Electrical Properties of Ice-Solid Interfaces
Paul R. Camp and David J. Halchin, University of Maine, Orono

In the ice-water system, the principal mechanical difference between the liquid and the solid, the inability of the liquid to support a shear, is reflected in the dielectric properties. In the liquid, the molecular dipole moments easily follow electric fields up to frequencies above $10^9$ Hz. In the solid, the structure prevents them from following fields above frequencies in the audio range. Thus dielectric measurements can tell us rather directly about a particular property which is important in determining the adhesive properties of ice, the rotational mobility of the molecules in the interfacial layer. We have used electrical measurements to study the nature of the molecules at two different ice-solid interfaces. One is the ice-ice interface which occurs between differently oriented grains of ice. The other is the ice-quartz interface. Measurements have been made over a frequency range of d.c. to 10 MHz and over a temperature range 0 to -20°C on both pure and NaCl doped samples. We find that the apparent thickness of the interfacial region depends on the frequency of measurement. That is, more molecules can follow a field of 100 kHz than of 1 MHz. It also depends strongly on temperature and impurity content. Trace impurities appear to play a dominant role in the d.c. conductivity at an ice-solid surface interface even when care has been taken to ensure clean surfaces.

We are concerned here with ice (water)-solid systems. For water, the principal difference between the liquid and the solid state (the inability of the liquid to support a shear) is directly reflected in the dielectric properties. Figure 1 (from Camp et al. 1967) shows the capacitance, which is proportional to the dielectric constant, and the conductance, which is proportional to the electrical conductivity, of a sample of pure ice as a function of frequency. A temperature dependent audio-frequency dispersion is the dominant feature. By contrast, the dielectric constant of water remains almost unchanged up to a frequency of above $10^9$ Hz (illustrated by the dashed horizontal line in Figure 1). At frequencies of the order of $10^9$ Hz, water shows a dispersion similar to that of ice at $10^3$ Hz. The difference in the two cases is that the water molecules can rotate much more easily under the influence of an applied electric field in the liquid than they can in the solid. Note that the average strength of the intermolecular bond in ice is changed by only about 10% when it
to discover a way of altering this region to reduce adhesion without dissipating much energy in the bulk. A mechanism for selectively depositing high energy density in this layer would be particularly exciting. Thus it is important that we understand fully the electrical and mechanical properties of the interfacial region.

Table 1. Energy costs of various processes.

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A knowledge of the molecular interactions in the interfacial region between two materials is essential to understanding the adhesive forces between them. When two materials adhere due to an interlocking structure, they are held together by the cohesion of whichever material breaks first. This is a special case of adhesion in which both materials are the same.

If one is to modify the adhesive forces and control them, one must alter the molecular interactions in this interfacial region. Because the region is usually very thin, the energy cost of modifying it is small compared to that of most mechanical processes associated with the separation of two materials such as ice and pavement. This situation is illustrated in Table 1 which shows the energy costs for various operations and compares them to the energy costs of simply driving a small truck down the highway without doing anything with it. It is clear that one would like

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melts. But the physical characteristics are changed dramatically and the dielectric relaxation frequency is shifted by seven orders of magnitude. Thus dielectric measurements tell us rather directly about a particular property which is important in determining the adhesive characteristics of ice. For a fairly current review of the dielectric properties of ice see Hobbs (1976). Some recent developments are reported by Granicher (1977).

In the interfacial, ice-solid region we have water molecules which are influenced both by the ice structure and by the solid structure. We expect that this interaction will disorder the local ice structure and create a more water-like interfacial region. (One must admit the possibility in certain conditions of creating a more rigid rather than a less rigid structure). Such a state, intermediate between ice and water, should exhibit a dielectric response also intermediate between ice and water. If it seems probable, there is a series of layers each having different properties, there will be a series of dispersions and the total dispersion curve will be broadened. Thus dielectric measurements would seem to provide a fairly sensitive test for water molecules in different states. For example, at a frequency of 10^5 Hz, the dielectric constant of pure ice is about 3.2 and that of water is about 80. Water-like molecules whose dispersion frequency is well above 10^5 Hz will respond as water. Thus the ratio 82/3.2 = 25 works in our favor: one water-like molecule has as much effect as 25 ice-like molecules. It turns out that in certain frequency regions, one has a still larger sensitivity through the measurement of conductance. Thus electrical measurements can contribute information about the thickness and properties of thin interfacial layers.

