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# Surface science and the atomic-scale origins of friction: what once was old is new again

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## Abstract

Long neglected by physicists, the study of friction's atomic-level origins, or nanotribology, indicates that sliding friction stems from various unexpected sources, including sound energy, and static friction may arise from physisorbed molecules. Progress in this field will be discussed, with an emphasis on how the field of surface science has influenced our understanding of friction. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Friction; Physical adsorption; Phonons; Energy dissipation

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## 1. Introduction

The fax from David Tabor came promptly, in response to my query about whether he and colleague Ken Johnson might be able to contribute to a special issue on “Fundamentals of Friction”, which I was guest editing for the *Bulletin of the Materials Research Society* [1]. Tabor, whose renowned work on friction spanned well over forty years, unfortunately was not going to be able to complete a manuscript in the time frame allowed. But his letter did not end with that. He went on to describe how he had been thinking about my experiments and also about how lattice commensurability effects should impact sliding friction levels. Solid–solid phase transitions, for example, should produce changes in friction that my experimental

techniques should be able to detect. As I thought about Tabor's research suggestions, I pondered whether forty years hence, at an age exceeding eighty, I too might still be investigating friction, and how fine it was that Tabor lived to participate in the current day renaissance in the topic of his life's work.

By most recent estimates, improved attention to friction and wear would save developed countries up to 1.6% of their gross national product, or over \$100 billion annually in the US alone [2]. The magnitude of the financial loss associated with friction and wear arises from the fact that entire mechanical systems, be they coffee makers or automobiles, are frequently scrapped whenever only a few of their parts are badly worn. In the case of an automobile the energy consumed in its manufacture is equivalent to that consumed in 100,000 miles of operation [3]. More extreme examples include aircraft, which can be entirely destroyed for loss of one part. The consequences of friction

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and wear also have great impact on national security and quality of life issues, so it can come as no surprise that tribomaterials, materials designed for use in moving contact (sliding, rolling, abrasive, etc.), have for decades attracted the interest of materials scientists and mechanical and chemical engineers. What is surprising however, is how little is known even now about the fundamental origins of friction and wear.

As important as tribomaterials are to technology, their discovery has usually been serendipitous. To be sure, materials scientists have frequently been able to provide explanations for why tribomaterials perform as well as they do [4,5], and have also been able to substantially improve the performance of tribomaterials through the development of new alloys, composites and/or improved surface engineering methods. They have, however, been far less successful at a priori design of tribomaterials with improved performance, largely because friction and wear processes have not been understood at the molecular level. Why is so little known on the topic? The answer lies primarily in the fact that friction and wear are surface and interfacial phenomena which occur at a myriad of buried contacts which not only are extremely difficult to characterize, but are continuously evolving as the microscopic irregularities of the sliding surfaces touch and push into one another.

The late 1980's marked the advent of a renewed interest in fundamental areas of tribology, sparked by a number of new experimental and theoretical techniques capable of studying the force of friction in geometries which were well defined even at nanometer length scales [6]. These techniques benefited directly from advances in surface science throughout the 1970's, whereby improvements in ultra-high vacuum technology allowed scientists to prepare unprecedented, well-characterized crystalline surfaces. Experimental techniques such as the quartz crystal microbalance (QCM), the surface forces apparatus and the lateral force microscope, could now record friction in geometries involving a single contacting interface, a vastly simpler situation than that of contact between macroscopic objects. Faster computers meanwhile allowed large-scale simulations of condensed sys-

tems to be increasingly comparable to experiment in a very direct fashion [7].

The increasing overlap of the previously distinct areas of surface science and tribology has given rise to increased optimism that major breakthroughs will be achieved in upcoming decades. Issues of particular importance include: (1) Understanding the chemical and tribochemical reactions which occur in a sliding contact, and the energy dissipation mechanisms associated with such a contact. To fully characterize a system's behavior, one must not only estimate friction levels but also account for the effects of the heat that the friction generates. Are chemical reactions triggered? Do the contact points melt, etc.? (2) Characterization of the microstructural and mechanical properties of the contact regions between the sliding materials. (3) Merging and coordinating information gained on the atomic-scale with that observed at the macroscopic scale. Much of the current information is fragmented, with linkages between individual experimental results yet to have been established. (4) Development of realistic interaction potentials for computer simulations of materials of interest to tribological applications, and (5) Development of realistic laboratory test set-ups which are both well-controlled and relevant to operating machinery.

## **2. Working outside of a vacuum: tribology before 1970**

The view of the Greek philosophers that vacuum was an impossibility hampered understanding of its basic principles until the mid-17th century (Fig. 1), greatly delaying progress in all vacuum-related fields [8]. The field of tribology by comparison dates well back to the construction of the Egyptian pyramids, if not hundreds of thousands of years earlier to the discovery of the use of flint stone for the sparking of fires [9]. Indeed, such tribological advances as Leonardo da Vinci's design of intricate gears and bearings [9] (some of which were not built until the industrial revolution provided sufficiently strong materials), and the landmark 18th century development of a timepiece allowing accurate longitudinal positioning of ships



Fig. 1. A highly publicized demonstration by Otto Van Guericke, describing his 1672 invention of a vacuum pump (from Ref. [8]). The ability to produce vacuum in laboratory conditions would centuries later give rise to the discovery of the electron. This revolutionary advance in physics gave rise to the field of modern surface physics. Electrons travelling through ultra-high vacuum conditions and high potential differences were first demonstrated to be highly sensitive probes of surfaces in 1967 (Fig. 7), and provided the vast majority of information on surface structure and chemical composition up until the invention of the scanning probe microscope in the 1980's.

at sea (accomplished via a self-lubricating wooden gear) [10] could easily be termed “modern”, given the overall longevity of the field. Modern study of friction began perhaps 500 years ago, when Leonardo da Vinci deduced the laws governing the motion of a rectangular block sliding over a planar surface (Fig. 2). Da Vinci's work had no historical influence, however, since his notebooks remained unpublished for hundreds of years. The French physicist Guillaume Amontons is credited with the first published account of the classic friction laws, which in 1699 described his observations of contacting solid surfaces [11].

Amontons observed that (1) the friction force that resists sliding at an interface is proportional to the “normal load”, or force which presses the surfaces together, where the “coefficient of friction” is defined as the ratio of the frictional force to the load, and (2) the friction force is independent of the apparent area of contact: A small block experiences as much friction as does a large block of the same material so long as their weights are equal. A third law is frequently included with these, attributed to French physicist Charles-Augustin de Coulomb (better known for his work in electrostatics) in the 18th century: the friction force

is independent of velocity for ordinary sliding speeds. Although the coefficient of friction is independent of the apparent contact area, loading force, and the sliding speed, it does in fact depend on whether the force is applied to an object at rest (“static friction”) or already moving (“sliding friction”). Considering its simplicity, Amontons' law is amazingly well obeyed for a wide range of materials such as wood, ceramics, and metals.

