The physics of sliding nanofriction at high temperature near the substrate melting point \( T_M \) is so far unexplored. We conducted simulations of hard tips sliding on a prototype non-melting surface, \( \text{NaCl}(100) \), revealing in this regime two distinct and opposite phenomena for plowing and for grazing friction. We found a frictional drop close to \( T_M \) for deep plowing and wear, but on the contrary a frictional rise for grazing, wearless sliding. For both phenomena we obtain a fresh microscopic understanding, relating the former to “skating” through a local liquid cloud, the latter to linear response properties of the free substrate surface. It is argued that both phenomena should be pursued experimentally, and much more general than the specific \( \text{NaCl} \) surface case. Most metals in particular possessing one or more close packed non-melting surface, such as \( \text{Pb}, \text{Al} \) or \( \text{Au}(111) \), that should behave quite similarly.

Thanks to the advent of increasingly sophisticated tip-based tools, the physics of nanofriction is now a field of growing importance. There is in particular a need for a deeper understanding of the physics of friction in extreme regimes including very high temperatures (HT) where the sliding materials approach their melting points. In everyday life, high frictional temperatures are routinely attained in a variety of situations including machining, motors, braking, etc \cite{1}. While rather complex phenomena are generally involved in many such practical situations, at the fundamental level even the very basic microscopic friction processes taking place close to the substrate melting point are not sufficiently explored, characterized and understood. For bare metals on metals, for example, a high speed drop of wear-related friction is generally reported \cite{2}, and reasonably attributed to softening caused by high (“flash”) temperatures ("if one could move fast enough, one could ski on copper mountains..." \cite{2}), but not yet pursued with surface science standards. Conversely, dry grazing friction between hard materials has been known to rise at HT, ostensibly due to the onset of some diffusion \cite{2}; again however that has not been further followed up microscopically. At the present stage, it is just not clear when, how and why closeness to the substrate melting point will imply a drop or a rise of frictional forces under controlled contact circumstances. Nanofriction presently offers a fresh opportunity to address the microscopic physical facts behind these phenomena which are receiving increasing attention. \cite{3} Recent simulation studies have addressed metallic friction between a hard indenter and a soft surface, at high velocities and at tip-driven local temperatures near and above the bulk melting point \cite{3}. Also the simulated motion of a rigid tip across a \text{Si} surface at room temperature showed an interesting tip and temperature driven local phase transition leading to a reduced friction \cite{3}.

Considering that most AFM nanotips slide normally at very low speed, and can hardly perturb the massive substrate, our attention is focused on friction under conditions of essential closeness to thermal equilibrium, however at temperatures arbitrarily near or even marginally above the substrate \( T_M \). We arrive at a first characterization of possible scenarios by means of simulation and theory. Our starting point are molecular dynamics (MD) simulations of sliding nanotips on the hard crystalline surface of a solid close to its bulk melting point \( T_M \). We actually recover both the high temperature friction drop for deep plowing and wear, and the frictional rise for weak load wearless sliding; and for both regimes we obtain a fresh microscopic understanding.

For a meaningful case study we require first of all a careful choice of surfaces and tips. In fact, close to \( T_M \) most solid surfaces wet themselves – in full equilibrium conditions and without any perturbing tips – with a microscopically thin film of melt (surface melting) \cite{3}. The liquid film will generally “jump to contact” with the tip long before closest approach – to some extent ruining the experiment, as indeed observed \cite{7} and predicted \cite{8} long ago. This unwanted complication could be avoided.
for example by resorting to tips that are not wetted by the substrate. Alternatively one could, as we do in the present work, choose a hard, non-melting crystalline substrate facet exhibiting no spontaneous surface melting at all—a surface that will spontaneously remain solid and crystalline up to \( T_M = 900 \text{ K} \). One added advantage of this choice is the possibility to distinguish between very different frictional regimes, such as deep plowing (involving plastic flow and heavy wear) and superficial (wearless) grazing friction, a distinction otherwise made impossible by surface melting. We did not consider inhomogeneous surfaces, simply kept from melting by some kind of protective coating, for they will be very difficult to control. Close-packed metal surfaces, such as Pb, Al or Au(111) are known to be nonmelting \[6, 9, 12, 14\] and would serve the purpose. Eventually, the very stable alkali halide NaCl(100) surface proved close to an ideal choice because of its extreme and recently understood nonmelting habit \[9\]. One added bonus of alkali halide surfaces is that they are already choice substrates for abundant experimental nanofriction work at room temperature \[10\].