We report below studies of the properties of this interfacial region as inferred from the electrical properties of various ice-solid configurations. Since interfacial regions are very thin, it is important to have large surface-to-volume ratios to provide enough molecules to give a measurable signal even with sensitive apparatus and the advantages cited above.

The Ice-Ice Interface

One way of obtaining large surface to volume ratios is to create ice having very small grains. Thereby one creates a large grain boundary surface area. This is an interesting approach also because it allows us to study what may be the simplest ice interface, namely the ice-ice interface. This is important in cohesion and therefore may be important in the adhesion of ice under conditions in which fracture occurs at grain boundaries rather than at the actual interface, for example when ice interlocks the solid. The analysis of a complex grain structure would be very difficult. However, if the grains can be made columnar, the grain boundaries are electrically in parallel with the grains themselves, and the analysis is simplified greatly.

Fine Grained Sample Preparation

We have developed a technique for making fine grained structures in which most of the grains are perpendicular to a given plane. This is accomplished by nucleating the growth at a very large number of sites on a plane surface. Then the surface is covered with a thin layer of water and cooled from the substrate. Because the heat of fusion is extracted through the base, the grains grow into the melt at the same rate with nearly perpendicular grain boundaries. The arrangement is illustrated in Figure 2. The myriad of small nuclei may be created by breathing on the cold substrate.

When a sample of the desired thickness has been prepared, it is melted free from the base and mounted in the measuring cell as shown in Figure 3. Our experience shows that, as a practical matter, grain sizes having a typical dimension of less than .01 mm are not easy to produce and use. This is because of the very rapid grain growth which occurs at temperatures close to melting (see Jellinek 1969). Another experimental matter which should be noted is the necessity of eliminating all air gaps between thin samples and the electrodes. A gap of 10μm with a 1 mm thick sample can seriously distort the measurement.

Fine Grained Sample Measurements

Several samples prepared and mounted in this manner have been studied and compared to similar samples of pure, single-crystal ice. From replicas of the samples taken after the measurements, we find typical grain sizes ranging from .05 mm on one sample to .12 mm on another. At low frequencies and -1°C, we find the conductivities of the different samples vary, one being just about the same as that for pure ice and others being several times as large. We attribute this variation to slight traces of impurity in the melt water. This suggests that for the purest ice, low frequency grain boundary conduction is very small. In the pure ice dispersion region (1 - 30 kHz), the bulk properties of the ice dominate our measurements and little information about the interface can be inferred.

At high frequencies one finds a significant increase in the conductivity for all samples and for some, a measurable decrease in the dielectric constant. The latter indicates that as the frequency increases, fewer and fewer molecular dipoles are able to follow the field. Thus at any given frequency the excess dielectric constant over 3.2, (the contribution due to the polarizability of the molecule itself, independent of rotation) provides a measure of the fraction of the dipoles which can follow the field. The argument is as follows: The measured dielectric constant, K_eff, is made up of two parts, a part due to a fraction, f_1, of molecules which rotate easily and are associated with the presence of grain boundaries, and a fraction f_2 which are normal bulk molecules.

The mobile molecules have a dielectric response similar to that of water (K = 80) and the immobile molecules a dielectric response due only to their polarizability (K = 3.2).

\[ K_{eff} = K_1 f_1 + 3.2 f_2 \]  

and therefore

\[ f_1 = \frac{K_{eff} - 3.2}{76.8} \]

If the change with frequency of the dielectric constant (well above the ice dispersion) is too small to measure but the change with frequency of the conductivity is large, we can also use this to give a rough value of f_1.