Amontons' and Coulomb's classical friction laws have far outlived a variety of attempts to explain them on a fundamental basis. Surface roughness, which Coulomb unsuccessfully attempted to attribute friction to (Fig. 3), was ruled out definitively as a possible mechanism for most friction in the mid 1950's. Molecular adhesion, though, remained a strong possibility, a conclusion due in large part to Bowden, Tabor and coworkers at Cambridge University, England. Their group found that friction, although independent of apparent macroscopic contact area, is in fact proportional to the true contact area. That is, the microscopic irregularities of the surfaces touch and push into one another and the area of these contacting regions is directly proportional to the friction force. The Cambridge group subsequently

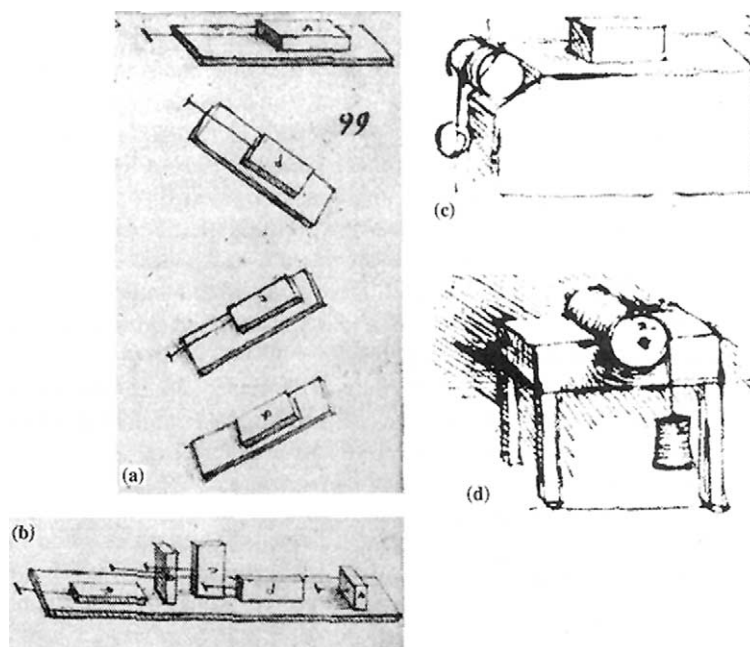


Fig. 2. Leonardo da Vinci's (A.D. 1452–1519) studies of friction. Sketches from the *Codex Atlanticus* and the *Codex Arundel* showing experiments to determine: (a) the force of friction between horizontal and inclined planes; (b) the influence of the apparent contact area upon the force of friction; (c) the force of friction on a horizontal plane by means of a pulley and (d) the friction torque on a roller and half bearing (from Ref. [9]).

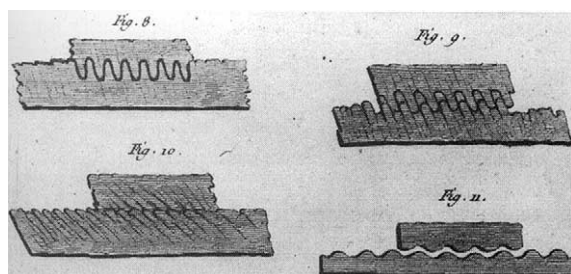


Fig. 3. Coulomb's representation of rough surfaces, published in 1785 (from Ref. [9]).

explored the possibility that friction arose from sufficiently strong bonding at the true contact points so as to produce continual tearing away of tiny fragments of material [12]. This explanation failed however to predict experimental observation. Indeed, it was proved incorrect by Tabor and one of his own graduate students, Jacob Israelachvili, who in the 1970's developed a "surface

forces apparatus" (SFA) (Fig. 4) for atomic-scale friction measurements, which definitively exhibited friction in the total absence of wear.

For decades thereafter, Tabor would continue to ponder the fundamental dissipative mechanisms of friction. In a 1991 plenary lecture at a NATO sponsored conference on the Fundamentals of Friction [14] (the first meeting to bring together long-established tribologists with surface scientists new to the field, like myself), he would conclude that friction in the absence of wear must be due to strains building up in the sliding contact which were being released in the form of atomic vibrations [15]. Phonons, as such vibrations are called, were first suggested by Tomlinson in 1929 [16], with subsequent independent derivations by both Gary McClelland at IBM Almaden and Jeffrey Sokoloff at Northeastern University [17]. Friction arising from phonons occurs when atoms close to one surface are set into motion by the sliding action of atoms in the opposing surface (Fig. 5).

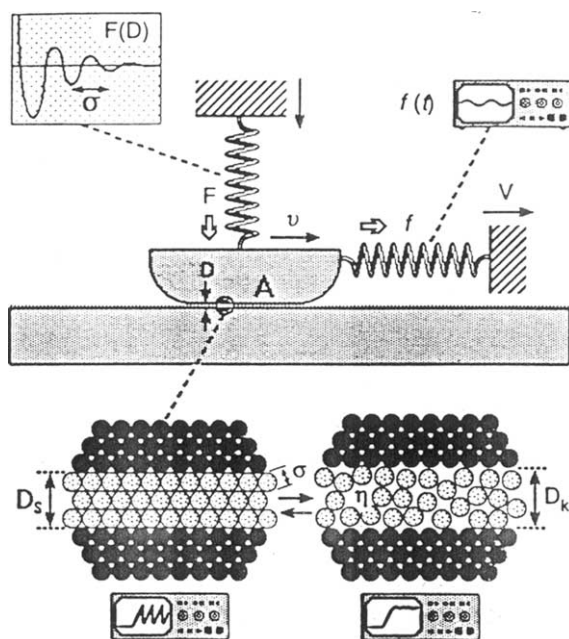


Fig. 4. Diagram of a SFA experiment (from Ref. [13]). The coiled springs are representative of any device used to measure the normal and shear forces between the samples. The SFA makes use of two cleaved mica surfaces, which are among the smoothest surfaces known. Investigators can place lubricant films, which can be as thin as a few molecules, between the mica surfaces and slide them about, to see how the films affect the friction.

The lattice vibrations are produced when mechanical energy needed to slide one surface over the other is converted to sound energy, which is eventually transformed into heat. Hence, to maintain the sliding motion, more mechanical energy must be added and one has to push harder.

In his presentation, Tabor could cite no experimental evidence, his own or otherwise, that phonons even existed, much less accounted for a major portion of the energy dissipation observed at the macroscopic scale. Nevertheless, by process of elimination he had decided that they must play an important role. Neither of us realized at the time that the sliding friction measurements of krypton monolayers which I had reported on a few months earlier [18] would prove to be the first definitive experimental evidence for the existence of phononic energy dissipation mechanisms in sliding

friction. For one crucial missing piece in the puzzle would not be forthcoming until 1994 [19].

### 3. Energy dissipation in adsorbed films: shakers and movers

Tribologists were in fact not the only community at the time to be pondering energy dissipation mechanisms at moving interfaces. An entirely distinct “vibrations at surfaces” community, which emerged in the 1980’s and 1990’s, was also exploring energy dissipation within the context of the damping of small vibrational motions of atoms on surfaces [20].

