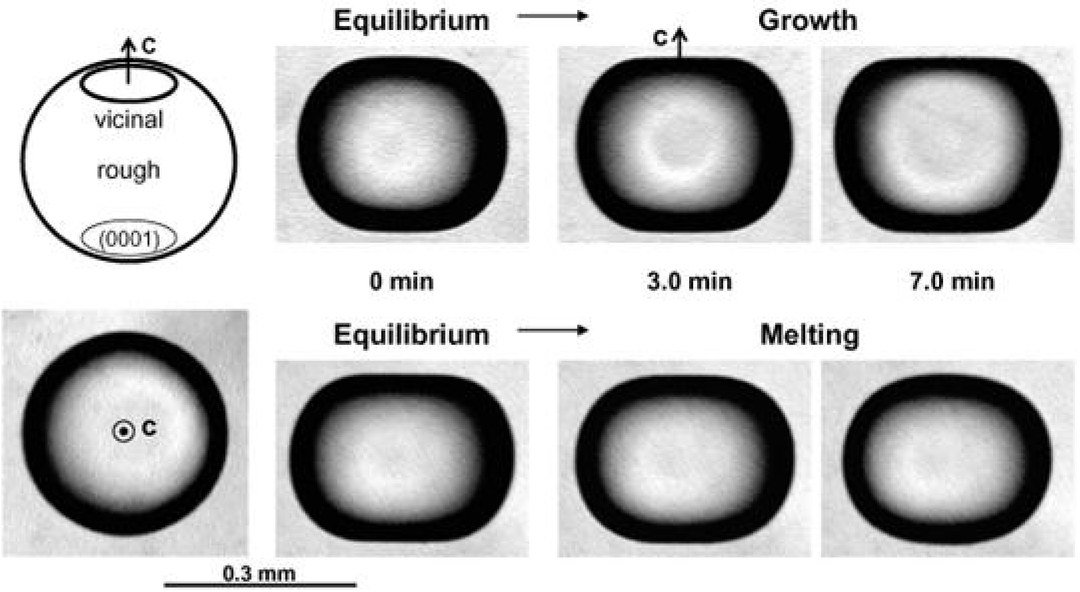
In slightly supercooled water at 1 bar, ice crystals grow as disks with the (0001) facets and a rounded side face in which all orientations, including prism faces, are molecularly rough. The rounded rough orientations grow rapidly and the smooth facets grow slowly; hence ice forms the shape of a disk. Here we focus on its side view in which facets and rounded surfaces are outlined. Strong attention is given to the rounded surfaces containing vicinal and rough surfaces. Using a high pressure anvil cell we produced a disk crystal, which was very thick and oriented with the c-axis perpendicular to the observation axis. The pressure was fixed at nearly 500 bar and hence the ice/water coexistence temperature was about -4C. If temperature is held constant, the ice crystal takes its equilibrium shape with a constant volume. During growth and melting the temperature is reduced and raised at a constant rate, respectively. Both growth and melt experiments were started after equilibrium was achieved at a fixed temperature. An equilibrium shape is partially faceted. When growth is initiated at a small drive, the rounded surfaces are grown and the facets are pinned. The vicinal regions near facet edges grow out of existence, leaving pinned facets that expand. The mean curvature of the rough regions decreases with their growth. During melting, however, the opposite phenomena occur in the vicinal and rough regions. We found asymmetry between growth and melt shapes of a disk crystal; (1) the vicinal surfaces gradually decay during growth but develop during melting; (2) the rough surfaces grow with decreasing curvature but melt with increasing curvature.



[PCI_1.jpg]

Growth enhancement of ice crystal by impurity effect of AFGP or AFP molecules adsorbed on ice/water interface

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Ice crystal growth in supercooled water containing of certain antifreeze glycoprotein (AFGP) or antifreeze protein (AFP type I) was observed in-situ using interference microscopy. The growth morphologies were observed as functions of the protein concentration and supercooling. Growth form diagrams of ice crystals in the aqueous AFGP or AFP solutions (0.0001 to 0.1wt% in concentration) were first determined. Growth forms strongly depended not only on the supercooling temperature but also on the protein concentration. Furthermore, we measured the growth rates of basal planes and along the a-axis directions, as functions of supercooling temperatures and protein concentrations using interference microscopy. The growth rates of basal planes were proportional to the supercooling temperature and were strongly "promoted" with increasing AFGP concentrations. This result is obviously different from the past understandings for the effect of AFGP or AFP type I molecules, in which the growth is strongly depressed by pinning the step motion at the adsorbed positions of molecules (namely, Gibbs-Thomson model, or pinning model). On the contrary, the growth rates along a-axis directions were suppressed in the polyhedral growth region, but enhanced in the stellar and dendritic growth regions.

These experimental results strongly indicate that the adsorption states of molecules depend on the crystallographic orientations of interfaces; namely, adsorbed protein molecules works as the **promoter** for the basal planes whereas the **inhibiter** for the prismatic planes. We propose a simple new model for the anisotropic adsorption of protein molecules, based on the characteristic adsorption depending on the structures of protein molecules.

Water vapor transport in snow under temperature gradient condition

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Snow in Arctic region is important as a cold source, when the heat balance on the climate was considered. It was clarifying by observation that the snow of the Arctic Circle such as Alaska, Finland is composed of depth hoar snow, because it changed under polar region low temperature less than -40C and large temperature gradient during severe winter. In this study, growth rate of depth hoar snow and mass transfer in snow, which developed in polar region, with water vapor sublimation were investigated experimentally. Experiments were carried out in the following way. Nylon mesh of 106μm size was stretched at a frame of the 250x250x25mm size. The lightly compacted snow, whose initial density and average diameter was 165kg/m3 and 2.7x10-4m, was put through a sieve into the frame, and the four frames were piled up. Between the frames, snow crystal could not move through the mesh, but water vapor can transfer. The snow sample was exposed to 530K/m temperature gradient condition. In this condition, the temperature of upper end was set to -65C, and lower end was -12C. The temperature of the snow sample was measured at six points; center of each frame, upper end, and lower end. After three days, mass change of each frame and growth of depth hoar snow were measured. Snow temperature distribution did not become linear; therefore, the temperature gradient is also different in the sample. It was proven that there was proportional connection between water vapor fluxes calculated from the snow temperature distribution on the growth rate of depth hoar snow. And, there was the good correlation between the distribution of mass flux calculated from the snow temperature distribution and that of experimentally measured value. From this result, it was proven that mass flux could estimate from the snow temperature distribution. The density decreased greatly at large water vapor flux layer, in which depth hoar snow largely grew. It was confirmed experimentally the weakness layer formation. It was clarified that water vapor transfer affects not only crystal growth but also mass balance under temperature gradient condition.

Prediction of the cellular microstructure of sea ice by morphological stability theory

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It is well known that seawater and saline solutions under most natural conditions freeze with a cellular interface, consisting of elongated vertical plates which are parallel within each grain. This plate spacing is the fundamental microstructure of sea ice. It determines the ice salinity, related to the brine entrapped between the plates, and is critical to model and understand many physical properties of sea ice as a porous medium. Previous attempts to correlate the plate spacing of sea ice in a simple manner with growth conditions, or to predict it theoretically, have been unsuccessful. Here it is shown that the plate spacing can be predicted from an approach based on morphological stability theory, if the latter is properly modified for the directional solidification of a cellular array. It is further demonstrated that solutal convection in a thin turbulent boundary layer below the cellular freezing interface has a strong impact on the plate spacing under most natural growth conditions. The resulting relationship between plate spacing and freezing rate does not show a constant slope, demonstrating why previous empirical correlation approaches have been unsatisfactory. Observations of the plate spacing during freezing of aqueous NaCl solutions and seawater have been carefully compiled from published laboratory and field studies. Although data at low growth velocities are sparse, it appears that the observations confirm the theoretical predictions of the plate spacing over five orders of magnitude in the freezing rate. The implications of the results for brine and salinity entrapment during the freezing of sea ice, marine ice shelves and in some other environments are pointed out.

The planar-cellular transition during freezing of natural waters

Maus S.[1]

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It is known that lake ice freezes with a planar interface, while ice growth on seawater proceeds vertically in form of cellular plates, oriented normally to its freezing interface and being parallel within each grain. In brackish waters both solidification modes have been observed. The present study demonstrates theoretically, at which solute concentration the transition from planar to cellular ice growth takes place during freezing of natural waters in the direction of gravity. The analysis involves a combination of morphological stability theory with a simple approach to model free turbulent solutal convection in a thin boundary layer below the ice-water interface. It leads to the prediction of a limiting water salinity, above which the interface is expected to become morphologically unstable and to evolve into a cellular solidification front.

Observations reveal the transition generally by an abrupt increase in the solute content of the ice. The theoretical results, in particular a predicted decrease in the transition water salinity with freezing rate, are in quantitative agreement with experimental data from several laboratory studies. The theory is also consistent with the limited field observations available. A comparison with published work on crystal fabrics of ice grown from saline solutions indicates, that the transition to cellular growth is associated with a transition to a horizontal c-axis orientation. Some implications of the planar-cellular transition in natural waters, as well as related physical applications due to its reasonable predictability, are discussed.

Flow-induced morphological instability in sea ice

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The interaction between the solidification of a binary alloy in the form of a dendritic layer of ice crystals and an external shear flow is investigated using trans-eutectic aqueous ammonium chloride solution in a laboratory flume. This dendritic layer is grown at a constant rate from the base of the flume, and a laminar shear flow is applied. We find a threshold speed above which convection is forced within the dendritic matrix leading to a spatiotemporal variation of the porosity with a planform wherein the long axis is transverse to the flow direction. We compare the growth pattern with a stability analysis which incorporates dissolution of the dendritic matrix and assess its importance to the formation of sea ice and associated salt fluxes.

Molecular-scale growth kinetics at ice-water interfaces: a molecular dynamics study using a new H_2O potential model

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The growth kinetics of ice from water, especially its anisotropy, is an important subject that should be investigated in detail on a molecular scale, because it is essential to understand the pattern formation of snow and ice, and the freezing of water in biological systems. It, however, still remains unclear, because it is quite difficult to observe by experiment. Computer simulations, such as molecular dynamics (MD) are a helpful tool to elucidate the growth kinetics of ice from water on a molecular scale. In order to elucidate it by MD simulations, we recently developed a new potential model of H_2O (the six-site model) [1]. The strength of the model is that it provides the stable structure of real ice near the melting point (Tm) at 1 atm. Moreover, Tm of ice in the model is very close to the real Tm of 273 K. Density curves of ice and water near Tm are also satisfactorily reproduced in the model. Using the six-site model, we carried out MD simulations of interfaces between ice and water near the real Tm at 1 atm [2, 3]. The anisotropic growth velocity among interfaces of {0001}, {1010} and {1120} planes of ice, which agrees with a macroscopic shape of ice, was obtained: The growth velocity was smaller on the {0001} plane than on the {1010} and the {1120} planes. Moreover, during growth on the {1120} plane, the {1120} plane disappeared and {1010} planes appeared instead, reflecting that the growth velocity was larger for the {1120} plane than for the {1010} plane.
The interface structure and growth kinetics was analyzed for all planes in detail. The results indicated that growth occurred by re-organization of the hydrogen-bonded networks in water near the interface. The results also indicated that both the interface structure and growth kinetics were strongly anisotropic. Details of the anisotropy and their relationship to a macroscopic shape of ice will be discussed at the presentation.

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FTIR study of the structure of antifreeze proteins at ice/water interfaces

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It is well known that ice crystal growth in supercooled solutions of antifreeze proteins (AFPs) and glycoproteins (AFGPs) is strongly inhibited by the adsorption of protein molecules at the ice/water interface. This property has attracted significant interest for their potential applications in medicine and industry where low temperature storage is required and ice crystallization is damaging. Although many experimental studies have been carried out, the mechanism of the anti-freeze effect has not been clarified yet. Toward this end, it is important to analyze the conformation of proteins at ice/water interfaces. However direct information about the adsorption state of protein molecules is limited because of the difficulty of in-situ observation of ice/water interface. Recently, Tsvetkova et al.[1] suggested the high flexibility of AFGP molecules which possibly reflects the necessity to expose more ice-binding groups. We conducted experiments to analyze the molecular structures of AFP and AFGP at ice/water interfaces using FTIR spectroscopy.

First, we carried out the one-directional crystal growth of ice in AFP and AFGP solutions and analyzed the protein structures by micro-FTIR spectroscopy in order to compare the structures of proteins at ice/water interfaces with those in the solutions. Furthermore, ATR spectroscopy was also used to analyze the structures of AFP and AFGP molecules adsorbed at ice surfaces. The role of the proteins at the ice/water interfaces for the mechanism of ice growth inhibition will be discussed.

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Adsorption of antifreeze proteins on hydrophilic and hydrophobic surfaces

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The adsorption behaviours of antifreeze proteins, control protein and control polymer on hydrophilic and hydrophobic surfaces are studied by quartz crystal microbalance with dissipation factor measurement (QCM-D). The desorption of the macromolecules are also studied. The differenct effects are also examined by contact angle measurements. Different adsorption behaviours of the tested proteins and polymer will help to understand the effects of them on the heterogeneous nucleation of ice and gas hydrate.

The growth of crystals and the transmission of light in frost surfaces

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Water ice is the dominant surface component on many surfaces in the solar system. Understanding interaction light with ice and a solute such as organic molecules is of prime importance to understanding many planetary objects include Mars, where the polar caps may contain organics at some depth; Titan, which appears to have organics in abundance and may have water ice; and comets, where the organics primordial and intermixed a icy crust. Light and other radiation impinging on these surfaces serves both as a probe of the surface composition (as measured with remote sensing and in situ instruments) and as a source of energy that modifies, often greatly modifies, the ice-organic systems. A particularly challenging problem is to develop a capability to reliably calculate the detailed radiation field within icy surfaces that exhibit significant scattering, such as surface frosts or extensively fractured ice.

Scattering properties within an icy mixture impose a spectral shape different from that found from (for instance) from transmission measurements on thin films. The spectral shape also depends with viewing geometry. Present scattering models use parameters that are difficult to tie to physical properties of the mixture, such as particle shape and absorption path length. As a consequence, it is not yet possible to accurately determine the composition of icy mixtures from remote sensing measurements, nor to set reliable detection limits for organic molecules that may reside within icy surfaces.

The size and shape of crystals within the ice matrix can change over time at a rate that is strongly affected by temperature. Size and shape affect the depth of penetration of radiation and the absorption path length within the ice. .The ice matrix itself is modified by radiation. This affects the transport of energy within the ice, the shape of ice spectra, and the amount of reactive species (e.g. ions and radicals) available for modifying included organics.

Ice crystals formed by deposition from the vapor phase on borosilicate substrates have particle sizes, as measured directly by environmental scanning electron microscopy measurements and by surface area (BET) measurements that are related to formation temperature. These sizes neither increase nor decrease at time scales accessible in the laboratory. The particle sizes do increase when the samples are annealed.

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Crystal growth of ice I/hydrate eutectic binary solutions

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As part of our ongoing investigation of chemical systems likely volumetrically important on Europa, we conducted laboratory experiments to examine the phase morphology and deformation behavior of several two-component, two-phase aggregates of salt hydrate + ice I: H_2O-Na_2SO_4, H_2O-$MgSO_4$, and H_2O-NaCl. The samples in this study were prepared by a eutectic solidification reaction in which cooperative, side-by-side growth of the two solid phases occurs in a supercooled, homogenous liquid solution. Thermocouples positioned within samples recorded the release of latent heat of crystallization allowing us to quantify growth rate during solidification. Microstructural analysis was performed using images obtained from Cryogenic Scanning Electron Microscopy (CSEM). Phases were identified using cryogenic x-ray diffraction (XRD) and energy dispersive x-ray (EDX) analysis. The observed microstructures consist of "colonies" of fine, ordered two-phase intergrowths. We found that the morphology of the intergrowth within a colony is unique to each ice/salt system, regardless of its bulk composition. In general this morphology is determined by the volume fraction of the constituent phases at the eutectic and by such factors as each of the phases' growth anisotropy. We present the three morphologies attributable to the above systems and compare them to nearly identical structures seen in metallurgy. Numerous studies on these analogous engineering materials have shown that the complex nature of the eutectic microstructure affects its mechanical response. Indeed, initial compressional creep tests have already given some indication that, like their counterparts in metallurgy, those systems that have significant volume fractions of salt at their eutectic are notably stronger and have far more complex rheologies. If this is the case, and if the crust of Europa, or any other icy satellite, formed via crystallization from a brine of such a system, then it could have a far greater viscosity than currently predicted from a pure ice model.

The firnification of snow measured by X-Ray-micro-tomography at the EPICA-Drill site Dronning Maud Land (DML), Antarctica

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The firnificaton of dry polar snow has been investigated with the means of X-ray micro-computer tomography (CT). The measurements were carried out on shallow firn cores and snow pit samples during the field campaign 2005/2006 at the EPICA (European Project of Ice Coring in Antarctica) DML-drill site, Antarctica. The CT-devices have been successfully tested in the field and offered us a novel method to study the fragile three dimensional structures of deposited snow and firn.

In this presentation we focus on the evolution of pore/ice cluster sizes and on the development of intergranular bonding. The parameters are derived from volume image analysis of the three-dimensional CT-reconstructions. We show that the number of bonds per cluster in samples near the surface is highly correlated to their respective density. Accordingly, the neck radii are anticorrelated to the density. Maxima of pore size and anisotropy are observed at depths where the metamorphism is dominated by temperature gradients. The relevance of experimental findings is discussed in relation to recent firnification models.

