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Operational and environmental conditions regulate the frictional behavior of two-dimensional materials



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ABSTRACT

The friction characteristics of single-layer h-BN, MoS₂, and graphene were systematically investigated via friction force microscopy measurements at various operational (e.g., normal force and sliding speed) and environmental (e.g., relative humidity and thermal annealing) conditions. The low friction characteristics of these single-layer materials were clearly observed from the normal force-dependent friction results, and their interfacial shear strengths were further estimated using a Hertz-plus-offset model. In addition, speed-dependent friction characteristics clearly demonstrated two regimes of friction as a function of sliding speed - the first is the logarithmic increase in friction with sliding speed regime at sliding speeds smaller than the critical speed and the second is the friction plateau regime at sliding speeds greater than the critical speed. Fundamental parameters such as effective shape of the interaction potential and its corrugation amplitude for these single-layer materials were characterized using the thermally-activated Prandtl-Tomlinson model. Moreover, friction of single-layer h-BN, MoS₂, and graphene was found to increase with relative humidity and decrease with thermal annealing; these trends were attributed to the diffusion of water molecules to the interface between the single-layer materials and their substrates, which leads to an increase in the puckering effect at the tip-material interface and interaction potential corrugation. The enhanced puckering effect was verified via molecular dynamics simulations. Overall, the findings enable a comprehensive understanding of friction characteristics for several classes of two-dimensional materials, which is important to elucidate the feasibility of using these materials as protective and solid-lubricant coating layers for nanoscale devices.

1. Introduction

Layered materials such as hexagonal boron nitride (h-BN), molybdenum disulfide (MoS₂), and graphite have been conventionally used as solid lubricants in a number of critical engineering applications based on their low friction characteristics. The weak interlayer bonding in the structure of these materials has been responsible for the remarkably low shear strength at contacting interfaces [1,2]. In addition, based on this weak bonding, single-layer h-BN, MoS₂, and graphene can be exfoliated from their bulk forms, and the ensuing two-dimensional (2D) materials have been extensively studied due to their notable material properties. For example, these single-layer materials with subnanometer thickness were found to have superior mechanical properties [3–5], high thermal stability [6–8], and outstanding oxidation resistance [9–11]. Such remarkable material properties indeed make single-layer h-BN, MoS₂, and graphene of considerable interest for use as protective and solid-lubricant coating layers for nanoscale devices [12]. These coating layers have been used to reduce the friction force generated at contacting interfaces between moving mechanical parts, which is one of the major sources of energy dissipation and damage in these devices. Hence, to elucidate the applicability of single-layer h-BN, MoS₂, and graphene for protective and solid-lubricant coating layers, a comprehensive understanding of their friction characteristics is essential.

In the literature, a number of studies have been conducted to investigate friction characteristics of single-layer h-BN, MoS₂, and graphene. Particularly, friction force microscopy (FFM) studies have demonstrated their low frictional behaviors [13–15]; in particular, the interfacial shear strength τ of single-layer graphene was estimated to be about 24 MPa, which was over one order of magnitude smaller than that of SiO₂ [13]. However, τ of single-layer h-BN and MoS₂ remain unexplored. Friction of these atomically-thin materials were also found

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to be dependent on the number of layers, in which friction increased as number of layers decreased, and the largest friction was measured on single-layer materials [16-20]. This thickness-dependent friction was proposed to be due to the dependence of the out-of-plane deformation or 'puckering effect' [16] and electron-phonon coupling effect [17,18] on number of layers. Other studies also demonstrated the strong influence of the interaction between atomically-thin materials and their underlying substrates on friction, which pointed out that friction could be increased or decreased when the materials were strongly or loosely bound to substrates, respectively, again due to the puckering effect [19,20]. Furthermore, friction characteristics of these atomically-thin materials were found to be highly affected by laser treatment [21], fluorination [22,23], hydrogenation [24–26], and oxidation [24,27]. The studies clearly showed an increase in friction due to an increase in bending stiffness, interaction potential corrugation, and surface roughness. Although rigorous efforts have been made to study friction characteristics of single-layer h-BN, MoS₂, and graphene, a comprehensive understanding of their frictional behaviors under various conditions remains limited.

Growth and deposition of 2D materials is the first and most important step to fabricate protective and solid-lubricant coating layers, and therefore has attracted tremendous attention. Large-area deposition of atomically-thin h-BN, MoS₂, and graphene via chemical vapor deposition (CVD) [28-30], physical vapor deposition [31,32], and epitaxial growth [33,34] have been recently realized. Although these methods have shown great potential in producing large-scale atomically-thin films, several problems including the crystalline quality and grain boundary structure still remain as compared to the pristine materials produced via mechanical exfoliation methods [29,35]. For example, CVD-growth MoS2 was recently found to exhibit poor friction characteristics compared to that of pristine MoS₂ [36]. To improve the quality of the CVD-growth MoS₂, efforts have been made to optimize the deposition conditions using the frictional behavior for pristine materials as the guideline [36]. Hence, a systematical investigation of friction characteristics for these pristine materials in various conditions is not only important for a comprehensive understanding of their frictional behaviors, but also for the improvement of other growth and deposition methods.

Apart from the challenges with growth and deposition, these 2D materials could also have tribological reliability and durability problems related to environmental conditions (e.g., relative humidity, RH), given that such problems have already been reported for the bulk forms of the materials. For example, bulk MoS₂ exhibited better tribological performance, including friction reduction and wear resistance, in vacuum and dry environments than in humid environments, whereas operating in vacuum and dry conditions resulted in significant degradation in tribological performance of graphite [37,38]. For singlelayer materials, it has also been shown that water molecules can diffuse to the material-substrate interface and form an 'ice-like' water adlayer, resulting in an increase in thickness and change in mechanical properties [39,40]. Given that friction of 2D materials is strongly dependent on mechanical properties and their interactions with the underlying substrates, diffused water molecules could have significant impact on frictional behaviors of the materials. Recently, friction of atomicallythin graphene was found to increase after exposure to humid conditions (\approx 95% RH) [41,42]. This friction enhancement was proposed to be due to the intercalated water layers at the interface between the graphene layers and mica substrate. Although these studies demonstrated an increase in friction for atomically-thin graphene after exposure to high RH, the change in friction for other RH conditions was not reported. Surprisingly, even less is known about the effect of RH on the frictional behaviors of single-layer h-BN and MoS₂.

In this work, friction characteristics of single-layer h-BN, MoS₂, and graphene were investigated using FFM measurements at various operational (e.g., normal force and sliding speed) and environmental (e.g., RH and thermal annealing) conditions. The motivation of this work was

to gain a fundamental understanding of frictional characteristics of pristine single-layer materials, associated with the interaction between the single-layer material and the substrate, so that a guideline for friction characteristics can be provided for other practical deposition methods for nanoscale devices. From the FFM, the dependence of topography, normal force, sliding speed, RH, and thermal annealing on frictional behaviors of these single-layer materials were observed. Furthermore, assisted by molecular dynamics (MD) simulations, the effect of water molecules on frictional behaviors of single-layer material was investigated. In all, the observations are useful not only to develop a more detailed understanding of the friction characteristics for single-layer h-BN, MoS₂, and graphene, but also to elucidate the general failure mechanisms in 2D materials for use as protective and solid-lubricant coating layers in nanoscale devices.

2. Materials and methods

2.1. Experimental measurements

Atomically-thin h-BN, MoS₂, and graphene were deposited onto Si wafers capped with a 300-nm thermally-grown SiO₂ layer via the mechanical exfoliation method. Atomically-thin specimens were located via optical microscopy (VK-X200, Keyence) and topographic images were obtained via intermittent-contact mode atomic force microscopy (AFM) (MFP-3D, Asylum Research) using Si tips (AC240, Olympus). Fig. S1a shows the topographic images of atomically-thin h-BN, MoS₂, and graphene along with the cross-sectional profiles. Based on the profiles, thicknesses were carefully determined. To confirm these values, Raman spectroscopy (Alpha300R, Witec) measurements were conducted, the results of which are shown in Fig. S1b. A 532-nm excitation laser wavelength and a $100 \times$ objective (NA \approx 0.9) were used, and to avoid surface damage induced by thermal effects [21], the laser power was kept well below 0.5 mW.