Whenever atoms or molecules adsorb on surfaces, new vibrational modes emerge which are not present in either an isolated surface or the adsorbate alone. The modes that appear include “internal”, stretching or torsional vibrations within a molecule, and “external” modes whereby the entire molecule or atom moves as a whole with respect to the surface. Before the mid 1980’s, the only external vibrations to have been studied were the “frustrated” (i.e. damped) vibrations of physisorbed molecules on graphite in directions perpendicular to the surface. Their energies were determined using inelastic scattering of thermal energy neutrons, the standard technique for vibrational studies in bulk materials [21]. Only graphite surfaces could be studied at the time on account of high surface area sample requirements. (It is interesting to note that such samples were obtained from the carbon industry, which manufactured high surface area graphite lubricants.) Frustrated vibrations parallel to a surface, perhaps more directly relatable to sliding friction, were reported for the system nitrogen on graphite in 1990 [22], but no connections with sliding friction were made at the time. Indeed, even if the notion had been advanced, it would not have been obvious that the dissipation associated with small molecular vibrations of atoms adsorbed on a surface was comparable to frictional energy dissipation of atoms sliding several lattice spacings or more along a surface.

The first direct observation of external vibrations of a molecule adsorbed on a non-graphitic

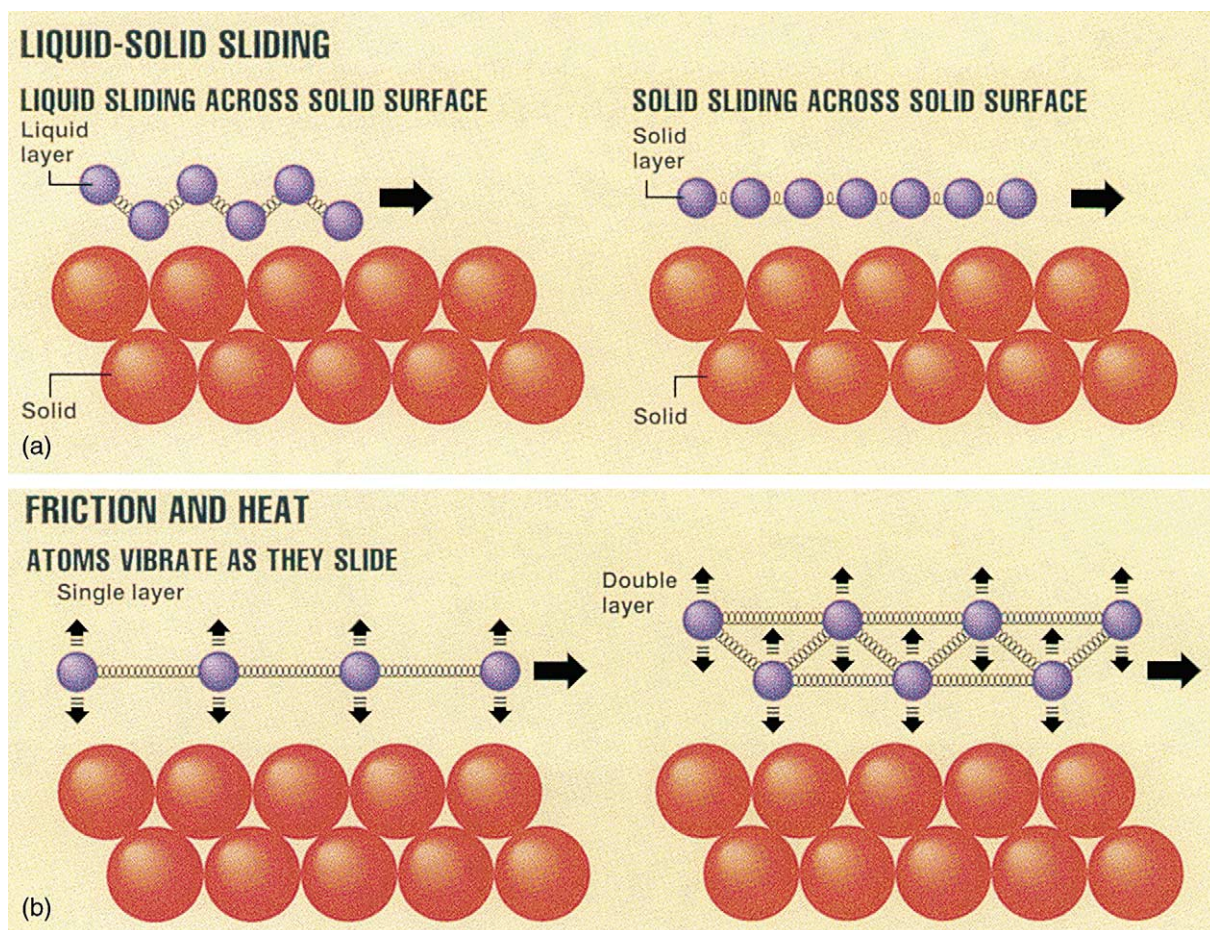


Fig. 5. Schematic of phonon friction (from Ref. [35]). Unlike matter in the visible world, a solid layer that's one atom thick (a) slides more easily over a solid surface than an equivalent liquid layer. That's because atoms in solids are more tightly bound together than atoms in liquids. Liquid atoms tend to fall between atoms of the surface beneath them, hindering their sideways movement. Solid atoms slip across the surface as a cohesive sheet. At the atomic level (b), a double layer of atoms is harder to slide over a solid surface than a single layer because the two layers of atoms jostle each other, producing extra heat. The extra heat creates more friction, and that means it takes more effort to slide the double layer of atoms.

substrate was reported in 1986 for CO molecules adsorbed on Pt(1 1 1) [23], obtained by means of the newly developed technique of inelastic scattering of thermal energy He atoms [24]. A large number of systems were subsequently explored by means of He scattering, and later advances in other fields also made possible the probing of external vibrational modes by means of electron energy loss spectroscopy [25], infrared spectroscopy [26], and Raman scattering [27]. Information on adsorbate vibration modes allows estimates to be made of the magnitude of a surface's

corrugation, or how much the binding energy to a surface varies as an atom moves from one position to another along a surface. Such information is essential for correct modeling of sliding friction at the atomic scale. If there were no corrugation in the potential, there could be no phononic component of sliding friction, irrespective of how strongly bound the atoms are to the surface, for one primary manifestation of phononic friction is its hypersensitivity to commensurability and interfacial orientation effects.

Separated in both time and topic, the vibrations at surfaces community was not destined to intersect with the tribology community before the mid 1990's [28–30]. When the intersection did occur, it was within two contexts: (1) The surface corrugation information generated by the vibrations community was an essential ingredient in computer simulations of phononic friction, and (2) theorists in the vibrations community noticed that energy dissipation rates of electronic friction mechanisms (discussed below) [31] observed for vibrational modes of adatoms were close to the frictional energy dissipation rates which I had measured by means of QCM for adsorbed monolayers. Could it be that the two communities were in fact studying the same phenomena? For an incommensurate contact, it is increasingly apparent that the energy dissipation mechanisms are in fact the same.

