A molecular dynamics study on the tribological behavior of molybdenum disulfide with grain boundary defects during scratching processes

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Abstract: The effect of grain boundary (GB) defects on the tribological properties of MoS₂ has been investigated by molecular dynamics (MD) simulations. The GB defects-containing MoS₂ during scratching process shows a lower critical breaking load than that of indentation process, owing to the combined effect of pushing and interlocking actions between the tip and MoS₂ atoms. The wear resistance of MoS₂ with GB defects is relevant to the misorientation angle due to the accumulation of long Mo–S bonds around the GBs. Weakening the adhesion strength between the MoS₂ and substrate is an efficient way to improve the wear resistance of MoS₂ with low-angle GBs.

Keywords: MoS₂; grain boundary; tribological behavior; molecular dynamics; misorientation angle

1 Introduction

In recent years, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have caused great attentions due to their excellent physical, mechanical and tribology properties [1–5]. As a representative of TMDCs, MoS₂ has a layered hexagonal crystal structure, which consists of one metal Mo layer and two S layers [6]. Due to its strong covalent bonding in molecular layer [7], single-layer MoS₂ (SL-MoS₂) shows extraordinary mechanical properties, such as the high effective in-plane Young's modulus [6, 8] and low bending modulus [9]. The weak van der Waals interactions in the interlayer of MoS₂ make shear more easily, which is the main reason for the low friction of MoS₂ [10–12]. Base on the excellent mechanical and tribological properties, MoS₂ is commonly used

as solid lubricant [13] and wear resistant coating [14], and is utilized as an additive in lubricating oils [13]. Due to the monolayer thickness, SL-MoS₂ and thin film MoS₂ present a number of potential applications to serve as lubricant materials in microelectromechanical systems (MEMS) [10, 11]. Under specific conditions, SL-MoS₂ and thin film MoS₂ even show a lower friction than graphene [15, 16]. Moreover, the super-lubricity phenomena are observed in MoS₂–MoS₂ [17] and MoS₂–Sb [18] contacts as well.

SL-MoS₂ with high-quality and large-area is required to achieve the application potentials above. However, it is still an enormous challenge to synthesize pristine (without GB defects) SL-MoS₂ with large-area by most advanced technologies, including chemical vapor deposition (CVD) and chemical exfoliation [19, 20]. Chemical exfoliation

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is used for the small flakes of MoS₂. Inevitably, it produces MoS₂ with native crystalline defects [21, 22]. The CVD synthesis is able to product large-area SL-MoS₂, but bicrystals and polycrystalline microstructures exist in the SL-MoS₂ due to the multiple nucleation sites on substrates [23, 24]. When adjacent MoS₂ crystals merge during the growth process, the grain boundaries (GBs) can be formed [20, 25, 26]. The GB defects, as well as point defects, dislocations and edges are classified as the intrinsic structural defects in SL-MoS₂ [27, 28]. The tribological properties of MoS₂ are sensitive to the testing and environment conditions, such as the pre-strain within MoS₂ [29–31], the magnitude and direction of friction velocity [32–34], the number of MoS₂ layers [32] and temperatures [35]. The intrinsic structural defects of MoS₂ have been deemed to be detrimental to its strength [24, 36–38]. Therefore, it is meaningful to investigate the effects of GB defects on the tribological behavior of MoS₂ for its potential tribology applications. It has been observed with AFM that the friction at the GB is obviously higher than that of pristine SL-MoS₂, possibly due to the defects at the GB [39]. In addition, the GBs of polycrystalline MoS₂ could cause a layer-dependent oscillatory friction, on account of the presence and absence of GBs in odd and even numbers of layers [40]. However, the wear mechanisms of the GB structure are not entirely understood. The study on the wear mechanisms of SL-MoS₂ with GB defects is urgently needed to provide guidelines for enhancing its tribological performances.

