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Molecular Dynamics Study on the Tribological Characteristics of Grain Boundary-Containing Graphene/*h*-BN Heterostructure Films

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Abstract: A heterostructure film composed of graphene and *h*-BN has superlubricity and long-term anti-corrosion performance, enabling its potential applications as low-friction and corrosion-resistant coatings, especially in marine environments. However, the grain boundaries (GBs) and point defects formed during the preparation process may significantly affect the performance of the film. In this study, the tribological properties and wear mechanism of heterostructure films with different GB misorientation angles were studied with the molecular dynamics method. The results show that the high-energy atoms generated by strain-induced hillocks along the GBs can lead to stress concentration, thus deteriorating the wear resistance of the heterostructure film. Furthermore, point defects occurring on high-energy atoms can significantly alleviate the stress concentration, which is conducive to improving the wear resistance of the film. This study sheds light on improving the tribological characteristics of a graphene/*h*-BN heterostructure coating by properly controlling its microstructure.

Keywords: heterostructure film; grain boundaries; graphene-based material; molecular dynamics



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1. Introduction

Reducing the friction and wear of dynamic interfaces has been a constant endeavor in the field of sustainability [1]. Graphene-based 2D materials have attracted widespread attention in the fields of lubrication and corrosion protection due to their excellent mechanical and tribological performance [2–5]. Moreover, their excellent chemical stability and impermeability also grant them excellent corrosion resistance [6,7]. In recent years, it has been proven that a heterostructure film composed of graphene and hexagonal boron nitride (*h*-BN) can achieve superlubricity and long-term anti-corrosion, thereby having potential applications to serve as high-performance coatings, especially in the marine environment [7–13]. However, 2D materials tend to exist in polycrystalline form, with adjacent grains merging at grain boundaries (GBs) [14–17]. The existence of GB structures can significantly affect the physical and chemical properties of the film [18,19]. Therefore, it is of great significance to investigate the tribological characteristics of GB-containing graphene/*h*-BN heterostructure films at the atomic scale.

In recent decades, the molecular dynamics simulation method has been introduced in many fields and its reliability has also been validated with experiments [20–22]. Scholars have delved extensively into the tribological properties of graphene-based materials through experiments and molecular dynamics (MD) simulations. Dienwiebel et al. [23] measured the friction between graphene layers by atomic force microscopy and observed

that the superlubricity phenomenon between graphene layers was closely related to the friction rotation angle. Bai et al. [24] found that the graphene could effectively lubricate the diamond-like carbon (DLC) film with MD simulation. Zhao et al. [25] studied the tribological properties of a graphene/*h*-BN heterostructure film and obtained the optimal structure with the lowest friction resistance under two-body abrasive contact. Additionally, the MD simulation results showed that compared with monolayer (graphene or *h*-BN) films, the tribological properties of heterostructured films could be significantly improved. Furthermore, the graphene/*h*-BN heterogeneous film had a higher load bearing capacity when scratched by a diamond tip, which also means that the graphene/*h*-BN heterogeneous film had superior wear resistance. After that, a “Rolling” command was developed for modeling the three-body abrasive contact in LAMMPS 2022 software, and the three-body abrasive tribological properties of the graphene/*h*-BN heterostructure film was investigated with the consideration of different kind of defects [26].

The large-size growth of single-crystalline graphene remains a major challenge for currently promising chemical vapor deposition (CVD) and epitaxial growth methods [14,15]. This means that graphene-based materials typically consist of grains of different sizes and orientation angles, and GBs are formed when any adjacent grains merge during the growth process [27]. Lahiri et al. [28] proved that the GBs of graphene sheets prepared by the CVD method are one-dimensional arrays formed by pentagonal/heptagonal pairs. Huang et al. [29] revealed the GB shape of graphene grown on copper through dark-field scanning transmission electron microscopy experiments. They also found that the GBs consisted of a set of continuous pentagonal/heptagonal pairs, which is consistent with several theoretical studies using atomic simulations such as the first-principles method [30,31].

The mechanical and tribological performances of the polycrystal graphene film have been investigated, and the GB structures were considered to be detrimental to the strength of graphene [18,19,29,32–34]. Huang et al. [29] grew single-layer graphene films on copper foils by the CVD method and found that grain boundaries severely weakened the mechanical strength of graphene films. Wei et al. [35] found that the tensile strength of polycrystalline graphene was significantly reduced, and that mechanical failure always began with the bond of the heptagon and hexagon rings. Zhang et al. [36] conducted ground-breaking work and studied the effect of GBs on the tribological properties of graphene with the MD method. They found that the wear resistance performance of polycrystalline graphene was affected by the indentation position and GB misorientation angle, and attributed the damage of polycrystalline graphene to the accumulation of long bonds at the grain boundaries.

