COMMENTARY

Tunable superlubricity of 2-dimensional materials

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Friction is responsible for an estimated 20 to 30% of world energy consumption (1). It is a major source of wear for both man and machine and causes most of the noise around us. But friction is also useful or even necessary, for example, to walk, drive, or skate, or to be able to use nuts and bolts to keep constructions together. In the example of a car, friction with the asphalt needs to be small while driving and large while braking. This calls for a tunable type of friction that is generally difficult to achieve, not in the least because we do not fully understand the microscopic mechanisms behind friction. In their article, Zhang et al. (2) demonstrate the existence of such tunable friction in a cleverly designed experiment, and provide a microscopic understanding of the tunability using molecular dynamics simulations.

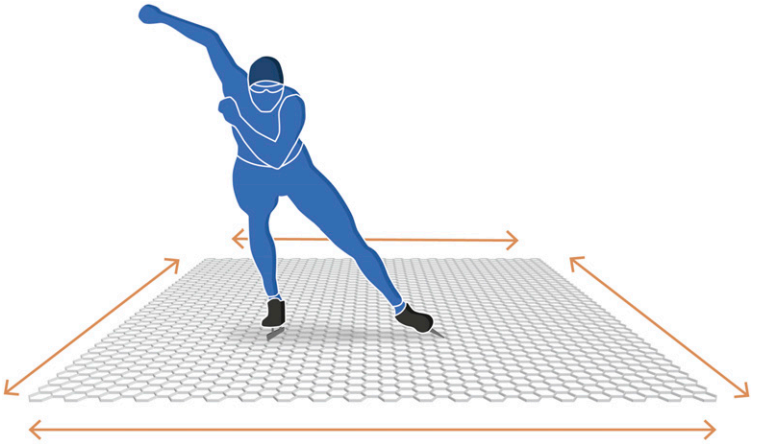

Fig. 1. Two-dimensional materials can be so slippery that one could skate on them. Zhang et al. (2) report a friction coefficient as low as 0.007 for an AFM tip on freely suspended graphene and show that it decreases to almost 0.001 when the graphene is stretched. For comparison, friction coefficients for AFM tips on 3D materials are usually above 0.1, while the optimal friction coefficient for a steel skate on ice is ∼0.01 (8). The low friction that Zhang et al. report on graphene is largely due to the weakness of the interaction between the graphene and the tip. By stretching the graphene, they suppress the freedom of the graphene to locally follow the precise contour of the tip surface and deform internally, to make individual carbon atoms of the graphene optimize their registry with respect to the tip atoms. This leads to a dramatic further lowering of the friction and introduces the exciting possibility of making friction tunable.

In itself, friction is everything but tunable. Leonardo da Vinci, in the first ever reported friction experiments, already showed that the friction coefficient of wooden blocks sliding over a wooden plane does not depend on the macroscopic contact area between the blocks and the plane. This is because of Amontons' law: The friction coefficient is the ratio of the friction force to the normal force, and both are proportional to the area of (true) contact (3). As a consequence, in designing machinery, engineers can look up friction coefficients, for instance of steel on steel, without having to worry about the surface roughness or even the shapes of the materials. How, then, to tune friction? It is true that some materials such as Teflon or ice are more "slippery" than others, but the molecular origin of this low friction is not well understood, and, in many applications, the choice of materials is imposed by other constraints.

In their paper, Zhang et al. (2) describe tunable friction induced by superlubricity, arguably the only friction phenomenon that has a sound molecular interpretation. The term *superlubricity* was coined originally for the extreme slipperiness predicted for the hypothetical geometry of 2 perfectly flat and crystalline surfaces sliding over each other in dry incommensurate contact (4). The required combination of flatness and crystalline perfection has been achieved only in a limited number of experimental systems, such as the microscopic contact between 2 graphite or graphene surfaces (5). The atoms in graphite or graphene are oriented in a hexagonal manner and form an atomic hill-and-valley landscape that looks like an egg carton. When the 2 surfaces are rotated into registry (every 60°), the friction force is high. When they are rotated out of registry, the friction is greatly reduced. This is like 2 egg cartons that slide over each other more easily when they are

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"twisted" with respect to each other. Thus, a relative rotation of the 2 surfaces allows one to tune the friction in these specific systems (5). Nowadays, the word superlubricity is used to indicate, more generally, that friction is very low, whether it originates from a lattice misfit or not.

