Sliding friction
*From microscopic contacts to Amontons’ law*
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Molecular Insight into the Slipperiness of Ice

C.1 Friction on different ice surfaces

The ice is cooled by a thermostat bath for temperatures down to $-25^\circ C$ and with liquid nitrogen for temperatures down to $-100^\circ C$. The surface temperature of the ice is measured by a thermocouple wire that is inserted into the setup and in contact with the ice surface. During the sliding, the normal force is varied between 0 and 5 N, the average friction coefficient obtained at these normal forces is plotted. The temperature dependence of the friction coefficient was measured on both polycrystalline and monocrystalline ice cut in the basal plane. The agreement between both curves (Figure C.1) confirms that grain boundary melting does not play a role in the frictional behavior. On heavy water ice, the temperature dependence of the friction coefficient is like that on normal water ice but shifted by roughly $4^\circ C$, the melting point difference between normal and heavy water.

C.2 Normal force dependence

At low temperatures, the friction force $F \propto N^{\frac{2}{3}}$, with $N$ the normal force, suggesting that the sphere is in elastic contact with the ice (Figure C.2). According to Hertz’ elasticity theory[1, 2], the elastic sphere-on-ice contact area is $A = \pi \left(\frac{3RN}{4E^*}\right)^{\frac{2}{3}}$, with $R$ the sphere radius and $E^*$ the effective elastic modulus of the ice. In most frictional systems[3], the friction force is proportional to the contact area, in this case giving $F \propto N^{\frac{2}{3}}$, as observed (Figure C.2). At near-melting temperatures, $F \propto N^{\frac{3}{2}}$, a relation that results from plastic
Figure C.1: The temperature dependence of the friction coefficient on different ice surfaces.

Figure C.2: The normal force dependence of the friction force at different temperatures. Inset: the ice surface after sliding at low (left top) and high (right bottom) temperatures.

contact in which the friction is dominated by ploughing through the ice.
C.3 Ploughing force

The ploughing cross section $A_p$, illustrated in Figure C.3 is given by

\[ A_p = \frac{2}{3} cd, \]  

with $c$ the contact arc length and $d$ the depth to which the sphere penetrates the ice, for $c \ll R$. We approximate $c \approx 2r$ and from the right-angled triangle with sides $R$, $r$ and $R - d$ we obtain $d \approx \frac{r^2}{2R}$ both for small contacts $c \ll R$. Plugging these approximations into the formula for the ploughing cross section we obtain $A_p = \frac{2r^3}{3\pi}$. The ploughing cross section multiplied with the penetration hardness gives the ploughing force. Assuming that the contact area during sliding is a half circle and that the contact pressure is equal to the penetration hardness we obtain a ploughing force:

\[ F_p = \frac{4N^{\frac{3}{2}}}{3\pi R} \sqrt{\frac{2}{\pi p_h}}. \]

C.4 Indentation experiments

We mount the 2.38 mm steel sphere that was used in the sliding experiments into a tensile tester to measure force vs. deformation curves for the sphere on ice contact. The sphere is loaded onto the ice surface at a constant rate of 20 N/minute up to a maximum force of 10 N after which the load is removed at the same rate. Meanwhile, the tensile tester measures the deformation with respect to the point of initial contact and plots this vs. the contact force (Figure C.4). We see that at low temperatures the contact is reversible and therefore elastic. The Hertzian relation between penetration depth $d$ and normal force $N$: $d = \left( \frac{3N}{4\sqrt{RE^*}} \right)^{\frac{2}{3}}$, with $R = 2.38$ mm the radius of the
Figure C.4: Indentation of the ice surface with a stainless steel sphere. At varying temperatures, the ice surface is indented with the stainless steel sphere that was used for the friction experiments. At temperatures below $-5\, ^\circ\text{C}$ we observe elastic behavior; the ice surface is reversibly deformed according to the Hertzian relation between penetration depth $d$ and normal force $N$: $d = \left( \frac{3N}{2\sqrt{RE^*}} \right)^{2/3}$, with $R = 2.38\, \text{mm}$ the radius of the sphere and $E^* = 0.84\, \text{GPa}$ the effective elastic modulus of the ice, in good agreement with its literature value[5]. At temperatures above $-5\, ^\circ\text{C}$, the contact becomes plastic and the ice does not push back when the sphere is lifted. At $-1\, ^\circ\text{C}$, the penetration depth $d$ is an order of magnitude larger than it was at temperatures below $-5\, ^\circ\text{C}$.

The penetration hardness obtained from the plastic loading curves is shown in Figure C.5.
C.5 Friction and contact area

In Figure C.6, we plot the friction force measured at $-16^\circ$C (Fig. 2) vs. the Hertzian contact area between the sphere and the ice calculated using $A = \pi \left( \frac{3RN}{4E^*} \right)^{\frac{2}{3}}$, with $R = 2.38 \cdot 10^{-3}$ m and $E^* = 0.84$ MPa. The friction is proportional to the contact area with $\tau = 1.2$ MPa, the shear strength of the interface. To demonstrate that this shear strength is low, we repeat the measurement replacing the ice with a float glass surface to obtain $\tau = 88$ MPa, using $E_{\text{glass}}^* = 64$ GPa (inset Figure C.6).