In this work, the effect of the GB defects on the tribological behavior of MoS₂ has been investigated by means of MD simulations. According to previous theoretical and experimental findings, eight specified zigzag-oriented GBs have been generated in different misorientation angles [20, 21, 37, 41]. The atomistic indentation and scratching processes have been simulated in order to calculate the carrying capacity and wear resistance of MoS₂ with different GB types. The results show that GB defects-containing MoS₂ is more easily broken during the scratching process owing to the

combined effect of pushing and interlocking actions between the diamond tip and MoS₂ atoms. MoS₂ with a low misorientation angle GB shows a weaker wear resistance due to the accumulation of the long Mo–S bonds around the GBs. Weakening the adhesion strength between MoS₂ and substrate is an efficient way to mitigate the negative effects of GBs on the wear resistance of MoS₂.

2 Simulation methods

In the atomistic models, a diamond tip is scratching against the SL-MoS₂ with GB defects. The SL-MoS₂ is coated on a deformable metallic Pt substrate, as shown in Fig. 1(a). The tip is cut from a diamond crystal with a (111) orientation, and its diameter is 30 Å. The dimensions of the SL-MoS₂ and the Pt (111) substrate are approximately 194.0 Å × 148.0 Å in the *x* and *y* directions, and 199.8 Å × 153.8 Å × 72.5 Å, respectively. The Pt (111) substrate contains 152,064 platinum atoms. For the SL-MoS₂ (including the MoS₂ with and without GB defects), the total number of Mo and S atoms ranges from 9,896 to 10,395. The SL-MoS₂ was placed above the substrate with an initial distance of 2.8 Å where their interaction energy was minimal. During the relaxation process, the diamond tip was placed 15 Å above the MoS₂ layer to insure there was no interaction between the tip and SL-MoS₂ layer. The Pt atoms which were on the bottom layer were constrained on the substrate to support the model, as shown in Fig. 1(a). The Mo and S atoms at the edge of the SL-MoS₂ were fixed in the *x* and *y* directions, while they can move freely in the *z* direction to prevent translational movement of the SL-MoS₂, as shown in Fig. 1(c). Periodic boundary condition was used along the *x* and *y* directions. The Langevin thermostat was applied to the atoms (circled in light-blue in Fig. 1) which were away from the contact region [42, 43]. This thermostat scheme in this work did not show artificial effects compared with another alternative scheme, as shown in Fig. S1 (in the Electronic Supplementary Material, ESM). It should be noted that the Langevin thermostat was used in an NVE ensemble, so as to

Fig. 1 (a, b) Simulation model of a diamond tip scratching against the GB defects-containing SL-MoS₂ that is coated on the Pt substrate, and (c) schematic of GB's formation process in bicrystal MoS₂.

maintain a constant temperature of 300 K.

During the process of MoS₂ crystal growth, GBs are formed when adjacent MoS₂ crystals merge due to the different orientation angles and sizes of MoS₂ crystals grains [25, 26]. Figure 1(c) shows a schematic of GB's formation process in bicrystal MoS₂. The GBs of MoS₂ crystals are composed of diverse dislocation cores which are dependent on the boundary misorientation angles of crystals. The dislocation cores not only include the conventional pentagon-heptagon (5|7) pairs [21, 41], but also exist in the form of quadrangle-quadrangle (4|4), quadrangle-hexagon (4|6), quadrangle-octagon (4|8) and hexagon-octagon (6|8) pairs [27, 28, 37, 44]. In contrast to graphene with 6-fold symmetry, MoS₂ with 3-fold symmetry has two types of 5|7 dislocation [37, 45]. In a microscopical view, there are two types of dislocation cores of the 5|7 pairs, including the Mo-rich 5|7 type (Mo5|7) and S-rich 5|7 type (S5|7) [37], as shown in Figs. 2(c, d). The zigzag-oriented SL-MoS₂ shows better tribological properties than other orientation [32–34]. In order to deeply study the GB defects' effect on the tribological performances of MoS₂, the GB defects are formed in the