The aforementioned studies mainly focused on the behavior of the GB-containing graphene film, but there have been few investigations on the tribological characteristics of GB-containing graphene/*h*-BN heterostructure films. Additionally, the point defect is inevitable in manufacturing and application processes for graphene-based two-dimensional materials, which can significantly affect the physical and chemical properties of the film [37–39]. The GB structure can be regarded as the defect for the heterostructure film resulting from the manufacturing process, and the effects of GBs and point defects on the tribological properties of a heterostructure film and their coupling behaviors need to be investigated at the atomic scale in detail.

In this study, a GB-containing graphene/*h*-BN heterostructure film scratched by a diamond tip was first modeled and studied with the MD method to analyze its tribological properties. Here, for the sake of simplicity, only the bicrystal structure present on the graphene layer was considered. The influence and the mechanism of the GB misorientation angle on the tribological characteristics of heterostructure films were discussed. Afterward, the role of different atoms located on GB structure were analyzed. Then, the point defects occurring on GB structures were investigated to reveal their influence on the tribological characteristics of heterostructure films.

2. Molecular Dynamics Modeling

A molecular dynamics (MD) model of a diamond tip sliding on a heterostructure film with a GB structure was established via the LAMMPS software, as shown in Figure 1a. The heterostructure film consisted of graphene and *h*-BN layers. The graphene layer was placed on the top and the *h*-BN layer under the graphene to separate it from the substrate. The heterostructure film has been proven to have excellent performance in friction reduction, wear resistance, and long-term corrosion resistance, and is suitable as a coating under marine environments [40–43]. Copper was employed as the substrate due to its good corrosion-resistant and mechanical properties [44].

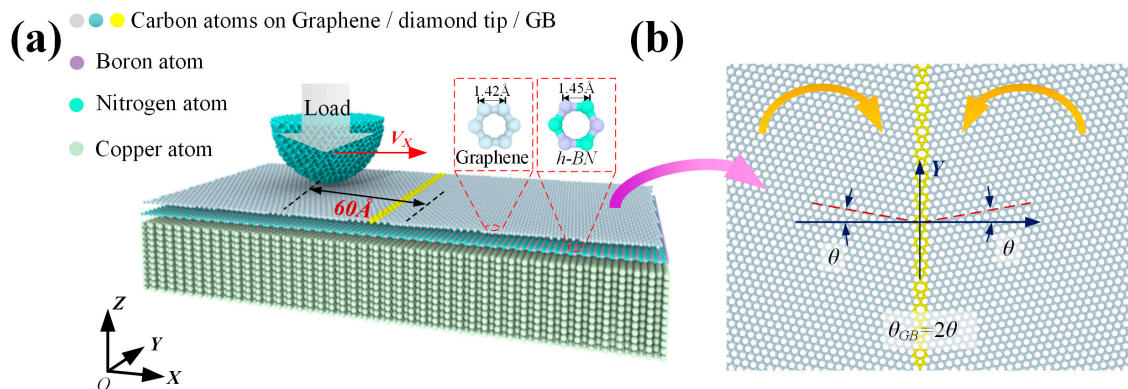


Figure 1. Schematic diagram of the MD contact model of (a) a diamond tip sliding on a GB-containing heterostructure film, and (b) the MD model of the GB-containing bicrystal graphene layer.

The dimension of the heterostructure film was respectively set to 200 Å and 150 Å along the *X* and *Y* directions, which contained 7661 carbon (C) atoms in the perfect graphene film as well as 3680 nitrogen (N) atoms and 3680 boron (B) atoms in the *h*-BN film. The thickness of the copper (111) substrate was 24 Å with a total of 12 layers, consisting of 42,588 copper atoms. The hemispherical diamond tip was assumed to be rigid with the radius of 25 Å and was composed of 5853 C atoms. The distance between the graphene and *h*-BN, and the distance between *h*-BN and the copper substrate, were all initially set to 4 Å. The diamond tip was placed 15 Å above the heterostructure film. The top eight layers of the copper substrate were set as heat-affected zones, and the bottom four layers were set as fixed layers to restrict the movement of the substrate, as conducted in Ref. [36].