The electrical analogy of a Debye dispersion is a pure resistance, R, in series with a pure capacitance C. At any frequency, this can be expressed as a frequency dependent conductance, G_p,
Figure 1. Debye dispersion for high-purity single crystal ice.

Figure 2. Technique for growing fine-grained ice with columnar grains perpendicular to the surface.

Figure 3. Measuring cell for fine-grained samples.
They are related by the following equations:

$$C_p = \frac{1}{\frac{R}{\omega^2} + \frac{C}{\omega^2}}$$

$$C_p = \frac{\omega_D}{\omega + \omega_D}$$

(4)

where $\omega_D$ is the Debye frequency in radians/sec, $\omega_D = \frac{1}{RC}$. This may also be written in terms of a complex permittivity $\epsilon' = \epsilon'' - i \epsilon''$ (Smyth 1955).

$$\epsilon' = \frac{(\epsilon_0 - \epsilon\omega_D)^2}{\omega + \omega_D}$$

(5)

where $\epsilon_0$ is the permittivity at frequencies large compared with $\omega_D$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon\omega_D) \omega_D}{\omega^2 + \omega_D^2}$$

(6)

Granicher (1957) has related $\omega_D$ to the average rate of dipole rotation $W$, by $\omega_D = \frac{1}{2} W_0$.

We assume that the rise in the conductivity over one decade of frequency is due to a single Debye dispersion having a dispersion frequency $\omega_D$ in the middle of the decade. (For these rough values, the results are not very sensitive to the details of the assumption such as whether a single dispersion or a distribution of dispersion should be used). If we call this change in conductivity $\Delta \sigma$ and the related change in dielectric constant $\Delta \epsilon_0$, we have from equation 4,

$$C_p = \frac{\epsilon_0 \Delta \sigma}{\epsilon_0 - \epsilon\omega_D}$$

$$\Delta \sigma = \frac{\omega_D}{\epsilon_0 - \epsilon\omega_D}$$

Since $RC = \frac{1}{\omega_D}$ and choosing $\omega = \omega_D$ we have

$$\omega_D = \frac{\Delta \sigma}{\epsilon_0 \Delta \epsilon_0} \Delta \epsilon_0 = \frac{\Delta \sigma}{\epsilon_0 \Delta \epsilon_0}$$

(7)

This is the contribution to $K_{eff}$ of the mobile molecules in the frequency region chosen and thus is equal to 80 f for the doped sample.

For a square grain, each of the four boundaries is shared by 2 grains. Thus if $t$ is the length of a side and $\delta$ is the thickness of the boundary region, $f_1 = 2 \delta/t$. This same relation may be used for irregularly shaped grains if $t$ is a suitable "characteristic" dimension of the grain.

For the sample which, from low frequency measurements, we believe to have been our purest fine grained specimen, we have a $\Delta \sigma$ at 5 x 10^6 Hz and -1°C of about 8.5 x 10^{-6} (ohm m)^{-1}. The typical grain dimension, $t$, was about 0.05 mm. This leads to a grain boundary thickness of 5 x 10^6 Hz of about 100 Angstroms. The argument is approximate (factor of 3) but it does show very thin grain boundaries even close to the melting point when the impurity content is low. This is in general agreement with grain boundary theory (Woodruff 1973). At 10^6 Hz, one would expect even thinner boundaries.