Possible use of Gaussian curvature for the 3D segmentation of snow grains from microtomographic data

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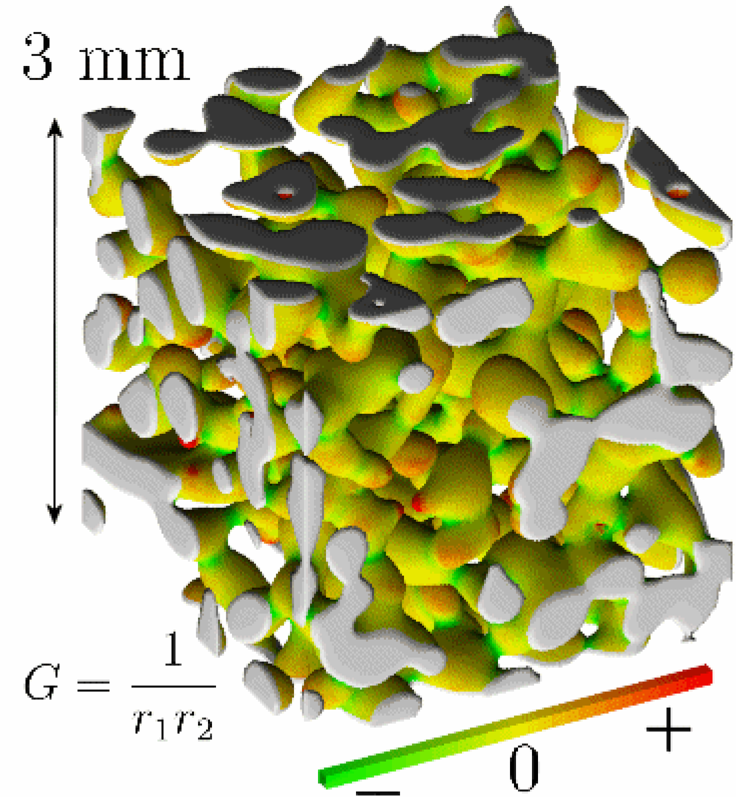
The Gaussian curvature G, namely the product of inverses of the principal radii of curvature, is a natural descriptor of necking regions on a surface. It was recently proposed as a means of segmenting raw triangulated data [1]. G can be computed also from raw voxel data by using the field of normal vectors of the 3D object [2]. To avoid digitization effects, this field can be computed on an adaptive neighborhood that accounts for singularities in the distance map of the image [3]. The use of G for sintered materials like snow may locate regions of potential stress concentration - that is - the most probable fracture surfaces of grains when extracted mechanically from the snow matrix. Such a segmentation process is expected to allow some realistic comparisons between the recent 3D data on snow and the existing wealth of snow grain data; this can be helpful for the parametrization of the microstructure behavior in field-scale models of snow cover. For snow layers evolved under low temperature gradients, regions where $G<0$ are also expected to comprise most of the grain boundaries, which may have interesting issues in further micromechanical studies.



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Ripple formation mechanism on icicles under a thin shear flow

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As one of examples of morphological instability in nature, ring-like ripples appear on the surface of icicles during ice growth when icicles are covered with a thin film of flowing supercooled water. The wavelength from peak to peak of the ripples is about 1 cm [1], which is similar regardless of variations in air temperature, icicle thickness, or growth rate. The fundamental building block of the morphological instability is the Mullins-Sekerka (MS) instability of a solidification front, which gives conditions for the growth of infinitesimal disturbances of a solid-liquid interface [2]. The dispersion relation in the MS theory for a pure material contains two characteristic lengths, which are the thermal diffusion length and the capillary length associated with the solid-liquid interface tension. As a result of competition between destabilization due to thermal diffusion and stabilization due to the Gibbs-Thomson (GT) effect (the melting temperature depression due to the curvature of the interface), a pattern with a specific wavelength is developed. However, since the thickness of flowing water film on the surface of icicles is about 100 micrometer, the thermal diffusion layer is not formed in the liquid. Furthermore, we can neglect the GT effect because the wavelength of the ripples on icicles is about 1 cm. Therefore, we have recently developed a quite new mechanism for the ripple formation on icicles [3,4], which is completely different from a previous theoretical model to predict the wavelength of ripples [5]. To the best of our knowledge, theoretical investigations have never been made on the morphological instability of solidification front in crystal growth from thin flowing liquid with one side being a free surface, on which restoring forces due to gravity and surface tension act. In our new model, the destabilization and/or stabilization of the solid-liquid interface is related to the magnitude of phase difference between the deformed solid-liquid interface and distribution of latent heat flux on it. The phase shift changes by the strength of restoring forces acting on the liquid-air surface, which depends on the wavenumber of the deformed solid-liquid interface. Our model also predicts that the solid-liquid interface moves upward direction, which is consistent with the observation that many tiny air bubbles trapped in just upstream region of protruded part of an icicle migrate in the upward direction during ice growth [1].

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UV photolysis of amino acids in crystalline water ice: Can they survive on Europa?

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We report the rate of decomposition by ultraviolet photolysis of 4 simple amino acids in crystalline water ice matrix at T=100K to constrain the survivability of these important organic molecules within ice lying near the surfaces of outer solar system bodies. As a specific example, we focus on Europa where subsurface liquid water or “warm ice” may be extruded onto the surface from a liquid water reservoir at depth during resurfacing events associated with the globally distributed linea and “bands”, long linear “cracks” [1-4], or during activity in the “chaotic terrain” [5, 6]. As an analog to some planetary ices, our liquid solution samples were frozen to form mm-thick crystalline phase hexagonal ices that appear “white” due to multiple scattering from internal microstructure. After irradiating the ice-amino acid mixtures with an Argon mini-arc UV continuum light source [7], the remaining fraction of amino acids was analyzed using a derivatization technique based on a fluorescence reaction [8]. Ice samples of 0.14, 0.28 and 1.6 mm thickness, prepared from ~10-4 M solutions of glycine, D,L-aspartic, D,L-glutamic, and D,L-phenylalanine were irradiated from 10 to 1020 minutes. We found that the half-lives for decomposition of the amino acids in ices are linearly proportional to their thickness as is expected for a layer with strong multiple scattering. Glycine is found to be the most resistant to destruction while phenylalanine is the most easily destroyed. For the 1.6 mm thick samples, under our lab conditions, we determined the half-lives of glycine, aspartic, glutamic and phenylalanine are 57, 21, 23, and 8 hours, respectively. For similar ices under solar irradiation at Europa, these results can be expressed as a “penetration velocity;” the depth to which half of the amino acids are destroyed in a year. We calculated that half of these amino acids in the upper meter of low latitude ice on Europa will be destroyed by solar UV on a timescale of ~2-300 years. We also measured UV transmission for phenylalanine ice samples in the 230-270 nm wavelength region and investigated the effects of irradiation on the strong absorption bands of phenylalanine (an aromatic amino acid) in water ice at 100K. UV transmission spectra show little or no change with the exposure time, however, the shape of the absorption differs significantly from that in the liquid, perhaps due to the formation of hydrogen peroxide during irradiation.

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Effects of additives and cooling rates on cryo-preservation process of rat cortical cells

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Cryo-preserved neurons offer some clear advantages over freshly dissociated cells: they provide flexibility to the culturing process and represent a ‘cell reserve’ that eliminates the need for timed pregnancy animals each time cell culture is initiated. However, neuron is one of the difficult cells to cryo-preserve with the usual protocol. The difficulty is mainly resulted from the uncertainties of cryo-preserving mechanism via the protocol. To overcome this difficulty, we should know the effects of additives and of cooling rates on the cryo-preservation of neurons. In this study, we examined both effects to reveal its precise mechanism. Primary rat cortical cells were prepared from neonatal SD rats at within 3 days. Neurons were suspended in the culture medium at a density of 1x10^6 in 1 ml solution. The medium included the following cryo-protecting additives: dimethyl sulfoxide (DMSO, 5 – 20 wt%), trehalose (100 – 500 mM), and the mixture of trehalose (10%) and methanol (10%). The cooling rate varied from slow (about 10^0 K/min) to rapid (10^2 K/min) for these cell suspensions. After storage of the sample at each temperature (at about 193 K for slow cooling-rate and at 77 K for rapid one) for a week, the sample were thawed in the warm bath (about 310 K) rapidly and cultured in the incubator (humidified atmosphere including 5% CO2 and at 310 K) after replacing the cryo-preserving additives with the culturing medium. The recovering of neurons was firstly determined by the microscopic observations of the cultured samples. The neurons in the recovered cells was confirmed with the neuron-specific markers microtubule associated protein 2 (MAP-2). After this rough classification of the effectiveness of cryo-preservation in each protocol, we measured the extra cellular potentials of the neurons to verify their function. Results indicated that there are some appropriate protocols to cryo-preserve the primary neurons. The effectiveness of additives and cooling rates on the results suggests the cryo-preservation mechanisms of neurons.

Monday 01:30 pm - 03:00 pm **116-P037**

Fluorescence microscopy studies of ice surface - antifreeze proteins interactions

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Antifreeze proteins (AFPs) protect animals from freezing by binding to extracellular ice and inhibiting its growth. Since the initial discovery of AFPs in fish, non-homologous types have been found in insects, plants, bacteria, fungi, and vertebrates. Different AFP types have diverse structures and varied activities. For example, AFPs produced by insects are much more active in inhibiting ice crystal growth compared to most AFPs found in some fish and plants. By conjugating biological fluorescent markers to various types of antifreeze proteins, we were able to visualize AFP binding to ice, to determine the ice crystal surfaces to which different types of AFPs adhere, and to follow the kinetics of AFP binding to ice. For the case of a pout fish AFP type III we were able to demonstrate, by lack of recovery after photo-bleaching, that there is no extensive exchange of AFP at the interface of the ice. This finding supports the models that assume tight binding of AFP to the ice surfaces. For the spruce budworm AFP which causes a large thermal hysteresis activity we identified accumulation of the proteins in particular crystallographic directions. We expect that direct visualization of various AFPs in interaction with ice within the thermal hysteresis gap will contribute to a better understanding of the mechanism of AFP activity and in particular the hyperactivity of insect AFPs.

Water adsorption on bio-membranes

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By employing temperature programmed desorption and time-of-flight secondary ion mass spectroscopy the adsorption of water on the hydrophilic and the hydrophobic surface of a lipid (DPPC) film has been investigated. It could be shown, that it is possible to prepare lipid films ex-situ with a preferential orientation of the lipid molecules on a solid support and to retain their specific properties under ultra high vacuum conditions. The water adsorption and desorption kinetics on the hydrophilic and hydrophobic surface provided by a lipid film are discussed in terms of their structural and chemical properties.

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Chemistry induced by implantation of reactive ions in water ice

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Solid surfaces of atmosphere-less objects in the Solar System are continuously irradiated by energetic ions (from solar wind and flares, from planetary magnetospheres, and cosmic rays). Reactive ions (e.g., H, C, N, O, S) induce all of the effects of any other ion including the synthesis of molecular species originally not present in the target. In addition these ions have a chance, by implantation in the target, to form new species containing the projectile. An ongoing research program performed at our laboratory has the aim to investigate the implantation of reactive ions in frozen ices (and mixtures) relevant to planetology, by using IR spectroscopy [1-4]. Here we present results obtained by implanting carbon, nitrogen and sulfur ions in water ice at 16 and 77 K. Carbon implantation produces carbon dioxide with a production yield of about 0.5 molecules per impinging ion. Nitrogen implantation does not produce any N-bearing species that is detectable by IR spectroscopy. We find that after sulfur implantation hydrated sulfuric acid is formed with high yield (0.7). All of the ions have also the capability to synthesize hydrogen peroxide at the two investigated temperatures. The results will be discussed in the light of the relevance they have for the chemistry induced by magnetospheric ions colliding with the surfaces of the icy Jovian moons.

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Monday 01:30 pm - 03:00 pm **121-P040**

Air Permeability and Microstructure of Polar Firn at Hercules Dome, Antarctica

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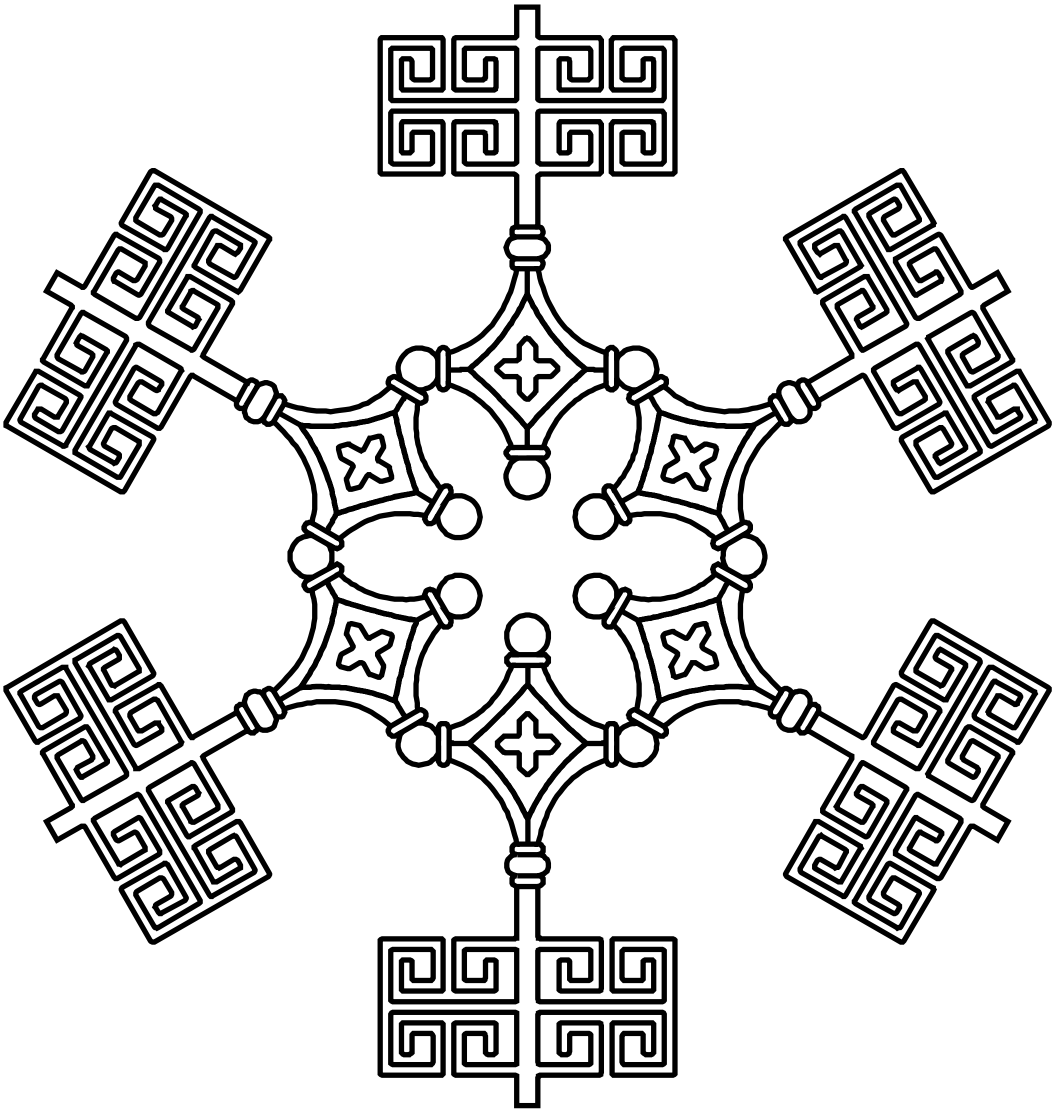
Air permeability of firn controls the transport of chemical species from the atmosphere into and out of the underlying firn. So far it is not known how to derive the permeability from microstructure measurements. The microstructure (and by that the permeability) is changing with depth and time due to meteorological impact and snow metamorphism.

In this study the air permeability of 220 samples from a 15meter deep firn-core from Hercules Dome (86°S, 105°W) has been measured. The measurements were carried out with a lab permeameter at the Cold Region Research Engineering Lab (CRREL). The permeability profile shows a maximum between 2 and 3 meter depth and at least one second, less pronounced maxima at 12 meter depth. Microstructure statistics have been obtained by stereological measurements on thick sections at CRREL and X-ray micro-computer tomography at the Alfred Wegener Institute (AWI). The permeability profile is presented as well as several microstructure parameters. The link between microstructure and air permeability is discussed.

Poster Session II



Wednesday 04:40 pm - 06:30 pm **003-P041**

Percolating networks and liquid-liquid transitions in supercooled water

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The existence of liquid-liquid transitions in isotropic one-component fluids may be attributed to the existence of several kinds of local ordering of molecules in the liquid. Upon cooling, aggregation of molecules with like local order may result in a liquid-liquid phase separation. The variety of the crystalline phases may be directly related to a diversity of local structures in the liquid [1] and therefore multiple liquid-liquid phase transitions may be expected for such fluids as water. Fluid-fluid phase transitions are closely related with the percolation transition of physical clusters [2]. In particular, in aqueous mixtures two-phase region approximately coincides with the concentration interval, where both components are above their percolation thresholds [3]. This observation can be used to determine the local structures, which may be responsible for the liquid-liquid separation in supercooled water. We performed extensive computer simulation studies of the liquid-vapor and liquid-liquid phase transitions of 5 non-polarizable models of water [4,5], which show multiple liquid-liquid phase transitions and up to four phases of amorphous water. To clarify the origin of the observed liquid-liquid transitions in supercooled water, we have analyzed the percolation behavior of water molecules, which show a specific local ordering. The lowest-density phase of amorphous water (analogue of LDA) is characterized by a presence of an infinite hydrogen-bonded network of tetrahedrally ordered four-coordinated water molecules. This network appears via percolation transition upon cooling the saturated liquid water and seems to be responsible for anomalous properties of liquid water [6]. In other phases of supercooled water, which are analogues of HDA and VHDA, such network is absent. The percolating hydrogen-bonded network of tetrahedrally ordered water molecules with arbitrary number of the neighbors in the first coordination shell exist in all amorphous water phases, excluding analogue of VHDA. Possible effect of the percolating networks on the properties of liquid water at ambient and supercooled temperatures is discussed.