The high temperature behavior of NaCl was simulated by the classic Born-Mayer-Huggins-Fumi-Tosi (BMHFT) two body potential \[11\]. Bulk molecular dynamics (MD) simulations \[9, 12\], as well as thermodynamic integration \[13\] yield for that model a bulk melting temperature \( T_M = 1066 \text{ K} \) (experimental value \( 1074 \text{ K} \)). The NaCl(100) surface was studied using periodically repeated slabs consisting of \( 12 \times 24 \text{ planes of 100 NaCl units} \) each separated by \( 100 \pm 120 \text{ Å} \) of vacuum. Computational details were similar to those of Ref. \[12\]. The perfect, tip free NaCl(100) was found to remain indefinitely solid and free of diffusion at all temperatures up to \( T_M \) and, in a metastable state, even above \( T_M \) up to a “surface spinodal temperature” \( T_S \approx 1200 \text{ K} \), for our longest simulation times \( \sim 200 \text{ ps} \). This qualifies NaCl(100) as a nonmelting surface, in agreement with its very poor melting point, and, in a metastable state, even above \( T_M \) up to the mean temperature (K)

\[
T_M = 900 \text{ K} \quad \text{and} \quad T_S = 1200 \text{ K}
\]

To simulate nanofriction we modeled a rigid diamond tip apex, for which deformations are negligibly small. For indentation and deep wear (plowing) simulations we used the sharp \( \sim 400 \text{ atoms conical tip} \) (Fig. 1a). For wearless (grazing) frictional simulations we used instead a blunt flat tip whose contact plane is composed of \( \sim 200 \text{ atoms} \) forming a diamond (111) plane of \( \sim 13 \text{ Å} \) diameter. We slid our tips at constant velocities and purposely avoided including any cantilevers with their mechanical deformations, and related stick-slip phenomena. Thanks to the relatively minor perturbation represented by the sliding tip, even in the plowing case no additional heat sink other than temperature control through standard velocity rescaling was necessary to ensure efficient dissipation of the Joule heat.

We address first of all plowing friction, with the aim of understanding wear forces and their dependence on temperature. For that, we indented the surface with the sharp tip and slid it at constant velocity \( v \) (generally between 25 and 50 m/s) parallel to the NaCl(100). Because under constant load at high temperatures the tip penetration will generally be unstable with time, we worked in a constant penetration mode, the tip wedge entering the NaCl(100) surface by a fixed depth \( d = 6 \text{ Å} \). The forces acting on the tip were collected during the simulated plowing along the \( x \) direction—parallel to the surface—across the \( 60 \times 60 \text{ Å}^2 \) wide surface.

The vertical and in plane forces \( F_z(t) \) and \( F_x(t) \) are shown in Fig. 2. The large noise reflects the discontinuous nature of wear, including plastic flow and the formation and displacement of debris. As a function of temperature, the mean frictional force \( \langle F_x(t) \rangle \) shown in Fig. 3 clearly shows two regimes.

Up to \( T = T_{\text{soft}} \sim 900 \text{ K} \equiv 0.85 T_M \), the plowing

\[
\langle F_x(t) \rangle \sim 0.85 F_{\text{as}} \quad \text{at} \quad T = 300 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 1.3 F_{\text{as}} \quad \text{at} \quad T = 900 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 1.7 F_{\text{as}} \quad \text{at} \quad T = 1200 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 2.0 F_{\text{as}} \quad \text{at} \quad T = 1500 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 2.5 F_{\text{as}} \quad \text{at} \quad T = 1800 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 3.0 F_{\text{as}} \quad \text{at} \quad T = 2100 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 3.5 F_{\text{as}} \quad \text{at} \quad T = 2400 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 4.0 F_{\text{as}} \quad \text{at} \quad T = 2700 \text{ K}
\]

\[
\langle F_x(t) \rangle \sim 4.5 F_{\text{as}} \quad \text{at} \quad T = 3000 \text{ K}
\]
frictional stress is approximately constant, corresponding to a friction coefficient \( \mu = \langle F_x / F_z \rangle \sim 1 \). This large value is naturally attributed to plastic deformation, breaking and reforming of atomic bonds, and the digging of a trough. For macroscopic indenters onto larger size substrates, plowing would in addition generally cause dislocations to appear. Our nanosized, poorly indented tip is in fact unable to generate dislocations and only leads to local plastic deformation and eventually local melting very near \( T_M \). The typical magnitude of \( F_z(t) \) is around 1 nN, which given the small tip active area is equivalent to a stress of about 6 GPa, a value close to the estimated yield stress of 8.3 GPa of NaCl against (100) shear near \( T_M \).

