

Origin of Nanoscale Friction Contrast between Supported Graphene, MoS₂, and a Graphene/MoS₂ Heterostructure

Mohammad R. Vazirisereshk,[†] Han Ye,[‡] Zhijiang Ye,[§] Alberto Otero-de-la-Roza,^{||} Meng-Qiang Zhao,[⊥] Zhaoli Gao,[⊥] A. T. Charlie Johnson,[⊥] Erin R. Johnson,[#] Robert W. Carpick,^{*,‡} and Ashlie Martini^{*,†}

[†]Department of Mechanical Engineering, University of California, Merced, California 95343, United States

[‡]Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

[§]Department of Mechanical and Manufacturing, Miami University, Oxford, Ohio 45056, United States

^{||}Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain

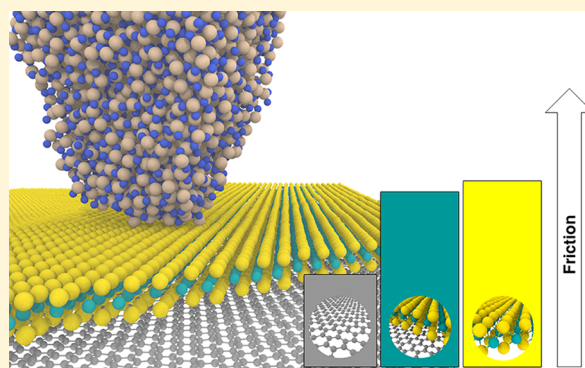
[⊥]Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

[#]Department of Chemistry, Dalhousie University, Halifax, NS B3H 4R2, Canada

S Supporting Information

ABSTRACT: Ultralow friction can be achieved with 2D materials, particularly graphene and MoS₂. The nanotribological properties of these different 2D materials have been measured in previous atomic force microscope (AFM) experiments sequentially, precluding immediate and direct comparison of their frictional behavior. Here, friction is characterized at the nanoscale using AFM experiments with the same tip sliding over graphene, MoS₂, and a graphene/MoS₂ heterostructure in a single measurement, repeated hundreds of times, and also measured with a slowly varying normal force. The same material systems are simulated using molecular dynamics (MD) and analyzed using density functional theory (DFT) calculations. In both experiments and MD simulations, graphene consistently exhibits lower friction than the MoS₂ monolayer and the heterostructure. In some cases, friction on the heterostructure is lower than that on the MoS₂ monolayer. Quasi-static MD simulations and DFT calculations show that the origin of the friction contrast is the difference in energy barriers for a tip sliding across each of the three surfaces.

KEYWORDS: Nanoscale friction, graphene versus MoS₂, heterostructure, atomic force microscope, molecular dynamics, density-functional theory



Two-dimensional (2D) materials offer unique and intriguing possibilities for structural and mechanical applications thanks to their extreme mechanical properties, including large in-plane stiffness and low bending rigidity.¹ Further, their weak interlayer van der Waals interactions enable easy lamellar shear and intrinsically low friction and adhesion.² These materials thus have a unique combination of properties that enable them to exhibit ultralow friction² and wear.^{3–6} These features make 2D materials attractive as ultrathin solid-lubricant coatings and as additives for liquid lubricants.^{2,7–11} For such applications, two of the most promising and frequently researched 2D materials are graphene and MoS₂.¹²

Graphene's ability to suppress wear is attributed in part to its mechanical strength; its in-plane elastic stiffness is equivalent to a Young's modulus on the order of 1 TPa.^{13,14} Additionally, graphene has been shown to be impermeable with respect to different liquids¹⁵ and gases,¹⁴ an important feature for

corrosion/oxidation-resistant coatings. Graphene and graphite also exhibit ultralow friction, as measured between an atomic force microscope (AFM) tip and a graphene or graphite substrate,^{7,11,16} or at graphene–graphene and graphite–graphite interfaces.^{17–19} Such studies have explored the dependence of friction on the number of graphene layers, chemical modification, environmental/operating conditions, and commensurability. These have revealed that friction decreases with increasing numbers of graphene layers⁷ and that this layer dependence is affected by a variety of factors, including out-of-plane stiffness⁷ and the structure of the interface,^{20–22} as well as graphene–substrate adhesion.^{23,24} Graphene properties can be tuned with chemical modification,

Received: May 17, 2019

Revised: June 25, 2019

Published: July 3, 2019

for example, fluorination,^{25–27} hydrogenation,²⁵ and oxidation.²⁵ These modifications lead to significant friction enhancement,^{26,27} attributed to increased corrugation of the potential energy surface²⁶ as well as an increase in the atomic-scale roughness.²⁸ Graphene and graphite are also sensitive to environmental and operating conditions: friction varies with humidity nonmonotonically,^{29,30} increases with decreasing temperature,^{31,32} and increases with increasing speed.^{32,33} Lastly, the orientation of graphene relative to the scan direction of an AFM tip or of adjacent graphene sheets has a significant effect on friction.³⁴ The lowest friction possible is achieved with incommensurate structures, leading to the observation of superlubricity^{35–37} for graphene sliding on graphene/graphite³⁸ and on gold.³⁹

Like graphene, MoS₂ has antiwear properties attributed in part to a high effective in-plane Young's modulus (0.33 TPa in the case of freely suspended MoS₂⁴⁰), and a low intrinsic friction response. Friction of various materials sliding against MoS₂ has been studied using AFM, and it has been shown that mechanically exfoliated MoS₂ exhibits layer-dependent friction similar to graphene.⁷ Like with graphene and graphite, the tribological behavior of MoS₂ is also sensitive to the environment and testing conditions. In atmospheric conditions, adsorption of chemical compounds (H₂O or O₂) can disrupt the easy shearing properties of the lamellae, which increases friction.⁴¹ Also, grain boundaries of polycrystalline MoS₂ can cause an oscillatory layer-dependent friction due to the absence and presence of polar grain boundaries with even and odd numbers of layers, respectively.⁴² In addition to environmental factors, temperatures above 350 K can lead to a substantial reduction in friction⁴³ and MoS₂ friction increases with increasing speed.⁴⁴ Lastly, MoS₂ frictional anisotropy has been measured with a periodicity of 60°,^{45–47} resulting from linearly aligned structures along the crystallographic axis of the honeycomb lattice structure.⁴⁷ This anisotropy has led to recent observations of superlubricity in MoS₂–MoS₂⁴⁸ and MoS₂–Sb⁴⁹ contacts.

Two recent studies have compared nanoscale friction on monolayer graphene and MoS₂ on SiO₂ substrates. In one study, a silver nanowire had lower friction when sliding on MoS₂ than for graphene.⁵⁰ In another study, friction measured with a Si AFM tip showed that the magnitude of the friction force was lower on MoS₂, but friction increased with normal force less strongly on graphene.⁵¹ In the former study, the difference was attributed to adhesion, but the latter study suggested puckering as the origin of the friction contrast. Importantly, in these studies friction was recorded on the two materials in separate measurements, i.e., the experiments were performed sequentially.

Previous research has shown that both graphene and MoS₂ can exhibit low friction and wear, but the behavior is sensitive to various conditions. In some cases, both materials exhibit similar trends (e.g., friction decreasing as temperature increases and orientation dependence), and in others different trends (e.g., environment dependence). Potentially, the properties of these two materials could be combined to leverage the unique features of both.⁵² Integration of dissimilar 2D materials without the constraints of crystal lattice matching is possible due to the weak van der Waals interlayer interactions of these materials.⁵² Recently, heterostructures of MoS₂ and graphene have been developed, and their macroscale tribological behavior characterized. A ball-on-disk friction test showed that reduced graphene oxide (RGO)/MoS₂ heterostructures,

used as oil additives and also dispersed in ethanol, decreased friction and wear compared to the lubricant with either RGO or MoS₂ alone.^{53–55} This improvement was attributed to the lattice mismatch between RGO and MoS₂, as well as the contribution of adsorbed RGO/MoS₂ structures to passivate the sliding interfaces, thereby reducing the wear rate.⁵⁵ At the atomic scale, an analytical study of the interlayer friction of a graphene/MoS₂ heterostructure revealed that the frictional energy for sliding graphene against MoS₂ was an order of magnitude smaller than that of homogeneous bilayers.⁵⁶ This observation is in agreement with a combined Raman-based experimental/first-principles study of superlubricity at atomic scale in graphene/MoS₂ heterostructures that showed the heterostructure had a lower interlayer lateral force constant than homogeneous bilayers.⁵⁷