C.6 Frictional heating

We calculate the temperature at the sphere on ice interface using the theory of heat diffusion, assuming that all frictional heat is absorbed by the sphere, there is no lateral heat diffusion and that the sphere is a semi-infinite solid (Figure C.7). In reality, the ice also absorbs heat and there is significant lateral heat diffusion while the heat capacity of the sphere is so large compared to the frictional heat flux that at the experimental time scales the sphere can be
Figure C.6: Friction per unit contact area. Using the effective elastic modulus $E^*$ obtained in the indentation experiment, the Hertzian contact area $A$ between the sphere and the ice can be calculated: $A = \pi \left( \frac{3RN}{4E^*} \right)^{\frac{2}{3}}$. The friction force obtained at low temperatures ($-16 \, ^\circ\text{C}$ data from Fig. 2) is proportional to $A$ with proportionality constant 1.2 MPa. We replace the ice with float glass and obtain a proportionality constant of 88 MPa between friction force and Hertzian contact area using the glass modulus $E_{\text{glass}}^* = 64 \, \text{GPa}$.

considered semi-infinite. The calculated surface temperatures therefore must be larger than the actual surface temperature in the experiment. Nonetheless, we see that the sphere surface temperature is hardly increased by the frictional heat, even at the highest sliding speeds (Figure C.7). The sphere follows a circular sliding path over the ice surface with radius 9 mm. Because the ice surface is not perfectly aligned with the sphere rotation plane, the sphere is not in contact with the ice during the full rotation (except for experiments conducted in the plastic regime where the sphere penetrates the ice deep enough to remain in contact during the entire rotation). As a result, the sliding distance for each rotation typically does not exceed 1 cm, strongly limiting the effect of frictional heating.
Figure C.7: The surface temperature of a semi-infinite steel solid warmed up by frictional heat. During sliding a heat flux $F_v A$ is generated by contact area $A$ due to friction force $F$ at sliding speed $v$. If this heat flux is absorbed by the steel sphere, which we model as a semi-infinite solid, the temperature at the sliding interface as a function of time $t$ is given by: 

$$T(t) = T_0 + \frac{2 F_v A}{\pi \rho c \kappa} \sqrt{\frac{t}{\pi \rho c \kappa}},$$

with, $T_0 = -50^\circ C$ the initial temperature, $\rho = 7.6 \cdot 10^3$ kg/m$^3$ the density of stainless steel, $c = 480$ J/kgK the specific heat of stainless steel, and $\kappa = 27$ W/mK the heat conductivity of stainless steel. We plot the relation between this surface temperature and the total sliding distance for sliding speeds ranging from $10^{-6} - 10^{-1}$ m/s, using a friction force $F = \mu \cdot 1$ N = 0.03 N and contact area $A = 5.15 \cdot 10^{-8}$ m$^2$, corresponding to the Hertzian contact area at 1 N normal force.
C.7 Sum-frequency generation spectroscopy

Details on the phase-resolved sum-frequency generation (SFG) setup can be found in [6]. Briefly, sum-frequency light generated at the surface of the ice sample is combined with a delayed sum-frequency signal generated at the surface of a gold mirror acting as a local oscillator. The sum-frequency response of the ice surface is extracted by Fourier filtering and normalized by a reference spectrum from z-cut quartz which gives a non-dispersive SFG response. Subsequently, the data are corrected for the Fresnel factors. The monocrystalline ice samples are measured in a liquid-nitrogen cooled closed sample cell in SSP-polarization configuration. The SFG experiments are performed on the basal plane of hexagonal ice (Ih). Details on the growth, characterization, and preparation of single crystal ice are given in [6].

C.8 Simulation protocols

C.8.1 Molecular dynamics simulation

We conducted molecular dynamics (MD) simulations at the basal face of ice (Ih) in contact with vacuum. We used the POLI2VS force field model for water molecules[7]. This model predicts a melting temperature of $265 \pm 5$ K and a surface tension of 60.6 mN/m without the long-range correction[8]. These are in reasonable agreement with experiment. In the MD simulation of the ice-vacuum interface, the simulation cell contained 1792 water molecules. We set the simulation cell size to $30.726 \times 30.411 \times 80$ Å, where 112 water molecules compose a bilayer of ice. The system thus consists of 16 bilayers. Periodic boundary conditions were used. The electrostatic forces were calculated with the Ewald method. The time step for the equations of motion was set to 0.4 fs. The reversible reference system propagator algorithm (RESPA) method was employed to integrate the equation of motion[9]. We prepared 26 independent samples for 170 K, 185 K, and 200 K and 16 samples for 230 K and 245 K. We performed over 400 ps MD runs for each sample at each target temperature for equilibrating the system in the NVT ensemble. We controlled the temperature by using the Nosé-Hoover chain thermostat[10]. We performed further MD runs for each sample to obtain the MD trajectories, which were used for analyzing the data and compute the SFG spectra. We obtained a total of 32.6 ns, 5.5 ns, 29.8 ns, 15.8 ns, and 6.0 ns NVT-MD trajectories for 150 K, 170 K, 185 K, 200 K, 230 K, and 245 K.
C.8 Simulation protocols