An approximate frictional energy balance at 300 K shows that about 20% is spent to plasticly deform and scratch the material, and the remaining 80% is dissipated as heat, similar to typical figures given in the literature [15]. The work-induced local melting of NaCl(100) near the tip occurs at essentially constant temperature, the mechanical energy transferred into heat of melting, plus phonons that are effectively absorbed by the temperature control through velocity rescaling. Above \( T_{\text{soft}} \sim T_M \sim 150 \) K, the frictional force drops and remains low across the \( T_M \) and above up to \( T_{\text{ss}} \sim 1200 \) K where the surface spontaneously melts. The drop of friction above \( T_{\text{soft}} \) resembles the experimental one reported for metals on metals, and is reminiscent of that observed for hard sliders on ice. In ice [15], the accepted view is that the low skating friction is due to a thin sliding-induced lubricating liquid layer. In our simulation, we find that indeed the frictional drop is accompanied by a thin local cloud of displaced Na and Cl ions which surround the tip with liquid-like mobilities (see Fig. 4). The local melting is motion-induced, and not due e.g. to uniaxial stress-induced lowering of the melting point. [16, 17] Coated by this nearly liquid shroud (Fig. 3) the tip effectively skates. The ease with which the tip wades through the solid is remarkable. The scratch produced by the moving tip, permanent at low temperatures, heals rapidly away at higher temperatures, (see movie in the supplementary material) with a characteristic time which is in the ps range at \( T_M \). The fast resolidification behind the tip restores the equilibrium solid nature of the NaCl surface at \( T_M \) [12], and the resulting latent heat is dissipated away as phonons.

Totally different from plowing friction are the results, shown in Fig. [5] for wearless friction of a large flat tip, grazing the NaCl(100) surface under zero load. Here the tip contacts the substrate by mere adhesion, the adhesive energy \( V_{\text{ad}} \) \( \sim 0.7 \) eV equivalent to an effective load \( F_z \sim -V_{\text{ad}} / h \) where \( h \) is of order of half the interplanar spacing (all results remain very similar for small positive loads). At low temperatures the strongly fluctuating frictional force \( F_z(t) \) (not shown) averages to a very small value, yielding a tiny friction coefficient \( \mu = \langle F_z / F_z \rangle \sim 0.007 \) at 300 K. Such nearly frictionless sliding of two hard incommensurate crystal lattices is not surprising, and resembles that recently reported for a rotated graphite flake on graphite [18]. As temperature grows, an initially moderate thermal growth of \( \langle F_z \rangle \) up to 900 K gives way to an important nonlinear frictional surge near \( T_M \). This high temperature frictional peak makes a sharp contrast with the high temperature drop just seen in plowing friction on the same surface. Here the grazing frictional energy is dissipated mostly through generation of phonons in the solid substrate, plus some modest tip-induced drift of diffusive surface atoms taking place at the highest temperatures. Unlike low temperature plowing, the solid surface is left, after dissipating away the small amount of frictional heat, very much in the same state it was before friction. This observation justifies an attempt at treating grazing friction within linear response theory, assuming a steady sliding state, and negligible influence of the tip on the surface.
Modeled as a hypothetical impurity-like particle, assumed free to move along \((xy)\) on the hot surface, a tip will experience random forces – Brownian kicks. In the absence of an external force, it would undergo 2D diffusion; under a planar force \(f\), it should drift with average velocity \(v\) proportional to \(f\). Simulations at 900 K with increasing velocities between 15 and 50 m/s confirmed an approximately linear increase of friction force. Here the viscous behavior of grazing friction is due to random kicks from large thermal vibrations, rather than to viscoelastic properties of the hot surface, still perfectly solid and crystalline. Assuming a Langevin equation \(\ddot{R} = -\eta \dot{R} + f(t)\) for the in-plane Brownian motion of the idealized (force-free) tip centered at \(\bar{R}\), the zero frequency self correlation of the random force \(f(t)\) is directly related to friction, in the simple form \[\eta = \frac{1}{3Mk_BT} \int_0^\infty dt \langle f(t)f(0) \rangle\] (1)

where it is moreover assumed, as usual that \(\langle f(t) \rangle = 0\). Within linear response, and for negligible tip influence over the surface, the random force acting on the tip can be taken to be proportional to the surface atom displacements \(u_i(t)\). Following Ying et al. [21][22] it is convenient to use 2D k-space \(u_i(t) = \int d^2q u_i(q(t)) e^{-iq \bar{R}}\), and write the random tip force in the form \(\langle f(t) \rangle = \sum_q C_q u_q(t)\) where \(C_q\) is a coupling function expressing the assumed proportionality between kicks onto the tip with individual displacements \(u_i(t)\) and the random force \(f(t)\) felt by the tip. Inserting this expression into the equation for \(\eta\), we obtain

