

Ionic Diffusion at the Ice-Solid Interface

R. P. Murrmann, D. M. Anderson, and J. W. Peek

Diffusion of $^{22}\text{NaCl}$ at the ice-aluminum interface was determined in investigating the nature of water at this junction. The average value of the diffusion coefficient of sodium ions, determined at 6 different times ranging from 8 to 28 days after introduction of the ions to the interface, was 9.4×10^{-8} and $4.5 \times 10^{-8} \text{ cm}^2/\text{sec}^{-1}$ at -5 and -10 C respectively. Comparison of these values with the diffusion coefficient for ionic diffusion in bulk liquid water, $D \cong 10^{-5} \text{ cm}^2/\text{sec}^{-1}$, and with that expected for ionic diffusion in ice, $D < 10^{-11} \text{ cm}^2/\text{sec}^{-1}$, indicates that the properties of the interface are considerably different from those of either bulk liquid water or ice. Lack of any consistent time dependence of the diffusion coefficient suggests that the nature of the interface was little disturbed by the addition of sodium chloride. These observations support the view that a transition zone 5 to 10 Å thick with liquid-like properties exists at this interface. A model of this concept of the ice-solid interface is proposed.

Development of methods for prevention or removal of adhering ice requires consideration of the factors that define each icing problem. A few of the most obvious and recurrent of these factors include the size and shape of the substrate surface, its physical location, micrometeorological conditions, and time and other economic considerations. Thus, a solution proposed for shipboard icing is not likely to be appropriate for treatment of aircraft wings, runways, power lines, windshields, antennas, refrigeration pipes, or roads. Faced with the diversity of icing problems and the different factors governing their occurrence, we might easily, if not inadvertently, deemphasize or overlook the essential aspects common to each. In attempting to create a condition at the ice-substrate interface that will preclude ice accumulation or facilitate ice release, we believe that an understanding of the nature of this interface is desirable and perhaps even essential, considering that up to now attempts to solve ice adhesion problems have with few exceptions resulted in limited success.

A few investigators of the phenomenology of ice adhesion have attempted to interpret their results in terms of the properties of the ice-substrate interface. Notable among several studies that have been undertaken from this point of view is that of Jellinek (8). He measured the shear and tensile strength of ice adhering to stainless steel, quartz, and several plastic surfaces directly. Although he found that cohesive breaks in bulk ice were common during the tensile experiments, adhesive breaks nearly always were observed with shear tests provided that the tests were carried out above -13 C. With decreasing temperature, however, shear strength increased until eventually only cohesive breaks occurred. To account for these results, Jellinek adopted Weyl's concept of a "liquid-like" interface (14), postulating that the properties of water there are intermediate between those of liquid water and ice. The specific properties of the interfacial zone were thought to be dependent on the nature of the substrate surface and temperature. Although Jellinek visualized a thickness of as much as 10^{-5} cm near 0 C, he felt that the thickness of the liquid-like zone surely decreased with decreasing temperature, accounting for the concomitant increase in adhesive strength. Jellinek explained the observed high tensile strength as being due to surface tension effects, whereas the relatively low shear strength was explained by the low frictional resistance of the liquid-like interface. This concept is supported by the results of many other types of experiments. Hoekstra (6), for example, has shown that glass beads embedded in ice migrate under the influence of a thermal gradient. This was explained as a consequence of a continual melting of ice and flow of water in a relatively thick film at the

warm side of a bead to the cold side where refreezing occurs, thus advancing the position of the bead. Hoekstra also used a similar argument to explain the mechanism of particle exclusion by an advancing ice front. Telford and Turner (13) investigated the rate of movement of a steel wire under an applied load through ice as a function of temperature. Calculations showed that the pressure of the wire on the ice would cause a freezing point depression of about 0.5 C. In harmony with this prediction, the velocity of the wire through the ice was observed to increase markedly with an increase in temperature above about -0.5 C. Surprisingly, however, the wire moved through the ice at temperatures below -0.5 C, the velocity decreasing with decreasing temperature. Because this movement could not be accounted for by the conventional concept of "pressure melting," the authors presented their results as evidence for the existence of a zone of liquid-like water at the steel-ice interface. They attributed the temperature dependence observed to changes in viscosity of the interfacial water that resulted from a concurrent decrease in film thickness and temperature.

