Adhesion-dependent negative friction coefficient on chemically-modified graphite at the nanoscale

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I. METHODS

A. Friction force microscopy (FFM):

Friction and lateral stiffness as a function of load, as well as adhesive forces, were obtained on highly oriented pyrolitic graphite samples cleaved with adhesive tape in laboratory air (\(\approx 25\%\) relative humidity (RH) at \(\approx 21\, ^\circ\text{C}\)). The applied load was varied by controlling the load in contact mode atomic force microscopy (AFM), using a triangle wave to approach and then retract the tip from the surface in a single image. The friction force was calculated at each applied load step, in the usual fashion, from the lateral force hysteresis loop. The average friction force was then calculated as half the difference between the trace and retrace lateral signals, to within a multiplicative lateral force calibration factor obtained using a diamagnetic lateral force calibrator\textsuperscript{S1}. Flexural spring constants were determined using the thermal noise method\textsuperscript{S2}. Load forces were calibrated in the usual way, by multiplying the flexural spring...
constant by the deflection sensitivity (slope of the vertical force-displacement curve) on a stiff (SiO₂) surface. Adhesive forces were determined from the applied load at which the AFM tip separates from the surface during retraction.

The friction experiments were performed using both silicon nitride and ultrananocrystalline diamond (UNCD) probes at room temperature in dry nitrogen (RH < 1 %), yielding similar results. The silicon nitride probe of radius \( R = (15 \pm 3) \) nm had a flexural stiffness \( k_N = (0.72 \pm 0.03) \) N/m; the two UNCD probe radii were \( R = (30 \pm 5) \) nm and \( (75 \pm 7) \) nm with \( k_N = (0.15 \pm 0.01) \) N/m and \( (0.120 \pm 0.002) \) N/m, respectively. Radii were determined post-experiment by scanning electron microscopy. Uncertainties in \( R \) are based on one standard deviation. Uncertainties in \( k_N \) were obtained from the usual Taylor series expansion for experimental uncertainty analysis. Scan sizes were 10 nm, and scan speeds were 40 nm/s. The measurement error in the friction-load plots is comparable to the size of the data points, and the scatter in the data is due to small inhomogeneities of the sample, as each data point is measured on a slightly different scan line. Scatter in the data is least for freshly cleaved graphite, but surface inhomogeneities emerge over longer exposure times, leading to greater scatter.

The lateral stiffness measurements were performed as a function of load using a lock-in amplification technique described elsewhere. In this technique, the tip remains in static contact with the sample surface (i.e., it does not slide) as the the sample is oscillated by a small amount in the lateral direction (parallel to the short axis of the cantilever). In the experiments here, we used a scanner oscillation rate of 1 kHz and a peak-to-peak amplitude of 0.56 nm, maintaining static contact. The AFM tip used to capture the data in Fig. 2b was the 30 nm UNCD probe described above.
B. Molecular Dynamics (MD) Simulations:

We simulated FFM using the MD setup as described in detail elsewhere. As shown in Fig. S1 below, the simulated graphite sample consisted of five 5.5 nm × 6.2 nm layers of graphene stacked in an ABAB order. The atoms at the edge of all layers in the x-direction and all atoms in the lowest layer were harmonically restrained in all three dimensions. A periodic boundary was imposed in the y-direction. A single-wall carbon nanotube (CNT) was used as the FFM tip scanning in the y-direction. The chirality, effective diameter, and height of the nanotube were (5,5), 1.2 nm, and 2.3 nm, respectively. During the simulated FFM scan, the upper half of the atoms along the height of the CNT were harmonically restrained and rigidly translated at a prescribed velocity of 5 m/s. The remaining atoms of the CNT interacted freely with the sample. A prescribed tip-sample contact force was maintained with feedback throughout each simulation. The contact force was varied from +10 nN in the repulsive (pushing) mode to the negative force in the adhesive (pulling) mode necessary to achieve loss of tip-sample contact (pull-off).

The carbon atoms within each layer of the sample and within the tip interacted via the bond-order potential. All tip-sample and interlayer van der Waals interactions were modeled by a Lennard-Jones pair potential with $\varepsilon = 7.5$ meV and $\sigma = 0.31$ nm and an interaction cut-off distance of 0.7 nm, yielding an interlayer cohesion of 42.8 meV/atom, in reasonable agreement with experiment and ab initio data. Additional simulations were performed with the tip-sample interactions increased two and five times the interlayer interaction. All simulations were performed at $T = 300$ K, maintained by the Langevin thermostat, as described in ref. S5. All scans were performed during a simulated period of 1.0 ns, corresponding to a total scan distance.
of 5.0 nm. The friction force averages were calculated from the last 750 ps of each simulation, allowing 250 ps for relaxation.