\[\eta = \frac{1}{3Mk_BT} \sum_q |C_q|^2 S(q, \omega = 0)\] (2)

where \(S(q, \omega = 0) = \int_0^\infty dt u_{-q}(t)u_q(0)\) is the two dimensional dynamical structure factor of the tip-free surface substrate, proportional to the substrate atom displacement auto-correlation functions. In this manner, the grazing friction \(\eta\) is reduced to a property of the unperturbed surface. In the simple present form, it could also be arrived at directly by observing that the dissipation rate takes in linear response theory a Fermi Golden rule form, \(|C_q|^2\) measuring the perturbation strength, and the dissipative part of the system’s linear response function giving the density of final states. Considering that the frequencies that are relevant for dissipation (long wavelength phonons and diffusional processes) are extremely small compared to e.g. the solid substrate Debye frequency, one can set \(\omega = 0\) recovering (disregarding factors) eq. (2) above.

We can now attempt a comparison of the temperature dependence predicted by linear response theory eq. (2) of grazing friction based on the dynamical properties of the tip-free surface with the actual simulated friction. Here we deliberately oversimplify by assuming a T independent coupling \(C_q\) – in reality, hard core interatomic potentials will generally imply a growing value with temperature, since vertical displacements, which eq. (2) disregards, will be more important at higher temperature. In \(q\) space, \(C_q\) will be nonzero for \(q < q_0 \equiv 2\pi/L\), where \(L\) is the lateral dimension of the tip (\(\sim 13\) Å) or roughly \(q_0 \approx 0.5\) Å\(^{-1}\). Since \(q_0\) is small, we can simply assume \(C_q = C_0 \Theta(q_0 - q)\), whence

\[\eta = \frac{1}{3Mk_BT} |C_0|^2 \int_{q<q_0} dq S(q, \omega = 0)\] (3)

To check the theory against frictional simulation, we extracted displacement auto-correlation functions of NaCl(100) from tip-free surface simulations. Fig. 6 shows \(S(\omega) = \int_{q<q_0} dq S(q, \omega)\) as a function of temperature, of surface atoms only. Comparison with Fig. 5 is qualitatively good, although as anticipated some increase of \(C_q\) would be needed to make the agreement quantitative at high temperature. The sharp rise close to \(T_M\) and \(\omega \to 0\) is attributable to large and eventually (close to \(T_M\)) catastrophic softening of the very anharmonic surface lattice, still solid but extremely compliant in this regime.

A well known analogue of this phenomenon is actually realized in the physics of type II superconductors close to \(H_{c2}\). Here the flux lattice – whose frictional depinning from the ion lattice and impurities determines the critical current – turns soft just before eventually disappearing [22]. This soft state is so compliant that the pinning force, and the critical current with it, develops a last sharp peak before dropping to zero at \(H_{c2}\), a phenomenon that has been described by very similar formulas to those of sliding friction [20][21]. It is thus reasonable to propose that the high temperature friction increase of a hard grazing slider we just described is the direct frictional analogue of this peak effect in type II superconductors.

In summary, the sliding of hard tips onto hard nonmelting surfaces (here modeled by NaCl(100)) reveals new phenomena in high temperature nanofriction. As the melting point is approached, friction may either drop as in skating, or rise as in flux lattice depinning. We believe that these phenomena should be more general than the specific NaCl surface context in which they emerged. In particular, most metals possess at least one close packed non-melting surface, such as Pb, Al or Au(111) [4], that should behave quite similarly to our results on NaCl(100). High temperature experiments on NaCl itself should be feasible. Because of the high vapor pressure (0.34 mmHg at \(T_M\)), and of a correspondingly high rate of evaporation (we estimate \(1.7 \times 10^{-5}\) s\(^{-1}\), for terraces 50 Å wide), the step flow velocity at sublimation conditions at \(T_M\) will be about \(10^{-5}\) m/s. So long as the tip velocity is larger than this value, our description of nanofriction is fully applicable. Moreover, irrespective of sublimation the terraces between the steps will still
be well represented by the flat, dry, stable solid surface described in our simulations. Thus the effects described will be readily observed, for example once the sliding tip velocity $v$ is faster than the step flow velocity.

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