The QCM (Fig. 6) is an instrument that operates on a time scale short enough to detect phonons, whose lifetimes are typically no longer than a few tens of nanoseconds. While for decades the QCM had been employed primarily for microweighing and time standard purposes, Allan Widom and I adapted it in the mid 1980's for sliding friction measurements of adsorbed layers on metal surfaces [32]. The basic component of a QCM is a single crystal of quartz that has very little internal dissipation (or friction). As a result it oscillates at an extremely sharp resonance frequency (usually 5–10 MHz) that is determined by its elastic constants and mass. The oscillations are driven by applying a voltage to thin metal electrodes that are deposited on the surface of the quartz in a manner that produces a crystalline texture, generally (1 1 1) in nature. Atomically thin films of a different material are then adsorbed onto the electrodes. The extra mass of the adsorbed layer lowers the resonance frequency of the microbalance, and the resonance is broadened by any frictional energy dissipation due to relative motion of the adsorbed layer and the microbalance. By simultaneously measuring the shift in frequency and the broadening of the resonance (as evidenced by a decrease in the amplitude of vibration of the microbalance), the sliding friction of the layer with respect to the metal substrate can be deduced. The friction can

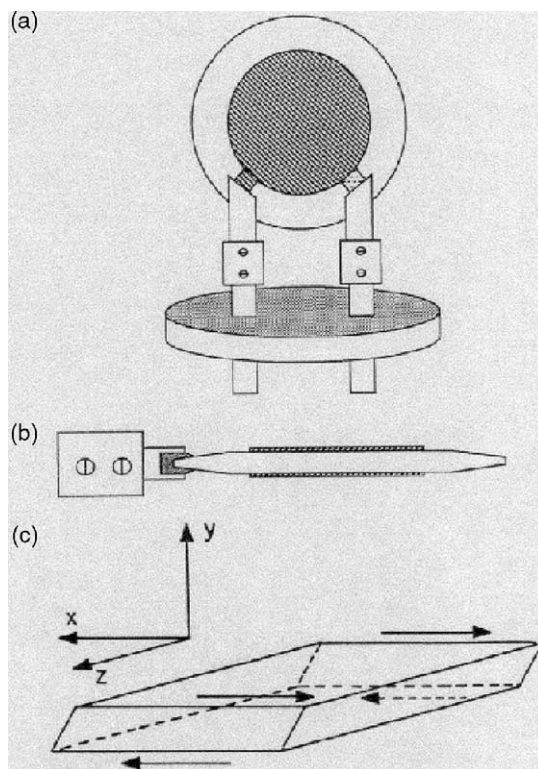


Fig. 6. Front (a) and side (b) views of a QCM. The shaded regions represent metal electrodes that are evaporated onto the major surfaces of the microbalance. Molarly thin solid or liquid films adsorbed onto the surface of these electrodes (which are parallel to the  $x$ - $z$  plane) depicted in (c) may exhibit measurable slippage at the electrode-film interface in response to the transverse shear oscillatory motion of the microbalance. The experiment is not unlike pulling a tablecloth out from under a table setting, whereby the degree of slippage is determined by the friction at the interface between the dishes (i.e. the adsorbed film material) and the tablecloth (i.e. the surface of the electrode).

be measured only if it is sufficiently low so as to result in significant sliding, which is accompanied by a measurable broadening of the resonance. For this reason, QCM measurements of sliding friction tend to be carried out on systems exhibiting very low friction, such as rare-gas solids adsorbed on noble metals. For the vast majority of other systems which exhibit higher friction (chemically bonded layers, etc.) the slippage of an adsorbed monolayer on the surface of the QCM is too small to produce a measurable broadening. In this case

interfacial slippage and/or bond breaking can be detected by performing measurements on micron-sized particles, whose larger inertial masses can more readily overcome the stronger frictional forces [33].

In 1991, I reported my group's QCM observations that solid monolayers of krypton sliding on gold exhibited five times less friction than liquid monolayers [18]. I had found the "slippery when dry" nature of krypton to be extremely counter-intuitive and had even delayed publication of the data for a year, as I could offer no physical explanation for the results. The explanation would be forthcoming in 1994, when Mark Robbins and coworkers' successfully modeled the data by assuming that the friction was due to phonons excited in the adsorbed layers [34]. Liquid layers, being more flexible and therefore slightly more commensurate with the underlying surface, exhibited higher friction than their solid counter parts. Phononic friction mechanisms were also found to explain monolayers and bilayers of xenon sliding on silver surfaces [35,36], and collectively these experimental and computational studies have supplied definitive proof of the existence, if not dominance of phononic friction in the adsorbed monolayer systems.

A surprising aspect of the excellent agreement between the numerical simulation data and the experiments is the fact that friction arising from electronic mechanisms was totally neglected. Such friction is related to the resistance felt by mobile electrons in a conducting material as they are dragged along by forces exerted by the opposing surface [37]. Could the simulations have slightly overestimated the friction, masking electronic contributions? The answer is probably yes, since there is just enough uncertainty in the best estimates for corrugation levels of Au(111) and Ag(111) substrates to allow for the presence of a moderate level of electronic friction to have been concealed [38]. Indeed both electrical resistivity measurements by Schumacher et al. [39], as well as our own group's measurements of nitrogen sliding on lead in its normal and superconducting state [40], indicate that electronic contributions are non-negligible for the first adsorbed layer of atoms on conducting metallic substrates.

One of the more remarkable properties of the friction of the adsorbed layers studied so far is the total absence of static friction: An arbitrarily small applied force is sufficient to induce sliding [18,34]. While this is entirely consistent with atomic-scale theories of friction (both phononic and electronic) at clean crystalline interfaces, it is unheard of in the macroscopic world [41]. This gives rise to the obvious question of how fundamental dissipation mechanisms such as phononic and electronic effects are manifested in systems characterized by different length and timescales. Do they play a substantive role in wear-free friction at the macroscopic scale, as Tabor had suspected, or are they simply the primary energy dissipation mechanisms in molecularly thin films adsorbed on open surfaces due to the simplicity of the systems under study? The answers to these questions remain outstanding. But a growing body of literature, particularly that focussed on the role of commensurability effects in sliding friction, is helping to shed light on this issue.

#### **4. Commensurability effects and static friction: a sticky topic**

One major manifestation of phononic friction is its hypersensitivity to the relative commensurability of the two surfaces in sliding contact: A transition from commensurate to incommensurate sliding conditions theoretically can reduce the sliding friction levels by many orders of magnitude [42]. Another manifestation of phononic friction is the theoretical prediction that static friction should vanish for nearly every pair of clean surfaces which deform elastically: The force to overcome friction is simply proportional to the sliding speed times a friction coefficient characteristic of the two surfaces in contact. But one of the most common everyday experiences with friction at the macroscopic scale is the ever present occurrence of static friction: The force to initiate motion (which itself is quite variable, depending for example on how long the two surfaces have been in contact) is larger than that required to keep an object in motion. A closely associated phenomenon is that of "stick slip" friction [43], whereby for certain



sliding speeds, the “velocity weakening” dependence of the transition from static to sliding friction leads to repetitive sticking and slipping at the interface, producing the all-too familiar screeching noises associated with brakes, fingernails, etc.

Stick–slip phenomena are frequently blamed for excessive interfacial wear rates, and as such have received much attention from the mainstream tribological community. The key to solving the mystery of static friction and stick–slip phenomenon appears to lie buried in the atomic-scale structure of the myriad of contacts formed between the two sliding surfaces, and the nature of molecules confined between them. These are not only extremely difficult to characterize, but are continuously evolving as the microscopic irregularities of the sliding surfaces touch and push into one another. The constant changing of the nature of the interfacial geometry of the contact areas (even in cases where the contact area is constant) gives rise to friction coefficients and stick slip event rates that are never exact numbers [43]. Moreover, the friction force at an individual asperity may or may not increase with applied load, depending on the structure of the contacting solids, and molecules confined within them [44,45].