To summarize, studies to date have demonstrated that both graphene and MoS₂ can exhibit extremely low friction, and recent developments in heterostructure synthesis and fabrication may enable further improvements. However, all previous nanoscale friction measurements on graphene, MoS₂, and graphene/MoS₂ heterostructures were performed only on one of those materials at a time, whereby the probe (e.g., an AFM tip) was slid against one material for some time period, then a different material. Therefore, the results could be affected by differences in parameters from experiment to experiment (e.g., tip size, morphology, and surface chemistry; sample preparation method and thus substrate surface chemistry; and environmental conditions, like humidity). The possibility of a significant change in the shape and/or the surface chemistry of the tip during an experiment is a particularly difficult challenge to address. While sequentially alternating from one sample to the other repeatedly is an effective approach, a more reliable approach is to directly compare the different substrate materials within a single AFM line scan. To accomplish this, here we produce graphene and MoS₂ monolayers on a single Si/SiO₂ substrate, establishing three surfaces: graphene on SiO₂, MoS₂ on SiO₂, and a heterostructure of MoS₂ on graphene on SiO₂, all accessible within the scan range of the AFM. Friction on these three surfaces is characterized using AFM and also by molecular dynamics (MD) simulations, complemented by density functional theory (DFT) calculations of surface energies. The approach enables, for the first time, direct comparison between friction on graphene, MoS₂, and a graphene/MoS₂ heterostructure.

A Si/SiO₂ sample with supported graphene and MoS₂ monolayers and graphene/MoS₂ heterostructures all simultaneously present was prepared based on the method discussed in [Methods](#). Optical images of the samples are shown in [Figure 1a,b](#). Atomic scale friction was measured using an Asylum MFP-3D AFM in contact mode with a diamond-like carbon (DLC) coated silicon tip. The measurements were performed at room temperature (~25 °C) with a sliding speed of 4.30 μm/s in a dry nitrogen environment with RH ~ 3%. A schematic of the experiment is shown in [Figure 1c](#). The slow scan direction was disabled so the same line was continually scanned as the normal force was varied from 25 to almost –5 nN, with the negative value resulting from sliding in the adhesive regime ([Figure S1](#)). The load range corresponds to estimated normal pressures from 3.62 to 1.90 GPa calculated using the continuum mechanics-based Derjaguin–Müller–Toporov (DMT)⁵⁸ model, which provides an approximation

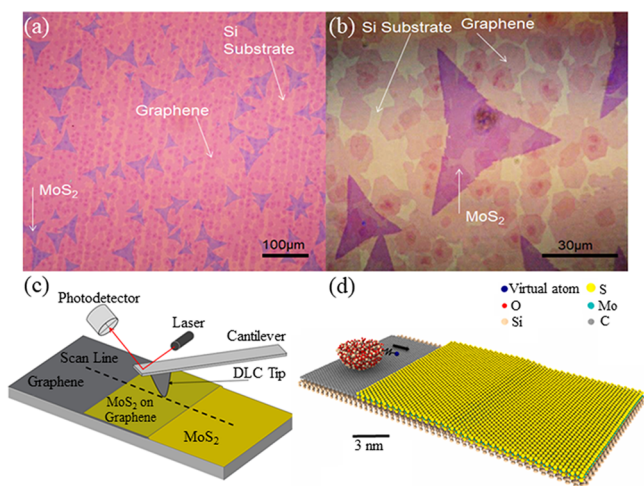


Figure 1. (a,b) Optical microscope images of the samples containing graphene, the graphene/MoS₂ heterostructure, and MoS₂ on Si/SiO₂. (c) Schematic of the AFM experiment and (d) snapshot of the corresponding MD simulation.

of the pressure in the absence of a specific model for 2D materials.

Complementary simulations were designed to capture the key aspects of the experiment and included the same three material systems. The model consisted of a graphene layer supported by a crystalline silicon (a-Si) substrate and an MoS₂ layer supported partially by the silicon substrate and partially by the graphene (see Figure 1d). The model tip was displaced laterally over the substrate with a constant speed of 2 m/s at normal loads ranging from 0.15 to 10 nN (corresponding to a pressure range from 5.2 to 9.3 GPa, calculated using the DMT model). Detailed information about the MD simulation setup can be found in [Methods](#). Density functional theory (DFT) calculations were performed to model the corrugation of the potential energy surface (PES) for methane sliding over graphene and MoS₂ bilayers (Figure S2a,b) and to calculate adhesion energies. DFT calculation details are given in [Methods](#).

Results and Discussion. The topography of a single region containing monolayer graphene, a heterostructure of MoS₂ on graphene, and monolayer MoS₂, measured by AFM is shown in Figure 2a. While some residual contamination can be seen, the heights of the various regions can be determined with respect to the substrate. The height profiles in Figure 2c show that the thicknesses of the monolayers of graphene and MoS₂ are 0.26 ± 0.12 and 0.76 ± 0.16 nm, respectively (see Section 3 of the [Supporting Information](#) for additional Raman spectra analysis). The theoretical thickness of single-layer graphene and MoS₂ are reported to be 0.35⁵⁹ nm and 0.65⁶⁰ nm.

Figure 2b shows the corresponding friction map, which indicates that friction is much higher on the SiO₂ substrate than for any of the 2D materials, as expected. The friction profile in Figure 2c enables direct comparison between the 2D materials and shows that friction on both monolayer MoS₂ and the heterostructure is larger than that on graphene. The same trend is seen in the simulations: friction is higher when the tip slides on MoS₂ as compared to graphene (see Figure S4 for a representative friction trace from the MD simulation). Figure S4 also demonstrates the stick–slip friction observed in the simulations. Although we did not resolve atomic lattice stick–slip behavior in the AFM experiments, preliminary work to be

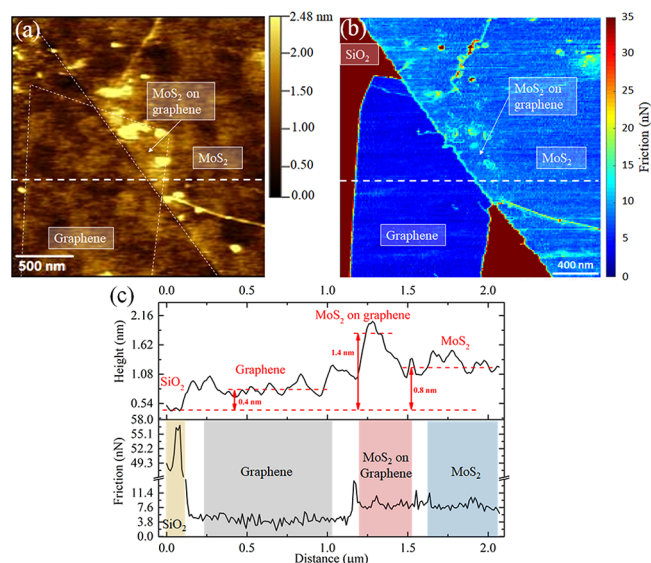


Figure 2. (a) AFM topographic image of graphene, MoS₂, and a graphene/MoS₂ heterostructure on a Si/SiO₂ substrate obtained using contact mode AFM, and (b) friction map corresponding to the topographic image. (c) Height and friction profiles corresponding to the white dashed line in (a,b) indicate graphene and MoS₂ are monolayers and show a clear friction contrast between MoS₂ and graphene. The AFM images in this figure are taken at 12.29 nN load and 22.54 $\mu\text{m/s}$ scanning speed. Some inhomogeneities are seen, which are attributed to remnant contamination from the poly(methyl methacrylate) (PMMA)-based transfer process and/or from adventitious carbon due to atmospheric exposure.

published in the future shows that we can observe atomic stick–slip on this sample at the same speeds and compliance values. Thus, we are confident we are measuring static friction behavior.

