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### Sliding friction

*From microscopic contacts to Amontons' law*

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# Molecular Insight into the Slipperiness of Ice

## 7.1 Abstract

The slipperiness of ice has fascinated scientists for over 130 years, but no real consensus has been reached as to its origin. Here we show that the friction coefficient of steel on ice, which is particularly relevant for ice skating, is very high at low temperatures ( $-100^{\circ}\text{C}$ ) and decreases steeply with increasing temperature. Very low friction is only found over the limited temperature range typical for ice skating. The strong decrease in the friction coefficient with increasing temperature exhibits Arrhenius behavior with an activation energy that closely matches the activation energy for the mobility of surface ice molecules. Through sum-frequency generation spectroscopy and molecular dynamics simulations we show that the high mobility is caused by weakly hydrogen-bonded surface molecules, that diffuse over the surface in a rolling motion and whose number increases with increasing temperature. The low friction at ice skating temperatures then results from this rolling motion of the mobile surface molecules that act as a lubricant.

## 7.2 Introduction

The presence of a thin film of liquid water is invariably invoked to account for the low friction on ice[1, 2]. The physical origin of this water layer is subject of debate; pressure melting was long regarded the main cause, even though the very same study that introduced this explanation for the slipperiness of ice showed that pressure melting under an ice skate can only occur at temperatures above  $-3.5^{\circ}\text{C}$  [3]. Nowadays, the two main hypotheses for

explaining why ice skating is possible are (i) the melting of the ice surface by frictional heating[4] and (ii) the existence of a premelted water layer on the ice surface[5]. Frictional melting fails to explain why ice remains slippery at low velocities[6] where the frictional heat has ample time to escape the contact zone[7]. It is clear from many experiments[8, 9, 10, 11, 12] that a possibly liquid-like layer exists at the free ice surface, with different dynamics than bulk molecules. However, even at temperatures close to the bulk melting point, this liquid-like layer has a reported thickness of only a few molecules or a few nanometers. That water spilled on a kitchen floor makes the floor slippery is often used as an argument for explaining why a water layer on ice makes skating possible[2]. However if one were to try and skate on that same wet kitchen floor, the water layer would be squeezed out between the two surfaces so rapidly that skating is impossible. Therefore it appears that an essential insight in the frictional behavior of ice is missing, notably a molecular level insight that explains its slipperiness.

### 7.3 Results

Here, we combine macroscopic studies of ice friction with molecular-level, surface-specific spectroscopy<sup>4</sup> and molecular dynamics (MD) simulations<sup>5</sup> to show that ice friction is caused by surface molecules that are very mobile and facilitate the sliding. To obtain the temperature dependent friction coefficient, we employ steel-on-ice sliding experiments over a large range of temperatures. To simplify the interpretation of the experiment, a sphere-on-planar surface contact geometry is used; a smooth stainless steel sphere is glued to a rheometer tool; through rotating the tool, the rheometer imposes sliding speeds for the sphere on the flat ice surface in the range of  $10^{-6}$  –  $10^{-1}$  m/s while simultaneously measuring the normal,  $N$ , and frictional force,  $F$ . The friction coefficient  $\mu = \frac{F}{N}$ , the ratio of the frictional to the normal force, is as low as  $\mu = 0.01$  at temperatures around  $-7^\circ\text{C}$  (Figure 7.1a); a value similar to that obtained in actual ice skating[13]. However, changing the temperature over a large range, we find a strong temperature dependence of  $\mu$ . A consequence of its dramatic increase at low temperatures is that at low temperatures, the ice surface is not slippery at all; the measured friction

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<sup>4</sup>The spectroscopy experiments were conducted by Wilbert Smit and Huib Bakker from AMOLF and Ellen Backus and Mischa Bonn from the Max Planck Institute for Polymer Research.

<sup>5</sup>The simulations were performed by Fujie Tang and Yuki Nagata from the Max Planck Institute for Polymer Research.