Friction characteristics were systematically investigated via FFM measurements under various operating (e.g., normal force and sliding speed) and environmental (e.g., RH and thermal annealing) conditions. In FFM measurements, an ultra-nanocrystalline diamond tip (NaDiaProbes, Advanced Diamond Technologies) with tip radius of about 40 nm was scanned across the surfaces of these specimens via contact-mode AFM. For the quantitative force measurements using AFM, normal [43] and lateral [44] force calibrations were performed prior to FFM measurements. The force calibration results showed that the normal spring constant and lateral force sensitivity of the diamond tip used for FFM measurements were about 0.15 N/m and 1.04 mV/nN, respectively. Friction force as a function of normal force and sliding speed for single-layer h-BN, MoS2, and graphene was parametrically investigated. The normal force was first varied in the range from -1 nN to 50 nN with sliding speed set to 375 nm/s. The sliding speed was then varied in the range of 10 nm/s to 14,650 nm/s with normal force set to 1 nN, 5 nN, and 7 nN. It should be noted that the maximum normal force (50 nN) selected for this work was minimized to eliminate the possibility of inducing surface damage during FFM measurements [45] and that the minimum normal force used here was dependent on the adhesion force between the AFM tip and the single-layer materials. In addition, the maximum sliding speed (up to 14,650 nm/s) was set to obtain reliable friction force data over the 300-nm scan length in the FFM measurements.

The humidity-dependent friction of these single-layer materials was characterized in the humidity cell (Humidity Sensing Cell, Asylum Research) at different RH. To control RH, a gas mixture consisting of dry nitrogen gas and nitrogen gas bubbled through a flask of water was continuously sent into the humidity cell. The RH in the cell was well controlled in the range between 5% and 75% by adjusting the gas ratio via two rotameters. The RH was initially decreased to 5% and then slowly increased to 75% with an interval time of 2 h. The thermally-annealed friction measurements were conducted using the temperature-



Fig. 1. (a) Friction loops consisting of friction forces measured in both the trace (forward scanning) and retrace (backward scanning) directions, (b) friction force as a function of normal force, and (c) interfacial shear strength for single-layer h-BN, MOS_2 , and graphene. In (a), the friction loops were obtained at $F_n = 5$ nN and 50 nN, and the dashed lines indicate the average of the trace and retrace friction force. In (b), the data were fitted to the HPO model in Eq. (S1). In (a)–(c), FFM measurements were conducted at 25% RH and 25 °C with a sliding speed of 375 nm/s. Error bars represent one standard deviation of the mean.

controlled stage (Polyheater, Asylum Research). In the annealing process, temperature was gradually increased from room temperature (≈ 25 °C) to 100 °C with a temperature rate of about 25 °C/2 h; the temperature was then maintained at 100 °C for 2 h before the cooling-down process naturally initiated. FFM measurements of these materials were conducted once the temperature reached room temperature with a RH of about 25%. In addition, the frictional behaviors of the single-layer materials under various temperatures including 30 °C, 50 °C, 75 °C, and 100 °C were also observed as shown in Fig. S2. Finally, variations in adhesion forces between the tip and materials were carefully monitored before and after FFM measurements to check for tip wear as shown in Fig. S3; no significant changes in adhesion were observed, which suggested that tip wear during FFM measurements was likely negligible.

2.2. MD simulations

MD simulations were conducted to provide atomic-level insights into the effect of water molecules at the interface between single-layer graphene and an Si substrate on its friction characteristics. Particularly, a hemispherical diamond tip apex with a tip radius of 10 nm was laterally moved across single-layer graphene on an Si substrate as illustrated in Fig. S4. The sizes of the single-layer graphene and Si substrate in x, y, and z directions were about $15.7 \text{ nm} \times 17.9 \text{ nm}$ and 15.7 nm \times 17.9 nm \times 2.2 nm, respectively. Periodic boundary conditions were applied to create an infinitely-large system, which can eliminate side-wall (boundary) effects during MD simulations. The diamond tip was initially located above the surface of single-layer graphene at a distance of ≥ 1 nm to avoid initial interactions between the tip and graphene. The covalent bonding between Si atoms in the substrate and C atoms in the graphene were described via Tersoff and reactive empirical bond-order (REBO) potential functions, respectively [46,47], where the potential parameters were determined from literature values.

The water molecules were added using a simple point charge/extended (SPC/E) model [48-50] and RATTLE algorithm [51,52], in which the electrostatic charges of oxygen and hydrogen atoms were about -0.8476e and 0.4238e, respectively. In addition, the interaction between water molecules was described by a Lennard-Jones (LJ) potential function and the potential parameters for oxygen and hydrogen atoms were taken from previous studies [48–50]. The number of water molecules trapped at the interface between graphene and the Si substrate were set to be about 0, 800, and 2700 molecules as shown in Fig. S4. The water molecules were evenly distributed on the Si substrate with a small amount of random shift in the horizontal direction for each water molecule to avoid perfectly-aligned conditions. The non-bonded interactions for Si-C (Si substrate-graphene), Si-O and Si-H (Si substrate-water molecule), C-O and C-H (graphene-water molecules) were simulated via a LJ potential function. The potential parameters for the interaction between non-identical atoms such as Si-C, Si-O, and C–O were obtained based on the Lorentz-Berthelot mixing rule [53]. In addition, potential parameters of Si and C atoms for non-bonded interactions were obtained from the literature [53,54].

At the initial stages of the simulation, the velocity of each atom was randomly assigned per the Maxwell-Boltzmann distribution. The relaxation process was then carried out for 5 ps to 50 ps to stabilize the system. Once the system was stable, the water molecules reached their minimum interatomic potential energy and the measurements of the thickness and friction force of single-layer graphene were conducted. In the friction force measurements, the diamond tip was initially brought into contact with the single-layer graphene at a normal force and speed of about 45 nN and 0.05 nm/ps, respectively. After contact was established and the system was stabilized for about 5 ps, the tip was dragged horizontally with the sliding speed of about 0.05 nm/ps and a scan length of about 1 nm. The friction force and deformation were carefully tracked during the sliding process. The temperature of the system was kept at about 300 K using a Nose-Hoover thermostat.

3. Results and discussion

3.1. Effect of operational conditions: normal force and sliding speed

Fig. 1a shows representative examples of friction loops obtained from single-layer h-BN, MoS_2 , and graphene at normal forces of 5 nNand 50 nN. A typical friction loop consists of trace and retrace friction profiles, which are obtained by sliding the AFM tip over a specimen surface in the forward and reverse directions, respectively. From the friction loops, friction values that fluctuated from their average values (dashed line) were taken to be friction fluctuations. As shown in Fig. 1a. a significant increase in friction fluctuation for single-layer h-BN, MoS₂, and graphene was qualitatively observed as the normal force increased from 5 nN to 50 nN. A quantitative assessment of the variation in friction fluctuation with normal force is shown in Fig. S5; from the data, it is clear that fluctuation monotonically increases with normal force. In addition, Fig. S6 shows topographic and FFM images of single-layer h-BN, MoS₂, and graphene obtained simultaneously via contact mode AFM under 50 nN normal force along with cross-sectional profiles, surface slopes, and friction loops. From these images, the correlation between topography and friction was clearly observed, where friction was found to increase and decrease as the tip traversed up and down, respectively, an asperity of given slope. This behavior is attributed to the 'ratcheting' mechanism in friction, which has been used to explain topography-induced contributions to friction force measured by FFM in previous studies [55,56]. In more detail, when an AFM tip slides over an asperity of angle δ with respect to the horizontal plane at constant normal force F_n , the slope of the asperity causes a variation in the friction force F_f as described by $F_f \sim \tan \delta \cdot F_n$. The variation in friction fluctuation is proportional to normal force, which explains the trends observed in Figs. 1a and S5. In addition to the slope effect, it was shown that the increase in friction measured when the tip climbed up an asperity was larger than the decrease in friction measured when the tip climbed down the asperity due to an initial 'collision' between the tip and asperity [57]. As a result, the effect of topography on friction measured by FFM could not be entirely eliminated by the subtraction of trace and retrace friction profiles [57], which is consistent with the friction force profiles (half of subtraction of trace and retrace) presented in Fig. S6f. This observation of topography-induced contributions to friction force could be useful when attempting to predict and interpret their frictional behaviors in systems with various topographical characteristics. For example, step edges at the surface of these atomicallythin materials could induce a considerable increase in friction force and even damage when the tip traversed up these steps, as previously found by other studies [58,59]. Although a number of mechanisms have been proposed to explain these observations, the change in slope and the mechanical impact of the AFM tip with the step edges could also strongly influence these behaviors.

