

# Measuring the Thickness of the Liquid-like Layer on Ice Surfaces with Atomic Force Microscopy

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Atomic force microscopy was used to study the surface melting of ice in a temperature range above  $-35$  °C. The thickness of the liquid-like layer ( $d$ ) on ice was determined from the jump-in distance of force-versus-distance curves. The layer thickness of ice formed from distilled water was roughly 32 nm at  $-1$  °C and 11 nm at  $-10$  °C. The temperature dependence of  $d$  could best be described by  $d \propto -\log \Delta T$ , where  $\Delta T$  is the difference between the melting temperature and the actual temperature. The addition of salt increased the thickness of the liquid-like layer, and the temperature dependency agreed with predictions by Wettlaufer (*Phys. Rev. Lett.* **1999**, *82*, 2516).

## 1. Introduction

Surface premelting has been detected on many different materials such as metals, semiconductors, rare gas crystals, and organic crystals. The melted layer on the surface does not necessarily have the same properties of normal liquids. Therefore, it is usually called a "quasiliquid" or a "liquid-like" layer. The first documented hypothesis of a liquid-like layer on ice was in a paper from 1859 by Faraday.<sup>1</sup> He deduced its existence from experiments on the adhesion of ice. The liquid-like layer plays an important role in the flow behavior of ice and snow, the adsorption of substances onto ice, and the low friction of solids on ice.<sup>2</sup> Nowadays, the existence of a liquid-like layer on ice is generally accepted. Measurements of its thickness, however, differ significantly, in some cases by a factor of 100.<sup>2</sup> Methods such as ellipsometry,<sup>3–6</sup> X-ray scattering,<sup>7,8</sup> proton channeling,<sup>9</sup> nuclear magnetic resonance (NMR),<sup>10–12</sup> scanning tunneling microscopy (STM),<sup>13</sup> and atomic force microscopy (AFM)<sup>14–18,20</sup> have been employed to examine its properties (for a review, see refs 2 and 21).

One important aspect is the temperature dependency of the layer thickness because the dependence contains information about the intermolecular forces which cause layer formation. We used AFM to measure systematically the thickness of the liquid-like layer versus temperature. With AFM, the mechanical properties of a surface are probed by measuring force-versus-distance curves. Hence,

the information complements the results from other techniques. In a typical force experiment, the sample mounted to a piezoelectric translator is moved toward the tip of an atomic force microscope cantilever. Forces between the tip and the sample lead to a deflection of the cantilever. Multiplying the deflection with the spring constant of the cantilever gives the value of the force. In experiments with the ice surface, the tip experiences an instability when approaching the ice surface. At a certain distance, it jumps through a layer which has mechanical properties similar to those of a liquid. We identify that layer with the liquid-like layer on ice; then the jump-in distance is, as a first approximation, equal to the thickness of the liquid-like layer. For this paper, we measured the dependence of the jump-in distance on temperature. To study the influence of ionic strength, we have compared the results obtained with pure ice to results with ice containing 10 mM KCl.

One reason for measuring the temperature dependency of the thickness of the liquid-like layer,  $d(T)$ , is that it contains information on the strength and distance dependency of the molecular interactions leading to its formation. There is no unique relation between  $d(T)$  and the molecular interactions. Still, assuming a force law for the molecular interactions leads to a prediction of  $d(T)$ , which can then be tested experimentally.

This can be illustrated with a model developed by Lacmann and Stranski,<sup>22</sup> Dash,<sup>23</sup> and Takagi.<sup>24</sup> In this model, the whole ice–vapor interface is divided into two interfaces, namely, the bulk ice–liquid-layer interface and the liquid-layer–vapor interface. The total surface energy

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of the ice–vapor interface,  $\gamma$ , is then considered to be the sum of three contributions: the interfacial energy of the bulk ice–liquid–layer interface ( $\gamma_{SL}$ ), the interfacial energy of the liquid–layer–vapor interface ( $\gamma_{LV}$ ), and a term which contains the thickness of the liquid-like layer ( $\Delta\gamma$ ). In the limit of vanishing layer thickness, the surface energy is equal to the surface energy of the bare solid ice surface:  $\gamma(d=0) = \gamma_S$ . At large layer thicknesses, the total surface energy is the sum of the two interfacial energies:  $\gamma(d \rightarrow \infty) = \gamma_{SL} + \gamma_{LV}$ . In the intermediate case, the surface energy is interpolated by a suitable function  $f$  according to  $\gamma(d) = \gamma_S + \Delta\gamma f(d)$ , with  $\Delta\gamma = \gamma_{SL} + \gamma_{LV} - \gamma_S$ . The function  $f$  becomes 0 for  $d = 0$ , and  $f$  becomes 1 for  $d \rightarrow \infty$ . The condition that in equilibrium the Gibbs free energy is minimal leads to an equation for the equilibrium thickness of the liquid-like layer:

