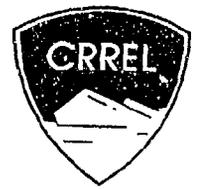


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# The Surface of Ice

Victor F. Petrenko

August 1994

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**Abstract**

This report examines the structure and physical properties of the surface of ice: a liquid-like layer on the ice surface, its thickness and molecular structure, surface conductivity, surface electric charge, surface potential, surface diffusion and so forth. The author reviews experimental results and theoretical models on ice adhesion, gas adsorption and ice sintering. Special attention is given to the results of studies from the last two decades. Among the experimental techniques under consideration are nuclear magnetic resonance, X-ray diffraction, optical ellipsometry, measurements of ice surface conductivity and dielectric permittivity, frictional electrification of snow and ice, proton channeling and others. In conclusion, the theoretical models of the ice surface structure and the results on molecular dynamics are considered.

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**US Army Corps  
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Cold Regions Research &  
Engineering Laboratory

## **The Surface of Ice**

Victor F. Petrenko

August 1994

Prepared in cooperation with  
THAYER SCHOOL OF ENGINEERING  
DARTMOUTH COLLEGE

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## PREFACE

This report was prepared by Dr. Victor F. Petrenko, Professor of Engineering, Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire. Funding was provided by the U.S. Army Research Office through contract DAAL 03-91-G-0164.

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## FOREWORD

At the present time, thousands and thousands of people around the world deal with ice, snow and permafrost. They are scientists, educators, engineers, navigators, meteorologists and others. While a small fraction of these people contribute to the knowledge base in ice physics, all of them use knowledge from it frequently. Moreover, successful applied research is based upon fundamental science—one more reason for ice specialists to have a textbook on ice physics on their desks.

The first modern ice physics text was Fletcher's book on *The Chemical Physics of Ice* (1970). Fletcher's book is in typical textbook format: it is reasonably brief and easy to understand. He touched on a few of the most important topics, but not all of them.

The most comprehensive book on ice physics to date was published by Hobbs in 1974. Hobbs considered almost all of the basic aspects of ice as understood at that time. Moreover, he described and compared several (sometimes opposing) viewpoints. This fundamental and rather large (837 pages) book is commonly known as the "Ice Bible" by specialists in the field. In 1974 and 1975, two CRREL Monographs on ice were produced by John Glen. These were briefly and clearly written and reviewed almost all ice-related subjects. This work was (and in some respects still is) a magnificent introduction to ice.

Finally, in 1981 Maeno wrote a simple, popular book for the express purpose of attracting people's attention to the subject.

During the past 20 years, a significant amount of new experimental and theoretical work has appeared, dramatically changing our views on ice physics. As a result, we are now able to formulate physical laws using more simple and direct methods. We have found some of the physical models used in the past to be completely wrong. The physics of ice is a much better developed subject than it was 20 years ago.

For the above reasons, I feel the time is ripe for a contemporary book on ice physics, incorporating the known and proven with almost 20 years worth of material not covered by previous works.

I have tried to prepare a "readable" book, and not one that requires the reader to be a uniquely educated person. It is my intent to present the material in such a way that any reader attracted by the title *Ice Physics* will be able to comprehend it. This is quite difficult for a book dedicated, not to a particular field of knowledge, but to a specific material. Indeed, for ice it means we have to consider a wide variety of subjects, including quantum chemistry, solid state physics, the theory of elasticity, ionic conductivity, synchrotron X-ray topography, crystal growth, the physics of surfaces and more.

The primary goal is to produce as simple a book as possible without sacrificing scientific accuracy. Experimental facts, physical ideas and theories will be strongly organized and bound together cohesively. The reader will be introduced to a wide variety of material on a step by step basis. Then the picture will be whole.

To accelerate publication, this book will appear first in the form of a series of joint CRREL-Dartmouth reports, later to be published in CRREL's Monograph series, on:

1. The structure of ordinary ice  
Part I: "Ideal" structure of ice. Ice crystal lattice  
Part II: Defects in Ice  
Volume 1: Point defects  
Volume 2: Dislocations and planar defects
2. Electrical properties of ice  
Part I: Conductivity and dielectric permittivity of ice  
Part II: Advanced topics and new physical phenomena

3. Optical properties
  4. Electro-optical effects in ice
  5. Thermal properties
  6. Mechanical properties of ice. Elasticity and anelastic relaxation. Plastic properties. Fracture of ice
  7. Electromechanical effects in ice
  8. The Surface of ice
    - Part I: Experimental results on the structure and properties of the ice surface
    - Part II: Theoretical models of the ice surface
  9. Other forms of ice and their properties
  10. Ice in space
  11. Ice research laboratories
- The reports will be prepared in a sequence convenient to the author. The present report is the fifth in the series.

## NOMENCLATURE

$a$	length of hop	$\varphi$	electric potential
$a_1^{-1}$	length of screening by Bjerrum defects	$\varphi_s$	surface electric potential
$a_2^{-1}$	length of screening by ions	$k$	absorption coefficient
$a^{-1}$	screening length when $ e_i \varphi_s  \gg k_B T$	$k_B$	Boltzman constant
$\alpha_0$	fraction of surface molecules in the liquid-like layer with dipole moments (i.e., protons) oriented towards the surface	$L$	thickness of the surface layer
$B$	magnetic induction	$\lambda_s, \lambda_{so}$	surface charge density
$C_s$	concentration of adsorbed molecules on the surface	$\lambda_{sa}$	surface charge absorbed on the ice interface
$C_M$	maximum concentration of adsorbed molecules	$\vec{m}$	dipole momentum of a water molecule
$d$	thickness of the quasi-liquid layer	$n$	refractive index
$D_i$	diffusion coefficient	$n_B$	concentration of Bjerrum defects
$\Delta, \psi, \vartheta$	angles	$n_{H_2O}$	water molecule concentration in ice
$E_a$	heat of adsorption	$n_i$	charge carrier concentration, $i = 1, 2, 3, 4$
$E, \vec{E}$	electric field strength	$n_i$	refractive coefficient of ice
$e_i$	electric charge of $i^{\text{th}}$ type of charge carrier, $i = 1, 2, 3, 4$	$n_w$	refractive coefficient of water
$\epsilon_0$	dielectric permittivity of vacuum	$n_{ion}$	concentration of ions
$\epsilon_s$	static dielectric permittivity of ice, $\epsilon_s \approx 100$ ( $T = -10^\circ\text{C}$ )	$\nu$	frequency of ion's hops
$E_s$	activation energy of surface conductivity	$P$	pressure
$E'$	effective electric field acting on a molecule	$\vec{P}$	polarization vector
$\epsilon_\infty$	high-frequency dielectric permittivity of ice, $\epsilon_\infty \approx 3.2$	$\vec{P}_e$	electronic polarization vector
$\Phi$	$= 3.85 k_B T r_{oc}$	$\vec{P}_M$	molecular polarization vector
$\phi$	wetting angle	$Q$	electric charge
$G$	Gibbs free energy	$\rho$	$r_{  } / r_{\perp}$
$g$	gyromagnetic constant	$\rho(x)$	density of the space charge
$\gamma$	surface energy	$\rho_L$	water density
$\gamma_{SL}$	surface energy of ice/water interface	$r_{\perp}$	reflection coefficient for light polarized perpendicular to the plane of incidence
$\gamma_{VL}$	surface energy of vapor/water interface	$r_{  }$	reflection coefficient for light polarized parallel to the plane of incidence
$\gamma_{VS}$	surface energy of vapor/ice interface	$r_o$	constant
$I$	current	$s$	surface area
$\eta$	viscosity	$\sigma_B$	Bjerrum defect conductivity
		$\sigma_B$	bulk conductivity
		$\sigma_{ion}$	ionic conductivity
		$\sigma_o$	low-frequency bulk conductivity
		$\sigma_s$	surface conductivity, $\Omega^{-1}$

$\sigma_{ss}$	specific bulk conductivity of the ice surface layer, $\Omega^{-1}\text{m}^{-1}$	$\tau_{MS}$	Maxwell relaxation time
$S_{st}$	adhesive strength	$T_m$	melting point of ice
$S_c$	entropy of fusion per unit mass	$v$	velocity
$\sigma_{\infty}$	high-frequency bulk conductivity	$x$	coordinate
$T$	temperature	$\omega$	angular frequency
$t$	time	$\omega_0$	resonance frequency
$\tau$	correlation time of molecular motion	$W_i$	electron work function of ice
$\tau_a$	mean lifetime of a molecule adsorbed on the surface	$W_m$	electron work function of a metal
$\tau_D$	Debye relaxation time	$\mu$	chemical potential
$\tau_{DS}$	Debye relaxation time of the surface layer of ice	$\mu_i$	charge carrier mobility, $i = 1, 2, 3, 4$ for $\text{H}_3\text{O}^+$ , $\text{OH}^-$ ions, D- and L-defects respectively

# The Surface of Ice

VICTOR F. PETRENKO

## INTRODUCTION

Since childhood, we have accustomed ourselves to matter being either solid or liquid or gas. Later, we become acquainted with the fourth kind of matter called plasma, which is very rarefied and has an extremely large electrical conductivity.

Can you imagine a simultaneous combination of certain properties of solid, liquid and plasma matter? It is present on the surface of the ice upon which we walk each winter, unsuspecting that it possesses such unique characteristics.

When we bump into a sharp corner or hurt ourselves with a needle or cut a finger with a knife, we confirm that surfaces of solids are indeed solid. This is true in so many cases that it necessarily becomes a rule.

In the case of ice, however, some simple observations make us doubt that it has a rigid and permanent surface. For example, if we bring two ice balls together, then right before our eyes, a small "neck" starts to grow between them (Fig. 1). In time, further growth will lead the two balls to become one. In this simple experiment, some substance can be considered to flow between the balls through the "neck." Since ice in bulk form is apparently solid (have you ever fallen on ice?), it is most likely the surface that flows.

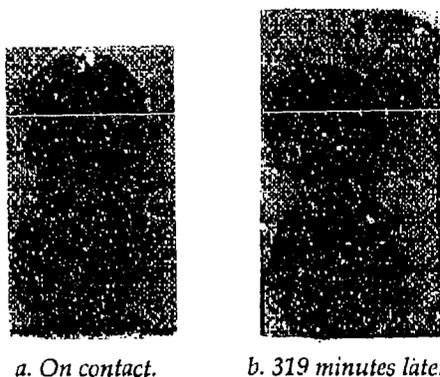


Figure 1. Growth of a neck between two ice spheres 0.5 mm in diameter at  $-6^{\circ}\text{C}$  (from Hobbs 1974).

In a process similar to the ice balls' unification, airy, fluffy snowflakes, after lying together for some time, sinter first into dense, heavy snow, and next into solid ice. It is this process, going on for thousands and thousands of years, that has formed the kilometer-thick ice sheets in Antarctica and Greenland (mass transport through the vapor phase and a plastic flow are also involved in this sintering process).

Evidently, the first documented guess for the existence of a special layer on the surface of ice was the work by Faraday (1859). On the grounds of his long-standing experiments on the adhesion of ice, Faraday called this layer a "liquid-like" layer. Another common expression is "quasi-liquid" layer. Now, the existence of some special layer on the ice surface has been proven by many experimental techniques. Hundreds of papers are dedicated to the investigation of the structure of this layer and its physical properties. The most essential contributions to the store of our knowledge about this liquid-like layer were made during the past two decades.

In the present report, I shall describe the results of the experimental research that provides direct information on the structure and thickness of this layer: X-ray diffraction, proton channeling, ellipsometry and NMR. Then, numerous results of studies of the physical properties of the ice surface will be considered. An analysis of these properties by means of comparing various models also allows us to obtain indirect information about the structure and thickness of the special layer on the ice surface. We shall not consider ice friction here, since several good reviews on this topic have been published recently (see, for instance, Aharon et al. [1988] and Colbeck [1992]). Nevertheless, when all the reports are united into a book, a chapter on ice friction will be included.

In conclusion, major known theoretical models, describing the structure and properties of the liquid-like layer, will be discussed.

## PART I. EXPERIMENTAL RESULTS ON THE STRUCTURE AND PROPERTIES OF THE ICE SURFACE

### X-RAY DIFFRACTION

When considering the structure of the quasi-liquid film on the ice surface, we must first answer the question: is the structure of the film ordered or not? That is, does the structure have a long range order? And if so, then is this structure different from that of ice? It seems that the easiest way to answer this question is to use any known X-ray diffraction technique. However, owing to the extremely small thickness of the film, it is difficult to differentiate its contribution to the diffraction from that of the ice bulk. I am aware of only one such attempt, where Kouchi et al. (1987) investigated X-ray diffraction at the surfaces of polycrystalline and monocrystalline ice in a temperature range of  $-0.5$  to  $-10^{\circ}\text{C}$ . Glancing beams were used (angle of incidence  $\approx 2^{\circ}$ ) to make the contribution of the surface as large as possible. The  $\text{K}\alpha$  line of the Cu X-ray spectrum was used in the experiments.

Figure 2 shows X-ray diffraction patterns of the surface of the polycrystalline ice sample obtained at  $-9.3$ ,  $-2.1$  and  $-1.1^{\circ}\text{C}$ . At  $T = -9.3$  and  $-2.1^{\circ}\text{C}$ , the diffraction peaks that are characteristic for the crystal are clearly visible, although their magnitude decreases at  $-2.1^{\circ}\text{C}$ . At  $T = -1.1^{\circ}\text{C}$ , those peaks virtually vanish, being replaced by a blurred, circular "halo" centered at  $2\theta \approx 26^{\circ}$ . This is a clear evidence that, at this temperature, the long-range order in the arrangement of surface molecules in the surface layer vanishes.

Since the intensity of the diffraction halo can be used to estimate the disorder in the surface layer thickness, it is interesting to study the temperature dependence of this intensity, which is illustrated in Figure 3. First, we can conclude from this figure that the layer's thickness is independent of the crystallographic orientation of the surface. Second, the layer ceases to be detectable by this method at  $T \leq -2^{\circ}\text{C}$ . Unfortunately, Kouchi et al. did not attempt to estimate an absolute magnitude of the layer's thickness.

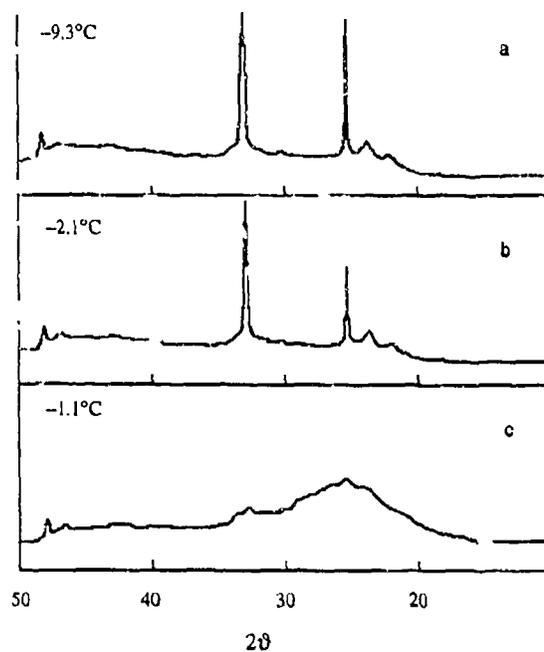


Figure 2. Intensity of the beam diffracted from the polycrystalline ice surface as a function of the angle between incident and reflected beams (after Kouchi et al. 1987).

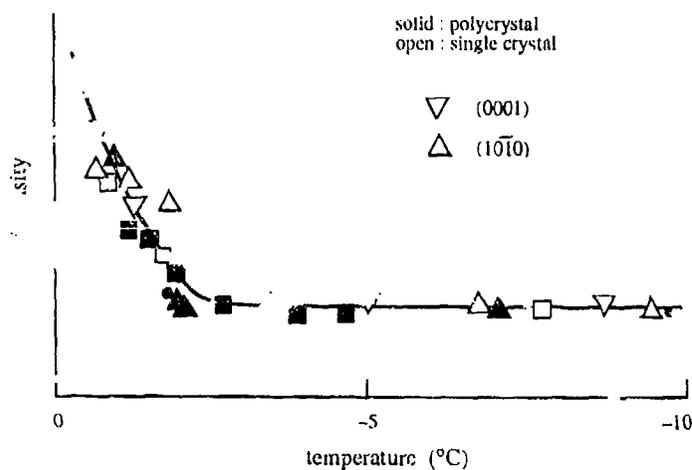


Figure 3. Changes in intensity of diffraction halo at  $2\theta = 28^{\circ}$  with temperature (after Kouchi et al. 1987).

## PROTON CHANNELING

Another interesting experimental method of determining the thickness and structure of the quasi-liquid layer was used by Golecki and Jaccard (1977, 1978). This is the so-called channeling effect, discovered by Oen and Robinson (1962). The channeling effect manifests itself in the fact that, if a beam of heavy charged particles (usually protons or  $\alpha$  particles) travels parallel to some crystallographic direction, then the particles of that beam experiencing low-angle scattering penetrate the crystal at very long distances and can stay inside the channels formed by atomic rows. The magnitude of this effect is usually expressed in terms of the ratio of the flux of backscattered particles when the direction of the flux coincides with one of the crystallographic directions to that when the direction is arbitrary.

The backscattering can take place only at nuclei of atoms that are much heavier than the particles in the beam and resembles the classic Rutherford scattering. The diffraction of such particles at the crystal lattice is insubstantial, since the characteristic de Broglie wavelength is several orders of magnitude less than the lattice constant.

Most of the backscattered particles experience only a single strong interaction with a lattice atom. Using the theory of Rutherford's scattering, we can calculate the energy of the reflected particle as a function of the scattering angle. Departures from this predicted value contain information about the depth at which the scattering took place (more exactly, about the path the particle has traveled back and forth within the matter). The loss of the kinetic energy of the particles is attributable to their interaction with the valence electrons and is almost independent of the direction of the motion. Having "calibrated" such losses for a particular material (or having calculated them theoretically), we can establish the depth at which the scattering took place with a rather high accuracy.

The channeling is extremely sensitive to the degree of perfection of a crystal structure and therefore can be efficiently used for measurements of the magnitude of thermal vibrations, the degree of disordering, the concentration of point defects and so forth. One of the comprehensive reviews on the subject is that by Gemmel (1974).