Figure S1 | The MD simulation setup using a CNT tip sliding along the y-direction at 5 m/s against the graphite surface, which consists of five layers of graphene stacked in ABAB order.

C. Finite Element Method (FEM) Simulations:

We used quasistatic FEM to simulate the process of an AFM tip scanning in contact with a graphite sample. For simplicity, we considered a two-dimensional case, where a cylinder rounded at its end (approximating the tip) slides against an elastic sheet, approximating the graphene layer(s), adhered to a substrate representing the graphite (Fig. S2). Both the tip and the substrate were assumed to be rigid. Tip-graphene and graphene-substrate interactions were prescribed by the cohesive zone model, which is derived from a Lennard-Jones potential. More specifically, the interaction stress, $\sigma$, between the elastic sheet (graphene) and the substrate as a function of inter-surface separation, $\delta$, follows the form
\[
\bar{\sigma} = 3.07\sigma_0 \left( \frac{1}{(\delta / \delta_0)^4} - \frac{1}{(\delta / \delta_0)^6} \right),
\]
where \(\delta_0\) is the equilibrium separation. During the simulation, the tip was first brought into contact with the elastic sheet and compressed against the substrate. Then the tip was retracted partially to achieve the desired normal load before performing a lateral sliding at that constant height. As this is a displacement-controlled system, tip-substrate separations beyond the experimental pull-off can be probed theoretically. In the main text, the friction-load plots do not extend all the way to full separation, as the goal was to emphasize the existence of the negative coefficient and its onset prior to the experimental pull-off. (See section VIII.B below for more details.)

For the FEM simulations, the elastic sheet (graphene) and substrate were both 2 \(\mu\)m long and fixed at their edges, while the tip had a radius of 30 nm. The elastic sheet had an effective Young’s modulus of 5.5 TPa and an effective thickness of 0.066 nm to represent the bending stiffness (0.85 eV) and in-plane stretching stiffness (within 340 \(\pm\) 50 N/m\(^S\)) of monolayer graphene by a continuum shell model\(^S\). The tip-graphene adhesion parameter, \(\sigma_0^{\text{tg}}\), was assumed to be equal to or greater than the graphene-substrate adhesion parameter, \(\sigma_0^{\text{gs}}\). We used \(\sigma_0^{\text{gs}} = 150\) MPa and \(\sigma_0^{\text{tg}}\) was varied from 150 MPa to 450 MPa to simulate the change in tip-sample adhesion. In the simulations, \(\delta_0\) was 0.33 nm for both interfaces. Note that the continuum approach demands the use of a much lower effective thickness than the interlayer spacing in order to comply with accepted values for the bending and in-plane stretching stiffness. Friction was introduced to the system using a constant shear strength of 30 MPa wherever the local normal stress was compressive within the tip-graphene interface. This value is within the range of values determined here experimentally for the shear strength of a silicon nitride tip sliding on supported monolayer graphene, as extracted from continuum fits to friction-load data.
Figure S2 | FEM simulation setup, showing the 30 nm radius, rigid spherical tip and 2 µm rigid substrate with single graphene surface layer.

II. SEM IMAGES OF AFM PROBES

Figure S3 shows three post-experiment high magnification scanning electron microscopy (SEM) images of the atomic force microscopy (AFM) tips used in the experiment. Figs. S3a and S3b correspond to the ultrananocrystalline diamond (UNCD) probes (Advanced Diamond Technologies, Inc., Romeoville, IL)\(^{S14}\) used throughout the manuscript. Figure S3c shows the silicon nitride probe (Olympus, Tokyo, Japan)\(^{S14}\) used for acquiring the data in Fig. S6 below. In previous work, some cases have been shown to result in flakes adhered to the tip\(^{S15,S16}\). Using SEM, we resolved no evidence of flake attachment. Moreover, we found that different sized tips extrapolated to the same friction coefficient at a given estimated work of adhesion (e.g., at the graphite exfoliation energy) (Fig. 2). Accordingly, if the ripple effect were occurring in flakes attached to the tips, the flakes would then have to be of the same size. Instead, we found that adhesive forces were commensurate with tip radius, consistent with the interface occurring between the tip and sample surfaces and not a (flat) flake and sample surface.
**Figure S3 | SEM images of AFM tips used for acquiring friction-load curves.**  
*a*, The UNCD AFM tip of radius, $R = (30 \pm 5)$ nm.  
*b*, The UNCD AFM tip with $R = (75 \pm 7)$ nm.  
*c*, The silicon nitride AFM tip of radius $R = (15 \pm 3)$ nm.  
All three images were taken at the end of their respective experiments.  
Scale bars: 100 nm.

