Transition from Thermal to Athermal Friction under Cryogenic Conditions

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Atomic scale frictional forces encountered as a function of temperature for the contact of a Si_3N_4 probe tip and the basal plane of MoS_2 have been measured with atomic force microcopy over the temperature range 100–500 K. Friction is observed to increase exponentially with decreasing temperature from 500 to 220 K. An Arrhenius analysis of the temperature dependent friction over this range yields an effective activation energy of ~0.3 eV for the thermally activated stick-slip motion of the probe tip on this surface. As temperature is reduced further below 220 K, a distinct transition to a largely athermal behavior is detected and is shown to result from the onset of interfacial wear, entailing an alternative energy dissipation pathway.

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Frictional energy losses accompany the sliding motion of all solid-solid contacts. A fundamental understanding of the mechanisms responsible for such losses is critical to the management of thermal equilibrium, mitigation of potential wear, and the design of interfaces in which such losses are minimized. The development of atomic force microscopy provides the opportunity to investigate the details of energy dissipation on an atomic scale [1–5].

The role of temperature in determining frictional responses has been considered from several perspectives. Macroscopic experiments have explored the frictional characteristics of a range of interfaces at cryogenic temperatures with a wide range of reported results [6–10]. From a microscopic perspective, Sang, Dubé, and Grant published a theoretical account of the thermal effects on atomic friction in the context of a ramped creep model, in which friction was predicted to scale with $T^{2/3}$ based on considerations of interatomic motions under the influence of an external (force) bias [2]. In contrast, Gnecco *et al.*, in investigating the velocity dependence of friction measurements, expressed the atomic scale stick-slip motion of an atomic force microscopy tip on a NaCl(100) surface under UHV in terms of activated jumps between relative interfacial positions of low potential energy [1]. In this context, the rate of motion can be expressed in terms of temperature through an exponential function of the quantity E_a/kT, where E_a represents a microscopic activation energy barrier. Krylov *et al.* have treated thermal lubricity through a similar consideration of activated rates in the regime of thermal drift, occurring at elevated temperatures for most systems [3]. None of these microscopic studies considered friction explicitly as a function of temperature.

Recently, accounts of atomic scale friction measured at cryogenic temperatures for contacts entailing silicon, diamond, and graphite substrates have been published, with a variety of results [5,11,12]. Here we present atomic scale friction measurements on MoS_2 in which discrete and reproducible transitions between a temperature dependent and a temperature independent behavior are active. The aim of this Letter is to describe the strong dependence of friction on temperature under cryogenic and dry sliding conditions in terms of energy dissipation mechanisms.

Molybdenum disulfide exists as a lamellar solid with a structure similar to highly oriented pyrolytic graphite and is widely employed as a solid lubricant [13,14]. In order to eliminate the effect of surface topography on friction, a single crystal MoS_2 sample exhibiting atomically flat surfaces extending over several microns was interrogated. Experiments were conducted using a variable temperature UHV atomic force microscopy system employing a beam deflection detection scheme and equipped with cooling and heating facilities providing access to the temperature range 25–750 K (Omicron Nanotechnology) [15]. The system operated at its base pressure of $\sim 2.0 \times 10^{-10}$ torr throughout the course of the measurements. The MoS_2 sample was cleaved *ex situ*, immediately introduced to the vacuum chamber, and annealed to 400 K. Si_3N_4 cantilevers (Digital Instruments) with a normal force constant of ~0.58 nN/m and a nominal tip radius of ~20 nm were used in the measurements. Zero applied normal load is defined as the force acting on the cantilever at its equilibrium deflection. Lateral forces were calibrated on a faceted $SrTiO_3$ (305) surface, employing a method proposed by Ogletree, Carpick, and Salmeron [16].

An atomic scale image of the MoS_2 surface at 260 K [Fig. 1(a)], generated by plotting the lateral force experienced at an applied load of 4 nN as a function of *xy* sample position, reveals the stick-slip motion of the tip across the surface. A representative friction loop, consisting of the friction force experienced during a single line scan for each of the two scan directions, is shown in Fig. 1(b) for 260 K. The average kinetic friction for a specific load and temperature condition is defined as one-half of the difference between the average friction for each sliding direction within the friction loop. Figure 1(b) also shows the change in friction signature as the temperature is reduced to 200 K