It has been remarked earlier that the low-frequency conductivity of the fine-grained samples varied from values close to those for pure ice to values several times larger. The extreme low-frequency case is direct current. Figure 4 (a) shows a plot of d.c. conductivity of fine-grained sample number 3 as a function of temperature from nearly 0°C to -20°C. It is seen that the conductivity rises rapidly as the temperature approaches 0°C. This indicates very rapid thickening of what are probably still very thin grain boundaries. Figure 4 (b) shows similar data for a sample of fine-grained ice grown from a 0.01 molar solution of NaCl. Note that the scale is roughly 2 orders of magnitude larger. The grain boundary effect decays much more slowly as the temperature is lowered. The two curves are well described by the empirical relations

$$\sigma = 1.18 \times 10^{-6} \exp(-0.3408) \text{(ohm m)}^{-1} \text{ for Sample 3}$$

$$\sigma = 2.8 \times 10^{-4} \exp(-0.1018) \text{(ohm m)}^{-1} \text{ for doped ice}$$

(Note: conductivity here means the grain boundary conductance per square meter of a sample one meter thick).

We would like to be able to interpret these numbers as being directly proportional to grain boundary thickness. However, because impurities segregate out along the grain boundaries, the concentration of impurities in the grain boundaries will tend to decrease as the boundary region thickens. This will tend to make the true grain boundary thickness curves somewhat steeper than the conductivity curves. We conclude that the grain boundaries of the deliberately doped sample are at least a factor of 50 thinner than those of the relatively pure sample # 3.

As will be shown shortly, we believe that the grain boundary width at -1°C for the doped sample as measured at 10^6 Hz is of the order of 12µ. This means that about 6% of the sample is grain boundary region. The total d.c. conductivity at this temperature is about 2.5 x 10^{-4} (ohm m)^{-1}. Thus, the conductivity of the grain boundary region must be about 4 x 10^{-3} (ohm m)^{-1}. This is substantially less than we would expect if the grains were composed of a .01 molar solution of NaCl. It seems probable that the effective grain boundary width for d.c. conduction is significantly smaller than that for 1 MHz relaxation or that ions are strongly rejected to the melt from the grain boundary regions. A frequency scan for the doped, fine-grained ice is shown in Figure 5. This is very different from that for pure ice. At the low frequencies we find a much larger conductivity, which is expected for relatively thick grain boundaries containing fairly significant concentrations of impurities. The apparent low-frequency dielectric constant, $K$, is anomalously high which is characteristic of an electrode effect, often referred to as "polarization", which is frequently a problem in working with doped samples.

In the middle frequency range there appears to be a Debye-type dispersion with a dispersion frequency of about 4 x 10^4 Hz and a dielectric strength of the order of 100. We believe this to be a true Debye dispersion for doped bulk ice. At the high frequencies, we see a rapidly rising conductivity and a decreasing dielectric constant, $K$. Here the change in $K$ is quite resolvable and we can infer directly from it something about the fraction of water molecules which are in a more mobile state than they would be in the ice lattice.

At 1 MHz (-1°C), well above the Debye dispersion, we measure a $K$ of 7.74. Since $K$ for pure ice at high frequency is 3.2, we have an excess of 4.64 which we attribute to dipoles which are able to rotate easily. Assuming the model in which the grain boundary region is in parallel with the bulk...
Figure 4. A pure fine-grained sample #3, d.c. conductivity vs. temperature. B Doped Sample (.01 M NaCl), d.c. conductivity vs. temperature

Figure 5. Frequency dependence of dielectric constant and conductivity of fine-grained ice grown from a .01 M NaCl solution (−1°C).
we find from equation 3 that at -1°C and 1 MHz, 
f_1 = 0.059. Similarly at 10 MHz K = 5.08 and 
f_1 = 0.024. It follows that about 6% of the molecules 
can easily follow the field at 1 MHz and only about 
2.4% at 10 MHz. From the previous analysis and the 
measured t of 0.4 mm for this sample, we conclude 
that the effective thickness of the grain boundaries 
in which the molecule can follow a 1 MHz field is 
about 12 µm and that for which they can follow the 
field at 10 MHz is about 5 µm. As might be expected, 
the grain boundaries comprise an inner core of very 
mobile molecules surrounded by layers of molecules 
which are successively more ice-like.