In 1977 and 1978 this effect was explored by Golecki and Jaccard for the investigation of the (0001) surface of ice crystals. The authors measured the backscattering (angle  $150^\circ$ ) of 100-keV protons from the surface of monocrystalline ice in

a wide temperature range from  $-2$  to  $-130^\circ\text{C}$ . They found that, at temperatures higher than  $-40^\circ\text{C}$ , the surface layer is characterized by much higher disordering in relation to the bulk. Analysis of the behavior of the disordering process prompted Golecki and Jaccard to conclude that the disordering is caused by a significantly higher magnitude of thermal vibrations of oxygen atoms near the surface, rather than the absence of symmetry in the structure. Thus, at  $T = -1.8^\circ\text{C}$  the average amplitude of the thermal vibrations of oxygen atoms near the surface exceeds that of the bulk by 3.3 times. Because of that, Golecki and Jaccard suggest not using the term 'liquid-like' layer at all.

To estimate the thickness of the special surface layer of ice, Golecki and Jaccard calculated an equivalent thickness of an amorphous layer (totally disordered) that would result in the same magnitude of scattering. The results of such calculations are depicted in Figure 4. It is worth noting that the half-thickness of the layer  $t/2$  obtained is extremely large. The temperature dependence of the thickness  $t$  was found to be

$$d(\text{nm}) = (94 \pm 17) - (54 \pm 14) \log(273 - T). \quad (1)$$

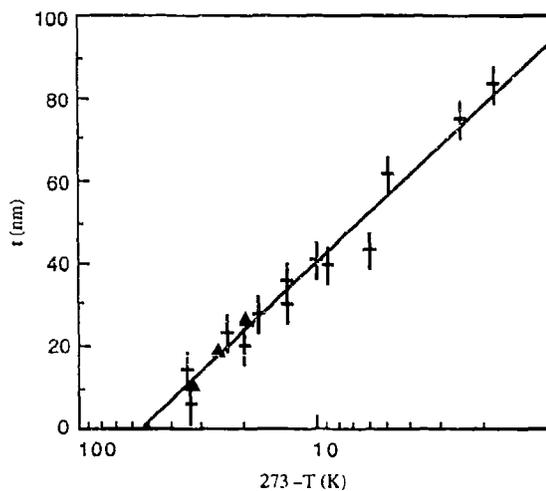


Figure 4. Equivalent "amorphous" thickness of the disordered region at the ice surface, deduced from the measurements with the aid of Meyer's (1971) theory. The solid line corresponds to least-squares fit. The density of the surface region was assumed equal to that of ice ( $0.917 \text{ g cm}^{-3}$ ) (after Golecki and Jaccard 1978).

## OPTICAL ELLIPSOMETRY

Ellipsometry is an optical reflectance technique in which the change of the state of polarization of light upon reflection from a surface is measured. Even though the method dates back to Drude (1889), ellipsometry has recently attracted considerable attention because of a wide variety of applications in modern solid state optics, especially in the physics of surfaces, interfaces and thin films. In the study of the ice surface, optical ellipsometry was used first by Beaglehole and Nason (1980), and later by Furukawa et al. (1987a,b).

The change of the state of polarization upon reflection can be expressed in terms of the ratio of two complex reflection coefficients  $r_{\parallel}$  and  $r_{\perp}$  for light polarized parallel and perpendicular to the plane of incidence,  $r$  being the ratio of reflected and incident electric field strength. The complex quantity

$$\rho = \frac{r_{\parallel}}{r_{\perp}} = \tan \psi \cdot \exp(i\Delta) \quad (2)$$

defines the two ellipsometric angles  $\Delta$  and  $\psi$ . The two angles completely determine the two optical constants  $n$  (refractive index) and  $k$  (absorption coefficient) of an isotropic reflecting medium. Mathematical dependence of  $n$  and  $k$  on  $\Delta$  and  $\psi$ , calculated from Fresnel's formula, was found, for example, by Bootsma and Meyer (1969).

The application of ellipsometry in surface physics is favored because in suitable cases a layer with average thickness as small as  $1/100$  of a monolayer can be detected, if in the layer  $n$  and  $k$  are different from that of the bulk.

Ellipsometric data are usually analyzed with computers because the two measured variations  $\delta\Delta$  and  $\delta\psi$  are not sufficient to determine all parameters (optical constants, thickness) even for a single surface film.

Beaglehole and Nason (1980) employed ice monocrystals grown following the Bridgeman method using twice-distilled water. The ice surface with the orientation (0001) (basal plane) or (10 $\bar{1}$ 0) (prismatic plane) was milled with a warm razor immediately before ellipsometrical tests. Water forming simultaneously on the ice surface was removed by the same razor, resulting in a surface of unruffled cleanness.

Measurements in the 0 to  $-30^{\circ}\text{C}$  temperature range revealed a considerable distinction in the behavior of the surface layer at the basal and prismatic planes. Assuming that the refractive coefficient of the surface layer is the same as that of

water, Beaglehole and Nason found that the film's thickness on the prismatic surface ( $d$ ) was about  $130 \text{ \AA}$  at  $T = -1.5^{\circ}\text{C}$ , decreasing slowly to a monoatomic thickness at  $T = -10^{\circ}\text{C}$ . They found a surface layer on the basal plane only at temperatures greater than  $-0.3^{\circ}\text{C}$ .

Furukawa et al. (1987a,b) significantly advanced use of the ellipsometry technique for determining the transition layer thickness on the surface of ice. First, they used improved, more perfect ice crystals, grown from twice-distilled and degassed water. The degree of purity of ice plays an important role, since even a small salt concentration can sizably alter the thickness of the transition (quasi-liquid) layer on the ice surface. Second, they examined atomically flat (0001) and (10 $\bar{1}$ 0) surfaces of the natural facets of a so-called negative crystal. A negative crystal is formed by pumping water vapor out of a small void inside a large monocrystal. Besides, they made their ellipsometric measurements under conditions of equilibrium between ice and its vapor.

Finally, Furukawa et al. interpreted their data, not using the assumption that the refractive coefficient of the surface film ( $n_i$ ) is the same as that of water ( $n_w$ ), but calculating it as a fitting parameter. They found that  $n_i = 1.330$  for both faces (0001) and (10 $\bar{1}$ 0), which is closer to water,  $n_w = 1.3327$ , than to ice,  $n_i = 1.3079$ . This implies that the density of the layer is quite close to that of water.

Figure 5 shows temperature dependence of the transition layer thickness as found by Furukawa et al. from their ellipsometrical measurements. As follows from this plot, the thickness of the transition layer drastically rises as temperature increases.

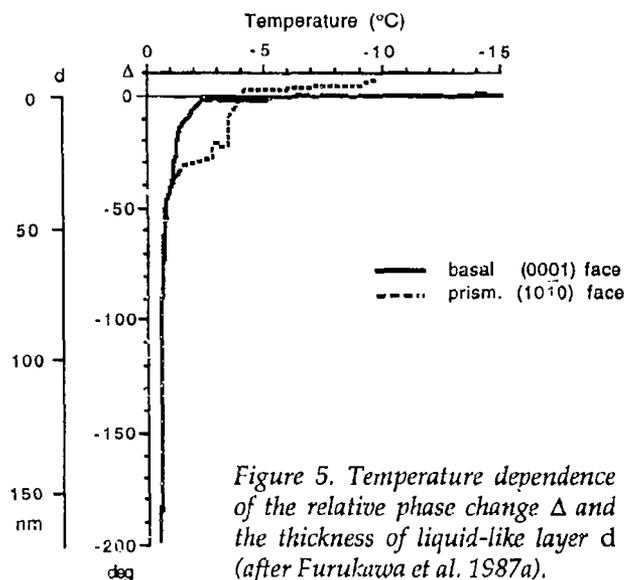


Figure 5. Temperature dependence of the relative phase change  $\Delta$  and the thickness of liquid-like layer  $d$  (after Furukawa et al. 1987a).

es above  $-1^{\circ}\text{C}$ , exceeding 150 nm. A difference between the film's thicknesses on the (0001) face and the (10 $\bar{1}$ 0) face is especially noticeable in the temperature range from  $-4$  to  $-1^{\circ}\text{C}$ . Optical ellipsometry can't detect the presence of a liquid film on an ice surface at temperatures below  $-4^{\circ}\text{C}$ .

Very recently, Elbaum et al. (1993) performed optical measurements of a liquid-like layer using a simplified ellipsometry technique, which was termed Brewster reflectometry. The idea was to measure the refractive index profile near a plane interface between uniform media. If a collimated light beam with a vector  $E$  lying in the plane of incidence falls at the Brewster's angle, then the intensity of the reflected light will be zero for an interface between two homogeneous media. But, since the interface has a finite thickness, the reflectivity is slightly different from zero. Elbaum et al. assumed that the interface is composed of water vapor or its mixture with air having the refraction coefficient  $n = 1$ , a liquid film of thickness  $L$  and  $n = 1.333$  (same as water) and, finally, ice with  $n = 1.309$ . Given such conditions, the problem of the intensity of the reflected light can be solved exactly, and they used this solution to calculate the thickness of the liquid film on the ice surface from the measurements of intensity of a polarized light reflected at the Brewster's angle. Though this method has a lower sensitivity compared to conventional ellipsometry ( $L \geq 12 \text{ \AA}$ , Elbaum et al. [1993]), the described work was the first where the effect of air on the thickness and conditions of existence of the quasi-liquid layer

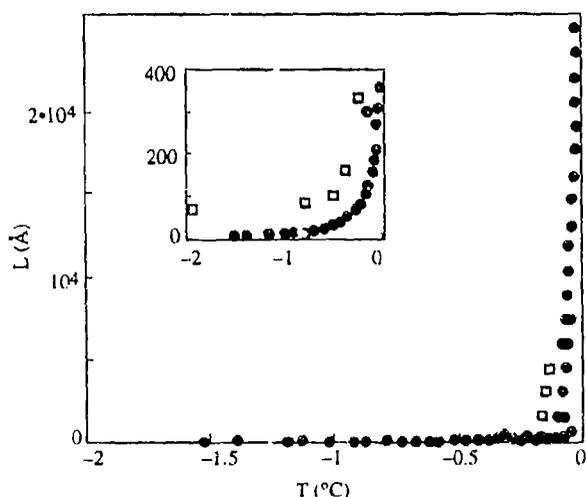


Figure 6. Collected results on the liquid-like film thickness from four reflection experiments. The inset shows the same results in smaller thickness range (after Elbaum et al. 1993).

was observed and investigated. In the absence of air, the quasi-liquid film could not be detected at the prismatic face of ice within the experimental error (12  $\text{\AA}$ ). At the same time, a very thick film was observed at the basal face (0001) under the same conditions (Fig. 6). The presence of air significantly increased the liquid film thickness at the (0001) face.

## NUCLEAR MAGNETIC RESONANCE

Clifford (1967), using Nuclear Magnetic Resonance (NMR) measurements on ice, observed a very narrow line ( $-0.2 \text{ G}$ ) that he attributed to some form of liquid water remaining in ice down to temperature of at least  $-12^{\circ}\text{C}$ . Kvlividze et al. (1970) demonstrated that this narrow resonant line is distinct from the NMR lines corresponding to protons in water and bulk ice and is caused by the liquid-like layer on the ice surface. Afterwards, NMR was used for studying the properties of the liquid-like layer on the ice surface by Bell et al. (1971), Kvlividze et al. (1974), Barer et al. (1977) and Ocampo and Klinger (1983a,b). The most comprehensive information about the physical properties of a liquid-like layer was obtained by Mizuno and Hanafuza (1987), to whom we are going to refer most often for this reason.

The phenomenon of NMR is an absorption of electromagnetic field quanta by nuclei that possess a magnetic moment and are placed in an external magnetic field  $B$  at resonance frequency  $\omega_0$

$$\omega_0 = g B \quad (3)$$

where  $g$  is the gyromagnetic constant.

The position of the resonant line, its shape and half-width, as well as the spin-lattice relaxation time, appear to be quite sensitive to the properties of a medium that surrounds the nuclear spins. Namely, those properties are the average distance and relative position of the spins in space, angular velocity and diffusion coefficient of molecules that contain the resonant nuclei.

Readers who are interested in this method should see the marvelous book by Abragam (1961) and also the paper by Burnett and Harmon (1972).

The NMR technique applied to ice, water or the quasi-liquid layer allows us first to distinguish three resonant lines associated with absorption by hydrogen nuclei in those three media. From the intensity of the liquid-like layer line, we can judge the approximate thickness of a particular layer. Besides, it is possible to determine the correlation

time of rotational motion of water molecules and a self-diffusion coefficient (Mizuno and Hanafusa 1987).

Since under normal conditions, the relative portion of molecules in the liquid-like layer is negligibly small, it is necessary first to increase the "surface-to-volume" ratio of the ice in question to observe NMR from this layer. The easiest way to achieve this is to pulverize water at a low temperature. As a result, microscopic ice balls are formed with a diameter about  $100\ \mu\text{m}$  and a net surface of about  $3\text{--}5 \times 10^2\ \text{cm}^2/\text{g}$ . This method was used for instance by Mizuno and Hanafusa (1987). Kvlividze et al. (1974) saturated water with air prior to freezing. This leads to an appearance of a great number of microscopic air bubbles inside the ice, with a net surface of the order of  $\sim 10^4\ \text{cm}^2/\text{g}$ . Frost forming on walls of a Dewar vessel filled with liquid nitrogen has an even larger specific area of  $1\text{--}2 \times 10^5\ \text{cm}^2/\text{g}$  (Kvlividze et al. 1970). Placing spherical Teflon particles ( $r \approx 350\ \text{\AA}$ ) (Kvlividze et al. 1974), or Aerosil particles ( $r \approx 100\ \text{\AA}$ ) (Barer et al. 1977) into water before freezing produced something comparable to the "frost" net surface of ice for NMR analysis. We have to take into account, of course, that the structure and properties of the liquid-like layer on the ice/(solid dielectric) interface might be different from ice/(water vapor + air) interface properties.

Figure 7 shows NMR spectra of the liquid-like layer of ice measured at various temperatures. To

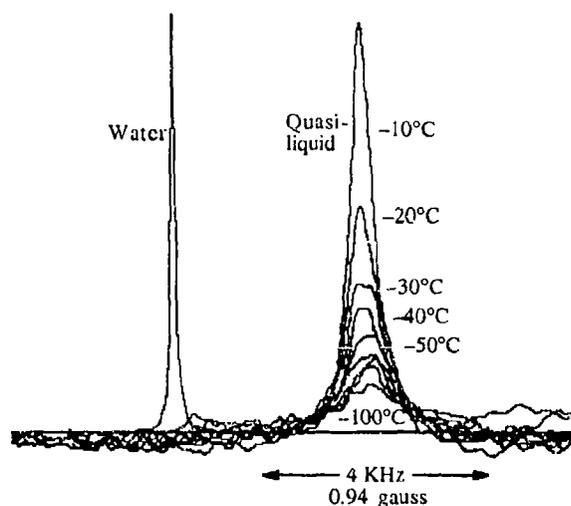


Figure 7. NMR spectra of the quasi-liquid layer of ice and water observed at 99.5 MHz. The signal of liquid water was taken at 5°C. Notice the difference in the line width between liquid water and the quasi-liquid layer (after Mizuno and Hanafusa 1987).

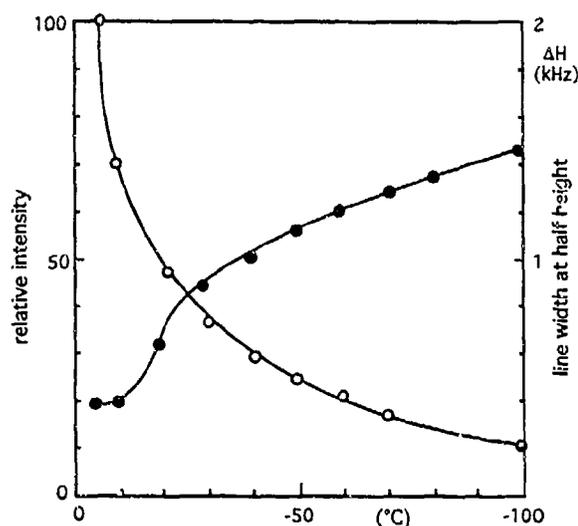


Figure 8. Intensity and line width of NMR of quasi-liquid layer against inverse temperature (after Mizuno and Hanafusa 1987).

increase the signal-to-noise ratio, the spectra were gathered 200 times at each temperature. The broad signal from crystalline ice is not seen within the range of the 20-kHz observational frequency (Mizuno and Hanafusa 1987).

The narrow signal was never detected at any temperature if bulk ice was used as a sample.

As is clear from Figure 7, the line width and the intensity vary with temperature and their temperature dependencies are shown in Figure 8. It should be noted that the line width of the liquid-like layer spectrum at  $-10^\circ\text{C}$  is about 7 times that of ordinary water at  $5^\circ\text{C}$ .

Since the temperature dependencies shown in Figure 8 were measured as temperature was increased from  $-100$  to  $-5^\circ\text{C}$ , and since at  $T \geq -10^\circ\text{C}$  a considerable sintering diminishes the total ice surface, the actual increase of the NMR signal at  $T \geq -10^\circ\text{C}$  could be greater than the one shown in Figure 8.

The temperature dependence of the correlation time for rotational motion  $\tau$  is shown in Figure 9. This time, which could be interpreted as the time it takes a water molecule to be reoriented in a liquid-like layer at  $T = -10^\circ\text{C}$ , appears to be closer to that time for water ( $\approx 10^{-12}$  seconds) than for ice ( $2 \times 10^{-5}$  seconds [Jaccard 1959]) at the same temperature. The activation energy of molecule reorientation in a liquid-like layer, which can be determined from the slope of the curve in Figure 9, is 0.291 eV and is also quite different from the corresponding value for the bulk ice (0.575 eV

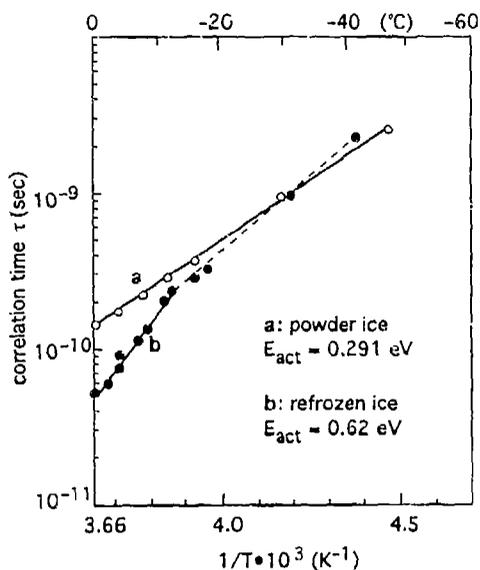


Figure 9. Correlation time for rotational motion  $\tau$  of quasi-liquid layer against inverse temperature (after Mizuno and Hanafusa 1987).