The load-dependence of friction for sliding on the three surfaces from experiment and simulation is shown in Figure 3. In both experiment (Figure 3a) and simulation (Figure 3b), the friction force on monolayer graphene is significantly lower than on either monolayer MoS₂ or the graphene/MoS₂ heterostructure (see Figure S5 for the topography corresponding to the friction data in Figure 3 and Figure S6 for another experimental data set). At some loads, there is also higher

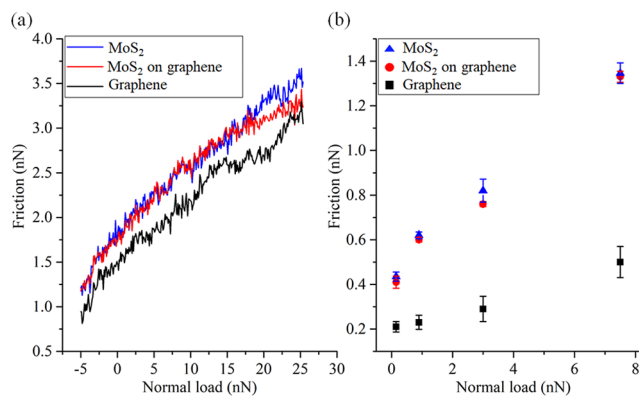


Figure 3. Friction as a function of load from (a) AFM and (b) MD. Friction on monolayer graphene is lower than on either monolayer MoS₂ or the graphene/MoS₂ heterostructure. The error bars in (b) represent the standard deviation of the measured friction force in the MD simulation.

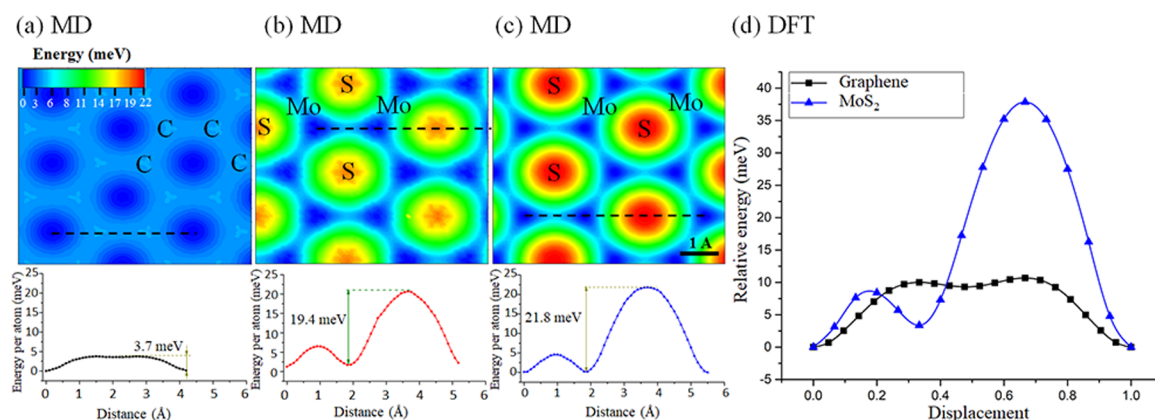


Figure 4. (a) Potential energy surfaces (PES) for the three surfaces calculated using quasi-static simulations for (a) graphene, (b) the graphene/MoS₂ heterostructure, and (c) MoS₂. A cross-sectional energy profile corresponding to the dashed line on the contour plot is shown below each contour. (d) Relative energy barrier calculated using DFT for translation of methane along the long diagonal of the hexagonal unit cell of graphene and MoS₂ bilayers. The *x*-axis represents the fractional displacement across the unit cell. Symbols correspond to the ab initio data; lines are guides for the eyes only.

friction force for MoS₂ on SiO₂ as compared to MoS₂ on graphene. This difference is only statistically significant in the simulations at a load of 3 nN, and it is only observed in about 14% of the experimental measurements (with at least 10% friction difference).

Comparing the simulations to experiments, the average friction force at each load in the experiments is higher than the average peak friction force at that same load in simulations. This is likely due to the larger tip used in the experiment (9.6 nm versus 2 nm radius in simulations), which will result in a larger contact area and, in turn, greater friction.⁶¹ Also, although the trends are the same, the difference between MoS₂ and graphene is greater in the simulations than in the experiments. This difference may be at least partially attributed to the presence of adsorbates in the experiments, which are not included in the model system. Such adsorbates are expected to increase friction by the same amount on both MoS₂ and graphene, such that the relative difference between MoS₂ and graphene is reduced in the experiments.

Several mechanisms of nanoscale static friction² might explain the friction contrast between the graphene and the two MoS₂ surfaces, and each of these is evaluated here. First, friction can be affected by thermal activation via the contribution of thermal energy to overcome local energy barriers and enable slip.⁶² However, the main factors affecting this friction mechanism are speed and temperature, which are the same for all three surfaces. The relative crystallographic orientation of the graphene and MoS₂ with respect to sliding direction can also affect the atomic scale friction in both experiments and simulation.² However, the experimental data shown in Figure 2 and Figure S5 were measured for samples having different orientations relative to the sliding direction, yet the same friction trend was obtained from both orientations in AFM, as well as in the MD simulations.

Static friction can also be enhanced when material removal occurs, that is, wear. The possibility of tip wear during the test was evaluated by comparing pre- and post-measurement transmission electron microscope (TEM) images of the tip and variation of friction and adhesion over time. TEM images (Figure S7) showed that some change in the tip shape occurred during the test. However, analysis of the lateral force calibration images and contact mechanics models^{63,64}

suggested that the observed wear likely occurred during lateral force calibration, such that the tip was unchanged during the friction measurements (see Section 7 of the Supporting Information). This is further confirmed by the fact that the difference between the pre- and post-test adhesion on each surface was less than the error associated with the adhesion measurement. Finally, capturing friction measurements of the three regions repeatedly in the same image, line after line, eliminated the possibility that friction differences seen were attributed to tip changes. The friction was consistent (with <3% standard error) at each normal load throughout the experiment. Moreover, no wear was observed in the MD simulations. Therefore, material removal cannot explain the friction contrast between the different materials.

Friction can also be affected by elastic deformation, that is, the out-of-plane deformation causes bending and stretching in the lattices and acts to enhance static friction.^{7,65} A direct experimental evaluation of the local deformation is not possible without sub-angstrom resolution indentation.⁶⁶ However, MD simulations provide detailed atomistic information on the buried contact between the AFM tip and substrate. As shown in Figure S8, the out-of-plane deformation of the 2D materials increases with load, but there is no statistically significant difference between the deformation of the three surfaces. We also investigated the possibility of the friction contrast being due to the difference in the surface roughness, which has been shown to enhance friction due to better interlocking of the atoms at the interface.²⁰ However, there is no consistent difference in the root-mean-square (RMS) roughness of the three surfaces observed in either AFM or MD (Figures S9 and S10), which indicates that roughness is not a dominant mechanism determining friction contrast.

Another important factor determining friction for nanoscale contacts is adhesion.⁶⁷ This effect can be measured in both experiments and simulations as the maximum adhesive force experienced as the tip is pulled away from the surface. The pull-off force is shown in Figure S11. Although the magnitude of the adhesive force differs between experiment and simulation, which we attribute primarily to the different tip sizes, the work of adhesion values calculated using the DMT model are comparable (Figure S12). Comparing graphene and MoS₂, adhesion is larger for graphene as measured from both

experiment and MD simulation, in agreement with previous measurements.^{51,68} This trend is also corroborated by binding energies calculated from DFT (Table S1). The breakdown of these energies shows that the base-functional energy has a positive contribution to the adhesion, indicating no favorable electrostatics and significant nonbonded repulsion. All of the adhesion energy originates from the dispersion term and, although the dispersion contribution to the binding is higher for MoS₂ than graphene, the total adhesion is weaker. This can be attributed to the larger atomic size of S, which would lead to greater repulsion for a similar methane-surface distance. DFT calculations were not performed for the heterostructure because the periodic boundary conditions would strain either the MoS₂ or graphene due to their misaligned lattice constants. Regardless, the adhesion difference between graphene and MoS₂ in DFT, MD, and experiments is opposite to the trend observed for friction, so adhesion cannot explain the friction contrast.