Similar measurements made on this sample at -14°C 
give a K at 1 MHz of 4.88 and a K very close to 3.2 
at 10 MHz. Thus the core which is mobile at 10 MHz 
is too thin to resolve in this way (less than .3 µm) 
and that which responds at 1 MHz has a thickness 
δ = 3 µm.

The temperature dependence of the conductance 
and the capacitance of this sample was measured at a 
frequency of 1 MHz. From these measurements, the 
effective grain boundary thickness for this frequency 
was evaluated as above. The results are shown in 
Figure 6. Because the analysis at low temperature 
includes the differences of nearly equal numbers, 
the base-line error is large and we cannot say, at 
this stage, whether or not the thickness is 
characterized by a single activation energy.

Ice-Quartz Interface

A series of experiments has been conducted on 
thin films of ice sandwiched between quartz plates. 
The basic experimental cell is shown in Figure 7. 
The quartz plates are separated by platinum spacers 
to which the lead wires are connected. However, to 
ensure good contact to the ice regardless of thermal 
contraction as the temperature is lowered, the actual 
electrodes are very thin layers of tin evaporated 
on to the quartz. Thus the ice makes a lap joint to 
the actual contacts. The cell is guarded and 
placed in a temperature controlled chamber.

Sample Preparation

Sample lengths of 3 mm and 15 mm and thicknesses 
of 10 µm and 40 µm were used. All samples were 6 mm 
wide. The samples were prepared by cleaning the 
cells and leaching them in demineralized distilled 
water. They were then filled from the side with 
a medicine dropper, capillary action drawing the water 
in. After filling, they were cooled to 1 or 2 degrees 
below freezing and then nucleated from the side with 
an ice crystal. In this way, they grew with 
relatively large regions nearly single crystalline 
as revealed by examination in polarized light. The 
direction of the c-axis relative to the direction of 
the applied field was not known. Both a.c. and d.c. 
measurements were made on a number of samples.

Measurements on Thin Films

The a.c. measurements showed a low frequency 
capacitance characteristic of an electrode process 
falling monotonically to what was probably a stray 
capacitance of a few tenths of a picofarad at 100 KHz. 
The conductance rose monotonically with frequency but, 
because samples of this geometry do not lend themselves 
to a.c. measurement, we cannot clearly separate the part 
which is due to the electrode effect from that 
due to the ice surface. This sample geometry is 
primarily intended for d.c. or low frequency a.c. 
conductance measurements.

A typical value for conductivity at 100 KHz was 
6 x 10^-4 (ohm-m)^-1 at -18°C, dropping off to a 
very nearly constant value of 10^-5 (ohm-m)^-1 at 1 KHz. 
The high frequency value is about two orders of 
magnitude greater than that found for pure bulk 
ices. This indicates a substantial surface effect.

Direct current measurements showed conductivities 
at -18°C which varied from sample to sample. The 
highest was about 8 x 10^-5(ohm-m)^-1 and the lowest 
about 10^-5(ohm-m)^-1. This is expected because 
d.c. conductivity is extremely sensitive to trace 
impurities. For high purity ice, the d.c. 
conductivity of the bulk should be less than 
10^-2(ohm-m)^-1 (Camp 1967, Von Hippel 1971).

Figure 8 shows the temperature dependence of the 
d.c. current (proportional to conductance) as a 
function of temperature for four samples of different 
geometries. Note that the values for the 3 mm by 
10 µm sample (indicated by the symbol, O ), 
have been divided by four to make the curve shape 
comparison easier. All samples show a very sharp 
increase in conductance as the melting point is 
approached and a much slower decrease at lower 
temperatures. The process is not a simple, thermally 
activated one and the range of temperatures 
accessible does not permit a resolution into two 
avivated processes. However we can say that if 
there is a characteristic activation energy for the 
high temperature process, it is larger than 40 K-
cal/mole. We find that the variation of sample 
length is in the right direction but that the 
variation with thickness is not consistent. This is 
what we would expect for a process in which the 
surface contribution was much larger than that of 
the bulk. Trace impurities would tend to segregate 
to the surface where they would have a large effect. 
Since thicker samples would contain more total 
impurity, they could easily have a larger surface 
conductance. From these thin-film experiments, we 
conclude that even for samples prepared under clean 
conditions, trace impurities are important and that 
the surface processes dominate. They seem to be 
very strong temperature effect close to the 
melting point. It is apparent that, for experiments with 
paving materials, much thicker ice layers can be 
used because of the impurities that will be present. 
This should simplify such measurements.

