# Nanotribology of transition metal dichalcogenide flakes deposited by chemical vapour deposition: the influence of chemical composition and sliding speed on nanoscale friction of monolayers

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#### Abstract

We present nanoscale frictional analysis of three commonly used transition metal dichalcogenide (TMD) monolayers, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub>, deposited by chemical vapour deposition (CVD). The monolayers were characterised by Raman spectroscopy, photoluminescence spectroscopy (PL), and X-Ray spectroscopy (XPS), to determine the composition of the coating and confirm monolayer structure. Nanoscale frictional analysis was performed by atomic force microscopy (AFM). Load-dependent frictional behaviour was measured at different sliding speeds to quantitatively assess friction on each sample. All samples experienced low nanoscale friction, with the lowest friction observed on WSe<sub>2</sub>. The friction was independent of sliding speed within the analysed range. Furthermore, monolayer TMDs significantly increase the operational load range by at least one order of magnitude when compared to SiO<sub>2</sub> substrate.

Keywords: Transition metal dichalcogenides, Atomic force microscopy, Nanotribology, Monolayers, Chemical vapour deposition

# 1 Introduction

The experimental discovery of graphene in 2004 [1] and increased fabrication capabilities in the subsequent years [2, 3] have led to an increase in the applications and research interest related to atomically thin 2D nanomaterials, including transition metal dichalcogenides (TMDs) and hexagonal boron nitride, as well as more complex structures such as carbon nanotubes [4]. Besides their more conventional applications in nano-electronics, photonics and sensing [5–7], 2D nanomaterials have also emerged as a promising candidate for modifying friction on the nanoscale [8]. In particular, the undesirable properties of Si-Si contacts present an operational challenge in the performance of micro/nano-electro mechanical systems (MEMS/NEMS) [9– 12]. Coating the contacting surfaces of these systems with 2D materials can provide a solution due to their favourable adhesion and frictional properties [13]. Understanding the behaviour of such materials within the small-scale contacts, namely the effects of friction and adhesion on their performance and wear, will help with further development of related materials and with the design of new components and systems incorporating them.

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Material	Atmosphere	$ ilde{\mu}^{-1}$	$ au$ $^2$	Ref.
		$({ m GPa}^{1/3})$	(MPa)	
Amorphous carbon	Air	$0.450 {\pm} 0.042$	/	[30]
Amorphous carbon	Argon	$0.158{\pm}0.022$		[30]
Diamond	Air	$0.158{\pm}0.061$		[30]
Diamond	Argon	$0.263 {\pm} 0.060$		[30]
C60	Argon	$0.67{\pm}0.22$	/	[30]
HOPG	Argon	$0.0012{\pm}0.0009$		[30]
$\operatorname{GeS}$	Air	$0.50{\pm}0.21$		[31]
Mica	Air	$0.14{\pm}0.05$		[31]
Mica	Argon	$0.16 {\pm} 0.04$		[31]
W-S-C coating	Air	/	36 - 91.2	28
W-S-C:Cr coating	Air	/	71 - 99.3	[27]

 Table 1: Nano-frictional properties of different materials.

<sup>1</sup> Effective coefficient of friction for point-like contact

<sup>2</sup> Contact shear strength

Group 6 transition metal dichalcogenides (e.g.,  $MoS_2$ ,  $WS_2$ ,  $MoSe_2$ ,  $WSe_2$  ...) are not new materials in the field of tribology. The patents involving the use of  $MoS_2$  in technical applications date as far back as the late-1920s [14].  $MoS_2$  and  $WS_2$  have been widely applied and studied as thin coatings for space applications since 1960s [15, 16] and extensively investigated throughout 1970s and 1980s [17, 18]. However, it was not until recently [19] that they have started receiving increasing interest as a material for reducing friction on the nanoscale. The low friction of bulk and multi-layered TMD systems is attributed to their lamellar structure, where weak van der Waals forces between the layers provide low shear resistance [20, 21]. On the other hand, low friction between a single monolayer and a second body is a result of surface inertness [22].