In order to describe the C–C interactions within the diamond tip and the graphene film as well as the interactions between them, the Adaptive Interatomic Reactive Empirical Bond-Order (AIREBO) potential energy was adopted [25]. In this way, the chemical bonds formed between the tip and the graphene can be used to characterize the adhesive wear on the sliding interface, as conducted in Ref. [45]. The interactions between B–B, N–N, and B–N atoms as well as C–B and C–N atoms are described with the Tersoff potential energy, as conducted in Refs. [46,47]. The atom interactions within the copper of the substrate were described with the EAM potential energy [48]. Furthermore, the Lennard-Jones (L-J) potential energy was adopted to describe the mechanical interactions between copper and other atoms [49,50]. All of the above potential energies are detailed in Appendix A. The parameters of the L-J potential energy are listed in Table 1.

Table 1. Potential parameters for the L-J potential in the MD simulation model.

L-J Potential	ϵ (eV)	σ (Å)
C-Cu	0.019996	3.225
B-Cu	0.0013009	3.3756
N-Cu	0.00080545	3.1872

Chemical vapor deposition (CVD) and epitaxial growth are the most common methods for fabricating the graphene film. In these methods, graphene tends to exist in a polycrystalline structure and consists of grains with different sizes and misorientation angles [14,15]. Grain boundaries are inevitable and form when adjacent grains merge during their growth [27]. The existence of GBs can significantly affect the physical and chemical properties of 2D materials [18,19,34,51]. In this study, a heterostructure film composed of a bicrystal graphene film and a perfect *h*-BN film was investigated for its tribological characteristics at atomic scale.

As shown in Figure 1b, two graphene grains were tilted reversely at the same angles θ for simplicity. The misorientation angle will destroy the continuity of the film at adjacent splices, thus forming the GB structure. The different misorientation angles can produce GB structures with different dislocation types and densities. According to the coincidence site lattice theory [52], six representative GB-containing bicrystal graphene layers were modeled by merging two adjacent graphene grains with corresponding certain misorientation angles θ_{GB} , as investigated in Ref. [36]. In each case, a series of coincidence points with a regular periodicity could be found in the grains to form steady GBs. More details about the GB modeling process can be found in Ref. [30].

Figure 2 displays bicrystal graphene films with six representative zigzag- and armchair-oriented GBs. Figure 2a–c displays the zigzag-oriented GBs corresponding to the misorientation angles of 7.34° , 13.2° , and 21.7° , which are denoted by ZZ-7.34, ZZ-13.2, and ZZ-21.7, and consisted of 7624 carbon atoms, 7627 carbon atoms, and 7632 carbon atoms, respectively. Correspondingly, Figure 2d–f shows the armchair-oriented GBs with the misorientation angles of 17.9° , 21.8° , and 27.8° , represented by AC-17.9, AC-21.8, and AC-27.8, respectively, and consisted of 7623, 7626, and 7632 carbon atoms, respectively. The pristine armchair and zigzag graphene samples are denoted as AC-0 and ZZ-0, consisting of 7661 and 7614 carbon atoms, respectively. From the figures, it is obvious that the GBs were predominantly composed of pentagon and heptagon ring defects, which were also observed in Refs. [31,53,54].