Fig. 1b shows friction force with respect to normal force for singlelayer h-BN, MoS₂, and graphene. The result shows that friction force for these single-layer materials increased from 0.04 nN to 2.18 nN as normal force increased from 0 nN to 50 nN, which generally demonstrates their low friction characteristics (e.g., at $F_n = 50$ nN and without consideration of adhesion, the coefficients of friction $\mu = F_f/F_n$ for single-layer h-BN, MoS₂, and graphene were \approx 0.04, almost an order of magnitude smaller than those for typical engineering materials). In addition, the normal force-dependent frictional behavior of these single-layer materials was found to be slightly different from each other. Particularly, as the normal force increased from 0 nN to 50 nN, single-layer MoS₂ exhibited a slightly larger increase in friction (0.04 nN to 2.18 nN) than those of single-layer h-BN (0.28 nN to 2.08 nN) and graphene (0.33 nN to 2.06 nN). This behavior could be attributed to differences in adhesion and mechanical properties for these single-layer materials [15,22]. For example, friction measured at small F_n for single-layer MoS₂ and graphene was recently found to be strongly affected by the adhesion between the tip and specimens, and as $F_{\rm n}$ increased, the increase in friction was strongly affected by mechanical properties [15]. In addition, the increase in friction with normal force for fluorinated graphene was found to be larger than that for pristine graphene, and this enhancement in friction was proposed to be due to the larger out-of-plane bending stiffness for fluorinated graphene [22]. Fig. S3 shows adhesion forces between the AFM tip and these single-layer materials obtained before and after FFM measurements. The average adhesion forces for single-layer h-BN, MoS2 and graphene at 25% RH were 7.01 nN, 5.17 nN, and 7.02 nN, respectively. Furthermore, the out-of-plane bending stiffnesses for single-layer h-BN, MoS₂, and graphene were earlier found to be 0.95 eV [60], 9.61 eV [61], 1.40 eV [62], respectively. Thus, the larger adhesion forces for single-layer h-BN and graphene could explain their larger friction values at small F_n , whereas the larger bending stiffness for single-layer MoS_2 could be responsible for its larger friction values at large F_n . Such understanding is important when these single-layer materials are used as coating layers for nanoscale devices, which are operated under various contact pressure conditions. For example, in low contact pressure situations (e.g., shunt switch) [63], large adhesion may cause stiction problems in the system, whereas in high contact pressure situations (e.g., wear resistance application) [12], large bending stiffnessinduced enhanced friction may deteriorate the lifetime of the protective coating layers and eventually cause severe damage in the system.

Friction force as a function of normal force data as shown in Fig. 1b also demonstrate the nonlinear dependence between $F_{\rm f}$ and $F_{\rm n}$, as predicted by several continuum models of the elastic contact in the single asperity regime [64–66]. To assess the interfacial shear strength τ (i.e., the stress required to slide the AFM tip across the surface) of the tipsurface interface, the normal force-dependent friction data was fitted to the modified theory of Derjaguin-Muller-Toporov and Maugis, also referred to as the Hertz-plus-offset (HPO) model (Supplementary material) [67,68]. Interfacial shear strengths for single-layer h-BN, MoS₂, and graphene were estimated to be $40.6 \text{ MPa} \pm 1.5 \text{ MPa}$, 74.8 MPa ± 2.0 MPa, and 50.5 MPa ± 1.0 MPa, respectively, as presented in Fig. 1c. The shear strength for the diamond tip sliding against single-layer MoS₂ was slightly larger than that for single-layer h-BN and graphene, with corresponds to the larger increase in $F_{\rm f}$ with $F_{\rm n}$ as shown in Fig. 1b. In previous work, the shear strength between an Si₃N₄ tip and single-layer graphene was found to be about 23.6 MPa, which represents a $2 \times$ decrease in shear strength relative to this work [13]. The differences in τ could be due to the different tip materials used in the FFM measurements. Particularly, the availability of C-C bonding with sp^2 configuration in the structure of the nanocrystalline diamond tip used here may offer commensurate contact between the tip and graphene [69], whereas Si-N bonding in the Si₃N₄ tip may cause incommensurate contact with graphene. For a given contact area, commensurate contact often exhibits larger friction, and hence larger shear strength, than incommensurate contact [70]. The τ values here were also found to be larger than those of their bulk forms; interfacial shear strengths for bulk MoS₂ and graphite were found to be about 25 MPa to 33 MPa [71] and 17.6 MPa [72], respectively, while understanding of the interfacial shear strength of h-BN remains limited. The differences could be attributed to the puckering effects in atomically-thin materials, which have been proposed as one of the major reasons for an increase in friction as the number of layers decreased. In addition, the out-of-plane elastic constants used for estimating the interfacial shear strengths here represent the values for bulk h-BN, MoS₂, and bi-layer graphene, which are expected to be larger than those for single-layer materials. Nonethe less, the estimated τ for single-layer h-BN, MoS₂, and graphene clearly demonstrate the low friction characteristics of these single-layer materials.

Fig. 2a shows friction force as a function of sliding speed under different F_n for single-layer h-BN, MoS₂, and graphene. The results demonstrate that under all normal forces investigated, friction of these single-layer materials logarithmically increased as the sliding speed increased. The results also show that the friction forces generally



Fig. 2. (a) Friction force as a function of sliding speed, and variations in the parameters (b) β , (c) β_{sin} , (d) F_c , and (e) E_0 as a function of normal force for single-layer h-BN, MoS₂, and graphene. In (a), $F_n = 1$ nN, 5 nN, and 7 nN. The friction force data in Fig. 1 was also included for clarity. FFM measurements were conducted at 25% RH and 25 °C. In addition, the speed-dependent friction data in (a) were fitted to the thermally-activated PTT model using Eq. (S3) and β , F_c , and v_0 as free parameters. In (b), β is a measure of the curvature of the interaction potential corrugation that governs the rate of increase in friction with sliding speed at low speeds. In (d), F_c is the friction force at zero temperature or the friction in the plateau regime. In (c) and (e), β_{sin} is the shape-related parameter and E_0 is the energy barrier or corrugation amplitude of the interaction potential assuming the interaction potential has a sinusoidal shape; β_{sin} and E_0 were estimated using Eqs. (S4) and (S5). Error bars represent one standard deviation of the mean.

reached steady-state values at speeds > 1000 nm/s. These trends are consistent with the thermally-activated Prandtl-Tomlinson (PTT) model (Supplementary material), which suggests that $F_{\rm f}$ increases with the sliding speed due to the thermal energy [73]. Based on the PTT model, two different regimes of friction as a function of sliding speed could be clearly observed - the first is the logarithmic increase in friction with sliding speed regime at sliding speeds smaller than the critical speed and the second is the friction plateau regime at sliding speeds greater than the critical speed. Therefore, per the PTT model, the observed sliding speed of about 1000 nm/s could be considered the critical speed for friction of single-layer h-BN, MoS₂, and graphene to reach their friction plateau regimes. Although these speed-dependent friction characteristics have been previously observed on various materials such as mica [73,74], NaCl (100) [75], Au (111) [76,77], and graphite (0001) [78], such observations on single-layer h-BN, MoS₂, and graphene have not been fully achieved.

The speed-dependent friction data in Fig. 2a was further examined with the PTT model using Eq. (S3) and β , F_{c} , and v_0 as free parameters. The parameter β is a measure of the curvature of the interaction potential corrugation, which governs the rate of increase in friction with sliding speed. In addition, F_c is the friction force at zero temperature or the friction in the plateau regime, and v_0 is the characteristic speed [73]. Based on the fitting results over the range of sliding speeds used in the FFM measurements, the friction data follow the low-speed trend very well (i.e., a logarithmic increase in friction with speed). The fitting results also show that friction of single-layer h-BN at $F_n = 1$ nN, 5 nN, and 7 nN reach the plateau regime at a critical speed of about 4000 nm/ s, which is similar to that for MoS_2 at $F_n = 1$ nN. The critical speed for friction of single-layer graphene at $F_n = 5 \text{ nN}$ and 7 nN was determined to be in the range 10,000 nm/s to 20,000 nm/s. Although the influence of normal force on critical speed was not clearly observed for all of the single-layer materials, the results do suggest that the critical speed for single-layer MoS₂ is generally smaller than that for h-BN and graphene.

Accordingly, the sliding friction of an AFM tip on the surface of singlelayer MoS_2 is thermally assisted over a smaller range of speeds than that for h-BN and graphene.

Fig. 2b and d show the variation in β and F_c as a function of F_n , respectively. As previously noted, β is the measure of the curvature of the interaction potential corrugation, and as such, the increase in β with $F_{\rm n}$ points to an increase in corrugation with normal force. The energy barrier or corrugation amplitude of the interaction potential E_0 was estimated using Eq. (S4), which assumes that the interaction potentials for these single-layer materials have a sinusoidal shape. The calculated values for E_0 in Fig. 2e clearly show an increase in E_0 with F_n . The increase in the corrugation of the interaction potential with increasing normal force found in this work is in good agreement with a previous study [73]. Furthermore, it is important to note that the corrugation amplitudes for single-layer h-BN, MoS₂, and graphene at $F_n = 5 \text{ nN}$ were found to be 0.19 eV, 0.26 eV, and 0.41 eV, respectively, which are small relative to those for mica ($\approx 1.3 \text{ eV}$, measured in air) [73] and NaCl ($\approx 0.5 \text{ eV}$, measured in vacuum) [79]. The small E_0 values as compared to other materials could be the basis for the low friction behavior in 2D materials.