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Wednesday 04:40 pm - 06:30 pm **006-P042**

Isothermal amorphous-amorphous-amorphous transitions in H_2O

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On compressing low-density amorphous ice (LDA) at 125 K up to 1.6 GPa two distinct density steps accompanied by heat evolution are observable in pressure-density curves [1]. Samples recovered to 77 K and 1 bar after the first and second step show the X-ray diffraction pattern of high-density amorphous ice (HDA) and veryHDA (VHDA), respectively. This implies a stepwise formation process LDA→HDA→VHDA, and is hence the first observation of an amorphous-amorphous-amorphous transition sequence in a single component material.

Comparison of pressure-density curves recorded at different compression rates shows, that the activation barrier between HDA/VHDA is higher than between LDA/HDA. We infer that the relation of HDA and VHDA is very similar to the relation between LDA and HDA except for a higher activation barrier between the former.

Multiple liquid-liquid transitions have also been found in difference near-IR spectroscopy [2] and computer simulations. These were found first on the example of supercooled ST2 water [3] and for a multistep potential [4]. Later, multiple transitions have been shown for six additional water models [5-7]. Whereas in some of the simulations three transitions have been observed, others show in agreement with our experiments just two: LDL→HDL→VHDL

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Observation of the glass transition of low density amorphous ice (LDA) and glycerol by isobaric volume-temperature experiments

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We investigated the glass to liquid transition of LDA and glycerol by isobaric heating in our material testing machine. A kink in the volume-temperature curves associated with a step change of the thermal expansion coefficient indicates that the glass has liquefied. For glycerol the glass transition temperature Tg~195 K (0.2 GPa) and Tg~230 K (1.0 GPa) is in agreement with earlier studies [1]. To confirm that we indeed observe the glass transition we varied the heating/cooling rate ratio and observed the expected over- and undershoot effects. In the case of LDA we find Tg~136-141 K in the pressure range up to 0.2 GPa. This is in agreement with our earlier determination by differential scanning calorimetry at ambient pressure [2-4].

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The local structure of ice VII determined by neutron total scattering

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The structural characterization of the local geometry of the H-bond network in Ice VII has been a long-standing problem in ice physics. Rietveld refinements of neutron powder-diffraction data have revealed an apparently short molecular O-D bond-length [1,2] in the average structure. The assumption that the real bond-length is close to that found in the (ordered) ice VIII structure has led to the proposal of site disorder of the oxygen atom in ice VII. Neutron total scattering (NTS) is a technique that includes the information content of the diffuse scattering in addition to that of the Bragg intensities. By performing in situ NTS measurements at 5.7 GPa, we have been able to make a direct measurement of the molecular bond-length that is entirely model independent. We observe that the O-D bond length in ice VII is identical to that of ice VIII to within our experimental resolution. Indeed, the local structure of the two phases looks very similar out to ~3.0 Å, beyond the extent of the first hydrogen bond. However, at higher radial distances, there are measurable differences between the two phases that are reasonably well described by a simple scaling of the local metric.

These results should have interesting implications for the interpretation of inelastic studies of the hydrogen-bond dynamics and may shed light onto the mechanism of bond centering at higher pressures.

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Structural studies of the P-T behaviour of high density amorphous ices

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The nature of high-density amorphous (HDA) ice is of considerable interest both because it is one of the few genuine examples of pressure-induced amorphisation and because of its proposed relationship to the high-density liquid form of water. We have found marked variability in the nature and behaviour of HDA in that annealing at high pressures produces the known densified form (VHDA) but annealing at pressures below ~0.8 GPa produces an 'expanded' form, in the sense that the d-spacing of the first diffraction peak increases, contrary to the change in forming VHDA. On recovery to ambient pressure, these forms differ markedly in their behaviour on warming both from each other and from the behaviour observed in unannealed HDA.

To explore the structural basis of these differences we have now carried out the first neutron diffraction studies of the P-T behaviour of amorphous ice under in-situ conditions. These studies reveal a strong pressure dependence of the first strong diffraction peak at low pressures with a cross-over in behaviour at ~0.8 GPa. The results of empirical potential structure refinement studies of the local structure of VHDA and e-HDA will be presented.

Hydrofluoric acid: a strong acid at low temperature

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The nature of aqueous acid solutions has been recently revisited and is once again [1] a very active topic as the development of ab initio molecular dynamics approaches allow very detailed mechanistic studies [2,3]. A molecular level understanding of the energetics and dynamics involved in acid dissolution in water is emerging as simulations indicate HF is strongly stretched but not dissociated in dilute solutions and in clusters. These results constrast with Giguère's model [4] of a strongly bound contact ion pair $F^{-}\cdot H_3O^{+}$ to explain the small dissociation constant (and other intriguing physical properties) displayed by dilute HF solutions at ambient pressure and temperature. We will report spectroscopic observations suggesting the complete dissociation of HF in thin (10-300 BL) amorphous H_2O and D_2O films. Binary films sampling the full compositional range (0.0-1.0 mole fraction HF in amorphous solid H_2O and D_2O) are grown in UHV at low temperatures (40-140K) on Pt(111) using molecular beams and are interrogated by reflection-absorption infrared spectroscopy. The strong acid behaviour implied by our results could highlight the delicate interplay between enthalpic and entropic contributions to the thermodynamic interpretation of this important process. Studies of the adsorption and uptake kinetics of HF at ice surfaces will also be briefly discussed.

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Raman scattering study of proton ordered ice-XI single crystal

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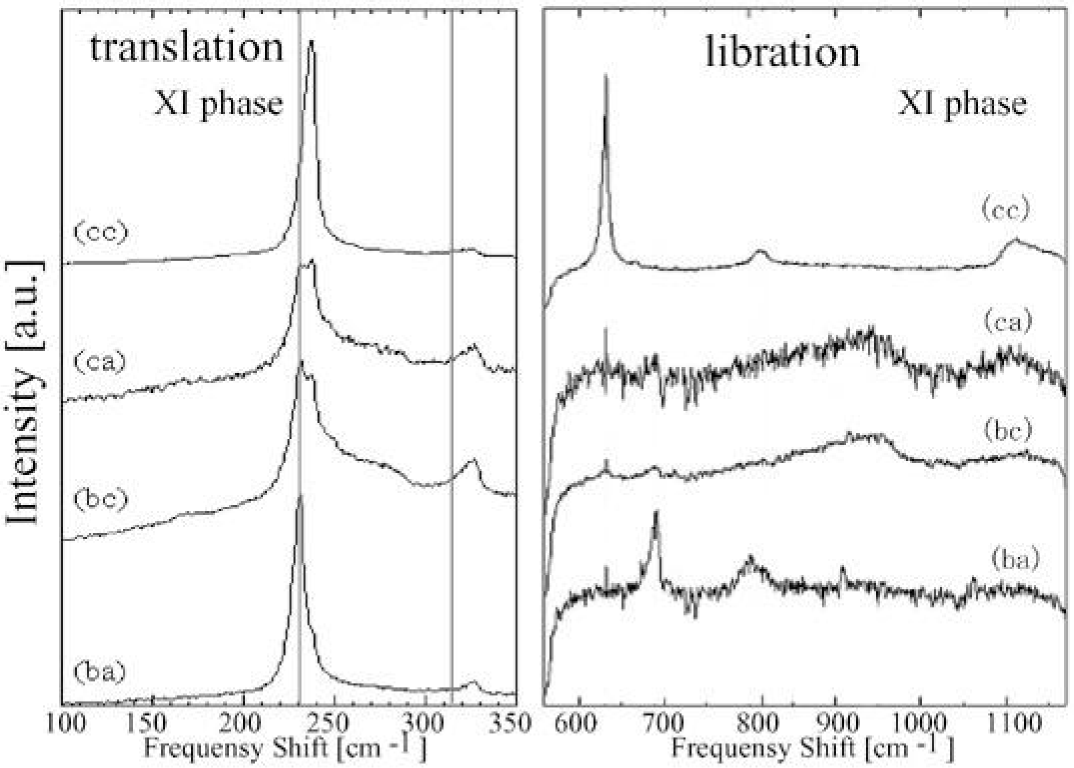
The phase transition to the proton-ordered phase of ice-XI can be realized below Tc=72K. by doping KOH as confirmed by calorimetric [1] and dielectric measurement [2]. In ice XI, H_2O molecules are ferroelectrically ordered with space group C2v-Cmc21 [3,4]. Some changes in Raman spectra by this transition have been reported [5]. But detailed mode assignment has not been made yet. In this study, we report the detailed polarization dependence of Raman spectra (Fig.1) and most of the modes in the translation and libration regions were successfully assigned for the first time.

In the translation region, E1g and E2g mode in Ih, have similar displacements in a-b layer and have the same energy 230cm-1[6]. Below Tc, it splits into two separate intense peaks at 230cm-1 in (ba) and 236cm-1 in (cc) spectra. The peak at 230cm-1 is assigned as A1 + B1 modes with displacement along a-axis and the peak at 236cm-1 is B2 + A2 modes with displacement along b-axis. The splitting by 6cm-1 is attributed to the depolarization field effect caused by the ordering of water molecules in ab-plane in XI phase.

In the libration region, an intense peak appears at 630cm-1 only in (cc) spectra reflecting the effect of the ferroelectric polarization along c-axis. The apparent resemblance in (ca) and (bc) spectra in Fig.1 may be attributed to the appearance of structural domains with different possible b-directions from hexagonal to the orthorhombic symmetry. From the group theoretical analysis for the 4 rigid water molecules and taking into account the combinations of wag, rock and twist modes, the observed libration modes can be assigned as 2A1+4A2+4B1+2B2.



[abe-fig1]

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The growth and structure of ice XI

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The complex behavior of water and the unusual nature of proton ordering in ice crystal continue to attract much interest. Neutron diffraction studies provide firm structural evidences that at high-pressure ices VIII and IX, which are the proton ordered phases of ices VII and III, exist as stable low-temperature phases. However, precious structure analysis of ice XI, which is considered to exist as the proton ordered phase of normal ice Ih at atmospheric pressure, has not been performed until now because of lack of a bulk crystal of ice XI, although previous neutron diffraction studies have provided an evidence of the transformation of very small fraction into ice XI (1, 2). The difficulty in obtaining the bulk of ice XI is due to a difficulty in the transition from ice Ih to XI.

To investigate the necessary condition for the phase transition, we have measured time-resolved neutron diffraction of ice containing minute impurities. We have carried out Rietveld analysis for the diffraction data, and obtained the mass fraction of ice XI and the detailed structure parameters. The analysis shows better conditions for the phase transition. We report the sample preparation, the necessary temperature condition, the growth mechanism, and the reliable structure analysis of ice XI. Furthermore, we discuss whether a fully proton-ordered ice exists or not.

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Wednesday 04:40 pm - 06:30 pm **030-P049**

Extended low-frequency vibrations of hydrogen-bond networks of high and low density amorphous ices

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The structure and vibrational properties of high- and low-density amorphous ices (HDA and LDA, respectively) have been determined using reverse Monte Carlo, molecular dynamics, and lattice dynamics simulations.

For the calculations on LDA ice we started from the LDA model [1] consisting of 1536 water molecules with density ρ=0.947 g/cm3 obtained from experimental structure factors using reverse Monte Carlo (RMC) analysis of the experimental data [2], [3]. The structure of this model was obtained by optimizing with a conjugate-gradient method employing a modified TIP4P potential for water. Ewald summation was used for summing the long range electrostatic interactions.

The structure of the HDA model used in present work was obtained from MD simulation by compressing the available LDA structure from zero pressure up to 15 kbar with a rate of pressure increase equal 30 bar/ps, followed by 500 ps relaxation at 15 kbar, and decreasing pressure with a 30 bar/ps rate down to zero pressure. The final LDA and HDA structures were obtained by additional optimization with a conjugate-gradient method. This resulted in an HDA amorphous structure having the structural characteristics and density (ρ=1.184 g/cm3 at ambient pressure) closely similar to the experimentally observed one [4]. The dynamical properties of the HDA, LDA, and Ih ices were estimated using the lattice dynamics (LD) calculations. A dynamical matrix was constructed and diagonalized to evaluate the normal-mode frequencies and eigenvectors. For comparison, an LD calculation on the ice Ih structure with density ρ=0.923 g/cm3 was also performed with $6\times6\times6$ k-point sampling inside the Brillouin zone to ensure convergence in the calculated quantities.

This combined approach leads to a more accurate and detailed structural description of HDA and LDA ices when compared to experiment than was previously possible. The water molecules in these ices form well connected hydrogen bond networks that exhibit modes of vibration that extend throughout the solid and can involve up to 80% of all molecules. However the networks display significant differences in their dynamical behaviour. In HDA, the extended low-frequency vibrational modes occur in dense, parallel 2-D layers of water that are approximately 1 nm thick. In contrast, the extended modes in

LDA resemble a holey structure that encapsulates many small pockets of non-participating water molecules

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Phonon dispersion of ordinary ice up to 0.5 GPa: implications on the negative thermal expansion and pressure-induced amorphization of ice.

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Ordinary ice (ice Ih) exhibits two very unusual properties at low temperatures, namely (i) negative thermal expansion at temperatures below ~ 60 K [1] and (ii) pressure-induced amorphization (PIA) when compressed above ~ 1.5 GPa at temperatures below 130 K [2]. In order to better understand these properties we have measured the phonon dispersion of ice Ih at pressures up to 0.5 GPa (T = 140 K) [3]. Our results show a pronounced softening of the low-energy phonon branches, especially for the transverse acoustic (TA) branch along the [100] direction and polarization in the hexagonal plane. By means of lattice dynamical calculations we may quantify this softening and directly link it to the macroscopically observed negative thermal expansion. Extrapolation to higher pressure indicates a complete softening of the above-mentioned [100] TA branch at ~ 2.5 GPa. The complete softening of an entire acoustic phonon branch has earlier been suggested by theory as being responsible for the PIA in ice Ih [4]. Our results give now the first experimental evidence that such scenario, i.e. mechanical melting, indeed represents the microscopic origin of PIA in ice Ih [3] and possibly more general in other solids exhibiting PIA.

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Mechanical strength and flow properties of ice-silicate mixture depending on the silicate contents and the silicate particle sizes

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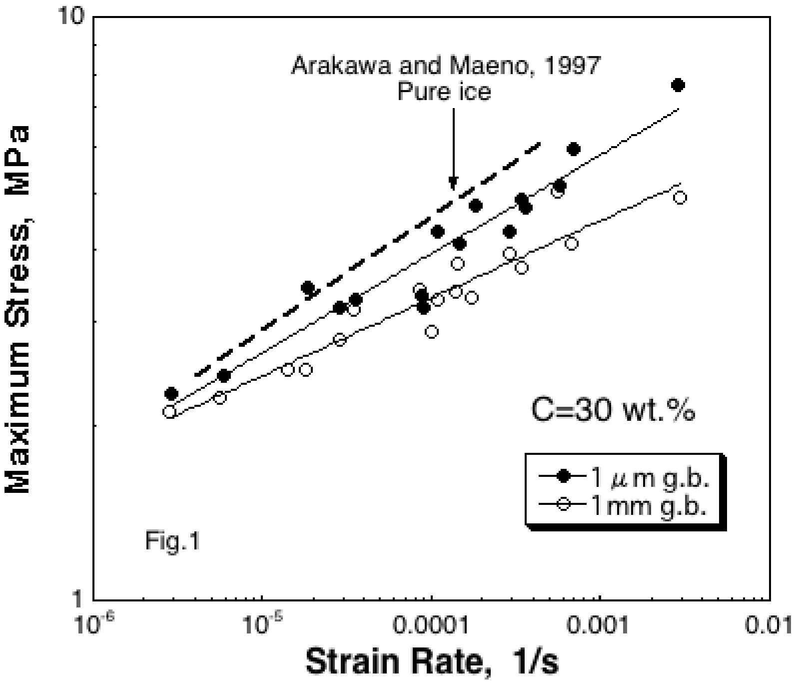
The icy crust and mantle of icy satellites are composed of the mixture of ice and silicates deduced by the mean density and the observation of reflection spectrum on the surface [1]. The stripe patterns showing the layered structures with the different sand contents are discovered on the polar cap of the Mars [2]. Therefore, the rheological properties of ice-silicate mixtures are important to study the tectonics of icy satellites and the flow dynamics of ice sheets on the Mars.

Thus, we have made deformation experiments of ice-glass beads (abbr. g.b.) mixtures in order to study the effects of silicate particles on the ice strength. The sample was prepared by mixing ice particles (1mm in the diameter) with glass beads (1mm or 1μm in the diameter), which contents (C) were from 0 to 50 wt.%. The cylindrical sample with the diameter of 30mm and the height of 60mm was deformed in the uniaxial compression at the strain rate from $3\mathrm{x}10^{-3}$ to $3\mathrm{x}10^{-6}$ s^{-1}. All of the experiments were conducted in a cold room regulating the temperature of –10°C.