zigzag-oriented bicrystal MoS₂. In terms of the coincidence site lattice (CSL) theory [46], eight specified GBs (consist of Mo5|7 and S5|7 pairs, respectively) were generated in various misorientation angles, as shown in Figs. 2(a, b). For the specified misorientation angle of two adjacent MoS₂ crystals, some periodic coincident points along a line could be found. An initial GB can be obtained by cutting the two MoS₂ crystals along the line [46]. In order to further optimize the GB's structures, the potential energy of the bicrystal MoS₂ has been minimized in the way of the conjugate gradient method. For convenience of representation, the zigzag-oriented GBs which consist of Mo5|7 cores are defined as M-51, M-94, M-132, and M-218, the misorientation angles (θ_{GB}) of which are 5.1°, 9.4°, 13.2°, and 21.8°, respectively, as shown in Fig. 2(a). Correspondingly, the reversed GBs which consist of S5|7 cores are defined as S-51, S-94, S-132, and S-218 corresponding to θ_{GB} = 5.1°, 9.4°, 13.2°, and 21.8°, as shown in Fig. 2(b). The schematic of the reversed GB could be found in Fig. S2 in ESM [44].

The intra-layer interactions within MoS₂ were described by the REBO potential [47,48], which has

Fig. 2 (a, b) Atomic structures of GB defects in bicrystal MoS₂ with different misorientation angles and (c, d) typical dislocation cores (Mo5/7 and S5/7 pairs) captured from GB in bicrystal MoS₂, and they are named in terms of the ring pairs characteristics, respectively.

been developed to simulate the break and recombination behaviors of Mo–S bonds and describe MoS₂'s covalently bonded systems [49]. The EAM potential for Pt system was applied to evaluate the interactions within the Pt substrate. The LJ potentials were used to model the interactions among the tip, SL-MoS₂ and the substrate. For C–Mo and C–S interactions, the LJ parameters of $\sigma_{C-Mo} = 3.01 \text{ \AA}$, $\varepsilon_{C-Mo} = 48.86 \text{ meV}$, $\sigma_{C-S} = 3.42 \text{ \AA}$, and $\varepsilon_{C-S} = 13.12 \text{ meV}$ were used, respectively [30, 50]. For Mo–Pt, S–Pt, and C–Pt interactions, the LJ parameters could be found in Table S1 in ESM [30]. Before indentation process, the whole system was well relaxed for 40 ps at 300 K. For the indentation course, the diamond tip was placed right above the GB of bicrystal MoS₂ and moved vertically to the GBs. For the scratching process, the diamond tip was positioned at an initial distance of 50 Å from the GB along the x direction to avoid the tip affecting the GB during the loading process, and moved laterally at different scratching depths. The total scratching distance of the diamond tip was 80 Å to ensure the diamond tip slides across the GB of bicrystal MoS₂ completely. The scratching depths were controlled by the tip's vertical displacement.

The speed of the diamond tip was set to 10 m/s in the process of indentation and scratch. Simulations have been performed based on the molecular dynamics simulation package LAMMPS. Every simulation has been repeated at least three times along different indentation positions and scratching routes to ensure the reliability of the results, which could be found in Fig. S3 in ESM. The tip atoms usually fall into different contact geometries with different GBs, the critical normal loads show small variations when the tip indents at different positions and scratches along different routes, as shown in Table S2 in ESM. It should be noted that the following results are based on indentation position 1 and scratching route 1 without further mention.

3 Results and discussion

3.1 The indentation and scratching process of MoS₂ with GBs

In order to research the GB defects' effects on the mechanical and tribological properties of MoS₂, the atomistic nano-indentation and nano-scratching

process of the bicrystal MoS₂ with GBs have been investigated. Figure 3(a) shows the schematic of indentation process. The diamond tip was placed right above the GB before indenting. In contrast, the tip was initially positioned away from the GB during scratching process, as shown in Fig. 3(b). According to previous tribological MD simulations on 2D materials, the bond permanent break has been used to characterize the indentation and scratching failure of 2D materials [30, 51–53]. In this work, the critical breaking loads of indentation and scratch were identified by the permanent break of Mo–S bonds, as shown in Fig. 3(c). For the pristine zigzag-oriented SL-MoS₂, the breaking loads of indentation and scratching process are respectively 106.6 and 94.4 nN, which are close to the previous works [30, 50]. Compared with the pristine MoS₂, the critical breaking loads for indentation on M-51 and S-51 models decrease by 19.37% and 27.12%, respectively. During the

indentation process, the critical breaking loads of GB defects-containing SL-MoS₂ increase with the misorientation angle. When the misorientation angle is greater than 20°, the critical breaking loads for indentation and scratching are close to those of pristine MoS₂. More interestingly, the critical breaking loads of all GB defects-containing MoS₂ during the scratching process are lower than those during indentation. It indicates scratching action imposes more extreme working condition than indentation for MoS₂.