Atomic force microscopy (AFM) is a powerful tool for probing surface properties, such as adhesion and friction. Due to a small tip size, it can be used to mimic a single nanoscale asperity contact [23], therefore offering a wide array of nanotribological investigations. AFM has been previously successfully employed to study nano- and atomic- scale tribological properties of several different 2D systems: graphite [24], graphene [19, 25], exfoliated TMDs [19, 26], sputtered TMDs [27, 28] or h-BN [19]. However, most of the above studies only focused on a specific normal force and solely observed the trends within the same sample, such as the influence of the number of layers on friction [19, 26], sample orientation [24], or the effect of substrate morphology [29].

In the framework of this work, we are interested in using AFM to study how the elemental structure of the TMD monolayer influences nanoscale friction between the bare silicon tip and the TMD surface. Due to different tools, methods, equipment, and sample preparation being used in various studies, a direct quantitative comparison between the frictional response of TMD materials from literature is almost impossible. To quantitatively compare the data of different TMD samples, we deposited WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub> monolayer flakes by an almost identical CVD procedure, and performed the analysis using the same setup (e.g., using the same probe, performing the measurements in a single session), thus minimising the external effects on the measurement. We present quantitative values of load-dependent friction behaviour on three major TMD monolayers (MoSe<sub>2</sub>, WS<sub>2</sub> and WSe<sub>2</sub>), according to Hertz-plus-offset model [30], which has been previously successfully applied to study nanoscale frictional properties and contact shear strength of many different materials (see Table 1). We used bare silicon tips, which offer a good depiction of a nanoscale tribo-system and accurately represent a contact in MEMS [12]. Furthermore, we examine the influence of sliding speed on nanoscale friction and compare how wear resistance and maximum applicable load differ between the TMD sample and the bare SiO<sub>2</sub> substrate.

Material	Precursors		Temperature for precursors		Gas inlet	Note	
			$T_1(^{\circ}C)$	$T_2(^{\circ}C)$			
$MoSe_2$	MoO <sub>3</sub>	Se	750	300	$ m H_2/Ar$		
$WS_2$	$WO_3$	$\mathbf{S}$	900	200	Ar	NaCl used	
$WSe_2$	$WO_3$	$\mathbf{Se}$	900	300	$ m H_2/Ar$		

 Table 2: CVD deposition parameters.

## 2 Materials and methods

### 2.1 Synthesis of TMDs

The transition metal dichalcogenide monolayer samples (WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>) were deposited by chemical vapour deposition (CVD) on 300 nm SiO<sub>2</sub>/Si substrate. The reaction was carried out in a 3 cm diameter quartz tube under atmospheric pressure. The substrates were loaded on a boat containing MoO<sub>3</sub> (or WO<sub>3</sub>) (Alfa Aescar, 99.9995% purity) and placed in the tube centre. NaCl was added during the deposition of WS<sub>2</sub>, to lower the high melting point of WO<sub>3</sub> and aid the vaporisation. Afterwards, another boat with sulphur (or selenium) (Alfa Aescar, 99.9995% purity) was placed at the upstream. After a 10 minute purge with 300 sccm Ar (or H<sub>2</sub>/Ar) (BOC, 99.999% purity), the flow rate was reduced to 30 sccm, and the furnace was programmed to heat the substrates (T<sub>1</sub> in Table 2). Concurrently, sulphur (or selenium) was heated (T<sub>2</sub> in Table 2), allowing its vapour to be transported to the substrate. The furnace was switched off after 15 minutes of deposition and naturally cooled-down.

#### 2.2 Characterisation of synthesised TMDs

Atomic force microscopy (AFM, Agilent Technologies, USA) was used to measure the surface morphology and flake thickness. The thickness of the flakes was measured in non-contact AFM mode. Raman spectroscopy (InVia Raman Spectrometer, 532 nm laser) was utilised to characterise the vibrational modes as well as photoluminescence (PL) spectra, and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Theta Probe XPS System MC03, Al K $\alpha$  source) was used to analyse the elemental composition of the flakes.