At about the same time, Raraty and Tabor (12) reported the results of shear experiments to determine the adhesive strength of ice to metal and polymer surfaces. Qualitatively, their results were remarkably similar to those of Jellinek; however, a different explanation was advanced. For metals, they explained the temperature dependence of the shear strength on the basis of a change in ductility of ice in the region near the interface during what was viewed as a cohesive failure. In agreement with Jellinek, they reported brittle fracture of ice at lower temperatures. In the case of plastics, they did find evidence of a true adhesive break, but in either case Raraty and Tabor hold that the adhesion strength of ice results from a direct bonding of ice to the substrate.

Landy and Freiberger (9) investigated the shear strength of ice to a series of plastic substrates having a wide range of surface characteristics. Water surface tension, thermal expansion, porosity, dielectric constant, and flexural modulus of various substrates were correlated with the measured adhesive strength of ice. When the plastics were grouped on the basis of similar surface bonding characteristics, it was possible to obtain a correlation between flexural modulus and adhesive strength. Thus, it appeared that in the case of these materials the ice-substrate bonding strength was so strong that mechanical deformation of the substrate occurred. Also, the adhesion strength depended on the various types of ice-substrate bonds formed.

The nature and properties of the interface between ice and silicate substrates recently were discussed by Anderson (1). From several lines of evidence it was concluded that the interfacial zone is fluid with a thickness greater than 15 Å near 0 C to about 3 Å at temperatures of -10 C and below. At low temperatures the mobility of the interfacial water appears to be very much diminished, and it may even possess the properties of a glass. A phase diagram showing the relationships that exist among the interfacial water, water vapor, and ice also was presented together with a discussion of the effect of changes in temperature and pressure.

Most recently, Bascom et al. (3) investigated the shear strength of ice on steel, on steel covered with monolayers of various adsorbents, and on plastic-coated metal surfaces. To better determine the mechanism of failure, they obtained plastic replicas of the sheared ice surface to reveal fracture markings and crystal defects. The replicas indicated that the dislocation density near an interface was much higher than that of bulk ice, and it appeared that the glide plane of these defects was parallel to the interface. This observation provides an alternate explanation of Jellinek's finding that the ice-substrate interface appeared stronger in tension than in shear. The dependence of the ice adhesive strength on temperature and the nature of the substrate was partially accounted for on the basis that differences in thermal conductivity between various substrates might well influence the rate of accumulation of defects at the interface. Materials with a relatively low thermal conductivity would be expected to have more interfacial defects because the cooling rate from 0 C to a given test temperature would be lower allowing more time for defect accumulation. Taking this view of this evidence, Bascom proposed, as did Itagaki (7) earlier, that it is more appropriate to consider the ice-substrate interface as a defect-rich solid rather than as a zone with liquid-like properties.

Thus, it appears from this somewhat abbreviated treatment of the recent literature that, although there is a general agreement in a qualitative sense among the various investigators on the importance of factors such as substrate type, surface roughness, temperature, and surface contamination, there are 2 distinctly different points of view as to the nature of the ice-solid interface. Clearly research on the mechanism of ice adhesion should be directed toward resolving this problem. Jellinek (8) has suggested several useful approaches. This paper deals with one of them, the measurement of diffusion coefficients at the ice-solid interface.

The rate of diffusion of a molecule through a liquid or solid matrix depends on the energy barrier encountered in moving from one equilibrium position to another. For a given substance in the liquid state where short-range order with weak intermolecular bonding exists, the diffusion coefficient of a molecule is high relative to that for diffusion through the same crystalline substance where long-range order with strong bonding between adjacent molecules exists. Hence, one possible way of determining whether the interfacial zone at the ice-substrate contact is relatively thick and liquid-like on the one hand or solid-like with many lattice defects on the other is to measure the diffusion coefficient of some suitable substance confined in this zone and to compare the values thus obtained to those measured in known liquids and solids. This combined with the measurement of the adhesive strength of ice to the same substrates should provide a better understanding of the nature and characteristics of this interface. In this investigation we report preliminary values for the diffusion coefficient of $^{22}\text{Na}^+$ at the ice-aluminum interface to serve as a basis for more refined measurements.