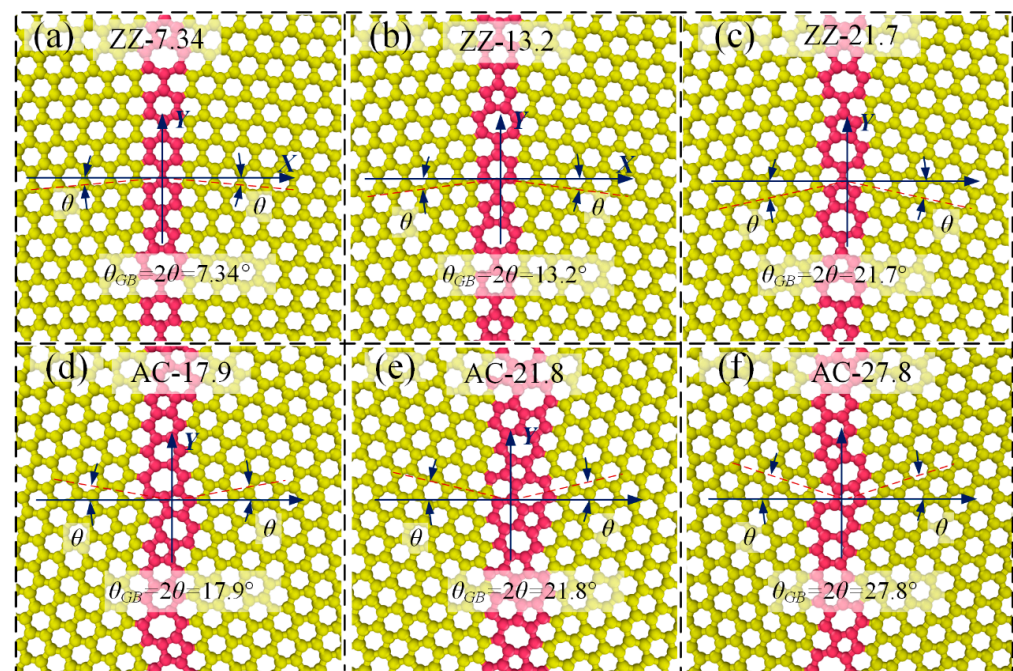


Figure 2. Zigzag-oriented GB structures of the bicrystal graphene layer with misorientation angles of (a) 7.34° , (b) 13.2° , and (c) 21.7° ; Armchair-oriented GB structures of the bicrystal graphene layer with misorientation angles of (d) 17.9° , (e) 21.8° , and (f) 27.8° .

The adopted coordinate system of the MD model is illustrated in Figure 1a, and the periodic boundary conditions were adopted in both the X and Y directions. The conjugate gradient method was first employed to achieve the potential energy minimization of the system. Then, the temperature was set to 300 K for all the atoms of the system, and a 20 ps relaxation was carried out through a Nosé–Hoover thermostat to achieve thermodynamic equilibrium, as conducted in Ref. [25]. The rigid diamond tip was 4 nm away from the grain boundary, which was selected to reduce the influence of the loading process on the grain boundary. In the whole simulation process, the total sliding distance was set to 6 nm along the X-axis. A constant sliding speed of 0.1 Å/ps was applied to the diamond tip with the time step of 0.5 fs, as conducted in Ref. [55].

In MD studies on the tribological properties between an abrasive and 2D film, the abrasive can be loaded with either a fixed load [36,56] or an indentation depth [37]. With the latter loading method, the abrasive slides against the heterostructure film without vertical motion. In this way, the reaction force between the abrasive and the film will vary simultaneously due to the wrinkle and step effects from the film as well as the grain boundary structure, thus posing some effect on the friction process. In this study, in order to determine the critical load of the GB-containing film with different misorientation angles and thus reveal the effect of the GB structure on the tribological properties of the film, a fixed load was exerted on the diamond abrasive particle to allow it to make contact with the film.

3. Results and Discussion

Based on the above models, the bicrystal graphenes with the aforementioned GB misorientation angles were first investigated to reveal their effects on the tribological performances of the heterostructure film adhesively scratched by a rigid diamond tip. Then, the GBs with differently located single-point defects were modeled and simulated to study their influences on the frictional characteristics of the heterostructure film including the friction coefficient and the anti-wear performance.

3.1. Effects of GBs with Different Misorientation Angles on the Tribological Performances of the Heterostructure Film

Figure 3a presents the average friction as the function of the normal loads for the scratching contact between a diamond tip and the heterostructure films containing bicrystal graphene with different GB misorientation angles. For each GB structure, the relationship between the lateral force and the normal load was determined by conducting a series of simulations in which an initial normal load was first exerted on the particle with a value of 100 nN, and then the load was gradually increased by 10 nN each time until wear of the film occurred. The wear failure was characterized by the emergence of the permanent breakage of the C–C bonds in the graphene sheet. In this study, the Ovito 2.9.0 software was used for the visualization and quantity processing of the covalent bonds. The formation and breakage of covalent bonds were detected by setting a cutoff distance with the value of 2.0 Å, which corresponded to the interaction cutoff distance in the AIREBO and Tersoff potentials, as conducted in Refs. [57,58]. If the distance between two atoms is shorter than the pre-set cutoff distance, a covalent bond is formed; otherwise, the covalent bond is broken.