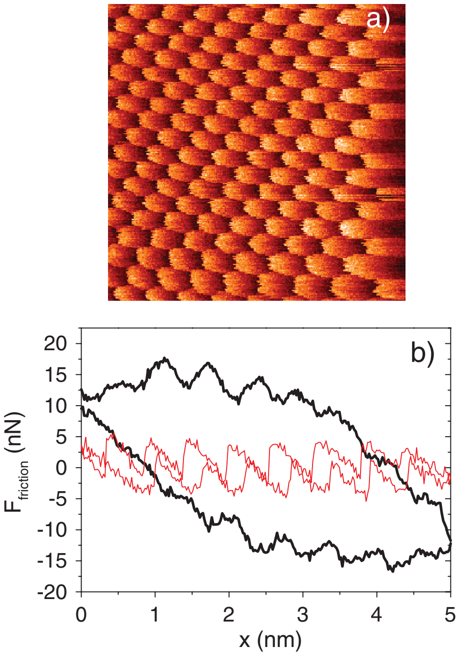
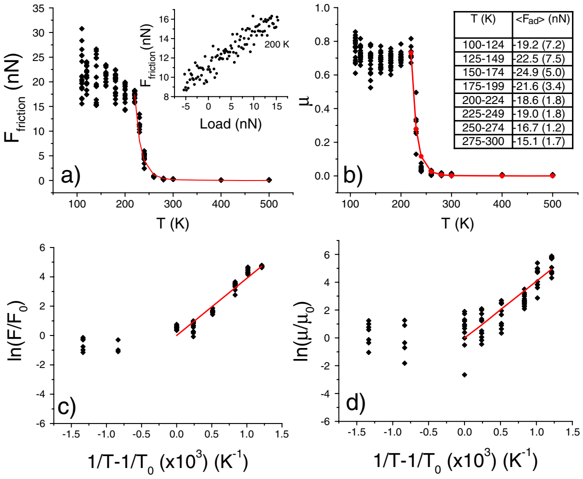


FIG. 1 (color). (a) Lateral force image of MoS_2 at 260 K. Scan size: 5 nm × 5 nm. Applied load: 4 nN. (b) Lateral force loops acquired at 200 K (black) and 260 K (red) reflecting the resolved stick-slip motion of the tip across the surface. Although the stick-slip motion of the tip is still resolved at 200 K, the friction loop reflects a significant increase in friction.



T (K)	$<F_{ad}>$ (nN)
100-124	-19.2 (7.2)
125-149	-22.5 (7.5)
150-174	-24.9 (5.0)
175-199	-21.6 (3.4)
200-224	-18.6 (1.8)
225-249	-19.0 (1.8)
250-274	-16.7 (1.2)
275-300	-15.1 (1.7)

FIG. 2 (color online). (a) Kinetic friction force, averaged over sliding distance and direction, measured on MoS_2 at 0 nN applied load as a function of surface temperature. (Inset) Average kinetic friction as a function of applied load at 200 K. (b) Microscopic friction coefficients derived from the plots of friction versus applied load (0–20 nN) data as a function of temperature. (Inset) Associated adhesion data (with standard deviations) as a function of sample temperature. (c) An Arrhenius analysis of normalized friction data in (a) over the temperature range 220–500 K. (d) An Arrhenius analysis of the friction coefficient data in (b) in the temperature range 220–500 K. Both analyses render an activation energy of ~0.3 eV.

under the same applied load condition. Clearly, the average kinetic friction, as indicated by area of the friction loop, is significantly increased.

An analysis of the temperature dependence of the system was conducted by measuring the average kinetic friction at a fixed applied load of 0 nN over the temperature range 100–500 K [Fig. 2(a)]. With decreasing temperature, the friction force increases exponentially below room temperature before reaching a plateau near 220 K. The system has been further characterized through load dependent friction measurements performed as a function of temperature [Fig. 2(a) inset]. In this case, the average kinetic friction has been measured as a function of applied load over the approximate range of 0–20 nN. The plot of this friction force versus applied load was found to be linear, with the slope in turn assigned as the microscopic coefficient of friction (μ). This procedure was repeated multiple times for a series of discrete temperatures between 100 and 500 K [Fig. 2(b)], demonstrating a significant increase in friction with decreasing temperature. Experiments entailing the purposeful introduction of water at cryogenic temperatures as well as separate temperature programmed desorption studies of water on MoS_2 confirmed that the reported effect does not arise from water condensation at the tip sample contact. In addition, the observed increase in friction cannot be attributed to changes in interfacial adhesion as a function of temperature.

The data of Figs. 2(a) and 2(b), for temperatures between 220 and 500 K, have been normalized to room temperature values and assessed via an Arrhenius model, considering friction forces as arising from the collective motion of the atoms of the tip through activated translation events. In this analysis, a plot of $\ln(F/F_0)$ or $\ln(\mu/\mu_0)$ vs $(1/T - 1/T_0)$ can be fit to a linear dependence with a finite slope. Within these plots, friction data corresponding to temperatures of 400 and 500 K have approached the detection limit of the microscope and therefore diverge statistically from the anticipated linear dependence of this analysis; as a result, they have been excluded in the determination of the slope. According to an Arrhenius analysis, the data of both Figs. 2(c) and 2(d) indicate that the sliding of a silicon nitride tip on the crystalline MoS_2 surface under cryogenic conditions can be described as an activated process characterized by an activation energy of ~0.3 eV. Based on the analysis of the data of Figs. 2(c) and 2(d), a 0.3 eV activation energy is used to generate the exponential curves shown in Figs. 2(a) and 2(b) as solid lines.