[Jaccard 1959]). Therefore, comparing the rotations of a water molecule in water, the liquid-like layer and ice, we could conclude that, according to this property, the liquid-like layer is intermediate between ice and water, but it nevertheless resembles water more closely.

However, if we try to compare self-diffusion coefficients in water, the liquid-like layer and ice

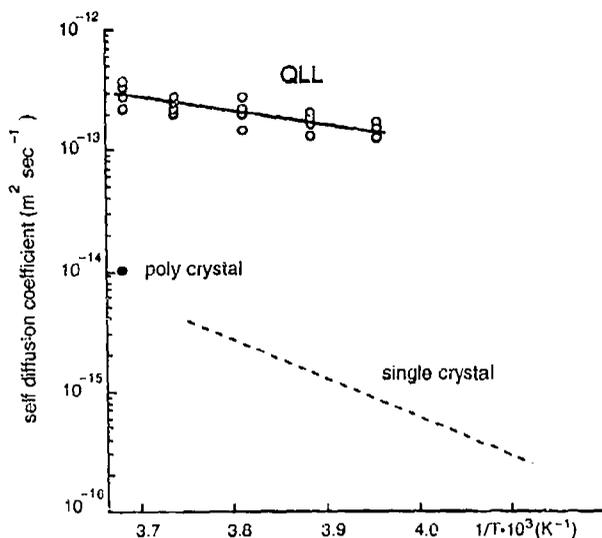


Figure 10. Diffusion coefficient of quasi-liquid layer against inverse temperature (after Mizuno and Hanafusa 1987).

(see Fig. 10), we will come to an opposite conclusion, because this coefficient at 0°C in the liquid-like layer turns out to be  $\approx 3 \times 10^{-12} \text{ m}^2/\text{s}$ , which is closer to ice ( $\approx 10^{-14} \text{ m}^2/\text{s}$ ) than to water ( $2 \times 10^{-9} \text{ m}^2/\text{s}$ ). At the same time the activation energy of self-diffusion in the liquid-like layer (0.24 eV) is closer to that of water ( $\approx 0.24 \text{ eV}$ ) than to ice (0.65 eV).

Barer et al. (1977) studied NMR from a liquid-like layer forming at the interface between ice and Aerosil microspheres, i.e., on a frozen aqueous suspension of Aerosil. Like Mizuno and Hanafusa, they tracked the existence of the liquid-like layer much further down on the temperature scale than measurements that could be obtained from X-rays or ellipsometry (see Fig. 11). The results of their estimations of the liquid-like layer thickness at various temperatures are given in Table 1.

Table 1. Temperature dependence of the thickness of a liquid-like layer on the ice/Aerosil interface (after Barer et al. 1977).

T (°C)	-12	-10	-8	-6	-4	-2
L (Å)	11	12	14	20	27	52

In the same work (Barer et al. 1977), the viscosity of a liquid-like layer on the ice/quartz interface was measured. At  $T = -10^\circ\text{C}$  the viscosity appeared to be  $\eta = 0.17 \text{ P}$ , which exceeds the viscosity of supercooled water at the same temperature by an order of magnitude.

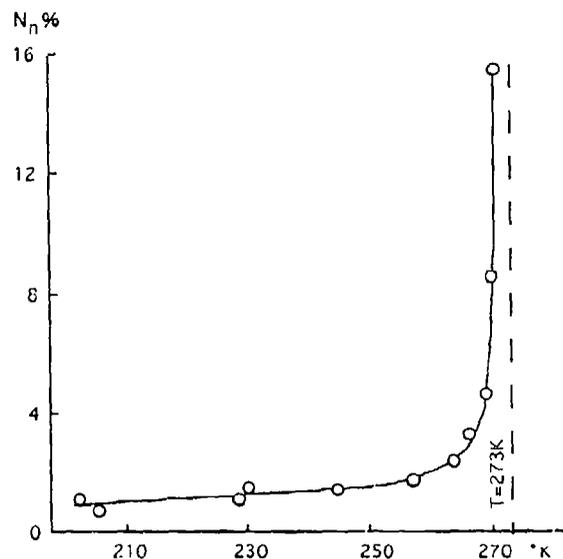


Figure 11. Temperature dependence of the relative concentration of the mobile aqueous suspension of Aerosil (after Barer et al. 1977).

## ELECTRICAL CONDUCTIVITY OF THE ICE SURFACE

As we have seen in the previous sections, the surface layer of ice differs from the bulk in its structure, optical properties, molecule reorientation time and self-diffusion coefficient. It is therefore also natural to expect the ice surface to be different from the bulk in its electrical properties.

We can name several possible things that could change electrical properties of ice near the surface. The first is an increase (or decrease) of the charge carrier concentrations within the screening length, assuming that there is a potential difference  $\phi_0$  between the surface and the bulk. Such a difference may arise because of differences in the chemical potentials of charge carriers in the bulk and on the surface (electrochemical potential must be uniform everywhere) or because of adsorption of electrically charged impurities that compensate the space charge of ice at the surface. The latter arises merely from differences in solubilities of positive and negative impurity ions in ice. Second, charge carrier mobilities and the mechanisms of interaction between them might be different in the disordered surface or quasi-liquid layer.

In fact, the ice surface has an extremely high net electrical conductivity that was discovered back in the 1950s and has been studied intensely over the past 30 years. At temperatures roughly above  $-15^\circ\text{C}$  in pure ice, the d.c. conductivity of the surface exceeds that of the bulk. A measurement of the surface conductivity is one of the simplest and most accessible ways to study the physical properties of the ice surface. In fact, a simultaneous measurement of the absolute value of the surface conductivity  $\sigma_s$  (with a dimension of  $\Omega^{-1}$ ) and of the specific volume electrical conductivity of the surface layer  $\sigma_{ss}$  (with a dimension of  $\Omega^{-1}\text{m}^{-1}$ ) would allow determination of the layer's thickness  $L$

$$L = \frac{\sigma_s}{\sigma_{ss}} \quad (4)$$

Measurement of charge carrier mobilities' values  $\mu_i$  and their concentrations  $n_i$  is essential to understanding the nature and the structure of the quasi-liquid layer, as well as for determining the activation energies of  $\mu_i$  and  $n_i$ . Researchers in this field have investigated the electrical conductivity and dielectric permittivity of the surface layer, as well as the Hall effect.

The major methodical problem in these experiments is the separation of currents flow-

ing on the surface from the bulk currents. Usually, this is done by means of so-called guard rings (Fig. 12). A guard ring, as can be seen from this figure, is separated from the central electrode by a thin insulating ring. The guard ring and the central electrode have nearly the same potential, which provides an orientation of electrical field strength vector  $\vec{E}$  (and consequently of currents) parallel to the surface of the cylinder. In this set-up all subsurface currents flow through the guard ring, and their magnitude is proportional to the voltage drop across the resistor  $R_s$ . In this schematic,  $R_s$  and  $R_B$  must be much smaller than the impedance of the specimen  $Z_s$  in the whole range of the investigated frequencies.

A great majority of researchers have used the configuration shown in Figure 12, although sometimes square ice samples were used instead of cylindrical ones. Caranti and Illingworth (1983a) used the same idea (making  $\vec{E}$  parallel to the surface and the use of a guard ring), although they employed a semi-spherical electrode frozen into ice.

Jaccard (1966, 1967) suggested that four-point electrodes, arranged in pairs at the opposite sides of a thin ice specimen, be used to determine the surface and bulk conductivities. However, we shall refrain from discussing this here because of serious criticism of this method expressed by Turner and Stow (1986).

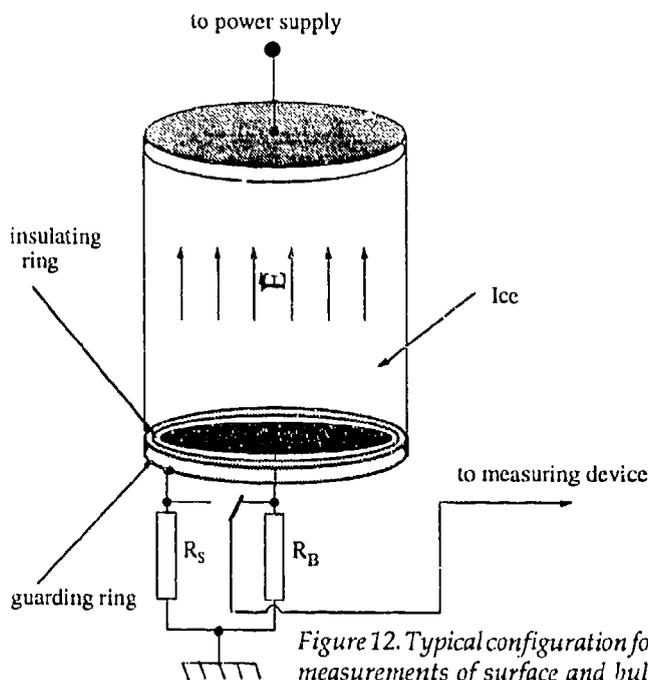


Figure 12. Typical configuration for measurements of surface and bulk conductivity.

Table 2. Surface conductivity of ice.

T (°C)	f (Hz)	$\sigma_s$ ( $\Omega^{-1}$ )	$E_s$ (eV)	Type of ice	Reference
-10	d.c.	$3 \times 10^{-8}$	$0.84 \pm 0.1$	pure polycrystals	Camp et al. (1969)
-10	d.c.	$3.9 \times 10^{-10}$	1.29	pure single crystals	Bullemer and Riehl (1966)
-10	d.c.	$3.9 \times 10^{-10}$	$\geq 1.3$	$3 \times 10^{-4}$ M HF	
-10	d.c.	$(1.5-6) \times 10^{-11}$	1.52	pure single crystals	Maeno (1973)
-10	d.c.	$(1-6) \times 10^{-11}$	1.19	pure single crystals	Maeno and Nishimura (1978)
-10	d.c.	$6 \times 10^{-8}$	0.44	$1.7 \times 10^{-4}$ M HF	
-10	0.1	$4 \times 10^{-9}$	1.0	pure polycrystals	Caranti and Illingworth (1983a)
-10	0.1	$6 \times 10^{-8}$	0.55	$10^{-3}$ M NaCl polycrystals	
-10	107	$2 \times 10^{-8}$	0.78	pure polycrystals	Caranti and Lamfri (1987)
-10	d.c.	$\approx 10^{-9}$	1.43	pure single crystals	Maidique et al. (1971)
-10	d.c.	$1.5 \times 10^{-10}$	1.29	pure single crystals	Ruepp and Käss (1969)
-11	d.c.	$(1.4-6.3) \times 10^{-10}$	—	pure single crystals	Jaccard (1967)
-53	d.c.	$\approx 1.5 \times 10^{-13}$ *	—	polycrystalline ice film	Chrzanowski (1988)
-10	d.c.	$\approx 4 \times 10^{-9}$ †	—	deposited onto a dielectric substrate	

\* Calculated from Chrzanowski's data assuming that the electrode's length was 5 mm.

† Calculated from Chrzanowski's data assuming that the activation energy is 1.2 eV.

Even a small amount of impurities in ice strongly affects the surface conductivity  $\sigma_s$ . This accounts for the considerable scatter in the experimental data obtained on  $\sigma_s$ . Data on low-frequency and d.c. surface conductivities of pure and doped ice at  $-10^\circ\text{C}$  are summarized in Table 2. As we can see from this table,  $\sigma_s$ , even for pure monocrystalline ice, assumes values in a wide range, from  $10^{-11} \Omega^{-1}$  (Maeno and Nishimura 1978) up to  $10^{-9} \Omega^{-1}$  (Maidique et al. 1971). Data on activation energies  $E_s$  for the same crystals vary from a minimum value of 1.19 to 1.52 eV, with an average value of about 1.3 eV. Even a slight doping of ice leads to a considerable increase in  $\sigma_s$  and, as a rule, a decrease of  $E_s$ .

Typical frequency dependencies of ice bulk and surface conductivities are plotted in Figure 13. This plot shows that the frequency dependence of the bulk conductivity  $\sigma_B$  follows Debye's dispersion, which is well known for ice

$$\sigma_B = \sigma_0 + \frac{(\sigma_\infty - \sigma_0) (\tau_D \omega)^2}{1 + (\tau_D \omega)^2} \quad (5)$$

where  $\sigma_0$  is the low-frequency limit of the conductivity (or d.c. conductivity) determined by minority charge carriers. In pure ice at  $-10^\circ\text{C}$ , those are  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions.  $\sigma_\infty$  is the high-frequency limit of the conductivity, equal to the sum of all partial conductivities of the charge

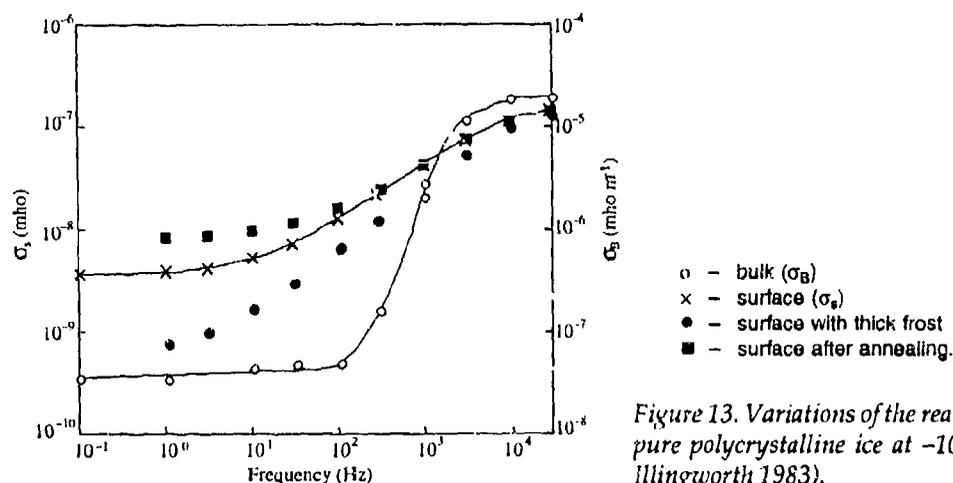


Figure 13. Variations of the real part of conductivity of pure polycrystalline ice at  $-10^\circ\text{C}$  (after Caranti and Illingworth 1983).

carriers. Under the conditions considered,  $\sigma_{\infty}$  practically coincides with the conductivity of the majority charge carriers—Bjerrum defects, that is L- and D-defects.  $\omega$  is the angular frequency and  $\tau_D$  is the Debye relaxation time. I refer readers who are more interested in the electrical properties of bulk ice to the latest review on this subject (Petrenko 1993). Let us just remember that a small (compared to  $\sigma_{\infty}$ ) value of  $\sigma_0$  results from lattice polarization arising from protonic charge carriers' motion. To prevent the polarization from increasing to infinity, ions and Bjerrum defects have to move in a consistent manner to keep their fluxes equal. An absence (or reduction) of any noticeable difference between  $\sigma_{\infty}$  and  $\sigma_0$  would imply either that such a correlation in the motion of ions and Bjerrum defects is absent (or reduced) or that partial conductivity of ions is close to the conductivity of Bjerrum defects.

As can be seen from Figure 13, the frequency dependence of  $\sigma_s$  is much less pronounced than that of  $\sigma_B$ . This is especially true for the ice surface after annealing, i.e., the smoothest surface. Since some fraction of the current flowing along the surface inevitably penetrates the bulk, the remaining slight frequency dependence can be ascribed to these accompanying bulk currents. The rougher the surface is, the greater is the "bulk" contribution of the "surface" conductivity, in excellent conformity with the results shown in Figure 13. Thus, we can tell that, at least in the frequency range of  $10^{-1}$  to  $3 \times 10^4$  Hz, there is either no correlation in the motion of ions and Bjerrum defects in the subsurface layer at all (as is the case in water) or that this correlation is weak.

An alternative explanation for the weak frequency dependence of  $\sigma_s$  can be that the corresponding dielectric relaxation time for the subsurface layer  $\tau_{DS}$  might be several orders of magnitude more than that of the bulk  $\tau_D$ . Therefore we would search for the Debye dispersion for the liquid-like layer in a very-high-frequency range, where the standard methods for measuring  $\sigma$  are not applicable.

Let us try to estimate the specific conductivity of the surface layer  $\sigma_{ss}$  (dimensions of  $\Omega^{-1}m^{-1}$ ), proceeding from the data in Table 2 and the results for the liquid-like layer thickness  $L$  given in the previous sections.

$$\sigma_{ss} = \frac{\sigma_s}{L} \quad (6)$$

Thus, taking  $L = 1.2 \times 10^{-9}$  m ( $T = -10^\circ\text{C}$  [Barer et al. 1977]) and  $\sigma_s = 10^{-10} \Omega^{-1}$ , we obtain

$$\sigma_{ss} \approx 10^{-1} \Omega^{-1}m^{-1} \quad (7)$$

If we substitute extreme values of  $\sigma_s$  for pure ice from  $10^{-11} \Omega^{-1}$  up to  $3 \times 10^{-8} \Omega^{-1}$ , we shall get

$$\sigma_{ss} \approx (10^{-2} - 3 \times 10^1) \Omega^{-1}m^{-1} \quad (8)$$

At the same temperature, the bulk low-frequency conductance  $\sigma_0$  falls in the limits ( $2.5 \times 10^{-8}$  to  $6.4 \times 10^{-10}$ )  $\Omega^{-1}m^{-1}$  (Petrenko 1993); i.e., it is from 6 to 11 orders of magnitude less than  $\sigma_{ss}$  from eq 8. The bulk high-frequency conductivity,  $\sigma_{\infty} = 1.6 \times 10^{-5} \Omega^{-1}m^{-1}$ , is also much less than  $\sigma_{ss}$ . If we assume that there is no correlation in the motion of ions and Bjerrum defects, then the characteristic dielectric relaxation time of the surface layer would be the Maxwell relaxation time  $\tau_{MS}$

$$\tau_{MS} = \frac{\epsilon_0 \epsilon_{\infty}}{\sigma_{ss}} \approx (10^{-12} - 3 \times 10^{-9}) \text{ s} \quad (9)$$

which corresponds to the frequency range

$$f = \frac{1}{2\pi\tau_{MS}} \approx (5 \times 10^7 - 1.6 \times 10^{11}) \text{ Hz} \quad (10)$$

where  $\epsilon_0$  is the vacuum dielectric permittivity and  $\epsilon_{\infty} = 3.2$ .