The maximum stress on the stress-strain curve in each experiment (C=30 wt.%) was plot against the strain rate on Fig.1. The relationships between the maximum stress and the strain rate can be expressed as the power law equation, $d\varepsilon/dt=a\sigma^n$. The n is calculated to be 5.6 and 6.5 for the 1μm g.b. sample and the 1mm g.b. sample, respectively. The difference of the strength between them is not so large, but it is clearly recognizable: the 1mm g.b. sample is weaker than the 1μm g.b. sample. It is also noticed that both mixed samples are weaker than polycrystalline pure ice [3].



[Fig1]

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Wednesday 04:40 pm - 06:30 pm **045-P054**

Effect of impurities on grain growth of ice

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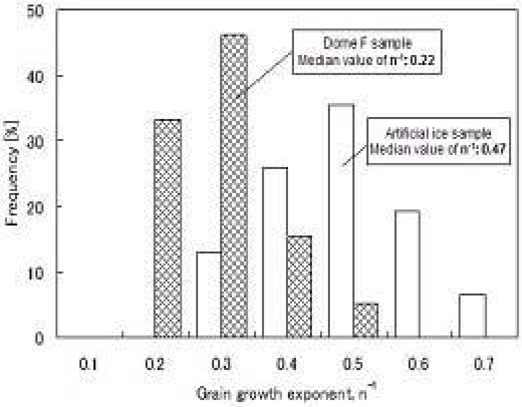
In order to investigate the effect of impurities on grain growth of ice normal grain growth experiments were carried out using polar ice sheet-ice and artificial ice which contains soluble and insoluble impurities. Each sample was pressurized up to 300 MPa in a teflon chamber filled with silicone oil at -233K for two hours and was depressurized to ambient pressure, which procedure produces very fine grain sample after nucreation/recrystallization process by phase change [1]. These samples were annealed at a given temperature and their grain sizes were measured intermittently with making thin sections. Seventy samples in total were examined in this study. The data of mean grain size with time were fit to a usual grain-growth curve given by $D=\alpha(t+t_0)^{1/n}$, where D is a mean grain size, an α^n (= K) is a grain growth constant which depends on temperature and the amount of impurites, t is time, t_0 is initial time and n is a grain growth exponent. From each grain growth curve a grain growth exponent, n and a grain growth constant K were determined.



[Fig.1]

As shown in Fig.1 it is found that the median value of grain growth exponent of the ice sheet samples (n =4.6) is larger than that of the artificial samples (n=2.1) which agrees with theoretical value (n=2) for normal grain growth. This result agrees with that the grain growth exponents of ice sheet-ice obtained from ice core analyses [2,3] show larger values (n>3 for Holocene ice) than the theoretical value. This implies that the grain growth theory which can be applicable to natural ice should be reconstructed.

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Methanol diffusion in ice

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Diffusion in ice has been the subject of several investigations recently however, results are inconsistent and show large discrepancies. We describe a new, highly sensitive method to measure very small diffusion coefficients for trace impurities in ice. Quantitative analysis of isothermal desorption rates of ice film samples doped with methanol reveals sublimation of mixed molecular solids follows a pseudo-Henry`s law. This allows us to interpret the isothermal desorption rates in terms of concentration depth profiles. Our method enables us to measure diffusion coefficients for methanol for a large range of temperatures (i.e., from 145 to 190K) as a function of impurity concentration. Our results show that diffusion rates and kinetics parameters are strongly influenced by the amount of impurity incorporated in the ice as well as its microstructure.

Effects of freezing on aqueous mixtures of formaldehyde and ethanol investigated by micro-Raman spectroscopy

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Incorporation of gases by freezing is an important process that occurs naturally in the atmosphere. Ice crystals can incorporate gases during their growth by collisions with supercooled droplets which subsequently freeze. To date, numerous studies were focused on the liquid-solid transition and formation mechanisms of binary or ternary solid aerosols composed of water and acid compounds under stratospheric or tropospheric conditions. However, light organics like ethanol and formaldehyde have received little attention although a wealth of organic species have been detected in snow particles [1]. Their gas phase composition may be modified by the interaction with frozen ice droplets. Moreover, in cryobiology, an enormous clinical interest is developed in avoiding ice formation within cells during rapid freezing for the cryo-preservation of living cells and tissues [2]. A comprehensive understanding of the mechanism and origin of the actions of protective additives at the molecular levels appears to be fundamental to avoid freezing damage of living systems. Although formaldehyde-ice / ethanol-ice systems are not yet of cryomedical importance, they could be regarded as model studies for future applications in cryo-protection.

In this work we report a micro-Raman spectroscopic study of frozen aqueous mixtures of ethanol and formaldehyde in the 800-3800 cm-1 spectral range. We investigate the effects of freezing on these systems at different temperatures and concentrations. In formaldehyde-ice systems, changes of the bands assigned to C-O and O-H vibrational modes are shown to partially reflect oligomer-water interactions and can be correlated with a structural transformation with the emergence of distinct crystalline phases (pI, pII) [3]. For the ethanol-ice system, our preliminary results reveal the formation of an ethanol hydrate at ~ 160 K for ethanol mixtures of ~ 23 and 65 mol% and ~ 170 K for the 40 mol% solution. Depending on the kinetics of cooling/heating, coexistence of two hydrates or a distinct hydrate is suggested to form for the 23 mol% solution. These results highlight the necessity to better characterize the solid-liquid phase diagram of these systems which are still incomplete. In correlation with these spectroscopic results, additional insight can be gained with molecular dynamics modeling to investigate the formation mechanism of the crystalline growing phase of frozen aqueous systems with respect to condensed ice-gas mixtures.

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Wednesday 04:40 pm - 06:30 pm **056-P057**

Grain boundary hierarchy in the EPICA-DML deep ice core, Antarctica

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Shape and distribution of grain and subgrain boundaries in ice samples from the EPICA (European Project for Ice Coring in Antarctica) DML (Dronning Maud Land) ice core have been mapped by using a CCD video camera system and a computer controlled xy-stage attached to an optical microscope. Most of the mapping was made in situ, in a subterranean laboratory built at the drilling site.
The boundaries were classified according to their shape, intensity and (in the case of sub-boundaries) inclination relative to the surrounding slip bands. We observed that microstructural processes like polygonization, grain growth and recrystallization are directly affected by the (sub-)grain boundary arrangement and hierarchy. An extensive pinning and bulging of grain boundaries by inclusions and subgrain boundaries have been identified, indicating that (sub)grain boundary migration seems to depend strongly on the deformation and impurity content, even at shallow depths. A surprisingly high amount of bent and polygonized slip bands have also been found at shallow depths, evidencing that the intracrystalline deformation is highly heterogeneous even close to the ice sheet surface. The origins of frequent subgrain islands are also discussed.

Freak patterns in the interface between polar ice and silicone oil

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In ice core studies, silicone oil is widely employed as a standard means of sealing and preserving the surfaces of thick and thin ice sections used in fabric analysis and microstructure mapping. We found, however, that its use can occasionally produce the contrary effect: for some unidentified reason, the interface between the polar ice sample and the silicone oil film may sporadically develop some curious, regular patterns with distinct characteristics in each grain. Interestingly, two neighboring samples of the same ice core, prepared under the same conditions and sealed with the same oil, may evolve differently: one forming surface patterns, while the other not.

On the other hand, if the upper face of a sample develops such patterns, then the lower face does necessarily the same. Also, every grain exposed at two section faces exhibits the same pattern on both. Finally, the question is raised about how to control this phenomenon, which should be avoided in the preparation of thick/thin sections, but can be useful in crystallographic studies.

Relaxation features in the EPICA ice cores

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During the tens of minutes of retrieval from the borehole, a deep ice core sample experiences severe temperature variations and a pressure release of many atmospheres. This represents a temperaturepressure shock which initiates a conspicuous relaxation process, characterized by noticeable changes in some microstructural features already in the first hours/days after retrieval.

In this work we present the most interesting relaxation features observed in the deeper parts of the ice cores retrieved from Antarctica (Dome C and Dronning Maud Land) and Greenland (GRIP and NorthGRIP), including the migration of grain boundaries during storage, the occurrence of "black dots" that transform first into plate-like inclusions and finally into bubbles, and the emergence of "dark dashes" parallel and perpendicular to basal planes, among others. We discuss also the genesis of such relaxation features and their consequences for ice core physics.

Investigation of structural disorder in ice Ih using neutron diffraction and Reverse Monte Carlo modelling

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Neutron powder diffraction experiments, using the NPD high resolution diffractometer in Studsvik NFL, have been carried out for (D_2O) ice Ih at 120, 200 and 260 K. All of the three measurements were total scattering experiments. In these cases the Bragg-scattering dominates the diffraction pattern; the Bragg-intensities have decreased strongly at the highest measured temperature. The intensity of the diffuse scattering, on the other hand, was already appreciable at 120 K and it has increased somewhat at 260 K.
Our primary aim was to study the structural disorder in ice Ih; for this purpose, the Reverse Monte Carlo (RMC) [1] technique was applied. RMC is a diffraction data based method for structural modelling in which large 3D particle configurations, containing thousands of atoms, are generated which are consistent with the measured total structure factors within errors. Here RMCPOW [2], a crystalline version of RMC, was used for modelling both Bragg- and diffuse scattering. From the resulting particle configurations, the (radially symmetric) O-O, O-H(/D) and H(/D)-H(/D) partial pair distribution functions (ppdf). All the three partials reflect longer range ordering, with oscillations extending well beyond the first and second coordination spheres; this is best observed on the O-O ppcf. Further details of the local geometry can be readily calculated from the collections of particle coordinates; distribution of bond angles, number of nearest and second nearest neighbours will also be presented.

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High-density amorphous ice: Relaxation and crystallization between 0.2 and 1.9 GPa

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High-density amorphous ice (HDA) was first prepared by pressure-amorphizing H_2O ice Ih at 77 K.[1] The crystallization kinetics of HDA and its dependence on heating rate and pressure was studied on isobaric heating between 0.2 and 1.9 GPa by displacement-temperature curves.[2] The crystalline phases, recovered at 77 K and 1 bar, were characterized by X-ray powder diffraction. The general pattern on isobaric crystallization of HDA is that of a parallel reaction, with one ice phase crystallizing slowly at low temperatures, and the other rapidly at higher temperatures. This requires that at a given pressure the rate constant for formation of one ice phase increases much more with temperature than that of the other. It follows that one ice phase forms predominantly on slow heating at low temperatures (called type 1), whereas the other forms mainly on rapid heating at higher temperatures (called type 2). The effect of pressure increase for a constant rate of heating is for type 1 ice phases to slow down further and suppress their formation, whereas for type 2 ice phases slowing down of kinetics leads to crystallization as type 1 phases. The ice phases crystallize with increasing pressure in the order ice Ih, ice IX, ice V, ice IV, ice XII, and ice VI as expected for their increasing density.

Density values of HDA under pressure are calculated from the volume changes during crystallization and the densities of the crystalline phases.[3] In the density versus pressure plot a pronounced change of slope occurs at ~0.8 GPa, with a slope of 0.21 g cm^{-3} GPa^{-1} below 0.8 GPa and a slope of 0.10 g cm^{-3} GPa^{-1} above 0.8 GPa. X-ray diffractograms and Raman spectra of recovered samples show that major structural changes occur up to ~0.8 GPa, developing towards those of very high-density amorphous ice (VHDA)[4], and that further increase of pressure has only a minor effect. In addition, the effect of annealing temperature (T_A) at a given pressure on the structural changes was studied by Raman spectra of recovered samples in the coupled O-H and decoupled O-D stretching band region: at 0.5 GPa structural changes are observed between ~100-116 K, at 1.17 GPa between ~121-130 K. Further increase of T_A or of annealing time has no effect, thus indicating that the samples are fully relaxed. The relaxation temperatures agree with a weak feature in the displacement-temperature curves obtained on isobaric heating of HDA.

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Apparent redistribution of impurities and air in the near-bedrock ice of the EPICA DML ice core, Antarctica

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In the field season 2005/06 the European Project for Ice Coring in Antarctica (EPICA) successfully finished the deep drilling of the second EPICA ice core at Kohnen Station by reaching subglacial water at 2774m depth. The measurements of the chemical composition of the ice by Continuous Flow Analysis (CFA) are already finished. Here we present the Ca2+ concentrations, relative air content, electrical conductivity of the ice and the melt water, as well as LineScan images of the lowermost 20m of the core. This section of the core is subject to strong temperature gradients due to the geothermal heat flux from the bedrock, which could be also responsible for the liquid water layer found below the ice sheet. Over a depth interval of only 5 meters the mean electrical conductivity of the melt water decreases by a factor of 4 while the variability of the signal strongly increases. The remarkable drop of the liquid conductivity ends around 1.5m above the water interface, below which it remains low and also the air content of the ice drops to essentially zero. The potential physical processes responsible for the apparent redistribution of trace elements and gas in this part of the ice are investigated.

First-principles study of Bjerrum defects in ice Ih: An analysis of formation and migration properties.

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We present a first-principles study of the structure and energetics of Bjerrum defects in ice Ih, considering both the thermal formation as well as the mobility of D and L defects. Our results are based on a density-functional-theory description within the generalized-gradient approximation, utilizing a periodic supercell containing 96 water molecules.

Considering the formation energetics, we compute the formation energy of a D-L Bjerrum defect pair as a function of the distance between them and, by means of asymptotic analysis, estimate the formation energy of an infinitely separated D-L defect pair as well as its effective charge. With regard to Bjerrum defect mobility, we estimate the energy barriers to L and D defect motion for a number of different L and D configurations. The results indicate that there is a fundamental difference between the mobility properties of D and L defects. It is suggested that this difference may be responsible for the experimental observation that only L-defects are mobile whereas D defects remain essentially trapped.

Finally, we compare the activation energy associated with L-defect motion with experimental estimates. While the DFT result for the net activation energy is in good agreement with experiment, we find that its two components, i.e. the formation and migration energies, are significantly larger and smaller, respectively, than the indirect experimental measurements. This result may be an indication of the activity of traps in doped ice in the temperature regime typically assumed to be controlled by the free migration of L defects.

First-principles study of molecular point defects in ice Ih: Interstitial vs. vacancy

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We present a first-principles study of the structure and energetics of a series of molecular point defects in ice Ih. Our results are based on a density-functional-theory description within the generalized-gradient approximation, utilizing a periodic supercell containing 96 water molecules in the defect-free crystal. In particular, we consider the energetics of the molecular vacancy vs. the molecular interstitial. In addition to the DFT total-energy part of the formation energies, we also compute the zero-point and finite-temperature energy contributions within the local approximation (including both inter and intramolecular vibrational mode changes) including effects related to thermal expansion. Specifically, we evaluate the formation free energies of 3 distinct interstitial structures, namely the Tc, the Tu and the B configurations, and that of the vacancy. To analyze effects due to the lack of long-range order in the molecular orientations, we considered 2 different replicas for each defect-type. We find that the formation free energies of the Tc and Tu interstitials, whose structures do not involve the formation of hydrogen bonds with the surrounding crystal, are systematically and significantly higher than that of the vacancy. On the other hand, the B interstitial, which does form hydrogen bonds to the surrounding lattice, shows a formation free energy that is essentially equal to that of the vacancy for temperatures near T=0 K but which decreases more rapidly with increasing temperature. This result suggests that the B interstitial is most the stable among the molecular point defects. On the other hand, given the proximity of the formation free energies of the B interstitial and the vacancy within the present level of description, a crossover scenario in which the vacancy is more stable below the crossover temperatures while the B interstitial becomes stable beyond this temperature, as suggested experimentally, appears plausible.

First – principles calculation of structure and dynamical properties of orientational defects in ice

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We present the results of density functional based computational studies of orientational defects in ice. In orientational defects the Bernal - Fowler´s ice rules [1] are broken such that in a Bjerrum D – defect there exist two hydrogens between nearest neighbour oxygens, and in a Bjerrum L - defect the bonds between nearest neighbour oxygens exist without any hydrogen [2]. These Bjerrum D and L defects are generated by molecular rotation and can travel to an adjacent site via thermal activation. The dynamics of these defects forms the basis of proton transport properties in ice.

The structure and dynamical properties of the ideal Bjerrum D and L defects for tetrahedrally fully coordinated ice Ih are studied within a periodic supercell constructed to contain both types of defects. Calculation of the relaxed defect structure is done using the ab-initio pseudopotential method using both the plane wave approach as employed in the CASTEP code [3] and the LCAO approach as employed in the SIESTA code [4]. In addition a controlled search within the core region of the defects is performed to find saddle points of possible diffusion pathways and barrier heights established. The microscopic picture of diffusion is further established through the evaluation of jump rates. Jump rates are evaluated using transition state theory [5] through the calculation of vibrational frequencies of configurations at both the energy minima and saddle point.

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Dielectric relaxation of ice samples grown from water vapor or liquid

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On dielectric properties of ice, a dielectric relaxation at audio and low radio frequencies is derived from re-orientation of water molecules as dielectric moments. The re-orientation behaviors of the molecules are restricted with some limitations as the Bernal-Fowler´s rules, existence of point defects and impurity ions, lattice imperfection, etc. The dielectric relaxation time of a pure ice sample, which for example was reported by Auty and Cole, has a value of 6x10(-5) s at -10 deg-C and its activation energy is 0.57 eV around the temperature. However ice samples contained impurities show lower values of the relaxation time and the activation energy.

