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Physical Mechanisms Responsible for Ice Adhesion

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We studied an electrostatic model of ice adhesion based on the existence of the surface states of protonic charge carriers on the surface of ice. At distances greater than one intermolecular distance, the model gives an order of magnitude for the adhesive energy, which is significantly greater than both chemical bonding energy and van der Waals forces. It also provides an understanding of the time- and temperature-dependent phenomena that explain the difference between adhesive properties of ice and water.

1. Introduction

Ice adhesion produces numerous problems in many areas of human activity: ice removal from roads and icing of airplane wings, helicopter blades, ships, and power lines. The development of materials with low adhesion to ice is a very important problem. Its solution requires a fundamental understanding of the physical mechanisms of bonding between ice and other solids. In particular, one needs to know the nature and strength of molecular bonding between ice and various solids. Why does ice adhere to any solid, even to hydrophobic materials? What changes occur over time in ice adhesion? To answer these questions, fundamental theoretical and experimental studies are needed.

It is reasonable to classify all possible mechanisms into one of three groups: a covalent or chemical bonding mechanism, a dispersion of or fluctuation in electromagnetic interaction (van der Waals forces), or a direct electrostatic interaction.¹

The first mechanism corresponds to the chemical reactions and the formation of interfacial compounds. In covalent or chemical bonding the adhesive energy results from lowering of the quantum-mechanical energy of the system due to overlap of the wave functions of the interacting solids. Such an interaction is essential only at a distance on the order of 0.1–0.2 nm. In addition, this type of adhesion is very sensitive to the chemical nature of adhesive solids. In a perfect contact, the chemical bonding mechanism can provide adhesive energy of ≥ 0.5 J/m². The latter value has been obtained from the definition of chemisorption (bonding energy higher than 0.5 eV per molecule²), so it can be considered the lowest value of adhesion energy for the chemical bonding mechanism.

In contrast to chemical bonding, van der Waals forces are long-range and act between all substances. These forces are defined only by the macroscopic characteristics of a solid (dielectric function at different frequencies), and for this reason they are rather insensitive to experimental conditions.^{3,4} This circumstance, together with the availability of an advanced theory of dispersion forces formulated by Dzyaloshinskii et al.,⁵ accounts for the ubiquity of this mechanism. In the case of ice this mechanism has been studied by Elbaum and Schick⁶ and by Wilen et al.⁷

In addition to chemical bonding and dispersion forces, two solids that contain noncompensated or spatially separated charges will also generate electrostatic forces. Historically this is probably the oldest mechanism recognized; it has been known

for more than 2000 years. Its importance has been rediscovered by Stoneham and Tasker⁸ rather recently. A detailed review of the role of electrostatics in adhesion has also been given by Hays.⁹ To the best of our knowledge, there have been no studies of the electrostatic contribution to ice adhesion. In this paper we describe a simple model that is based on a theory of the electrical properties of the surface of ice (Petrenko and Ryzhkin¹⁰). The model reveals a connection between the ice adhesion problem and other properties of ice. We compare our model with van der Waals forces, with the chemical bonding mechanism, and with experimental results.

The main conclusion is that the electrostatic interaction plays a significant, if not major, role in ice adhesion. The key point of our model is the ordering of water molecules adjacent to the ice/solid interface or, in other words, the appearance of the surface states for protonic charge carriers. So the problem is reduced to the study of water molecule behavior at the solid surface, which can be done by computer simulation. However, in the following sections we will simply assume that there exist surface states that can be occupied by protonic point defects. The occupancy of these surface states is defined by the interplay between the Coulomb energy of captured charge carriers and the energy depth of the surface states. Then, either the occupancy coefficient of a surface state (in the nonequilibrium case) or the energy depth of the surface state will be taken as a parameter.

Finally, we shall study the effect of surface charge density on the energy of the interaction between ice and a metal plate. This electrostatic mechanism will be compared with others, and ways to improve our model in future studies will be discussed.