Unfortunately, I am not aware of any attempts to measure  $\sigma_s$  as a function of frequency in the specified range, which could give more accurate values of  $\sigma_{ss}$  in conformity with eq 9. If in the future such measurements are carried out, then this will also allow more accurate determination of the liquid-like layer thickness  $L$  using eq 6.

The result of estimating the charge carrier concentration in the liquid-like layer using the following formula is quite interesting

$$n_i = \frac{\sigma_{ss}}{\mu_i e_i} \quad (11)$$

If we take  $\sigma_{ss} \approx 3 \times 10^1 \Omega^{-1}m^{-1}$  and  $\mu \approx 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  for ions and  $\mu \approx 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  for Bjerrum defects (Petrenko 1993), then an estimation using eq 11 for the  $n$  of ions and Bjerrum defects gives  $3 \times 10^{27} \text{ m}^{-3}$  and  $5 \times 10^{28} \text{ m}^{-3}$  respectively. (We used  $e_1 = 0.62e$  and  $e_3 = 0.38e$  [Hubmann 1979].) These are extremely large values if we recall that the concentration of water molecules in ice is about  $3 \times 10^{28} \text{ m}^{-3}$ .

The above estimations can be much more accurate if we employ for our calculations the correlation time for rotational motion of water molecules at the ice surface, found in NMR experiments by Mizuno and Hanafuza (1987) (see Fig. 9). In bulk ice, this time coincides with the dielec-

tric relaxation time  $\tau_D$  and is related to the conductivity  $\sigma_s$  by the following formula

$$\tau_D^{-1} = \Phi \left( \frac{\sigma_{ion}}{e_1^2} + \frac{\sigma_B}{e_3^2} \right) = \Phi \frac{\sigma_s}{e_3^2} \approx \Phi \frac{\sigma_{ss}}{e_3^2} \quad (12)$$

where  $\Phi = 3.85 k_B T r_{00}$ ,  $r_{00} = 2.76 \text{ \AA}$  is oxygen-oxygen distance, "ion" and "B" subscripts correspond to ionic and Bjerrum defect conductivity and  $e_1$  and  $e_3$  to the electrical charges of ions and Bjerrum defects. Substituting  $\tau_D \approx 10^{-10} \text{ s}$  (from Fig. 8),  $T = 263 \text{ K}$  and  $e_3 = 0.38e$  into eq 12, we obtain for the net conductivity of the surface layer

$$\sigma_{ss} \approx 11 \Omega^{-1} \text{ m}^{-1} \quad (13)$$

i.e., a value close to the upper limit found in eq 8. The corresponding concentration of Bjerrum defects in the surface layer according to eq 11 will be

$$n_B = 2 \times 10^{28} \text{ m}^{-3}. \quad (14)$$

If there is no correlation between fluxes of ions and Bjerrum defects in the liquid-like layer, we should use eq 9. Then

$$\sigma_{ss} = 0.3 \Omega^{-1} \text{ m}^{-1}, n_B = 5 \times 10^{26} \text{ m}^{-3}. \quad (15)$$

Thus, we can conclude that the charge carrier concentration in the ice surface exceeds by many orders of magnitude that of the bulk and in some cases might correspond to a superionic state, i.e., a state in which all (or nearly all) molecules are ionized and mobile.

Caranti and Illingworth (1983a) remark in their paper that, in a.c. measurements of real and imaginary parts of the complex surface conductivity, the phase angle was always small, showing surface currents to be predominantly resistive. This is exactly what must be the case for an ordinary conductivity (without correlation between charge carrier fluxes) at frequencies much less than  $\tau_D^{-1}$ .

Temperature dependencies of the surface conductivities of pure and doped ice are plotted in Figures 14 and 15. The behavior of this dependence is different at temperatures above and below  $-6^\circ\text{C}$ . It is quite possible that a sharp rise of  $\sigma_s$  at  $T \geq -6^\circ\text{C}$  is associated with an appearance of the liquid-like layer on the ice surface, which is detected by optical ellipsometry and X-ray diffraction methods (see previous sections). An interesting observation is the difference in  $\sigma_s$  corresponding to different crystallographic surfaces of ice (Fig. 15). The conductivity of the basal

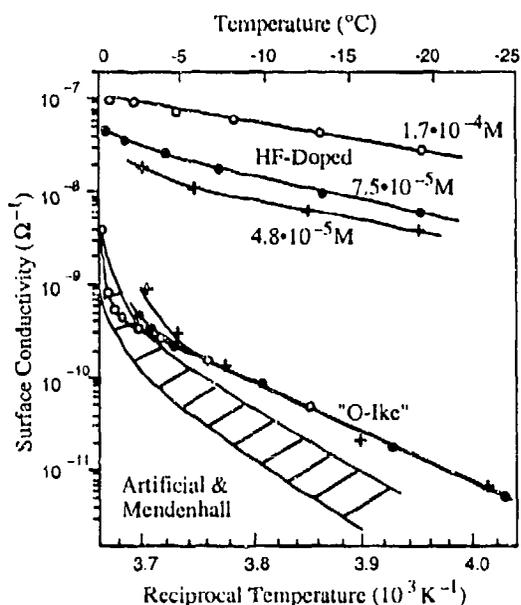


Figure 14. Temperature dependence of surface conductivity of the (0001) plane for pure and doped ice. "O-Ike" stands for ice from O-Ike pond near the Syowastation in Antarctica, "Mendenhall" stands for ice from Mendenhall Glacier, Alaska (after Maeno and Nishimura 1978).

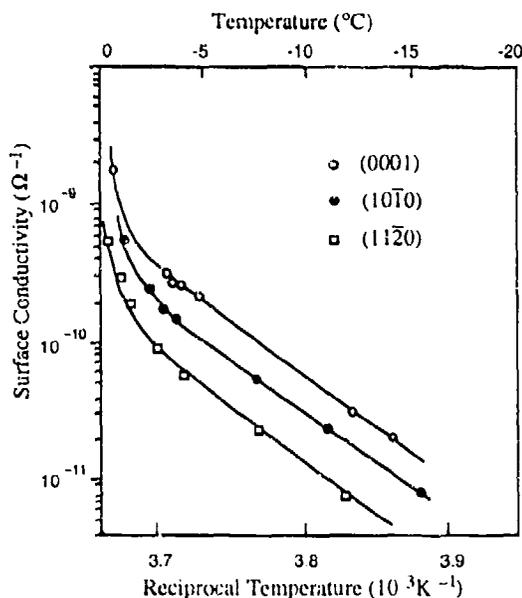


Figure 15. Surface conductivity of ice as a function of crystallographic orientation and temperature. Ice single crystals were taken from the Mendenhall Glacier, Alaska (after Maeno 1973).

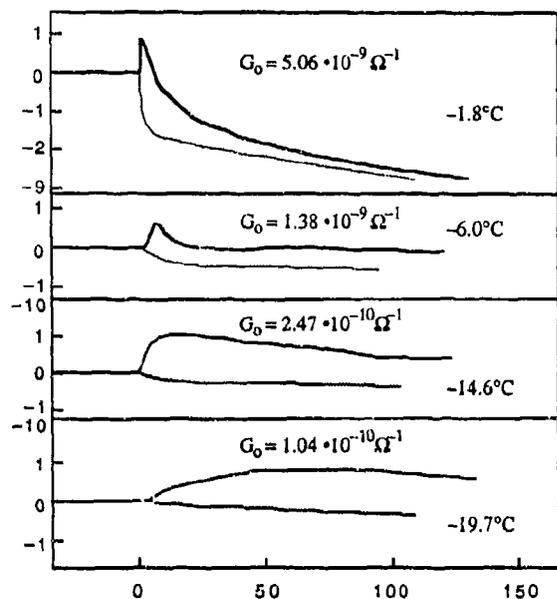


Figure 16. Variations of surface conductance after evacuation of pure water for "pure" natural ice (O-ike pond). Dotted lines indicate expected variations of the conductance calculated from measured temperature of the ice surface (after Maeno and Nishimura 1978).

(0001) surface was maximum. This result is in agreement with optical measurements by Elbaum et al. (1993) but is opposed to the results of optical ellipsometry (where liquid-like layer thickness is greater on the prismatic (10 $\bar{1}$ 0) surface) and X-ray diffraction (where the difference between the (0001) and (10 $\bar{1}$ 0) surface is negligible).

Maeno (1973) and Maeno and Nishimura (1978) found that an intense pumping out of water vapors from above the ice surface changes the surface conductivity considerably (Fig. 16). Pumping out of water vapors accelerates evaporation from the surface and its cooling. Aside from this trivial effect, a lower partial pressure of water vapor above the ice increases the surface conductivity. The phenomenon discovered by Maeno shows the degree to which the conductivity of the surface layer is sensitive to physical conditions at the ice interface.

An interesting result was obtained in the work by Chrzanowski (1988), who investigated the d.c. conductivity of thin ice films deposited onto a high resistance dielectric substrate (high quality glass or quartz plate). Figure 17 demonstrates that the conductance of an ice film grows rapidly with the film's thickness until it thickens to 0.3–0.5  $\mu\text{m}$ . Then, the rate of the conductance growth diminishes considerably. This result implies that the lay-

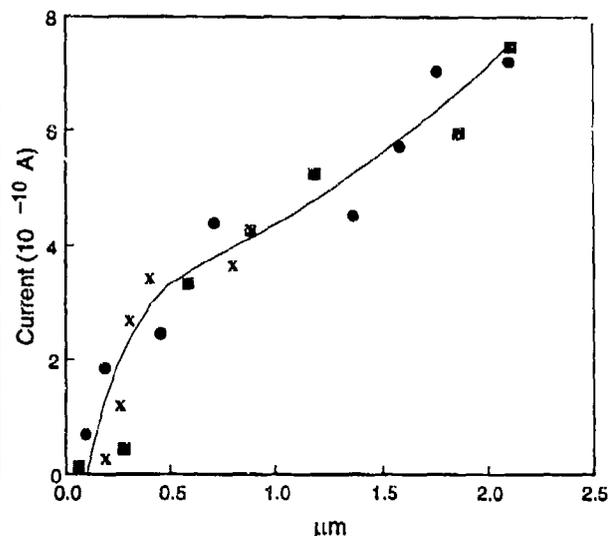


Figure 17. Typical thickness dependence of the measured current intensity obtained for ice films deposited onto a glass substrate of temperature 220 K. Three different experimental runs are shown (after Chrzanowski 1988).

er close to the ice/dielectric interface has a much larger specific conductivity than the bulk and that the thickness of this layer is about 0.3–0.5  $\mu\text{m}$ . This thickness (taking also into account the temperature of 220 K) exceeds considerably values found in other works. I believe that this quantity can be associated only with the screening length in ice, which was considered in detail by Petrenko and Ryzhkin (1984).

Caranti and Lamfri (1987) made a very interesting attempt to determine charge carrier mobilities in the ice surface layer. The authors used for this purpose measurements of the Hall effect and surface conductivity. Owing to the very small mobilities of charge carriers in ice, the measurements of the Hall effect are quite complicated. Caranti and Lamfri used an a.c. setup with two distinct frequencies of the magnetic field (50 Hz) and the driving current (107 Hz), measuring the Hall effect at the total frequency 157 Hz. Figure 18 shows the temperature dependence of the carrier mobilities in the ice surface determined by Caranti and Lamfri. An unusually large value of mobility ( $3 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) is striking. This is three orders of magnitude greater than the mobility of ions in water and ice and four orders greater than the mobility of Bjerrum defects in ice (Petrenko 1993). Moreover, such high mobility can not be attributed to

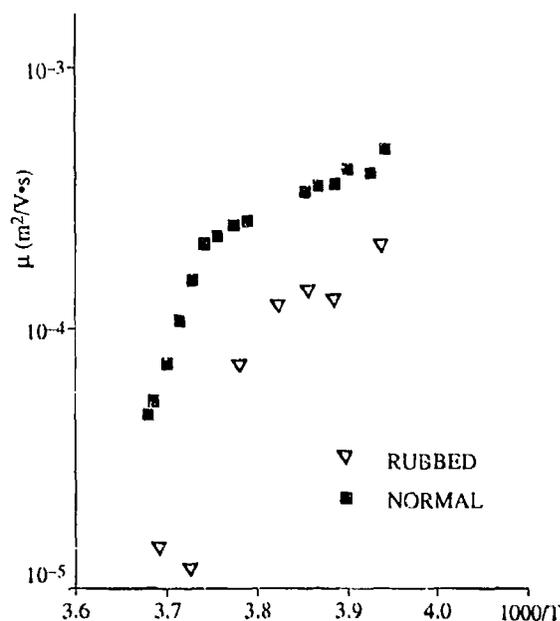


Figure 18. Hall mobility  $\mu$  ( $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ ) at 157 Hz as a function of temperature for normal and rubbed surfaces. The magnetic field  $B_0$  was 0.38 T (after Caranti and Lamfri 1987).

Nonetheless, the result of Caranti and Zamfri is indirectly confirmed by earlier measurements of Bullemer and Riehl (1968), who tried to measure a bulk Hall effect in ice and obtained  $\mu = 1.4 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$  at  $T = -8^\circ\text{C}$ . Although Bullemer and Riehl used guard rings at the Hall electrodes to eliminate the effect of surface currents, they apparently did not succeed because they did not observe the Hall effect, which is forbidden for bulk ice in principle (Sokoloff 1973, Gosar 1974). Hence, Bullemer and Riehl also determined the surface Hall mobility. It is remarkable that their result (although they used d.c. measurements) is in a good agreement with the Caranti and Lamfri result. Then, with what is this extremely high mobility associated? Perhaps with electrons in the ice surface? We do not know the answer.

Finally, Camp and Halchin (1979) studied the electrical properties of ice/ice (grain boundaries) and ice/quartz interfaces in the temperature range from 0 to  $-20^\circ\text{C}$  and in the frequency range from d.c. to  $10^7$  Hz. They found that the widths of the "electrical" interfaces (ice/ice and ice/dielectric), estimated from the conductivity measurements, depend on the frequency. The higher

Table 3. Summary of estimates of grain boundary thickness  $\delta$  (after Camp and Halchin 1979). The measuring frequency is indicated in parentheses.

Sample	Type of measurement	Effective grain boundary thickness
		$-1^\circ\text{C}$
Pure no. 2	From high frequency	$\delta (5 \times 10^6) = 100 \text{ \AA}$ (order of magnitude)
Pure no. 3	From capacitance data	$\delta (10^6) = 700 \text{ \AA}$
	From d.c. compared to doped ice	$\delta$ (d.c.) = 2400 $\text{ \AA}$ (order of magnitude)
Pure no. 1	From capacitance data	$\delta (10^6) = 1000 \text{ \AA}$
Doped	From capacitance data	$-1^\circ\text{C}$
		$-14^\circ\text{C}$
		$\delta (10^6) = 12 \text{ \mu m}$ 3 $\text{ \mu m}$
		$\delta (10^7) = 5 \text{ \mu m}$ 0.3 $\text{ \mu m}$

ions at all. Even in the case of an activation-free diffusion motion of ions, their mobility cannot exceed the value

$$\mu \approx \frac{vca^2}{k_B T} \quad (16)$$

where  $v$  = frequency of ion's hops between molecules

$e$  = charge

$a$  = length of a hop ( $\approx 10^{-10}$  m).

To explain  $\mu \approx 3 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ , we have to accept that  $v \approx 10^{15} \text{ s}^{-1}$ , which is much greater than all possible phonon frequencies in ice (as well as in any other material).

the frequency, the thinner the surface layer in which the dielectric relaxation time is small enough for water molecules to be able to reorient. That is, the surface layer is not homogeneous: the charge carrier concentration is greater near the surface and decreases away from the surface into the bulk (see Table 3, which is a summary of results of Camp and Halchin).

#### SURFACE CHARGE AND SURFACE POTENTIAL

The study of the surface potential of ice and electric charges at the ice surface has quite a long history and continues to attract the attention of

numerous scholars. Such interest in the electrostatic properties of the surface of ice is stimulated by both fundamental problems associated with it and certain practical issues. Fundamental questions, which the study of the surface potential and the ice surface might help to resolve, include the issue of the structure of the surface of ice. For instance, if all the molecules at the ice surface are oriented "proton-outwards," as some theoretical models suggest (Fletcher 1968), this must lead to a positive charge at the surface  $\lambda_s$  and a positive potential of the ice surface  $\phi_s$ . Both  $\lambda_s$  and  $\phi_s$  are determined by the thickness of the surface layer  $d$  and the fraction of the oriented water molecules contained in this layer. Thus, measurement of  $\lambda_s$  and  $\phi_s$  in conjunction with other data ( $d$ , for example) might provide valuable information on the microscopic structure and nature of the ice surface layer.

The practical issues stimulating the study of electrical properties of the ice surface, incorporate, first of all, the problem of atmospheric electricity (see details in Hobbs 1974) as well as the problem of adhesion and friction of ice and snow (Petrenko 1994).

Before we proceed to a review of experimental data, let us consider basic theoretical relationships defining the electrostatic properties of the ice surface and the most frequently employed experimental techniques used to determine of  $\lambda_s$  and  $\phi_s$ .

Figure 19 shows schematically the distribution of the electric charge density  $\rho$  in ice near the surface ( $x = 0$ ). The coordinate scale is chosen deliberately. First, since ice is a conductor, in equilibrium, the electric field within the bulk must be zero, i.e.,  $E(+\infty) = 0$ . If we use the formula for the

electric field strength above a charged surface

$$E \approx \frac{\lambda_s}{2\epsilon_0} \quad (18)$$

we shall obtain an apparent result

$$E(+\infty) \approx \frac{1}{2\epsilon_0} \int_0^{+\infty} \rho(x) dx = 0. \quad (19)$$

In other words, the sum of all charges in the surface layer of ice must be zero.