We have measured dielectric properties of ice samples and also of samples aggregated with ice particles, as like snow samples. Undoped ice samples, grown from water liquid, show a simple dielectric dispersion as the Debye-type with the ordinary relaxation time which is consistent with the Auty-Cole´s result. But crushed ice samples (aggrigated with particles of several mm diameter, made of the undoped ice) show a dielectric dispersion as the Davidson-Cole type with the ordinary relaxation time. On the other hand, we have measured aggregation samples of hoer-frost ice particles which were grown from water vapor. These samples show a dielectric dispersion as the Davidson-Cole type with shorter relaxation times. Natural snow samples, which also were grown from water vapor in the sky, show a complex dielectric dispersion as the Havriliak-Negami type with shorter relaxation times. Snow samples generally contain several impurity ions and are inhomogeneous aggregations of ice particles with several sizes.

These results may suggest the relaxation process of ice is different not only between pure and impure ice but also between ice samples grown from water vapor and liquid. Ice grown from the vapor is expected that the ice crystal has many lattice defects as vacancies, which can make the water molecules re-orientate easily. This hypothesis is able to offer an explanation for previous reports as snow, hoar-frost and poler ice samples, which sometimes were expected with low impurity concentration, show shorter dielectric relaxation times than its of ordinary ice.

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Microstructural deformation features in polar ice cores (EDML, Antarctica) and artificially deformed ice

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The records from deep ice cores from polar ice sheets provide information about the climatic changes during the past but require careful interpretation and understanding of other processes affecting the ice. Flow and deformational processes can change stratigraphic sequences by folding and interruption of layers as well as crystal orientations, sizes and shapes. Amongst other processes the bending of grains and splitting into smaller grains is an important consequence when load acts on polycrystalline ice. In this polygonization process the evolution of new grain boundaries viz. sub-grain boundaries plays an important role. A sublimation method [1] reveals grain- and sub-grain boundaries as etch grooves on the surface of the sections and other features like inclusions and slip lines inside the sample, which are recorded as microphotographs. This method has been applied to thick sections from the deep ice core EDML, Antarctica. Detailed analysis on sub-grain boundary occurrence in selected depths revealed that these features are frequent in all depth ranges. Remarkable is that sub-grain boundary formation starts at very shallow depths. For correct interpretation of these detailed analysis in terms of deformation history knowledge about the formation processes of microstructural deformation features is required.

Investigations on deformation tests, where the initial state and the deformed state can be observed, can help to understand these processes. Therefore creep tests using artificially produced polycrystalline ice are recently carried out under the condition of grain growth occurrence. Uniaxial compression deformation at stresses of the order of 0.1 MPa produces microstructures. The same sublimation method revealing deformation features as applied to ice core samples is used to observe artificially deformed ice. The aim is to produce the observed features by creep tests and compare their occurrence and to gain understanding on their formation processes and conditions.

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Formation of photoproducts and structural alterations in photon-irradiated crystalline and amorphous ices. A NEXAFS study.

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We have used the X-ray absorption spectroscopy technique at the oxygen K-edge to characterise the evolution of the structure and the chemical composition of cold ice films of various structures (porous-ASW, ASW and Ic) upon X-ray irradiation (1-1000 eV) at 20 K, and how they further evolves when annealed to 150 K. Radical and molecular species can be directly identified on the NEXAFS spectra of the irradiated films. OH, O, HO_2, O_2 and H_2O_2 are observed, with concentrations that differ in irradiated Ic and in irradiated porous-ASW. Structural changes induced by irradiation also depend on the initial structure of the film. Irradiation of porous-ASW lead to an amorphous structure consistent to the high-density (HDA) form of ice, whereas irradiation of ice Ic and ASW leads to structures close to the normal Low density amorphous (LDA) form of ice, in line with recent predictions [1]. Further evolutions are observed when warming the films, which will be also shown.

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High-pressure gas hydrates

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The clathrate hydrates are model systems for the study of hydrophobic interactions and many of them are commonly found in nature both on the Earth and in other parts of the Solar System. Studies of the high-pressure behaviour allow the distance dependence of the interactions to be explored and provide information directly relevant to Earth and planetary modelling.

Recent work has shown that, in several significant cases, gas hydrates have very wide ranges of stability and may persist into the megabar range. The consequences of this will be reviewed along with the possibilities for stability of polar gas hydrates at high pressure.

Experimental and theoretical analysis of clathrate sII vibrations

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Diamond anvil cell measurements [1,2] demonstrated that up 5 weight percent of hydrogen can be stored in clathrate hydrates. This experiment established calthrates and related molecular compounds as new class of potential hydrogen storage materials. The development of viable storage materials is considered to be one of the great challenges for the transition to a hydrogen based economy. To enhance the stability range of clathrate in temperature and pressure additional guest molecules are currently being tested experimentally.

In this paper, we used experimental and theoretical methods to characterize the vibrational properties of the clathrate sII structure. We conducted inelastic neutron scattering experiments on the FANS spectrometer at the NIST Center for Neutron Research, Gaithersburg MD. Neutron scattering is sensitive to the motion of hydrogen atoms and has the advantage over optical spectroscopy methods that it does not depend on any selection rules.

We compared the experimental spectra with lattice dynamics calculations based on the TIP4P force field. We obtained a very good overall agreement allowing us to distinguish between phonon and libron bands, and to study the associated isotope shifts. We can further characterize the properties of different phonon and libron excitations. In the phonon band, we distinguish between breathing and cage-deformation modes. In the libron band, we can characterize changes of the rotational axis of water molecules in the cage structure. The presented vibrational analysis will help us the characterize clathrate structures with different stabilizing guest molecules.

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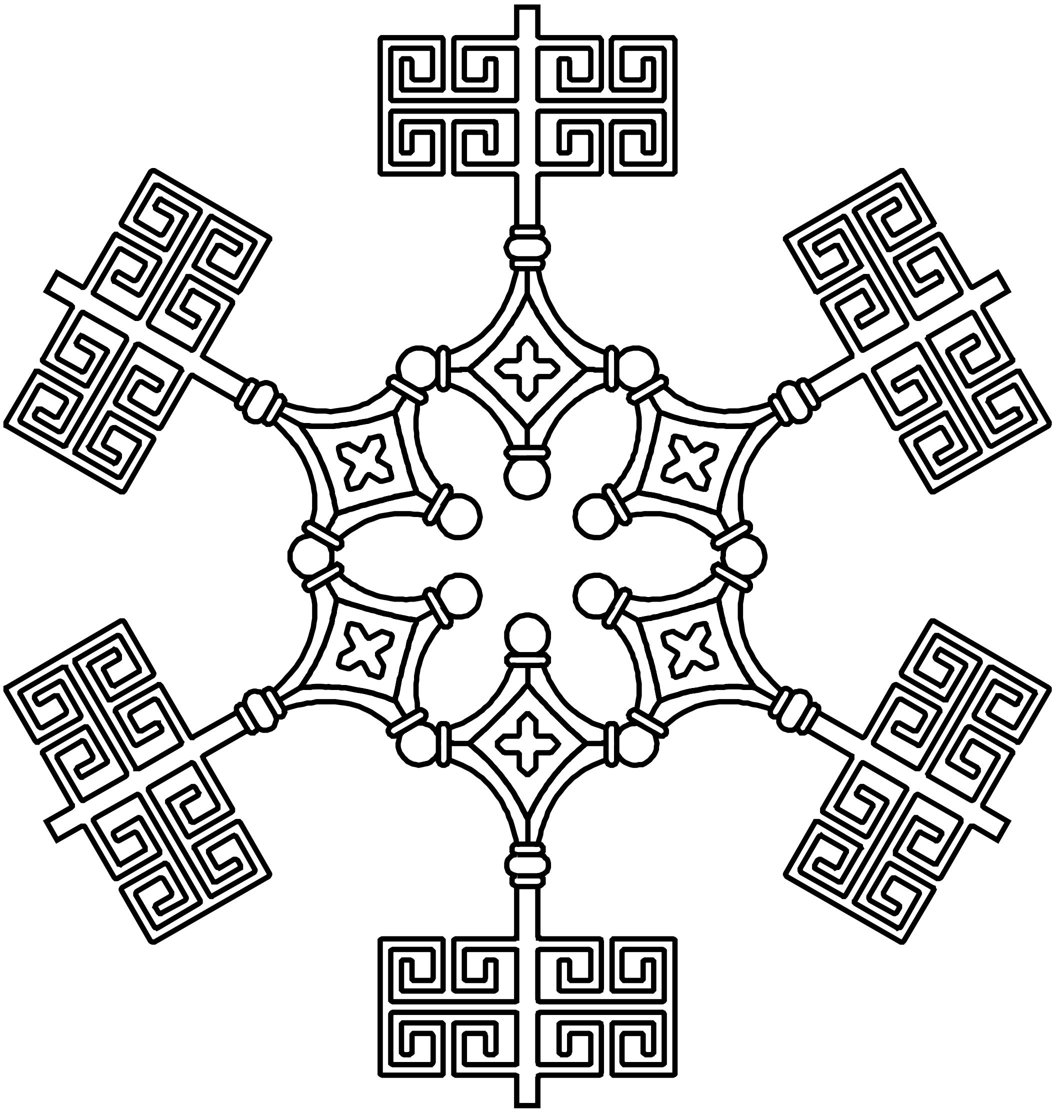
Poster Session III



Friday 01:30 pm - 03:00 pm **001-P070**

Cryo-Atomic Force Microscopy (AFM) along Ice Surfaces

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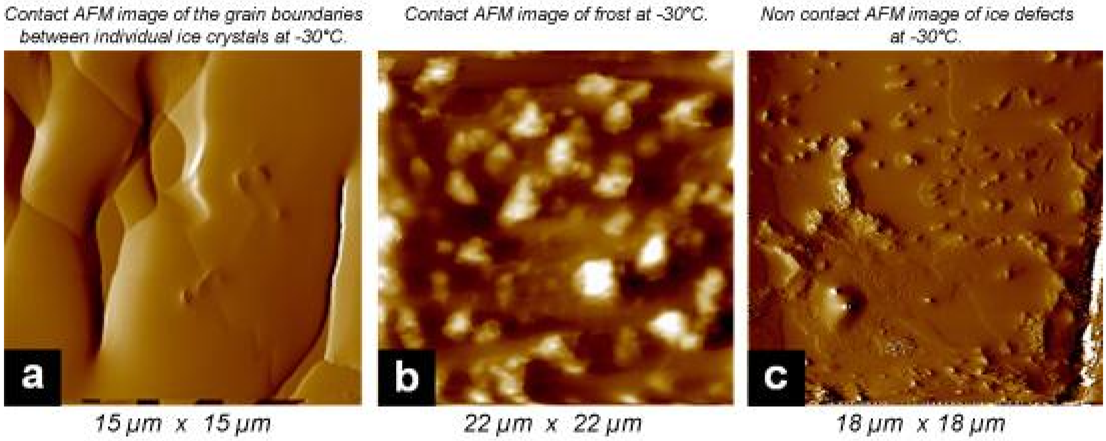
Atomic Force Microscopy (AFM) has been applied to investigate the properties of bulk ice surfaces [1-3] and for the measurement of liquid-like layers on the ice surfaces [3-4]. Most of the investigations were done at super- or undersaturated conditions [5-7]. Aims of our studies are the characterisation of ice and snow surfaces to obtain information about crystallization and alteration processes, in particular about the formation and metamorphosis of natural snow. We use a commercial Atomic Force Microscope (PicoSPM, Molecular Imaging). The temperature of the purpose-build sample stage (Peltier cooler with copper plate) can be controlled down up to -35°C. The AFM investigations are performed in a glove box at about 20°C to avoid condensation. The experimental setup allows for a control of relative humidity and for exposures of the ice surface to other gases in addition to pure water vapor. Preliminary investigations of the ice surface demonstrate different structures along the ice surface at -30°C strongly depend on the relative humidity:

(a) Grain boundaries between individual ice crystals (freezing process and AFM-investigation outside glove box at rel. hum. of ~50%). During longer scanning times, smaller grains recrystallize into large grains.

(b) Nucleations of frost (freezing process at 5% rel. hum. in glove box, afterwards increasing the rel. hum. up to ~50%). Individual frost crystals can be removed by the tip during the scanning.

(c) Defects of ice (freezing process and AFM-investigation inside glove box at rel. hum. of 5%). The obtained images indicate etch pits of up to some hundred nanometers in depth and up to 2 µm in diameter.



Contact AFM image of the grain boundaries between individual ice crystals at -30°C.

Contact AFM image of frost at -30°C.

Non contact AFM image of ice defects at -30°C.

[Structures along ice surface.]

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Experimental studies concerning photochemical reactions in snow

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In the recent years, we have performed laboratory experiments concerning the photochemical reactions of several photolabile compounds in artificial snow samples [1, 2]. We investigated reactions of compounds like hydrogen peroxide, formaldehyde, and nitrogen-containing compounds like nitrate and nitrite, which are always present in variable amounts in natural snow samples. The experiments indicated that large fractions of the impurities are present in the surface layer of the ice crystals. The experiments also showed that a rather diverse chemistry is occurring in this surface layer: hydrogen peroxide was quickly destroyed under the applied experimental conditions while formaldehyde was rather stable in comparable experiments. The results of experiments with varying initial amounts of nitrate and nitrite demonstrate that the transformation of nitrate is not a simple cascade of reactions leading to the direct formation of nitrogen oxides like NO and NO_2. Instead, the transformation of nitrate and nitrite involves a range of nitrogen compounds, which establish several reaction cycles for the re-cycling of nitrate and nitrite. For example, in the experiments with high initial concentrations of nitrite a significant increase of nitrate concentrations in the snow was observed. However, final products are still the nitrogen oxides, which are able to escape to the gas phase. Using all available experimental data we will present a comprehensive reaction mechanism for photochemical reactions in snow, which can also be applied to the conditions of natural snow covers. The implication of such reactions for the post-depositional loss of reactive compounds from the snow and the impact on the composition of the atmosphere due to the release of newly formed compounds will be discussed.

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Molecular dynamics simulation of an ice nanocluster in supercooled water

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The structural properties of an ice/water interface were studied for an nanocluster of Ih ice with 600 molecules immersed in a supercooled water shell of about 1.5 nm width. The SPC/E water model was used. The temperature of the system increased from 200 to 250 K. The radial profiles of the local density, energy, electric potential, and the normal component of the pressure tensor were calculated. Laplace equation was used to estimate the interfacial tension the water/ice curved surface. The results are compared with those for the similar methane hydrate nanocluster placed into a water shell. For the latter the nonmonotonical dependence of the interface tension on temperature was observed within this temperature interval.

The work was supported by the INTAS grant No 03-51-5537.

Comparison of a simple model of speedskate ice friction with measurements

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The classic work of Evans Nye and Cheeseman (1976) has been extended and adapted to produce a simple theory of ice friction for speed skates. The theory is compared with measurements by de Koning et al. (1992), who used an instrumented skate worn by competitive speedskaters to record ice friction during actual skating. While there is broad agreement between the theory and the experiments, the detailed differences are a key to understanding the variability of ice friction during skating, and possibly improving both skate and ice design in order to improve overall speedskating performance.

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Friday 01:30 pm - 03:00 pm **013-P074**

AFM and SEM studies of frozen NaCl solutions

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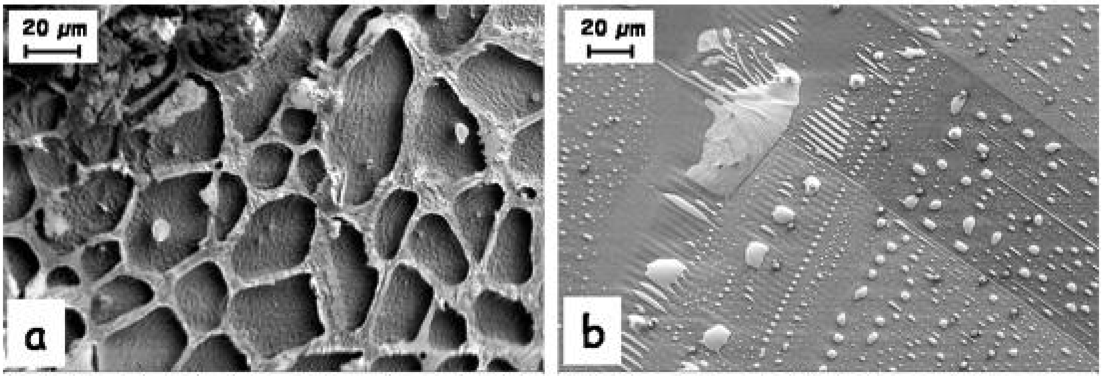
Both AFM and SEM techniques were used to characterize the surfaces of frozen NaCl solutions in different freezing processes. The advantages of Cryo-AFM are: high vertical resolution of surfaces, in-situ characterization of structure changes, detection of liquid layers on ice surfaces [1, 2] and investigations under controlled relative humidity [3, 4]. The SEM investigations were carried out to determine the composition of impurities and to check images obtained from AFM technique for artefacts. The conditions of preparation as well as measurement techniques showed a clear influence on the surfaces studied. For the AFM investigations, the NaCl aqueuos solutions were cooled slowly (cooling rate 1.5 K/min) at the temperature controlled stage down to -30°C inside the glove box (at 20°C with a relative humidity of 5%). The images obtained after 30 min showed a fine grained lamellar structure with individual sizes of some µm in diameter and ~150 nm in hights. After ~3 h of scanning the lamellar structure changed into cubic crystals (probably NaCl) of some µm size. For the SEM investigations NaCl aqueuos solutions were treated in two different ways: slow cooling, similar to those of AFM investigations, and rapid cooling in liquid nitrogen. Inside the SEM cryo-chamber some etching of the samples was observed. In the slow cooling case the surface of the samples were changed, after sublimation (5–15 min), from relative uniform structures into the NaCl skeleton (Fig. 1a.). In contrast, in the rapid cooling case the NaCl concentrates in domains showing a characteristic pattern with undulations and scattered droplets on the frozen surface. (Fig. 1b.).