When the normal load is larger than the critical load, the film will be worn during the scratching process, resulting in greater friction due to the step and wrinkle effects of the torn cavity. As shown in Figure 3a, the abrupt increase in friction with the normal load indicated the occurrence of the wear, and the load at the abrupt point corresponded to the critical normal load of the current heterostructure film. Accordingly, Table 2 lists the critical normal loads of different GB-containing heterostructure films. The critical normal loads obviously depend on the GB misorientation angle of graphene layers. In the bicrystal case, the critical load increased with the misorientation angle, and the larger the orientation angle of the GB structure, the more inclined the critical load is to the monocrystal layer case. This

indicates that the bicrystal structure can weaken the wear resistance performance of the heterostructure film, but with the increase in the GB misorientation angle, this weakening effect gradually decreases, which is consistent with the conclusions obtained in Ref. [36].

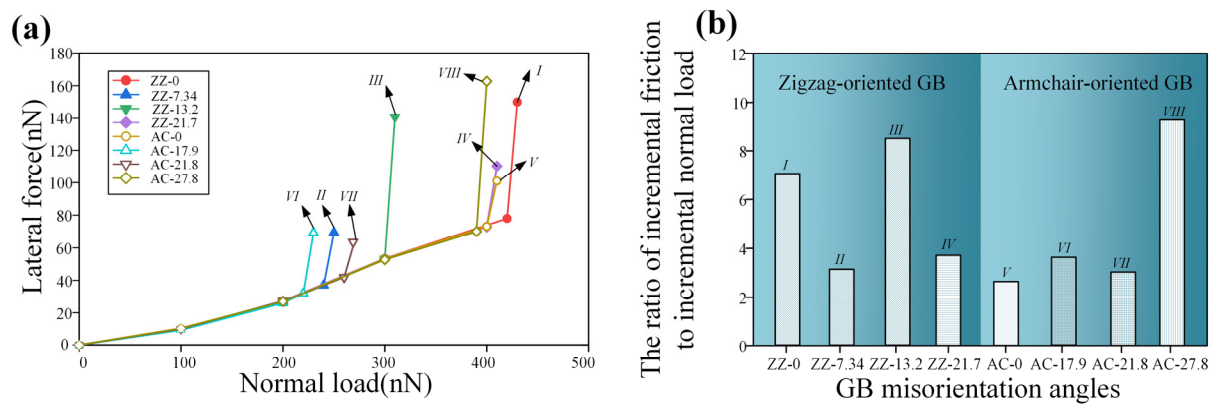


Figure 3. (a) The average friction as the function of the normal loads for the scratching contact between a diamond tip and GB-containing heterostructure films with different misorientation angles, and (b) the ratio of incremental friction to incremental normal load after wear initiation.

Table 2. The critical normal loads of the heterostructure film containing bicrystal graphenes with different GB misorientation angles.

	Zigzag-Oriented				Armchair-Oriented			
	ZZ-7.34	ZZ-13.2	ZZ-21.7	ZZ-0	AC-17.9	AC-21.8	AC-27.8	AC-0
F_{cn} (nN)	250	310	410	430	230	270	400	410

For the intact GB-containing heterostructure film (i.e., no wear failure occurs in the film), the misorientation angle of the GB structure had little influence on the friction experienced by the diamond tip sliding on different heterostructure films, as shown in Figure 3a. In detail, Figure 4a,b demonstrates the variations in friction during the sliding process for films with different GB misorientation angles under normal loads of 200 nN and 300 nN, respectively. The positive lateral force represents the thrust, and the negative force represents the friction resistance on the tip. Under the load of 200 nN, all of the aforementioned GB-containing films remained intact, and the frictions almost fluctuated around a constant. The different misorientation angle of the bicrystal graphene layer posed different pinning effects on the sliding tip, inducing a slightly different stick-slip period during the sliding process. Under the load of 300 nN, an abrupt rise in friction was produced when the tip scratched through the GBs with misorientation angles of AC-17.9, ZZ-7.34, and AC-21.8. In these cases, the increase in the friction mainly resulted from the step and wrinkle effects of the torn cavity initiated at the GB structures. This indicates that the existence of the above GBs deteriorated the wear resistance of the heterostructure film, and thus reduced the critical normal load.

Figure 5 shows the wear initiation of heterostructure films with different GBs under the corresponding loads marked I to VIII (shown in Figure 3a), respectively. The ratio of incremental friction to incremental normal load compared to the critical case is shown in Figure 3b to characterize the initiated wear. It is clear that the greater the ratio, the more severe the wear. In cases of ZZ-7.34 and ZZ-13.2, the wear initiation of the films occurred at the GB structures. This can also demonstrate the weakening effect of these two GBs on the wear resistance of the heterostructure films. Similarly, the wear initiation of the AC-17.9 and AC-21.8 oriented films also occurred at GBs. However, when the misorientation angle increased up to ZZ-21.7 and AC-27.8, the wear initiated in the graphene grains rather than on GBs. The reason is that these two GB structures did not significantly reduce the critical

normal load (shown in Figure 3a), and thus their wear resistance mainly depended on the strength of graphene monograins under the current orientation angles.