A very thin layer of the surface charge per se, with the density  $\lambda_{so}$ , is composed of ions adsorbed by the surface from the air, electrons entrapped in the surface layer, etc. This layer is screened on the inner side by a much thicker layer of a space charge, composed of mobile charge carriers, i.e., predominantly Bjerrum defects and ions. Using Poisson's equation, we obtain

$$\frac{dE}{dx} = \frac{\rho(x)}{\epsilon_0 \epsilon_\infty} \quad (20)$$

and as  $d\phi/dx = -E$ , we can easily find the relationships between  $\rho$ ,  $E$  and  $\phi$

$$E(x) = \int_0^x \frac{\rho(\xi)}{\epsilon_0 \epsilon_\infty} d\xi; \quad \phi(x) = - \int_0^x E(\xi) d\xi. \quad (21)$$

$\epsilon_\infty$  is high-frequency dielectric permittivity of ice.

To estimate a fraction of water molecules oriented along the electric field, i.e., with dipole moments oriented normally to the surface, we have to find the component of the polarization vector  $\vec{P}$

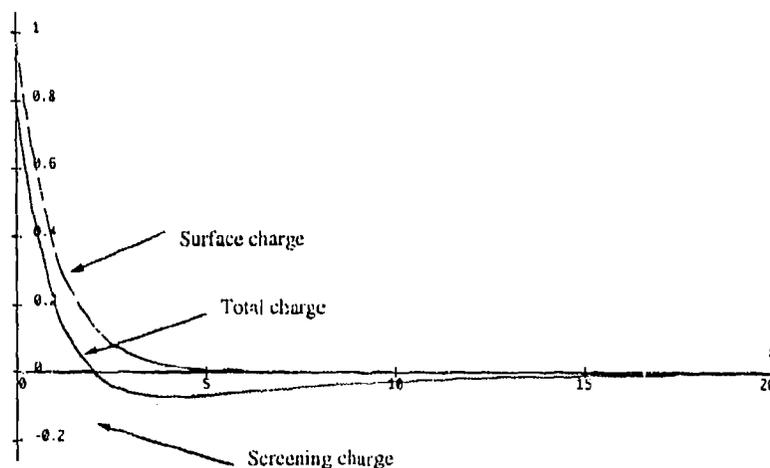


Figure 19. Space distribution of electric charges in ice near the surface. Scales are arbitrary.

that is determined by the reorientation of water molecules ( $\vec{P}_M$ )

$$\vec{P}_M = \vec{M} \left( \frac{n_{\perp}}{n_{H_2O}} \right) n_{H_2O} \quad (22)$$

where  $n_{H_2O}$  and  $n_{\perp}$  are water molecule concentration in ice and the concentration of water molecules oriented along the field respectively. Since

$$\vec{P}_M = \epsilon_0(\epsilon_s - \epsilon_{\infty}) \vec{E} = \left( \frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_{\infty}} \right) \int_0^x \rho(\xi) d\xi \quad (23)$$

then

$$\frac{n_{\perp}}{n_{H_2O}} = \frac{P_M}{M n_{H_2O}} = \left( \frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_{\infty} M n_{H_2O}} \right) \int_0^x \rho(\xi) d\xi. \quad (24)$$

Here,  $\epsilon_s$  is the static dielectric permittivity of ice and  $M$  is the molecular dipole moment ( $M \approx 8.66 \times 10^{-30}$  °C m [Hobbs 1974]).

This molecular "ordering" reaches its maximum at the surface where

$$\frac{n_{\perp}}{n_{H_2O}} = \frac{\epsilon_s - \epsilon_{\infty}}{\epsilon_{\infty} M n_{H_2O}} \lambda_{sa} \quad (25)$$

$$\lambda_{sa} = \int_0^d \rho(\xi) d\xi. \quad (26)$$

Note that the fraction of ordered molecules in eq 25 depends only upon the density of charge  $\lambda_{sa}$  adsorbed by the ice surface. In other words, this result will still hold if, owing to the change of temperature or doping, the concentration of charge carriers changes, resulting in a change of the screening charge  $\rho(x)$  in the bulk. Therefore, eq 25 provides a remarkable and simple way to study the ordering of water molecules in the surface layer through a measurement of the electric charge  $\lambda_{sa}$  adsorbed in a thin surface layer. The thickness of this layer is much less than the screening radius  $\alpha^{-1}$ .

Above we have considered the electric charge absorbed by the ice surface as a reason for the ordering orientation of water molecules. There can be an inverse phenomenon when an ordering of water molecules on the ice surface generates a surface charge. In its turn, the ordering of dipole moments of water molecules may be caused, for example, by dipole-dipole and dipole-quadrupole interactions (Fletcher 1968). Suppose this ordering is associated with polarization  $P(x)$  that reaches its maximum at the surface and decays

somehow to zero when  $x \rightarrow \infty$  since the ice bulk is disordered. Then the surface charge  $\lambda_s$  associated with this polarization is

$$\lambda_s = \int_0^{\infty} \frac{\partial P}{\partial x} dx = \vec{P}_x(0). \quad (27)$$

To find the other quantity that can be measured from an experiment, namely, the surface potential  $\phi_s$  (using eq 21), we have to know how the charge  $\rho(x)$  is distributed in ice; in other words, we have to know the laws of screening of an electric charge in ice. The screening of the charge  $\lambda_s$  will occur differently, depending on the ratio of the average thermal energy  $k_B T$  to the electrostatic energy of the charge carriers  $|e_i \phi_s|$ . If the surface potential is small, so that

$$k_B T \gg |e_i \phi_s| \quad (28)$$

then in this case, as was shown by Petrenko and Ryzhkin (1984)

$$E(x) \approx \frac{\lambda_{sb}}{2\epsilon_0 \epsilon_{\infty}} \exp(-\alpha_1 x) + \frac{\lambda_{sa}}{2\epsilon_0 \epsilon_s} \exp(-\alpha_2 x) \quad (29)$$

where  $\alpha_1^{-1}$  and  $\alpha_2^{-1}$  are the two screening lengths determined by the major charge carriers (Bjerrum defects) and minor charge carriers (ions) respectively

$$\alpha_1^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_{\infty} k_B T}{e_3^2 (n_3 + n_4)}} \quad (30)$$

$$\alpha_2^{-1} = \sqrt{\frac{e_2^2 k_B T}{e^2 \Phi (n_1 + n_2)}} \quad (31)$$

$$\Phi \approx 3.85 k_B T \text{ roo}. \quad (32)$$

Since  $\epsilon_{\infty} \ll \epsilon_s$ , a large fraction of electric field (and potential) decays according to eq 29 at the distance  $\alpha_1^{-1} \ll \alpha_2^{-1}$ . This happens because of screening by major charge carriers. The rest of the potential decays at the characteristic length  $\alpha_2^{-1}$ , determined by minor charge carriers.

In the case of strong fields (large densities of the surface charge), when

$$k_B T \ll |e_i \phi_s| \quad (33)$$

the screening is described by a system of nonlinear differential equations, which apparently does

not have an analytical solution. Petrenko and Maeno (1987) have found a solution by making an approximation that ignores the difference between fractional values of the electric charges of Bjerrum defects and ions. Assuming  $e_3 = e_1 = q$ , we obtained

$$E = \frac{\lambda_{sa}}{2\epsilon_0\epsilon_\infty} \frac{1}{1 + x\alpha^{-1}} \quad (34)$$

where the screening length  $\alpha^{-1}$  now depends on  $\lambda_{sa}$

$$\alpha^{-1} = \frac{4k_B T \epsilon_0 \epsilon_\infty}{q \lambda_{sa}} \quad (35)$$

Equation 33 can be used in the subsurface region to a depth where the potential  $|\phi_s, e_1|$  becomes comparable to  $k_B T$ . Further down, we should use eq 29.

Before proceeding to the discussion of experimental data, I shall point out an apparent relationship that exists between  $\lambda_{sa}$  and the component of the surface conductivity  $\sigma_s$ , which is determined by the layer  $\lambda_s$  of the screening charge of the protonic carriers. If in the bulk ( $x = +\infty$ ), the charge carrier concentrations are denoted as  $n_i(+\infty)$ , then the corresponding values of concentrations at the surface will be

$$n_i(0) \cong n_i(+\infty) \exp\left(-\frac{e_i \Phi_i}{k_B T}\right) \quad (36)$$

In reality one of the four types of charge carriers always dominates, hence the high-frequency surface conductivity is given by

$$\sigma_s = \sum_{i=1}^4 |e_i \mu_i| \int_0^{+\infty} n_i dx = |\lambda_s| \mu_i \quad (37)$$

Petrenko (1994) and Petrenko and Colbeck (in press) studied an electrification arising from friction between metal and dielectric sliders on ice. Thin films rubbing against the surface of a rotating ice cylinder were used as sliders. The experiments were conducted in the  $-4.5$  to  $-31.5^\circ\text{C}$  temperature range and in the  $0.5$ - to  $8\text{-m s}^{-1}$  velocity range; the maximum pressure exerted on the ice by a slider was  $1\text{ kPa}$ . In these experiments, we found that during sliding, the sliders pick up a significant positive charge from ice. In the case of metal sliders (stainless steel and aluminum), a large potential difference of  $1600\text{ V}$  arises between the ice and the slider (velocity =  $8\text{ m/s}$ ,  $T = -31.5^\circ\text{C}$ ). When dielectric sliders were used (under the same conditions) strong electric fields  $E =$

$2.1 \times 10^6\text{ V m}^{-1}$  were produced at the ice/slider interface. From the measurements of the current  $I$  passing through an electrometer used as a current meter, we found that a coupled ice and slider acted as a charge generator. Thus

$$I = \frac{dQ}{dt} = \lambda_s \frac{ds}{ds} \quad (38)$$

where  $Q$  = electric charge

$\lambda$  = surface charge density which the slider picks up from the ice surface

$s$  = swept area

$t$  = time.

Similar results were obtained in the course of field experiments on sliding of alpine skis on ice. The value of the electric charge density found is enormous:  $\lambda_s = 1.6 \times 10^{-2}\text{ C m}^{-2}$ . But even this value must be considered as the low limit for  $\lambda_s$  since, first, the slider is unlikely to pick up the entire charge; second, if the slider penetrated to some depth into the ice, some fraction of the unwanted screening charge can be entrapped along with  $\lambda_s$ .

It is interesting to make some estimates based on the value of  $\lambda_s$  that we found. First, such a high density of the surface charge corresponds to  $0.01$  electron charges per water molecule in the ice surface. Second, let us estimate the fraction of water molecules on the surface that are directed perpendicularly to the surface

$$\frac{n_{\perp}}{n_{\text{H}_2\text{O}}} = \frac{P(0)}{M} \quad (39)$$

Substituting  $\lambda_s = 1.6 \times 10^{-2}\text{ C m}^{-2}$  into eq 27, we find from eq 39 that

$$\frac{n_{\perp}}{n_{\text{H}_2\text{O}}} = 0.2. \quad (40)$$

And remember this is the lower limit! It means that a significant fraction of water molecules at ice surface must be polarized.

Finally, using eq 37 to calculate the surface conductivity  $\sigma_s$ , we obtain

$$\begin{aligned} \sigma_s &= 1.6 \times 10^{-2}\text{ C m}^{-2} 1.8 \times 10^{-8}\text{ m}^2\text{ V}^{-1}\text{ s}^{-1} \\ &\approx 3 \times 10^{-10}\text{ } \Omega^{-1} \end{aligned} \quad (41)$$

where the value of the mobility of L-defects (which must be the major charge carriers screening a positively charged surface) at  $T = -10^\circ\text{C}$  (Jacard 1959) was used. The estimated value of  $\sigma_s$  found in eq 41 agrees in the order of magnitude to

experimental data at  $T = -10^\circ\text{C}$  (see Fig. 14 and 15). Although it seems unlikely that in such a way all properties of  $\sigma_s$  can be explained (the temperature dependence of  $\mu_4$  and  $\sigma_s$  is different, for instance), the conformity found is hardly purely incidental and implies that this process significantly contributes to the surface conductivity.

Buser and Jaccard (1978) studied a charge exchange between very small (10- $\mu\text{m}$ ) ice particles and various metal targets, doing the experiments at  $T = -45^\circ\text{C}$  and collision velocities of 10 m/s. They found that the amount and the sign of the charge transferred during a collision depended upon the work function of the metal target as well as the value and the sign of the external electric field, in which the particles were polarized prior to collision. To interpret their experimental results, Buser and Jaccard assumed the presence of electronic states at the ice surface in an analogy to semiconductors. These states participate in the electron exchange between ice and metal during a short ( $10^{-7}$  seconds, in the described experiments) collision. The lower limit of the density of electron surface states was found to be  $\lambda_{sa}/e \geq 10^{16} \text{ m}^{-2}$ . If we assume that the amount of charge  $\Delta Q$  that passes between the ice and the metal during the collision is proportional to the difference in their work functions ( $W_i - W_m$ ), then  $W_i$  can be defined as the point of intersection with the horizontal axis on the graph of  $\Delta Q$  versus  $W_m$ . In this manner, Buser and Jaccard found that  $W_i = 4.3 \text{ eV}$ . A similar result was obtained in experiments of the same kind by Buser and Aufdermaur (1977). Caranti et al. (1985), who used the same method to determine the work function of ice, found a somewhat smaller value for  $W_i$  of  $4.11 \pm 0.2 \text{ eV}$ .

Another method used by many authors is Kelvin's method. Figure 20 illustrates the principle of measurement of the difference between a work function of the studied material (in our case  $W_i$ , the work function of ice) and that of an oscillating electrode  $W_m$ . In this method, ice (or another material) is connected electrically to the electrode that is oscillating above its surface. If  $W_m \neq W_i$ , electrons flow from the ice into the metal if  $W_m >$

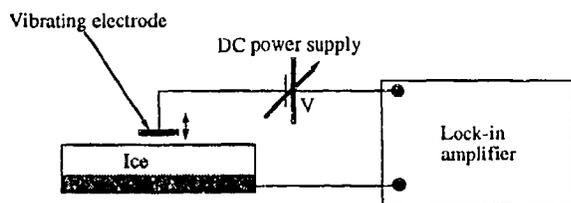


Figure 20. Kelvin's method.

$W_i$  or in the opposite direction if  $W_m < W_i$ , until the equilibrium potential difference  $\Delta\phi$  is established

$$\Delta\phi e = W_m - W_i. \quad (42)$$

This potential difference produces an electric field in the space between the ice and the oscillating electrode, which forms a flat capacitor. When the electrode oscillates, the capacitance also oscillates, resulting in an alternating electric charge at the capacitor and an electric current in the circuit. At the voltage  $V = -\Delta\phi$ , the magnitude of the current is minimal, which allows  $W_m - W_i$  to be determined. To find the absolute value of  $W_i$ , we need to find  $W_m$  using some other method (from the extrinsic photo-effect, which has been done already for all pure metals, for instance). Kelvin's method was used to determine the work function of ice by Takahashi (1969a,b, 1970), Mazzeda et al. (1976), Caranti and Illingworth (1980, 1983a,b,c) and Caranti et al. (1985).

The approximate value of  $W_i$  found in these experiments appeared to be quite sensitive to such ambient conditions as humidity, temperature and, to a smaller degree, ice doping. A characteristic maximum value by which  $W_i$  was altered due to a change in the ambient conditions was  $|\delta W_i| \leq 200 \text{ meV}$ . Thus, for example, Takahashi (1970) observed a buildup of a positive potential (30–80 mV) at the ice surface at the beginning of the condensation process. During further condensation, the surface potential changed its sign and reached a value of  $-250 \text{ mV}$ . The effect was more pronounced at the basal (0001) plane as compared to the prismatic plane. Condensation and evaporation at the ice surface were produced through its heating or cooling, respectively; the ambient temperature was maintained constant.

The same author observed a negative potential buildup at the ice surface after its rubbing (Takahashi 1969b). This result is in qualitative agreement with the observations of Petrenko and Colbeck (in press), although we found a much larger effect.

Mazzeda et al. (1976) studied variance in  $W_i$  as a function of temperature. In these experiments, the ice surface was in equilibrium with the saturated vapor throughout the entire temperature range of 223–273 K; thus, the effect of condensation and evaporation should not have manifested. Figure 21 shows a typical temperature dependence of  $\Delta W_{im}$

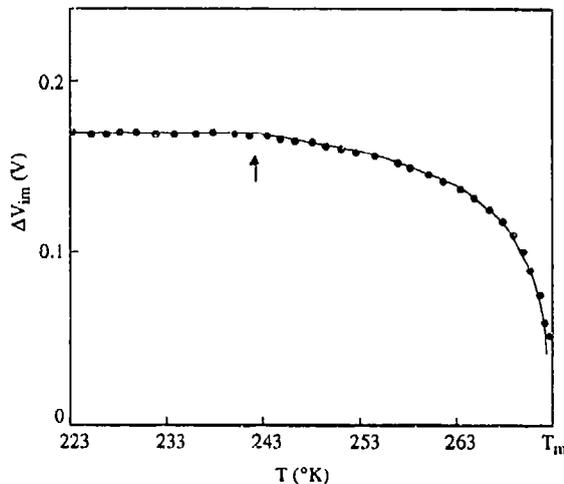


Figure 21. Temperature dependence of  $\Delta W_{im} = 1/|e| (W_m - W_i)$  (after Mazzeda et al. 1976).

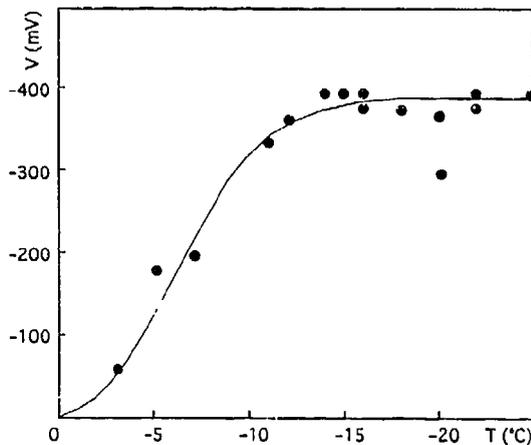


Figure 22. Change in ice surface potential when the surface was rimed with supercooled droplets (after Caranti and Illingworth 1983c).

$$\Delta W_{im} = \frac{1}{|e|} (W_m - W_i). \quad (43)$$

The arrow in Figure 21 indicates the temperature ( $\approx -30^\circ\text{C}$ ) at which there is a transition from a weak linear dependence to a stronger logarithmic dependence. The surface potential grew more positive relative to the bulk and reference electrode when it approached the melting point, which can be explained in terms of the formation of a double charge layer near the surface, as shown in Figure 19. Such charge distribution arises if the molecules at the surface are oriented oxygen-outwards, entrapping a positive compensating charge from the atmosphere.