C.8.2 SFG spectra calculation

The resonant part of the SFG signal can be calculated via the truncating response function formalism[11]:

\[ \chi_{xxz}^{\text{res}}(\omega, r_t) = iQ(\omega) \int_0^\tau R_{xxz}^{(2)}(t, r_t) f(t) e^{-i\omega t} dt \]  

(C.1)

where the z-axis is the surface normal and the xy-plane is the ice surface. The \( \chi_{xxz}^{\text{res}}(2) \) component corresponds to the SFG signal at the ssp-polarization configuration of the sum-frequency, visible, and infrared beams.

\[ Q(\omega) = \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}} \]  

(C.2)

is the harmonic quantum correction factor[12]. \( \beta = \frac{1}{k_b T} \), with \( k_b \) the Boltzmann constant, \( f(t) \) is the Hann window function,

\[ f(t) = \begin{cases} \cos^2(\pi t/2\pi) & \text{for } 0 < t < \tau, \\ 0 & \text{for } t > \tau \end{cases} \]  

(C.3)

where we used \( \tau = 1.024 \) ps to compute the SFG spectra.

The time correlation function \( R_{xxz}^{(2)}(t, r_t) \) is given by

\[ R_{xxz}^{(2)}(t, r_t) = \left\langle \sum_i g_{sc}^3(z_i(0)) \mu_{z,i}(0) \alpha_{xx,i}(t) \right\rangle, \]  

(C.4)

where \( \mu_{a,i}(t)(\alpha_{ab,i}(t)) \) is the \( a \) component of the molecular dipole moment (the \( ab \) component of the molecular polarizability) of water molecule \( i \) at time \( t \). Here, we considered only the autocorrelation function and neglected the cross-correlation terms such as \( \mu_{z,i}(0)\alpha_{xx,j}(t) \) for \( i \neq j \), because the free O-H stretch SFG signal at \( \sim 3700 \) cm\(^{-1} \) is dominated by the autocorrelation terms.

Since the two ice surfaces are identical in the slab model, the dipole moments of the two interfaces cancel out. In order to avoid this cancellation, we multiplied the dipole moment by the screening function

\[ g_{sc}(z) = \text{sign}(z) \times \begin{cases} 0 & \text{if } |z| \leq z_{c1} \\ \cos^2\left(\frac{\pi(|z| - z_{c2})}{2(z_{c1} - z_{c2})}\right) & \text{if } z_{c1} < |z| \leq z_{c2}, \\ 1 & \text{if } z_{c2} < |z| \end{cases} \]  

(C.5)

where \( z \) is the z-coordinate of the oxygen atom of a water molecule. Here, we set \( z_{c1} = 7 \) Å and \( z_{c2} = 8 \) Å, where the origin point is set to the center of mass.
of the system. The range of $z_{c1} < |z| < z_{c2}$ is located in-between the bulk ice bilayers.

To compensate the nuclear quantum effects on the frequency shift of the O-H stretch mode, we multiplied the factor of 0.9585 [13]. Furthermore, since the classical correlation function cannot predict properly the temperature dependence of the spectral amplitude, we scaled the maximum height of the simulated 3700 cm$^{-1}$ peak to that of the experimental data.

**C.8.3 Definition of free O-H group of water**

To identify the water molecules which have free O-H group(s), we used the geometry-based definition. In this definition, we categorized the hydrogen atoms of water into the non-hydrogen bonded sub-ensemble and the hydrogen-bonded sub-ensemble. When the possible water dimer $(i,j)$ conformation has an intermolecular $O_i\ldots O_j$ distance ($R$) less than 4 Å and the $O_i$-$H_i\ldots O_j$ angles ($\phi$) are larger than 135°, we defined that the $i$-$j$ water dimer forms the hydrogen bond through the $H_i$ atom (see the schematic in Figure C.9). When a H atom does not form any hydrogen bonds, its O-H
Figure C.9: Schematic of water dimer. $R$ and $\phi$ are used for defining the free O-H groups.

group is categorized as a free O-H group. The criteria for $R$ and $\phi$ were chosen such that the selected free O-H groups can reproduce a positive $3700 \text{ cm}^{-1}$ SFG spectral feature of the water–air and ice–air interface. More detailed discussion is given in reference [13].