Zhang et al. (2) start out from such low friction between a graphene surface and an atomic force microscopy (AFM) tip; clearly, the superlubricity is not between 2 rotated crystal lattices but reflects the absence of registry between the network of atoms in the silicon nitride AFM tip and the weave of carbon atoms in the graphene. In addition, they add a twist by showing that friction can be lowered by straining the graphene surface and hence changing the distance between the carbon atoms. They do so by placing the graphene on a substrate with holes. By applying a pressure difference over this structure, they controllably stretch the graphene over the holes. Sliding the AFM tip over the stretched and unstretched areas of graphene, they observe a systematic variation of the frictional behavior with the degree of stretching. The authors put these outcomes in the perspective of the common stick–slip picture of atomic-scale friction (6); as the tip is pulled sideways over the graphene, it first sticks, with the lateral force building up until it is high enough to force the AFM to slip over a single period of the graphene lattice, after which the cycle repeats itself. Zhang et al. find that, when they stretch the graphene, the stick–slip amplitude and the average lateral force decrease. This effect is completely reversible: When the stretching is reduced, the stick–slip amplitude increases again.

The friction force in their experiment (2) is small for a number of reasons (Fig. 1), one of them being the superlubricity due to the lack of lattice matching between the AFM tip and the graphene. In addition to this geometrical effect, there is relatively little adhesion between the tip and the 2-dimensional (2D) graphene sheet: Compared to a 3D material, the number of carbon atoms that interact with the tip via, for example, the van der Waals interaction is very small (7). Yet this is not the whole story, because, in this experiment, the authors go beyond the level of natural adhesion between the graphene and the tip by superimposing an extra normal force on top of the adhesion force. Friction remains low, because the strength of the interaction between the tip and the graphene shows little variation with lateral position. This is to be expected, since, in graphene, each of the carbon atoms is sp2-hybridized and therefore chemically very inert; it has 3 carbon neighbors and therefore does not chemically bind to either the silicon or the nitrogen atoms of the tip. Zhang et al. (2) verify this in their computer simulations (with the tip modeled as pure silicon), in which they describe the strong Si–Si and C–C bonds by Stillinger–Weber potentials and the weak adhesive interaction between the graphene and the tip by a Lennard-Jones potential. In these calculations, the low friction directly reflects the weakness of the graphene–tip interaction, which varies extremely weakly as a function of the lateral position of the tip with respect to the graphene.

The interpretation of the reported strain effect is strongly linked to 2 special types of deformability that are associated with a purely 2D material, that is, with a single atomic layer such as graphene. The first of these is the freedom of the sheet to "drape" itself over the surface features of a rough substrate, much like a carpet draped over a staircase. Where the rigidity

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of 2 hard materials such as graphite and silicon prevents them from making intimate contact everywhere, flexible graphene can follow the contours of the silicon surface faithfully. When the graphene is subjected to increasing tensile stress, however, it will be forced to give up more and more of this intimacy, thus gradually reducing its true contact area with the silicon tip. The other deformability is related to this effect, but is slightly more subtle. In addition to the freedom of the graphene to be deformed in the perpendicular direction, it can also be distorted within the plane. Regions within the graphene can be translated and rotated within the plane, away from their ideal, regular configuration. Of course, such distortions are associated with a penalty in elastic energy. However, this penalty can be offset by the contact with the silicon, if that brings individual carbon atoms into energetically favorable configurations with respect to the silicon atoms. Just like the first type of deformability, this second type is also reduced when the graphene is put under tensile stress. As a result, when pressure is applied and the graphene is stretched, there is a reduction not only in the true contact area of the graphene but also in the "quality" of contact in the regions that stay "in touch." Zhang et al. (2) verify these ideas by performing atomic-scale computer simulations of the complete contact between a graphene sheet and a silicon tip. These simulations reveal an effect of the stretching of the graphene on the friction force similar to the experiments, but also show that the changes cannot be ascribed solely to a reduction in true contact area between the graphene and the tip. Part of the reduction of the friction force is indeed due to the reduction in contact quality.

What we learn here is that friction of atomically thin materials can be fundamentally different from usual friction. The 2D materials introduce degrees of freedom into the game that are absent or, at least, orders of magnitude weaker for the surfaces of regular, 3D materials. As the measurements and simulations in ref. 2 show, it is possible to control these degrees of freedom, presenting an exciting pathway toward the practical realization of the tribologist's dream: tunable friction.

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