$$q_m \frac{\Delta T}{T_m} = - \frac{\Delta\gamma}{\rho_L} \frac{\partial f}{\partial d} \quad (1)$$

where  $q_m$  is the latent heat of fusion,  $\Delta T = T_m - T$  is the difference between the melting temperature ( $T_m$ ) and the actual temperature ( $T$ ), and  $\rho_L$  denotes the density of the liquid. The choice of  $f(d)$  depends on the surface force acting between the solid–liquid and the liquid–vapor interfaces. For van der Waals forces,  $f(d) = d^2/(d^2 + \sigma^2)$  was suggested,<sup>22,25</sup> where  $\sigma$  is a typical interatomic distance. Inserting this and assuming that  $d \gg \sigma$  leads to

$$d = \left( -\frac{2\sigma^2 \Delta\gamma T_m}{\rho_L q_m \Delta T} \right)^{1/3} \quad (2)$$

A more general expression,  $d = (-2\sigma^2 \Delta\gamma / \rho_L q_m \times T_m / \Delta T)^\alpha$ , is derived from  $f(d) = d^n / (d^n + \sigma^n)$ , with  $\alpha = 1/(1+n)$  (see also ref 26). For an exponentially decaying force between the two interfaces,  $f(d) = 1 - \exp(-d/\lambda)$  is expected. Here,  $\lambda$  is the decay length. This leads to a logarithmic dependence of the equilibrium thickness on the temperature.<sup>21</sup>

$$d = \lambda \ln \left( -\frac{\Delta\gamma}{\rho_L q_m \lambda} \frac{T_m}{\Delta T} \right) \quad (3)$$

The parameters  $n$  and  $\lambda$  can be determined experimentally.

The advantage of this simple model of the ice surface is that it allows the interpretation of measured layer thicknesses in a relatively universal way. One should, however, keep in mind that severe assumptions are made and that it is not a thermodynamic model in a strict sense. One assumption is that the liquid-like layer wets the bulk ice. The validity of this assumption was questioned by Makkonen.<sup>27</sup> He observed contact angles larger than 25° between water and ice. The total surface energy is a thermodynamic function which can in principle be measured under equilibrium conditions. The quantity of  $\gamma_S$ , however, is not. The surface energy is strictly defined for equilibrium conditions, and a bare solid ice surface is not at equilibrium with its vapor (at a given temperature). Hence,  $\gamma_S$  should only be considered as a parameter of the model. The energies of the water–ice and the water–vapor interfaces can in principle be measured and are thermodynamic quantities. However, if the liquid-like layer is not similar to bulk water, then  $\gamma_{SL}$  and  $\gamma_{LV}$  are also not thermodynamic quantities and should only be

considered as parameters of the model. Another limit of the model is that it does not account for a possible inhomogeneity of the liquid-like layer. Hence, if there is no real interface between the liquid-like layer and the bulk ice but the viscoelastic properties gradually change, the model is not valid. Despite these limitations, a power law dependency of the layer thickness on  $\Delta T$  is confirmed by detailed calculations considering van der Waals forces between the molecules.<sup>28,29</sup>

## 2. Methods and Materials

All AFM measurements were done with the commercial Multimode NanoScope III (Digital Instruments). We used two different kinds of V-shaped cantilevers: silicon nitride cantilevers (Digital Instruments; 110  $\mu\text{m}$  long, 0.6  $\mu\text{m}$  thick, gold-coated on the backside, resonance frequency  $\sim 40$  kHz) with a spring constant of about 0.2 N/m and tip curvature radii of 25–60 nm<sup>30</sup> and silicon cantilevers (Silicon-MDT Ltd., Zelenograd Research Institute of Physical Problems, Moscow, Russia; 290  $\mu\text{m}$  long, 1  $\mu\text{m}$  thick, resonance frequency  $\sim 10$  kHz) with a spring constant of typically 0.12 N/m. Their backsides were coated with aluminum, and the tips had radii of curvature smaller than 20 nm and were coated with about 10 nm of silicon nitride. In previous experiments, Preuss and Butt<sup>31</sup> demonstrated that in the temperature range from 22 to 200 °C the spring constant does not change. Therefore, it is unlikely that the spring constants depend significantly on temperature between –30 and 0 °C. Cantilevers were tilted by roughly 7° with respect to the sample surface. Cantilever deflection was determined by focusing the beam of a laser diode (initial power 1 mW) onto the back of the cantilever. To avoid significant heating of the tip,<sup>32</sup> we reduced the intensity of the laser beam to 0.1 mW with an optical filter.<sup>18</sup> A segmented photodiode was used to measure the position of the reflected beam. The time resolution of the electronics was fast compared to the resonance frequency of the cantilever. The z-component of the piezo scanner was calibrated at room temperature, as described in ref 33. It changed by roughly 0.5%/°C.