The remaining factor is the tip-sample interaction energy. In the classical Prandtl–Tomlinson (PT)^{62,69} model, at zero temperature static friction is directly proportional to the height of the energy barrier that the tip must overcome to slip forward, that is, the corrugation of the interfacial potential energy surface.⁷⁰ To quantify this for the three surfaces, we used quasi-static MD simulations in which an oxygen atom was used to raster scan over each surface and calculated the minimum energy at each lateral position. Figure 4 shows the complete potential energy surface (PES) for each region. The maximum energy barrier is much smaller for graphene than either MoS₂ or the heterostructure (~16 meV smaller). Further, the heterostructure energy barrier is slightly smaller (2.4 meV smaller) than that for MoS₂. Because these simulations were based on an empirical potential, the energy barriers for MoS₂ and graphene were also calculated using DFT. The methane molecule (in two different configurations, as shown in Figure S2c,d) was translated diagonally over the three surfaces. DFT results (Figure 4d and Figure S13) for both methane configurations are consistent with the empirical model in terms of the relative differences between energy barriers for the graphene and MoS₂ surfaces.

Importantly, the energy trends found from empirical simulations of an oxygen atom and DFT calculations of methane are consistent with the friction observed in the MD simulations of an SiO₂ tip and experiments with a DLC tip. In the case of an atom sliding over these barriers, one can expect the atom to slide over the saddle points with lower barriers leading to almost identical friction between these materials. However, during the AFM experiment or MD simulation, the tip apex consists of an ensemble of atoms in the buried contact, some of which will necessarily move over energy barrier maxima. This suggests that energetic barriers to sliding explain the friction contrast between the three materials.

Interestingly, we observe slightly higher adhesion between the tip and graphene compared with the adhesion between the tip and MoS₂. However, the relative difference of the adhesion to these two surfaces in our AFM experiments and MD simulations (see Table S3) is small with respect to the relative friction contrast observed. Moreover, increased adhesion will increase contact area, according to most contact mechanics models, and it has been seen to increase the interfacial shear strength.⁷¹ In both cases, this would increase interfacial friction. We thus attribute the increased friction to the increased energy barrier with adhesion making little difference.

Although the energy barriers were obtained from static calculations at 0 K, the barrier heights are expected to determine friction contrast at finite temperatures and speeds. According to the thermal PT model, the approximate relationship between friction (F), temperature (T), and speed (v) is $F = F_C - \left| \beta k_B T \ln\left(\frac{v}{v_c}\right) \right|^{2/3}$, where F_C is the maximum friction at 0 K, β is a parameter determined by the shape of the potential, k_B is Boltzmann's constant, and v_c is the critical speed, above which friction starts to become speed-independent.⁶¹ The magnitude of F_C is directly proportional to barrier height. The second term in the equation increases sublinearly with barrier height due to the dependence of β and v_c on F_C ; thus, the net effect of increasing barrier height will be larger friction at any temperature and speed.

Next, we consider why the energy barriers are different for these three surfaces. Comparing graphene and MoS₂ energy barriers from DFT, the difference is due entirely to the dispersion contributions (see Table S2). At the minimum-energy configurations, there is greater dispersion binding of the model tip to MoS₂, which stems from the sulfur anions in MoS₂ being more polarizable than carbon atoms in graphene. Coupled with the atomic corrugation of the MoS₂ surface, which reduces the dispersion binding at the maximum-energy configuration, this leads to higher sliding barriers for MoS₂ relative to graphene.⁷² The finding that friction contrast between MoS₂ and graphene is due to sliding energy barriers also may explain the difference between our results and those from a previous study that showed friction is lower on MoS₂ than graphene.⁵⁰ Friction in that study was measured with a silver nanowire, and the nature of the interaction of silver with graphene or MoS₂ is likely different from those we observe with nonmetallic, nonreactive materials.

DFT calculations were not performed for the heterostructure as it would require introducing unphysical lattice strain, as mentioned earlier. However, the energy barrier difference between the MoS₂ and the heterostructure could be explained by the quasi-static MD simulations. Analysis of the relative contributions of the layers to the energy barrier, which consists entirely of van der Waals interactions in the MD simulation, showed that the contribution of the upper MoS₂ layer was the same for the monolayer and the heterostructure (18.5 ± 0.2 meV). However, the graphene layer in the heterostructure contributes 1.0 meV to the energy barrier, while the silicon substrate beneath the MoS₂ monolayer contributes 3.1 meV. Therefore, the heterostructure has a slightly lower energy barrier because the graphene contribution is less than that of the silicon. This difference is small, which explains why the friction in dynamic simulations and in experiments, which is determined both by potential energy and thermally driven hopping over energy barriers, is only sometimes observed to be smaller for the heterostructure. This interpretation is limited by the fact that the relative twist orientation of the MoS₂ and graphene layers in the heterostructure was not known; further study is required to determine how strongly friction depends on this twist angle.

Conclusions. In this study, we report a direct comparison of nanoscale static friction between a diamond-like carbon AFM tip and monolayer graphene, monolayer MoS₂, and a graphene/MoS₂ heterostructure, all supported on an Si/SiO₂ substrate. Both experiments and MD simulations showed that MoS₂ has higher friction than graphene across a wide range of normal loads. The friction measured for sliding on the

graphene/MoS₂ heterostructure was comparable to, but occasionally lower than, that for monolayer MoS₂. The origin of the friction contrast between sliding on graphene versus MoS₂ was shown not to be scanning speed, tip change, roughness, adhesion, or other environmental factors. Instead, quasi-static simulations with an empirical potential and with DFT calculations demonstrated that the origin of the friction contrast is the difference in energy barriers to sliding on the two surfaces. The energy barrier difference between MoS₂ and graphene is due to the higher dispersion contribution to the sliding barrier for MoS₂ due to the higher polarizability of S atoms compared to C. The quasi-static MD simulations showed that the difference in friction between sliding on MoS₂ and sliding on the heterostructure results from the dispersion contribution of the underlying material (graphene versus silicon) to the energy barrier. These findings have implications for continued development and application of heterostructures with unique and potentially tunable properties.

Methods. Sample Preparation. The substrate was a die cut from a Si(100) wafer with 285 nm of thermally grown SiO₂. Discontinuous graphene flakes were grown on a copper foil using atmospheric-pressure chemical vapor deposition (CVD) based on an established method.⁷³ Briefly, Cu foils (Alfa Aesar Item #46365) were cleaned with 5.4% HNO₃ for 40 s and two DI water baths for 2 min. The Cu foils were then loaded into the furnace (Lindberg blue M, TF55035). The furnace was ramped to 1050 °C at a rate of 60 °C/min in a flow of 500 sccm Ar + 30 sccm H₂. After 5 min annealing, graphene flakes were grown by introducing 2.5 sccm CH₄ (1% in Ar) for 15 min. After growth, the reactor was rapidly cooled to room temperature in a flow of 10 sccm H₂ and 1000 sccm Ar. Discontinuous graphene flakes were then transferred onto the Si/SiO₂ substrate using the bubble transfer method.⁷⁴ During the bubble transfer procedure, a layer of poly(methyl methacrylate) (PMMA) was spin-coated on the graphene on the copper substrate at 3000 rpm for 60 s. The spin-coated sample was baked at 100 °C for 2 min and then immersed in a 0.05 mol/L NaOH aqueous solution with applied 20 V voltage between the copper foil and the solution. PMMA-supported graphene was delaminated from the Cu foil by hydrogen gas bubbles formed at the graphene–Cu surface. The floating PMMA/graphene film was washed with distilled water (resistivity of 18.2 MΩ cm), and then carefully placed in contact with the Si/SiO₂ die. After drying, the PMMA was removed by treating in acetone overnight, washed with isopropyl alcohol (IPA), and then annealed in vacuum (4×10^{-4} Torr) at 600 °C for 150 min,⁷⁵ leaving the graphene/Si/SiO₂ sample. The monolayer MoS₂ was CVD-grown on another Si/SiO₂ substrate⁷⁶ and transferred onto the graphene/Si/SiO₂ sample. The transfer involved spin coating the MoS₂ with PMMA and etching the SiO₂ interface by the 1 M KOH method.⁷⁷ The floating PMMA/MoS₂ film was washed with distilled water twice and placed on the top of the graphene/Si/SiO₂ sample. The PMMA was removed by treating in acetone for 2 h, washed with IPA, and annealed in vacuum at 600 °C for 150 min to remove the PMMA. Optical images (Olympus BX51 Microscope with Olympus C-5050Z camera) of the samples are shown in Figure 1a,b. Raman spectroscopy (NT-MDT NTEGRA) shown in Figure S3 confirms that monolayer graphene and monolayer MoS₂ were present on the sample. The possibility of oxidation of the materials during sample preparation was analyzed and

determined to be negligible, as discussed in Section 13 of Supporting Information.