Conclusions

By electrical measurements, we have been able to 
show that the ice-ice interface comprises a core of 
molecules which are much more fluid than are those 
of the bulk ice. They are surrounded by molecules 
having less and less mobility as one progresses 
away from the core toward the ice. Thus the 
effective grain boundary thickness depends on the 
frequency at which it is measured. At the specific 
frequency at which the thickness is defined, most 
of the molecules within this thickness can rotate to 
follow the a.c. field. For pure ice, the grain 
boundaries are probably so thin even at -1°C that 
only molecules in a layer a few tens of monolayers 
thick are able to rotate at frequencies significantly 
above those of the bulk ice dispersion. Even trace 
impurities contribute significantly to the 
thickness of the grain boundary and with the 
addition of .01 N NaCl, the grain boundaries thicken 
to the order of micrometers. Typical values are reviewed in Table II. Under 
these conditions, it is possible to show how the 
thickness of the interfacial layer varies both
Figure 6. Grain boundary thickness vs. temperature for doped fine-grained ice.

Figure 7. Cell and cell holder for thin film experiments.
Figure 8. Temperature dependence of d.c. current for four thin film samples of different geometry with 3 volts applied.

- O length 3 mm, thickness 10µm, x length 3 mm, thickness 40µm,
- + length 15 mm, thickness 10µm, Δ length 15 mm, thickness 40µm.

**NOTE:** O values are reduced by factor of 4 to fit on graph.
with temperature and with the frequency at which the measurements are made.

Table 2. Summary of Estimates of Grain Boundary Thickness.

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<tr>
<td>Pure #2</td>
<td>From High Frequency</td>
<td>$\delta \left(5 \times 10^6\right)$ 100 A (Order of Magnitude)</td>
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<tr>
<td>Pure #3</td>
<td>From Capacitance Data</td>
<td>$\delta \left(10^6\right)$ 700 A</td>
</tr>
<tr>
<td></td>
<td>From d.c. Compared to Doped</td>
<td>$\delta \left(d.c.\right)$ 2400 A (Order of Magnitude)</td>
</tr>
<tr>
<td>Pure #1</td>
<td>From Capacitance Data</td>
<td>$\delta \left(10^6\right)$ 1000 A</td>
</tr>
<tr>
<td>Doped</td>
<td>From Capacitance Data</td>
<td>$\delta \left(10^6\right)$ 12 µm</td>
</tr>
<tr>
<td></td>
<td>$\delta \left(10^7\right)$ 5 µm</td>
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Effective grain boundary thickness at -1°C and -14°C.

Unless otherwise noted, values are believed to be within a factor of 2.

Direct current measurements show the grain boundary conductance dropping off with decreasing temperature, but not as rapidly as does the grain boundary thickness. Perhaps this is due to the increasing concentration of ions as the grain boundary grows thinner. The d.c. conductance appears low for the salt concentration used, suggesting that the region in which ions are easily transported is much thinner than that in which dipole rotation at 1 MHz is easy, or that even in the grain boundaries significant rejection of impurities to the melt takes place.

Thin film experiments also show a strong temperature dependence of the conductivity of the surface region. They substantiate the importance of trace impurities and indicate that valid measurements can be made on practical (dirty) interfaces, such as paving materials, using fairly thick ice layers. This fact should greatly simplify such measurements.

References