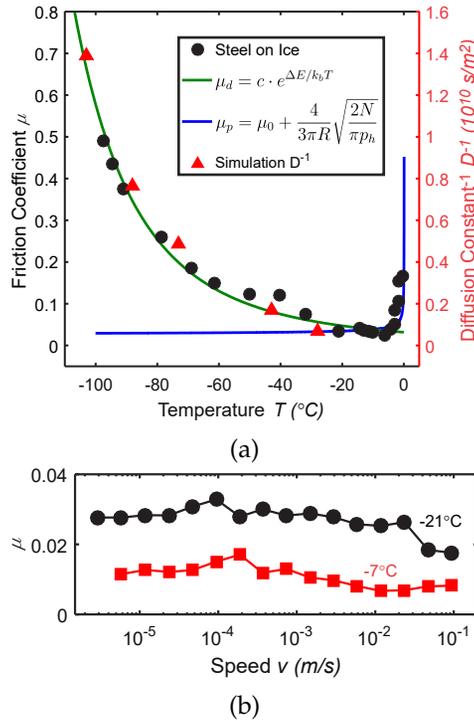


Figure 7.1: (a) The steel-on-ice friction coefficient  $\mu$  as a function of temperature measured at a constant sliding speed of 0.38 mm/s (black circles). Close to the melting point, the friction coefficient increases strongly, in agreement with a calculation of the friction coefficient resulting from plastic ploughing through the ice, using the temperature dependence of the penetration hardness of the ice,  $p_h$ , obtained from indentation experiments (Appendix C), a normal force  $N = 1$  N and the surface friction contribution  $\mu_0 = 0.03$  (blue line). At low temperatures, both the friction coefficient and the calculated inverse ice surface diffusion constant (red triangles) are found to follow Arrhenius temperature dependence with an activation energy of  $\Delta E \sim 11$  kJ/mol (green line). (b) Sliding speed dependence of the friction coefficient.

coefficient of  $\mu = 0.5$  at  $-100^{\circ}\text{C}$  is typical for dry friction such as that between the same steel sphere and a glass surface (Appendix C).

At temperatures above  $-5^{\circ}\text{C}$ , the friction coefficient rises sharply (Figure 7.1a). Visual inspection of the ice surface shows that when the friction coefficient becomes high in this temperature range, the sphere leaves a clearly visible ‘ploughing’ track (Appendix C): the ice has plastically deformed. Our

contact geometry allows us to calculate the ploughing force based on the penetration hardness of the ice and the resulting contact area between the steel and the ice. The experimental friction coefficient for temperatures close to melting agrees well with this simple calculation (blue line in Figure 7.1a and Appendix C). Furthermore, independent penetration experiments in which the sphere is pressed onto the ice surface and retracted again, indeed show that at temperatures above  $-5^{\circ}\text{C}$  the contact becomes fully plastic (irreversible) while at temperatures below  $-5^{\circ}\text{C}$  the contact is purely elastic and the ice surface is not affected. In this elastic regime, the friction force is proportional to the steel-on-ice contact area predicted by Hertzian[14] (elastic) contact mechanics (Appendix C); any small scale irregularities on the ice surface are likely flattened plastically since the Hertzian contact pressure is close to the ice penetration hardness. The interesting observation is now that the elastic properties of the ice do not vary greatly with temperature[15], and therefore the contact area does not either. In general, the friction force is always found to be proportional to the contact area[16]. The consequence is that the change in friction observed at temperatures between  $-100^{\circ}\text{C}$  and  $-5^{\circ}\text{C}$  must result from a change in "quality of contact" *i.e.*, frictional shear stress. The presence of such a temperature-dependent effective 'lubrication' mechanism at the ice surface has indeed been suggested recently[7].

To investigate the nature of this lubrication, we vary the sliding velocity over more than four orders of magnitude (Figure 7.1b). Perhaps surprisingly, we find that the friction is independent of sliding velocity. The observation of velocity-independent friction is inconsistent with the frictional melting hypothesis since the sliding velocity controls the contact temperature[7, 17, 18] (Appendix C). Moreover, as the latent heat for melting ice is roughly 80 times larger than the specific heat required to raise the temperature of ice by one degree, the ice volume that can be melted for a particular friction force, is not strongly dependent on the ice temperature, unlike the measured friction coefficient (Figure 7.1a). Finally, even if substantial amounts of liquid water are formed at the contact, this water would be squeezed out immediately, since the viscous drag of a liquid water layer would depend linearly on the sliding speed, again in disagreement with the data (Figure 7.1b).