**III. STICK-SLIP FRICTION MEASUREMENTS**

Figure S4 shows stick-slip friction loops on aged graphite at different applied loads during tip retraction, using the UNCD probe shown in Fig. S3b.  
Also considering the stick-slip data using the silicon nitride probe (main text, Fig. 3a), regardless of tip material the width of the friction loops decreases with increasing load, and the average slip height increases with applied normal load.  
We note that the friction loops of Fig. S4a exhibit some double-slip events due to the softer cantilever and larger tip size relative to the silicon nitride probe.  
Figure S4b shows a plot of the lateral forces in Fig. S4a as a function of applied load, where we compare slip height with the overall friction force (one-half times trace minus retrace).  
Slip heights decrease with decreasing load due to changes in atomic corrugation, as shown elsewhere$^{517-519}$.  

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Figure S4 | Load dependence of atomic friction. a, Stick-slip friction loops at different applied loads (right), using the 30 nm-radius UNCD probe on aged graphite; trace (black) and retrace (gray) directions are indicated by the arrows. b, Slip height (open red triangles) and average friction force (open blue squares) as a function of load, corresponding to the friction loops in (a).

IV. CYCLING OF FRICTION-LOAD MEASUREMENTS

Cycled load-variation experiments were performed on an aged graphite surface using the 30 nm-radius UNCD probe. To test whether the observed friction-load relationship is reversible, we cycled the load multiple times. Figure S5a shows both friction and applied load for two such cycles as a function of time (represented by scan line); the direct plot of friction versus load for these data (Fig. S5b) shows that the negative coefficient is reproducible. Friction increases with load during the first tip approach and subsequently decreases with load and retraces itself thereafter with repeated cycling of the load. The repeatability of the initial retraction data supports reversible partial exfoliation and eliminates tip or sample damage as the main effect.

Figure S5 | Reversible friction-load curves on graphite. a, Friction force and applied load plotted as a function of scan line, using the 30 nm-radius UNCD probe, where the load was cycled through approach and retract twice before pulling off (1st approach = black crosses, 1st retract = open red circles, 2nd approach = open blue squares, and 3rd retract = solid green triangles). Each data point (image scan line) corresponds to an elapsed time of 0.5 s. b, The same data in (a) replotted as a function of load instead of scan line. The cluster of data at (0, 0) are the out-of-contact data recorded during the initial approach.

V. NEGATIVE FRICTION COEFFICIENT ON SUPPORTED MULTILAYER GRAPHENE AND THE APPLICATION OF CONTINUUM MODELS

Figure S6 shows three representative friction-load curves taken with a silicon nitride probe in ambient air on supported trilayer, bilayer and monolayer regions of graphene. The graphene flakes were prepared by mechanical exfoliation of natural graphite onto the surface of a 300 nm-thick silicon dioxide layer on silicon substrate and exposed to laboratory air for > 300 h. The number of graphene layers were measured based on AFM topography and Raman spectra. Figure S6a shows a slightly negative slope of the friction-load curve on the graphene trilayer, while friction increased with load for bilayer and monolayer graphene. As a result of stronger adhesion of the monolayer to the SiO2 substrate compared with the graphene-graphene...
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exfoliation energy, no lifting occurs until there are a sufficient number of subsurface graphene layers. In the main text, we calculate the exfoliation energy to be ≈ 0.32 J/m²; whereas, monolayer-SiO₂ adhesion of 0.45 J/m² has been demonstrated elsewhere, based on experiments on pressurized graphene membranes\(^\text{S20}\). We note that the bilayer exhibits a possible onset in the negative load regime starting from -5 nN (Fig. S6b).