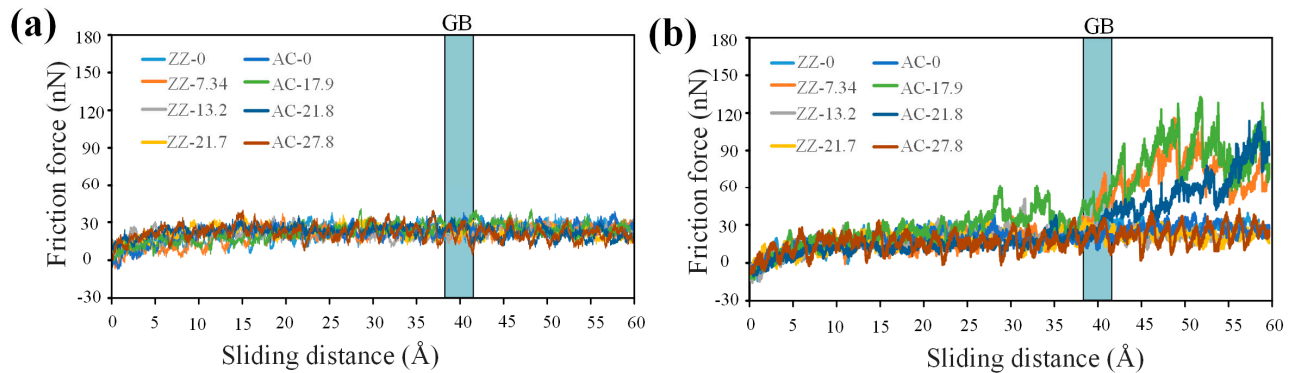


Figure 4. The variations in friction experienced by the diamond tip sliding on the GB-containing heterostructure films with different misorientation angles under normal loads of (a) 200 nN and (b) 300 nN.

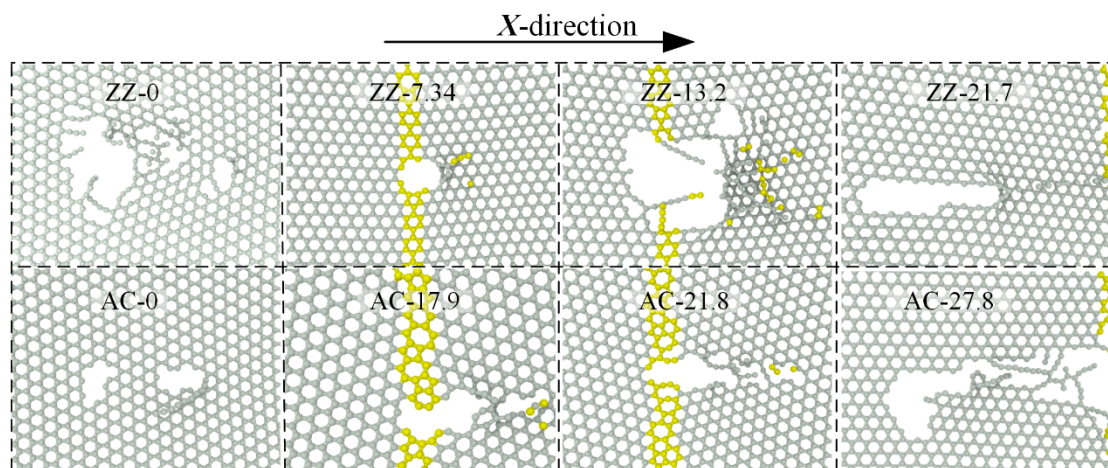


Figure 5. The comparison of wear initiation for heterostructure films with different GBs.

3.2. Weakening Mechanism of GBs on the Wear Resistance of Heterostructure Films

In this subsection, the weakening mechanism of the above four bicrystal graphene layers on the wear resistance of heterostructure films is explored. Figure 6 compares the wear initiation and propagation of the heterostructure film containing bicrystal graphene layers of ZZ-7.34, ZZ-13.2, AC-17.9, and AC-21.8 during the scratching process under corresponding loads marked II, III, VI, and VII (shown in Figure 3a), respectively. It was found that the film wear initiated at the atoms shared by heptagon and hexagon rings at the GBs. This phenomenon is similar to the fracture of GB-containing graphene subjected to uniaxial tensile [59,60], where the fracture at the GBs is attributed to the high pre-strain of the critical bond shared by the heptagon and hexagon rings. However, in this study, heterostructure films were subjected to extrusion and bonding interaction from the diamond tip, which makes it more complex for the wear mechanism of the GB-containing heterostructure film.