Surface scientists new to the field of tribology have abandoned the approach of characterizing innumerable hidden interfaces. Instead, well-defined interfaces at nanometer length scales are prepared in advance of the measurements, usually involving contact at one, rather than multiple asperities [6]. The techniques which they employ benefit directly from progress in surface science in decades prior, whereby improvements in ultra-high vacuum technology allowed preparation of unprecedented, well-characterized crystalline surfaces. Three major advances in the period 1950–1970 gave rise to the ability to prepare well characterized surfaces: (1) The development and construction of routinely de-mountable vacuum-tight metallic enclosures in which residual pressures between  $10^{-9}$  Torr and  $10^{-10}$  Torr could be established and maintained without excessive difficulty, (2) The use of these enclosures to perform the elemental analysis of the constituents of a surface by means of Auger electron spectroscopy, and (3) The deployment of the diffraction of low-

energy electrons (LEED) for structural studies of single crystal surfaces (Fig. 7). A great number of LEED/Auger studies were carried out starting in the 1970’s on the structure of a wide range of single crystal surfaces, and the two-dimensional phases of atoms and molecules adsorbed on them [49–51] (Fig. 8).

Further advances in the structural characterization of surfaces came with the development of scanning probe microscopes in the 1980’s, which were quickly adapted for non-conducting surfaces and for probes of microscopic-scale friction. Indeed, inspired by the concept of phonon friction, Gary McClelland collaborated with C. Mathew Mate at IBM Almaden in the mid 1980’s to measure nanometer-scale friction. They did so by adapting a newly invented instrument: the atomic-force microscope, for measurements of lateral forces. With it, they published their first observations of friction, measured atom-by-atom, in a landmark 1987 paper. Their instrument revolutionized studies of friction at atomic-length scales [52].

An atomic-force microscope consists of a sharp tip mounted at the end of a compliant cantilever (Fig. 9). As the tip is scanned over a sample surface, forces that act on the tip deflect the cantilever. Various electrical and optical means (such as capacitance and interference) quantify the horizontal and vertical deflections. In the early 1990’s, the IBM researchers succeeded in setting up their friction-force microscope in ultra-high vacuum, with a contact area estimated to be less than 20 atoms in extent. Their measurements yielded a friction force that exhibited no dependence on normal load [54]. According to the classical friction laws, this result would have implied zero friction. But not only was friction evident, the shear stress, or force per area required to maintain the sliding, was enormous: one billion newtons per square meter, or 150,000 pounds per square inch! That force is large enough to shear high-quality steel. Could there be frictional energy dissipative mechanisms as yet undetermined which are giving rise to such high levels?

Energy dissipation mechanisms and the fundamental origins of friction are the focus of ongoing efforts by Miquel Salmeron, University of

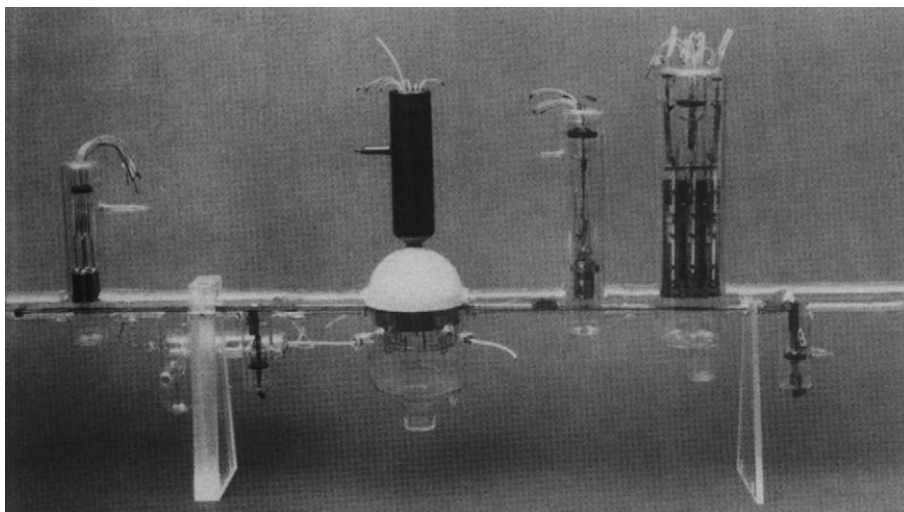


Fig. 7. This first ultra-high vacuum system became the first LEED/Auger Spectrometer when in 1967. R. Weber observed the differentiated Auger peaks of silicon and cesium [46] (from Ref. [8]). L.A. Harris made the first practical Auger Electron Spectroscopy measurements in 1968 using an electrostatic velocity analyzer [47], and Weber's demonstration of the use of the LEED apparatus for this purpose opened up a new era in surface physics. The system shown was originally built by P. Palmberg and used for his graduate research in W.R. Peria's Physical Electronics Laboratory [48]. Weber modified the system and also used it for his graduate research of alkali metal layers on semiconductor surfaces.

California, Lawrence Berkeley Laboratories, whose members are among an elite group worldwide who have succeeded at the difficult task of performing well-controlled atomic-force microscopy measurements in an ultra-high vacuum environment [45,55]. It is interesting to note that even in AFM geometry involving a single contacting asperity on a single crystal surface, static friction and stick–slip phenomenon are ever present. In the vast majority of cases, one stick–slip event is observed per unit cell of the substrate, even in cases where the atomic cell contains more than one species. Accounting for such phenomena in terms of energy dissipation, which is distributed among the tip, substrate, and cantilever, is an ongoing issue in the AFM community. The high-energy dissipation rates associated with AFM geometries may in fact be due to the creation of point defects and/or atom transfer to and from the tip. Carpick and Salmeron have published a comprehensive treatment of AFM measurement for studies of the fundamentals of friction [45]. It should be considered required reading material for scientists entering the field.

Among tribologists, AFM researchers are not the only ones to have adapted their techniques to UHV conditions. Many tribologists now routinely employ Auger Spectroscopy for surface chemical analysis of regions that have been exposed to sliding with and without the presence of a lubricant [56]. But the most direct merging of mainstream surface science with tribology has occurred in the laboratory directed by Andrew Gellman at Carnegie Mellon [57]. Gellman and coworkers have constructed a “UHV tribometer”, which allows the tribological properties of two single crystal metal surfaces to be measured under the ultra-high vacuum conditions of a surface analysis apparatus (Fig. 10). The experiment allows measurements of both friction and adhesion between two single crystal surfaces brought into contact under a wide range of loads, and sheared with a wide range of sliding velocities. The experiments performed to date have systematically varied a number of surface characteristics in order to observe their effect on tribological properties, including the relative orientation of the single crystal lattices. Experiments with Ni(100) reveal varia-