To understand the reason of the lower critical breaking load for GB defects-containing MoS₂ during scratching process, MoS₂ structural deformations for indentation and scratching have been investigated. Unlike graphene has only one C atom layer, SL-MoS₂ consists of a Mo atom layer sandwiched by two S layers. Therefore, the deformation mechanism of SL-MoS₂ is more complicated, such as the existence of the out-of-plane

Fig. 3 Schematic diagrams of (a) indenting and (b) scratching processes. (c) Critical breaking loads of pristine MoS₂ and GB defects-containing MoS₂. The values were obtained by averaging the results from the repeated simulations.

compression deformation of SL-MoS₂ [54]. The structural deformations of MoS₂ could be better described with the length of Mo–S bond ($L_{\text{Mo-S}}$). The out-of-plane compressive and in-plane tensile deformation of MoS₂ could be described by the $L_{\text{S-S}}$ (distance between the relative S atoms) and $L_{\text{Mo-Mo}}$ (distance between the adjacent Mo atoms) [30]. The radial distributions of the $L_{\text{Mo-S}}$, $L_{\text{Mo-Mo}}$, and $L_{\text{S-S}}$ have been calculated under the same load, which is the critical breaking load of M-51 model during the scratching process (scratch depth of 5.4 Å), as shown in Figs. 4(a–c). For the indentation course, the structural deformations of MoS₂ exhibit a better symmetry, while the deformations of MoS₂ display an obvious asymmetry during the scratching process, as shown in Figs. 4(a–c). Severe out-of-plane compressive and in-plane tensile deformations are mostly distributed in front of the diamond tip during scratching process. It should be noted that the scratching process exhibits a larger in-plane tensile deformation than indentation process, as shown in Fig. 4(b). To better represent the deformation, the MoS₂ atoms are colored on the basis of the

relative displacements in the x direction, as shown in Figs. 4(d) and 4(e). In the contact area [55], MoS₂ is stretched under indentation owing to the differences of the atom relative displacement, which is accordance with a previous study [7]. For the scratching process, the MoS₂ deforms plastically in the contact area at the same load of indentation. Under the pushing force of diamond tip atoms, the MoS₂ atoms in the contact area move forwards along the x direction, which is contrary to the indentation process. A larger local stretching occurs in front of the tip due to the nonuniform relative displacement of MoS₂ atoms in the contact area.

The combined effect of pushing and interlocking actions during the scratching process also leads to the difference in the critical breaking load between indentation and scratching processes. Figure 5 shows the failure mechanisms during the scratching process which are caused by pushing and interlocking actions. During the course of scratch, the diamond tip atoms are easily interlocked in the MoS₂ lattice due to the abundant hollow positions

Fig. 4 Radial distributions of (a) $L_{\text{Mo-S}}$, (b) $L_{\text{Mo-Mo}}$, and (c) $L_{\text{S-S}}$ for MoS₂ at the load depth of 5.4 Å. (d, e) Relative displacements of MoS₂ atoms in x direction regarding to their initial positions for indentation and scratching processes of M-51 Model at the load depth of 5.4 Å. The edge of the tip was marked by dashed circles.