#### 2.3 Friction and nanoscale wear measurement by AFM

Surface friction maps and topography were collected simultaneously by AFM (Agilent 5500, Agilent Technologies, USA) in contact mode. Frictional maps were used to examine the qualitative frictional contrast between the TMD sample and the substrate. We used a PPP-LFMR (Nanosensors, USA) probe at low contact loads and 1 Hz scan rate.

Load dependent frictional behaviour was measured using the same setup. A single PPP-LFMR probe was used to perform all the measurements, with the purpose of reducing measurement error due to discrepancies in the probe shape, calibration factors, or probe mounting. The normal spring constant was determined in-situ using a built-in thermal noise method [32] (k = 0.109 N/m). Lateral forces were calibrated according to the wedge calibration method [33] on commercial TGF11 (µMasch, Bulgaria) gratings ( $\alpha = 278$  nN/V).

Measurements with incremental increasing or decreasing normal load were performed at three different sliding speeds (0.5, 1.0 and 1.5  $\mu$ m/s) over 0.5 x 0.5  $\mu$ m area. A total of 10 different loads were used, including negative loads to study the behaviour between the tip and the sample at very low loads (see Table 3). The value of minimum load was determined empirically on each sample, as the lowest load at which the tip did not lose contact with the surface during continuous sliding. The value of applied negative load had to be lower than the force of adhesion to ensure that the tip does not snap out of contact due to local

 Table 3: LFM experimental parameters.

Sample	$F_{min}$ (nN)	$F_{max}$ (nN)	$F_{pull-off}$ (nN)
$WS_2$	-0.6Fpull-off	30	7.5
$MoSe_2$	-0.7Fpull-off	30	11.4
$WSe_2$	-0.7Fpull-off	30	7.5

differences in adhesion, contact area, or surface roughness. A custom script was employed to automatically control contact loads and sliding speeds during the experiments.

Nanoscale wear was evaluated in terms of surface damage and wear caused to the tip. We used stiffer probes (PPP-NCH, k = 51 N/m), which allowed us to reach much higher contact pressure required to induce any changes on the surface. The loads up to 10 µN were used. As a reference, the measurements on the TMD flakes were compared to sliding on SiO<sub>2</sub>.

## 3 Results

#### 3.1 Sample characterisation

**WS<sub>2</sub>:** The samples were characterised by Raman spectroscopy using a 532 nm laser. As displayed in Figure 1a, the 2LA (353.1 cm<sup>-1</sup>) and  $A_{1g}$  (420.1 cm<sup>-1</sup>) peaks are indicative for a monolayer [34, 35]. In addition, PL spectrum in Figure 1b shows an emission peak at 620.2 nm, further confirming monolayer WS<sub>2</sub> structure.

The XPS spectra of monolayer WS<sub>2</sub> flakes in Figure 1c and d display the W 4f peaks at 34.7 and 32.5 eV, which are assigned to the  $4f_{5/2}$  and  $4f_{7/2}$  orbitals of WS<sub>2</sub>, respectively [36, 37]. The W 5p core level at 37.4 eV suggests the existence of W<sup>6+</sup>, likely residual WO<sub>3</sub> on the as-deposited sample [38]. 163.5 and 162.3 eV peaks belong to the S doublets:  $2p_{1/2}$  and  $2p_{3/2}$  [36]. All the results are indicative of WS<sub>2</sub> crystal with the atomic ratio between W and S of ~1:2.

**MoSe<sub>2</sub>:** The lateral sizes of the CVD deposited MoSe<sub>2</sub> nanoflakes were approximately 10-30 µm. Raman peaks at 238.3 cm<sup>-1</sup> and 285.2 cm<sup>-1</sup> (Figure 2a) were related to  $A_{1g}$  and  $E_{2g}$  modes, respectively [39, 40]. Additionally, we observed an unknown peak at 250.4 cm<sup>-1</sup>. This peak can be often seen in the literature (see [40], [41] and [42]), but the authors did not comment on it. The 794.1 nm peak in the PL spectrum (Figure 2b) belongs to single-layer MoSe<sub>2</sub> [43, 44].