2. Model and Basic Results for Electrostatic Mechanism

Ice consists of polar water molecules that strongly interact with any solid substrate which has dielectric permittivity different from that of ice. In addition, there is a great deal of theoretical and experimental evidence for the existence of a surface charge in ice.^{10,11} This surface charge can also interact with the substrate. Here we assume that the surface charge originates from the capture of protonic charge carriers by the ice surface. The captured defects are presumably D defects, H₃O⁺ ions, or protons. Actually, positive ions are smaller in size than negative ones, because they have fewer electrons or do not have them at all and exist as protons. Thus we can use the image charge theory for smaller distances, where the potential energy of the charge and its image may be less than the charge energy within the ice. For negative ions of larger size it is much more difficult to reach this. At thermal

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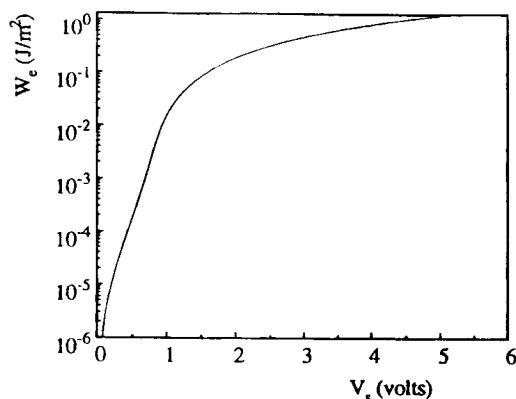


Figure 1. Graph illustrating the electrostatic energy of the screening layer of ice per surface unit, W_e , vs surface potential, V_s ($T = -10^\circ\text{C}$).

equilibrium the occupancy of surface states cannot be perfect, because the gain in energy due to captured charge carriers is compensated for by the rise in electrostatic energy. However, the electrostatic energy itself can be reduced significantly by charge redistribution inside the substrate (by induced charges). This could lead to perfect occupancy of the surface states and rather high adhesion energy (close to the electrostatic energy).

The spatial distribution of charge carriers in the subsurface layer of ice has been calculated by us previously.¹⁰ The first integral of Poisson's equation can be written in the following form:

$$E = \frac{\sigma_0}{\epsilon\epsilon_0} f(V) \quad (1)$$

where E and V are the electric field strength and electrostatic potential, respectively (both are functions of the space coordinate z); $\sigma_0 = e_B \lambda N$; e_B is the effective charge of Bjerrum defects; N is the concentration of water molecules; λ is the screening length given by $\sqrt{\epsilon\epsilon_0 kT/e_B^2 N}$; ϵ and ϵ_0 are the dielectric permittivities of ice (≈ 3.2) and a vacuum, and k and T are the Boltzmann's constant and the temperature, respectively. The function $f(V)$ is defined by the following equations:

$$f(V) = \sqrt{\ln(a(V) a(-V) b^2(V) b^2(-V))} \quad (2)$$

$$a(V) = \frac{\exp(E_f/2kT) + (4/3) \exp(e_i V/kT)}{\exp(E_f/2kT) + 4/3} \quad (3)$$

$$b(V) = \frac{\exp(E_B/2kT) + \exp(e_B V/kT)}{\exp(E_B/2kT) + 1} \quad (4)$$

Here we used Bjerrum defects as charge carriers being captured in the surface states. Equation 1 holds at any point of the ice crystal. Applying it to the ice surface, we get the relationship between the surface charge density σ_s and the surface potential V_s : $\sigma_s = \sigma_0 f(V_s)$.

It is now easy, using eqs 1–4, to calculate the electrostatic contribution to the adhesion energy of ice. First, let us calculate the electrostatic energy of the screening layer of ice as a function of the surface potential. This energy is very important, because it gives the upper limit for the adhesion energy. Using the definition of electrostatic energy and eq 1, we get

$$W(V_s) = \int_0^\infty \frac{\epsilon\epsilon_0}{2} E^2 dx = -\frac{\sigma_0}{2} f(V) \frac{dV}{dx} dx = \frac{\sigma_0}{2} \int_0^V f(V) dV \quad (5)$$

The graph of W_e vs V_s is pictured in Figure 1. Perfect occupancy

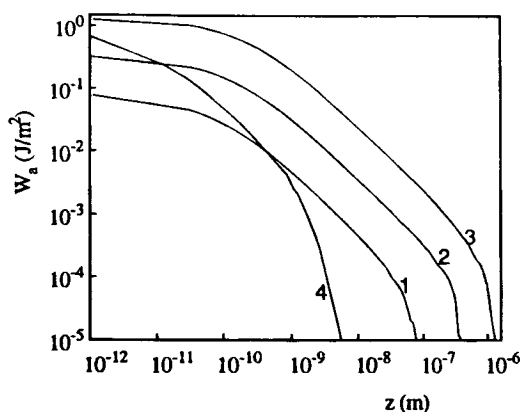


Figure 2. Graph illustrating the adhesive energy of the ice/metal interface per surface unit, W_a , as a function of distance, z . Curves 1, 2, and 3 correspond to perfect occupancy by D defects, H_3O^+ ions, and protons, respectively (fixed occupancy curves). Curve 4 depicts the equilibrium dependence of adhesion energy on distance for proton surface states ($T = -10^\circ\text{C}$).

by Bjerrum D defects, positive ionic defects H_3O^+ , or protons gives the values of the surface potential $V_s \approx 1.47, 2.50$, and 5.13 V, respectively. According to Figure 1, complete occupancy of the surface states by Bjerrum defects, H_3O^+ ions, and protons would correspond to an upper limit of adhesion energy of $0.8, 0.32$, and 1.35 J/m², respectively. The smaller values are for imperfect occupancy. Using the relationship between the surface charge density and surface potential, it is easy to recalculate this energy vs surface charge density.