To obtain force-versus-distance curves, we converted the original deflection-versus-position curves by  $z = z_{\text{piezo}} - z_{\text{def}}/m_{\text{cl}}$ . The variable  $z$  is the distance between the tip and the sample surface;  $z_{\text{piezo}}$  is the piezo scanner position in nanometers,  $z_{\text{def}}$  the deflection signal of the cantilever in volts, and  $m_{\text{cl}}$  the slope of the linear, retracting part of the contact line in volts per nanometer. The term  $z_{\text{def}}/m_{\text{cl}}$  is the deflection of the cantilever in nm. It corrects for the cantilever bending. The force is  $F = K z_{\text{def}}/m_{\text{cl}}$ .  $K$  denotes the spring constant. We would like to point out that for determining the jump-in distance, this conversion was not necessary. Hence, the jump-in distance did not depend on the spring constant or the conversion factor  $m_{\text{cl}}$ .

A new sample was used for each experiment. All experiments were done in a freezer which could be cooled to –40 °C. The air humidity determined with an electronic thermohygrometer was  $85 \pm 5\%$ . Temperature was measured with a thermocouple device (accuracy 0.5 °C absolute), which was positioned directly above the ice. The temperature difference between the position of the thermocouple and the ice surface was less than 1 °C.

Ice samples were prepared in two different ways. The first method is freezing a drop of  $\sim 100$   $\mu\text{L}$  of Millipore water (conductivity 0.06  $\mu\text{S}/\text{cm}$ ) on a freshly cleaved mica sheet at a temperature lower than –30 °C. Since the water layers were only  $\sim 1$  nm thick, they froze within seconds. We have no possibility of determining the crystalline properties of our samples. Ice frozen in this way is probably polycrystalline. The second method of preparation is cooling Millipore water on a freshly cleaved mica sheet by evaporation in a vacuum. The water

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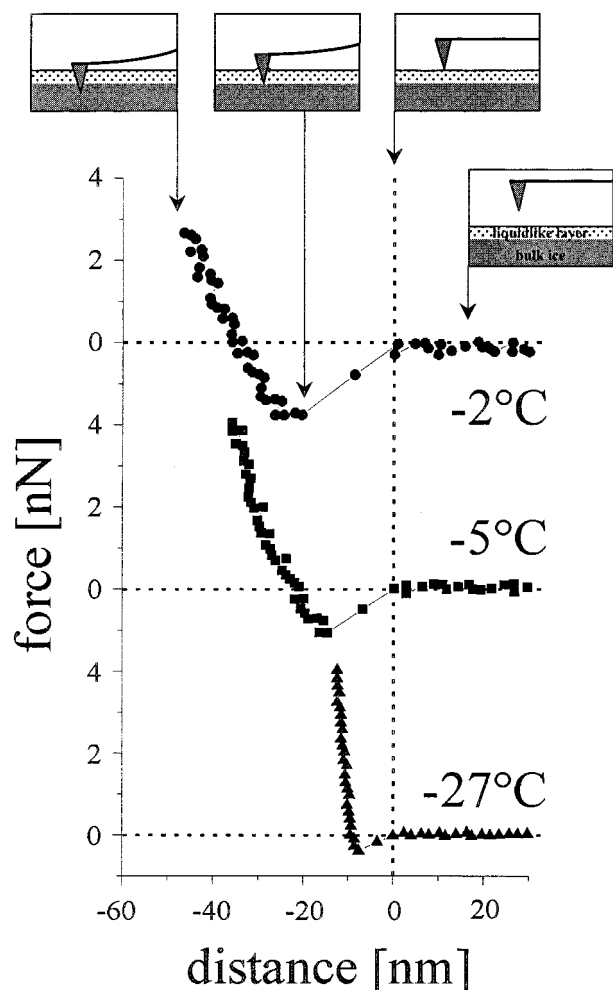
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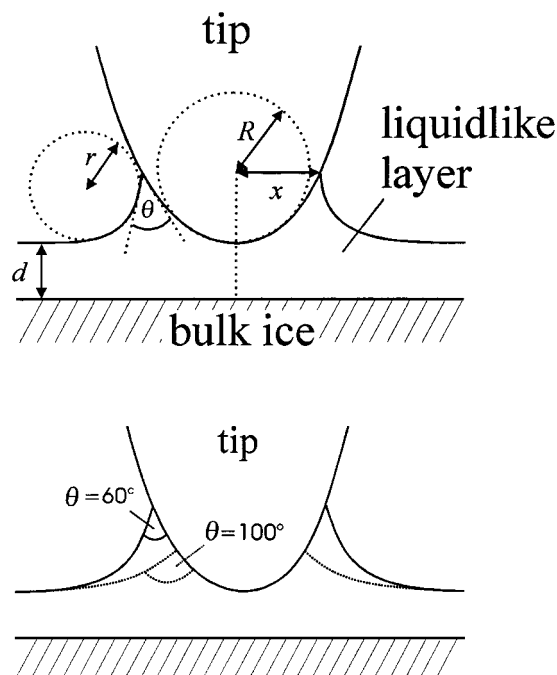