The curvature of the interaction potential corrugation can also be calculated using Eq. (S5), which also assumes that the potentials for these single-layer materials have a sinusoidal shape. The resulting values for β_{sin} are shown as a function of F_n in Fig. 2c. A comparison between the measured values for β and the calculated values for β_{sin} provided useful insight into the shape of the interaction potentials for single-layer h-BN, MoS₂, and graphene. For single-layer h-BN, the results show good agreement between β and β_{sin} , which suggests that its interaction potential is well described with a sinusoidal shape. In contrast, β_{sin} was found to increase less rapidly than β with F_n for single-layer MoS₂ and graphene, which suggests that their interaction potentials may take a different shape. This finding is important when looking to understand the fundamental frictional behaviors of these atomically-

thin materials based on the PTT model.

In summary, the corrugation amplitude and effective shape of the interaction potential of these single-layer materials were characterized via their speed-dependent friction characteristics. This characterization is critical for a fundamental understanding of the frictional behaviors. From a practical viewpoint, the speed-dependent friction data could also provide useful information on surface characteristics such as wettability. For example, it was demonstrated that as sliding speed increases, a partially hydrophilic surface exhibits a logarithmic decrease in friction, whereas a partially hydrophobic surface exhibits a logarithmic increase in friction [80]. Hence, per the logarithmic increase in friction for single-layer h-BN, MoS₂, and graphene with increasing sliding speed, surface hydrophobicity of these single-layer materials could be clearly inferred. This observation is consistent with other studies that noted surface hydrophobicity for single-layer h-BN [81], MoS₂ [82], and graphene [83] via water contact angle measurements. For applications that use these materials as protective and solidlubricant coatings, surface hydrophobicity could aid in self-cleanability, decreased dirt retention, and extended life expectancy by reducing water concentration on the top surface. However, it has been found that water molecules diffuse to the interfaces between the single-layer materials and their underlying substrate in humid environments, which leads to the formation of ice-like water adlayers at these interfaces. The diffused water molecules were shown to increase the thickness and change the mechanical properties of these materials [39,40]. Given that friction in 2D materials is strongly influenced by mechanical properties and substrate interactions, the diffused water molecules could, in turn, also affect their frictional behaviors [41]. Therefore, the effect of RH and thermal annealing should be well characterized to enhance the reliability and durability of these single-layer materials.

3.2. Effect of environmental conditions: relative humidity and thermal annealing

The effect of RH on friction characteristics of single-layer h-BN, MoS₂, and graphene was investigated via FFM measurements at different RH conditions ranging from 5% to 75%. Fig. 3a and b show normal force-dependent and speed-dependent friction measurements obtained at various RH levels, respectively. For the friction results in Fig. 3a, the sliding speed was 375 nm/s and F_n varied from -1 nN to 50 nN. For the friction results in Fig. 3b, F_n was 7 nN and the sliding speed varied from 10 nm/s to 3000 nm/s at 5%, 45%, and 75% RH and 10 nm/s to 14,650 nm/s at 25% RH. Interestingly, the results show that at a given normal force and sliding speed, the friction of single-layer h-BN, MoS₂, and graphene generally increased with RH, despite the surface hydrophobicity discussed earlier. Fig. 3a shows both the non-linear dependence between F_n and F_f at various RH and the increase in F_f at a given F_n with RH. The interfacial shear strengths were estimated by fitting this data to the HPO model in Eq. (S1). The resulting τ values are shown in Fig. 3c; the data point to an increase in τ with RH.

Fig. 3b clearly shows a logarithmic increase in friction with increasing sliding speed for single-layer h-BN, MoS₂, and graphene and that such speed-dependent friction characteristics exist for all RH conditions investigated. The results also show that only the critical speeds for single-layer MoS₂ were experimentally observed at all RH values; as such, the critical speeds for single-layer MoS₂ were determined to be between 1000 nm/s and 2000 nm/s. The speed-dependent friction data were fitted to the PTT model in Eq. (S3). Based on the fitting results, the critical speeds for single-layer h-BN and graphene were predicted to be in the range of about 8000 nm/s to 10,000 nm/s and 4000 nm/s to 9000 nm/s, respectively, which were in good agreement with the observed values at 25% RH. Thus, the critical speeds for single-layer MoS₂ were smaller than those for single-layer h-BN and graphene, as also shown in Fig. 2. Moreover, no significant change in critical speed with respect to RH was clearly observed. Fig. 3d and e show the parameters β and $F_{\rm c}$ from the PTT model as a function of RH, respectively. From the results, it is clear that β and F_c increase with RH, which suggests that the rate of increase in friction with sliding speed and the friction in the plateau regime both increase with RH. The increases in β and F_c further indicate an increase in the interaction potential corrugation with RH. Per the PTT model, the friction force increased as the interaction potential became more corrugated [79]. Analogous situations have been reported in the literature for hydrogenated and fluorinated graphene (i.e., increased friction with increased interaction potential corrugation) [23,25].

Early research on the friction force of graphite showed that $F_{\rm f}$ was large in dry or vacuum environments and small in humid environments [37]. The authors suggested that this trend was due to the adsorbed layers of vapors, such as water, at the sliding interfaces. For MoS₂, a previous study has shown the opposite response, which is intriguing given MoS₂ and graphite have a similar lamellar structure. Here, the interaction of water between MoS₂ planes during contact sliding was found to be responsible for the trends [38]. These observations clearly highlighted the different roles that water interactions can have on the friction of layered materials. Recently, it was proposed that the thickness-dependent friction of water layers intercalated between graphene and mica may be associated with a change in the vibration modes of graphene [41,42]. Despite these advances, however, a clear understanding of water interactions and their role at the interfaces between tip and single-layer materials and between single-layer materials and substrate remains limited. To this end, it is first paramount to determine if the increases in $F_{\rm f}$ with RH are due to water menisci and the associated capillary forces between the AFM tip and the single-layer materials. The adhesion force between single-layer h-BN, MoS₂, and graphene and the AFM tip were carefully monitored during FFM measurements at various RH as shown in Fig. S7a. The results show no appreciable change in adhesion force as a function of RH. In addition, from Fig. 3b, a logarithmic increase in friction with sliding speed was consistently observed across the range of RH. As discussed earlier, this trend is indicative of a hydrophobic surface, which would preclude water adsorption on the top surface and thus minimize any capillary forces between the tip and surface.

Fig. 3f shows the thickness of single-layer h-BN, MoS₂, and graphene as a function of RH. The thicknesses were determined from topographic images at various RH conditions as shown in Fig. S7b. The results indicate that thickness generally increased with RH. This increase in thickness is likely due to water diffusion at the interface between these single-layer materials and their underlying SiO₂ substrates, as shown in previous studies [39,40,84]. In more detail, the studies demonstrated that water molecules can diffuse into the interface between single-layer materials (e.g., MoS₂ and graphene) and their underlying substrates (e.g., SiO₂ and mica) in humid environments, which leads to increases in thickness, wrinkle formation, and changes in mechanical properties [39,40]. Moreover, as RH increases, the number of diffused water molecules also increases, which increases the distance and decreases the adhesion between the materials and substrate. This could eventually lead to an increase in friction due to an enhancement in the outof-plane deformation or puckering during sliding [16,20] or changes in the vibration modes [41,42].

In previous work, it was proposed that in the ice-like water layer, the oxygen atoms in the diffused water molecules were oriented toward the SiO₂ substrate [40,85], and the hydrogen atoms were likely oriented toward the single-layer materials as demonstrated in Fig. S8. Thus, a localization of hydrogen atoms with partial positive charges right beneath the single-layer materials could lead to a local variation in their interaction potential during FFM measurements. The local variation becomes more significant as the formation of these ice-like water adlayers increases, which could also be responsible for the increase in the interaction potential corrugation with increasing RH as previously discussed. This behavior is similar to what was found in the work of Li et al. [23], which also described an increase in friction for fluorinated graphene due to an increase in corrugation. The authors



Fig. 3. (a) Normal force-dependent friction, (b) speed-dependent friction, and variations in the parameters (c) τ , (d) β , (e) F_c , and (f) thickness as a function of RH and thermal annealing for single-layer h-BN, MoS₂, and graphene. In (a), the sliding speed was 375 nm/s and the data were fitted to the HPO model in Eq. (S1) with τ as the free parameter. In (b), F_n was 7 nN and the data were fitted to the PTT model in Eq. (S3) with β , F_c , and ν_0 as free parameters. The friction force data in (a) was also included for clarity. In (f), the thicknesses were determined from topographic images obtained via intermittent-contact mode AFM as shown in Fig. S7. In (c)–(f), dashed lines are guides to the eye. Error bars represent one standard deviation of the mean.

found that the localization of fluorine atoms with large negative charge resulted in a strong local variation in the interaction potential, which eventually led to an increase in friction for the fluorinated graphene [23].