Now let us consider a metallic plate at a distance d from an ice surface. The nonuniform charge distribution in the ice will induce a surface charge on the metal and, therefore, an electric field between the ice and the metal plate. The total electrostatic energy of the system per unit area can be written in the following form:

$$W_e(d, V) = \frac{\sigma_0^2 d}{2\epsilon\epsilon_0} \left[f(V) - \frac{\sigma}{\sigma_0} \right]^2 + \frac{\sigma_0}{2} \int_0^V dV \quad (6)$$

However, V in eq 6 is the surface potential of ice, which has to be found from minimization of the energy for each value of distance d . Note that at this time we consider surface charge density to be a constant. Physically, that could correspond to a nonequilibrium occupancy of the surface states. Performing a minimization procedure for $W_e(d, V)$, we arrive at the adhesion energy per unit area as a function of d :

$$W_a(d) = W_{\min}(d) - W_{\min}(\infty) \quad (7)$$

This function is pictured in Figure 2 for the same cases of perfect occupancy by the Bjerrum D defects, positive ionic defects H_3O^+ , and protons, shown as curves 1, 2, and 3, respectively.

Under equilibrium conditions the surface charge density of ice, σ , increases with a decrease in the distance, d , because of screening of the ice surface charge by an induced charge on the metal plate. Indeed, in this case the Coulomb energy of captured charge carriers decreases, so higher occupancy becomes possible. In considering this case one first has to sum up the electrostatic energy, the energy gain due to occupancy of the surface states, and the entropy contribution of the surface defects:

$$F = \frac{d\sigma_0^2}{2\epsilon\epsilon_0} \left[f(V) - \frac{\sigma}{\sigma_0} \right]^2 + \frac{\sigma_0}{2} \int_0^V f(V') dV' - \frac{\sigma}{e} E_0 + \frac{kT}{e} \left[\sigma \ln \left(\frac{\sigma}{\sigma_m} \right) + (\sigma_m - \sigma) \ln \left(1 - \frac{\sigma}{\sigma_m} \right) \right] \quad (8)$$

Here E_0 is the energy of surface states (assuming $E_0 = -0.5$ eV), $\sigma_m = e/S$, and S is the surface area of one water molecule. Then the free energy F has to be minimized over V and σ . This procedure also assumes that the chemical potential of the ice bulk is kept constant and equals zero. Doing so for every value of d , we arrive at the equilibrium free energy as a function of the distance or equilibrium adhesion energy. This is pictured in Figure 2 (curve 4, for protons).

A similar procedure enables us to find the equilibrium occupancy of the surface state or the surface potential of ice as a function of the energy of surface states E_0 or temperature. Let us assume that the metallic plate is infinitely far from the ice surface. Then, to minimize the first infinite element in eq 8, we have to assume $\sigma = \sigma_0 f(V)$. Then F becomes a function of only one parameter, either V or σ . It is somewhat easier to perform the final minimization over V , but the results can be recalculated as a function of σ as well. The occupancy coefficient of the surface states with D defects plotted vs surface state energy is shown in Figure 3. The surface state energy level is measured with respect to the chemical potential of D defects in the bulk.

3. Discussion and Future Studies

As can be seen from our results, typical values of the adhesion energy are located between 1.3 and 0.08 J/m², depending on the type of charge carriers and the energy of their surface states. This magnitude is comparable to or even higher than the experimentally measured adhesion energy of ice/metal interfaces at -20°C which were found in the range 0.093–0.104 J/m² for four different metals.¹³ In fact, it is as high as values for the chemical bonding mechanism. However, in contrast to the latter, the electrostatic mechanism remains significant up to a larger distance (about $10r_{00}$; $r_{00} = 0.276$ nm). Thus, at distances larger than r_{00} , the electrostatic mechanism is significantly more important than the chemical bonding one. Our calculations also show that at distances greater than r_{00} , the electrostatic energy exceeds that of the van der Waals forces, if the Hamaker constant equals 3×10^{-20} J.¹ Note that the last estimation concerns an ice/ice (or water/water) interface, but not an ice/metal interface, as do curves 1, 2, 3, and 4 in Figure 2. The van der Waals interaction between ice and metal, which is also a long-ranged one, has not been considered in this paper, and this will be the subject of our future research.