**Figure 1.** Approaching part of force curves measured at  $-27^{\circ}\text{C}$  (triangles),  $-5^{\circ}\text{C}$  (squares), and  $-2^{\circ}\text{C}$  (circles). "Zero distance" was defined at the surface of the liquid-like layer. The assumed position of the tip is indicated schematically for the force curve taken at  $-2^{\circ}\text{C}$ .

was thermally insulated from the bottom and sides of the vacuum chamber. This leads to the formation of a single crystal, as described in ref 34. Unfortunately, we cannot determine the orientation of the crystal. Contamination due to ions desorbing from the mica surface can probably be neglected. Even if one ion per unit cell is dissolved in the ice, the ion density is only about  $5\ \mu\text{M}$ .

### 3. Results and Discussion

**Interpretation of Force Curves.** Figure 1 shows the approaching parts of force-versus-distance curves (called "force curves") measured at temperatures of  $-27$ ,  $-5$ , and  $-2^{\circ}\text{C}$ . They were measured at a frequency (measured force curves per second) of 10 Hz. The frequency influences the force curves only at frequencies smaller than about 2 Hz.<sup>18</sup> While the tip is far away from the ice, the force on the tip is zero. At a certain distance the tip jumps into contact with the surface. We call that distance the "jump-in" distance (Figure 2). When the tip is in contact and the sample is perfectly rigid, one expects a vertical line in the force-versus-distance curve, since the position of the tip with respect to the sample surface should not change anymore. Force curves measured on ice deviate from a straight vertical line because the tip penetrates the ice. Such a penetration was observed and discussed before.<sup>16–18</sup>



**Figure 2.** Sketch of the AFM tip image just after touching the liquid-like layer on the ice surface after meniscus formation but before jump-in (top). For a hydrophilic tip with a low contact angle, the meniscus rises higher than on a hydrophobic tip with a high contact angle; but even on a hydrophobic tip, the meniscus is still present (bottom).

Detailed calculations using a modified plastic deformation model indicate that it is probably caused by time-dependent plastic deformation of the ice.<sup>17,19</sup> We assume that the observed change in the slope of the force curve between the jump-in and the contact parts separates the processes of surface melting and plastic deformation. In this paper, we do not discuss the penetration but concentrate on the jump-in distance.

The jump-in is probably caused by the capillary force. As soon as the tip comes into contact with the surface of the liquid-like layer, it is wetted by the liquid. The bending of the water surface at the meniscus causes a negative Laplace pressure, which pulls the tip onto the ice surface. This process is fast and limited only by the resonance frequency of the cantilever. A simple estimation shows that the capillary force is strong enough to pull the tip onto the surface. The capillary force can be approximated by  $F_{\text{cap}} \approx \gamma_{\text{LV}} \pi x^2 / R \approx 4\pi R \gamma_{\text{LV}} \cos \theta$ . Here,  $R$  is the tip radius of curvature,  $\gamma_{\text{LV}}$  is the surface tension of the liquid-like layer, and  $\theta$  is the contact angle of the liquid-like layer on the tip surface. The parameter  $x$  is shown in Figure 2. Using typical values of  $R = 20\ \text{nm}$ ,  $\gamma_{\text{LV}} = 0.076\ \text{N/m}$  (at  $T = 0^{\circ}\text{C}$ ), and  $\theta = 0$ , we obtain a force of 19 nN. In addition, the surface tension of water causes a downward force<sup>35</sup> of  $2\pi x \gamma_{\text{LV}}$ .