(a) Slowly cooled samples down to -30°C (cooling rate 1.5 K/min, relative humidity 5% in the glove box).

(b) Rapidly cooled samples in liquid nitrogen.

[Fig.1. SEM images of frozen NaCl aqueous solutions]

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Grain boundary melting in polycrystalline ice

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A recent study of impurity driven grain boundary melting (Benatov and Wettlaufer, 2004.) found theoretical evidence for a wetted liquid layer separating individual grains within polycrystalline ice. Other numerical simulations and theory have also supported the idea of disorder along grain boundaries within polycrystalline solids. However, direct experimental access to the interface of two crystals in thermodynamic equilibrium remains difficult.

Auspiciously, the transparency, birefringency, and melting temperature of polycrystalline ice lend it to experimental probing. Here, using light scattering by a 4mW Helium-Neon laser, we directly explore the boundary in an ice bicrystal, prepared within a thin ice growth cell. Reflected light intensity is measured as a function of the thermodynamic variables, temperature and impurity concentration. C-axis orientation of individual crystals can be determined by systematically measuring the difference between incident and transmitted polarized beams. Assuming the index of refraction for bulk water, for any melted layer, we anticipate a greater than 10% change in reflected signal strength for a 15 Angstroms melt layer. Experimental and theoretical results are compared.

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Substrate effects on the interface melting of ice

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Ice interfaces play a key role in many technological and environmental phenomena. Yet the properties of the ice interfaces are not fully understood, especially at conditions close to the melting point. It is well established that surface melting occurs at the free ice surface. However only very few and contradictory measurements exist for the melting of ice at buried interfaces. Interface melting can be influenced by the presence of impurities as well as changes in the chemistry and microscopic/mesoscopic morphology of the substrate. In this work we focus on the effect of substrate chemistry. We have investigated the temperature dependence of the structure of ice at the interface to different substrates by x-ray reflectivity measurements exploiting a high energy x-ray beam from a 3rd generation synchrotron source. The large penetration depth of this probe allows us to investigate interface phenomena through macroscopic amounts of material. From the analysis of reflectivity curves we obtain the density profile of the ice interface with atomic resolution.

Comparison of the specific surface area of natural and artificial snow samples measured using methane adsorption at 77 K and micro-tomography

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Nitrogen oxides, volatile organic compounds and acidic gas play important roles in atmospheric chemistry, such as production of hydroxyls radicals (OH) and the related formation of tropospheric ozone. Knowing sources and sinks of those compounds is therefore extremely important. Snow can cover a significant amount of land especially during winter time and it can influence the chemical composition of our atmosphere by up taking those compounds on its surface and acting as a sink or a source if heterogeneous reactions take place. Quantities of uptake studies have been done to determine the portioning of atmospheric relevant compounds between the snow and the gas phase. Nonetheless, to interpret such experiments requires a good understanding of both the microphysical uptake processes and the micro morphology of the snow. One important parameter to extrapolate laboratory results to the snow cover is to know the specific surface area (SSA) of snow. In this study, we compare the specific surface area of different natural and artificial snow samples measured using both micro-Tomography and methane adsorption at 77 K. The results of further investigations on the micro-morphology of the snow samples using the micro-Tomography are also presented.

Surface melting of ice away from equilibrium

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Surface melting occurs when a liquid wets its own solid in the form of a stable thin liquid layer disjoining the solid/vapor interface at temperatures below the bulk transition temperature, Tm. It is an equilibrium phenomenon driven by the tendency to reduce the interfacial free energy of the system. The process occurs in many classes of solids (metals, semiconductors, solid rare gases and molecular solids, including ice), and typically begins at T < 0.9 Tm, with a film thickness of a few monolayers, which thickens gradually with increasing T, and diverges at Tm. Because of its high vapor pressure, ice provides an ideal material for detecting disequilibrium effects. This requires that the dynamics of such interfaces be for a conserved order parameter. Accordingly, we treat surface melting at disequilibrium using a Cahn-Hilliard (CH) equation for mean particle density. The CH equation is solved in four regions: bulk vapor, surface melted film, and at the two interfaces. The coupled motion of the two interfaces is described at steady-state and yields the thickness of the film as a function of environmental parameters.

Dynamics of ice Ih films upon methanol adsorption: quasielastic neutron scattering experiments and molecular dynamics simulations

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Quasielastic neutron scattering experiments and classical molecular dynamics simulations have been performed in similar conditions to investigate the effect of methanol adsorption on the dynamics of an ultra-thin ice Ih film (5 water layers thick) grown on a crystalline MgO(001) substrate. Experiments have been performed in the 220-270K temperature range and for a CH_3OH monolayer coverage. At T=250K, about 20 % of the whole film is in the liquid state according to the measured molecular translational and rotational diffusion coefficients. At 270 K, our measurements show that this liquid fraction reaches almost 50 % of the whole film. Comparing these experimental results to those obtained for pure water/MgO(001) [1] in the same temperature range indicates that the observed mobility is more probably due to methanol molecules rather than water molecules.

These interpretations of the experimental data are supported by the results of the molecular dynamics simulations. Indeed, the calculated translational and rotational diffusion coefficients for the methanol/water/MgO system show that methanol molecules are much more mobile than water molecules between 250 and 270 K, and that the methanol layer behaves as a liquid-like layer adsorbed above rigid ice layers. Moreover, the comparison with results of simulations performed on the water/MgO system without methanol show that the adsorbed methanol molecules strongly hinder the mobility of the underlying water molecules.

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Ionisation of HCl on ice at very low temperature

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We have studied by X-ray absorption spectroscopy the adsorption of HCl at 20 K and 90 K on crystalline water ice films deposited under ultrahigh vacuum. We have found that HCl dissociates at temperatures as low as 20 K, in agreement with the prediction of a barrierless ionisation [1]. We show that the hydrogen-bonding of HCl with the native water "dangling" groups of the surface only account of 20% of the ionisation events. A further mechanism drives the rest of the dissociation process. We suggest that the weakening of the ice surface hydrogen-bond network after the initial HCl adsorption phase facilitates the generation of new dissociation/solvation sites, increasing the uptake capacity of ice. This gives insights on the molecular mechanisms of the early formation of a "quasi-liquid" layer at the very low temperatures when acid species adsorb on ice.

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Vibrational probe of the ice single crystal surface

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We will report on our results with methodology for growing single crystal, I_h ice samples, authenticating orientation of the *c* axis, and vibrational spectroscopy of the single crystal ice surface. Results show that the vibrational spectrum varies with temperature in the range 77-220 K. The well-known broad hydrogen-bonded peak of water that extends from 3000-3650 cm^{-1} collapses upon cooling. At 77 K, the spectrum consists of one very strong, narrow band (about 40 cm^{-1} width) and a much weaker broad band. It is the weaker broad band that nearly disappears on cooling. The spectroscopic technique used to probe the interface is the surface specific probe, sum frequency generation. We will discuss the spectroscopic technique as well as the implications of the spectrum.

Water monolayers and ice films on Ru(0001) investigated with He atom scattering: Structure and stability under electron irradiation

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Recently the structure of water(D_2O) adlayers on the Ru(0001) surface has given rise to a pronounced controversy [1-5]. Since, there is conclusive evidence that water adlayers on Ru exhibit a rather low threshold for beam damage when investigated with electrons, we have employed He-atom scattering (HAS), where electron beam damage (either through primary or secondary electrons) can be strictly excluded. In contrast to all previous studies, our results reveal that a stable water bilayer with a high-order commensurate structure exists on this surface. On top of such a bilayer, which had been adsorbed within 30 min at 160 K, ordered multilayer ice films could be grown at 130 K.

Experiments using a standard LEED system have revealed that the water adsorbates are indeed very sensitive to electrons, even short exposure of the bilayer in front of the LEED instrument led to the formation of the well-known ($\sqrt{3}$x$\sqrt{3}$)R30° structure. However, the reported preparation condition did not result in layers which gave good He diffraction. HAS data recorded during electron irradiation showed that the effect of electrons is both, electron induced desorption and electron-induced dissociation. A structural model for the ground state of the bilayer on the Ru(0001)-surface and a comparison of the effect of electrons on multilayers and bilayers will be presented on this poster.

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Microscopic model of structural phase transition in hydrates under pressure

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The major generalization of the existing theory of clathrate hydrates, so that the new model allows taking into account the influence of guest molecules on the host lattice and permit to describe in detail structural phase transition in hydrates under pressure., are suggested.

Combined statistical mechanical modeling, molecular dynamics (MD) method and lattice dynamics (LD) method was used for numerical modeling of structural, dynamic and thermodynamic properties of the considered clathrate hydrates.

Within the framework of this theory for modeling hydrate phases the supercells was chosen containing such number of unit cells what will allow to describe hydrates with different degrees of filling of host lattice cavities. Using known potentials of intermolecular interactions at fixed temperature and pressure the optimization of the shape of supercell and coordinates of molecules in it by MD and LD approach was performed. The initial coordinates of molecules was taken from experiments. For these structures numerical calculations of dynamic, thermodynamic characteristics of studied hydrates was carried out with the use of the software package designed by the authors of the project.

For determination of phase equilibria lines between different hydrate phases and lines of structural phase transitions the chemical potentials of water molecules forming hydrate lattices and guest molecules placed in different cages was calculated numerically. For investigation of equilibria hydrate-ice also thermodynamic functions of different ice phases will be determined with the proper intermolecular potentials between water molecules. These potentials will be used then also for calculations of hydrate lattices. Equilibrium compositions of hydrate phases will be found numerically from the conditions of equality of chemical potentials for guest and host molecules on the phase equilibria lines.

The influence of guest molecules (hydrogen, argon, methane and xenon) on the host lattice of hydrate of cubic structures I, II and H was investigated. Results of these calculations was to construct the phase equilibria lines in these hydrates.

Effects of additives on formation rates of CO_2 hydrate films

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The inhibitors of gas hydrates have been developed mainly in the petroleum industries for prohibiting the gas-hydrate plugs during the production, transportation, and processing. Such additives from natural materials are very feasible to the circumstances. A lot of studies to control the living body and freeze of foods have been done with adding the cryo-protecting materials, such as sugars and anti-freeze proteins (AFPs). Recently, a kind of AFPs was also found to inhibit the crystal growth of clathrate hydrates with cubic structure II [1, 2]. It is therefore considered that AFPs are one of the potential inhibitors. However, because these materials have been thought to interact specifically with the certain ice crystal surface and restrain the crystal growth by blocking the formation kinetics, this finding has provoked a great deal of controversy about the cryo-protecting process with additives. We then observed the formation process of CO_2 hydrate films (cubic structure I) with adding two kinds of cryo-protecting materials: trehalose (a disaccharide of glucose) and type-III AFP (RD3-N1, retrieved from Antarctic eel pout [3]. The lateral growth rate of CO_2 hydrate films measured at the interface between liquid CO_2 and solutions of trehalose (concentrations ranged up to 50 wt%) or of AFP (from 10 to 10^3 ppm). The results indicated that both materials reduced the growth rates remarkably compared with those in the pure water-liquid CO_2 system at pressures ranged from 4 to 6 MPa and temperatures about 263K.

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Molecular dynamics simulations for structure-H hydrates of hydrocarbon large molecular guest substances

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Clathrate hydrates are crystalline compounds composed of hydrogen-bonded host water molecules and guest molecules. The guest molecules are enclosed within cages of the host water molecules. There are several types of the clathrate hydrates, including structure-I, -II, and –H. Structure-H hydrates were found by Ripmeester, et al. in 1987 [1], and several advantages of using the structure-H hydrates for storage and transportation were reported by Khokhar et al.[2] Structure-H hydrates are composed of three types of cages of the water molecules and two types of guest substances. Guest substances with a small molecular size (typically, methane, xenon etc) are located in small cages, while those of another type—termed large molecule guest substances (LMGSs)—are located in larger cages. The phase equilibrium conditions of the structure-H hydrate forming systems depend on the molecular spices of the LMGS. It is required to study the dependence of the size and shape of the LMGS molecules on the phase equilibrium conditions at the molecular level for the best selection of the LMGS to be used with natural gas in the storage/transportation applications. Molecular dynamics simulations of the structure-H hydrates were performed with one site Lennard-Jones potential model for LMGS molecules.[3,4] However, there has been no investigation on molecular dynamics simulation with multi-site model for LMGS.

In this study we adopted the molecular dynamics simulation of structure-H hydrate to observe the static and dynamic behavior of LMGS of hydrocarbon, such as neo-hexane, in the large cages. Molecular dynamics simulations were performed under constant pressure and constant temperature with 6120 TIP4P water molecules, 900 OPLS-UA methane molecules, and 180 multi-site modeled OPLS-UA LMGS molecules. All simulations are performed on special computers for molecular dynamics simulation, MDGRAPE-2. We will present the radial distribution function g(r) and the density of the states of the vibrational modes g(w).

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Classification of low-energy configurations of polyhedral water clusters from cube up to backminsterfullerene

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Polyhedral water clusters (PWC) possess a large variety of features that make them extremely convenient and attractive for theoretical analysis of unusual properties of water and ice. The extensive theoretical analysis of PWC energy profile was provided by Singer, Ojamäe et al. [1] and also by Anick [2,3]. In these works, PWC are considered to be complex systems with complicated interactions. The purpose of using this statistical approach is to determine correlations between bond energy of a cluster and topology of hydrogen bonding.

We propose an alternate approach based on the analysis of specific features of molecular interactions with the nearest, second, third and etc. neighbors. The first discrete topological model [4] takes into account energy nonequivalence of trans- and cis-conformations of H-bonds. Earlier, within the framework of this strong and weak bond (SWB) model, all configurations of PWCs have been classified according to the number of trans and cis-conformations (strong and weak H-bonds) [4,5]. New discrete model is based on a concept of effective pair interaction energy [6]. The strong and weak effective bond (SWEB) model takes into account the peculiarities of interactions with the second and third neighbors. The new discrete model is in a good agreement with the Anick's statistical analyses [3]. In this work a classification of the most stable configurations is presented for neutral clusters from water cube up to water buckminsterfullerene. The classification describes all topologically-distinct configurations of two lowest energy levels in each cluster in accordance with SWEB model. The linear combinatorial optimization methods based on the max-plus algebra were used for proving the completeness of discrete optimized classes of configurations in big PWCs. The symmetry of these configurations is analyzed with allowance for the antisymmetry operation changing the directions of all H-bonds [5]. Calculations with pair-additive potential TIP4P have shown the splitting of the two lowest energy levels in most cases. The validity of this classification has been demonstrated by the similarity of results obtained using different potentials: TIP4P, TIP5P and TTM2-F.

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Energy optimization of gas hydrate frameworks on the basis of discrete models of inter-molecular interactions

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Gas hydrates studies are very important for various reasons. Special interest for theoretical analysis is due to the fact that here there is only one hydrogen bond type. In contrast to hexagonal ice, all hydrogen bonds between water molecules in gas hydrate frameworks are mirror-symmetrical as in cyclic water clusters and polyhedral water clusters. The stability and other properties of such systems essentially depend on the proton positions on hydrogen bonds.

A new computational algorithm was developed for quick random generation of H-bond frameworks Structure I (sI) and Hexagonal Structure (sH) according to the Bernal-Fowler rules and periodic boundary conditions, for any size of simulation cell. The simulated annealing method was used in order to optimize the energy and the total dipole moment of the H-bonded frameworks. The total dipole moment was evaluated as a sum of all H-bond dipoles. The energy was calculated using the discrete models of inter-molecular interaction. The first strong and weak bond (SWB) model [1] takes into account specific features of the interactions with the nearest neighbor molecules. Within the framework of SWB model, lowest energy configurations have the maximal number of strong H-bonds corresponding to trans-configurations of H-bonded dimers. On the basis of concept of effective pair interactions [2], we have developed a new three-dimensional discrete model that takes into account specific features of inter-molecular interactions between second- and third-neighbor molecules. This bottom-up approach directly connects the local structure with the local energetics of gas hydrate frameworks.

All the lowest and highest energy configurations of unit cell of gas hydrate frameworks sI and sH according to the nearest-neighbour SWB model were found. Some calculations were carried out for different size of simulation cell and for zero total dipole moment. More exact results were obtained using the new middle-range discrete model. The predictabilities of the two models were evaluated by comparison with calculations using pair-additive potentials TIP4P and TIP5P.

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Inelastic x-ray scattering studies on the vibrational dynamics of clathrate hydrates

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The vibrational dynamics of clathrate hydrates of methane hydrate was studied with inelastic x-ray scattering using synchrotron radiation under ambient and high pressure. The results reveal resonant scatterings betweeen guest and lattice vibrations [1]. The strength of the coupling decreases with pressure [2]. At high pressure, methane hydrate transformed into the filled-ice phase [3] and the guest vibrations can no longer be regarded as localized oscillators. The effect of the resonant scattering is examined further with kryton hydrate where site specific nuclear resonance inelastic scattering technique [4]. The unexpectedly large anharmonic motion of the Kr is the cause for the glasslike thermal conductivity of the clathrate hydrates.