EXPERIMENTAL

The substrate selected for this preliminary investigation was aluminum. This selection was made because aluminum is a common metal used in many applications in which ice adhesion is an important problem. To obtain a suitable configuration for the experiment, we used polished aluminum weighing dishes. Although the dishes were carefully cleaned to remove organic surface films and soluble salts, no attempt was made to remove or to prevent formation of aluminum oxide at the air-aluminum interface. Thus, the existence of an oxide layer may be assumed. Two sets of dishes were filled with distilled water to a depth of approximately 1 cm and frozen. One set was kept in a cold room maintained at -5 C and the other set was kept in a second room maintained at -10 C . Although some air bubbles were observed in the ice, the ice-aluminum interface was bubble-free. This simple method of preparing the samples was adopted after it was found that more elaborate methods did not seem to yield significant improvements. For example, considerable time was devoted to the development of a closed system for degassing the carefully cleaned surfaces prior to forming the ice-solid interface without exposure to the atmosphere. Although it was found that the shear strength of the ice-substrate bond increased and that the scatter in the data decreased slightly relative to values obtained by direct freezing in a cold room, the small improvement hardly warranted the elaborate effort required. The most important factor in obtaining reproducible shear strength values seemed to be the degree to which gross contaminants were removed from the test surfaces.

After equilibrating for 24 hours, the samples were treated as shown in Figure 1. The dishes containing the ice were inverted and a small hole was made through the aluminum in the bottom center of each dish by means of a dissecting needle. Next, a $1\text{-}\mu\text{l}$ aliquot of carrier-free, aqueous $^{22}\text{NaCl}$ solution having a total activity of about $0.05\ \mu\text{C}$ was carefully introduced through the hole onto the ice by means of a $10\text{-}\mu\text{l}$ liquid syringe. Upon contacting the ice, the droplet froze upward, excluding $^{22}\text{NaCl}$ and leaving the isotope free to diffuse from the ice-air interface into the ice-aluminum interfacial region surrounding the point of deposition.

Use of a radiotracer keeps contamination of the interface to a minimum because the detection sensitivity of a radiotracer is very high. Consequently, a very small amount of tracer suffices. The proper choice of radioisotope depends primarily on the detection method that can be used for a given experiment. In any case, the radioisotope used should be in a carrier-free, high specific activity, neutral pH form. In this case,

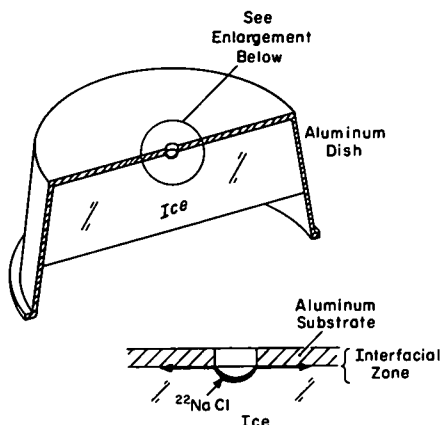


Figure 1. Application of $^{22}\text{NaCl}$ to the ice-aluminum interface.

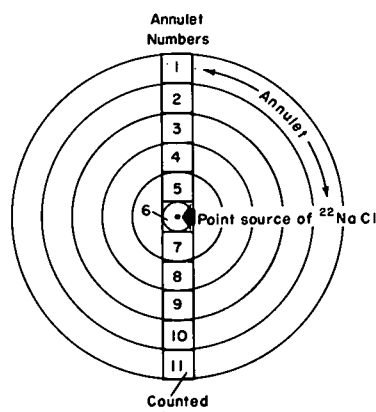


Figure 2. Determination of radial distribution of ^{22}Na at the ice-aluminum interface.

$^{22}\text{NaCl}$ was a convenient choice because in the analysis the sample was sectioned and separated during counting so that gamma radiation from adjacent sections did not interfere with the measurement. If the sample could not have been sectioned, direct-counting or an autoradiographic method using a weak beta-emitting isotope might have been employed.