in MoS₂. The atomistic interlock results in a high friction [42]. When the scratching time (t) is 445 ps, the atom A of the tip is interlocked with the atom 1 and 2 of MoS₂. When $t = 470$ ps, the atom 2 of MoS₂ is pushed away by the atom A. Meanwhile, the atom B is interlocked with the Mo–S bond between the atom 3 and 4. Then the Mo–S bond is broken because the atom B moves forwards. Similarly, when $t = 505$ ps, the atom C is interlocked with the atom 5 and 6. The atom C exerts a lateral force to atom 6, which leads to a bond break between atom 5 and 6, as well as breaks the bond nearby which is indicated by a black dotted circle in Fig. 5. Those interlocking and pushing behaviors iteratively occur during the scratching process, which result in a possibility to break the Mo–S bonds of MoS₂. In contrast, there are less interlocking and pushing actions because of lacking the interfacial sliding movements during indentation process. Similar interlocking and pushing actions also happen in S-51 model as shown in Fig. S4 in ESM. In addition, the effect of misorientation angles on these above interactions has been further discussed, as shown

in Fig. S5 in ESM. For the SL-MoS₂ with the low-angle GB, the GB structure shows a greater deformation after the diamond tip slides over the GB. With the misorientation angle increasing, the deformation degree and the number of broken Mo–S bond reduce due to the increase of the GB dislocation density [56].

3.2 Wear mechanism of MoS₂ with GB defects

Researches show that the pristine SL-MoS₂ which is supported on a substrate can effectively reduce the friction [30, 50]. To investigate the tribological behavior and wear mechanism of MoS₂ with GB defects, the diamond tip has been used to scratch each GB defects-containing SL-MoS₂. The variations of friction with scratching distance were calculated to show the effect of GB defects on friction, which is shown in Fig. 6(a). For the pristine MoS₂, the friction force increases with scratching distance on the early stage of scratching process, and then stays stable. The similar phenomena also can be observed before the tip reaches to GB defects in the GB defects-containing models. Taking M-51

Fig. 5 Schematic of the specific tip atoms and MoS₂ atoms of M-51 Model during the scratching process at the load depth of 5.4 Å. The top S layer is hidden to show the structural changes of MoS₂ clearly. The representative atoms of the tip and MoS₂ were marked by red and blue color, respectively. In order to trace the bond-breaking actions, the interaction force and broken bond were marked by red arrow and black circle, respectively. The interaction force was individually obtained by calculating the interaction between each specific tip atom and specified MoS₂ atoms. For display the interaction in a two-dimensional plane, only x and y components were used to find out the resultant force. The detailed interaction forces between the tip atoms and MoS₂ atoms could be found in Tables S3 and S4 in ESM.

Fig. 6 At a scratching depth of 5.4 Å, the change of friction force and the average number of broken Mo–S bonds during the scratching process of (a) pristine MoS₂ and (b) M-51 model. The average number of broken bonds is averaged with an interval of 1 Å. The top S layer is hidden to show the structural changes of MoS₂ directly. The Mo and S atoms around the MoS₂ pairs are marked by blue color.

model as an example, the friction force increases and becomes unstable when the tip is close to the GB defects, as shown in Fig. 6(b). The coefficient of friction follows the same trend as the friction force as shown in Fig. S6(a) in ESM. Owing to the lamellar structure of 2D materials the wear is hard to be quantified by the continual volume of material removed. Instead, the number of broken bonds can be used to analyze the wear for 2D materials [53]. Figure 6(b) shows the relationship between the average number of broken Mo–S bonds and scratching distance in M-51 model. The number of broken bonds shows a sharp increase when the tip scratches to GB defects, while it is almost zero in pristine MoS₂ model. Therefore, the GB defects could accelerate the local Mo–S bond breaking and rupture initiation of MoS₂, which leads to a reduction on the wear resistance of MoS₂.

