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FRICTION AT THE ATOMIC SCALE

Long neglected by physicists, the study of friction's atomic-level origins, or nanotribology, indicates that the force stems from various unexpected sources, including sound energy

I used to dread the first week of December. It wasn't the darkness or Boston's pre-snow drizzle the darkness or drizzle that made me gloomy, and it wasn't the nonexistent parking at holiday-frenzied shopping malls. This was the week when abstracts were due for the annual March meeting of the American Physical Society, the meeting of condensed-matter physicists. In 1986 my colleague Allan Widom and I had developed an experimental technique that could measure the frictional force of one-atom-thick films sliding along flat solid surfaces. The problem was, I could find nowhere to classify my atomic-scale friction abstract within a myriad of March meeting subject categories.

It was not that research on friction did not exist. I had always been welcomed by the multidisciplinary American Vacuum Society, in sessions on macroscopic-scale friction or nanometer-scale science. But mainstream physicists seemed to have no interest in the topic. With near unanimity, they would attribute the origins of friction as something to do with surface roughness. Given the everyday familiarity and economic impact of friction, one would have thought that they might have been more interested. (By most estimates, improved attention to friction and wear would save developed countries up to 1.6 percent of their gross national product, a whopping $116 billion for the U.S. alone in 1995.)

In fact, I wasn't really alone in my research interests. The late 1980s marked the advent of many new techniques, including my own, that could study the force of friction, either experimentally, by sliding atoms on crystalline substrates, or theoretically, using new computer models. I first referred to the field as "nanotribology" -- friction, or tribology, studied in well-defined geometries on the nanometer scale --in a January 1991 publication, and others began using the term as well. What was once a grassroots

community of isolated researchers was progressively becoming an accepted scientific field in its own right.

Since then, nanotribologists have been regularly discovering that atomic-scale friction can differ significantly from what is observed at the macroscopic level. Friction has very little to do with microscopic surface roughness, and in some instances, dry surfaces are actually slicker than wet ones. The force is complex enough that, even if we can perfectly characterize a sliding interface, we cannot accurately predict the friction that will occur at that interface. If the precise nature between microscopic contacts and macroscopic materials could be determined, then better understanding of friction could lead to such industrial innovations as improved lubricants and wear-resistant machine parts.

Such technological considerations have driven humans to attempt to understand friction since prehistoric times. More than 400,000 years ago, our hominid ancestors in Algeria, China and Java were making use of friction when they chipped stone tools. By 200,000 B.C.E., Neanderthals had achieved a clear mastery of friction, generating fire by the rubbing of wood on wood and by the striking of flint stones. Significant developments also occurred 5,000 years ago in Egypt, where the transportation of large stone statues and blocks for the construction of the pyramids demanded tribological advances in the form of lubricated wooden sledges.

Writing the Classics

Modern tribology began perhaps 500 years ago, when Leonardo da Vinci deduced the laws governing the motion of a rectangular block sliding over a flat surface. (Da Vinci's work had no historical influence, however, because his notebooks remained unpublished for hundreds of years.) In the 17th century the French physicist Guillaume Amontons rediscovered the laws of friction after he studied dry sliding between two flat surfaces.

Amontons's conclusions now help to constitute the classic laws of friction. First, the friction force that resists sliding at an interface is proportional to the "normal load," or the force that squeezes the surfaces together. Second, and perhaps counterintuitively, the amount of friction force does not depend on the apparent area of contact. A small block sliding on a surface experiences as much friction as does a large block of the same weight. To these rules is sometimes added a third law, attributed to the 18th-century French physicist Charles-Augustin de Coulomb (better known for his work in electrostatics): the friction force is independent of velocity once motion starts. No matter how fast you push a block, it will experience nearly the same amount of resistance.

Amontons's and Coulomb's classical friction laws have far outlived a variety of attempts to explain them on a fundamental basis in terms of, say, surface roughness or molecular adhesion (attraction between particles in the opposing surfaces). By the mid-1950s, surface roughness had been ruled out as a viable mechanism for most everyday friction. Automobile makers and others had found, surprisingly, that the friction between two surfaces is sometimes less if one of the surfaces is rougher than the other [see "Friction," by Frederic Palmer; SCIENTIFIC AMERICAN, February 1951 l. Furthermore, friction can increase when two surfaces are made smoother. In cold welding, for instance, highly polished metals stick together quite firmly.

