“Friction” is so much part of everyday experience that our language generalizes the idea to the relations between individuals and nations. To manage and optimize this fact of life has always been an engineering problem, but the present is an age when scientists often choose problems for their complexity and relevance—and what could be more relevant than friction? Careful economic studies estimate that an annual sum of money equivalent to 1% of the GNP (gross national product) could be saved if use were made of known methods to reduce friction and wear. With advances in understanding one should do better than this.

The relevance is not just to machinery, though machinery is the classical justification to study friction. Can we justify with honest scientific answers why we lubricate our eyes with tears—the artificial tears containing hydrophilic polymers? Why joggers’ knees? Why artificial hips and other biomedical implants? Neither our machinery nor our bodies could operate unless polymers—synthetic in some of these examples, biological in others—mediated what happens. These problems of “low-pressure” friction become especially urgent not only in biological contexts but also in the burgeoning fields of MEMS and microfluidics.

The point of this essay is to highlight the related opportunities to do fundamental and interesting science. In fact, objects in sliding contact present among the best model systems to study nonequilibrium polymer physics of which one can conceive. It is the system that matters. Numerous conjoint variables come into simultaneous play: polymer, shear rate, and solid surface, to which polymers adhere or not as they flow. The thermodynamic variables (temperature, pressure) are inhomogeneous—in time and in spatial position within the sample. Pressure is inherently spatially inhomogeneous when surfaces are squeezed together. Temperature is inherently inhomogeneous because the local viscous dissipation, and the local sliding-induced activation of potential chemical reactions, depends on the local pressure at each given point within the sliding system.

Thus, a sliding contact presents a convenient microcosm in which, to study systems driven far from equilibrium. The friction problem is “driven physics”—a problem distinctly different from the extensive mainstream focus on equilibrium properties in polymer science, those properties susceptible to analysis by statistical thermodynamics. The small thickness and very high shear rate when solids are in sliding contact make this problem attractively amenable to molecular dynamics simulation.

Polymers are used ubiquitously to control friction and wear but with insufficient recognition, on the engineering side, that their physical responses differ from those of small molecules. In the lubrication of magnetic disks, the lubricant is a polymer—but the literature on this subject is unclear why perfluoropolyethers are more effective than competing polymers. In the regulation of the viscosity of engine oils, polymers are used too. Classically, when dealing with metal-based machinery, the maximum pressure (load divided by area of actual contact between adjoining rough surfaces) is on the order of GPa, yet in softer contexts, involving polymers, it is 2–3 orders of magnitude less.
The unique aspect of having polymers in sliding contact is that the normal pressure, squeezing two adjoining surfaces together, is so relatively small—as is commonly the situation in “soft materials” applications.

Friction is energy dissipated into heat. Too little is understood about the link between friction and events at the scale of molecules. The National Science Foundation recently sponsored a workshop charged to assist in deciding how scarce research funding resources might be allocated to most effectively address the most important outstanding challenges. This workshop concluded1 that “New tools are required to monitor phenomena that occur at the tribological interface and to characterize the nature of buried interfaces… (they) include spectroscopic… and imaging techniques.” In this endeavor the potential is evident to apply modern spectroscopic methods—fluorescence spectroscopies to assess dynamics and vibrational spectroscopies to assess molecular orientation.2 Yet advances conducted in this spirit have hardly gone beyond proof-of-concept studies. Mechanically-based measurements of friction are well developed—but accompanying spectroscopic measurements of lubricant orientation and spatial segregation are not. This is a nearly unexplored field of study. The phenomenological observation is that the concept of “friction coefficient” (friction normalized by load) describes many sliding situations, yet little fundamental understanding exists of how energy dissipated in sliding couples to force squeezing sliding surfaces together with lubricant in between.

Another hopeful area, too little explored yet: to understand chemical reactions during sliding. Mechanical influences can result in chemical transformations—this is known from engineering practice, but how does it happen? This is the field known as mechanochemistry. Can mechanical stress shift the energy level of the higher-energy “transition state” of a chemical reaction, through which reactants pass before becoming products? If so, mechanical stress could thus lower the activation threshold of certain reactions, and so make it easier to kick-start them. According to the magnitude of stress applied, future research might even show how to switch them off and on. The complexity of polymers’ internal architecture means that stress transmission differs fundamentally from atomic systems, which lack orientational degrees of freedom, but too little is known about this fascinating possibility. Our vision is that in chain molecules, the internal architecture of the molecule focuses large stresses to weaker chemical bonds with resulting stress-induced scission of chemical bonds in these materials.3 The engineering proof that these considerations matter is the practical experience, in the field of friction engineering, that “friction polymers” are created when surfaces slide over one another, separated by lubricant.

Slow or even forbidden chemical reactions can perhaps be activated by mechanical stress. Chemical reactivity is known to depend on the relative orientation of the reactant molecules. Could one employ mechanical deformation to place anisotropic molecules into a more favorable alignment for reaction? Directional friction and confinement offer versatile ways to align molecules. This too will be an interesting avenue for possible further progress.

We conclude by mentioning vast untapped problems4 some of which may take generations to fully resolve:

- First, when driven far from equilibrium, what surface alignment results? The near-surface molecular alignment of polymers has potential technological relevance in fields from how magnetic lubricants work, to how skis function in snow when they slide downhill while coated with wax. Solutions to this problem will bring the field into closer contact with emerging issues of polymer processing and, more generally, the boundary conditions for fluid flow over a surface.

- Second, how do polymers respond to a severe and sudden change of environment, for example local temperature or pressure—as commonly occurs when solids slide over one another? Until now, the field of polymer friction studies has concentrated on systems that are subject to steady external conditions: constant shear rate, and so forth. But it often happens that polymers sustain ultrafast and transient alteration of film thickness, temperature, pressure, and deformation rate. We do not yet have good ways to think about how polymers respond to an extreme change of environment that might last for less than a second.

- In seeking to control friction, one must recognize the friction force and normal force might be decoupled, or nearly so. A thought experiment shows the idea. Imagine that the repulsive force between the surfaces carrying the same electric charge is balanced by a force that pushes them together. Although end-attached polymers in solvent (polymer brushes) strongly resist being pressed together when in good solvent situation, their resistance to interfacial forces, being dominated by an entirely different physical mechanism, is far less. Thus, decoupling, which can cause friction forces to remain small even as normal forces become large, constitutes an approach to minimizing friction that is particularly well-adapted to polymer systems.

- In minimizing wear and degradation of the solids beneath them, these thick end-attached polymers layers also offer useful sacrificial layers. The relation between friction (the minimizing of energy loss in sliding contact) and wear (the degradation of the solid surfaces underneath) is too little explored.

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Is it realistic to expect a general theory of surfaces in sliding contact? For a long time, it has been clear that—intriguingly—much of the flow behavior of high-viscosity confined fluids so much resembles granular materials (sand, powder, and colloids) that an observer could not distinguish between them if the experiment were performed in a black box. Too often, the models proposed for a given system are specific to that system—but common responses strongly suggest more universality. This could reflect the fact that high-density, short-range packing, and dynamical rearrangements of structure by instability are interrelated. The challenge, then, is to predict, is to predict from theory, rather than by empiricism, what makes polymer lubricants of one chemical structure more effective in lowering friction forces and wear than those of another.

REFERENCES AND NOTES