In contrast to other materials[6] (glass, brass and granite) we find that below  $-5^{\circ}\text{C}$  our steel ball does not adhere to or plough through the ice surface so that there is no adhesive or ploughing contribution to the friction coefficient (Appendix C). Both observations indicate that the interaction between steel and ice is not important for the low friction and that the latter is rather related to the surface of ice; steel on glass, in contrast, has a

high friction coefficient (Appendix C). This leaves us with an ice surface layer that apparently differs from the bulk, and that lubricates the contact. To shed more light on the molecular nature of steel-on-ice friction and its temperature dependence, we investigate the properties of that molecular surface layer with surface-specific vibrational sum-frequency generation (SFG) spectroscopy[19]. Although friction is inherently a non-equilibrium phenomenon, both the lack of plastic deformation (below  $-5^{\circ}\text{C}$ ) and the absence of any velocity-dependence indicate that the friction occurs in a near-equilibrium regime. Indeed, a previous SFG study on the role of water in friction between two solid sliding objects has revealed that macroscopic sliding does not affect the microscopic structure of interfacial water[20]. As such, the equilibrium spectroscopy results should be directly relevant for explaining friction. In the SFG experiments, the vibrational response of specifically the outermost molecular layer of the ice is recorded, by irradiating the ice surface with infrared and visible laser pulses. When the infrared is resonant with the O-H stretch vibration of interfacial water molecules, the sum-frequency signal of the two pulses is strongly enhanced. Our SFG measurements therefore probe the vibrational response of only the interfacial  $\text{H}_2\text{O}$  molecules at temperatures ranging from  $-28^{\circ}\text{C}$  to  $-103^{\circ}\text{C}$ . To connect our SFG response to the microscopic structure of the ice surface, we performed molecular dynamics (MD) simulations using the POLI2VS model of  $\text{H}_2\text{O}$ [21]. The MD trajectories were used for computing the SFG spectra as well as the mean square displacement (MSD) of the water molecules at the ice–air interface (Appendix C).

The experimentally measured SFG responses in the spectral region of the free O-H stretch vibration are plotted in Figure 7.2a. Previously[22] it was demonstrated that this free O-H stretch response is governed by two distinct types of water molecules: molecules with one donating (D) and two accepting (A) hydrogen bonds (notation: DAA), and molecules donating and accepting one hydrogen bond (DA). The DAA and DA water molecules have stretch frequencies of the free O-H centered at  $3695$  and  $3715\text{ cm}^{-1}$ , respectively[23]. The SFG spectra of the free O-H stretch vibrations at different temperatures can indeed be well described with two Gaussian lineshapes centered around these frequencies (Figure 7.2a). With increasing temperature, the amplitude of the DAA band decreases, while that of the DA band increases. This interconversion of different interfacial water species is quantitatively reproduced in the calculated SFG spectra (Figure 7.2b). Both SFG experiment and simulation thus show that the DAA-type water molecules lose a hydrogen bond with increasing temperature, thereby changing from DAA to DA.