Caranti and Illingworth (1980, 1983a,b,c) studied variations in the surface potential when the

ice surface was rimed with supercooled droplets from an ultrasonic generator (of  $50\text{-}\mu\text{m}$  radius; 1- to  $2\text{-g m}^{-3}$  water content). A drastic change in the surface potential was observed (Fig. 22). The effect of doping by  $\text{NH}_3$ ,  $\text{NaCl}$  and  $\text{HF}$  (up to concentrations of  $10^{-2}\text{ M}$ ) on the amount of variation in potential was insignificant. The authors came to the conclusion that the variation in the surface potential of ice during its riming is a result of the disordered ice produced by rapid freezing of the supercooled water, since this change is proportional to the rate of freezing and relaxes with a time constant comparable to that of a mechanical relaxation.

## SURFACE ELECTROCHEMICAL POTENTIAL

When the impurity concentration in ice varies from place to place, a static electric field arises from inhomogeneity in the distribution of impurities, which are the effective sources of protonic charge carriers in ice. As a result of this inhomogeneity of impurity concentration, a gradient of the charge carriers' concentrations  $n_i$  arises. The fluxes of ions and Bjerrum defects are correlated since they alter the orientation of the water molecule when they pass through it. The mathematical description of the general case, when both diffusive and drift fluxes of all four types of charge carriers must be taken into account, is quite complicated. Nevertheless, we can easily make rough estimations of the magnitude of the arising electric fields, using a simplified consideration.

Let us regard the case of one type of charge carrier of electric charge  $e_i$  and concentration  $n_i$  at a temperature  $T$ . If a diffusive flux  $j_D$  arises from inhomogeneous doping, in equilibrium it must be balanced by the opposite drift flux  $j_{DR}$

$$j_D = j_{DR} \quad (44)$$

$$j_{DR} = \mu_i \times E; \quad j_D = -D_i \text{ grad}(n_i). \quad (45)$$

Then, employing the Einstein relationship

$$D_i = \mu_i \times k_B T / e_i \quad (46)$$

we obtain for the electric field strength  $E$

$$n_i \times E = (k_B T / e_i) \times \text{grad}(n_i). \quad (47)$$

In eq 44-47,  $D_i$ ,  $\mu_i$  and  $e_i$  are the diffusion coefficient, the mobility and the electric charge of

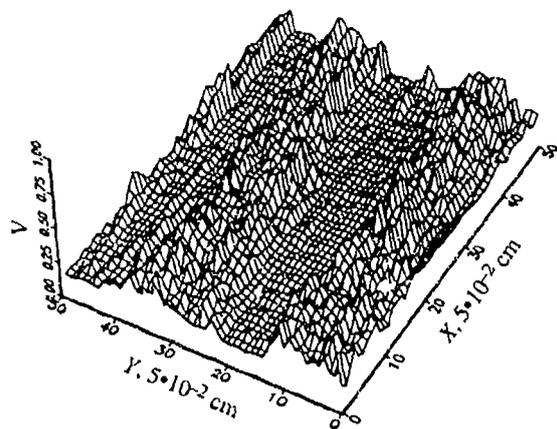


Figure 23 Static electric potential at the surface of freshwater columnar ice. An area of  $2.5 \times 2.5 \text{ cm}^2$  is shown. The columns lie along the x-axis. The potential is given in volts;  $T = -20^\circ\text{C}$  (from Petrenko 1992).

the  $i$ th charge carrier respectively;  $k_B$  is Boltzmann's constant. For the potential difference  $\Delta\phi$  between two points

$$\Delta\phi = (\phi_1 - \phi_2) = (k_B T / e_i) \times \ln(n_{2i} / n_{1i}) \quad (48)$$

where  $n_{1i}$  and  $n_{2i}$  are the concentration at points 1 and 2. Equation 48 gives  $\Delta\phi = 97 \text{ mV}$  for Bjerrum defects (L- and D-defects) at  $T = 263 \text{ K}$  and  $n_{2i} / n_{1i} = 10$ . A typical magnitude of the electric field associated with Bjerrum defects in ice is about  $1\text{--}5 \text{ V/cm}$  (see Fig. 23). Since  $\Delta\phi$  depends upon a ratio of impurity concentration, such an electric field exists even in very pure single crystals of ice.

I (Petrenko 1992) have studied electric potential on the surface of natural and artificial ice using a scanning microprobe connected to an electrometer (Fig. 24). The central element of the experimental setup is an X-Y pen recorder, in

which a pen is replaced by a thin stainless steel electrode with a ball of  $0.3 \text{ mm}$  diameter at its end. A computer controls the position of the electrode scanning over a given area of an ice sample. Scanning was from  $1 \times 1 \text{ mm}$  to  $5 \times 5 \text{ cm}$ , with resolution better than or equal to  $\pm 0.5 \text{ mm}$ . The pressure on the electrode was adjusted so finely that the electrode did not produce visible tracks on or damage to the ice surface. The velocity of the mobile electrode and the measuring time can be changed within a wide range, so that the electrode is able to measure a correct value of an electrochemical surface potential. I found that an electrode velocity of less than  $10 \text{ mm s}^{-1}$  and a measuring time longer than  $10 \text{ ms}$  were satisfactory. The potential was amplified by an electrometer preamplifier with input impedance  $R_{\text{input}} \geq 10^{12} \Omega$  and then stored in the computer. The smooth surface of the ice samples was prepared using a microtome.

An example of the electric potential over the surface of freshwater columnar ice is shown in Figure 23. The ice columns lie along the x-axis. A comparison of the electric potential pattern with an optical image of the ice sample placed between two crossed polarizers reveals their similarity or even identity. In Figure 23 "rough" and "smooth" bands belong to different individual columns. The most significant gradient of potential, and hence electric field strength  $E = \text{grad}(\phi)$ , is located at or near grain boundaries. Generally, the distribution of the electric potential in ice follows the structural pattern of the ice: arrangement of grains, columns and boundaries between the regions of doped and normal ice.

Figure 25 depicts the electrical potential over the surface of a two-part ice sample. One part was grown from very pure deionized water and one was grown from water doped with  $10^{18}$  molecules  $\text{cm}^{-3}$  of KOH. Those two halves, with ideal flat

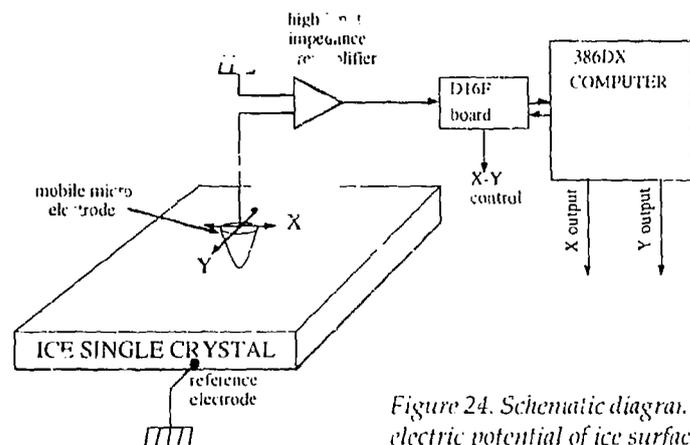


Figure 24. Schematic diagram of experimental setup for measurements of static electric potential of ice surface (from Petrenko 1992).

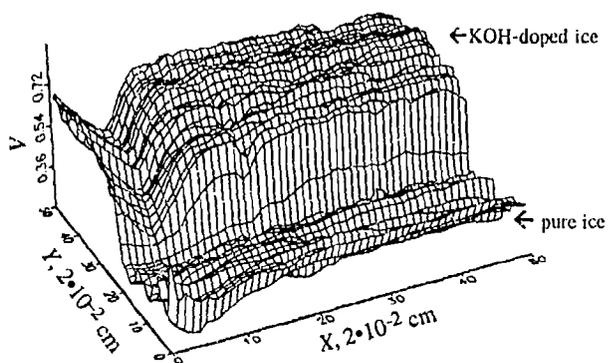


Figure 25. Electric potential on the surface of ice sample assembled of pure and KOH-doped ice. The steep step of the potential is located on the boundary between the pure and doped ice. A "ditch" seen in the potential of the doped (more positive) half corresponds to locations of grain boundaries. Dimension of the area shown is  $1 \times 1$  cm;  $T = -19.5^\circ\text{C}$  (from Petrenko 1992).

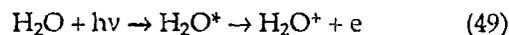
and smooth surfaces, were pressed together for 10 minutes at  $T = -5^\circ\text{C}$ , so that they built a monolithic block. Doping ice with KOH provides negatively charged, extrinsic mobile defects: L-defects and  $\text{OH}^-$  ions (Howe and Whitworth 1989). Their diffusion into pure ice makes the pure part of the sample negatively charged and the doped part positively charged. That is precisely what we can see in Figure 25. At temperatures higher than approximately  $-15^\circ\text{C}$  for pure ice and  $-22^\circ\text{C}$  for saline ice, the existence of a conductive, quasi-liquid layer on the ice surface masks (or screens) the electric potential measured with this technique

#### PHOTO-EMISSION OF ELECTRONS FROM THE ICE SURFACE

Nason and Fletcher (1975) studied photo-emission of electrons (extrinsic photo-effect) from the surface of ice and water. They found that the threshold of photo-emission for both ice near  $-10^\circ\text{C}$  and water near  $10^\circ\text{C}$  is about  $195 \pm 5$  nm. This wavelength corresponds to the energy of  $6.3 \pm 0.2$  eV. The emission efficiency for liquid water was about half that for ice. Photo-emission from ice decreases steadily with decreasing temperature, apparently without any shift in the threshold value, and vanishes below approximately  $-160^\circ\text{C}$ . This decrease of photo-emission with temperature was not related to the decrease of conductivity of ice, since the same temperature dependence of photo-emission was found for ice heavily doped with HF (5%). On the basis of

similarity of photo-emissions from ice and water, the authors concluded that a quasi-liquid layer exists at the ice surface at temperatures  $T > -160^\circ\text{C}$ . Since the threshold is extremely sensitive to the value of the surface potential, its weak sensitivity to temperature variations implies, as the authors believe, that the electric structure ( $\lambda_{sa}$ , the screening length) of the surface layer of ice and water remains unchanged within the whole temperature range ( $-160$  to  $10^\circ\text{C}$ ). Nason and Fletcher believe that the most probable source of photo-electrons is the process of ionization of  $\text{OH}^-$  ions in the surface layer of ice and water. This hypothesis, obviously, contradicts the fact that a change in pH of ice from 1 to 14 does not affect photo-emission significantly.

At the present time, we can suggest an interpretation that is different. It is known that illuminating ice with light having a wavelength  $\lambda \leq 190$  nm excites a bulk photo-conductivity according the following reaction



where  $\text{H}_2\text{O}^*$  denotes an excited water molecule (Khusnatdinov and Petrenko 1992). The electrons produced in this reaction can tunnel out of the ice, provided that its surface has a negative potential. Since the reaction (eq 49) begins with the excitation of a water molecule, it is not surprising that it is insensitive to the change in pH. The temperature dependence of photo-emission (as well as the difference in its values for ice and water) might result from the change in the surface electric field, since this field causes tunneling of electrons out of the subsurface layer of the ice.

#### SURFACE OPTICAL ABSORPTION IN INFRARED REGIONS

Interesting results about the molecular structure of the ice surface were obtained most recently from the study of infrared optical absorption spectra (Bush and Devlin 1991, Rowland and Devlin 1991, Callen et al. 1992, Devlin 1992, Nixon et al. 1992, Rowland et al. 1993). Those studies and the resulting implications were supported by computer simulations using molecular dynamics simulation methods (Bush and Devlin 1991).

The above-mentioned measurements are based on the possibility of distinguishing between lines in the IR spectra corresponding to the stretching and bending mode oscillations of non-saturated hydrogen bonds (i.e., dangling bonds) at the ice surface. The frequency of these oscilla-

tions appears to be extremely sensitive to the way in which a given water molecule is bonded to other molecules—by two or by three hydrogen bonds (2-coordinated or 3-coordinated water molecules). Molecules in the bulk are 4-coordinated. Therefore, a comparison between the intensities of 2-coordinated and 3-coordinated molecules allows us to estimate their relative concentrations. The IR absorption spectra observed in the experiments are better interpreted because of the high sensitivity of the eigen frequencies of dangling bond oscillations to the isotopic substitution of H with D. Moreover, these frequencies are quite sensitive to the process of adsorption of various gases. Thus, such measurements allow us to study ion adsorption by the ice surface at low temperatures.

Specimens of ice with large surface-to-volume ratios were produced either in the form of microscopic ice clusters suspended in gas or by vapor condensation onto a substrate, forming thin ice films. In experiments by Rowland et al. (1993), for example, crystalline ice clusters ~25 nm in diameter formed when mixtures of an inert carrier gas containing a small amount of water vapor, with a gas/H<sub>2</sub>O ratio of ~200/1, were introduced rapidly into a cooled cluster cell to pressures of 33 kPa ( $1/3$  bar) at temperatures below ~120 K. Increasing temperature and load pressures create larger clusters with consequently smaller surface-to-volume ratios and reduced relative surface-mode band strengths (Rowland et al. 1991).

Computer simulations using molecular dynamics methods have demonstrated that when water molecules collect to produce a small cluster, the following phenomena occur: 1) there are no molecules possessing two dangling OH bonds; 2) both 2- and 3-coordinated molecules form on the surface in approximately equal amounts, provided that the temperature is quite low (~20 K); and 3) in the annealed clusters, the 3-coordinated species are dominant. The concentration of dangling bonds is small ( $\ll 1$ ) even at these low temperatures. The results of spectral studies performed in the above works are in agreement with the results of computer simulations.

#### REGELATION (REFREEZING), SINTERING AND ADHESION

In retrospect, the studies of the quasi-liquid layer at the ice surface began with studies of thermo-mechanical effects: regelation, sintering and

adhesion. The data on the physical parameters of the ice surface layer, obtained during those studies, are ambiguous and much less accurate than those obtained by modern methods. But we should keep in mind that, first, it was these phenomena that aroused such a great interest in the ice surface. Second, these phenomena are still of great practical importance. Therefore, a brief retrospective view of these studies is presented below.

Faraday (1850) observed an interesting phenomenon: if two pieces of ice are brought into slight contact at 0°C or a higher temperature, they freeze together. This discovery initiated a long and interesting argument between Faraday and Tyndall on one side and J. Thomson, his brother W. Thomson (Lord Kelvin) and Helmholtz on the other side. The Thomsons and Helmholtz held to the opinion that regelation is caused by melting under pressure in the contact zone between two pieces of ice. When the pressure is removed, water freezes again, bonding the pieces together. Faraday performed several simple but ingenious experiments that proved the erroneousness of the Thomsons' hypothesis, suggesting a regelation mechanism that is very close to the modern concept of this process. He assumed that at temperatures close to the melting point, a thin liquid film always exists at the ice surface. When two blocks of ice touch, this film first forms a "neck" connecting the two blocks. Then, since the inner part of the neck gradually turns into a bulk region of ice, it freezes, forming a solid joint between the two.

Nakaya and Matsumoto (1953) did some experimental work to verify the existence of the liquid-like layer at the ice surface. They suspended small spheres of ice (from 1.5 to 4 mm in diameter), prepared from distilled water, on cotton threads in a pendulum-like fashion. One of these pendulums was moved laterally, bringing the spheres in contact with a very small force, estimated by the authors to be less than 0.01 dyn. Then, the suspension point of one of the spheres was displaced laterally until the spheres broke free; the force can be calculated from the value of the angle  $\vartheta$  (with respect to the vertical) at which they separated. Nakaya and Matsumoto also tested ice spheres containing 0.1% NaCl. In this case we would expect a thicker film on the ice surface. To explain their results, the authors had to assume that a transitional liquid-like layer exists at the ice surface at temperatures below 0°C.

Hosler et al. (1957) did similar but more accurately controlled experiments in a temperature

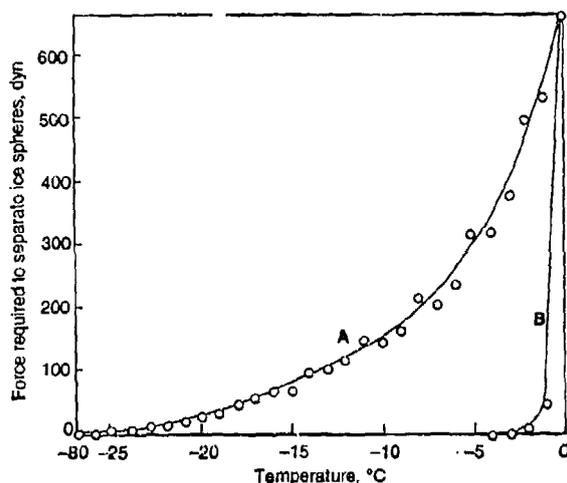


Figure 26. Separation force as a function of temperature: A—water-vapor saturated atmosphere; B—dry atmosphere (after Hosler et al. 1957).

range from  $-80$  to  $0^{\circ}\text{C}$  in both dry and water-saturated atmospheres. Between  $-80$  and  $-40^{\circ}\text{C}$ , they observed no adhesion between spheres (Fig. 26). The lowest temperature at which adhesion was measurable in a saturated atmosphere was about  $-25^{\circ}\text{C}$ , whereas in a dry atmosphere the adhesion practically ceased at  $-3^{\circ}\text{C}$ . They explained this difference in terms of a rapid evaporation of the liquid-like layer from the ice surface in a dry air, which makes it very thin. Hosler et al. also found that the temperature dependence of the force at which separation occurs can be expressed in terms of a Boltzmann equation with the activation energy of  $0.46$  eV.

Jellinek (1957a,b; 1959; 1960; 1962), investigating the adhesive properties of ice, conducted shear and tensile experiments with ice frozen onto stainless steel and optical flat quartz plates and various polymers. In his tensile experiments, only cohesive breaks through ice were observed. Shear tests resulted in adhesive breaks along the interface, the strength of which depended on the loading rate, surface polishing, temperature and the type of the material used. A temperature dependence of the shear strength for the case of ice-snow confined between stainless steel disks is shown in Figure 27.