Friction Force Measurements. Friction was measured using an Asylum MFP-3D AFM (DLC) coated silicon tip (Budget-Sensors ContDLC) with a radius of curvature of 9.6 ± 0.4 nm estimated from TEM images (JEOL F200 TEM, Figure S7). The normal and lateral cantilever force constant calibrations ($k_{\text{normal}} = 0.087$ N/m, $k_{\text{lateral}} = 28.3$ N/m) were performed via the thermal tune method⁷⁸ and the wedge method,⁷⁹ respectively. Friction was measured as a function of applied normal load, starting at a maximum load and then reducing the load by 0.1 nN per scan line until the tip pulled off the sample. This was accomplished using a program provided by Asylum Research Technical Support to ramp the normal force set point after each friction loop with the feedback still engaged, thus reducing wear and any changes in load due to changes in local surface height. The scan location was carefully chosen so that the AFM tip scanned across the three surfaces of interest: (1) monolayer graphene on the SiO₂ substrate, (2) monolayer MoS₂ on monolayer graphene on SiO₂, and (3) monolayer MoS₂ on SiO₂.

MD Simulation. The MD model consisted of a graphene layer and an MoS₂ layer supported partially by the silicon substrate and partially by the graphene (see Figure 1d). To incorporate the compliance of the AFM cantilever, we coupled the model tip (2 nm radius) to an interaction-free particle (virtual atom in Figure 1d) via a harmonic spring (stiffness of 1.6 N/m) representing the cantilever.⁶¹ The substrate and the atoms at one end of the graphene and MoS₂ sheets were fixed in place and the tip was treated as a rigid body. The potentials used for interactions within each material were AIREBO for graphene⁸⁰ and REBO⁸¹ for MoS₂. A Lennard–Jones 6-12 potential was employed to describe all interactions between the materials (parameters in Table S4). The simulations were performed at 300 K in NVT (constant number of atoms, volume, and temperature) ensemble using a Nosé–Hoover thermostat⁸² (excluding the direction of sliding from the temperature calculation), consistent with previous simulations of atomic friction.^{83–85} The simulations were performed with the LAMMPS⁸⁶ code and the atomic configurations were imaged using OVITO.⁸⁷ During a simulation, the tip was first brought in contact with the substrate and the entire system was relaxed for 0.7 ns at which point the vertical position of the tip varied less than 0.05 Å. Then, friction tests were performed by displacing the virtual atom laterally with a constant speed of 2 m/s at normal loads ranging from 0.15 to 10 nN. The sliding speed in simulations was orders of magnitude larger than that in the experiments due to the femtosecond-scale time step in the simulations. Although the speed gap between simulations and experiments can be addressed using simulations with parallelization in time,⁸⁸ that approach was not viable here because the large model size required the available computational resources be used for spatial parallelization. Further, it has been shown that the same friction trends can be obtained using AFM and MD with very different sliding speeds.^{16,29} We therefore used this approach here. During each sliding simulation, the lateral force on the virtual atom was recorded. The lateral force exhibited stick–slip behavior in all cases and friction was calculated as the average of the peak lateral forces, that is, static friction.⁸⁹

DFT Calculations. In order to model the corrugation of the potential energy surfaces (PES) for a methane sliding over graphene and MoS₂ bilayers (Figure S2a,b), DFT calculation

were performed. All calculations used the B86bPBE^{90,91} functional with the exchange-hole dipole moment dispersion model (XDM),^{92,93} implemented in the Quantum ESPRESSO package.⁹⁴ The XDM damping function coefficients have the canonical values for the B86bPBE functional ($a_1 = 0.6512$, $a_2 = 1.4633$). The projector-augmented wave (PAW) method⁹⁵ with data sets from the Quantum ESPRESSO pslibrary⁹⁶ were used. The cutoff energies were 80 Ry for the wave functions and 800 Ry for the density. A uniform k-point sampling of $5 \times 5 \times 1$ was used for graphene and $2 \times 2 \times 1$ for MoS₂. The atomic positions and in-plane lattice constants of graphene and MoS₂ bilayers were relaxed, whereas the surface-normal dimension of the unit cell was kept fixed, providing 30 Å of vacuum between each surface and its periodic image. The energy and force convergence thresholds were 10^{-6} Ry and 10^{-5} Ry/bohr, respectively, and these same values were used for all geometry relaxations in this work.

To generate the sliding PES, a single methane molecule was used to represent the AFM tip, as in our previous work.⁹⁷ Although this does not at all match the dimensions of the tips used in the MD simulations and experiments, the DFT calculations are limited to model tips of molecular dimensions. The resulting barriers should represent an upper bound to the corrugation of the PES, because incommensurability resulting from larger tips will tend to reduce this corrugation. Adsorption of the model methane tip on the surface was considered in two different configurations, shown in Figure S4c,d. The methane was adsorbed on the equilibrium geometries of the graphene or MoS₂ bilayers, using 3×3 supercells to prevent methane–methane self-interactions. The horizontal coordinates of the methane molecule on the surface and the atomic positions of the graphene and MoS₂ layers were kept fixed, whereas the vertical position of methane molecule was allowed to relax. A 6×6 uniform sampling of methane positions was used to explore the two-dimensional sliding PES. In addition, calculations of methane sliding along the long diagonal of the hexagonal unit cell (Figure S4) were carried out for both bilayers. These sliding-energy barriers have been shown to control friction in the low-temperature limit, according to the PT model, and scale well with experimental nanoscale friction measurements.^{26,70}

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b02035.

Additional information, figures, and tables (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: amartini@ucmerced.edu.

*E-mail: carpick@seas.upenn.edu.

ORCID

Mohammad R. Vazirisereshk: 0000-0001-8122-7749

Meng-Qiang Zhao: 0000-0002-0547-3144

Zhaoli Gao: 0000-0003-3114-2207

A. T. Charlie Johnson: 0000-0002-5402-1224

Erin R. Johnson: 0000-0002-5651-468X

Robert W. Carpick: 0000-0002-3235-3156

Ashlie Martini: 0000-0003-2017-6081

Author Contributions

M.R.V. and H.Y. contributed equally to this work. H.Y. carried out the experiments, advised by R.W.C. M.R.V. performed the MD simulations, advised by A.M. M.Q.Z. and Z.G. prepared the sample, advised by A.T.C.J. A.O.R. and E.R.J. performed the DFT calculations. Z.Y. contributed to the preliminary design of the MD simulation setup. The manuscript was written through contributions of all authors.

Funding

A.M., M.R.V., H.Y., and R.W.C. acknowledge the support of the National Science Foundation, awards CMMI-1762384 and CMMI-1761874. M.Q.Z. and A.T.C.J. acknowledge support from the National Science Foundation EFRI-2DARE program, Grant ENG-1542879. A.O.R. thanks the Spanish Ministerio de Economía y Competitividad (MINECO) for a Ramón y Cajal fellowship (RyC-2016-20301). E.R.J. thanks the Natural Sciences and Engineering Research Council of Canada for financial support.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation Grant ACI-1548562. The authors acknowledge the University of Pennsylvania's Singh Center for Nanotechnology, an NNCI member supported by NSF Grant ECCS-1542153, technical support and discussion from K. Hasz, Dr. H. Khare, Dr. M. Brukman, Dr. J. B. McClimon, J. Hilbert, K. Tian, Dr. J. Lefever, Dr. C. Naylor, and Dr. Z. Milne.

■ ABBREVIATIONS

AFM, atomic force microscope; MD, molecular dynamics; DFT, density functional theory; DLC, diamond-like carbon; RH, relative humidity; DMT, Derjaguin–Müller–Toporov; RMS, root-mean-square; PT, Prandtl–Tomlinson; PES, potential energy surface; CVD, chemical vapor deposition; PMMA, poly(methyl methacrylate); IPA, isopropyl alcohol; TEM, transmission electron microscope.