Given the increases in $F_{\rm f}$ with RH and the prospect that these increases were due to water molecules at the single-layer material-SiO₂ substrate interface, subsequent efforts focused on the removal of these water molecules by a simple thermal annealing process and FFM measurements to investigate their role in friction. The FFM measurements were performed at various normal forces and sliding speeds at 25% RH and 25 °C. The normal force-dependent and speed-dependent friction results for the thermally-annealed materials are shown in Fig. 3a and b, respectively. The results clearly show that friction significantly decreases after the thermal annealing process. Furthermore, by fitting the normal force-dependent data to the HPO model in Eq. (S1) and the speed-dependent data to the PTT model in Eq. (S3), it was found that τ , β , and F_c also decreased with thermal annealing. Fig. 3f also shows that the thicknesses decreased after thermal annealing, and in most cases, were smaller than those at the small RH conditions. This result suggests that water molecules are present at the interface even at small RH, and that these molecules can be diffused out by a thermal annealing process [84]. The decreased amount of water molecules at the interface would consequently decrease the friction force, which could lead to the added benefit of improving the surface damage resistance and wear protection. Thus, a simple thermal annealing process could effectively enhance the tribological performance of these singlelayer materials. This finding is of practical importance for their usage as protective and solid-lubricant coating layers.

To provide more atomic-level insights, the effect of water molecules trapped at the interface between single-layer graphene and an Si substrate on its friction characteristics was investigated via MD simulations. In these simulations, a hemispherical diamond tip apex was scanned across a single-layer graphene surface supported by an Si substrate under a normal force of 45 nN with various amounts of water molecules trapped at their interfaces. The number of water molecules at the interface was set to 0, 800, and 2700 prior to the sliding simulations to simulate different levels of water diffusion. The deformation and friction force from the MD simulations are shown in Fig. 4. As the number of water molecules increased from 0 to 800 to 2700 molecules, the thickness of the single-layer graphene increased from 0.32 nm to 0.51 nm to 0.64 nm, respectively. It is important to note at this juncture that these thicknesses are indicative of the experimental results for thermally-annealed graphene, graphene at small RH (\approx 5% RH), and graphene at moderate RH (\approx 45% RH), which enables a direct comparison between FFM experiments and MD simulations. To enable this comparison, the average friction forces were quantified; from the MD simulations, it was found that $F_{\rm f}$ increased from 0.23 nN to 0.65 nN to 1.06 nN as the number of molecules increased from 0 to 800 to 2700 as shown in Fig. 4a. On the surface, the calculated values in Fig. 4a seem at odds with the experimental values in Fig. 3a. At $F_n = 45 \text{ nN}$, F_f ranges from 0.23 nN to 1.06 nN in the MD simulations and from ≈ 1.0 nN to 2.2 nN in the FFM experiments. However, there are two important



Fig. 4. MD simulations of a hemispherical diamond tip apex scanned across a single-layer graphene surface supported by an Si substrate with various amounts of water molecules at the interface. (a) Friction force and (d) histograms of vertical positions for individual C atoms in the graphene layer during the sliding. Snapshot: (b) cross-sectional and (c) deformation images as a function of number of water molecules. The friction force measurements were simulated under a normal force and sliding distance of about 45 nN and 1 nm, respectively. The number of water molecules at the interface was set to 0, 800, and 2700. In (a)–(b), the average friction forces and the leading edges for the diamond tip were denoted by the dashed lines and white dashed circles, respectively. In (c), the diamond tip was hidden for clarity. The snapshots in (b)–(c) and histogram in (d) were obtained at a sliding distance of about 0.8 nm.

considerations that need to be addressed prior to making a comparison: differences in (1) contact pressure and (2) sliding speed. On point (1), the tip radius R was 40 nm for the experiments and 10 nm for the simulations, which resulted in a mean contact pressure of 0.9 GPa for the experiments and 3.0 GPa for the simulations. From Eq. (S1), it can be shown that $F_{\rm f} \sim (RF_{\rm n})^{2/3}$ for $F_{\rm n} \gg F_{\rm a} - F_{\rm off}$, which is true for $F_{\rm n} = 45$ nN. In terms of contact pressure, the same expression can be written as $F_{\rm f}$ ~ $(RP_na^2)^{2/3}$, where P_n is mean contact pressure and *a* is contact radius. For constant P_n , the MD results for R = 10 nm and a = 2.2 nm can thus be converted to their FFM analogues for R = 40 nm and a = 4 nm via the ratio $F_f^{\text{FFM}}/F_f^{\text{MD}} = (R^{\text{FFM}}/R^{\text{MD}})^{2/3}(a^{\text{FFM}}/a^{\text{MD}})^{4/3} = 5.6$. Thus, for R = 40 nm, F_f ranges from 1.3 nN to 5.9 nN in the MD simulations. On point (2), the sliding speed was 375 nm/s for the experiments and 0.05 nm/ps for the simulations. From Fig. 3b, the sliding speed in the MD simulations is well within the plateau regime of the speed-dependent friction data, suggesting that the associated values for $F_{\rm f}$ (1.3 nN to 5.9 nN at R = 40 nm) are upper bounds. After a correction for sliding speed, the corrected $F_{\rm f}$ from MD simulations (1.3 nN to 5.9 nN) would be in good agreement with the FFM experiments (1.0 nN to 2.2 nN) for the RH range investigated.

As discussed earlier, in a humid environment, water molecules diffuse into the interfaces between these atomically-thin materials and

their substrates, which leads to an increase in their frictional behaviors. It was proposed that this friction enhancement may be associated with the vibration modes of graphene [41,42]. Additionally, it is plausible that the friction enhancement is further attributed to an increase in deformation and the puckering effect during contact sliding. To evaluate this hypothesis, the deformation of single-layer graphene during the sliding simulations was carefully examined as shown in Fig. 4b to d. Particularly, Fig. 4b and c show cross-sectional and deformation images during sliding simulations as a function of number of water molecules, respectively. From Fig. 4b, it can be clearly seen that as the number of water molecules increased, the distance between the graphene layer and substrate significantly increased. In addition, out-of-plane deformation was clearly observed in Fig. 4b and c, and this deformation increased as the number of water molecules increased. To further quantify the degree of puckering in graphene, histograms of vertical positions (i.e., height) for individual C atoms in the graphene layer during the sliding simulations were generated as shown in Fig. 4d. In the histograms, the vertical positions of the undeformed C atoms were 0, and due to the nature of the puckering effect, only the number of C atoms with positive heights were included. For 0 water molecules, there are \approx 4797 atoms deformed vertically, with a largest deformation of \approx 0.09 nm. As the number of water molecules increased from 800 to

2700, the number of C atoms deformed vertically increased from 5769 to 6675 and the largest deformation increased from 0.10 nm to 0.14 nm, respectively. These results clearly indicate that the level of out-of-plane deformation in graphene increases with the number of water molecules, which partially leads to the increase in friction observed in Fig. 4a. The enhanced puckering effect was previously attributed to a decrease in adhesion between the materials and their substrates with an increase in the number of water molecules. Particularly, as the number of water molecules at the interface increased, the distance between the materials and substrates increased, which resulted in a decrease in adhesion. In fact, based on the Lorentz-Berthelot mixing rule, the well depth ε (one of the LJ potential parameters) of Si–C and O-C was determined to be 0.65 kJ/mol and 0.4 kJ/mol, respectively [53,54,86]. These parameters indicate that the interaction strength between graphene and water molecules was much smaller than that between graphene and an Si substrate. Thus, as the distance between graphene and its substrate increased due to water molecules, their interaction strength decreased, which led to an increase in the out-ofplane deformation during contact sliding.

However, it is important to note that the increase in friction force with number of water molecules cannot solely be explained by the enhanced puckering effect. In recent work [42], FFM and first-principles density functional theory calculations were used to examine isotope- and thickness-dependent friction of graphene on mica with intercalated water layers. For single-layer graphene, the authors clearly showed that specimens intercalated with H₂O exhibited friction twice that of specimens intercalated with H₂O + D₂O, despite nearly identical average heights for the water adlayers (0.37 nm for H₂O and 0.38 nm for $H_2O + D_2O$). The increase in friction for H_2O as opposed to $H_2O + D_2O$ was explained by the increased spectral range of the vibrational modes of the graphene in the presence of water. In more detail, the out-of-plane phonon modes of the water layers interacted strongly with the flexural modes of the graphene, which created more phonon channels to dissipate the frictional energy from the graphene to the mica. Interestingly, the results presented in ref. [42] and the results presented herein may represent the opposite ends of a spectrum with regards to the dominant mechanism responsible for increases to friction with intercalated water layers. At high RH [42], 1 to 3 water layers existed between the graphene and substrate, which yielded significant changes to the flexural modes of the graphene and additional phonon channels to dissipate the frictional energy to the substrate. In contrast, at low RH (Figs. 3 and 4), < 1 water layer (on average) existed between the graphene and substrate, which increased the relative significance of the out-of-plane deformation or puckering effect during contact sliding.