If we assume that the shear strength in shear-type experiments at temperatures above  $-13^{\circ}\text{C}$  is determined by viscous flow of the quasi-liquid layer, then

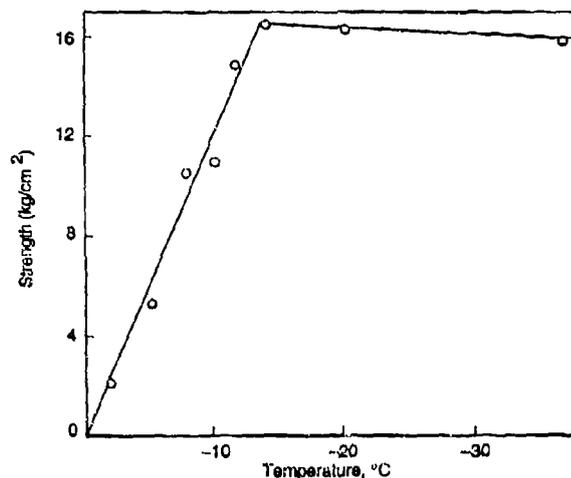


Figure 27. Strength as a function of temperature for snow-ice sandwiched between stainless steel disks, obtained by shear. Cross-sectional area  $1.54$   $\text{cm}^2$ ; height  $0.2$  to  $0.4$  cm. Adhesive breaks at  $T > -13^{\circ}\text{C}$  and cohesive breaks at  $T < -13^{\circ}\text{C}$ . Each point represents an average of at least 12 tests (after Jellinek 1959).

$$\frac{dS_{\text{st}}}{dv} = \frac{\eta}{L} \quad (50)$$

where  $\eta$  and  $L$  are film viscosity and thickness respectively. The ratio of  $\eta/L$  found by Jellinek at  $T = -4.5^{\circ}\text{C}$  was  $6.99 \times 10^4$  N s/m for ice-stainless steel and  $1.5 \times 10^4$  N s/m for ice-quartz. In eq 50 we have two unknowns,  $\eta$  and  $L$ . If the value of  $L = 2.7 \times 10^{-9}$  m, found by Barer et al. (1977) at  $T = -4^{\circ}\text{C}$  (see Table 1), is used, then the resulting viscosity of the quasi-liquid layer between ice and quartz will be  $\eta = 0.41$  Pa s, as compared to  $0.017$  Pa s found by Barer et al. at even lower temperatures.

Raraty and Taber (1958) did some adhesion experiments. Their results are essentially in agreement with those of Jellinek.

A large number of experimental and theoretical works dealt with the issue of sintering of ice. Sintering plays a major role in the process of snow densification, which transforms falling snow into ice in mountain glaciers and the polar caps of Greenland and Antarctica. Several physical phenomena, such as surface and bulk diffusion, surface tension, plastic deformation and water transfer through water vapor, contribute to the sintering. The relative effect of each of the mechanisms above depends largely on conditions during sintering: temperature, humidity, impurity composition and size of ice particles. Because of this, interpreting the data on ice sintering is usually very difficult. The phenomena of small particle migra-

tion (Itagaki 1967a) on the ice surface and regelation are also similar to sintering. Studies of these things, although contributing significantly to the development of practical applications, were of little use for the determination of the fundamental parameters of the ice surface layer owing to difficulties in interpretation. As examples of excellent studies on ice sintering, I can recommend to interested readers the following papers: Kingery (1960), Hobbs and Mason (19641), Itagaki (1967c) and Maeno and Ebinuma (1983).

### ADSORPTION OF GASES ON THE ICE SURFACE

When gas molecules of a mass  $m$  strike a solid surface, they can either bounce or get stuck to the surface (be entrapped) for a certain time. The latter case is called an adsorption of the molecule. If the gas molecules are in thermal equilibrium with the solid surface, the equilibrium surface concentration  $C_s$  of adsorbed molecules will depend on the flux of oncoming molecules, i.e., on the gas pressure  $P$  and temperature  $T$  and on the average time that a molecule spends on the surface.

Langmuir (1916) assumed that the maximum concentration of the adsorbed molecules  $C_M$  corresponds merely to a mono-molecular layer. Therefore, a molecule coming from a gas and colliding with an already adsorbed molecule must instantly bounce off the surface. On the basis of this assumption, simple kinetic considerations lead to the so-called Langmuir's adsorption isotherm

$$\frac{V_s}{V_M} = \frac{k_1 P}{1 + k_1 P} \quad (51)$$

where  $V_s$  is the actual volume of the adsorbed gas (which corresponds to  $C_s$ ) and  $V_M$  (which corresponds to  $C_M$ ) is the volume of the adsorbed gas when the entire adsorbent surface is covered with a monolayer.

$$k_1 = \frac{1}{(2\pi m k_B T)^{1/2}} \frac{\tau_a}{C_M} \quad (52)$$

Brunauer et al. (1938) extended the result of Langmuir to the case of multilayer adsorption. This equation is known as a BET equation. They found that

$$\frac{P}{V_s(P - P_0)} = \frac{1}{V_M k_2} + \frac{(k_2 - 1)P}{V_M k_2 P_0} \quad (53)$$

where

$$k_2 = \exp\left(\frac{E_a - E'_a}{k_B T}\right) \quad (54)$$

$E_a$  and  $E'_a$  are the heats of adsorption (i.e., the amounts of heat liberated when a molecule is adsorbed) corresponding to the first and all succeeding layers;  $P_0$  is the saturation pressure of a gas over a plane surface at temperature  $T$ .

As we can see from eq 53, a plot of  $P/V_s(P - P_0)$  versus  $P/P_0$  must be a straight line with a slope of  $(k_2 - 1)/V_M k_2$  and an intercept with a horizontal axis of  $1/V_M k_2$ . In this way constants  $V_M$  and  $k_2$  can be determined; then, the surface area of the solid can be calculated. We can also find  $E_a$ , provided that the value of  $E'_a$  is known (it is usually taken to be equal to the latent heat of evaporation of the adsorbate in a liquid form). Readers interested in the theories of adsorption can find them in the book by Steele (1974), for example.

Experimental studies of gas adsorption on the ice surface are of a great practical importance for the physics of the atmosphere, meteorology, climatology and astrophysics. In addition, such studies contribute to the understanding of the ice surface structure, since adsorption is quite sensitive to both surface structure and the presence of various defects at the surface, as well as to the local fields (from the molecular dipoles, for instance) existing near the surface.

Gas adsorption by ice has been studied in a wide temperature range: from 77 to 273 K. The adsorption of gaseous nitrogen was studied by Adamson et al. (1967), Ocampo and Klinger (1983a) and Schmitt et al. (1987); the adsorption of  $\text{CO}_2$  was studied by Ocampo and Klinger (1983); the adsorption of hydrogen was examined by Smoluchowski (1983; theoretical study); and Orem and Adamson (1969) studied the adsorption of non-polar hydrocarbon vapors (n-alkanes). In these experiments, the surfaces of amorphous, cubical and hexagonal ice, cleaved at 77 K and annealed at higher temperatures, and natural snow were investigated.

Cubic ice, produced by the direct condensation of water vapor onto the walls of a vessel at a liquid nitrogen temperature, has the maximum net surface ( $11.8 \text{ m}^2/\text{g}$  [Adamson et al. 1967]). This surface was reduced after the ice had been annealed, and was about  $1 \text{ m}^2/\text{g}$  in the case of natural snow. The value of the adsorption heat found exceeds the heat of evaporation:  $2700 \pm 20 \text{ J mol}^{-1}$  at 77 K for the adsorption of  $\text{N}_2$  reported by Schmitt et al. (1987); a similar value of  $2512 \pm 250 \text{ J/mol}$  was reported by Adamson et al. (1967). The adsorption heat is gen-

erally reduced after annealing (down to  $1067 \text{ J mol}^{-1}$  after 4 days [Ocampo and Klinger 1983a]).

The results of studies performed by Orem and Adamson (1969) showed that there exists a significant difference in the character of adsorbent-adsorbate interaction above and below  $-35^\circ\text{C}$ . Between  $-35$  and  $-196^\circ\text{C}$ , ice acts as a low-energy adsorbent and the adsorption energy is associated with dispersion interactions, with no effect of local dipole fields. However, at temperatures above  $-35^\circ\text{C}$ , the ice surface acquires an adsorption capability close to that of a water surface. These observations conform to the model of a quasi-liquid film at the ice surface. A similar temperature transformation in the adsorption process, just at a lower temperature ( $-40^\circ\text{C}$ ), was also noted by Ocampo and Klinger (1983a). They also found a considerable decrease in the entropy of the adsorbed gas at  $T > -40^\circ\text{C}$ . Such an entropy decrease could be explained in terms of the ordering of adsorbate molecules in a strong electric field of ordered water molecules at the ice surface. As we have seen previously, this also conforms to the model of the quasi-liquid layer.

## SURFACE ENERGY

A net surface free energy or simply surface energy is defined as the work required to increase the interface area by a unit area (at a constant temperature). We shall need, for a theoretical analysis, the energies of the interfaces between solid ice ( $S$ ), liquid phase ( $L$ ) and water vapor ( $V$ ). We denote them as  $\gamma_{SL}$ ,  $\gamma_{VS}$  and  $\gamma_{VL}$  for solid/liquid, vapor/solid and vapor/liquid interfaces respectively. All of these quantities are temperature dependent; it does not make sense to give a value to  $\gamma$  without indicating the temperature. The best known quantity is the most easily measured,  $\gamma_{VL}$ , which can be determined by a variety of experimental techniques based on the measurement

of the surface tension of water. (These techniques include measurement of the height of water rise in a capillary and measurement of the wavelength of surface waves, excited by an ultrasonic generator, for example.) At the melting temperature,  $\gamma_{VL} = 75.7 \text{ mJ m}^{-2}$  and increases with increasing temperature. The two other energies  $\gamma_{SL}$  and  $\gamma_{VS}$  cannot be measured quite so easily, and to determine them a certain ingenuity is required.

We shall not describe here the early and less accurate works, and shall proceed to an interesting technique suggested by Ketcham and Hobbs (1969). That technique was also used later by Hardy (1977). The technique is based on the measurement of equilibrium angles at the interfaces between two ice seeds and water vapor or water (Fig. 28). As can be seen from this figure, the triple junction in a grain-boundary groove is subjected to three forces of surface tension. Therefore, for equilibrium, the following conditions must be satisfied

$$\gamma_{gb} = 2\gamma_{VS} \cos(\theta_{VS}/2) \quad (55)$$

$$\gamma_{gb} = 2\gamma_{LS} \cos(\theta_{LS}/2) \quad (56)$$

Since there are three unknowns  $\gamma_{gb}$ ,  $\gamma_{LS}$  and  $\gamma_{VS}$ , we need a third equation in addition to eq 52 and 53. This equation can be the condition of equilibrium among vapor, liquid and ice in the case of incomplete wetting ( $0 < \phi < \pi$ ). In this case

$$\gamma_{VS} = \gamma_{LS} + \gamma_{VL} \cos\phi \quad (57)$$

Using this technique for determination of the surface energies, Ketcham and Hobbs (1969) found that at  $0^\circ\text{C}$

$$\begin{aligned} \gamma_{VS} &= (109 \pm 3) \text{ mJ m}^{-2} \\ \gamma_{LS} &= (33 \pm 3) \text{ mJ m}^{-2} \end{aligned} \quad (58)$$

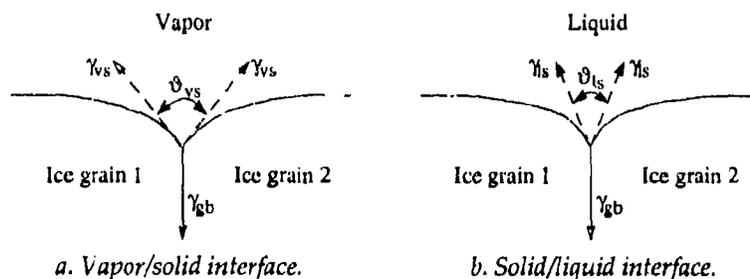


Figure 28. Schematic of grain-boundary grooves (after Ketcham and Hobbs 1969).

$$\gamma_{gb} = (65 \pm 3) \text{ mJ m}^{-2}.$$

The reader can find the data on the values of the angle  $\phi$  in the papers by Knight (1966, 1971). Ketcham and Hobbs also calculated that the anisotropy of  $\gamma_{VS}$  and  $\gamma_{LS}$  with respect to orientation is probably small and falls within the experimental error. The value of  $\gamma_{gb}$  depends, of course, on the grain boundary type and must tend to zero as the angle of misorientation between the seeds tends to zero. Hardy (1977) using a similar technique, found in the case of water/ice interface a more exact value

$$\gamma_{LS} = (29.1 \pm 0.8) \text{ mJ m}^{-2}. \quad (59)$$

Recently, Makkonen (in press) concluded from results of measurements of  $\phi$  ( $37^\circ$ ) that  $\gamma_{LS} = 77 \text{ mJ m}^{-2}$  for ice at  $-25^\circ\text{C}$ .

Finally, Kuroda and Lacmann (1982), from the number of broken bonds at the ice surface and the value of heat of sublimation of  $8.5 \times 10^{-20} \text{ J molecule}^{-1}$ , estimated  $\gamma_{VS}$  on the basal (0001) and prismatic (10 $\bar{1}$ 0) faces to be

$$\begin{aligned} \gamma_{VS} (0001) &= 121 \text{ mJ m}^{-2} \\ \gamma_{VS} (10\bar{1}0) &= 128 \text{ mJ m}^{-2} \end{aligned} \quad (60)$$

## SUMMARY OF MAIN EXPERIMENTAL RESULTS

Before we proceed to the review of theoretical models developed to explain the structure and physical properties of the ice surface, let us summarize the major experimental results so that we have a starting point for comparing them with theories. The reader undoubtedly already anticipates the difficulty of that task. The range of discrepancies in the results of different authors is too large, especially when different experimental techniques are used.

Nonetheless, let us try to establish the facts that either conform to the majority of results or to the most reliable of them. I shall also try to point out major discrepancies.

All results can be classified into several issues:

1. The presence or absence at the ice surface of a special layer, which has physical properties different from those of the bulk ice.
2. The layer thickness and its temperature domain of existence.
3. The molecular structure of this layer.
4. A comparison between measured properties

of the ice surface layer (diffusion, electric conductivity, refraction coefficient, etc.) and those of water and ice.

After this is done, we shall see whether it is possible to assemble some consistent picture of the ice surface layer.

### Existence of a special layer

The greatest consistency is achieved here. Experimental papers published over the past 20 years never address the question of the existence of the special layer. All authors admit to its existence. Let us join them, keeping in mind an impressive listing of experimental evidence considered above.

### Thickness of the layer and the domain of its existence

Since in all cases, a strong temperature dependence of the surface properties was observed, we cannot discuss the question of the layer thickness without referring to its temperature dependence.

Figure 29 attempts to summarize all the measurements of the thickness of the surface ice layer. In those cases when a temperature dependence of some property of this layer (e.g., surface conductivity) rather than the absolute thickness was measured, this temperature dependence, normalized by the value at some temperature  $T_0$ , is plotted.

At first glance, the results presented in Figure 29 are awesome, so great are the discrepancies.

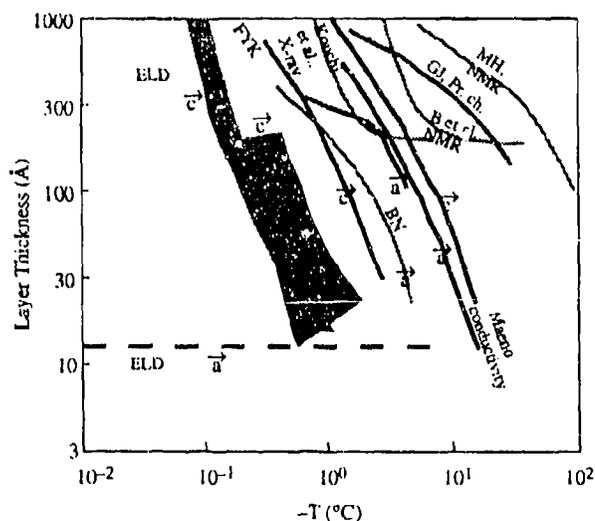


Figure 29. Temperature dependencies of quasi-liquid layer thickness taken from the papers cited in this review. Capital letters at the curves stand for first letters of the authors' names.

Thus, the layer thicknesses found by different authors differ by one to two orders of magnitude (at  $-10^{\circ}\text{C}$ ,  $L \approx 10 \text{ \AA}$  [Elbaum et al. 1993] and  $L \approx 1000 \text{ \AA}$  [Golecki and Jaccard 1978], for instance).

The width of the temperature domain of existence also differs by two orders of magnitude ( $\Delta T \approx 1^{\circ}\text{C}$  [Elbaum et al. 1993] and  $\Delta T \geq 100^{\circ}\text{C}$  [Mizuno and Hanafusa 1987]). Taking into account the thoroughness of the measurements and control of the conditions in these experiments, I feel that it is most unlikely that the described discrepancies are attributable to errors in measurement or some other error. On the contrary, I believe that all measurements were correct, but absolutely different layers on the surface of the same ice  $I_h$  were measured. In other words, the surface layer must consist of several layers, each possessing specific physical properties, different from that of the bulk.

In fact, optical investigations, based on the measurement of intensity of the light reflected from the surface, are sensitive to the molecular density of the layer. Such investigations indicate the presence of an optically dense film at the ice surface in the temperature range from 0 to approximately  $-4$  to  $-5^{\circ}\text{C}$ . The refractive index of this film  $n = 1.330$ , determined by Furukawa et al. (1987a,b), is very close to the refractive index of water at  $0^{\circ}\text{C}$   $n = 1.333$ .

The thickness of this thinnest, "external" dense film depends not only on the temperature, but also on the type of crystallographic face, as well on the presence or an absence of air (Elbaum et al. 1993). In approximately the same temperature interval ( $-2.5$  to  $0^{\circ}\text{C}$ ), Kouchi et al. (1987) observed by means of X-ray diffraction a film with no long-range order, which is characteristic of a liquid phase.

Thus, we can conclude that in the temperature range from  $0^{\circ}\text{C}$  to "minus several degrees Celsius," a film similar in structure and density to water exists on the surface of pure ice.