Diffusion was allowed to proceed for periods ranging from 8 to 28 days to check on the time-dependence of the diffusion coefficient. At appropriate times, samples were then transferred to a freeze-dry apparatus where the ice was sublimed away from the interface leaving $^{22}\text{NaCl}$ in place on the aluminum substrate. The aluminum dishes were carefully sectioned as shown in Figure 2. First, the side of the dish was cut away, and a strip 0.4 cm wide and 4.4 cm long was cut from the bottom of the dish. Each strip was then further subdivided into 11 segments 0.4 cm on edge. The center segment from the strip contained the hole through which $^{22}\text{NaCl}$ had originally been injected. The ^{22}Na activity of each segment was then determined by using a scintillation detector in conjunction with a timer-scaler. The radial distribution of ^{22}Na was found by calculating the total activity in an "annulet" from the activity of a given segment. As Figure 2 shows, this procedure resulted in 2 values for each annulet.

The boundary conditions of this experiment correspond closely to those defining diffusion outward from an instantaneous point source over an infinite planar surface. The solution of Fick's law for this case is given by Crank (4) as

$$C = \frac{M}{4\pi Dt} \exp\left(\frac{-r^2}{4Dt}\right) \quad (1)$$

where in this case C is the activity of ^{22}Na in cpm, M is the total ^{22}Na activity added as determined by summing the activities for each annulet in cpm, D is the diffusion coefficient in $\text{cm}^2/\text{sec}^{-1}$, t is time in sec, and r is the radial distance from the point of application to the center of a given annulet ring in cm. Inasmuch as Eq. 1 can be rewritten as

$$-\log_{10}\left(\frac{C}{M}\right) = \log_{10}(4\pi Dt) + \frac{r^2}{9.2Dt} \quad (2)$$

the diffusion coefficient of $^{22}\text{Na}^+$ in the interfacial zone can be evaluated from the slope of a plot of $-\log(C/M)$ versus r^2 . Although D can also be calculated from the intercept, there is more error involved because of uncertainty in the value for M .

RESULTS AND DISCUSSION

Plots of $-\log_{10} (C/M)$ versus r^2 made by using data obtained for 6 times ranging from 8 days to 28 days at both -5 and -10 C are shown in Figure 3. The lines drawn through the points represent a least squares fit. Although there is a fairly high degree of scatter in the distribution of data points for each experimental condition, it is clear that the data are best represented by a straight line as predicted by the model described earlier. The reason for the scatter is undetermined, but it could have been caused by a redistribution of $^{22}\text{NaCl}$ that may have resulted from sample handling or during the sublimation step of the experimental procedure.

The values of the interfacial diffusion coefficients calculated from the slope of the lines shown in Figure 3 are given in Table 1. At -5 C, the diffusion coefficients at different times ranged from 7.0×10^{-8} to 13.0×10^{-8} with an average value of 9.4×10^{-8} $\text{cm}^2/\text{sec}^{-1}$. Similarly, at -10 C, a range of 2.1×10^{-8} to 6.4×10^{-8} with an average of

