

## NANOSCALE FRICTION

## Distorted by the tip

Peaks of energy dissipation arising from distortions of a charge density wave have been observed by oscillating the tip of an atomic force microscope a few nanometres above a surface of a layered dichalcogenide.

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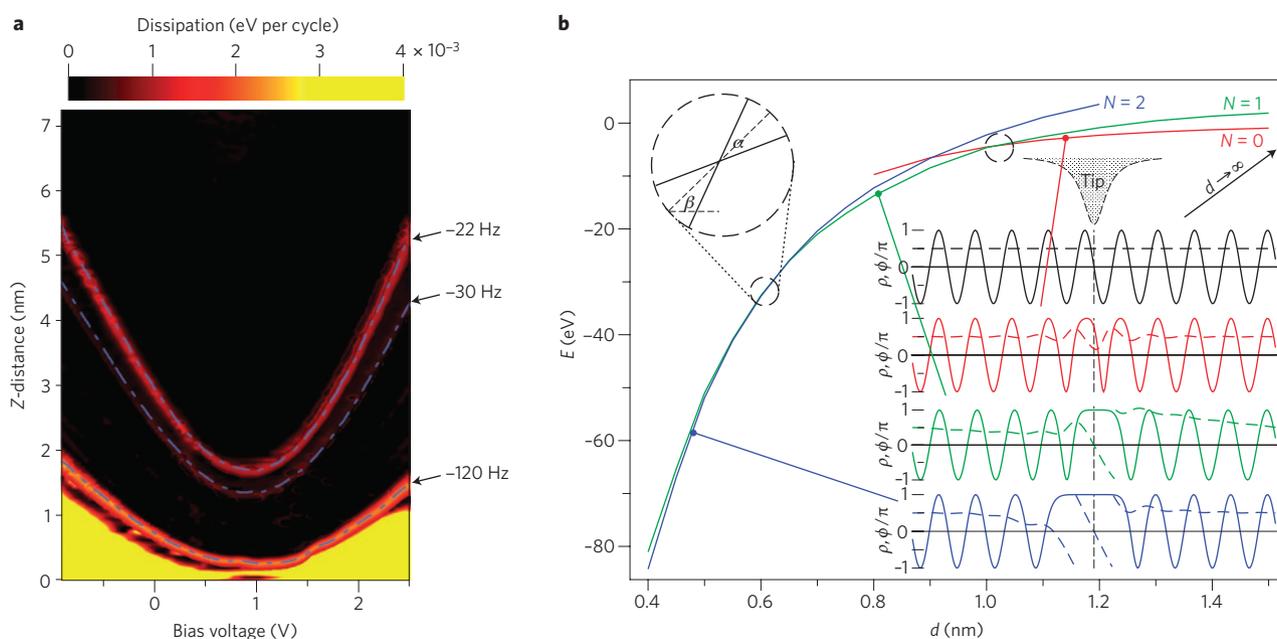
When two macroscopic bodies in contact slide, energy is dissipated. However, at the nanoscale, tiny amounts of energy can also be dissipated when the sliding bodies are not in contact with each other. Such non-contact form of friction — the origin of which has been associated with van der Waals (vdW) forces — has been measured with highly sensitive atomic force microscopy (AFM). In a friction force microscope, the tip scans over a surface and provides the well-characterized conditions needed to determine the relations between the applied load, the lateral friction force and the energy dissipated during sliding. Reporting in *Nature Materials*, Marcin Kisiel and colleagues now show that dynamic AFM is able to detect the energy dissipated in the creation of tip-induced local distortions in the electronic spatial distribution associated

with the charge density wave (CDW) of the low-temperature ground state of NbSe<sub>2</sub> — a layered dichalcogenide<sup>1</sup>.

At the microscopic level, friction force microscopy has revealed that the energy dissipation during contact sliding is associated with stick-slip motion: chemical bonds at the contact region are stretched (stick), and eventually broken and re-formed (slip) as the tip moves laterally<sup>2</sup>. The mechanical energy stored during the stick stage is released during the slip stage, converted into atomic vibrations (phonons), and finally dissipated as heat. However, extending these studies to the single-chemical-bond level requires the atomic force microscope to be operated in the so-called dynamic mode<sup>3</sup>. In this case, the tip mounted at the end of a micrometre-sized cantilever oscillates vertically — that is, in the direction normal to the surface — to

minimize and control the contact area. The tip-sample interaction can then be detected by the changes induced in the oscillation amplitude and frequency that characterize the cantilever dynamics, and the energy dissipated can be monitored through the energy that has to be added to keep the oscillation amplitude of the cantilever constant.

In dynamic operation mode, AFM can also detect the elusive, non-contact friction arising from vdW interactions, which is mediated by the long-range electromagnetic fields created by thermal and quantum fluctuations of the electronic density and, in some cases, by static surface charges arising from material inhomogeneities or a bias voltage<sup>4</sup>. Yet sensing non-contact friction requires ultrasoft cantilevers oscillating like a pendulum over the surface. In fact, such an AFM design has recently



**Figure 1** | Non-contact friction between a NbSe<sub>2</sub> surface and an atomic force microscope tip oscillating as a pendulum above the surface<sup>1</sup>. **a**, Non-contact energy dissipation at 6 K versus tip-sample distance and bias voltage. The amount of energy loss per cycle within each of the three dissipation branches (red curves) is independent of the bias voltage. Blue lines, representing constant-frequency-shift contours, confirm that each dissipation branch corresponds to a particular value of the total force. **b**, Energy as a function of tip-sample distance for a model of an elastic CDW. The crossings between different states (dashed circles), which are characterized by  $2\pi N$  phase slips and stabilized by the tip interaction, result in a force-hysteresis cycle and lead to energy dissipation. Bottom inset: Solid and dashed lines represent the density  $\rho$  and phase  $\phi$  of the CDW, respectively. The tip position is indicated by the dashed vertical line. Top inset: The angle between the energy curves  $\alpha$  and the average slope at the crossing point  $\beta$  determine the area of the force-hysteresis cycle, and thus the dissipated energy.

been able to measure the suppression of electronic friction when a metal undergoes a superconducting transition, a situation where many of those fluctuations become energetically forbidden as a result of the presence of a gap in the energy spectrum<sup>5</sup>.