A layer with increased conductivity can be detected at the ice surface at much lower temperatures ( $-25$  to  $-35^{\circ}\text{C}$ ). Its maximum thickness is limited by the value of the screening length. An idea of the latter can be obtained from the work by Chrzanowski (1988):  $L \approx 0.5 \mu\text{m}$  at  $T = -53^{\circ}\text{C}$ . Charge carrier concentration and conductivity increase within this layer as they approach the surface. Estimates made in the section on the surface charge and the surface potential indicate that the concentration of ions and Bjerrum defects near the surface can reach a value comparable to the

molecular concentration. (see eq 14 and 15). Such a large concentration of defects itself can be sufficient reason for a disordering of the structure.

A layer with an abnormally large amplitude of thermal vibrations is observed at even lower temperatures ( $\approx -50^{\circ}\text{C}$  [Golecki and Jaccard 1978]). The thickness of this layer at  $T \approx -1^{\circ}\text{C}$  reaches the value of  $1000 \text{ \AA}$ .

Even larger is the temperature domain ( $T \geq -100^{\circ}\text{C}$ ) of a layer detected by means of NMR (Mizuno and Hanafusa 1987). This layer can be characterized as having a spin-lattice interaction different from that of the bulk, or as a layer with increased self-diffusion coefficient and rate of molecule reorientation. The thickness of this layer at the ice/ aerosil interface is  $11 \text{ \AA}$  at  $T = -12^{\circ}\text{C}$  (Barer et al. 1977).

### Molecular structure of the layer

We have several sources of information about the surface layer structure. First, as was shown by Kouchi et al. (1987), in the temperature interval 0 to  $-2.5^{\circ}\text{C}$ , there is no long-range order at the ice surface, which is characteristic of liquids. The disordering probably remains at lower temperatures, but the technique used does not have the necessary sensitivity to detect this. An interesting fact is that the thickness of the "liquid" layer, which is measured by X-ray diffraction, appears to be the same for (0001) and (0110) surfaces, which contradicts ellipsometrical measurements. Therefore, we cannot rule out the possibility that in these investigations different layers were observed.

Golecki and Jaccard (1977, 1978), who used a proton channeling technique, observed the presence of a disordered layer down to  $-50^{\circ}\text{C}$ . This layer, with a thickness of about  $1000 \text{ \AA}$  at  $T = -1^{\circ}\text{C}$ , was interpreted as having a much greater amplitude of the thermal vibrations or oxygen atoms rather than having an amorphous structure.

Additional indirect evidence of the disordering in the ice surface layer comes, as we have seen in the section on surface conductivity, from a comparison of NMR data with the data on the values of the concentrations and the mobilities of charge carriers (see eq 11-14). We found that the concentration of defective hydrogen bonds (Bjerrum defects) equals  $2 \times 10^{28} \text{ m}^{-3}$  and is comparable to the molecular concentration of  $3 \times 10^{28} \text{ m}^{-3}$ . Obviously, in this case it is impossible to preserve an ordered structure interconnected by hydrogen bonds corresponding to ice  $I_h$ . Moreover, since the activation energy of the L-defect mobility

(0.23 eV) is close to that of  $\tau^{-1} \propto \sigma_{ss}$  (0.29 eV, Fig. 9), then according to eq 11 such high Bjerrum concentration and consequent inevitable disordering will persist down to very low temperatures ( $-60^{\circ}\text{C}$ ). We should keep in mind, however, that since the amplitude of the NMR signal decreases with decreasing temperature, the thickness of this layer must also decrease. Finally, let us remember that the results of experiments on the surface charge density and gas adsorption imply that a fraction of water molecules in the subsurface layer (at least within a single monomolecular layer) must have their dipole moments oriented normally to the surface. Such orientation is also an ordering of some kind.

#### **Physical properties of the surface layer as compared with water and ice**

As we discussed earlier, certain physical properties of the surface ice layer are intermediate between water and ice. This holds for viscosity and self-diffusion coefficient, for instance. But there are two remarkable exceptions to this rule. First, the optical density of the quasi-liquid film practically coincides with that of water at  $0^{\circ}\text{C}$ . Second, the net electric conductivity of the ice surface exceeds by many orders of magnitude the electric conductivities of both ice and water and corresponds to the upper boundary of conductivity of superionic materials.

## PART II. THEORETICAL MODELS OF THE ICE SURFACE

We have seen in Part I how complicated the structure of the ice surface is and what diverse physical properties it possesses. It is clear, therefore, how difficult it is to create a theoretical model describing such physical objects as the surface layer of ice, and nobody has yet been able to devise one. Theoretical models do exist, although there are very few, that in the best case can describe satisfactorily only one of the phenomena associated with the ice surface in a limited temperature range. However, probably all the physical reasons that make the ice surface as it is were analyzed in these works. Therefore, it seems reasonable, in spite of a very limited application of existing theories, to consider and discuss them briefly.

The most simple and clear is the phenomenological model based on the idea of a possible gain in the free energy of the ice/vapor interface resulting from the formation of a liquid film on the ice surface. Obviously, this is possible only if

$$\gamma_{VS} > \gamma_{LS} + \gamma_{VL} \quad (61)$$

Within the framework of this theory, the surface layer of ice is considered to be simple, ordinary water. If we denote the change in the Gibbs free energy per unit area resulting from melting as  $\Delta G$ , obviously in thermodynamical equilibrium

$$\left(\frac{\partial \Delta G}{\partial d}\right)_T = \rho_L \Delta \mu(d) = 0 \quad (62)$$

where  $\mu$  is the chemical potential,  $\rho_L$  is the water density and  $d$  is the water film thickness. The water film thickness  $d$  enters into  $\Delta G$  twice

$$\Delta G = (\rho_L S_L \Delta T) d + \Delta \gamma(d) \quad (63)$$

where  $\Delta T = T_m - T$ ,  $S_L$  is the entropy of fusion per unit mass and  $\Delta \gamma$  is the change in the free energy of the surfaces

$$\Delta \gamma(d) = \gamma_{VL} + \gamma_{SL} - \gamma_{VS} \quad (64)$$

$\Delta \gamma$  depends on the film's thickness implicitly because, at thickness values comparable to the interatomic distances, two interfaces begin to "sense" the presence of each other. Usually, it is assumed that

$$\Delta \gamma(d) = \Delta \gamma(\infty) \left[ 1 - \left(\frac{r_0}{d}\right)^2 \right] \quad (65)$$

where  $r_0$  is a constant on the order of interatomic distance (see for example Dash [1991] and Takagi [1990]). A solution of the system of eq 62-65 gives for the water film thickness

$$d = \left( \frac{2r_0^2 \Delta \gamma(\infty)}{\rho_L S_L (T_m - T)} \right)^{1/3} \quad (66)$$

The reader can find examples of these calculations in the paper by Dash (1991), who also considered an ice/solid interface and took into account a small correction due to thermomolecular pressure acting on the melted layer; also in the paper by Takagi (1990), who incorporated corrections due to surface curvature. Figure 30 shows the results of such a calculation.

Fukuta (1987) and Makkonen (in press) suggested that the surface can melt because of the pressure applied to the subsurface layer by the bulk. The nature of this pressure becomes clear if we recall that a molecule on the surface is subjected to the attraction forces from the rest of the molecules and the net force is directed inside the crystal. Since the pressure lowers the melting temperature of ice, the surface melts. Fukuta, analyzing the intermolecular forces and using the dependence  $T_m(P)$ , valid for microscopic quantities of water and ice, estimated the thickness of the liquid film as

$$d = \frac{1.5 \text{ nm}}{\sqrt{T_m - T}} \quad (67)$$

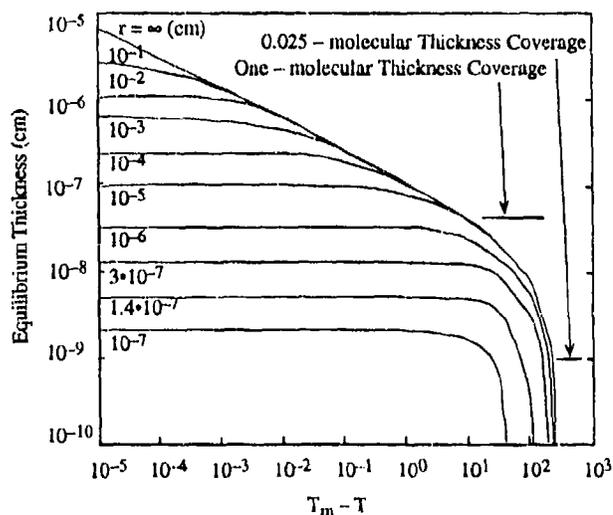


Figure 30. Calculated temperature dependence of a thickness of liquid film on an ice surface (after Takagi 1990).

Makkonen (in press), who found experimentally that eq 61 is not valid, predicted

$$d = \frac{3.5 \text{ nm } ^\circ\text{C}}{(T_m - T)} \quad (68)$$

Within the context of Fukuta's model, the liquid film must vanish at temperatures  $T < -22^\circ\text{C}$ , where the pressure just transforms ice  $I_h$  into its high pressure forms ( $I_{II}$ ,  $I_{III}$  and  $I_{IX}$ ) rather than into liquid.

Thus, the models just described could have been applied to the optical observations of a dense liquid film on the ice surface close to the melting point, although the estimation using eq 67 gives a much thinner thickness compared to experimental data (for example at  $T = -1^\circ\text{C}$ ; see Fig. 29). In addition, these phenomenological models can give nothing more in terms of properties of the liquid film than the properties of ordinary water. And these properties do not coincide at all with the properties of the liquid-like layer of ice, as we have seen previously (electrical conductivity and self-diffusion coefficient, for instance).

During a rather long period, a model proposed by Fletcher has attracted (and still continues to attract) considerable attention (see Fletcher 1962, 1963, 1968). (Note that Fletcher recently returned to the problem of the ice surface structure at much lower temperatures [see Fletcher 1992].) The key idea in Fletcher's (1968) model is the assumption that, at the ice surface, a significant fraction of molecules (denoted as  $\alpha_0$ ) is oriented with their dipole moments (i.e., protons) pointing outwards, as opposed to the bulk where molecules are oriented randomly. This would result in a large buildup of positive polarization charge at the surface. Fletcher came to his conclusion about molecule orientational ordering by analyzing the interaction between dipole and quadrupole moments of water molecules close to the surface. Fletcher estimated the energy of this interaction as  $10^{-20}$  J per molecule, which exceeds an average thermal energy  $k_B T \approx 4 \times 10^{-21}$  J.

As we have seen in the section on surface charge and surface potential, a positive electric charge of a high density, which is unambiguously related to the water molecule dipole ordering, was indeed discovered on the ice surface.

All other predictions of Fletcher's model are consequences of the molecule ordering in the surface layer. In fact, since in the bulk there is no ordering ( $\alpha_0 = 1/2$ ), between the surface and the bulk, there should be a transitional layer with a large concentration of defective hydrogen bonds

allowing molecules to reorient. This transitional disordered layer, according to Fletcher, is the liquid-like layer. Fletcher finds the equilibrium thickness of this layer thermodynamically by minimizing the Gibbs free energy of the surface and incorporating the following components of this energy: the energy associated with the surface orientation of the layer; the energy associated with the interaction of the molecular quadrupoles with the gradient of the electric field; the interaction of molecular dipoles with the total electric field; and the interfacial energy between the liquid-like layer and the ice. In addition, a "volume" reduction in  $G$  because of the melting of the layer and a lowering of the entropy because of molecule orientation are apparently also considered. An unknown fitting parameter of the theory is  $\epsilon_2$ , the energy required to form an L-defect in the liquid-like layer. Finally, Fletcher minimizes the free energy  $G$  as a function of  $\alpha_0$  and the layer thickness  $d$ . I deliberately do not present the mathematical details of Fletcher's calculation because it is quite cumbersome and, more importantly, might be made more accurate in the future. Nevertheless, Fletcher's analysis of the problem and the insight that he has achieved into the physical nature of the layer are absolutely remarkable. Let us note also that within the context of this model, an unusually high electrical conductivity of the surface layer has an obvious explanation: it is ascribable to a high concentration of L-defects in the liquid-like layer. Figure 31

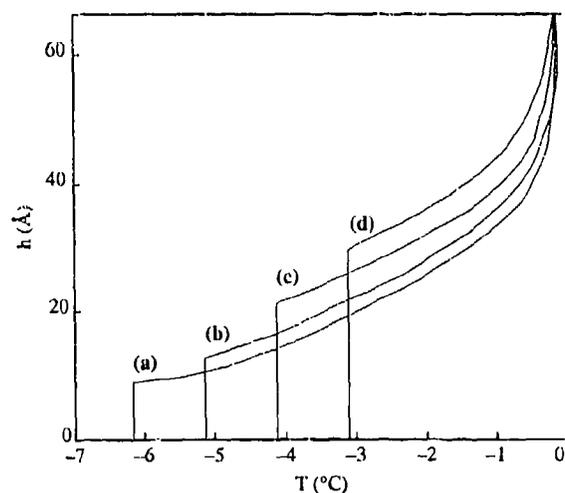


Figure 31. Calculated dependence of the equilibrium thickness,  $L$ , of the liquid-like layer on ice for various assumed values of  $\epsilon_2$ , the energy of formation of diffuse L-defects in the liquid-like layer (after Fletcher 1968).  
 a— $\epsilon_2 = 6.25 \times 10^{-3}$  eV;    b— $\epsilon_2 = 0.0188$  eV;  
 c— $\epsilon_2 = 0.0625$  eV;        d— $\epsilon_2 = 0.1875$  eV.

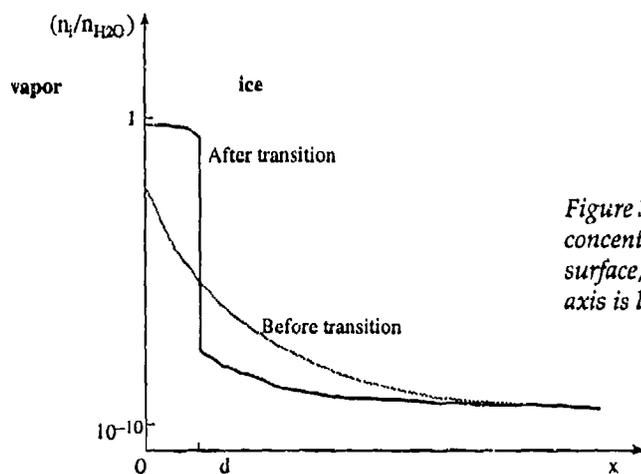


Figure 32. Schematic representation of protonic point defects concentration,  $n_i$ , as a function of a distance from the ice surface,  $x$ ;  $d$  is the thickness of a superionic layer. The  $n_i/n_{H_2O}$  axis is logarithmic.

shows the calculated thickness of the liquid-like layer as a function of temperature. Later, in his invited review paper, Fletcher (1973) gave an approximate expression for the thickness  $d$  of the liquid-like layer

$$d(\text{\AA}) = (20 \text{ to } 50) - 25 \log_{10}(273 - T). \quad (69)$$

Fletcher's (1992) recent calculations suggest that, at much lower temperatures, the ice surface is reconstructed by an orientation of surface dipoles into a superlattice. Such a reconstruction should occur on the (0001) basal plane below approximately 30 K and on the (01 $\bar{1}$ 0) prismatic plane below approximately 70 K.

On the basis of the model of the superionic state of ice invented by Ryzhkin (1985), Ossipyan and Petrenko (1988) suggested a purely electrostatic reason for surface melting that accounts for a high surface electric conductivity and the appearance of a rather thick (up to the screening length) disordered layer. The reasons for the formation of the layer are as follows. As was shown by Ryzhkin (1985), upon the increase of charge carrier concentration above a certain critical value (on the order of  $10^{-8}$  to  $10^{-4}$  of the molecular concentration), the activation energy of ion and Bjerrum defect formation drastically decreases, leading to a catastrophic growth of defect concentration up to 0.1–1 of the molecular concentration. This is equivalent to a phase transition into a superionic state, which can not have a regular lattice owing to a high defect concentration.

If the surface of ice is charged (which is the case in reality, as we have already seen in the section on surface charge and surface potential), this charge will be screened by ions and Bjerrum defects coming from the bulk, as shown in Figure 32. By taking into account the transition into a disordered

superionic state, we can transform a smooth curve of the screening charge concentration distribution into the curve with a thin superionic layer near the surface. Within the framework of this model, the high surface conductivity of ice, the formation of the quasi-liquid disordered layer and the sharp interphase boundary (detectable by optical methods) can be quantitatively accounted for. To my knowledge, Dr. Ryzhkin is currently working on the improvement of this model.

There exists a very nontrivial and unusual model of the structure and properties of the ice layer at temperatures close to the melting point. Dzyloshinskii et al. (1961) showed that a fluid that is less polarizable than its solid phase is attracted to the solid, causing a liquid film to grow at the solid/vapor interface. Elbaum and Schick (1991) applied this idea to the ice surface. Figure 33 shows the result of their calculations. If we compare this

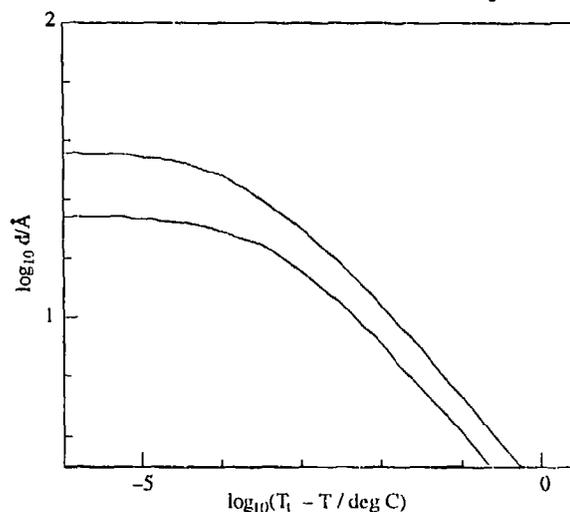


Figure 33. Calculated temperature dependence of the liquid film on ice thickness (after Elbaum and Schick 1991).

figure to the experimental results (Fig. 29), it becomes apparent that the contribution of this mechanism to the experimentally measured thickness of the quasi-liquid film is extremely small. Kroes (1992) used a molecular dynamics

computer simulation to study the surface of a small cluster of water molecules. He found such ice surface characteristics as premelting and partial polarization of molecular dipoles.

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