Irrespective of the direction of temperature change, a transition between athermal and thermal friction behavior was observed to reproducibly occur at or near 220 K for the Si_3N_4-MoS_2 interface. A series of correlated measurements provides evidence that the transition originates from the onset of interfacial wear that occurs on the atomic scale and results in frictional interactions occurring through an alternative mechanism of energy dissipation. First, topographic probes of the MoS_2 surface sought to directly identify wear products following friction measurements conducted below 220 K; however, little evidence of plastic deformation of the substrate was observed. Instead, characterization of the tip radius before and after continuous interfacial sliding at 180 K for a period of 4 hours was found to have produced an increase in radius of ~25% during this time. A similar protocol conducted at room temperature produced no increase in tip radius. Thus, for the transitions observed in Figs. 2(a) and 2(b), we conclude that friction increases exponentially with decreasing temperature until a point where the barriers to interfacial shear approximate the energy needed to break chemical bonds. While the energies calculated using common contact mechanics models, measured lateral forces, and corresponding unit cell dimensions produce energies insufficient to break bonds within the basal plane, energies on the order of 10 eV (or GPa shear stresses) are found when the same energy considerations are applied to atomic scale asperities on the tip. Such energies would result in the onset of atomic scale wear, which, in this case, occurred on the probe tip.

Second, the potential influence of wear of the MoS_2 substrate was explored through the purposeful introduction of defect structures within the basal plane. This was accomplished by lightly sputtering the surface with 500 eV Ar^+ at 5×10^{-6} torr for 30 s. The influence of this procedure is depicted through the comparison of STM images of a 300 nm × 300 nm area collected before and after the sputtering procedure (Fig. 3). Typical peak-to-valley height measurements on the sputtered surface are on the order of only 0.3 nm; thus the surface has been roughened only on the atomic scale. The temperature dependence of frictional forces measured at zero applied load as a function of temperature on this sputtered surface are presented in Fig. 3(c). Friction at the disordered or defective surface is observed to be higher than that of the pristine surface at room temperature, and to exhibit a weaker temperature dependence in approaching the friction values observed in the plateau region observed in Fig. 2(a). These data portray a situation in which multiple modes of energy dissipation (wear and friction) are active and, importantly, further demonstrate the strong influence of atomic scale wear on the temperature dependence of friction.

Historically, the atomic scale stick-slip motion of the tip across a crystalline surface has been accounted for through classical mechanical models [17–20]. More recently, models have ascribed the temperature dependence of friction to a variety of mechanisms [2,3]. In particular, those in which an activated behavior is predicted consider friction in terms of the motion of the tip within an environment described by a coupled potential [3]. The potential represents the superposition of an atomic corrugation on a harmonic potential characteristic of a lever-spring sensor. Within this model, local energy maxima associated with specific atomic pathways are encountered as energy is stored in the system as a function of the translation of the tip. The net motion of the tip is then described in terms of the probability of crossing these barriers. The individual rates determining this probability are the source of the temperature dependence, being defined in terms of a thermally activated process.

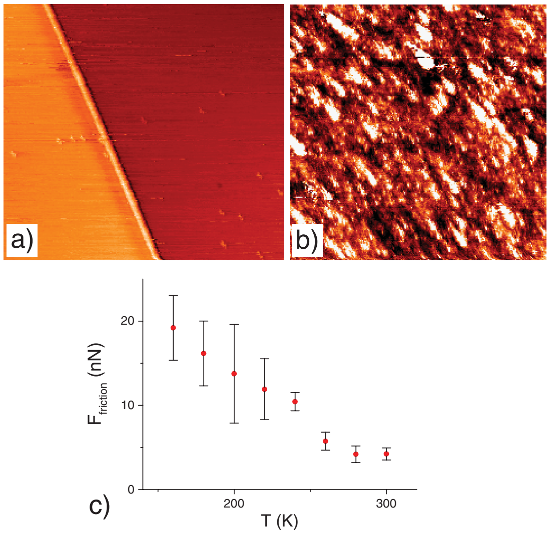


FIG. 3 (color). STM images of (a) atomically flat MoS_2 and (b) lightly sputtered MoS_2 surfaces. Scan size, 300×300 nm^2; bias, −0.2 V; tunneling current, 0.2 nA. The height of the step running across the flat surface is 0.6 nm; maximum feature heights on the sputtered surface are only 0.4 nm. (c) Average kinetic friction forces measured as a function of temperature on the sputtered surface exhibit a marked difference in temperature dependence from that displayed in Fig. 2(a), underscoring the influence of atomic scale wear on such friction measurements.