As evident from the XPS spectra in Figure 2c and d, the 232 and 228.8 eV peaks correspond to the Mo  $3d_{3/2}$  and  $3d_{5/2}$  orbitals, respectively; the Se 3d peaks at 54.9 and 54 eV originate from the  $3d_{3/2}$  and  $3d_{5/2}$  doublets [45, 46]. An atomic ratio of 1:2.05 is extracted for Mo and Se under this circumstance. Note that Raman spectroscopy was performed on the same sample as used later in AFM analysis, while PL and XPS spectra were obtained on a separate monolayer MoSe<sub>2</sub>.

**WSe<sub>2</sub>:** The lateral size of chemical vapour deposited triangular WSe<sub>2</sub> nanofilms was 5-20 µm. Two Raman peaks at 249.2 and 258.9 cm<sup>-1</sup> belong to the  $E_{2g}$  and  $A_{1g}$  modes of WSe<sub>2</sub>, respectively. As the van der Waals force can induce the interactions between neighbouring layers, a peak at ~308 cm<sup>-1</sup> can be detected for multi-layered WSe<sub>2</sub>. Thus, the absence of this specific peak has been used to confirm the singlelayer nature of WSe<sub>2</sub> instead of the frequency difference between  $E_{2g}$  and  $A_{1g}$  modes [47, 48]. Evidently, there is no  $B_{2g}^1$  peak at ~308 cm<sup>-1</sup> as demonstrated by the inset of Figure 3a, so we can conclude that the as-grown WSe<sub>2</sub> consists of a single layer. Additionally, the emission peak at 752.5 nm also indicates the single-layer nature of the WSe<sub>2</sub> sample (3b) [48].

As for the XPS spectra in Figure 3c and d, the peaks at 32.5 and 34.7 eV are the W  $4f_{7/2}$  and W  $4f_{5/2}$  doublets; the weak peak at 37.4 eV may result from the WO<sub>3</sub> residues on the sample surface; the 54.8 and 55.7 eV peaks are ascribed to the Se  $3d_{5/2}$  and Se  $3d_{3/2}$  orbits; the atomic ratio of W and Se was calculated to be 1:1.98, which is close to the stoichiometric 1:2 [49].

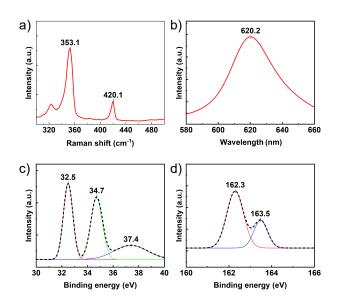


Figure 1: Characterisation of WS<sub>2</sub> nanoflakes synthesised on  $SiO_2/Si$  substrate by the CVD method. (a) Raman spectrum and (b) PL spectrum with 532 nm laser excitation. XPS spectra of (c) W 4f and (d) S 2p orbitals of a monolayer.

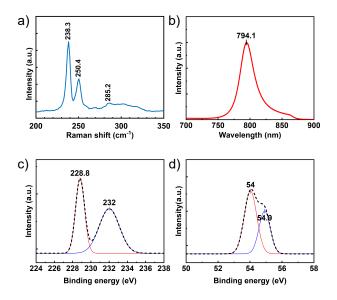


Figure 2: Characterisation of chemical vapour deposited  $MoSe_2$  nanoflakes on  $SiO_2/Si$  substrate. (a) Raman spectrum and (b) PL spectrum with 633 nm laser excitation. XPS spectra of (c) Mo 3d and (d) Se 3d orbitals.

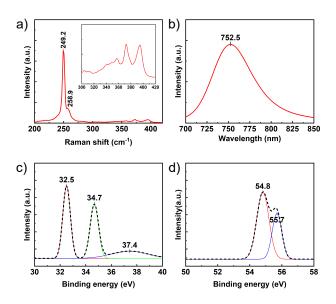


Figure 3: Characterisation of WSe<sub>2</sub> nanoflakes synthesised on  $SiO_2/Si$  substrate by CVD method. (a) Raman spectrum and (b) PL spectrum with 532 nm laser excitation. XPS spectra of (c) W 4f and (d) Se 3d orbitals of a monolayer.