The average friction forces around GB defects were calculated to accurately evaluate the GB defects effect on the anti-friction performance of MoS₂. Figure 7(a) shows the relationship between the average friction force and the scratching depth during the scratching process. The scratching processes on the substrate covered with the SL-MoS₂ show an extremely low friction force at a scratching depth below 2 Å, which is accordance with the previous study [50]. The average friction force on the GB defects-containing SL-MoS₂ is

lower than that on the Pt substrate only, when the scratching depth is below 5 Å. It indicates that the MoS₂ with GB defects still can be used as an effective solid lubricant at low load. With the increasing scratching depth, a sudden increase of the average friction force happens in all the lines in the Fig. 7(a). It corresponds to a number of Mo–S bond breaks, and then leads to a total failure of MoS₂. The critical breaking loads for wear failure are identified by the permanent break of Mo–S bonds. Compared with the pristine MoS₂, the critical breaking loads for wear failure on M-51 and S-51 GBs are reduced by 22.9% and 30.7%, respectively, as shown in Table 1. The wear resistance of GB defects-containing SL-MoS₂ increases with the misorientation angle, but less than that of the pristine MoS₂. The GB dislocation density of bycrystal MoS₂ increases with the misorientation angle. The strain fields which are caused by these dislocations can be canceled and overlapped, resulting in the improvement of the GB structural stability [56]. In addition, the failure of MoS₂ with GB defects under uniaxial tensile owes to the higher pre-strain in the Mo–S bonds around GBs [37]. The longest Mo–S bond length of each model has been calculated as shown in Fig. S7 in ESM. The longest bond length decreases with the increase of the misorientation angle. However, the MoS₂ layers under the diamond tip suffers more complex local strains and stresses

Fig. 7 (a) Relationship between average friction force and the scratching depth when the tip scratches on bare Pt substrate, pristine MoS₂ and MoS₂ with GB defects. (b) Variation of the average number of long Mo–S bonds with the scratching distance in M-51 model. The number of long bonds is averaged with an interval of 1 Å. The diamond tip is positioned at an initial distance of 50 Å from the GB along the *x* direction. (c) Relationship between the length of the critical bond 1–4 and scratching distance. (d) At the load depth of 5.4 Å, the distributions of the long Mo–S bonds for M-51, M-94, M-132 and M-218 models at two sliding distances of 37 and 45 Å, respectively. The long Mo–S bonds are marked in red, and the MoS₂ pairs along the GB defects are colored with bisque. The critical bonds within GBs are numbered by 1–4 and highlighted in blue.

during the scratching process than in uniaxial tensile tests. More complex wear failure mechanisms of GB defects-containing SL-MoS₂ could be investigated, which is concerning on the effect of misorientation angle.

To further explore the wear failure mechanisms, the other MoS₂/7- and S5/7-containing models

were also scratched under the critical breaking load of M-51 and S-51 models, respectively. The characteristics of Mo–S bonds were further considered. Here, the critical bond length of Mo–S bonds is defined as 2.75 Å, which is greater than the longest length of the pre-strain Mo–S bond within GB defects-containing SL-MoS₂ at equilibrium.

Table 1 Longest pre-strain Mo–S bond length at equilibrium and the critical breaking load for wear failure.

Model	Longest pre-strain bond length (Å)	Critical breaking load (nN)
M-51	2.73	72.77
M-94	2.70	77.67
M-132	2.69	82.94
M-218	2.67	89.40
S-51	2.74	65.37
S-94	2.73	74.29
S-132	2.72	78.09
S-218	2.69	83.69
Pristine MoS ₂	2.61	94.35

In the contact area between the SL-MoS₂ and the tip, the long Mo–S bonds were tracked (bond length is longer than 2.75 Å but less than the maximum cutoff radius of MoS₂). The distributions of long Mo–S bonds at two scratching distances of 37 and 45 Å were shown in Fig. 7(d). For all MoS₂-containing models, the long Mo–S bonds were scattered in the contact area at a scratching distance of 37 Å. When the tip scratched to 45 Å, most of the long Mo–S bonds emerged around the GB of M-51 model. In addition, the quantity of the long bonds around the GB defects decreased with the increase of the misorientation angle. The average number of the long Mo–S bonds was calculated to show the variation trend of the long bonds, as shown in Fig. 7(b). It should be noted that the number of long Mo–S bonds does not include the broken bonds. As the tip scratches to the GB defects, the quantity of long Mo–S bonds increases. But its growth trend decreases with increasing misorientation angle. For low-angle GB defects, the accumulation of those long bonds leads to the permanent break of critical bond-1, as shown in Figs. 7(c) and S7(c) in ESM. But for other models with large-angle GBs, the critical bonds are able to recover after the diamond tip slides over the GBs under the same load, which stops the further damage of MoS₂. Therefore, for low-angle GB defects, more Mo–S long bonds translate into the broken bonds when the tip scratches to GB defects, which can confirm that the accumulation of the long bonds around the GB defects leads to the

lower wear resistance of GB defects-containing SL-MoS₂.