The jump-in caused by the capillary force is relatively independent of the tip properties. The reason is that a certain degree of wetting is expected even if the contact angle of the liquid on the tip surface is significantly larger than  $0^{\circ}$ . The liquid meniscus rises around the tip until it has formed the equilibrium contact angle at the three-phase contact line. For a hydrophilic tip with a low contact angle, the meniscus rises higher than on a hydrophobic tip with a high contact angle (Figure 2, bottom). However,

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since the capillary force is so strong, even hydrophobic tips immediately jump to the surface.

There are serious doubts that the liquid-like layer on pure ice is completely homogeneous and can be treated as a separate phase. It could well be that there is a transition layer from the solid to the vapor phase.<sup>49,50</sup> Our experiments done at temperatures lower than  $-2\text{ }^{\circ}\text{C}$ , however, all showed a clear step change of the viscoelastic properties of the ice surface. At this step, the ice becomes much harder and stops the jump-in movement of the tip. Only force curves taken at temperatures around  $-1\text{ }^{\circ}\text{C}$  showed a gradual transition, and no clear change in the slope of the force curve was observed after the jump-in.

#### Corrections and Exclusion of Possible Artifacts.

The jump-in distance is not precisely equal to the thickness of the liquid-like layer. Two corrections have to be considered. First, the distance between two data points is 2 nm. This experimental uncertainty results in an offset between 0 and 2 nm, which we cannot determine more precisely. Therefore, we have subtracted the mean value 1 nm from all our results. Second, the van der Waals attraction can cause a jump-in even before the tip touches the liquid-like surface. For a tip with a radius of curvature  $R$  interacting with a plane, the van der Waals force can be approximated by  $F_{\text{vdW}} = HR/6d^2$ .  $H$  is the Hamaker constant. For solids or liquids interacting across gas it is on the order of  $H \approx 5 \times 10^{-20}\text{ J}$ . An attractive force leads to a jump-in of the tip when the gradient of the attraction exceeds the spring constant of the cantilever. For the cantilevers used in our experiments, the van der Waals force leads to a jump-in at about 1 nm above the liquid-like layer. It is not possible to determine this distance exactly, since the radii of the tips and the spring constants of the cantilevers are difficult to measure, but even for unfavorable combinations (large radius and small spring constant or vice versa), it is never more than 2 nm. This distance has to be subtracted from the jump-in distance to obtain the thickness of the liquid-like layer. Fortunately, both corrections are small compared to measured jump-in distances.

An additional factor which might have increased the jump-in distance is the deformability of the liquid-like layer. Before the tip actually touches the liquid surface, attractive forces might lead to a bulging-up and a locally increased thickness. Also, the vapor might condense into the closing gap between the tip and ice surface and form a meniscus. A number of observations, however, indicate that these two effects were not significant:

- We used a relatively high driving speed of the piezo ( $20\text{ }\mu\text{m/s}$ ), and the jump-in distance did not change when force curves with frequencies above 2 Hz were taken.

- We measured force curves with tips made hydrophobic by silanization with dichlorodimethylsilane. Contact angles on similarly prepared planar surfaces were around  $90^{\circ}$ . If capillary condensation or a bulging-up of the liquid-like layer was significant, jump-in distances obtained with silanized tips should be smaller than with original hydrophilic tips. Experiments, however, did not show reduced jump-in distances.

- As will be shown, jump-in distances on ice made of distilled water differ from jump-in distances on ice containing 10 mM KCl. Such a difference would not be expected if capillary condensation or a deformation of the liquid-like layer would contribute significantly.

- If capillary condensation were significant, we would expect a similar jump-in on hydrophilic samples such as mica. Jump-in distances on mica were, however, significantly smaller. We found a constant jump-in distance of about 4 nm between  $+20$  and  $-20\text{ }^{\circ}\text{C}$ .

A jump-in due to electrostatic forces is unlikely: Bluhm and Salmeron<sup>20</sup> have determined the thickness of the liquid-like layer by comparing contact mode and scanning polarization force microscopy (SPFM) images. In SPFM, a bias voltage is applied to a conducting tip with respect to the grounded sample holder, which induces a polarization charge distribution on the sample surface. From the fact that the SPFM images were similar at both positive and negative biases, Bluhm and Salmeron concluded that the contribution from contact potential differences is minimal.