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Structure H hydrate kinetics studied by NMR spectroscopy

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Nuclear Magnetic Resonance (NMR) spectroscopy was employed to monitor structure H hydrate growth kinetics. Three well-known structure H hydrate formers (LMGS) with methane were studied: 2,2-dimetylbutane (NH), methylcyclohexane (MCH), and tert-butyl methyl ether (TBME). Hydrates were formed from ~0.15g freshly ground ice powder packed in the NMR cell and with excess of LMGS. The NMR cell was pressurized with 99% deuterated methane (CD4) to 45 bars at 253K. Proton (1H) and deuterium (2H) NMR spectra were employed to distinguish the spectra from LMGS and methane, which were recorded for 20 hours. The NMR spectra obtained from the gas and liquid phase appeared as sharp lorentzian lines and the solid phase appeared as broad Gaussian lines. Hence the distribution of methane in the gas, dissolved in LMGS and hydrate phase was able to be quantified. The 2H NMR spectra revealed the diffusion rate of methane in LMGS and the conversion rate of ice into hydrate. Methane diffused into TBME and NH faster than MCH. Hydrates were found to grow relatively fast for the first ~5 hours before slowing down mainly due to the formation of a hydrate film which blocked contact of the ice surface with methane and LMGS. The conversion achieved was found only about 35%, 19%, and 16% for the TBME, NH, and MCH systems, which were still far from the expected maximum values. However, ramping the temperature above the icepoint and using ´memory ice´ proved to speed up the kinetics and enhance further ice conversion into hydrate. The distribution of LMGS between ice particles was also observed by 1H micro-imaging NMR. The imaging study showed that each LMGS interacted with the ice particles differently, which affected the kinetics. The contact of TBME with ice particles was reasonably homogeneous but not so for the NH and MCH systems. The degree of packing of ice particles also influenced the kinetic results. Highly packed ice had less surface contact with LMGS so that further conversion of ice into hydrate was limited due to the isolation of ice. This study confirms that the hydrate growth rate obtained by NMR spectroscopy agrees with the results from gas uptake measurements, which suggests TBME to be the best structure H hydrate former to improve the kinetics during hydrate formation, followed by NH and MCH.

Investigation of local pressure and network of hydrogen bonds in methane hydrate – ice Ih system

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Effect of anomalous preservation of gas hydrates in their thermodynamic instability region ("self-preservation" effect) has remained in the focus of research efforts for many years, but the nature of this effect is still poorly understood. We are suggesting a microscopic-level model of methane hydrate clusters immersed in ice matrix. The difference in thermal expansion coefficients for methane hydrate and ice Ih leads to the appearance of excess pressure in the hydrate phase, which shifts the latter into its thermodynamic stability field. The hydrate cluster is stabilized by the formation of hydrogen bonds network at the ice-hydrate interface. We have constructed two models of methane hydrate immersed in ice. In the first model the spherical methane hydrate core (95 methane molecules and ca. 550 water molecules) was surrounded by 1 nm thick ice shell containing ca. 1700 water molecules (to a total of 2350 molecules). MD simulations were performed to obtain local pressure and density profiles of this system. It was found that the hydrate cluster immersed in ice cluster remains stable up to the melting point of the ice shell. The calculated temperature dependence of the surface tension at the ice-hydrate interface correlates with the experimentally observed dependence of hydrate decomposition rate on temperature.

The second model consisted of a methane hydrate sphere, surrounded by bulk ice Ih. Methane hydrate is modeled as supercell containing 63 molecules of methane and about 1100 water molecules; ice Ih contained more then 5000 water molecules (to a total of 6287 molecules). In this model periodic boundary conditions were applied to describe the bulk hydrate-ice system. The application of periodic boundary conditions leads to the increase of the ice melting point. The excess pressure in methane hydrate at such conditions was found to be sufficient to move the gas hydrate into the region of thermodynamic stability on the phase diagram. The results of calculations are in good agreement with our assumption.

Effects of large guest species on thermodynamic properties of structure-H hydrates

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Structure-H (s-H) hydrate has three kinds of hydrate cages, called S-, S'-, and U-cages. Its unit-cell consists of three S-cages, two S'-cages, and one U-cage [1]. Large guest species can occupy only the U-cage because of its size. Small guest species (help gases, for example, methane and xenon) occupy both the S- and S'-cages. The s-H hydrate helped by methane can be generated under lower pressure than the methane structure-I hydrate. The large guest species enable us to handle hydrates, which contain methane, under moderate conditions. This is why the s-H hydrates attract much attention as a medium for energy storage and transportation [2].

It is very important for developing the technology to elucidate thermodynamic properties of the s-H hydrates. In the present study, phase equilibria of the s-H hydrates helped by methane were investigated in the pressure region up to 10 MPa. In addition, s-H hydrate single-crystals were analyzed under four-phase equilibrium state (gas + water + s-H hydrate + large guest species) by means of Raman spectroscopy. Dimethylcyclohexane (DMCH) stereo-isomers, methylcyclohexane (MCH), cyclooctane (CO), and methylcyclopentane (MCP) were used as large guest species. It was suggested that there were limitation of the U-cage occupancy between the DMCH stereo-isomers. The s-H hydrate helped by methane is generated in MCP, cis-1,4-DMCH, cis-1,2-DMCH, CO, MCH, and 1,1-DMCH systems [3,4,5,6]. The equilibrium pressures decrease in that order under isothermal conditions. Methane + trans-1,4-DMCH s-H hydrate was not generated. It is suggested that the border of the U-cage occupancy is laid between the 1,4-DMCH stereo-isomers. Thermodynamic stability of s-H hydrate depends largely on how suitable shape and size of large guest species are for the U-cage. The results reveal that 1,1-DMCH has the most suitable shape and size for the U-cage in DMCH stereo-isomers.

Raman shifts of 1,1-DMCH enclathrated in the s-H hydrate are different from that of 1,1-DMCH phase. Raman spectra of enclathrated methane in methane + 1,1-DMCH s-H hydrates consist of two kinds of peaks. The lower peak corresponds to methane, which is enclathrated in the S'-cage, and the higher peak is that of S-cage. Peak area ratio of methane enclathrated in the S-cages to the S'-cages agrees well with that of the previous report (methane + MCH s-H hydrate system) [7]. It is suggested that the cage occupancies of methane for the S-, S'-cages have weak pressure dependency.

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Elastic properties of single-crystalline methane-ethylene hydrate under high pressure

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Natural methane hydrate (NMH) is an important material with respect to both a substantial future energy resource and a powerful greenhouse gas contributing to global warming. Therefore, elastic properties of gas hydrates with a variety of constituents are important for the safe extraction of methane gas and the estimation of the amount of natural methane hydrate in the deep sea sediment. However, there are few studies on detailed elastic properties of gas hydrates. Therefore, in order to estimate the elastic properties of NMH, we firstly apply the high-pressure Brillouin spectroscopy to a single crystal of binary methane-ethylene hydrate (MEH), and estimate the role of guest molecules in host water cages by comparing with the previous result of methane hydrate with structure I [1]. A single crystal of structure I MEH was synthesized in a high-pressure diamond anvil cell from pure water and a gas mixture containing 25 mol% CH_4 and 75 mol% C_2H_4, where this 1:3 gas mixture is the same ratio of S- to M-cages in the unit cell of structure I. The computational analysis for Brillouin experimental results of a single-crystalline MEH yielded three ratios of elastic constants to density (C_{ij}/ρ) and the elastic anisotropy ($A = 2C_{44}/(C_{11}-C_{12})$); $C_{11}/\rho = 13.2$ km^2/s^2, $C_{12}/\rho = 7.68$ km^2/s^2, $C_{44}/\rho = 4.07$ km^2/s^2, and $A = 1.46$ at 0.13 GPa. In spite of the heavier molecular weight of ethylene than methane, C_{ij}/ρ's are close to the values of methane hydrate. However, the elastic properties of MEH seem to be different from those of methane hydrate, since the elastic anisotropy A of MEH is apparently 23% larger than that of methane hydrate ($A = 1.19$ at 0.08 GPa). Moreover, we will speculate the mechanical stability of MEH on the basis of pressure dependences of elastic constants, bulk modulus, elastic anisotropy, and Cauchy violation.

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Microscopic observation and in-situ Raman studies on some single-crystalline gas hydrates under high pressure

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Recent high-pressure X-ray and neutron diffraction studies clarified the pressure-induced phase transformations of Ar hydrate, nitrogen hydrate, methane hydrate, and Xe hydrate at room temperature. These results indicate that the initial clathrate structure I or structure II eventually transforms to "filled ice" structure through a hexagonal phase with increasing pressure. On the other hand, the direct observations and in-situ high-pressure Raman studies have revealed the change of the occupation number of host water cages by guest atoms or molecules. As it is hard to find out such a change without structural transformation by means of X-ray and neutron diffraction methods, these results suggest that the microscopic observation and in-situ high-pressure Raman experiment are very effective in finding the change of cage occupancy. In the cases of nitrogen and methane hydrates, Raman scattering measurements for intramolecular vibrations of guest molecules are useful for finding out the change of cage occupancy, because their frequencies are sensitive to the surroundings of guest molecules. In the MH-II (hexagonal) phase of methane hydrate [1] and the structure II phase of nitrogen hydrate [2], the abrupt changes of cage occupancy were found at 1.3 GPa and 0.5 GPa, respectively. On the other hand, for krypton hydrate, the microscopic observation and the pressure dependence of the peak frequencies of lattice and O-H vibrations were very effective in finding the change of cage occupancy [3], because the increase of the occupation number of host water cages by guest krypton atoms at 1.0 GPa produced the released water as fine patches observed in hydrate crystals and the elongation of hydrogen bond of host water cages, namely, the frequency jumps of Raman signals of host water cages.

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Formation of metastable gas hydrates structures and time dependency of their transformation into the stable crystalline form

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There are repeated observations of the formation of gas hydrates in one of the two main cubic crystalline forms of the Stackelberg type I and II (sI and sII). We report here on experiments forming metastable hydrates starting from ice powder and using CO_2 and methane-ethane mixtures. Metastable sII CO_2 hydrates were observed earlier by us in in-situ neutron diffraction experiments and are analysed here in terms of their transformation kinetics. Mixed methane-ethane hydrates were prepared using a constant feed gas composition (97.3 mol% CH_4) at 270 K and 50 bar. After different reaction times samples were investigated via synchrotron X-ray diffraction and Raman spectroscopy. Initially sII hydrate was formed as the dominant phase together with sI hydrate. Afterwards, the sII hydrate transformed into sI as the thermodynamic stable phase. The sII-sI transformation takes place in our experiments over many days up to several months. Raman spectroscopy shows that for the methane-ethane mixtures the sII form is distinctly richer in ethane than the final sI form. In the sII hydrates the ethane resides in the $5^{12}6^4$ cavities as evidenced by the C-C stretch. The experiments are interpreted in terms of a kinetically favoured nucleation of the sII structure with a slow transformation into the stable sI form by a complete regrowth of the sample. The regrowth kinetics is most likely slow (1) because the difference in free energies of the two forms is small and (2) because the reconstruction of a type II structures has a high activation energy. At similar conditions a few degrees below melting/ decomposition the regrowth of gas hydrate takes orders of magnitude longer than the regrowth of hexagonal ice e.g. during Ostwald ripening.

Friday 01:30 pm - 03:00 pm **081-P098**

High-resolution Raman spectra of N_2 and O_2 guest molecules in natural clathrate hydrates

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Raman spectroscopy provides much information about molecular dynamics of clathrate hydrates and is a valuable analytical tool for the determination of hydrate structure, composition and cage occupancy [1].

It is known that N_2 and O_2 clathrate hydrates form clathrate structure II, which consists of two types of water cages with different sizes. Since N_2 and O_2 molecules enter both cages, one can expect that the guests each have two Raman bands; one is from molecules in the small cages and the other is from molecules in the large cages. However, only a single peak was observed for both hydrates [2]. It is believed that the two bands are too close to be resolved.

In order to clarify the above point, we performed high-resolution Raman experiments on natural air clathrate hydrates in the Dome Fuji Antarctic ice core. The single peaks were resolved into two lines, as was expected. Contrary to a well-known general trend that "the larger the cavity, the lower the frequency" [3], analysis of the data indicated that the low-frequency bands were from molecules in the small cages and the high-frequency bands were from molecules in the large cages. Judging from the intensity of the bands, the amount of N_2 molecules in the small cages was about the same as that in the large cages while most of O_2 molecules occupied the small cages.

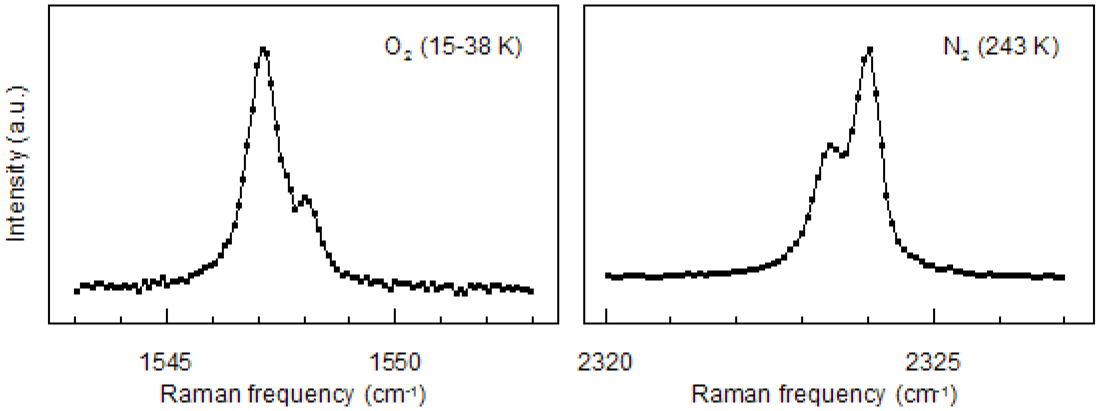

Fig.1 Raman spectra of a clathrate hydrate in Dome Fuji Antarctic ice from 1570 m.

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On the use of the Kihara potential for hydrate equilibrium calculations

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Due to their diversified field of applications (e.g. flow assurance in oil and gas pipelines in the oil industry, gas storage and transportation, potential use as an energy source, carbon dioxide oceanic sequestration, desalination, gas separations, etc.) gas hydrates have attracted significant attention from the international industrial and scientific community. Research efforts have focused on characterizing hydrates, obtaining their properties experimentally, developing theoretical models to describe various aspects of their behavior, and identifying their presence in nature. In general, while the existence of experimental data is useful for theory verification and model validation, predictive models can function as inexpensive tools for obtaining data for cases when no experimental data exist. The Van der Waals-Platteeuw theory for hydrate equilibrium calculations, and the subsequent improvements, is considered as one of the best examples of a theory based on statistical thermodynamics and successfully utilized to accurately solve real-world problems.

However, the long-lasting success of the theory, combined with the demand to accommodate the new areas of interest has resulted in stretching the theory to its limit, with some unintentional side effects. A typical example is the inability to define a unique set of Kihara potential parameters for each gas. Therefore, there is a significant difference between the different sets of parameters obtained from fitting different sets of hydrate equilibrium data. Furthermore, the parameters obtained through hydrate equilibrium calculations can differ significantly from those obtained from second virial coefficients or viscosity data. Current hydrate applications span a very wide range of conditions, including those falling outside the range for which the theory was originally developed (e.g. multiple cage occupancy). Therefore, the current theory tends to be correlative instead of having the powerful attribute of being completely predictive. The purpose of this study is to identify some of the aforementioned issues and discuss their implications. An extensive database of Kihara potential parameters, obtained from different methods (second virial coefficients, viscosities, hydrate equilibrium calculations) is gathered and analyzed. In addition, suggestions on how to remove the inconsistencies are explored and discussed.

Formation of carbon dioxide gas hydrates in freezing sediments and decomposition kinetics

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As is known permafrost section is the favorable environment where natural gas hydrate accumulations (methane hydrate, CO_2 gas hydrate and others) can be formed and exist. Necessary P/T conditions for gas hydrate formation here can be created by freezing processes which promote concentration of natural gas in porous media, to cooling gas saturated sediments and to increase pore pressure. It allows to consider permafrost and underpermafrost sediment layers as the possible environment for a storage of greenhouse gases, mainly CO_2 in gas hydrate form.

In this connection carrying out of special experiments for study gas hydrate and ice formation in CO_2 saturated sediments and behavior of frozen hydrate contained sediments under nonequilibrium conditions is obviously important.