3.3 Weakening the negative effects of GB defects on the tribological properties of MoS₂

According to the above discussions, the existence of GBs will degrade the tribological properties of MoS₂. With the decrease of misorientation angle between MoS₂ crystals, the deterioration of GB defects is more pronounced on the tribological properties of MoS₂. Therefore, weakening the negative effects of GBs (especially the low-angle GBs) is significant to enhance the quality of MoS₂ coatings for their potential applications. Researches show that the adhesive strength of the interfaces could affect the performance of coatings [57, 58]. The adhesive strength of the interfaces between MoS₂ and Pt substrate is changed by altering the LJ parameters, as shown in Tables 2 and S5 in ESM. It should be noted that the parameters of LJ-3 were used in the above simulations. The ideal work of adhesion between MoS₂ and Pt substrate could be calculated by the following formula:

$$W = \frac{E_1 + E_2 - E_{12}}{A_c} \quad (1)$$

where E_1 and E_2 are the total energies of the SL-MoS₂ and Pt substrate at equilibrium, respectively. E_{12} is the total energy of the SL-MoS₂ and Pt substrate when they contact each other at equilibrium. A_c is the contact area of the interface [59].

For the M-51 model, with the interfacial work of adhesion increasing, the critical breaking load for wear reduced as shown in Fig. 8(a). The same effects of the adhesive strength on critical load are observed in S-51 model. From what has been discussed above, the accumulation of those long

Table 2 LJ potential parameters and the work of adhesion.

	ε_{S-Pt} (meV)	ε_{Mo-Pt} (meV)	Work of adhesion (J/m ²)
LJ-1	88.92	330.71	1.03
LJ-2	133.38	496.06	1.57
LJ-3	177.84	661.41	2.13
LJ-4	266.76	922.12	2.64

Fig. 8 (a) Critical breaking load for wear failure of M-51 and S-51 model with different work of adhesion between MoS_2 and Pt substrate. (b) Average number of the long Mo-S bonds of S-51 model with different adhesive strengths at the load depth of 4.6 $\text{\AA}$.

bonds around the GB defects influences the wear resistance of the MoS_2 . The average number of long Mo-S bonds under different adhesive strengths has been calculated at same normal load (the critical breaking load of LJ-4), as shown in Fig. 8(b). During the scratching course, the quantity of the long bonds increases with the adhesive strength between MoS_2 and Pt substrate. Similar effects of the adhesive strength on the number of the long Mo-S bonds have been observed in M-51 models, as shown in Fig. S8 in ESM. Therefore, a lower adhesion strength of the interface could weaken the negative effects of GB defects on the tribological properties of MoS_2 . This result is opposite to the previous experiment [60] and simulation works on graphene [45]. They pointed out that the increase of adhesion between substrate and film could suppress the pucker effect [45, 60]. Although the interface quality could be enhanced by suppressing the pucker effect [61], the resistances of SL- MoS_2 and monolayer graphene against the pucker effect are different. The lower out-of-plane bending stiffness of 2D materials is the major causes of the pucker effect. Compared with monolayer graphene, the SL- MoS_2 shows higher bending stiffness owing to the larger thickness and the angular and pairwise interactions between Mo and S atoms [9]. The SL- MoS_2 presents an advantage over graphene on resisting against puckering owing to its bending modulus is about 7 times higher than

graphene [30]. In addition, Yang et al. [58] observed the controllable friction of SL- MoS_2 on different substrates and found that greater adhesion between substrate and SL- MoS_2 film resulting in higher friction force, which was consistent with the results in this work. Therefore, there could be other major reasons instead of the pucker effect for the increase of wear resistance of GB defects-containing SL- MoS_2 by decreasing the adhesion strength.