We should emphasize the long-range character of the electrostatic mechanism: the adhesive energy equals 0.01 J/m² even at $z \approx 90r_{00}$ for the maximum density of a surface charge. Note also that the adhesive energy for a nonequilibrium detaching experiment should be higher than that for an attaching one. The latter can be explained by the almost perfect screening of electrostatic energy by a metallic plate when ice and metal are in contact. It is rather easy to understand the behavior of adhesion energy with distance in equilibrium experiments. At small distances a metallic plate screens the electrostatic energy and we have high adhesive energy, because the occupancy of surface states is high. However, when the distance increases, the electrostatic energy increases as well, and we arrive at the lower occupancy coefficients and a lower surface charge density. Compare curves 3, 2, and 1 in Figure 2. These are equivalent to the more rapid decay of free energy with distance than in the case of constant occupancy.

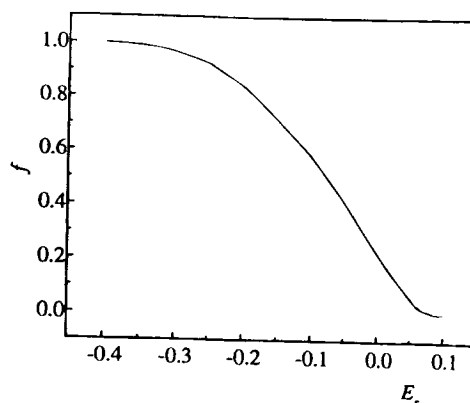


Figure 3. Graph illustrating the occupancy coefficient of the surface states for D defects, f , as a function of surface states energy, E_s ($T = -10^\circ\text{C}$).

We also studied the behavior of the occupancy coefficient (for the model of the surface states for D defects) as a function of the surface state energy, E_s . The occupancy coefficient is close to zero when $E_s \approx 0.1$ eV, Figure 3. One reason for the charge carriers being captured into the surface states with positive energy has to do with the entropy gain in the free energy. For the same reason, defects exist in the ice bulk. Note that for the bulk D defects the "creation energy" equals 0.34 eV per defect, and this energy is significantly greater than 0.1 eV. Eventually this leads to an "occupancy coefficient" for the bulk states on the order of 3×10^{-7} .

We did not consider any time-dependent phenomena associated with ice adhesion; however, we should note here that such phenomena are inherent in our model. In order to enter or leave the surface state, defects have to overcome some electrostatic barrier, and this leads to nonequilibrium situations and time-dependent phenomena.

Since the key element of the proposed model is electrostatic attraction between the ice surface charges and the charges induced in metals, the very same mechanism is applicable to the ice/insulator interface. The only difference is in the magnitude of the induced charges. A charge q on the ice surface induces the "image charge" $-q$ in a metal, while the very same charge q will induce a smaller "image" charge q' in the insulator:

$$q' = q \frac{\epsilon - 1}{\epsilon + 1}$$

where ϵ is the dielectric permittivity of the insulator. In most of solid dielectrics ϵ is much bigger than 1 and the induced charges are comparable with ones induced in metals. The lower ϵ is, the lower the electrostatic-related adhesion is. For instance, Teflon, with its lowest $\epsilon = 2.04$, is well-known for its low adhesion to ice. But of course, accurate calculations of W_a for insulators are needed. This work is now in progress.

Finally, we would like to explain why ice is more adhesive than water. In our model, the answer to this question is very simple and intuitive. Due to much higher concentrations of charge carriers in water, the screening of the surface charge in water (if it is present) is much more effective than in ice (the corresponding initial electrostatic energy is much less than in ice). Thus the screening of the electric field due to the substrate cannot lower the energy significantly. Note that at temperatures close to the melting point of ice a thin liquid layer may appear on the ice/solid interface.¹² We are currently working on a model that includes the effect of surface premelting on ice adhesion.

4. Conclusions

The electrostatic model of ice adhesion reveals the relationship between the electrical properties of the surface of ice and ice adhesion. The model gives a correct order of magnitude for the adhesive energy. The electrostatic interaction between ice and metals supplies energy that is significantly higher than chemical bonding energy and van der Waals forces at distances greater than intermolecular ones. It also provides an intuitive way to understand the time- and temperature-dependent phenomena that help explain the difference in adhesive properties of ice and water.

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