In the main text, we estimate the tip-sample work of adhesion based on continuum Johnson-Kendall-Roberts (JKR) theory\(^\text{S21}\). This is based on the fact that we observe a trend toward JKR-like behavior for single layer graphene supported by SiO₂. Further, when compared with the exfoliation energy of 0.319 J/m², the JKR limit more closely predicts the force required to exfoliate a surface graphite layer. A reduction in interlayer binding by \(W = 0.283\) J/m² corresponds to a separation of the graphite layer from its equilibrium spacing by \(≈ 0.32\) nm, or nearly one layer spacing\(^\text{S8}\). This reversible partial exfoliation is exemplified in Fig. 2, where \(|\alpha|\) increases faster with \(|L_c|\) as the tip-surface work of adhesion approaches the exfoliation energy. Given that our MD and FEM results predict the tip-sample work of adhesion must be enhanced relative to the exfoliation energy for lifting to occur, it should be surprising that the tribomechanical behavior of the graphite surface mimics that of single layer of graphene under tip retraction when the work of adhesion is simply comparable to the exfoliation energy. However, we emphasize that our experimental adhesion values represent a lower limit.
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**VI. XPS ANALYSIS OF THE AGED GRAPHITE SURFACE**

The x-ray photoemission spectroscopy (XPS) measurements, performed in parallel with the friction-load experiments demonstrated that oxygen was chemisorbed to the graphite surface with exposure time in laboratory air, as discussed in the main text. Figure S7a shows the evolution of the oxygen content (O1s atomic %), where the remaining content is attributed to the carbon 1s peak (not shown). No nitrogen or other species could be identified by XPS.
Figure S7b shows the emergence of two oxygen 1s region peaks as surface oxygen content grew. The peak at (531.9 ± 0.2) eV was observed to emerge shortly following the peak at (533.1 ± 0.2) eV. These peaks have been shown to correspond to O₂ chemisorption and H₂O wetting, respectively, and they emerge simultaneously as a result of O₂ adsorption forming a more hydrophilic surface than freshly cleaved graphite. We believe this increases tip-sample adhesion through greater electrostatic interaction and possible meniscus formation.

**Figure S7** | **a**, XPS spectra (open circles) showing O₂ chemisorption (∼ 532 eV) and H₂O wetting (∼ 533 eV) peaks (both dashed lines) emerging as a function of exposure time in laboratory air. **b**, Corresponding surface oxygen content (total O₁s peak intensity from solid line-fit in (a)) as a function of exposure time.

**VII. LINEAR DEPENDENCE OF FRICTION ON LOAD**

We note that the friction force at a given load increased linearly with the magnitude of the adhesive force, |Lₖ|. Figure S8 shows two load examples (L = 0 nN and 40 nN) for the 30 nm radius diamond probe on graphite, where different exposure times have been combined to produce the variation in Lₖ, as in Fig. 2 of the main text. α exhibited a stronger than linear
dependence on $|L_C|$ (Fig. 2a), while the friction force at a given load varied linearly with $L_C$ (Fig. S8). Assuming friction is proportional to contact area, the nonlinear behavior of $\alpha$ cannot be accounted for by a straightforward scaling with contact area, as that would require $\alpha$ to have a linear dependence on $L_C$, as well. For example, normalization of $\alpha$ vs. $L_C$ to the corresponding friction at zero load, $F_0$, (thus, to the presumed contact area) does not collapse the friction-load plots (e.g., Fig. 1) onto a single line. As shown in Fig. S8b, an $L_C$-dependent slope remains, as a result of a more fundamental change in the tip-sample interaction and the mechanical behavior of the top surface layer.

**Figure S8 | Linear dependence of friction force on adhesive force.** a, Friction is plotted versus the magnitude of the adhesive force, $|L_C|$, for zero applied load and a load of 40 nN. b, Normalization of $\alpha$ to $F_0$ yields linear behavior, suggesting $\alpha$ is not directly related to contact area.

Based on the linearity of the friction-load data during tip retraction and the corresponding increase in FEM-simulated barrier height, it may be possible to represent the deformation of the top layer while sliding by an existing plowing model previously established for surfaces coated
by Langmuir-Blodgett layers. As is typical of continuum models, this approach begins by assuming a proportional relationship between friction, $F$, and contact area, $A$:

$$F = \tau A,$$  \hspace{1cm} (S1)

where $\tau$ is the interfacial shear strength. When rippling or plowing occurs, $\tau$ is pressure-dependent, \textit{i.e.}, $\tau = \tau_{\text{int}} + \alpha P$, with $P$ the average contact pressure, $\alpha$ a constant (herein referred to as the nanoscale friction coefficient), and $\tau_{\text{int}}$ the intrinsic interfacial shear strength. With $P = L/A$, equation (S1) may be written as

$$F = F_{\text{int}} + \alpha L,$$  \hspace{1cm} (S2)

where the interfacial term $F_{\text{int}} = \tau_{\text{int}} A$, $F_0 = F_{\text{int}} (L = 0)$, and $A$ depends on $L_C$. For continuum models of single asperity contacts, $A(L = 0) \propto L_C^{4/3}$; however, the observed linear dependence of $F_0$ on $L_C$ (section VII) suggests that the contact area follows a different relation. The second term in equation (S2) represents the rippling of the lifted graphene layer. This pressure-dependent term assumes an increase in material pile-up, \textit{i.e.}, more material impeding lateral motion, with load. Though originally understood to be a positive value, indicating greater rippling at higher loads, we observed larger deformations on graphite as the applied load was reduced. The strong linear dependence of friction on applied load during retraction suggests that the plowing term dominates at the onset of lifting, where this term represents the compressive stresses at the outermost edges of the tip-sample contact.