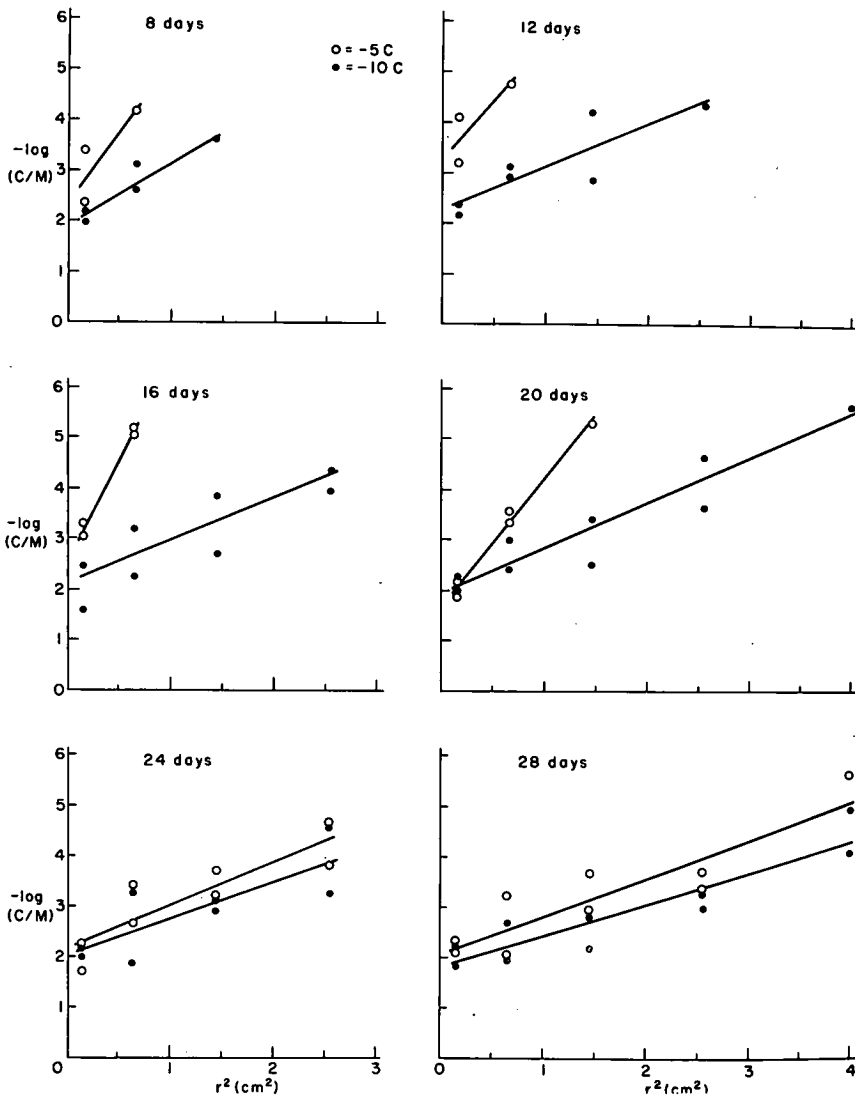


Figure 3. Calculation of diffusion coefficient of Na^+ at the ice-aluminum interface.

$4.5 \times 10^{-8} \text{ cm}^2/\text{sec}^{-1}$ was observed. Thus, decreasing the temperature from -5 to -10 C decreased the value of the diffusion coefficient by about a factor of two. Lack of a clear-cut and consistent trend in the observed diffusion coefficient as a function of time suggests that the variation in values obtained at both temperatures arises from experimental error. For the experiment conducted at -5 C, even though the values do not change by more than a factor of two with time, the data given in Table 1 might indicate a real time dependence. If the trend is real, because diffusion obviously is more rapid at -5 C than at -10 C, it might be explained by a depletion of tracer at the source. It should be noted that if diffusion were a result of freezing point depression effects caused by the $^{22}\text{NaCl}$ solute, the diffusion coefficients would be expected to decrease with time because of progressive dilution. However, the lack of a strong time dependence supports the view that the added $^{22}\text{NaCl}$ did not appreciably disturb the interfacial zone.

Values of the diffusion coefficients of a soluble salt in liquid water are of the order of $10^{-5} \text{ cm}^2/\text{sec}^{-1}$ (5). Although the diffusion coefficients of salts in ice have not been determined, the values are not expected to exceed $10^{-11} \text{ cm}^2/\text{sec}^{-1}$, the value for the self-diffusion coefficient of water molecules in ice (11). The diffusion coefficient of Na^+ obtained during this investigation is intermediate to these values. The value obtained is, if anything, closer to that for diffusion in liquid water than that expected in ice. This finding indicates that Na^+ is highly mobile at the ice-aluminum interface compared to its mobility in ice. Although these results do not rule out either the liquid-like interface concept or the solid but defect-rich interface concept, it is clear that the interfacial zone possesses characteristics that definitely distinguish it from normal ice. Also, the observed diffusion rates are hardly compatible with a liquid-like interfacial zone several hundred molecular diameters thick as Jellinek (8) suggested might be present; they are too low. The diffusion coefficients obtained in this study are comparable in magnitude to those obtained by Murrmann et al. (10) in an earlier study of sodium self-diffusion in a frozen clay-water matrix. From the evidence advanced by Anderson (1), there can hardly be any doubt that the interfacial zone in the clay-water matrix consists of unfrozen, liquid-like water; and, as shown by Anderson and Hoekstra (2), the thickness of this interface at -5 and -10 C is of the order of 10 and 5 Å respectively. From this correspondence, it appears that if the ice-aluminum interface is viewed as also consisting of a layer of liquid-like unfrozen water, its thickness must be comparable, that is to say 5 to 10 Å. A representation of the ice-aluminum substrate that is compatible with this view is given in Figure 4. The diagram is drawn roughly to scale, but the thickness of the interfacial zone is slightly exaggerated to