#### Liquid-like Layer of Ice from Distilled Water.

Figure 3 shows the thickness of the liquid-like layer as a function of  $\log \Delta T$ . Ice samples were prepared by freezing water at temperatures lower than  $-30\text{ }^{\circ}\text{C}$  (Figure 3a) and by evaporation in a vacuum (Figure 3b). In both cases, the thickness of the liquid-like layer increased with increasing temperature from  $\sim 11\text{ nm}$  at  $-10\text{ }^{\circ}\text{C}$  to  $\sim 32\text{ nm}$  at  $-1\text{ }^{\circ}\text{C}$ . We observed no significant difference between curves measured on differently prepared ice samples. The dependence of the layer thickness on temperature can best be described with  $d = a - b \log \Delta T$ , where  $a = 32\text{ nm}$  and  $b = 21\text{ nm}$ . These parameters are the mean values of six different experiments. Three experiments were done on ice samples frozen in the freezer (resulting in  $a = 35\text{ nm}$  and  $b = 22\text{ nm}$ ). The other three samples were prepared in the vacuum chamber (resulting in  $a = 30\text{ nm}$  and  $b = 20\text{ nm}$ ). In both cases, the statistical error for the parameters of one experiment was about  $\pm 5\%$ .

The statistical errors do not represent the measured variations of  $a$  and  $b$  in separate experiments under the same conditions. For  $a$ , we found values between 23 and 43 nm;  $b$  varied between 12 and 27 nm. We have no explanation for this variation. Systematic errors might result from small changes of air humidity, impurities in the ice, or different orientations of crystal faces.

Assuming a power law dependence of the layer thickness on temperature ( $d \propto \Delta T^{-\alpha}$ ), we found exponents  $\alpha$  between 0.5 and 0.9. The mean value was  $\alpha = 0.65$ . The resulting parameter varied by  $\pm 9\%$ , which is significantly greater than with the logarithmic fit. In addition,  $\alpha$  depended on the temperature range where it was determined. If only values measured below  $-10\text{ }^{\circ}\text{C}$  were taken into account, the exponents became higher, and the mean value shifted to  $\alpha = 0.92$ . This variation of  $\alpha$  and the larger error

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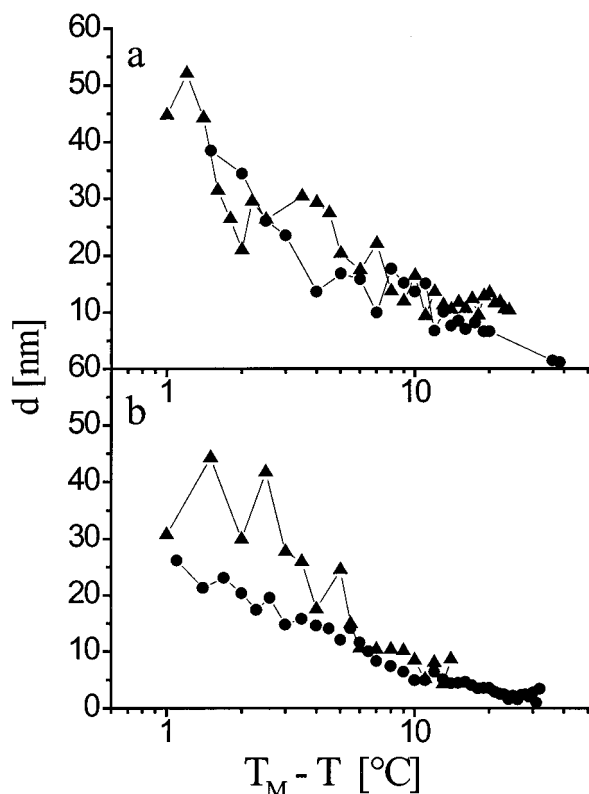
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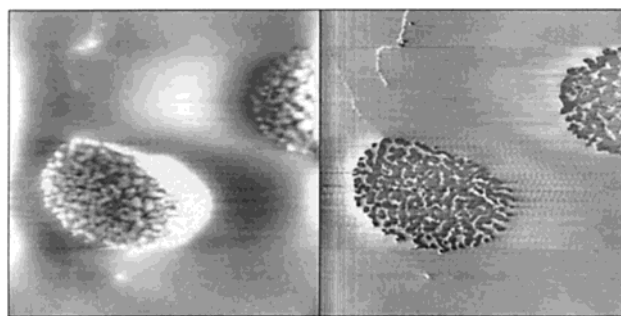
**Figure 3.** Thickness of the liquid-like layer on ice ( $d$ ) vs the difference between the melting temperature ( $T_M$ ) and the actual temperature ( $T$ ). The ice samples were frozen (a) below  $-30\text{ }^\circ\text{C}$  in a freezer and (b) by evaporation in a vacuum. The layer thickness is equal to the jump-in distance minus 2 nm. Triangles and circles correspond to different experiments done under the same conditions.

underline that the behavior of the layer thickness can better be described with  $d \propto -\log \Delta T$ , which does not systematically change with the selected temperature range.