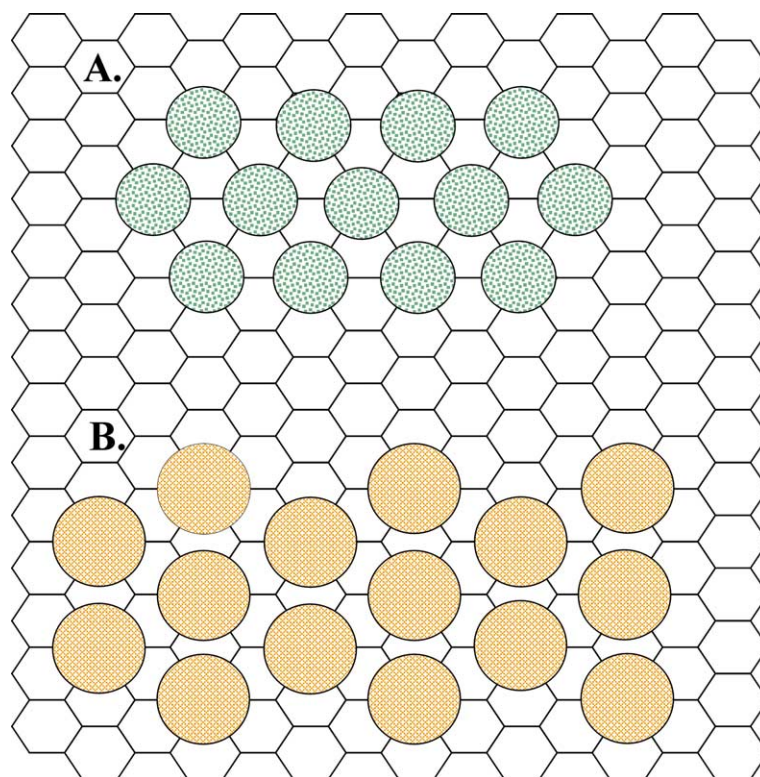


Fig. 8. Arrangement of molecules adsorbed in a commensurate fashion on the (0001) face of graphite. (It is interesting to note that graphite samples were obtained from the carbon industry, which manufactured high surface area graphite lubricants.) (a) Arrangement of molecules of a diameter less than 4.26 Å, and (b) molecules of a diameter greater than 4.26 Å [49].

tions in friction (by about a factor of five) with relative orientation of the lattices [58]. While Gellman attributes the variation with orientation in this system to plastic deformation within the bulk solids, the result reveals how ubiquitous is the dependence of friction on interfacial commensurability, irrespective of the time or length scale under study. It is also routinely observed in surface forces apparatus [59] and atomic-force microscopy studies measurements [60,61].

Even though friction is routinely observed to depend on lattice commensurability, the variation is generally less than an order of magnitude, not the many orders-of-magnitude change (up to 14!) [42] predicted by theories of phononic dissipation mechanisms. Perhaps the discrepancy simply reflects the degree to which phononic dissipation mechanisms contribute to the total frictional observed. To shed light on the issue, our group is

presently pursuing a detailed QCM study of friction as an adsorbed layer undergoes a transition from incommensurability to commensurability (Fig. 8) with the underlying substrate. In such a simple system we expect to observe changes in friction which are far closer to theory, just as adsorbed monolayers are to date the only systems to exhibit no static friction.

The question of course remains as to why static friction can be so ubiquitous when theoretically, two clean interfaces in sliding contact are not expected to exhibit it. The answer may ultimately prove to lie in “third body” effects, whereby additional adsorbed molecules act to initially pin the interface. Mark Robbins and coworkers have recently suggested that static friction is likely to be related to adhesive forces of thin adsorbed films (water, hydrocarbons, etc.) [41] which are known to be present on most surfaces: They have

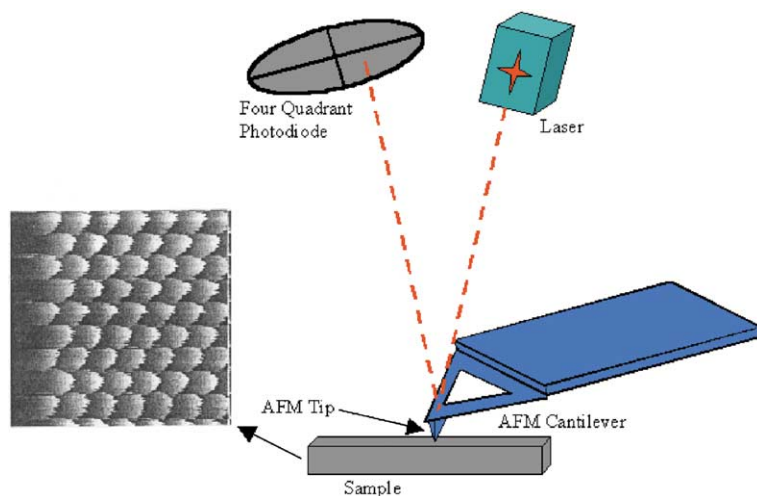


Fig. 9. Schematic of an atomic force microscope (AFM). The image at left is a lateral force image of MoS<sub>2</sub> taken from Ref. [53]. In contact AFM mode, the AFM tip is brought into contact with the sample surface, and then raster scanned across the sample surface. The AFM tip maintains contact with the sample, and the AFM cantilever moves in response to the sample's morphology and frictional forces between the sample and the AFM tip. A laser beam is reflected off of the back of the AFM cantilever and onto a four-quadrant photodiode. In this way, small angular motions of the cantilever can be detected. The position of the laser on the photodiode provides both a map of the sample surface and a frictional measurement.

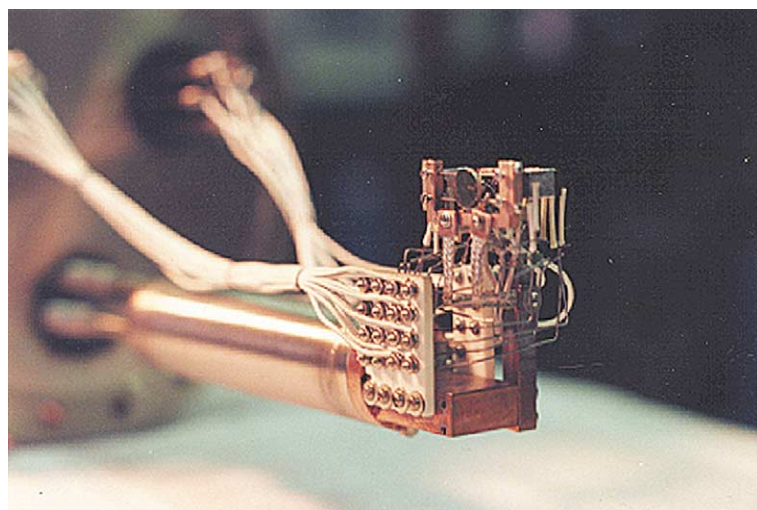


Fig. 10. Photograph of the UHV tribometer. One of the single crystal surfaces is the circular disk in the upper right of the photograph.

demonstrated this with computer simulations which indicate that these ubiquitous films behave like marbles which roll to the open niches of an incommensurate interface composed of, for example, ping-pong balls in contact with tennis balls. The marbles always find a local energy min-

imum (Fig. 11), so it always takes some energy to initiate sliding.