TABLE 1
DIFFUSION COEFFICIENT OF Na^+ AT THE ICE-ALUMINUM INTERFACE

Time Following Application of $^{22}\text{NaCl}$ (days)	$D \times 10^2 (\text{cm}^2/\text{sec}^{-1})$	
	-5 C	-10 C
8	13.0	5.7
12	12.5	4.5
16	9.4	2.1
20	7.2	2.4
24	7.0	6.4
28	7.2	5.9
Avg.	9.4	4.5

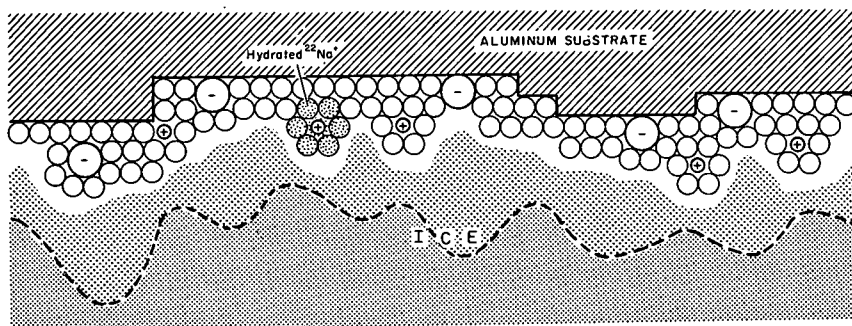


Figure 4. Schematic diagram of the ice-aluminum interface.

show the possibility of fully hydrated ions and a defect-rich zone in the adjacent ice. The soluble substances may be impurities but, in any case, are always present because of dissolution of the substrate interface. Although on the present balance of evidence, we favor the concept shown in Figure 4, it must be acknowledged that the data do not rule out the defect-rich solid interface concept of Itagaki (7) and Bascom (3). This controversy probably will not be resolved until the crucial experiments are done on substrates for which the surface roughness is known to be less than the presumed thickness of the interfacial zone, say 3 Å or less. Further work designed to decide this issue is planned.

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Informal Discussion

H. H. G. Jellinek

It is unfortunate that I used the term liquid-like layer about 15 years ago when some of this work was done. It would have been better to have called it a transition layer, meaning that there is a transition in coming from bulk ice to bulk water. Now, in his experiments, Bascom postulates a high number of defects in the interface. With that method you would not be able to determine any of the liquid interface; it would miss the transition layer altogether. But if there are no defects, of course, then it is a question of semantics as to whether you call that a transition layer or you call the liquid side the transition layer. I think the idea of starting with the defects and then going into a more liquid-like structure is the right approach. As far as the diffusion

is concerned, we have recently measured the diffusion of radioactive cesium in polycrystalline ice, and at -6 C it is on the order of 10^{-10} . The diffusion coefficient is dependent on the concentration of the cesium. You have to consider 2 types of diffusion in polycrystalline ice: the bulk diffusion going through the ice grains and the grain boundary diffusion, which is the same type of diffusion as in metals. Mr. Murrmann shows that the diffusion coefficient depends on the time. We have measured the grain size distribution in polycrystalline ice. If you measure the distribution as a function of time, or the average diameter of the grain as a function of time, it increases with time—small ones disappear and the interfacial area becomes smaller—so the diffusion should get smaller as time goes on, and I think that is what Mr. Murrmann found.

Murrmann

We found that the diffusion coefficient did become smaller.

Jellinek

That means the grains become larger with time, and of course the boundary diffusion is slower than the grain boundary diffusion. There is less grain boundary as you go on in time. That is my explanation of the dependence of diffusion coefficient on time.