VIII. SIMULATIONS SUPPLEMENT

A. MD

Movie S1 shows a cross-sectional view of the CNT tip sliding on the graphite substrate for the 5:1 enhancement under an applied load of -6 nN. A deformed (lifted) region follows the tip position as it slides over the surface.

Figure S9 shows the vertical deflection data from Fig. 4a (5:1 at -6 nN applied load) along with the corresponding deflection profiles for a load of 0 nN. Figure S9 | MD vertical deflection profiles (out-of plane deviation from average height) of the three topmost graphene layers during sliding. Deflections are shown for zero applied load and just prior to pull-off (-6 nN load) for the 5:1 tip-graphene to graphene-graphene interaction ratio. The profiles have been shifted so that 0 on the vertical axis corresponds to their zero deflection positions. The gray zone refers to the region over which thermally excited deflections occur naturally at room temperature.
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B. FEM

Movies S2-S5 show FEM-simulated profiles during sliding at displacements of 0.27 nm, 0.33 nm, 0.37 nm, and 0.43 nm (from pressing to lifting) for the 3:1 case, where tensile and compressive stresses are indicated by a corresponding color gradient. Comparing lifting (e.g., Mov. S5) with pressing (e.g., Mov. S2) while sliding, the lifting case leads to the transfer of the most compressive stresses from the central region around the tip apex to the outer perimeter of the contact zone. We note that this new stress distribution could lead to a different functional form for the area-load relation than a regular centrally compressed contact configuration. When the tip retracts, the central contact area reduces quickly at the beginning and later gradually levels off because of the lateral spread in the lifted region (Fig. 4c). However, because of the enlarged lifted region, more force is needed to push the enlarged lifted region forward. This mechanism, together with the increase in out-of-plane deformability of the lifted layer, leads to the usual increase in friction. We note that this result is derived from the continuum assumption of an interfacial shear stress in our FEM model. Although a complete understanding of the process may require combination of both continuum and atomistic analyses, our FEM results demonstrate that a reversible partial delamination of the topmost atomic layer(s) can indeed lead to this unusual friction behavior.

As mentioned above, in a load-controlled experiment, pull-off would occur at the minimum load. In this displacement-controlled simulation, we calculated friction at several additional displacement values for each data set to capture the contact behavior under retraction at displacements beyond the maximum tensile load (pull-off) points shown in Fig. 4d. Fig. S10 combines the friction data of Fig. 4d with these additional data—all plotted as a function of tip-sample displacement (Fig. S10a) and calculated normal load (Fig. S10b). A dip and abrupt rise
in friction upon retraction in the 2:1 case is followed by a slope lower in magnitude than in the 3:1 case. This intermediate behavior is a result of a competition between adhesion of the graphene layer to the substrate versus the tip, leading to changes in the amount by which the rippling increases with retraction. In the typical behavior for a JKR-like contact between isotropic materials, friction decreases with decreasing contact area, even as the normal load increases again after what would be the pull-off point in a load-controlled experiment. Conversely, Fig S10 shows that friction increases in this regime. We believe friction would eventually decrease again, as the tip fully separates from the substrate.

Figure S10 | FEM simulation results for friction beyond the maximum tensile load. a, Friction force as a function of tip-substrate displacement, $h_{t,s}$, during retraction (solid arrows) for different enhancement ratios up to the same maximum tip-substrate displacement ($h_{t,s} = 0.43$ nm); the graphene layer and substrate are located at $h_{r,s} = 0.33$ nm and $h_{r,s} = 0$, respectively. b, The same data plotted as a function of average normal load. The curve turns around at the maximum tensile load (pull-off point in AFM), after which the load increases with
increasing $h_{c,s}$ while the total contact area continues to decrease. A JKR-like plot (red dashed line) qualitatively illustrates what might be expected for a typical (isotropic) system with similar pull-off force and positive load behavior. For comparison, dashed arrows indicate how four of the data points might map onto the JKR curve.

References for Supplementary Information


S14. The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST or that they are necessarily the best materials, instruments, software or suppliers for the purposes described.