The linear dependence of the layer thickness on the logarithm of  $\Delta T$  was first proposed on theoretical grounds by Fletcher<sup>36</sup> in 1973. He found the approximation  $d(\text{nm}) \approx 2-5 - 2.5 \log \Delta T$ . This logarithmic dependence of layer thickness on temperature was found experimentally by Lied et al.<sup>37</sup> They have studied the surface melting of ice  $I_h$  single crystals by glancing-angle X-ray scattering. Both Fletcher and Lied et al. found layer thicknesses significantly smaller than our values. Our results are on the same order of magnitude as those determined by Golecki and Jaccard<sup>9,38</sup> using proton channeling. They found that  $d(\text{nm}) = (94 \pm 17) - (54 \pm 14) \log \Delta T$ , which is about two times higher than our results. The parameter  $a$  is the layer thickness at  $-1\text{ }^\circ\text{C}$ . Other authors have also found, at this temperature, layer thicknesses significantly larger than  $10\text{ nm}$ <sup>5,6,9,38</sup> (for review, see ref 2).

Petrenko also used AFM to determine the jump-in distance on ice.<sup>15</sup> At a temperature of  $-10.7\text{ }^\circ\text{C}$ , he found a mean value of  $3.5\text{ nm}$ , which is smaller than our values, although in two cases he found similar jump-in distances of  $13$  and  $16\text{ nm}$ , which agree with our measurements. Bluhm et al.,<sup>20</sup> using AFM and SPFM, found a layer thickness of  $5 \pm 0.5\text{ nm}$  between  $-20$  and  $-10\text{ }^\circ\text{C}$  for thin layers of ice on mica.

According to the previously described theory, the observed logarithmic growth of the liquid-like layer indicates that surface melting of ice is not dominated by long-range van der Waals forces, but by exponentially decaying interactions between the bulk ice-liquid and



**Figure 4.** Height (left) and friction (right) image of a frozen  $10\text{ mM}$  KCl aqueous solution at  $-26\text{ }^\circ\text{C}$ . The scan size is  $14\text{ }\mu\text{m}$ . The domains show that the KCl partly crystallized out.

liquid-vapor interfaces. An exponential function is characterized by its decay length. To find this decay length  $\lambda$ , we can write eq 3 in the form

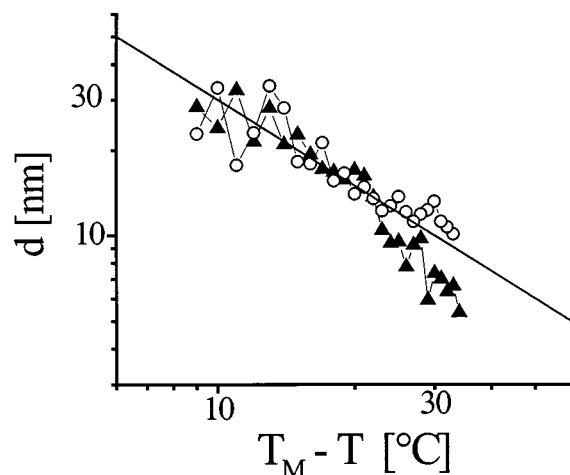
$$d = \lambda \ln \left( -\frac{\Delta \gamma T_m}{\rho_L q_m \lambda} \right) - 2.3 \lambda \log \Delta T = a - b \log \Delta T$$

Since both terms are independent, we can determine the decay length  $\lambda$  directly by  $\lambda = b/2.3 \approx 9\text{ nm}$ . Using  $a = 32\text{ nm}$ ,  $\lambda = 9\text{ nm}$ ,  $\rho_L = 998\text{ kg/m}^3$  (water at  $-10\text{ }^\circ\text{C}$ ), and  $q_m = 334\text{ kJ/kg}$ , we obtain  $\Delta \gamma = \gamma_{SL} + \gamma_{LV} - \gamma_S = -0.384\text{ J/m}^2$ . To estimate  $\gamma_S$ , we have to assume certain values for  $\gamma_{SL}$  and  $\gamma_{LV}$ . The surface stress of the ice-water interface has been measured to be around  $0.13\text{ J/m}^2$ .<sup>43,44</sup> Other measurements gave a lower value of  $0.01\text{--}0.035\text{ J/m}^2$ .<sup>45</sup> If  $\gamma_{LV}$  is assumed to be similar to the surface tension of water ( $76\text{ mJ/m}^2$  at  $0\text{ }^\circ\text{C}$ ), the estimated surface energy of a bare solid ice surface would be  $\gamma_S \approx 0.5\text{ J/m}^2$ . This is in the same range as that of surface energies of ionic crystals.<sup>46,47</sup>