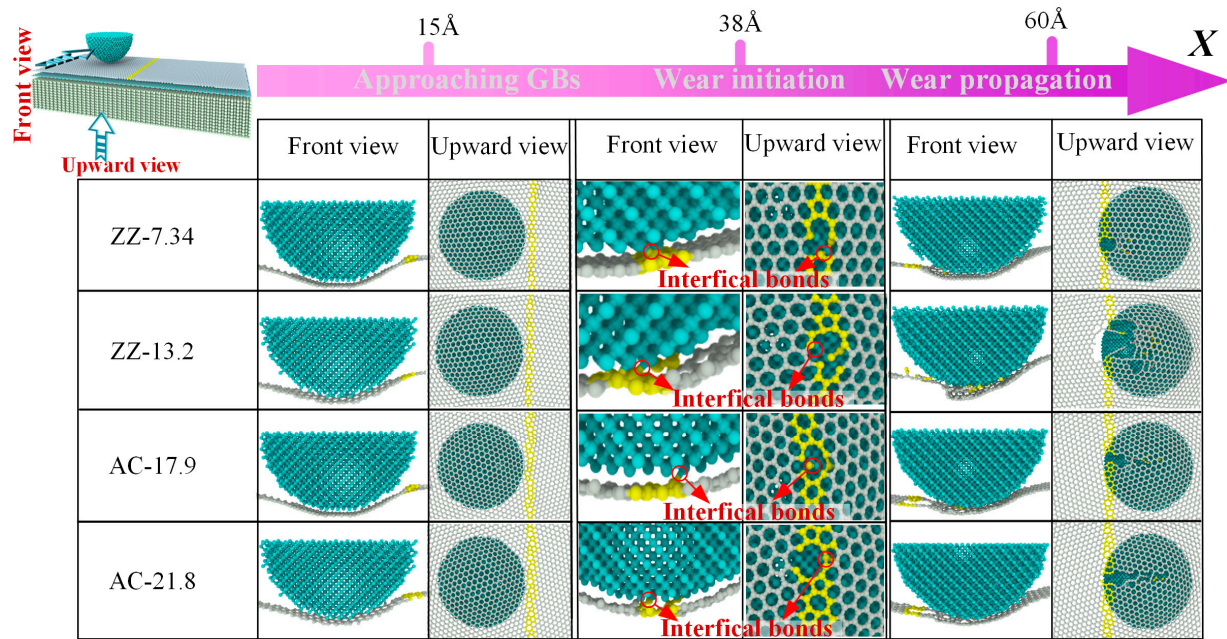


Figure 6. The comparisons of the wear initiation and propagation of GB-containing heterostructure films containing bicrystal graphene layers of ZZ-7.34, ZZ-13.2, AC-17.9, and AC-21.8 scratched by a sliding diamond tip under each corresponding critical normal load.

The wear resistance behavior is closely related to the frictional performance of the heterostructure film under sliding contact [25,26]. Figure 7 presents the variation in the lateral forces as well as the changes of numbers in the graphene in-plane broken and the graphene-tip interfacial bonds in the cases of ZZ-7.34, ZZ-13.2, AC-17.9, and AC-21.8. When the tip scratches approach the GBs, the strain-induced hillocks along the GBs can produce high contact stress between the tip and graphene layer, resulting in the formation of graphene-tip interfacial bonds. These interfacial bonds can largely increase the tensile stress within the GB-containing graphene layer and thus easily initiate the wear at about the sliding distance of 38 Å. As shown in Figure 6, some atoms shared by the heptagon and hexagon rings on the GBs can easily form interfacial bonds with the diamond tip. These atoms can be regarded as dangerous atoms and act as pioneers for the breakage of in-plane C–C bonds.

These dangerous atoms could be easily removed from the heterostructure film by the sliding diamond tip, thus initiating wear and generating more dangling bonds. Dangling bonds can produce more interfacial bonds with the diamond tip, and in turn further exacerbate the propagation of wear. In other words, the defect on the heterostructure film will expand from the point defects to larger defects due to the adhesion of the interfacial bond. The friction experienced by the diamond tip was positively correlated with the number of in-plane broken bonds and interface bonds due to the stick-, step-, and wrinkle-effects of the deformable layer, as found in Ref. [24]. The detailed wear evolution process can be found in Movie S1, Supplementary Materials.