Murrmann

A second explanation, of course, is the fact that as you put a point source you are introducing a contaminant at the interface and this may effectively create a liquid-like layer itself. The effect of this would be that the diffusion coefficient would decrease with time because of the dilution that occurs with time. In another case at -10 C , it seemed to be constant within the experimental results that we had; so it is hard to make a point of this. This is certainly something that must be taken into consideration when an approach like this is used. The idea is to find under what conditions an interfacial zone exists or does not exist. The other point that Dr. Jellinek brought out is one that should be taken more seriously; that is, when do you start calling something defect-rich and liquid-like? This becomes a matter of debate, which is a waste of time as far as I am concerned. A great deal of evidence accumulated indicates that the molecules next to a surface, maybe not the adjacent molecules but the layer next to that, are highly mobile and also, in many cases, highly associated. Therefore, things happen in these layers of water very close to surfaces that you would not expect to happen in bulk ice—a surface chemical activity one might observe.

H. R. Kivisild

I agree that which of the ideas is right is really a point of semantics. Because we found out that the large effects of roughness could be explained by the assumption of a liquid-like layer and could not be explained by the assumption of interfacial deformation, we rather favor the change to a liquid-like form.

Jerrold L. Colten

Have you been able to determine any effect on rate of cooling of the substrate when you come down very rapidly in your freezing test? I am alluding to the rate of crystalline growth within the ice itself.

Murrmann

We have not studied this ourselves. We have in preliminary work drawn ice at different temperature and different cooling rates and tried to do some shear tests. Allowing an aging period of a day or two, we were not able to tell much difference. Others have investigated these different factors. I think that what is important apparently, judging from what other investigators report, is the fact that a recrystallization near the interface does occur, and that in making shear tests such as we did you must allow a sufficient period of time for this reorientation to occur near the inter-

face or else it will occur during the course of the experiments and will shed some doubt on what you are doing.

Lorne W. Gold

Do you take into account in any way the possible thickness of the diffusing layer at the surface?

Murrmann

There is really no way to tell whether you are dealing with a thick layer or a thin layer. I can only mention what we have done with other systems that are colloidal minerals in which you can actually measure the thickness between adjacent clay plates. There is also other evidence that leads you to believe what the thickness would be between, say, clay plates and different minerals and ice surfaces. In these cases we have found that the diffusion coefficient is the same order of magnitude as I have pointed out. Also, we have been able to measure the thickness directly; actually it was done by Dr. Hoekstra and Dr. Anderson at USACRREL. In this case it turns out to be 10 Å units, or 9 units. The point I would like to make is that, if there is a liquid-like layer, we feel that very probably it is very close to the surface and very thin. Then it becomes semantics again where it ends in terms of the defect structure.

David Brohm

I would like to make an observation from the practical point of view. For many years, some excellent observations have been made by good practical people that road chemicals commonly used appear to act most beneficially in breaking the ice-to-pavement bond in the interface region. The practical point made by highway maintenance staff and by technical representatives of the firms selling winter ice control chemicals was the augur action of salt and calcium chloride in crystal form, which penetrated through the ice or snow layers to the interfacial region where it broke the ice-to-pavement bond. It is in this bond-breaking that we get the most efficient and most economical use of our chemicals.

According to Mr. Carey's remarks this morning, in some instances 35 tons of chemical per lane mile may be applied to a highway for winter ice control. Extend this to the 12- to 14-lane expressway and the aggregate exceeds 400 tons of chemical per linear mile. We can only describe this as an unacceptable level of environmental pollution. We propose additional research is most warranted to determine better ways to apply and use the chemical to optimize the bond-breaking mechanism to determine the minimum amounts of chemical necessary to give the necessary bond-breaking at the interface, and to develop all of these considerations as steps to optimum ice control with a minimum of pollution.

Murrmann

I hope that the main benefit to the sort of research that I have described here and what Dr. Jellinek has described in the past will create a better understanding of the problem. Things move faster when you understand what is going on. I am not proposing that this research will lead to a practical solution, though perhaps it can.

Jellinek

I mentioned in my paper that very small amounts of inorganic chemicals decrease the mechanical strength of ice very effectively, not by melting it but by going into the grain boundary and decreasing the mechanical strength. You need only 10^{-3} molar lithium chloride or sodium nitrate or some other salts or some organic substances. For instance, 3 ppm of hydrogen fluoride decreases the mechanical strength of ice by one-half. So you need only very small amounts of chemicals to get a weak interface. This has been shown by Smith-Johanssen at General Electric and by Pounder at McGill. You do not need to put tons of inorganic chemicals on the road to melt the ice. Very small amounts make the interface weak, and then it can be pushed off very easily.