#### 3.2 Nanotribology: Friction maps and load-dependent frictional behaviour

The topography of the chosen  $WS_2$ ,  $MoSe_2$  and  $WSe_2$  flakes for nanotribological analysis, together with their corresponding friction maps and load-dependent frictional response is shown in Figure 4. Note that the flakes presented in this section are not the exact same monolayers used for characterisation in the previous section, due to their small size and different methods used to characterise the samples. However, the flakes used for frictional experiments and for structural characterisation were taken from the same sample (i.e., from the same CVD batch), unless otherwise noted.

The surface topography of the specific flakes was obtained just before performing each friction experiment. As shown in Figure 4a, WS<sub>2</sub> and WSe<sub>2</sub> formed triangular crystals, indicating well-controlled crystal growth, while MoSe<sub>2</sub> resulted in 'snowflake-like' flake shape. Nevertheless, the scan on MoSe<sub>2</sub> displays triangular grain boundaries within the flake, thus indicating that the single grains are, in fact, triangular. The 'snowflake-like' shape is a consequence of recrystallisation due to longer deposition time [42]. We have checked the analysed flakes using Raman spectroscopy (see Figure 2a), which confirmed the monolayer structure. Furthermore, friction measurements on MoSe<sub>2</sub> were comparable with the other two (in absolute value and load-dependent behaviour), further ensuring the quality and crystallinity of the surface. For example, poor crystallinity or low crystal quality should result in increased friction due to the presence of dangling bonds.

The measured values of thickness vary substantially between the samples. WS<sub>2</sub> and MoSe<sub>2</sub> flakes show no height difference compared to the substrate, while the measured thickness of WSe<sub>2</sub> was  $1.10 \pm 0.12$  nm. The same structure was observed on additional WS<sub>2</sub>, WSe<sub>2</sub> and MoSe<sub>2</sub> flakes (Supporting Information, Figure S1), showing that the structure is comparable between the flakes on the same sample. We must note that because these measurements were performed in contact mode, the measured thickness can differ from the actual value. The discrepancy can be attributed to the cross-talk between the lateral and normal response of the probe. Due to the low spring constant of the probe, the observed frictional contrast between the sample and the substrate can mask or amplify small height differences. Cross-talk is a common artifact experienced in contact mode and is further discussed in literature [33, 50]. To avoid the effect of cross-talk and obtain

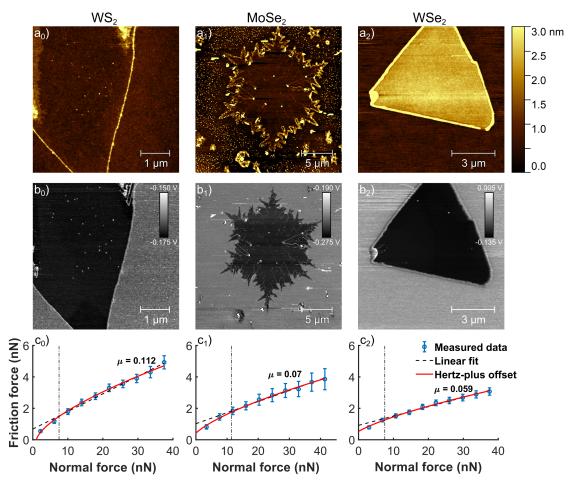


Figure 4: Surface characterisation of the analysed monolayer  $WS_2$ ,  $MoSe_2$  and  $WSe_2$  flakes. Topography  $(a_0-a_2)$ , corresponding friction maps  $(b_0-b_2)$  and load-dependent friction  $(c_0-c_2)$ . Normal force represents the combined force of adhesion and applied load. Zero applied load is marked by a dotted dashed line.

meaningful values of the thickness, the flakes were also measured in tapping mode. The obtained thickness values of  $\sim 0.75$  nm,  $\sim 0.78$  nm and  $\sim 0.76$  nm, for WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub>, respectively, agree well with the reported values for monolayer flakes [48, 51–55].