Molecular adhesion, though, was a strong possibility, a conclusion reached in large part because of the ingenious work of F. P. Bowden, David Tabor and their co-workers at the University of Cambridge. They also found that friction, though independent of apparent macroscopic contact area, as Amontons had stated, is in fact proportional to the true

contact area. That is, the microscopic irregularities of the surfaces touch and push into one another. The sum of all these contact points constitutes the true contact area. Having established that some kind of intimate link existed between friction and adhesion, the Cambridge group presumed that friction resulted primarily from adhesive bonding at true contact points that was so strong that tiny fragments were continually being worn away.

But this explanation was wrong. It simply could not explain the fact that substantial friction exists even in cases in which wear is negligible. Indeed, under Tabor's own supervision in the 1970s, a gifted Ph.D. candidate, Jacob N. Israelachvili, developed a "surface-forces apparatus" for atomic-scale friction measurements and found clear evidence of wear-free friction. The measurement left Tabor to puzzle over where that friction might be coming from.

Israelachvili's apparatus explores the lubricated contacts between uniform mica surfaces. It takes advantage of the fact that mica is atomically smooth: cleaving a piece of mica leaves a surface that has atomically flat areas spanning as much as one square centimeter, a distance of more than 10 million atoms. (In contrast, typical surfaces might stay flat for a distance of 20 atoms, whereas smooth metals might go on for 300 atoms.) When two mica surfaces touch, an interface free of atomic pits or mountains ("asperities") is formed. In the device the backs of the mica surfaces are generally glued onto crossed half-cylinders that can be moved in two directions in the horizontal plane. To measure the contact area and separation, researchers shine a coherent light beam across the gap and look at a resulting optical effect called an interference pattern, a series of dark and light bands. Deflections of springs connected to the half-cylinders indicate the frictional force.

Early on, the surface-forces apparatus allowed atomic-scale verification of the macroscopic deduction that friction is proportional to the true contact area. But it would be nearly two decades before Israelachvili, now a full professor at the University of California at Santa Barbara, and his colleagues would establish the elusive link between friction and adhesion. They discovered that friction did not correlate with the strength of the adhesive bond itself. Rather friction was connected to adhesive "irreversibility," or how differently surfaces behave when they stick together as compared with when they are in the process of becoming unstuck. But in their triumph, the investigators could not address the explicit physical mechanism that gave rise to the friction they were measuring.

James A. Greenwood of the University of Cambridge, a world authority on tribological contact between rough surfaces, summed up the situation in 1992 when he wrote, "If some c]ever person would explain why friction exists, and is proportional to the [true] area of contact, our problem would be solved."

Good Vibrations

A leading candidate for that clever person is Gary M. McClelland of the IBM Almaden Research Center. In the 1980s he derived a very simple model for wear-free friction based on vibrations of atomic lattices. Unknown to McClelland, the model had been published by G. A. Tomlinson of the British National Physical Laboratory in 1929, as had a far more sophisticated treatment by Jeffrey B. Sokoloff and his coworkers at Northeastern University in 1978. But these works had received little attention.

Friction arising from atomic-lattice vibrations occurs when atoms close to one surface are set into motion by the sliding action of atoms in the opposing surface. (The vibrations, which are really just sound waves, are technically called phonons.) In this way, some of the mechanical energy needed to slide one surface over the other is converted to sound

energy, which is eventually transformed into heat. To maintain the sliding, more mechanical energy must be added, and, hence, one has to push harder.

The amount of mechanical energy transformed into sound waves depends on the nature of the sliding substances. Solids are much like musical instruments in that they can vibrate only at certain distinct frequencies, so the amount of mechanical energy consumed will depend on the frequencies actually excited. If the "plucking" action of the atoms in an opposing surface resonates with one of the frequencies of the other, then friction arises. But if it is not resonant with any of the other surface's own frequencies, then sound waves are effectively not generated. This feature opens the exciting possibility that sufficiently small solids, which have relatively few resonant frequencies, might exhibit nearly frictionless sliding.