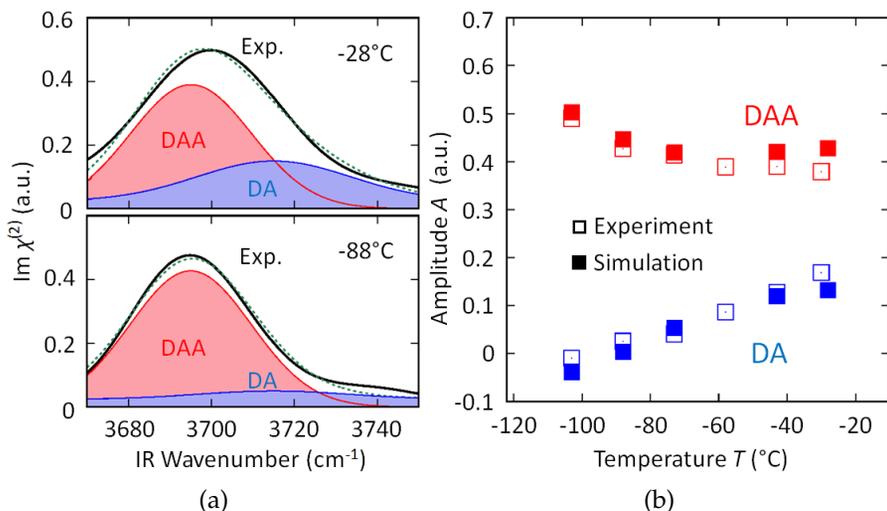


Figure 7.2: (a) Experimentally measured SFG spectra of the free O-H stretch mode at the ice-basal face for  $-88^{\circ}\text{C}$  and  $-28^{\circ}\text{C}$ . DAA and DA molecules (see text) are fitted to the experimental data using two Gaussians centered at  $3695\text{ cm}^{-1}$  (red) and  $3715\text{ cm}^{-1}$  (blue), respectively. (b) Amplitude of the DAA and DA contributions as a function of temperature for both experimental and simulated SFG spectra.

The interconversion of DAA water to more weakly interacting DA molecules entails an increase in the mobility of water molecules across the surface; a lower number of hydrogen bonds lowers the energetic barrier for translational motion. The energetic barrier for translational motion on the surface is directly relevant for friction; skating on polytetrafluorethylene (PTFE) skating rinks for example is possible because the activation energy for the slippage between crystalline PTFE slices is low, causing high wear and low friction on PTFE[24]. In friction at the nanoscale, the energy barrier for translational motion of an AFM tip over a surface can become small compared to the thermal energy resulting, again, in very low friction; temperature acts as a lubricant because the energy required to locally move from one potential minimum to the next, is supplied thermally[25]. The thermally driven high lateral mobility of water molecules on an ice surface has been demonstrated previously: experiments on the merging of ice spheres have conclusively shown that macroscopic quantities of water molecules can be transported over millimeter length scales on a timescale of minutes at temperatures as low as  $-25^{\circ}\text{C}$ [26]. We quantify the lateral mobility of the surface molecules

and link it to macroscopic ice friction using the time evolution of the in-plane two-dimensional (2D) mean square displacement ( $MSD$ ) of the topmost  $H_2O$  molecules with free O-H group(s) in the simulations:

$$MSD(t) = \frac{\langle \theta(0) | r(t) - r(0) |^2 \rangle}{\langle \theta \rangle}$$

where  $\theta(t)$  is 1 when a surface molecule has a free O-H group at time  $t$ , and 0 otherwise. While heating the ice from  $-103^\circ C$  to  $-28^\circ C$ , we see a marked increase in the mean square displacement of the surface molecules (Figure 7.3a). If surface diffusion indeed facilitates the sliding, we would expect an inverse relation between friction and diffusion; the higher the diffusion coefficient, the lower the friction. This is exactly what we observe; in Figure 7.1a we plot the inverse diffusion coefficient,  $D^{-1}(T)$ , together with the friction coefficient as a function of temperature:

$$D = \lim_{t \rightarrow \infty} \frac{\langle \theta(0) | r(t) - r(0) |^2 \rangle}{4t \langle \theta \rangle}$$

Friction and diffusion follow the same Arrhenius temperature dependence with an activation energy:  $\Delta E \sim 11$  kJ/mol (Figure 7.1a), almost half of the hydrogen-bond energy of 21 kJ/mol.