The experimentally found expression  $d(\text{nm}) = 32 - 21 \log \Delta T$  can be used to calculate the temperature  $T_S$  at which surface melting starts. We obtain  $T_S = -34\text{ }^\circ\text{C}$ . The fact that even below  $-22\text{ }^\circ\text{C}$  a liquid-like layer exists does not agree with the theories of Fukuta<sup>48</sup> and Makkonen.<sup>27</sup> They assumed that forces of the molecules from the ice interior acting on surface molecules cause a pressure which is so high that the surface ice melts. Pressure melting, however, is only possible above a temperature of  $-22\text{ }^\circ\text{C}$ .

**Influence of Salt.** Salt in the ice is one possible contribution to surface melting (see Wettlaufer).<sup>39</sup> Elbaum et al.,<sup>3</sup> who used an optical reflection technique, even concluded that "it appears that the presence of air or other contaminants induces surface melting". To study the influence of salt, we measured force curves on ice by cooling water containing  $10\text{ mM}$  KCl. During the freezing process, part of the salt crystallized out. Figure 4 shows height (left) and friction (right) images of a frozen  $10\text{ mM}$  KCl aqueous solution at  $-26\text{ }^\circ\text{C}$ . Friction was determined by measuring the lateral deflection of the AFM tip. The scan size is  $14\text{ }\mu\text{m}$ . Salt domains on the surface are clearly visible. Force curves were measured in regions without salt domains.

On ice containing  $10\text{ mM}$  KCl, the thickness of the liquid-like layer was higher than on pure ice (Figure 5). At  $-10\text{ }^\circ\text{C}$  for instance, the thickness was  $\sim 28\text{ nm}$  compared to  $\sim 13\text{ nm}$  on pure ice. In addition, the dependence on temperature was steeper. Above  $-9\text{ }^\circ\text{C}$ , force curves could not be measured anymore because the adhesion force exceeded the force range accessible with the AFM. When fitting the thickness of the liquid-like layer with  $d = a - b \log \Delta T$ , we found  $a = 66\text{ nm} \pm 8\%$  and  $b = 38\text{ nm} \pm 11\%$ . A fit with  $d \propto \Delta T^{-\alpha}$  leads to  $\alpha = 1.0 \pm 11\%$ . In both cases, the standard deviations are on the same order of mag-



**Figure 5.** Thickness of the liquid-like layer on a frozen 10 mM KCl aqueous solution. The solution was frozen at  $-35\text{ }^{\circ}\text{C}$  in a freezer. The layer thickness is equal to the jump-in distance minus 2 nm. The solid line represents the temperature dependence of  $d \propto \Delta T^{-1}$ . Triangles and circles correspond to different experiments done under the same conditions.

nitide. Therefore, we cannot determine which function better describes the curves, but we can conclude that the presence of salt increases the surface melting significantly.

Wettlaufer<sup>39</sup> has theoretically investigated the influence of salt in ice using DLVO theory.<sup>40–42</sup> He calculated van der Waals and Coulombic interactions within interfacial solution films and found that the liquid-like layer thickens with increasing salt content and that for sufficiently large salt concentrations the melting behavior is dominated by the power law  $d \propto \Delta T^{-1}$ . The solid line in Figure 5 represents an exponent of  $\alpha = 1$ . It is in good agreement with our experimental results.

#### 4. Conclusions

With AFM, it is possible to measure the thickness of the liquid-like layer  $d$  at  $\leq -1\text{ }^{\circ}\text{C}$ . This thickness determination is based on the difference in mechanical properties of bulk ice and the liquid-like layer. The temperature dependence of  $d$  of ice formed from distilled water indicates that long-range exponentially decaying interactions are responsible for the formation of the liquid-like layer. In the presence of 10 mM monovalent salt,  $d$  increases significantly, and the temperature dependency agrees with the predictions of Wettlaufer.<sup>39</sup> This indicates that impurities play a major role.

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