Friction maps (Figure 4b) show high friction contrast between the flakes and the SiO<sub>2</sub> substrate. All the analysed TMD flakes experienced much lower friction than the substrate, indicating superior frictional characteristics. This indicates that coating a single surface in the MEMS/NEMS contacts with a TMD monolayer can offer a great performance improvement. Load dependent frictional behaviour of the three samples is shown in Figure 4c. Only the results obtained at 1  $\mu$ m/s are shown here, despite performing the measurements at various sliding speeds; the speed dependence is discussed later. No stick-slip motion was observed on any of the samples. The measurements were consistent for a total of three different WS<sub>2</sub> and WSe<sub>2</sub> flakes and two separate locations on the MoSe<sub>2</sub> flake. No significant difference was observed between the loading and unloading curves on any of the samples, which can be expected for an elastic contact, where a layer has good adhesion to the substrate (Supporting Information, Figure S2). Thus, only the data with increasing normal force are shown in Figure 4c for clarity.

We observed only minor fluctuation of friction with sliding speed across the analysed range (Supporting Information, Figure S3), which can be attributed to measurement uncertainty and internal equipment error. The only obvious difference in the response is on the  $MoSe_2$  sample at increasing load (Supporting Information, Figure S3b) at 0.5 Hz (0.5  $\mu$ m/s). However, it is the only measurement that deviates from the rest, and it was the first measurement that was taken on that sample. Therefore, we can conclude that the difference in response was a consequence of surface or tip contamination. The amount of contamination was very low, and it was completely removed after the initial scan, which is evident from the other measurements on the same sample. Even the measurement with decreasing load (Supporting Information, Figure S3e) at 0.5 Hz, performed right after in the same area, did not show any deviation between the sliding speeds anymore. Besides that, all three samples exhibit the same behaviour, indicating that nanoscale friction of TMDs is independent of sliding speed within the analysed range.

#### 3.3 Nanotribology: Wear resistance

The experiments above were performed at relatively low loads to prevent possible damage to the tip or to the substrate. Following that, we increased the maximum load up to 10  $\mu$ N to analyse the WS<sub>2</sub> monolayers for potential rupture and tip wear. A pre-worn probe was used to prevent the tip shattering solely due to high pressure, which could give inconsistent results. In fact, a measurement with a new sharp probe resulted in the probe shattering at 6  $\mu$ N on WS<sub>2</sub> (Supporting Information, Figure S4). Therefore, we only present the results obtained by the pre-worn probe here. Additionally, we performed the reference scans on the SiO<sub>2</sub> substrate.

We have not observed any sample wear on either  $SiO_2$  or  $WS_2$ . However, high friction between the tip and the  $SiO_2$  surface caused the tip to start wearing off above 1000 nN, which resulted in the transfer of material from the tip to the surface (see the insets in Figure 5a). Probe wear is quantitatively evaluated in Figure 5a; the total volume difference was determined between the surface topography after each wear measurement and the initial topography scan at 0 nN. As expected, the volume differences are negligible on WS<sub>2</sub>, but we see an almost linear increase after 500 nN on the SiO<sub>2</sub>.

The bars in Figure 5a show the distance to failure (e.g. the point at which we could visually notice the changes on the surface) at the loads where tip wear was observed. The total scanned distance at each load was 768  $\mu$ m, indicating that even though we measured noticeable amounts of tip wear at 1000 nN, it only happened towards the end of the experiment. The distance reduced significantly at higher loads; at 1500 nN it reduced down to 40  $\mu$ m whereas at 2000 nN the transfer of the material occurred after only 15  $\mu$ m of sliding. Therefore, the limit of usable loads on SiO<sub>2</sub> is around 1000 nN. On the other hand, sliding on WS<sub>2</sub> did not result in similar behaviour; even near the technical limit of our setup at 10  $\mu$ N, there was no tip wear (Figure 5b). The complete scans on both surfaces after all analysed loads are shown in (Supporting Information, Figure S5).