4. Conclusions

In summary, this work presented a systematical investigation of friction characteristics for single-layer h-BN, MoS₂, and graphene via FFM measurements under various conditions. The dependence of topography, normal force, sliding speed, RH, and thermal annealing on friction was thoroughly investigated. Particularly, topography-induced friction fluctuations were observed, and it was found that these fluctuations increased with normal force. The low friction characteristics were clearly observed from the normal force-dependent friction results, and their interfacial shear strengths were estimated using the HPO model. Interestingly, the shear strength between an Si₃N₄ tip and single-layer graphene was found to be about 23.6 MPa in previous work, which represented a $2 \times$ decrease in shear strength relative to this work [13]. The differences in τ could be due to the different tip materials used in FFM measurements; the availability of C-C bonding with sp² configuration in the structure of the nanocrystalline diamond tip used here may offer commensurate contact between the tip and graphene [69], whereas Si-N bonding in the Si₃N₄ tip may cause incommensurate contact. In addition, speed-dependent friction characteristics clearly showed two regimes of friction as a function of sliding

speed – the first is the logarithmic increase in friction with sliding speed regime at sliding speeds smaller than the critical speed and the second is the friction plateau regime at sliding speeds greater than the critical speed. From the PTT model, the results show that the critical speed for single-layer MoS₂ is smaller than that for h-BN and graphene, which suggests that the sliding friction of single-layer MoS₂ is thermally assisted over a smaller range of speeds than that for h-BN and graphene. Furthermore, the results for β and β_{sin} imply that the interaction potential for single-layer h-BN is well described with a sinusoidal shape, whereas the interaction potentials for single-layer MoS₂ and graphene may take a different shape.

The effect of RH on friction characteristics of single-laver h-BN. MoS₂, and graphene was investigated via FFM measurements at different RH conditions. The normal force-dependent friction results generally pointed to an increase in τ with RH. The speed-dependent friction characteristics clearly demonstrated two regimes of friction as a function of sliding speed. From the PTT analysis, it was shown that critical speed was constant with RH, but that β and F_c increased with RH, the latter of which points to an increase in the interaction potential corrugation. It was surmised that the changes with RH were due to: (1) water menisci and the associated capillary forces on the AFM tip or (2) water diffusion at the material-substrate interface. The first possibility was likely to be limited, given the hydrophobic nature of these singlelayer materials. The second possibility, however, was explicitly demonstrated via changes in thickness and friction as a function of RH and annealing. Particularly, it was shown that thickness and friction increased with RH and decreased with thermal annealing, presumably due to the diffusion of water molecules into and out of the interface. These trends were further elucidated via MD simulations of single-layer graphene. As the number of molecules in the simulation increased from 0 to 2700 molecules, the thickness increased from 0.32 nm to 0.64 nm and the out-of-plane deformation increased from 0.09 nm to 0.14 nm, both of which lead to increased puckering and friction. Perhaps even more astonishing is the level of agreement between the FFM experiments and MD simulations; after accounting for differences in both contact pressure and sliding speed, the corrected $F_{\rm f}$ from the MD simulations (1.3 nN to 5.9 nN) were in good agreement with the FFM experiments (1.0 nN to 2.2 nN). Future work will look to better match tip geometry, specimen orientation, applied load, temperature, and system compliance in the FFM experiments and MD simulations, as this will facilitate a more direct comparison between the results, and more generally, a predictive MD simulation for FFM experiments on other 2D materials [76,77]. Additional future work will investigate the phonon density of states for h-BN, MoS_2 , and graphene on SiO_2 with interfacial water, as this will offer further insight into the main mechanism responsible for increases to friction with RH (i.e., puckering vs. vibrational modes).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.03.249.

References

- L. Spanu, S. Sorella, G. Galli, Nature and strength of interlayer binding in graphite, Phys. Rev. Lett. 103 (2009) 196401.
- [2] H. Li, J. Wang, S. Gao, Q. Chen, L. Peng, K. Liu, X. Wei, Superlubricity between MoS2 monolayers, Adv. Mater. 29 (2017), https://doi.org/10.1002/adma. 201701474 (1701474-n/a).
- [3] A. Falin, Q. Cai, E.J.G. Santos, D. Scullion, D. Qian, R. Zhang, Z. Yang, S. Huang, K. Watanabe, T. Taniguchi, M.R. Barnett, Y. Chen, R.S. Ruoff, L.H. Li, Mechanical properties of atomically thin boron nitride and the role of interlayer interactions, Nat. Commun. 8 (2017) 15815.
- [4] S. Bertolazzi, J. Brivio, A. Kis, Stretching and breaking of ultrathin MoS2, ACS Nano 5 (2011) 9703–9709, https://doi.org/10.1021/nn203879f.
- [5] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the elastic properties and intrinsic strength of monolayer graphene, Science. 321 (2008) 385–388, https:// doi.org/10.1126/science.1157996.
- [6] N. Kostoglou, K. Polychronopoulou, C. Rebholz, Thermal and chemical stability of hexagonal boron nitride (h-BN) nanoplatelets, Vacuum. 112 (2015) 42–45, https:// doi.org/10.1016/j.vacuum.2014.11.009.
- [7] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Single-layer MoS2 transistors, Nat. Nanotechnol. 6 (2011) 147–150.
- [8] K. Kim, W. Regan, B. Geng, B. Alemán, B.M. Kessler, F. Wang, M.F. Crommie, A. Zettl, High-temperature stability of suspended single-layer graphene, Phys. Status Solidi (RRL) 4 (2010) 302–304, https://doi.org/10.1002/pssr.201000244.
- [9] S. Chen, L. Brown, M. Levendorf, W. Cai, S. Ju, J. Edgeworth, X. Li, C.W. Magnuson, A. Velamakanni, R.D. Piner, J. Kang, J. Park, R.S. Ruoff, Oxidation resistance of graphene-coated Cu and Cu/Ni alloy, ACS Nano 5 (2011) 1321–1327, https://doi. org/10.1021/nn103028d.
- [10] L.H. Li, J. Cervenka, K. Watanabe, T. Taniguchi, Y. Chen, Strong oxidation resistance of atomically thin boron nitride nanosheets, ACS Nano 8 (2014) 1457–1462, https://doi.org/10.1021/nn500059s.
- [11] H.S. Sen, H. Sahin, F.M. Peeters, E. Durgun, Monolayers of MoS2 as an oxidation protective nanocoating material, J. Appl. Phys. 116 (2014) 083508, https://doi. org/10.1063/1.4893790.
- [12] J.C. Spear, B.W. Ewers, J.D. Batteas, 2D-nanomaterials for controlling friction and wear at interfaces, Nano Today 10 (2015) 301–314, https://doi.org/10.1016/j. nantod.2015.04.003.
- [13] Z. Deng, N.N. Klimov, S.D. Solares, T. Li, H. Xu, R.J. Cannara, Nanoscale interfacial friction and adhesion on supported versus suspended monolayer and multilayer graphene, Langmuir 29 (2013) 235–243, https://doi.org/10.1021/la304079a.
- [14] X. Li, J. Yin, J. Zhou, W. Guo, Large area hexagonal boron nitride monolayer as efficient atomically thick insulating coating against friction and oxidation, Nanotechnology. 25 (2014) 105701.
- [15] B.T. Khac, K. Chung, Quantitative assessment of friction characteristics of singlelayer MoS2 and graphene using atomic force microscopy, J. Nanosci. Nanotechnol. 16 (2016) 4428–4433, https://doi.org/10.1166/jnn.2016.11004.
- [16] C. Lee, Q. Li, W. Kalb, X. Liu, H. Berger, R.W. Carpick, J. Hone, Frictional characteristics of atomically thin sheets, Science 328 (2010) 76–80, https://doi.org/10. 1126/science.1184167.
- [17] T. Filleter, J.L. McChesney, A. Bostwick, E. Rotenberg, K.V. Emtsev, T. Seyller, K. Horn, R. Bennewitz, Friction and dissipation in epitaxial graphene films, Phys. Rev. Lett. 102 (2009) 086102.
- [18] T. Filleter, R. Bennewitz, Structural and frictional properties of graphene films on SiC(0001) studied by atomic force microscopy, Phys. Rev. B 81 (2010) 155412, , https://doi.org/10.1103/PhysRevB.81.155412.
- [19] Q. Li, C. Lee, R.W. Carpick, J. Hone, Substrate effect on thickness-dependent friction on graphene, Phys. Status Solidi B 247 (2010) 2909–2914, https://doi.org/10. 1002/pssb.201000555.
- [20] D. Cho, L. Wang, J. Kim, G. Lee, E.S. Kim, S. Lee, S.Y. Lee, J. Hone, C. Lee, Effect of surface morphology on friction of graphene on various substrates, Nanoscale 5 (2013) 3063–3069, https://doi.org/10.1039/C3NR34181J.
- [21] B.C. Tran Khac, K. Jeon, S.T. Choi, Y.S. Kim, F.W. DelRio, K. Chung, Laser-induced particle adsorption on atomically thin MoS2, ACS Appl. Mater. Interfaces 8 (2016) 2974–2984, https://doi.org/10.1021/acsami.5b09382.
- [22] S. Kwon, J. Ko, K. Jeon, Y. Kim, J.Y. Park, Enhanced nanoscale friction on fluorinated graphene, Nano Lett. 12 (2012) 6043–6048, https://doi.org/10.1021/ nl204019k.
- [23] Q. Li, X. Liu, S. Kim, V.B. Shenoy, P.E. Sheehan, J.T. Robinson, R.W. Carpick, Fluorination of graphene enhances friction due to increased corrugation, Nano Lett. 14 (2014) 5212–5217, https://doi.org/10.1021/nl502147t.
- [24] I.S. Byun, D. Yoon, J.S. Choi, I. Hwang, D.H. Lee, M.J. Lee, T. Kawai, Y.W. Son, Q. Jia, H. Cheong, B.H. Park, Nanoscale lithography on monolayer graphene using hydrogenation and oxidation, ACS Nano 5 (2011) 6417–6424, https://doi.org/10. 1021/nn201601m.
- [25] Y. Dong, X. Wu, A. Martini, Atomic roughness enhanced friction on hydrogenated graphene, Nanotechnology 24 (2013) 375701.
- [26] G. Fessler, B. Eren, U. Gysin, T. Glatzel, E. Meyer, Friction force microscopy studies on SiO2 supported pristine and hydrogenated graphene, Appl. Phys. Lett. 104 (2014) 041910, https://doi.org/10.1063/1.4863832.
- [27] J. Ko, S. Kwon, I. Byun, J. Choi, B. Park, Y. Kim, J. Park, Nanotribological properties of fluorinated, hydrogenated, and oxidized graphenes, Tribol. Lett. 50 (2013) 137–144, https://doi.org/10.1007/s11249-012-0099-1.
- [28] L. Song, L. Ci, H. Lu, P.B. Sorokin, C. Jin, J. Ni, A.G. Kvashnin, D.G. Kvashnin, J. Lou, B.I. Yakobson, P.M. Ajayan, Large scale growth and characterization of atomic hexagonal boron nitride layers, Nano Lett. 10 (2010) 3209–3215, https://