In order to further explain the effects of the adhesion strength on the wear resistance of GB defects-containing SL- MoS_2 , the structural deformations of MoS_2 have been studied during the scratching process, as shown in Fig. 9. The out-of-plane compressive and in-plane tensile deformation of MoS_2 could be described by $L_{\text{Mo-Mo}}$ and $L_{\text{S-S}}$, as shown in Figs. 9(b) and 9(c). It should be noted that for smaller $L_{\text{S-S}}$, the corresponding out-of-plane compression deformation is larger. With the adhesion strength increasing, the value of $L_{\text{Mo-Mo}}$ rises to a high level which indicates that the MoS_2 is suffering from a larger in-plane tensile deformation. The reduction of $L_{\text{S-S}}$ is also responsible to more out-of-plane compressive deformation of MoS_2 . Thus, both the in-plane tensile and out-of-plane compression deformations of MoS_2 increase with the adhesion strength, resulting in the rupture of SL- MoS_2 . Unlike graphene, the out-of-plane compression deformation of the SL- MoS_2 is the main cause of the rupture Pt-supported SL- MoS_2

Fig. 9 Relation curves of (a) $L_{\text{Mo-S}}$, (b) $L_{\text{Mo-Mo}}$, and (c) $L_{\text{S-S}}$ with scratching distance in S-51 model with different work of adhesion at a load depth of 4.6 Å.

[30, 50]. Therefore, SL-MoS₂ undergoes severe structure deformations under a high adhesion strength between SL-MoS₂ and substrate, resulting in more serious wear failure of GB defects-containing SL-MoS₂. The above reasons could explain the different findings in this work and previous works on graphene [45, 60]. That is, the adhesion strength changes the wear resistance of GB defects-containing SL-MoS₂ by influencing the structure deformations of MoS₂. Therefore, the wear resistance of GB defects-containing SL-MoS₂ could be enhanced by decreasing its interfacial adhesion strength to the substrate under certain conditions. A number of efforts have been made to reduce the adhesion strength between MoS₂ and substrate, such as the post-processing of vacuum plasma, increasing the layers of MoS₂ and deposition of MoS₂ on oxides (SiO₂ or Al₂O₃) substrate [58], which can offer a way to improve the wear resistance of MoS₂ with low-angle GB defects.

4 Conclusions

In this work, the effects of GB defects on the tribological behavior of MoS₂ have been investigated by using MD simulations. The GB defects-containing MoS₂ is more easily broken during the scratching course owing to the combined effect of pushing and interlocking between the diamond tip and MoS₂ atoms. In contrast, GB defects-containing MoS₂ is able to

withstand a larger load during the indentation process owing to the lack of relative sliding between the interfaces of the tip and MoS₂. The wear resistance and carrying capacity of MoS₂ with GB defects are relevant to the misorientation angle. Compared with the pristine SL-MoS₂, the critical breaking load of GB defects-containing MoS₂ with a low misorientation angle is significantly reduced. It should be noted that the critical breaking loads for wear failure on M-51 and S-51 GBs are reduced by 22.9% and 30.7%, respectively. The critical load of MoS₂ with GB defects increases with the misorientation angle. The accumulation of the long Mo–S bonds around the GBs results in the wear failure of GB defects-containing SL-MoS₂ during the scratching process. The GBs with low misorientation angles are easier to accumulate long bonds than large-angle GBs, which is severely decreased the wear resistance of MoS₂. Weakening the adhesion strength between MoS₂ and substrate is an efficient way to eliminate the negative effects of GB defects on the wear resistance of MoS₂. The adhesion strength changes the wear resistance of GB defects-containing SL-MoS₂ by influencing the structure deformations of MoS₂. When the interfacial work of adhesion reduces from 2.13 to 1.03 J/m², the wear resistance on M-51 and S-51 GBs are increased by 11.3% and 13.7%, respectively. These results show the importance of controlling the microstructure, such as the low-angle GB defects, and provide guidelines to enhance the wear resistance of GB defects-containing SL-MoS₂.

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