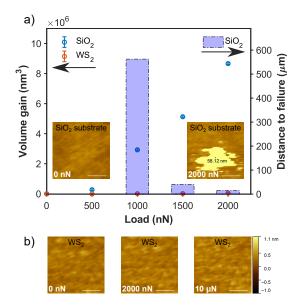


Figure 5: Tip wear on SiO<sub>2</sub> substrate and WS<sub>2</sub> samples. (a) Sample volume gain and distance to failure. The insets show the surface topography after the experiments performed on SiO<sub>2</sub> substrate at 0 nN and 2000 nN. (b) WS<sub>2</sub> monolayer surface topography after the experiments at 0 nN, 2000 nN and 10  $\mu$ N. The height bar applies to all topography scans. The lateral scale bars correspond to 500 nm

### 4 Discussion

The standard approach to frictional analysis is to obtain the slope  $\mu$  of the increasing friction with applied load L, similar to linear Amontons' law on the macro scale [56]. Obviously, at the nanoscale the friction does not vanish at zero load due to the effects of adhesion; therefore, the friction force at zero load  $F_0$  needs to be considered. Adhesion is initially included in total normal force  $F_N = L + F_{adh}$  [30], leading to a formulation of Amontons' law with included effects of adhesion:

$$F_f = \mu F_N + F_0. \tag{1}$$

The formulation is straight-forward and readily comparable with the approach to understanding friction on the macro-scale. However, it can only serve as an initial assessment of the analysed measurements and can only be applied in cases when the observed behaviour is linear. Its major drawbacks include general inapplicability at low loads and its dependence on the contact geometry. Furthermore, it is only applicable to compare the measurements obtained with the same probe.

By observing the friction graphs in Figure 4c, we see the linear trend from ~10 nN onward, whereas at lower loads, the frictional response deviates from linear behaviour. Note that below 10 nN we are already entering the adhesive regime, where the surfaces are kept in contact solely by adhesion. By assuming the onset of linear behaviour at higher loads, we have only considered the data above 10 nN normal load when fitting the linear model. The resulting values of  $\mu$  and  $F_0$  are collected in Table 4.

Because adhesion plays a major role in contact properties of nanoscale contacts, a more suitable approach is to include adhesive contact models from solid mechanics [57]. Several models have been suggested to study the contact interactions in the AFM contact [30, 58, 59], proposing either JKR [60], DMT [61], or transition regime to model the adhesive contact. The benefit of these models is that they incorporate contact geometry (usually approximated by sphere-on-flat contact) and adhesion and thus allow for a much more accurate comparison between the measurements performed using different probes and systems.

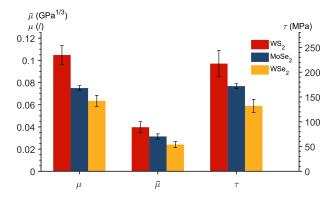


Figure 6: Averaged frictional and contact parameters.

Table 4: Contact properties of TMD samples measured by LFM.

Sample	$\mu~(/)$	$F_0$ (nN)	$ ilde{\mu}~({ m GPa}^{1/3})$	$\tau$ (MPa)	$F_{off}$ (nN)	$F_{adh}(nN)$	$R^2 \; (/)$
$WS_2$	0.112	0.7	$0.0413 \pm 0.0014$	226.1	1.1	7.5	0.9947
$MoSe_2$	0.073	0.8	$0.0308 \pm 0.0015$	168.6	0.3	11.4	0.9910
$WSe_2$	0.059	0.9	$0.0255 \pm 0.0009$	139.6	-2.9	7.5	0.9955

One of such models, which is commonly [27, 28] used to fit lateral force data is Hertz-plus-offset model for a sphere on flat contact [30]:

$$F_f = \tilde{\mu} R^{2/3} (F_N - F_{off})^{2/3}.$$
(2)