This suggests that the mechanism by which mobile water molecules on the ice surface can lubricate the frictional contact relies on the thermally activated breaking of hydrogen bonds. The simulations allow us to monitor how the interfacial water molecules diffuse. We compute the MSD of an interfacial water molecule that continuously keeps a free O-H group between time 0 and time  $t$  using:

$$MSD_c(t) = \frac{\langle |r(t) - r(0)|^2 \int_0^t \theta(t') dt' \rangle}{\langle \int_0^t \theta(t') dt' \rangle}$$

This is shown in the inset of Figure 7.3a for a temperature of  $-43^\circ C$ . In contrast to the average MSD of an interfacial water molecule that was considered before, the MSD for this type of molecule, surprisingly, remains nearly constant after  $t = 2$  ps. This means that an interfacial water molecule with a free O-H group no longer moves unless the free O-H group forms a new hydrogen bond.

The MD trajectories displayed in Figure 7.3b demonstrate that a water molecule at the ice surface moves by exchanging its hydrogen bond partner. This exchange occurs through breaking the hydrogen bonds of the topmost

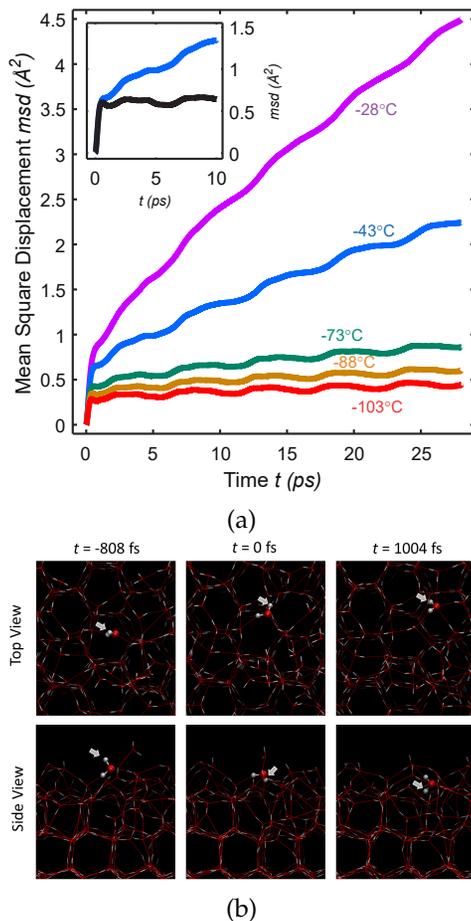


Figure 7.3: (a) Calculated 2D mean square displacement of the interfacial water molecules with free O-H group(s) at different temperatures. Inset: comparison of the mean square displacement of the interfacial water molecules which have free O-H group(s) at time 0 (blue) with that of the interfacial water molecules which keep free O-H group(s) during time 0 to  $t$  (black), both simulated at  $-43^\circ\text{C}$ . (b) Snapshots of the MD trajectory of the ice–air interface at  $-43^\circ\text{C}$ . Top and bottom panels show the top and side views of the interface. The water molecule with the free OH group which forms the new hydrogen bond at positive  $t$  is highlighted.

water molecules. As is evident from the SFG spectra of the free O-H stretch peak, by increasing temperature, the hydrogen-bond tends to be broken, converting DAA water molecules to DA water molecules and increasing

the surface mobility. During frictional sliding, we submit that these weakly bonded surface molecules determine the friction coefficient. We therefore conclude that at temperatures close to melting ice is slippery due to highly mobile DA water molecules that diffuse over the ice surface in a rolling motion that involves a change in hydrogen bond partner: there is one molecular layer of mobile water at the surface that lubricates the contact.

## 7.4 Conclusion

The MD trajectories displayed in Figure 7.3b demonstrate that a water molecule at the ice surface moves by exchanging its hydrogen bond partner. This exchange occurs through breaking the hydrogen bonds of the topmost water molecules. As is evident from the SFG spectra of the free O-H stretch peak, by increasing temperature, the hydrogen-bond tends to be broken, converting DAA water molecules to DA water molecules and increasing the surface mobility. During frictional sliding, we submit that these weakly bonded surface molecules determine the friction coefficient. We therefore conclude that at temperatures close to melting ice is slippery due to highly mobile DA water molecules that diffuse over the ice surface in a rolling motion that involves a change in hydrogen bond partner: there is one molecular layer of mobile water at the surface that lubricates the contact.



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