Experimental determination of the structure of films trapped between solid surfaces, and not just the structure of the surface contact points, thus remains one of the most important goals of the

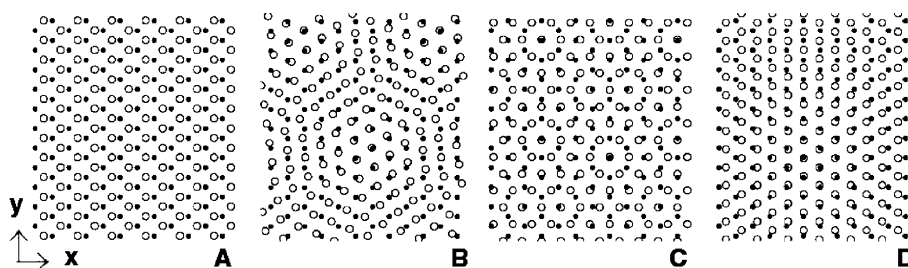


Fig. 11. Projections of atoms from the bottom ( $\bullet$ ) and top ( $\circ$ ) surfaces into the plan of the walls. In (a)–(c) the two walls have the same structure and lattice constant, but the top wall has been rotated by 0, 11.6 or 90°, respectively. In (d) the walls are aligned, but the lattice constant of the top wall has been reduced by 12/13. Note that the atoms can only achieve perfect registry in the commensurate case (A) (from Ref. [41]).

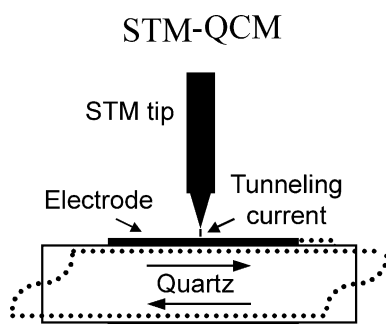


Fig. 12. Schematic of the STM-QCM apparatus. The STM tip scans the surface of a QCM which oscillates in transverse shear mode. This geometry provides a single asperity contact with nanometer scale contact area. The response of the QCM resonance to the applied normal force of the tip combined with STM images of the surface results in a unique view of a sliding contact and a powerful technique for studying the fundamentals of friction and lubrication [63].

nanotribology community. Current efforts to characterize the detailed atomic structure of films confined at an interface include combined synchrotron X-ray/Surface forces apparatus methods [62], and a combined STM-QCM apparatus. [63, 64] (Figs. 12 and 13).

### 5. Nanoscale machine lubrication: The squeaky wheels will get no grease

If the precise nature of the contacting asperities between macroscopic objects in sliding contact is determined, including the role of uncontrolled adsorbed species, the results of nanotribological

studies can be directly implemented into mainstream tribological considerations. Meanwhile, the results of fundamental investigations of surfaces can be more readily applied to solid–vapor or solid–liquid interfaces, where the complicating factors associated with asperity contacts are less of an issue, and to micro-electro-mechanical systems (MEMS)/nano-electro-mechanical systems (NEMS) related issues, where machine components with incredibly small dimensions are rapidly approaching the length scales routinely probed by the nanotribological community. To name just one recent example, the design of a two-dimensional “car” complete with pulling power and an “engine” was recently published by Porto et al. [65]. It is “driven” by frictional push-off forces along a surface and bears a striking resemblance to the atoms and springs considered in the Tomlinson models. While the authors are quick to point out that the actual “cars” built according to their design need not be so small in scale (the general concept scales up in size to the mesoscale), the design illustrates how astoundingly small future machine components are envisioned.

Are such designs the way of the future, or just pure fancy? Consider, for a moment “ordinary” (i.e. macroscopic) motor vehicles, which in their early days were quite operational, but far from optimal mechanical devices. Ownership of an automobile in 1916 involved an overwhelming maintenance schedule requiring daily servicing of the lubricants, and major maintenance every 500 miles [3]. Without the major improvements in lubrication engineering that occurred subsequent to its

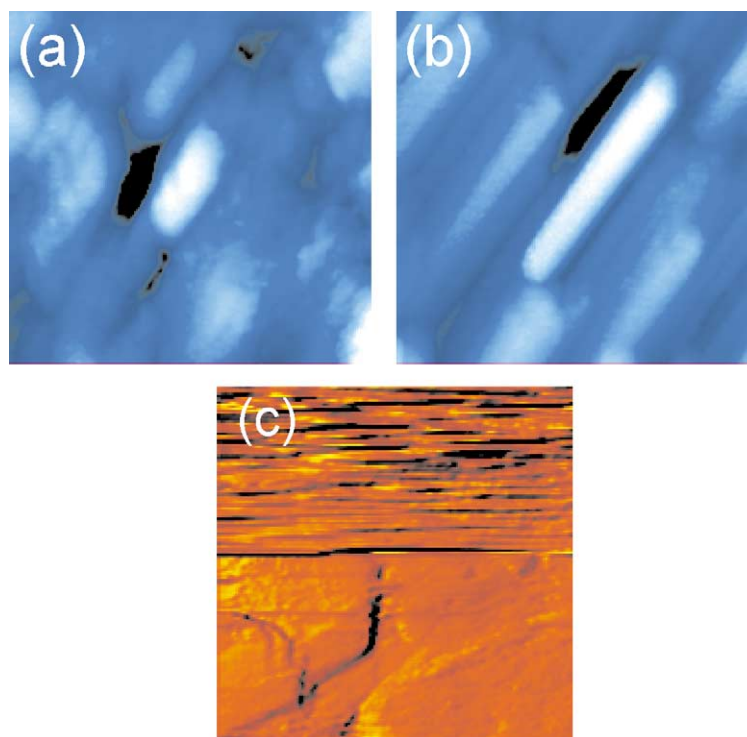


Fig. 13. Images recorded with the STM-QCM apparatus. Images (a) and (b) are a pair of STM images showing the surface of a QCM while stationary (a) and vibrating (b). The images are  $177 \times 177 \text{ nm}^2$ , and the full vertical range is 15 nm. The quartz sample is a thin disk 8 mm in diameter. Both of its surfaces are coated with a thin (150 nm) metal film, which acts as an electrode for exciting the resonance of the quartz through piezoelectric coupling. This crystal has a 5 MHz fundamental frequency and vibrates in transverse shear mode, whereby vibration is in the plane of the surface. The direction and amplitude of vibration can be determined by comparing the stationary and vibrating images. Since the oscillation occurs very rapidly compared to the image acquisition time, vibrating features such as the prominent central mound appear smeared according to the extent of motion back and forth. Measurements of the amplitude and frequency reveal that the quartz surface readily achieves speeds over 1 m/s. Such speeds are typical for everyday objects in sliding contact. Therefore, the STM-QCM is capable of studying friction on the nanometer scale under realistic sliding conditions. In (c), an STM image ( $350 \times 350 \text{ nm}^2$ ) of TBPP, a well-known lubricant additive, on a platinum QCM electrode at room temperature. The additive was vapor-deposited to form a 1 nm thick film on the surface. The underlying quartz crystal is vibrating in the bottom half of the image and stationary in the top half. Interestingly, the STM is unable to image the surface unless the quartz is vibrating. Most likely, the mobile and insulating lubricant is brushed away from the tip by the vibrating action of the surface, allowing the tip to image the conductive platinum surface [64].

invention, the motor vehicle would not have risen to its present status in society. Similarly, while there is widespread belief that the future will be revolutionized by MEMS and/or NEMS devices, the enormous promise will not materialize without substantial progress in overcoming the stiction, friction and wear associated with such devices [66]. Because MEMS devices must react to mechanical signals, many employ construction topologies that require physical motion. Suspended plates and beams that are fabricated a few microns away

from their supporting substrates are in common use, and these structures typically have relatively large areas and very small stiffness. These combined characteristics makes MEMS devices highly susceptible to surface forces which can cause the suspended member to deflect towards the substrate, collapse and/or adhere permanently to the substrate [67]. With the current impetus towards device components extending well into the nanometer regime, the surface-related complications currently encountered with MEMS are expected to

be even more severe: an atomistic understanding of the devices' material properties will be tantamount to their ability to function reliably, and it is clear that liquid and grease-like lubricants developed for macroscopic machinery will be of no use on such machines.