■ REFERENCES

- (1) Androulidakis, C.; Zhang, K.; Robertson, M.; Tawfik, S. Tailoring the mechanical properties of 2D materials and heterostructures. *2D Mater.* **2018**, *5* (3), 032005.
- (2) Berman, D.; Erdemir, A.; Sumant, A. V. Approaches for Achieving Superlubricity in Two-Dimensional Materials. *ACS Nano* **2018**, *12* (3), 2122–2137.
- (3) Klemen, A.; Pastewka, L.; Balakrishna, S. G.; Caron, A.; Bennewitz, R.; Moseler, M. Atomic Scale Mechanisms of Friction Reduction and Wear Protection by Graphene. *Nano Lett.* **2014**, *14* (12), 7145–7152.
- (4) Vasić, B.; Matković, A.; Ralević, U.; Belić, M.; Gajić, R. Nanoscale wear of graphene and wear protection by graphene. *Carbon* **2017**, *120*, 137–144.
- (5) Berman, D.; Erdemir, A.; Sumant, A. V. Reduced wear and friction enabled by graphene layers on sliding steel surfaces in dry nitrogen. *Carbon* **2013**, *59*, 167–175.
- (6) Mungse, H. P.; Khatri, O. P. Chemically Functionalized Reduced Graphene Oxide as a Novel Material for Reduction of Friction and Wear. *J. Phys. Chem. C* **2014**, *118* (26), 14394–14402.
- (7) Lee, C.; Li, Q.; Kalb, W.; Liu, X.-Z.; Berger, H.; Carpick, R. W.; Hone, J. Frictional Characteristics of Atomically Thin Sheets. *Science* **2010**, *328* (5974), 76.

- (8) Kim, K.-S.; Lee, H.-J.; Lee, C.; Lee, S.-K.; Jang, H.; Ahn, J.-H.; Kim, J.-H.; Lee, H.-J. Chemical Vapor Deposition-Grown Graphene: The Thinnest Solid Lubricant. *ACS Nano* **2011**, *5* (6), 5107–5114.
- (9) Shin, Y. J.; Stromberg, R.; Nay, R.; Huang, H.; Wee, A. T. S.; Yang, H.; Bhatia, C. S. Frictional characteristics of exfoliated and epitaxial graphene. *Carbon* **2011**, *49* (12), 4070–4073.
- (10) Berman, D.; Deshmukh, S. A.; Sankaranarayanan, S. K. R. S.; Erdemir, A.; Sumant, A. V. Macroscale superlubricity enabled by graphene nanoscroll formation. *Science* **2015**, *348* (6239), 1118.
- (11) Egberts, P.; Han, G. H.; Liu, X. Z.; Johnson, A. T. C.; Carpick, R. W. Frictional Behavior of Atomically Thin Sheets: Hexagonal-Shaped Graphene Islands Grown on Copper by Chemical Vapor Deposition. *ACS Nano* **2014**, *8* (5), 5010–5021.
- (12) Akinwande, D.; Brennan, C. J.; Bunch, J. S.; Egberts, P.; Felts, J. R.; Gao, H.; Huang, R.; Kim, J.-S.; Li, T.; Li, Y.; Liechti, K. M.; Lu, N.; Park, H. S.; Reed, E. J.; Wang, P.; Yakobson, B. I.; Zhang, T.; Zhang, Y.-W.; Zhou, Y.; Zhu, Y. A review on mechanics and mechanical properties of 2D materials-Graphene and beyond. *Extrem. Mech. Lett.* **2017**, *13*, 42–77.
- (13) Lee, G.-H.; Cooper, R. C.; An, S. J.; Lee, S.; van der Zande, A.; Petrone, N.; Hammerberg, A. G.; Lee, C.; Crawford, B.; Oliver, W.; Kysar, J. W.; Hone, J. High-Strength Chemical-Vapor-Deposited Graphene and Grain Boundaries. *Science* **2013**, *340* (6136), 1073.
- (14) Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Impermeable Atomic Membranes from Graphene Sheets. *Nano Lett.* **2008**, *8* (8), 2458–2462.
- (15) He, K. T.; Wood, J. D.; Doidge, G. P.; Pop, E.; Lyding, J. W. Scanning Tunneling Microscopy Study and Nanomanipulation of Graphene-Coated Water on Mica. *Nano Lett.* **2012**, *12* (6), 2665–2672.
- (16) Egberts, P.; Ye, Z.; Liu, X. Z.; Dong, Y.; Martini, A.; Carpick, R. W. Environmental dependence of atomic-scale friction at graphite surface steps. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88* (3), 035409.
- (17) Liu, Z.; Yang, J.; Grey, F.; Liu, J. Z.; Liu, Y.; Wang, Y.; Yang, Y.; Cheng, Y.; Zheng, Q. Observation of Microscale Superlubricity in Graphite. *Phys. Rev. Lett.* **2012**, *108* (20), 205503.
- (18) Feng, X.; Kwon, S.; Park, J. Y.; Salmeron, M. Superlubric Sliding of Graphene Nanoflakes on Graphene. *ACS Nano* **2013**, *7* (2), 1718–1724.
- (19) Sinclair, R. C.; Suter, J. L.; Coveney, P. V. Graphene–Graphene Interactions: Friction, Superlubricity, and Exfoliation. *Adv. Mater.* **2018**, *30* (13), 1705791.
- (20) Ye, Z.; Balkanci, A.; Martini, A.; Baykara, M. Z. Effect of roughness on the layer-dependent friction of few-layer graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96* (11), 115401.
- (21) Li, S.; Li, Q.; Carpick, R. W.; Gumbsch, P.; Liu, X. Z.; Ding, X.; Sun, J.; Li, J. The evolving quality of frictional contact with graphene. *Nature* **2016**, *539*, 541.
- (22) Smolyanitsky, A.; Killgore, J. P.; Tewary, V. K. Effect of elastic deformation on frictional properties of few-layer graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85* (3), 035412.
- (23) Li, Q.; Lee, C.; Carpick, R. W.; Hone, J. Substrate effect on thickness-dependent friction on graphene. *Phys. Status Solidi B* **2010**, *247* (11–12), 2909–2914.
- (24) Cho, D.-H.; Wang, L.; Kim, J.-S.; Lee, G.-H.; Kim, E. S.; Lee, S.; Lee, S. Y.; Hone, J.; Lee, C. Effect of surface morphology on friction of graphene on various substrates. *Nanoscale* **2013**, *5* (7), 3063–3069.
- (25) Ko, J.-H.; Kwon, S.; Byun, I.-S.; Choi, J. S.; Park, B. H.; Kim, Y.-H.; Park, J. Y. Nanotribological Properties of Fluorinated, Hydrogenated, and Oxidized Graphenes. *Tribol. Lett.* **2013**, *50* (2), 137–144.
- (26) Li, Q.; Liu, X.-Z.; Kim, S.-P.; Shenoy, V. B.; Sheehan, P. E.; Robinson, J. T.; Carpick, R. W. Fluorination of Graphene Enhances Friction Due to Increased Corrugation. *Nano Lett.* **2014**, *14* (9), 5212–5217.
- (27) Kwon, S.; Ko, J.-H.; Jeon, K.-J.; Kim, Y.-H.; Park, J. Y. Enhanced Nanoscale Friction on Fluorinated Graphene. *Nano Lett.* **2012**, *12* (12), 6043–6048.
- (28) Dong, Y.; Wu, X.; Martini, A. Atomic roughness enhanced friction on hydrogenated graphene. *Nanotechnology* **2013**, *24* (37), 375701.
- (29) Hasz, K.; Ye, Z.; Martini, A.; Carpick, R. W. Experiments and simulations of the humidity dependence of friction between nanoasperities and graphite: The role of interfacial contact quality. *Phys. Rev. Mater.* **2018**, *2*, 126001.
- (30) Arif, T.; Colas, G.; Filleter, T. Effect of Humidity and Water Intercalation on the Tribological Behavior of Graphene and Graphene Oxide. *ACS Appl. Mater. Interfaces* **2018**, *10* (26), 22537–22544.
- (31) Zhang, Y.; Dong, M.; Gueye, B.; Ni, Z.; Wang, Y.; Chen, Y. Temperature effects on the friction characteristics of graphene. *Appl. Phys. Lett.* **2015**, *107* (1), 011601.
- (32) Jansen, L.; Hölscher, H.; Fuchs, H.; Schirmeisen, A. Temperature Dependence of Atomic-Scale Stick-Slip Friction. *Phys. Rev. Lett.* **2010**, *104* (25), 256101.
- (33) Peng, Y.; Wang, Z.; Li, C. Study of nanotribological properties of multilayer graphene by calibrated atomic force microscopy. *Nanotechnology* **2014**, *25* (30), 305701.
- (34) Choi, J. S.; Kim, J.-S.; Byun, I.-S.; Lee, D. H.; Lee, M. J.; Park, B. H.; Lee, C.; Yoon, D.; Cheong, H.; Lee, K. H.; Son, Y.-W.; Park, J. Y.; Salmeron, M. Friction Anisotropy-Driven Domain Imaging on Exfoliated Monolayer Graphene. *Science* **2011**, *333* (6042), 607.
- (35) Baykara, M. Z.; Vazirisereshk, M. R.; Martini, A. Emerging superlubricity: A review of the state of the art and perspectives on future research. *Appl. Phys. Rev.* **2018**, *5* (4), 041102.
- (36) Leven, I.; Krepel, D.; Shemesh, O.; Hod, O. Robust Superlubricity in Graphene/h-BN Heterojunctions. *J. Phys. Chem. Lett.* **2013**, *4* (1), 115–120.
- (37) Dienwiebel, M.; Verhoeven, G. S.; Pradeep, N.; Frenken, J. W. M.; Heimberg, J. A.; Zandbergen, H. W. Superlubricity of Graphite. *Phys. Rev. Lett.* **2004**, *92* (12), 126101.
- (38) Liu, Y.; Song, A.; Xu, Z.; Zong, R.; Zhang, J.; Yang, W.; Wang, R.; Hu, Y.; Luo, J.; Ma, T. Interlayer Friction and Superlubricity in Single-Crystalline Contact Enabled by Two-Dimensional Flake-Wrapped Atomic Force Microscope Tips. *ACS Nano* **2018**, *12* (8), 7638–7646.
- (39) Kawai, S.; Benassi, A.; Gnecco, E.; Söde, H.; Pawlak, R.; Feng, X.; Müllen, K.; Passerone, D.; Pignedoli, C. A.; Ruffieux, P.; Fasel, R.; Meyer, E. Superlubricity of graphene nanoribbons on gold surfaces. *Science* **2016**, *351* (6276), 957.
- (40) Castellanos-Gomez, A.; Poot, M.; Steele, G. A.; van der Zant, H. S. J.; Agrait, N.; Rubio-Bollinger, G. Elastic Properties of Freely Suspended MoS₂ Nanosheets. *Adv. Mater.* **2012**, *24* (6), 772–775.
- (41) Zhao, X.; Perry, S. S. The Role of Water in Modifying Friction within MoS₂ Sliding Interfaces. *ACS Appl. Mater. Interfaces* **2010**, *2* (5), 1444–1448.
- (42) Lavini, F.; Calò, A.; Gao, Y.; Albisetti, E.; Li, T.-D.; Cao, T.; Li, G.; Cao, L.; Aruta, C.; Riedo, E. Friction and work function oscillatory behavior for an even and odd number of layers in polycrystalline MoS₂. *Nanoscale* **2018**, *10* (17), 8304–8312.
- (43) Zhao, X.; Phillpot, S. R.; Sawyer, W. G.; Sinnott, S. B.; Perry, S. S. Transition from Thermal to Athermal Friction under Cryogenic Conditions. *Phys. Rev. Lett.* **2009**, *102* (18), 186102.
- (44) Sheehan, P. E.; Lieber, C. M. Friction between van der Waals Solids during Lattice Directed Sliding. *Nano Lett.* **2017**, *17* (7), 4116–4121.
- (45) Onodera, T.; Morita, Y.; Nagumo, R.; Miura, R.; Suzuki, A.; Tsuboi, H.; Hatakeyama, N.; Endou, A.; Takaba, H.; Dassenoy, F.; Minfray, C.; Joly-Pottuz, L.; Kubo, M.; Martin, J.-M.; Miyamoto, A. A Computational Chemistry Study on Friction of h-MoS₂. Part II. Friction Anisotropy. *J. Phys. Chem. B* **2010**, *114* (48), 15832–15838.
- (46) Sheehan, P. E.; Lieber, C. M. Nanotribology and Nanofabrication of MoO₃ Structures by Atomic Force Microscopy. *Science* **1996**, *272* (5265), 1158.