In any case, McClelland, excited by the fact that not only wear-free but also nearly friction-free sliding was a theoretical possibility, proceeded to collaborate with his colleague C. Mathew Mate and others. To measure nanometer-scale friction, they adapted a newly invented instrument: the atomic-force microscope. With it, they published their first observations of friction, measured atom by atom, in a landmark 1987 paper.

An atomic-force microscope consists of a sharp tip mounted at the end of a compliant cantilever. 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. The microscope can detect friction, adhesion and external loading forces as small as a piconewton, or 10[Sup -12] newton. (Loosely speaking, a piconewton is to a fly's weight as a fly's weight is to an average person's.) By the early 1990s, the IBM researchers had set up their friction-force microscope in ultrahigh vacuums, allowing them to study the sliding of a diamond tip over a crystalline diamond surface with a contact area estimated to be less than 20 atoms in extent.

McClelland and his colleagues' measurements yielded a friction force that exhibited no dependence on normal load. 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 fracture top-grade steel. It was becoming clear that even if the atomic nature of the sliding contact was completely known, our ability to predict the friction force occurring at that contact was virtually nonexistent.

To date, nanotribologists have collectively observed a remarkable range of shear stresses, from 0.01 newton to 10 billion newtons per square meter. For example, Roland Luthi, Ernst Meyer and coworkers at the Institute of Physics at the University of Basel have pushed "islands" of one-molecule-thick buckminsterfullerene ("buckyballs," or carbon 60) along a crystalline salt surface with a modified atomic-force microscope tip approaching single-atom dimensions. They found shear stresses of 10,000 to 100,000 newtons per square meter, orders of magnitude lower than those associated with typical macroscopic-scale solid lubricants, such as graphite powder. (The shear stress appears high only because it is measured over a square meter of true -- not apparent contact area, which in general is orders of magnitude smaller than the apparent contact area. When graphite is used, say, to lubricate a lock cylinder, even the apparent contact area is quite small, so the actual friction encountered can be rather low.) The researchers also measured the force needed to slide the tip over the top of the buckyball island and found it to be

"stickier" than the salt.

Shear stresses orders of magnitude lower have been observed in my own laboratory by means of a quartz crystal microbalance, a device that for decades has been used to weigh samples as light as a few nanograms. It consists of a single crystal of quartz that stably oscillates at high frequency (five to 10 million times a second). We deposit metal-film electrodes onto its surfaces and then condense single-atom-thick films of a different material onto the electrodes. The condensation onto the microbalance lowers the frequency, providing a measure of how well the film particles can track the shaking of the underlying quartz substrate. The smaller the resulting amplitude of vibration, the greater the friction from the "rubbing" action of the film sliding about on the substrate.

The quartz microbalance is currently the only experimental apparatus operating on a timescale short enough to see how atomic-scale friction depends on velocity. Although the third classic law of friction states that friction is independent of velocity, researchers later found this rule to be untrue. (Coulomb himself suspected as much but could not prove it.) For example, to decelerate an automobile uniformly and stop it without a jerk, the driver must ease up on the brake in the final moments, demonstrating that friction increases with slower speeds. Such macroscopic velocity dependencies are almost always attributed to changes at the microscopic contact points (which can melt at high sliding speeds and can increase in area at low speeds, where they "tear apart" more slowly and hence have more time to form bonds). But for a geometry in which the contact area remains fixed, such as that of our quartz microbalance, friction is in fact predicted to exhibit just the opposite behavior, increasing in direct proportion to the sliding speed. We recently confirmed this observation for one-atom-thick solid films sliding over crystalline silver and gold surfaces.

Slippery when Dry

But analytic theories did not predict our surprising discovery in 1989 that krypton films sliding on crystalline gold surfaces were slipperier when dry. We observed that friction forces for liquid films were about five times higher than for solid films, with shear stresses for the solid films being a minuscule 0.5 newton per square meter for sliding speeds of one centimeter per second. The effect was so counterintuitive to me that I held off publishing the result for more than a year after discovering it.