doi.org/10.1021/nl1022139.

- [29] Y. Zhan, Z. Liu, S. Najmaei, P.M. Ajayan, J. Lou, Large-area vapor-phase growth and characterization of MoS2 atomic layers on a SiO2 substrate, Small 8 (2012) 966–971, https://doi.org/10.1002/smll.201102654.
- [30] K. Kim, H. Lee, C. Lee, S. Lee, H. Jang, J. Ahn, J. Kim, H. Lee, Chemical vapor deposition-grown graphene: the thinnest solid lubricant, ACS Nano 5 (2011) 5107–5114, https://doi.org/10.1021/nn2011865.
- [31] S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgaard, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher, Atomic-scale structure of single-layer MoS₂ nanoclusters, Phys. Rev. Lett. 84 (2000) 951–954.
- [32] J.A. Garlow, L.K. Barrett, L. Wu, K. Kisslinger, Y. Zhu, J.F. Pulecio, Large-area growth of turbostratic graphene on Ni(111) via physical vapor deposition, Sci. Rep. 6 (2016) 19804.
- [33] C. Virojanadara, M. Syväjarvi, R. Yakimova, L.I. Johansson, A.A. Zakharov, T. Balasubramanian, Homogeneous large-area graphene layer growth on 6H-SiC(0001), Phys. Rev. B 78 (2008) 245403, https://doi.org/10.1103/PhysRevB. 78.245403.
- [34] D. Dumcenco, D. Ovchinnikov, K. Marinov, P. Lazić, M. Gibertini, N. Marzari, O.L. Sanchez, Y. Kung, D. Krasnozhon, M. Chen, S. Bertolazzi, P. Gillet, i.M. Fontcuberta, A. Radenovic, A. Kis, Large-area epitaxial monolayer MoS2, ACS Nano 9 (2015) 4611–4620, https://doi.org/10.1021/acsnano.5b01281.
- [35] Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, L. Cao, Controlled scalable synthesis of uniform, high-quality monolayer and few-layer MoS2 films, Sci. Rep. 3 (2013) 1866.
- [36] D.L.C. Ky, B. Tran Khac, C.T. Le, Y.S. Kim, K. Chung, Friction characteristics of mechanically exfoliated and CVD-grown single-layer MoS2, Friction (2017), https://doi.org/10.1007/s40544-017-0172-8.
- [37] B.K. Yen, B.E. Schwickert, M.F. Toney, Origin of low-friction behavior in graphite investigated by surface X-ray diffraction, Appl. Phys. Lett. 84 (2004) 4702–4704, https://doi.org/10.1063/1.1760597.
- [38] X. Zhao, S.S. Perry, The role of water in modifying friction within MoS2 sliding interfaces, ACS Appl. Mater. Interfaces 2 (2010) 1444–1448, https://doi.org/10. 1021/am100090t.
- [39] M.J. Lee, J.S. Choi, J. Kim, I. Byun, D.H. Lee, S. Ryu, C. Lee, B.H. Park, Characteristics and effects of diffused water between graphene and a SiO2 substrate, Nano Res. 5 (2012) 710–717, https://doi.org/10.1007/s12274-012-0255-9.
- [40] K. Jinkins, J. Camacho, L. Farina, Y. Wu, Examination of humidity effects on measured thickness and interfacial phenomena of exfoliated graphene on silicon dioxide via amplitude modulation atomic force microscopy, Appl. Phys. Lett. 107 (2015) 243107, https://doi.org/10.1063/1.4938068.
- [41] H. Lee, J. Ko, J.S. Choi, J.H. Hwang, Y. Kim, M. Salmeron, J.Y. Park, Enhancement of friction by water intercalated between graphene and mica, J. Phys. Chem. Lett. 8 (2017) 3482–3487, https://doi.org/10.1021/acs.jpclett.7b01377.
- [42] H. Lee, J. Ko, H.C. Song, M. Salmeron, Y. Kim, J.Y. Park, Isotope- and thickness-dependent friction of water layers intercalated between graphene and mica, Tribol. Lett. 66 (2018) 36, https://doi.org/10.1007/s11249-018-0984-3.
 [43] J.L. Hutter, J. Bechhoefer, Calibration of atomic-force microscope tips, Rev. Sci.
- [43] J.L. Hutter, J. Bechhoefer, Calibration of atomic-force microscope tips, Rev. Sci. Instrum. 64 (1993) 1868–1873, https://doi.org/10.1063/1.1143970.
- [44] B.C. Tran Khac, K. Chung, Quantitative assessment of contact and non-contact lateral force calibration methods for atomic force microscopy, Ultramicroscopy 161 (2016) 41–50, https://doi.org/10.1016/j.ultramic.2015.10.028.
- [45] B. Tran Khac, F.W. DelRio, K. Chung, Interfacial strength and surface damage characteristics of atomically thin h-BN, MoS2, and graphene, ACS Appl. Mater. Interfaces 10 (2018) 9164–9177, https://doi.org/10.1021/acsami.8b00001.
- [46] J. Tersoff, Empirical interatomic potential for silicon with improved elastic properties, Phys. Rev. B 38 (1988) 9902–9905, https://doi.org/10.1103/PhysRevB.38. 9902.
- [47] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, S.B. Sinnott, A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons, J. Phys. Condens. Matter 14 (2002) 783–802.
- [48] Q. Zhang, K. Chan, N. Quirke, Molecular dynamics simulation of water confined in a nanopore of amorphous silica, Mol. Simul. 35 (2009) 1215–1223, https://doi.org/ 10.1080/08927020903116029.
- [49] T. Werder, J.H. Walther, R.L. Jaffe, T. Halicioglu, P. Koumoutsakos, On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes, J. Phys. Chem. B 107 (2003) 1345–1352, https://doi.org/10. 1021/ip0268112.
- [50] R.S. Taylor, L.X. Dang, B.C. Garrett, Molecular dynamics simulations of the liquid/ vapor interface of SPC/E water, J. Phys. Chem. 100 (1996) 11720–11725, https:// doi.org/10.1021/jp960615b.
- [51] H.C. Andersen, Rattle: a "velocity" version of the shake algorithm for molecular dynamics calculations, J. Comput. Phys. 52 (1983) 24–34, https://doi.org/10. 1016/0021-9991(83)90014-1.
- [52] R.J. Sadus, Molecular Simulation of Fluids: Theory, Algorithms, and Object-orientation, Elsevier, 2002.
- [53] L. Xie, P. Brault, A. Thomann, L. Bedra, Molecular dynamic simulation of binary ZrxCu100 – x metallic glass thin film growth, Appl. Surf. Sci. 274 (2013) 164–170, https://doi.org/10.1016/j.apsusc.2013.03.004.
- [54] M. Neek-Amal, Reza Asgari, M.R. Rahimi Tabar, The formation of atomic nanoclusters on graphene sheets, Nanotechnology 20 (2009) 135602.
- [55] R. Overney, E. Meyer, Tribological investigations using friction force microscopy, MRS Bull. 18 (1993) 26–34, https://doi.org/10.1557/S0883769400047096.
- [56] S. Grafström, J. Ackermann, T. Hagen, R. Neumann, O. Probst, Analysis of lateral force effects on the topography in scanning force microscopy, J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom. 12 (1994) 1559–1564, https://doi.org/10.1116/1.587286.
- [57] S. Sundararajan, B. Bhushan, Topography-induced contributions to friction forces

measured using an atomic force/friction force microscope, J. Appl. Phys. 88 (2000) 4825–4831, https://doi.org/10.1063/1.1310187.