- (47) Lee, J. H.; Lee, S.; Jeon, J. H.; Oh, D. Y.; Shin, M.; Lee, M. J.; Shinde, S.; Ahn, J.-H.; Roh, C. J.; Lee, J. S.; Park, B. H. Universality of strain-induced anisotropic friction domains on 2D materials. *NPG Asia Mater.* **2018**, *10*, 1069–1075.
- (48) Li, H.; Wang, J.; Gao, S.; Chen, Q.; Peng, L.; Liu, K.; Wei, X. Superlubricity between MoS₂ Monolayers. *Adv. Mater.* **2017**, *29* (27), 1701474.
- (49) Dietzel, D.; Brndiar, J.; Štich, I.; Schirmeisen, A. Limitations of Structural Superlubricity: Chemical Bonds versus Contact Size. *ACS Nano* **2017**, *11* (8), 7642–7647.
- (50) Zeng, X.; Peng, Y.; Lang, H.; Yu, K. Probing the difference in friction performance between graphene and MoS₂ by manipulating the silver nanowires. *J. Mater. Sci.* **2019**, *54* (1), 540–551.
- (51) Khac, B.-C. T.; Chung, K.-H. Quantitative Assessment of Friction Characteristics of Single-Layer MoS₂ and Graphene Using Atomic Force Microscopy. *J. Nanosci. Nanotechnol.* **2016**, *16* (5), 4428–33.
- (52) Liu, Y.; Weiss, N. O.; Duan, X.; Cheng, H.-C.; Huang, Y.; Duan, X. Van der Waals heterostructures and devices. *Nat. Rev. Mater.* **2016**, *1*, 16042.
- (53) Song, W.; Yan, J.; Ji, H. Fabrication of GNS/MoS₂ composite with different morphology and its tribological performance as a lubricant additive. *Appl. Surf. Sci.* **2019**, *469*, 226–235.
- (54) Hou, K.; Wang, J.; Yang, Z.; Ma, L.; Wang, Z.; Yang, S. One-pot synthesis of reduced graphene oxide/molybdenum disulfide heterostructures with intrinsic incommensurateness for enhanced lubricating properties. *Carbon* **2017**, *115*, 83–94.
- (55) Chen, J.; Xia, Y.; Yang, J.; Chen, B. Fabrication of monolayer MoS₂/rGO hybrids with excellent tribological performances through a surfactant-assisted hydrothermal route. *Appl. Phys. A: Mater. Sci. Process.* **2018**, *124* (6), 430.
- (56) Jiang, J.-W.; Park, H. S. A Gaussian treatment for the friction issue of Lennard-Jones potential in layered materials: Application to friction between graphene, MoS₂, and black phosphorus. *J. Appl. Phys.* **2015**, *117* (12), 124304.
- (57) Wang, L.; Zhou, X.; Ma, T.; Liu, D.; Gao, L.; Li, X.; Zhang, J.; Hu, Y.; Wang, H.; Dai, Y.; Luo, J. Superlubricity of a graphene/MoS₂ heterostructure: a combined experimental and DFT study. *Nanoscale* **2017**, *9* (30), 10846–10853.
- (58) Jacobs, T.; Mate, C. M.; Turner, K.; Carpick, R. W. Understanding the tip-sample contact: An overview of contact mechanics at the nanoscale. In *Scanning probe microscopy for industrial applications: nanomechanical characterization*; Yablon, D. G., Ed.; Wiley Publishing, 2013; pp 15–48.
- (59) Gupta, A.; Chen, G.; Joshi, P.; Tadigadapa, S.; Eklund, R. Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films. *Nano Lett.* **2006**, *6* (12), 2667–2673.
- (60) Lee, Y.-H.; Zhang, X.-Q.; Zhang, W.; Chang, M.-T.; Lin, C.-T.; Chang, K.-D.; Yu, Y.-C.; Wang, J. T.-W.; Chang, C.-S.; Li, L.-J.; Lin, T.-W. Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv. Mater.* **2012**, *24* (17), 2320–2325.
- (61) Dong, Y.; Vadakkepatt, A.; Martini, A. Analytical Models for Atomic Friction. *Tribol. Lett.* **2011**, *44* (3), 367.
- (62) Prandtl, L. Ein Gedankenmodell zur kinetischen Theorie der festen Körper. *Z. Angew. Math. Mech.* **1928**, *8* (2), 85–106.
- (63) Reedy, E. D. Contact mechanics for coated spheres that includes the transition from weak to strong adhesion. *J. Mater. Res.* **2007**, *22* (9), 2617–2622.
- (64) Jacobs, T. D. B.; Ryan, K. E.; Keating, P. L.; Grierson, D. S.; Lefever, J. A.; Turner, K. T.; Harrison, J. A.; Carpick, R. W. The Effect of Atomic-Scale Roughness on the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. *Tribol. Lett.* **2013**, *50* (1), 81–93.
- (65) Deng, Z.; Smolyanitsky, A.; Li, Q.; Feng, X.-Q.; Cannara, R. J. Adhesion-dependent negative friction coefficient on chemically modified graphite at the nanoscale. *Nat. Mater.* **2012**, *11*, 1032.
- (66) Gao, Y.; Kim, S.; Zhou, S.; Chiu, H.-C.; Nélis, D.; Berger, C.; de Heer, W.; Polloni, L.; Sordan, R.; Bongiorno, A.; Riedo, E. Elastic coupling between layers in two-dimensional materials. *Nat. Mater.* **2015**, *14*, 714.
- (67) Waghmare, A. K.; Sahoo, P. Adhesive friction at the contact between rough surfaces using n-point asperity model. *Engineering Science and Technology, an International Journal* **2015**, *18* (3), 463–474.
- (68) Li, P.; You, Z.; Cui, T. Molybdenum disulfide dc contact MEMS shunt switch. *J. Micromech. Microeng.* **2013**, *23* (4), 045026.
- (69) Tomlinson, G. A. CVI. A molecular theory of friction. *Philos. Mag.* **1929**, *7* (46), 905–939.
- (70) Socoliuc, A.; Bennewitz, R.; Gnecco, E.; Meyer, E. Transition from stick-slip to continuous sliding in atomic friction: entering a new regime of ultralow friction. *Phys. Rev. Lett.* **2004**, *92* (13), 134301.
- (71) Carpick, R. W.; Agrait, N.; Ogletree, D. F.; Salmeron, M. Variation of the Interfacial Shear Strength and Adhesion of a Nanometer-Sized Contact. *Langmuir* **1996**, *12* (13), 3334–3340.
- (72) Ye, Z.; Otero-de-la-Roza, A.; Johnson, E.; Martini, A. Oscillatory motion in layered materials: graphene, boron nitride, and molybdenum disulfide. *Nanotechnology* **2015**, *26* (16), 165701.
- (73) Gao, Z.; Zhang, Q.; Naylor, C. H.; Kim, Y.; Abidi, I. H.; Ping, J.; Ducos, P.; Zauberman, J.; Zhao, M.-Q.; Rappe, A. M.; Luo, Z.; Ren, L.; Johnson, A. T. C. Crystalline Bilayer Graphene with Preferential Stacking from Ni–Cu Gradient Alloy. *ACS Nano* **2018**, *12* (3), 2275–2282.
- (74) Lerner, M. B.; Matsunaga, F.; Han, G. H.; Hong, S. J.; Xi, J.; Crook, A.; Perez-Aguilar, J. M.; Park, Y. W.; Saven, J. G.; Liu, R.; Johnson, A. T. C. Scalable Production of Highly Sensitive Nanosensors Based on Graphene Functionalized with a Designed G Protein-Coupled Receptor. *Nano Lett.* **2014**, *14* (5), 2709–2714.
- (75) Xie, W.; Weng, L.-T.; Ng, K. M.; Chan, C. K.; Chan, C.-M. Clean graphene surface through high temperature annealing. *Carbon* **2015**, *94*, 740–748.
- (76) Naylor, C. H.; Kybert, N. J.; Schneier, C.; Xi, J.; Romero, G.; Saven, J. G.; Liu, R.; Johnson, A. T. C. Scalable Production of Molybdenum Disulfide Based Biosensors. *ACS Nano* **2016**, *10* (6), 6173–6179.
- (77) Dumcenco, D.; Ovchinnikov, D.; Lopez Sanchez, O.; Gillet, P.; Alexander, D. T.; Lazar, S.; Radenovic, A.; Kis, A. Large-area MoS₂ grown using H₂S as the sulphur source. *2D Mater.* **2015**, *2* (4), 044005.
- (78) Hutter, J. L.; Bechhoefer, J. Calibration of atomic-force microscope tips. *Rev. Sci. Instrum.* **1993**, *64*, 1868–1873.
- (79) Ogletree, D.; Carpick, R. W.; Salmeron, M. Calibration of frictional forces in atomic force microscopy. *Rev. Sci. Instrum.* **1996**, *67* (9), 3298–3306.
- (80) Stuart, S. J.; Tutein, A. B.; Harrison, J. A. A reactive potential for hydrocarbons with intermolecular interactions. *J. Chem. Phys.* **2000**, *112* (14), 6472–6486.
- (81) Liang, T.; Phillpot, S. R.; Sinnott, S. B. Parametrization of a reactive many-body potential for Mo-S systems. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *79* (24), 245110.
- (82) Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* **1984**, *81* (1), 511–519.
- (83) Kobayashi, K.; Liang, Y.; Amano, K.-i.; Murata, S.; Matsuoka, T.; Takahashi, S.; Nishi, N.; Sakka, T. Molecular Dynamics Simulation of Atomic Force Microscopy at the Water–Muscovite Interface: Hydration Layer Structure and Force Analysis. *Langmuir* **2016**, *32* (15), 3608–3616.
- (84) AlMotasem, A. T.; Bergström, J.; Gård, A.; Krakhmalev, P.; Holleboom, L. J. Atomistic Insights on the Wear/Friction Behavior of Nanocrystalline Ferrite During Nanoscratching as Revealed by Molecular Dynamics. *Tribol. Lett.* **2017**, *65* (3), 101.
- (85) Adams, H. L.; Garvey, M. T.; Ramasamy, U. S.; Ye, Z.; Martini, A.; Tysoe, W. T. Shear-Induced Mechanochemistry: Pushing Molecules Around. *J. Phys. Chem. C* **2015**, *119* (13), 7115–7123.
- (86) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117* (1), 1–19.