The model introduces the effective coefficient of friction for point-like contact  $\tilde{\mu} = \pi \tau / K^{2/3}$ , where  $\tau$  is contact shear strength and K is the effective contact elastic modulus.  $\tilde{\mu}$  is a more valid coefficient for comparison of the frictional behaviour of materials on a small scale than the conventional coefficient of friction because it is independent of the contact geometry. The force of adhesion is initially approximated by measuring pull-off force ( $F_{adh} \approx F_{pull-off}$ , which leads to  $F_N = L + F_{pull-off}$ ). However, due to the uncertainty in the determination of pull-off force, an offset ( $F_{off} \ll F_{pull-off}$ ) is introduced, which corrects for any discrepancy in adhesion measurement. R is the radius of the probe, which was determined by scanning a standard calibration grating TGT1 (ND-MDT, Russia), and calculated using the envelope method [62]. The obtained radius was 33.4 nm. As the manufacturer specified radius for a new probe is less than 10 nm, this indicates some wear occurred throughout the measurements. However, because no visible signs of wear were observed on the scans during friction measurements, we can assume that the majority of the probe wear occurred during the initial contact of the tip with the sample and throughout the initial topography measurements. As reported by J. Liu et al. [63] and D.S. Grierson et al. [64], the sharp apex of Si tip could shatter almost immediately after contact with the surface. A slight increase of the probe radius after the measurements is therefore expected.

The results of the fit are summarised in Table 4. Hertz-plus-offset is equivalent to DMT contact model, which is consistent with many AFM measurements, when the surfaces are atomically flat, sufficiently hard, and can be approximated by a sphere on flat contact [30]. We observe a very good fit to the model ( $R^2 >$ 0.99,  $F_{off} < F_{adh}$ ) for all three samples, which further confirms wear-less friction and fully elastic contact and thus shows that the friction is proportional to the contact area.

The averaged frictional parameters of the measurements on all three  $WS_2$  and  $WSe_2$  flakes and on both regions on the  $MoSe_2$  flake, are shown in Figure 6. All three samples exhibit low friction, but there are observable differences between the samples. Both selenium containing samples showed lower friction than the sulphur-based monolayer (WS<sub>2</sub>). This indicates that the chalcogenide atom has a major influence on the friction of TMD monolayers, although the influence of the metal atom is not negligible. Thus, we can conclude that friction of clean layers is mainly driven by the interatomic forces between the contacting bodies, with structural properties of the layers taking a secondary role.

Since there were no large differences in measured pull-off forces among the three TMD samples, we can conclude that the difference in friction between different samples was not related to difference in adhesion. In fact, the same pull-off force was measured on samples with the highest and the lowest measured friction.

Comparing our measured values with the values of  $\tilde{\mu}$  from the literature, we see that the values obtained on TMDs are substantially lower than the majority reported in Table 1, except for highly oriented pyrolytic graphite (HOPG) measured in argon atmosphere. Due to the high quality of HOPG crystals, they contain fewer surface defects compared to CVD grown monolayers, which are more prone to defects due to shorter time scales used for deposition [65]. Furthermore, our measurements were performed in air; therefore, we can expect some degree of organics and water adsorbed on the surface [66]. Both effects can contribute significantly to the final frictional response. Therefore, eliminating them on TMD surfaces could further decrease friction and make them potentially more comparable with HOPG. Nevertheless, the quantitative friction observed on all the TMD samples was very low.

### 5 Conclusions

We have shown that all the measured TMD monolayer samples exhibited low nanoscale friction, therefore indicating good tribological behaviour. The exact elemental structure of the clean samples had some effect on the frictional response; however, all three monolayers showed similar behaviour.  $WS_2$  monolayer experienced the highest values of the lateral force and  $WSe_2$  experienced the lowest. The results indicate that selenides would result in lower friction than sulphides. The samples also did not show any dependence on sliding speed. Furthermore, we have shown that the TMD monolayers can significantly reduce and delay the onset of wear in high load applications.

We can conclude that precisely selecting a single TMD for a specific sliding application is less important than ensuring that the deposited monolayer crystal would be of high quality, contain a low number of defects and be free of contamination.

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