While consistent with the temperature dependent data presented here, for a number of reasons this model does not appear to be physically complete. First, the sliding contact of the physical interface is not fully described by a one-dimensional model, as multiple atomic contacts exist with no certainty of equivalent registries. As a result, the picture of a single energetic barrier appears overly simplistic. Second, in terms of a multiple atom contact, the net effective barrier does not change explicitly with sliding distance as in the case of the one-dimensional model. Instead, the motions of individual tip atoms with respect to substrate atoms are intrinsically two-dimensional and independent of one another on the time frame of microslip events, which significantly complicates the effective energy landscape.

We propose here two alternative mechanisms by which an activated friction response may be observed. First, we postulate that the motion of the tip could be described in analogy to recent considerations of stress-assisted, activated propagation of dislocations [21–23]. In this context, the tip-surface contact is viewed as a dislocation residing at the substrate surface. The motion of this dislocation, parallel to the surface, would then be subjected to a periodic Peierls-Nabarro-like force imposed by the substrate lattice. The existence of such a force provides the framework to describe the stick-slip motion of a multiple atom contact. The motion of contact would then be expected to exhibit an activated behavior in analogy to the well-understood temperature dependence of dislocation motion. Recent analytical considerations of friction in terms of dislocation drag point to contributions of viscous behavior for systems characterized by low Peierls stresses over a broad velocity range [21]. In particular, these dissipative processes are associated with phonon processes that reduce dislocation mobility and generate heat. With this view of dislocation motion, Merkle and Marks [21] argue that frictional forces could increase exponentially with decreasing temperature, which would ultimately produce an alternative (deformative) interaction of the tip-surface contact with a different temperature dependence.

Second, we postulate that the dissipative component of the interaction may exhibit a thermally activated form. While the precise physical mechanism is not yet clear, we are reminded of shear flow in liquids and glasses which, in a manner somewhat analogous to tribology, involves the activated dissipative response of materials to shear loads. While the dynamics of individual atoms in such a system can be described in terms of Newtonian mechanics, their collective behavior is dissipative in nature and can frequently be characterized as an activated process through the Vogel-Fulcher equation [24]. Moreover, as is well known, the ability of a glass to shear essentially disappears at the glass transition. It is possible to view these friction experiments in the same manner. In particular, while a tip with a single-atom contact might be viewed as a Newtonian system, a real tip will generally have a large number of atoms in contact. The number, identity, and configuration generally change under both environmental and tribological conditions. It is therefore not unreasonable that the collective behavior of such a system might also be described in terms of dissipative behavior. Moreover, in this framework, the crossover to athermal wear behavior would be analogous to the glass transition. In contrast to previous models, these constructs account for the observed temperature dependence while not imposing the single barrier, one-dimensional constraints on the physical stick-slip events.

The proposed models of thermally activated motion of the contact can also describe earlier results of atomistic measurements of temperature dependent friction. A prior account of thermally activated friction on a highly oriented pyrolytic graphite surface reported an activation energy of $\sim$0.1 eV for friction measured at temperatures between 140 and 750 K [12]. Subsequent studies have identified a transition to athermal behavior below this temperature, with the transition occurring at a similar friction force (friction coefficient) value. In addition, a previous study of the frictional properties of a silicon point contact detected an increase in friction coefficient with decreasing temperature to 100 K, followed by a reduction below this point [5]. Within the model presented here, thermal activation of the energy dissipation process accounts for the increase in friction with decreasing temperature, while potential wear events at lower temperatures may account for the observed transition. The presence of native oxides and the likelihood of interfacial bonding in this system held in vacuum would introduce further complexities. In a similar vein, the weak temperature dependence of experimental measurements of the temperature dependent shear strength of diamond-diamond contacts in vacuum [11] are reminiscent of the modified temperature-friction behavior of the lightly sputtered MoS_2 system.

The frictional interactions of a Si_3N_4 probe tip and the basal plane of MoS_2 measured over the temperature range 220–500 K exhibit an activated behavior with an activation barrier of $\sim$0.3 eV. We conclude that this barrier is associated with energy dissipation in analogy to recently observed activated propagation of dislocations. Below 220 K, a largely athermal behavior is detected, which is the result from the onset of interfacial wear. These data provide atomistic insight into fundamental mechanisms of energy dissipation at cryogenic temperatures as well as the temperature dependence of macroscopic friction measurements of low wear systems [25].

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