- (87) Stukowski, A. Visualization and analysis of atomistic simulation data with OVITO—the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18* (1), 015012.
- (88) Liu, X.-Z.; Ye, Z.; Dong, Y.; Egberts, P.; Carpick, R. W.; Martini, A. Dynamics of Atomic Stick-Slip Friction Examined with Atomic Force Microscopy and Atomistic Simulations at Overlapping Speeds. *Phys. Rev. Lett.* **2015**, *114* (14), 146102.
- (89) Carpick, R. W.; Salmeron, M. Scratching the Surface: Fundamental Investigations of Tribology with Atomic Force Microscopy. *Chem. Rev.* **1997**, *97* (4), 1163–1194.
- (90) Becke, A. On the large-gradient behavior of the density functional exchange energy. *J. Chem. Phys.* **1986**, *85* (12), 7184–7187.
- (91) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.
- (92) Otero-de-la-Roza, A.; Johnson, E. R. Van der Waals interactions in solids using the exchange-hole dipole moment model. *J. Chem. Phys.* **2012**, *136* (17), 174109.
- (93) Becke, A. D.; Johnson, E. R. Exchange-hole dipole moment and the dispersion interaction revisited. *J. Chem. Phys.* **2007**, *127* (15), 154108.
- (94) Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Nardelli, M. B.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys.: Condens. Matter* **2017**, *29* (46), 465901.
- (95) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50* (24), 17953.
- (96) Dal Corso, A. Pseudopotentials periodic table: From H to Pu. *Comput. Mater. Sci.* **2014**, *95*, 337–350.
- (97) Ye, Z.; Otero-de-la-Roza, A.; Johnson, E. R.; Martini, A. Effect of tip shape on atomic-friction at graphite step edges. *Appl. Phys. Lett.* **2013**, *103* (8), 081601.