Kisiel and co-authors have used the pendulum-AFM set-up to determine the energy dissipation when the tip approaches the surface of a NbSe<sub>2</sub> crystal in its low-temperature CDW ground state (the CDW corresponds to a joint distortion of the lattice and the electron density, and has an incommensurate periodicity and a long-range coherent phase that extends over hundreds of lattice spacings). They detected three distinctive dissipation peaks at particular distances that seem to correspond to well-defined values for the tip-sample interaction (Fig. 1a), which is at odds with the expected monotonic increase in friction as the tip-sample distance is reduced. The authors also performed measurements with a tuning-fork tip operated in the conventional dynamic AFM mode (tip oscillating normal to the surface), which systematically showed the presence of the three dissipation maxima, thus confirming the general nature of these phenomena. Kisiel and colleagues connect the dissipation processes with tip-induced local changes in the electron density modulation associated with the CDW. This is supported by the temperature dependence of the dissipation peaks, which disappear above the CDW transition temperature, as well as by experiments on similar layered materials that do not present the CDW phase; these only show a smooth, monotonic increase in the dissipation energy when the tip-sample distance is reduced<sup>1</sup>.

To understand the source of the dissipation peaks, one can resort to a concept that pervades the interpretation of friction: force hysteresis. When the tip

is laterally and cyclically moved on top of the surface — or, in the case of dynamic AFM, when the tip approaches and retracts from the surface — the different forces in opposite directions define a hysteresis cycle, whose area determines the energy dissipated per cycle. Force hysteresis arises because of the presence of energy barriers between the ground state and excited configurations of the system. As the tip-sample interaction can stabilize one of these excited configurations, energy barriers can prevent the relaxation back to the ground state during tip retraction. Hence, the system is in different states during tip approach and retraction, which provides a quantitative understanding of the energy dissipated in tip-sample adhesion at the level of a single atomic bond<sup>6</sup>. Following this idea, Kisiel and co-workers suggest that the observed dissipation peaks result from the hysteresis cycle formed by the crossing between CDW states with phases differing by  $2\pi$  that are stabilized by the interaction with the tip (Fig. 1b).

The ground state of the CDW can be visualized as a periodic charge-density modulation (Fig. 1b, black curve). The coherence of the state is reflected in the constant phase value (Fig. 1b, dashed horizontal black line), which is fixed by the boundary conditions. Other higher energy solutions with a non-uniform charge and phase distribution are possible (Fig. 1b, green and blue curves), provided that the phase changes by  $2\pi N$  (with  $N$  being an integer ‘winding number’ that characterizes the different CDW states) to satisfy the boundary conditions. During approach, the attractive interaction between the tip and the sample can stabilize these excited CDW solutions through the energy balance between the gain in potential energy when extra charge density is brought under the tip and the cost of the spatial variation of the

phase needed to create this additional charge modulation. In the retraction stage, the orthogonality among these states prevents an immediate relaxation back to the ground state, defining a force-hysteresis cycle that leads to energy dissipation.

Although the explanation of energy dissipation in terms of phase slips in the CDW state is appealing, we are still far from a complete understanding of the process. For example, it is not clear what effect the geometrical configuration and the chemical nature of the tip have on the dissipation peaks, which are of the order of a few meV per cycle for the pendulum atomic force microscope yet 100 times larger for the tuning-fork measurements. Also, although the spatial decay and strength of the electrostatic and vdW forces at play are quite different, their role seems almost equivalent. In fact, when changing the bias polarity, a solution with charge depletion close to the tip could be stabilized, yet the dissipation energy per cycle is symmetric with respect to the bias voltage (Fig. 1a). Nevertheless, it is clear from Kisiel and colleagues’ work that dynamic AFM is a powerful tool for exploring the collective electronic effects that are responsible for exotic phases like CDWs, superconductivity and spin density waves in real materials. □

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## THERMOELECTRIC POLYMERS

# Behind organics’ thermopower

Conjugated polymers with high electrical conductivity and high thermopower are now demonstrated. The electronic structure of these materials is that of a semi-metal, a previously unreported state for organic conductors.

Michael Chabinyk

Since the discovery that the electrical properties of polymers can be engineered to display insulating, semiconducting or near-metallic behaviour, these organic materials have been considered as model systems for the study

of one-dimensional charge transport<sup>1</sup>. In their undoped and doped state, conjugated polymers have been successfully used in thin-film electronics as well as in optoelectronic applications — a striking example being organic light-emitting diodes,

now commercialized in mobile phones and large-area displays<sup>2</sup>. The emerging interest for organic materials in thermoelectric applications has now brought more attention to the precise control of electrical doping. There has been recognition that conjugated