In this work we presented experimental data of CO_2 hydrate formation in gas saturated wet sediments during cooling and hydrate decomposition kinetics in frozen CO_2 hydrate contained sediments. The initial CO_2 gas pressure inside chamber with sediment sample was 3,5-4,0 MPa. The study on hydrate and ice formation in carbon dioxide saturated samples we carried out at cyclic temperature changing: from +20°C to slightly above zero (+1-3°C), then to negative temperatures (-7°C÷-8°C) and to +20°C again. In each experiment 2-3 cycles gas hydrate formation has been lead. We finished each experiment by completely freezing the sample at (-7°C÷-8°C). Then the pressure inside the chamber was reduced to atmospheric pressure. Processing included analysis time change of temperature and pressure in the chamber, determination of phase transition parameters, estimation of water phase composition and also study of petrophysical characteristics of frozen hydrate-containing sediments [1, 2]. The influence of composition of mineral skeleton on the porous water supercooling degree, conditions and rate of CO_2 hydrate crystals growth and also on the hydration saturation in the studied samples was shown. The experimental study of CO_2 hydrate decomposition kinetics in frozen samples when pressure release allow to observe self-preservation effect of CO_2 hydrate in porous media. The experimental data shows that this process depend on temperature conditions, macro- and micromorphological features, degree of hydrate and ice pore space filling, composition and properties of sediment matrix.

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Friday 01:30 pm - 03:00 pm **090-P101**

Investigation of methane hydrate dissociation through decay of radiation-induced methyl radical in methane hydrate

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We investigated the thermal stability of gamma-ray-induced methyl radicals in methane hydrate using the electron spin resonance (ESR) method at atmospheric pressure and 210-260 K. The methyl radical decay proceeded with the second-order reaction and ethane molecules were generated from the dimerization process [1]. The methyl radical decay proceeds by two different temperature-dependent processes, that is, the respective activation energies of these processes are 20.0 ± 1.6 kJ/mol for the lower temperature region of 210-230 K and 54.8 ± 5.7 kJ/mol for the higher temperature region of 235-260 K [2]. The former agrees well with the enthalpy change of methane hydrate dissociation into ice and gaseous methane, (18.13 to 23.37 kJ/mol in literatures [3-5]), while the latter agrees well with the enthalpy change into liquid water and gaseous methane, (54.19 to 67.85 kJ/mol in literatures [3, 5, 6]). These findings reveal that methane hydrates dissociate into liquid (supercooled) water and gaseous methane in the temperature range of 235-260 K, thus methyl radical decay model may be connect with self-preservation effect of methane hydrate, which emerges in similar temperature range.

Additionally, we observed the amount of methane remaining in the hydrate after heating. Although methyl radicals completely decay in the temperature region at 253 K, the methane still remains 80% amount of original gas, which is confirmed by comparison of induced methyl radical density in hydrate before and after 3-hours annealing at 253 K.

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Investigation of formation and phase diagrams of double gas hydrates H_2 –CH_4 - H_2O at pressures up to 250 MPa.

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Hydrogen storage in the form of clathrate hydrate $(H_2)x*17H20$ is an important but difficult problem because of a low decomposition temperature of this hydrate (140 K at 0.1MPa [1]). However, the stability of the system can be significantly increased by adding certain chemical compounds to the initial components of the hydrate. One of compounds that can be used for increasing stability of hydrogen hydrate is methane. The advantage of the double hydrate system H_2 – CH_4 - H_2O is that upon melting it emits gas mixture consisting of burning gases which can be used as a fuel. These considerations indicate that hydrogen storage in double hydrate H_2 – CH_4 - H_2O has certain technological prospects.

In this work we investigated a part of the phase diagram of the system H_2 – CH_4 - H_2O at pressures up to 250 MPa and in a wide range of concentrations of hydrogen in the initial gas mixture. The obtained data show that increase of hydrogen fraction the in initial gas mixture leads to a decrease in the of decomposition temperature of the double hydrates.

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Determination of volume changes upon phase transformations in the argon-water system

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For the first time, volume changes accompanying structural transformations in argon hydrates and the dissociation of cubic structure II (CS-II) argon hydrate were determined in the pressure range of 1.5-10 kbar at room temperature and at ~ 800 bar in the temperature range of 283-305 K. Three argon hydrates were known to exist below 10 kbar in the argon-water system [1]. One phase that is stable up to 4.6 kbar appears to be CS-II gas hydrate with a variable degree of filling of the large cavities. Another hydrate existing in the pressure range of 4.6–7.7 kbar possesses a hexagonal structure. One more hydrate forms in the pressure range of 7.7–9.5 kbar and belongs to the tetragonal structural type. Two series of experiments were carried out. In the first part of this work, high-pressure argon hydrates were synthesized from thoroughly ground ice and an excess of argon. After an equilibrium was established, the pressure was reduced slowly in a regular steps, and a volume changes were determined from the piston`s shift.

In the second part of this work, the experiment with CS-II argon hydrate was performed at ~ 800 bar. The temperature was increased from 283 K and the pressure was kept constant. A sharp volume change was observed at the dissociation point of the hydrate.

By this method, we observed volume changes corresponding to a phase transitions from tetragonal structure to structure H and from structure H to CS-II argon hydrate as well as the dissociation of the CS-II argon hydrate to water and gaseous argon.

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Ordering mechanism of H_2O and gas molecules during growth of a gas clathrate hydrate

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A molecular dynamics simulation was carried out for a three-phase system including a gas clathrate hydrate, liquid water and a gas phase at a temperature above 0 degree C. The interaction between a pair of H_2O molecules was estimated using the six-site model [1], and the interaction between a pair of gas molecules were estimated using the Lennard-Jones potential with a parameter set for a spherically-approximated CH_4 molecule. The purpose of this study was elucidating the growth mechanism of a gas clathrate hydrate from a dilute solution in a real system.

By applying a high pressure to the system, growth occurred on interfaces between the clathrate and the liquid water. The transfer process of gas molecules from the gas phase, through the liquid water, to the clathrate-water interface was analyzed. The results clearly indicated a very low frequency of dissolution of gas molecules in the liquid water and slow diffusion of them in the liquid water, reflecting that the transfer of gas molecules was the rate-determinant factor for growth of the clathrate. The slow diffusion of gas molecules in the liquid water originated from a stable hydrogen-bonded network in the first hydration shell around each gas molecule. However, no cage-like structure was found in the hydration shell.

The ordering processes of H_2O and gas molecules on the interface were also analyzed in detail. The results clearly indicated that the ordering of gas molecules occurs smoothly on the interface, prior to the surrounding H_2O molecules' formation of cage structures. It should be noted that the subsequent ordering of H_2O molecules occurred only in restricted regions surrounded by the gas molecules, which were arranged on the interface. This ordering of H_2O molecules in restricted regions is analogous to the ordering of H_2O molecules confined in a closed nano-scale space, such as in a carbon nanotube. The present results strongly suggest that a cage structure is not related to the growth unit for the clathrate. In other words, the clathrate does not grow by a "cage-by-cage" process.

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From ice to CO_2 hydrates and back – The nature of formation and decomposition processes

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In spite of the great efforts placed upon understanding the physical chemistry of gas hydrates, final conclusions have not been reached yet. The kinetics of formation/decomposition is a complicated multi-phase process, details of which are still largely unknown. A better understanding may enable a wide range of new industrial and scientific applications. Previous publications dealing with formation kinetics of hydrates starting from well defined ice powder consisting of particles with known geometry point to a multistage process [1,2]. Both in-situ diffraction experiments as well as gas consumption measurements were used to follow the transformation process; electron microscopy was helpful to get microstructural information at various stages of the reaction on samples recovered during the process. The reaction starts with nucleation-and-growth and later changes to a diffusion controlled formation. The nucleation and pre-nucleation processes are difficult to access and remain largely unknown. However, there is good evidence that nucleation starts at multiple sites on the ice surface accessible to the reacting gas. New data from formation experiments gave us a better understanding on the fast initial processes. The first stage ends when the whole available surface is covered. Then, the transport of gas/water to/from the ice phase is increasingly hampered and ultimately can only be achieved by solid-state diffusion. Correspondingly, the system shows a transition from a reaction-limited to a diffusion-limited formation process. As the size of the ice particles shows some dispersion, there is a smooth transition between the stages. Much less is known about the mechanism of hydrate decomposition and specific models need to be developed for this case. Nevertheless, the reaction also produces many nucleation sites, clearly seen in SEM images at the surface of hydrate grains [3]. Moreover, the existence of so-called anomalous preservation creates additional difficulties for modelling the decomposition of gas hydrates. In a temperature interval from ~ 240 to 273 K the decomposition is anomalously slowed down leading to a stabilization of gas hydrate outside the thermodynamic stability field even for geological time-scales. Combination of interrupted decomposition runs with electron microscopy seems to be a very promising way of investigation. We will present new observations on formation/decomposition of the hydrates in a broad range of pressures and temperatures.

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The hydrogen bonding nature of water molecules in methane hydrates as studied by in-situ low temperature IR spectroscopy

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Methane hydrate has recently attracted much attention as a potential new natural resource. It is a clathrate hydrate in which a methane molecule is surrounded by cages of water molecules bound by hydrogen bonding. Its structure has been mainly investigated by X-ray diffraction and Raman spectroscopy. However, the hydrogen bonding nature of water molecules and their interaction with methane molecule have not been investigated. This kind of interaction might provide better understanding of behaviors of methane hydrates, especially for their phase changes and decomposition. In order to study hydrogen bonding natures of methane hydrates, we have conducted in-situ infrared (IR) spectroscopy at low temperatures under atmospheric pressure. Methane hydrate films were prepared from water-ice films on a CaF_2 plate in liquid nitrogen (-190 C) under methane gas pressure (10 MPa). The obtained film on the CaF_2 was then put on an aluminum foil on a cooling stage set under an IR microscope. IR transmission-reflection spectra of the methane hydrate film (a few micrometers thick) on the Al foil were measured through the CaF2 at temperatures of –120 to –20 C with 20 C intervals.

IR spectra of methane hydrates at -120 to -80 C show a sharp peak around 3250 cm-1 with a shoulder around 3400cm-1 due to OH stretching vibration similar to ice. Bending vibrations of molecular water are also observed at around 2200 and 1630 cm-1. Since the 2200 cm-1 band is present in pure water but not in pure ice, the water molecular cages in methane hydrates have both similarity to and difference from water molecular clusters in pure ice. Besides these water bands, contributions of two broad bands are recognized around 3000 cm-1 and 1400 cm-1 at –60 to –20 C. These are considered to be due to C-H stretching and bending vibrations of methane, respectively. IR spectra of pure ice at the same temperature were subtracted from the IR spectra of methane hydrates to eliminate effects of coexisting pure ice. The resulted difference spectra of methane hydrates minus ice show absorption bands at 3400, 2200 and 1630 cm-1 bands similar to liquid water together with 3000 and 1400 cm-1 bands due to methane. The hydrogen bonding nature in methane hydrate is thus much closer to that in liquid water than that in ice, based on the present in-situ IR spectroscopy.

Gas hydrates in sediments imaged by cryogenic SEM (CSEM): Insights from lab experiments on synthetic hydrates as interpretive guides

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Using CSEM, we have investigated the physical states of hydrates produced in our lab and those in drill core taken from hydrate-bearing sediment from Arctic permafrost and marine environments and ultimately preserved in liquid nitrogen. Samples from nature to date are all partially decomposed and altered during drilling, their transit to the surface, surface handling, and the preservation process. As such, they contain to varying degrees hydrate that may or may not be changed from its original textural and composition state, hydrate decomposition products, including ice, trapped gas, and frozen pore water, and possibly also non-clathrated hydrates such as sulfate and chloride hydrates and chlorides. Finally, such samples can be subject to damage under the electron beam and sublimation under vacuum; these processes can pose challenges for investigating some hydrate structures and compositions, limiting the time available for observation. Alternatively, these variations in sublimation rates may be used for identification purposes. At imaging conditions of ~ 105 K, vacuum below 10-5 mbar and < 2 kV accelerating voltage, these solids sublimate under the beam in the following order (high to low): sI and sII gas hydrates > ice I > non-clathrate hydrates (sulfate and chloride hydrates). Drill core material with a significant fraction of preserved hydrate have been obtained for CSEM investigation from only a few sites worldwide and the following trends are apparent for the grain and pore textures in them: (1) Massive domains of polycrystalline hydrate that contains isolated gas-filled pores that are sometimes lined with euhedral hydrate crystals. The pores are typically 5- 50 microns in diameter and occupy roughly 10-30% of the volume of the domain. Hydrate grain sizes, where visible, are commonly several tens of microns in diameter. (2) Grain boundaries are often replaced by a tabular mesoporous material that stands out above the hydrate and is believed to be bubbly ice (based on its location and its slower sublimation rate) produced by hydrate decomposition along the boundary. (3) Larger domains of nano-to-micro porous “spongy” to frothy ice that are believed to represent hydrate decomposition products produced during drill-core transport and handling or pore water frozen by this exothermic reaction and by exposure to liquid nitrogen. Lab experiments indicate that these materials are not stable at in situ natural conditions above 0°C.

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Friday 01:30 pm - 03:00 pm **111-P110**

Microstructures of gas hydrates in porous media

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Most natural gas hydrates are stored in ocean floor deposits and commonly formed in sediments. Laboratory investigations of the microstructure of gas hydrates in porous media will help to understand the formation processes of gas hydrates in various sediment compositions as a function of p-T conditions and supersaturation. Moreover, it may also allow the prediction of accumulation /decomposition rates of some natural gas hydrates in the corresponding geological settings. Synthetic samples of gas hydrates were obtained in different porous media: (a) quartz, (b) quartz with kaolinite and (c) quartz with montmorillonite. Samples recovered at various stages of the formation or decomposition reaction were investigated using high resolution field-emission scanning-electron microscopes (FE-SEM) equipped with a cryo-stage. In addition to high vacuum working conditions we also plan to present first results obtained under low vacuum or extended low vacuum conditions. In the electron micrographs gas hydrates, formed by the transformation of liquid water, appeared as cement like materials between quartz grains. Kaolinite particles separated from the gas hydrate cement and accumulated on the surface of methane hydrate. In contrast, when using montmorillonite, the cement appeared to be a mixture of clay particles and hydrates. The gas consumption was recorded during hydrate formation indicating different formation kinetics for the various media used.

Special aspects of air hydrates in deep ice cores

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In the large ice sheets, air bubbles convert to air clathrate hydrates in the depth range between 500 and 1500 m. Statistical analysis shows that,on average, smaller bubbles transform earlier than larger bubbles. On the other hand, microstructure mapping indicates also that there are horizons (from some millimeters to one or two centimeters in width), within the air bubble-air hydrate transition zone, where all bubbles seem to have been converted to hydrates more or less simultaneously and independently of size. It seems that the presence or absence of some impurities may cause this sudden and size-independent conversion.

In the transition zone, air hydrates form a wide variety of shapes. Below about 1500 m, the number of shapes reduces dramatically to mainly round and oval hydrates. Subdivision, size- or shape-dependent instability, growth, recrystallization, or other processes may lead to air hydrates with smoother outlines. Noteworthy is also that air hydrates in ice from below about 2300 m depth (in the EPICA DML ice core) appear covered with ´black dots´ while air hydrates in ice from the last glacial maximum, which has a much heavier load in impurities, look ´clean´. Should this mean that such ´dirty´ air hydrates have collected/attracted impurities?

Effect of snow accretion to the GPS antenna on positioning performance

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Recently, GPS has been using positively in railway-system [1]. When the snow accreted the GPS-antenna, occasionally, the positioning ability was decreased. We examined the effect of snow accretion to the GPS antenna on the positioning performance. We compare a snow-accreted-antenna (accreted like a column) with a non-snow-accreted antenna about the number of satellites (which can use for positioning) and carrier-to-noise power rate(C/N0). In this examination, we used the compacted snow (<Fi>0.5mm) which had been accumulated naturally and GSC-001 antenna which was made by FURUNO ELECTRIC CO. LTD. First, we accreted dry snow (content-of-water/c.w.0% [2]). When we changed the thickness of snow from 0 to 400mm,dry-snow did not decrease positioning ability. Second, we accreted wet snow (c.w.39%). When we changed the thickness of snow from 0 to 400mm, wet-snow decreased positioning ability. When the thickness was between 0 and 50mm, snow got thicker, positioning ability got lower. And, when thickness was more than 50mm, C/N0 was about 30dB which meant that it couldn't position. Next, in order to examine the effect of the water volume which the accreted snow contented, we used tree types of wet snow (c.w.17, 24, 39%). In this case, if it cannot position, C/N0 is always about 30dB. This means we can not compare. So, we use the data which the thickness of snow was between 0.5 and 50mm. As a result, when the accreted snow got wetter, positioning ability got lower. Summary, the accretion of dry-snow to the GPS antenna (GSC-001 antenna) did not decrease positioning ability. However, accreted snow got wetter and thicker, positioning ability got lower. And, when the content-of-water was more than 40% and the thickness was more than 50mm, it could not position.

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Ice clusters in the size range of tens to thousands of water molecules

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A joint computational (Buch, Kazimirski) and experimental (Baurecker, Devlin and Buck) effort was directed towards understanding of large solid water clusters. The computations included structure optimizations and calculations of OH stretch spectra for select sizes in the range n=20-931. The measurements focused predominantly on OH stretch spectroscopy as a function of mean particle size. FTIR spectra are discussed for the size range of tens to hundreds-of-thousands of molecules. Photofragment spectroscopy in molecular beams is shown to be a sensitive probe of the outer cluster surfaces. The crucial element of the different experimental approaches is the control and the estimation of the mean cluster sizes. The combined experimental and computational results are consistent with a physical picture of quasi-spherical nanocrystals with disordered reconstructed surface layers. The surface reconstruction can be viewed as outcome of recombination of surface dangling atoms, to increase the number of hydrogen bonds.

The hydrogen bonds within the mostly crystalline subsurface layer are stretched by the interaction with the disordered component. The emergence of the (strained) crystal core occurs at a size of a few hundred molecules. Smaller clusters are described as compact-amorphous.

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