Why should a liquid layer cause more friction on the atomic scale when in most situations in everyday life it lubricates two surfaces? Computational studies have supplied the crucial link, for they open a rare window into molecular behavior that is unattainable by any other means. Several researchers have broken new nanotribological ground with the computer. They include Uzi Landman of the Georgia Institute of Technology, who pioneered simulations of point contacts; Judith A. Harrison of the U.S. Naval Academy, who modeled interfacial chemical effects; and James Belak of Lawrence Livermore National Laboratory, who analyzed machining and wear.

It was Mark O. Robbins and his co-workers at Johns Hopkins University, though, who answered the question of liquid friction when they simulated one-atom-thick krypton films sliding on crystalline gold surfaces. They demonstrated that liquid krypton atoms, being more mobile than solid krypton, could "get stuck" more easily in the gaps between the solid gold atoms. Note that the shearing takes place between a solid and a liquid surface, a situation different from macroscopic cases of liquid lubrication. In those instances, the shearing takes place within the bulk of the liquid (that is, at a liquid-liquid interface), which usually offers less resistance to shearing than does a solid-liquid interface.

The near-perfect agreement between Robbins's model and our experimental result is both surprising and revealing, because all the friction in his calculations was attributed to lattice vibrations (sound waves). His model neglected friction from electrical effects. For insulating surfaces, such friction arises from the attraction of positive and negative charges that have separated at the interface. (A similar attraction is achieved when a balloon is rubbed on hair and left to cling to a wall.) When one or both of the surfaces in contact are metal, however, then the buildup of charge should not be significant. Rather another type of electronic friction may occur, as suggested by Mats Persson of Chalmers University of Technology in Goteborg, Sweden, and extensively investigated by theorist Bo N. J. Persson of the Julich Research Center in Germany. That friction is related to resistance felt by mobile electrons within the metallic material as they are dragged along by the opposing surface.

Physicists know that such friction exists but not how important it is (which is why small solids might exhibit nearly frictionless, instead of completely frictionless, sliding). The success of the model calculated by Robbins and his colleagues seemed to imply that electronic effects play no significant role in friction.

To investigate this Issue further, we recently measured the force needed to slide one- and two-atom-thick solid films of xenon along a crystalline silver surface, and we observed that friction increased by approximately 25 percent for the two-atom-thick xenon film.

Did this 25 percent increase stem from electronic effects? Probably not. Bo Persson, Robbins and Sokoloff have performed independent computer simulations of the xenon-silver system, and their preliminary computational results indicate that the friction associated with sound waves is much greater for two layers than for one. Basically, two layers make for a more elaborate "musical instrument," so there are more resonant frequencies to excite and hence more friction. Electronic friction undoubtedly exists, but its strength may be determined in large part by only those atoms immediately adjacent to the interface. The parameters selected to represent metal surfaces in a simulation could easily mask it. But as theoretical and simulational efforts become increasingly sophisticated, we should eventually be able to estimate with precision the proportion of energy loss that is associated with electronic effects and lattice vibration.

Rewriting the Rules

The recent progress in nanotribology clearly demonstrates that the laws of macroscopic friction are inapplicable at the atomic scale. We can now rewrite the laws of friction in a more general way. First, the friction force depends on how easily two surfaces become stuck relative to becoming unstuck: it is proportional to the degree of irreversibility of the force that squeezes the two surfaces together, rather than the outright strength of the force. Second, the friction force is proportional to the actual, rather than apparent, area of contact. Finally, the friction force is directly proportional to the sliding speed of the interface at the true contact points, so long as the surfaces are not allowed to heat up and the sliding speed remains well below the speed of sound. (Near that speed, it levels off because the lattice vibrations cannot carry away the sound energy rapidly enough.)

The discrepancy between microscopic and macroscopic frictional phenomena greatly diminishes if one notes that the true area of contact between macroscopic objects is likely to be proportional to the squeezing force. The harder you squeeze, the more area comes into contact. So friction appears to be proportional to the normal load, as Amontons stated.