- [58] H. Hölscher, D. Ebeling, U.D. Schwarz, Friction at atomic-scale surface steps: experiment and theory, Phys. Rev. Lett. 101 (2008) 246105, https://doi.org/10. 1103/PhysRevLett.101.246105.
- [59] Y. Qi, J. Liu, J. Zhang, Y. Dong, Q. Li, Wear resistance limited by step edge failure: the rise and fall of graphene as an atomically thin lubricating material, ACS Appl. Mater. Interfaces 9 (2017) 1099–1106, https://doi.org/10.1021/acsami.6b12916.
- [60] J. Wu, B. Wang, Y. Wei, R. Yang, M. Dresselhaus, Mechanics and mechanically tunable band gap in single-layer hexagonal boron-nitride, Mater. Res. Lett. 1 (2013) 200–206, https://doi.org/10.1080/21663831.2013.824516.
- [61] J. Jiang, Z. Qi, H.S. Park, T. Rabczuk, Elastic bending modulus of single-layer molybdenum disulfide (MoS2): finite thickness effect, Nanotechnology 24 (2013) 435705.
- [62] Q. Lu, M. Arroyo, R. Huang, Elastic bending modulus of monolayer graphene, J. Phys. D 42 (2009) 102002.
- [63] P. Li, Z. You, T. Cui, Molybdenum disulfide dc contact MEMS shunt switch, J. Micromech. Microeng. 23 (2013) 045026.
- [64] D. Maugis, Adhesion of spheres: the JKR-DMT transition using a dugdale model, J. Colloid Interface Sci. 150 (1992) 243–269, https://doi.org/10.1016/0021-9797(92)90285-T.
- [65] R.W. Carpick, D.F. Ogletree, M. Salmeron, A general equation for fitting contact area and friction vs load measurements, J. Colloid Interface Sci. 211 (1999) 395–400, https://doi.org/10.1006/jcis.1998.6027.
- [66] R.W. Carpick, M. Salmeron, Scratching the surface: fundamental investigations of tribology with atomic force microscopy, Chem. Rev. 97 (1997) 1163–1194, https:// doi.org/10.1021/cr960068q.
- [67] U.D. Schwarz, O. Zwörner, P. Köster, R. Wiesendanger, Quantitative analysis of the frictional properties of solid materials at low loads. I. Carbon compounds, Phys. Rev. B 56 (1997) 6987–6996, https://doi.org/10.1103/PhysRevB.56.6987.
- [68] U.D. Schwarz, A generalized analytical model for the elastic deformation of an adhesive contact between a sphere and a flat surface, J. Colloid Interface Sci. 261 (2003) 99–106, https://doi.org/10.1016/S0021-9797(03)00049-3.
- [69] M. Mohr, A. Caron, P. Herbeck-Engel, R. Bennewitz, P. Gluche, K. Brühne, H. Fecht, Young's modulus, fracture strength, and Poisson's ratio of nanocrystalline diamond films, J. Appl. Phys. 116 (2014) 124308, https://doi.org/10.1063/1.4896729.
- [70] T. Onodera, Y. Morita, R. Nagumo, R. Miura, A. Suzuki, H. Tsuboi, N. Hatakeyama, A. Endou, H. Takaba, F. Dassenoy, C. Minfray, L. Joly-Pottuz, M. Kubo, J. Martin, A. Miyamoto, A computational chemistry study on friction of h-MoS2. Part II. Friction anisotropy, J. Phys. Chem. B 114 (2010) 15832–15838, https://doi.org/10. 1021/jp1064775.
- [71] I.L. Singer, R.N. Bolster, J. Wegand, S. Fayeulle, B.C. Stupp, Hertzian stress contribution to low friction behavior of thin MoS2 coatings, Appl. Phys. Lett. 57 (1990) 995–997, https://doi.org/10.1063/1.104276.
- [72] C. Langlade, S. Fayeulle, R. Olier, New insights into adhesion and lubricating

properties of graphite-based transfer films, Wear. 172 (1994) 85–92, https://doi. org/10.1016/0043-1648(94)90303-4.

- [73] E. Riedo, E. Gnecco, R. Bennewitz, E. Meyer, H. Brune, Interaction potential and hopping dynamics governing sliding friction, Phys. Rev. Lett. 91 (2003) 084502, , https://doi.org/10.1103/PhysRevLett.91.084502.
- [74] J. Chen, I. Ratera, J.Y. Park, M. Salmeron, Velocity dependence of friction and hydrogen bonding effects, Phys. Rev. Lett. 96 (2006) 236102, https://doi.org/10. 1103/PhysRevLett.96.236102.
- [75] E. Gnecco, R. Bennewitz, T. Gyalog, C. Loppacher, M. Bammerlin, E. Meyer, H.-J. Güntherodt, Velocity dependence of atomic friction, Phys. Rev. Lett. 84 (2000) 1172–1175, https://doi.org/10.1103/PhysRevLett.84.1172.
- [76] Q. Li, Y. Dong, D. Perez, A. Martini, R.W. Carpick, Speed dependence of atomic stick-slip friction in optimally matched experiments and molecular dynamics simulations, Phys. Rev. Lett. 106 (2011) 126101, https://doi.org/10.1103/ PhysRevLett.106.126101.
- [77] X. Liu, Z. Ye, Y. Dong, P. Egberts, R.W. Carpick, A. Martini, Dynamics of atomic stick-slip friction examined with atomic force microscopy and atomistic simulations at overlapping speeds, Phys. Rev. Lett. 114 (2015) 146102, https://doi.org/10. 1103/PhysRevLett.114.146102.
- [78] L. Jansen, H. Hölscher, H. Fuchs, A. Schirmeisen, Temperature dependence of atomic-scale stick-slip friction, Phys. Rev. Lett. 104 (2010) 256101, https://doi. org/10.1103/PhysRevLett.104.256101.
- [79] A. Socoliuc, R. Bennewitz, E. Gnecco, E. Meyer, Transition from stick-slip to continuous sliding in atomic friction: entering a new regime of ultralow friction, Phys. Rev. Lett. 92 (2004) 134301, https://doi.org/10.1103/PhysRevLett.92.134301.
- [80] E. Riedo, F. Lévy, H. Brune, Kinetics of capillary condensation in nanoscopic sliding friction, Phys. Rev. Lett. 88 (2002) 185505, https://doi.org/10.1103/PhysRevLett. 88.185505.
- [81] X. Li, H. Qiu, X. Liu, J. Yin, W. Guo, Wettability of supported monolayer hexagonal boron nitride in air, Adv. Funct. Mater. 27 (2017), https://doi.org/10.1002/adfm. 201603181 (1603181-n/a).
- [82] A.P.S. Gaur, S. Sahoo, M. Ahmadi, S.P. Dash, M.J.-F. Guinel, R.S. Katiyar, Surface energy engineering for tunable wettability through controlled synthesis of MoS2, Nano Lett. 14 (2014) 4314–4321, https://doi.org/10.1021/nl501106v.
- [83] R. Raj, S.C. Maroo, E.N. Wang, Wettability of graphene, Nano Lett. 13 (2013) 1509–1515, https://doi.org/10.1021/nl304647t.
- [84] J. Song, Q. Li, X. Wang, J. Li, S. Zhang, J. Kjems, F. Besenbacher, M. Dong, Evidence of Stranski-Krastanov growth at the initial stage of atmospheric water condensation, Nat. Commun. 5 (2014) 4837.
- [85] D.B. Asay, S.H. Kim, Evolution of the adsorbed water layer structure on silicon oxide at room temperature, J. Phys. Chem. B 109 (2005) 16760–16763, https://doi. org/10.1021/jp0530420.
- [86] I.-H. Sung, D.-E. Kim, Molecular dynamics simulation study of the nano-wear characteristics of alkanethiol self-assembled monolayers, Appl. Phys. A 81 (2005) 109–114, https://doi.org/10.1007/s00339-004-3036-9.