While the “MEMS train” has yet to leave the station, computer disk drive technology has soared forward with lightening speed [68]. The miniaturization of computer hard-disk storage devices is so advanced that many of the devices shipped today rely on a single layer of lubricant molecules adsorbed on a sub-micron thick hard protective coating of amorphous carbon to control the static friction and wear between the read/write head and the disk surface. The frictional properties of hard coating and lubricant molecules attached to solid surfaces are thus a matter of major interest to both fundamental and applied tribologists. (It is important make a distinction here between low frictional properties of an adsorbed film, and its overall ability to lubricate. More important, in many cases than low friction, is a lubricant's ability to remain on the surface.) Perry and co-workers at the University of Houston [69] have employed AFM with standard surface analytical methods to investigate the frictional properties of potential hard-coating material, vanadium carbide (VC), as a function of surface oxidation. In this study, a single-crystal VC sample was prepared under ultra-high vacuum conditions by sputtering and annealing, then characterized by LEED and

Auger electron spectroscopy. Using a UHV-AFM, the frictional forces between a silicon nitride tip and the clean VC surface were measured as a function of the applied load. The surface was then exposed to a saturation coverage of molecular oxygen, known to react predominantly with the vanadium atoms of the VC surface, and then re-investigated in situ with AFM. The results of the frictional measurements appearing (Fig. 14) indicated a 38% reduction in the coefficient of friction upon surface oxidation. Oxidation is of interest for tribological considerations on account of its common occurrence, particularly in sliding contacts, under ambient conditions. The exact mechanism of the friction reduction observed is still being explored, within the context of phononic and electronic dissipation mechanisms, with electronic mechanisms appearing to be the most likely candidate.

AFM, as well as numerical simulations have also probed the frictional properties of model lubricant chain molecules. The average frictional forces of alkylsilane molecules containing two to eighteen carbon atoms adsorbed on silicon substrates decreases with chain length up to eight carbon atoms, and then remains relatively constant [70]. Salmeron and coworkers have proposed that the chain length dependence arises from the interplay between packing energy of the monolayer film and local deformations in the film [71], since below eight carbon atom chain lengths, the molecules are relatively disordered. Energy

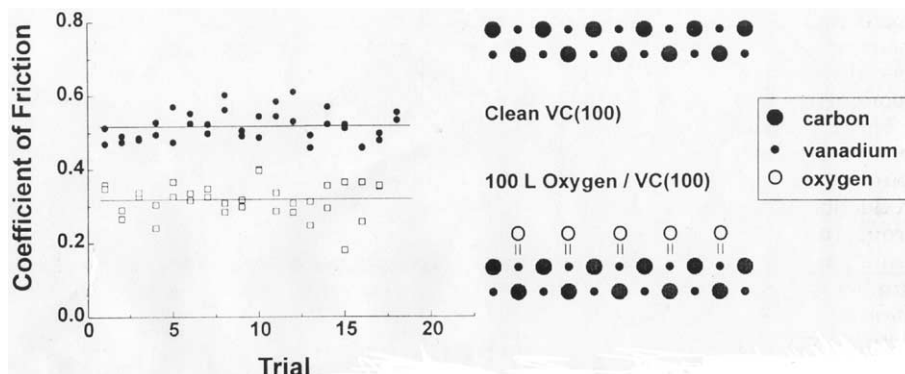


Fig. 14. Frictional forces measured using AFM under ultra-high vacuum conditions as a function of surface oxidation of single crystal VC (from Ref. [69]).

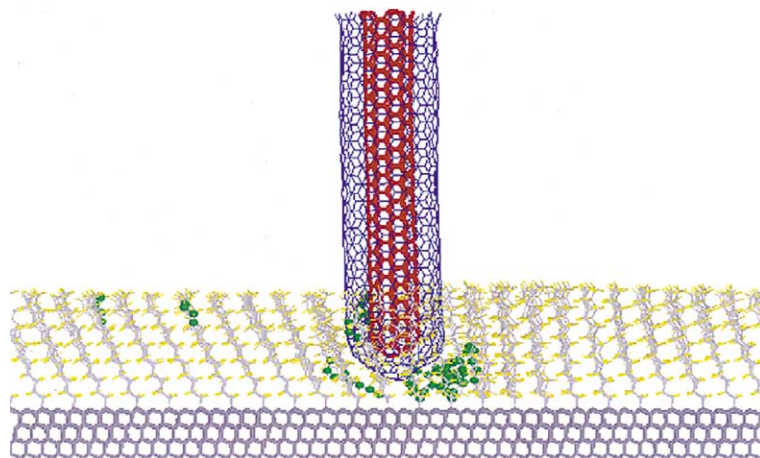


Fig. 15. Snapshot of a molecular dynamics simulation depicting a carbon, double-wall nanotube indenting a monolayer of *n*-alkane chains attached to diamond (1 1 1) (colored gray). The chains have 13 carbon atoms and are attached in a  $(2 \times 2)$  arrangement (colored gray and yellow) to the diamond substrate. The nanotube is composed of a (5,5) capped nanotube (colored red) inside a (10,10) capped nanotube (colored blue). Gauche defects introduced into the monolayer by the indentation are depicted as large green spheres (from Ref. [72]).

dissipation mechanisms to be considered in such systems must go beyond simple electronic and phononic mechanisms, as now the vibrations within individual molecules (the “internal” vibrations as referred to by the vibrations at surfaces community), as well as the creation of kinks and Gauche defects (deformation of extended chains) must be taken into account. Judith Harrison at the US Naval Academy is incorporating these effects into numerical simulations [72], and is rapidly converging on a solution to the problem, investigating all of the chain lengths which have been experimentally probed (Fig. 15).

## 6. Tribology and surface science: One slick partnership for now and the future

It is clear that fundamental surface scientists have now joined their materials science and engineering colleagues in efforts to speed progress in the area of tribology. Is the surface science community, which has been so highly successful at determining the structure and chemical composition of an open surface, up to the task of performing such characterizations at buried interfaces which are constantly moving? Only the future will tell. Meanwhile, pressed on by a confluence of

forces ranging from environmental concerns over energy consumption to the ever shrinking nature of mechanical systems, the need to be able to a priori design tribomaterials is ever increasing. Whether for macroscopic applications in the automotive industry, or small-scale applications such as those involving MEMS, and ultimately NEMS, there is no doubt that the role of surface scientists will be critical.

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