And what ever became of surface roughness? Alas, its importance seems to shrink. Physicists had presumed that surface irregularities played a role in stick-slip friction, in which surfaces gliding past one another momentarily cling and then let go. Notable examples include screeching train brakes and fingernails on blackboards. Roughness was thought to cause the random nature of the sticking and the slipping. But Steve Granick and his colleagues at the University of Illinois recently observed stick-slip friction in lubricated contacts between nominally "perfect" mica surfaces. They applied millions of repetitive cycles of a sinusoidal force to confined liquids without wear and observed results suggesting that randomness (specifically, so-called 1/f noise) may be intrinsic to the stick-slip friction itself.

Considering the current race to manufacture machine components with astoundingly small dimensions, what is today considered fundamental research on the atomic scale may give way tomorrow to direct application. For instance, we now know why substances made of branched-chain molecules make better lubricants than straight-chain molecules, even though the branched-chain ones are, in bulk form, more viscous. (They remain as a liquid under greater forces than do the straight-chained molecules and thus are better able to keep two solid surfaces from touching.) Nanotribologists working with known contact geometries may one day help chemists understand friction-induced reactions taking place on surfaces or aid materials scientists in designing substances that resist wear. As the need to conserve both energy and raw materials becomes more urgent, physicists' rush to understand basic frictional processes can be expected only to accelerate.

PHOTO (COLOR): GRINDING wears away sliding surfaces. Such instances of friction had always been associated with permanent damage to the surfaces. But new studies have shown that friction can persist at high levels even in the absence of wear or damage.

PHOTOS (BLACK & WHITE): EARLY STUDIES OF FRICTION, such as those done in the 18th century by the French physicist Charles-Augustin de Coulomb, helped to define the classical laws of friction and attempted to explain the force in terms of surface roughness, a feature that has now been ruled out as a significant source.

DIAGRAM: QUARTZ-CRYSTAL MICROBALANCE can measure friction between its electrode and a layer of material only one or two atoms thick deposited on the electrode. Changes in the vibrational properties of the quartz indicate how much the deposited layer slips on the underlying surface. Computer simulations of the sliding layers, such as that of a liquid layer of krypton (white in inset) on top of gold (blue), are used to confirm the findings of the microbalance.

DIAGRAM: SURFACE-FORCES APPARATUS makes use of two cleaved mica surfaces, which are 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 sliding (insets).

DIAGRAM: LATERAL-FORCE MICROSCOPE is a variation of the atomic-force microscope. It employs a fine needle mounted on a cantilever. The tip deflects as it drags along the sample's surface. Light reflecting off the tip indicates the degree of deflection, thus providing a measure of the friction between the tip and the surface. Researchers have used the microscope to push "islands" of carbon 60 (green crystals in inset) across a salt surface. SHEAR STRESS, the amount of force per unit of true contact area needed to maintain the sliding of one object on another, is one measure of friction that has been explored with several instruments. Collectively, they have recorded a range of stress

spanning 12 orders of magnitude, all in experimental geometries free of wear, surface damage and roughness.

PHOTO (COLOR): CONTACT POINTS are the places where friction occurs between two rough surfaces sliding past each other (top). If the "normal load" -- the force that squeezes the two together -- rises, the total area of contact increases (bottom). That increase, and not the surface roughness, governs the degree of friction.

DIAGRAMS: CHEMICAL REACTIONS can occur between two sliding interfaces. In this setup, an ethane molecule, composed of two carbon atoms (green) and six hydrogen atoms (blue), is sandwiched between two diamond surfaces, which are terminated with hydrogen atoms (1). As the surfaces slide, the ethane loses a hydrogen atom (2), becoming an ethyl radical. The free hydrogen subsequently removes a hydrogen atom from the diamond and bonds with it to form a molecule of hydrogen gas (3). The ethyl radical eventually becomes chemically bound to one of the diamond surfaces (4). The diagram is based on computer simulations conducted by Judith A. Harrison and her co-workers at the U.S. Naval Academy.

DIAGRAM: DIAMONDLIKE TIP made of carbon (blue) and hydrogen (yellow) slides across the face of a similar material, a diamond surface made of carbon (green) and terminated with hydrogen atoms (red). Such computer simulations help in tribochemistry, or the study of friction-induced reactions. In this particular computation, the tip and surface deformed, but no chemical reactions occurred.

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