It is notable from Figure 6 that in the cases of ZZ-7.34, AC-17.9, and AC-27.8, the propagation of the wear was not significant with the sliding of the tip after its initiation in GB zones, and only a small cavity was created near the GBs. It can also be seen in Figure 8 that the number of in-plane broken bonds tended to be stable after a sliding distance of about 45 Å. This also indicates that the graphene monograins had a larger strength than the above GB structures. Furthermore, when the wear was no longer extended, the friction also decreased significantly, indicating that the friction increase was mainly caused by the wear of the graphene layer. In the ZZ-13.2 case, there were two dangerous atoms on the GB structure, as shown in Figure 6. As the sliding process progressed, two cavities sprouted at the dangerous atom simultaneously, then gradually expanded, and finally merged into a

large worn hole. The gradual expansion was mainly due to the excessive weakening of the above two cavities on the strength of the graphene monograins.

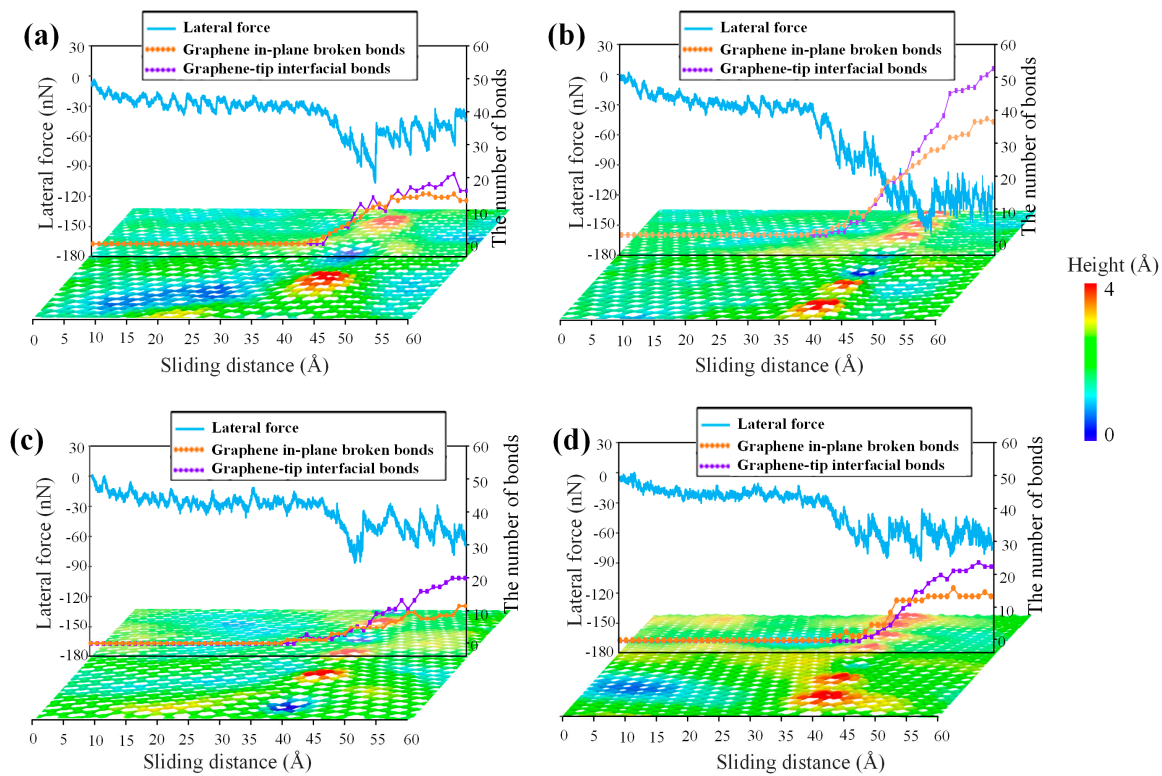


Figure 7. Variations in the lateral forces as well as changes in the numbers of the graphene in-plane broken and graphene-tip interfacial bonds during diamond tip scratching on the GB-containing heterostructure films with different misorientation angles of (a) ZZ-7.34, (b) ZZ-13.2, (c) AC-17.9, and (d) AC-21.8.

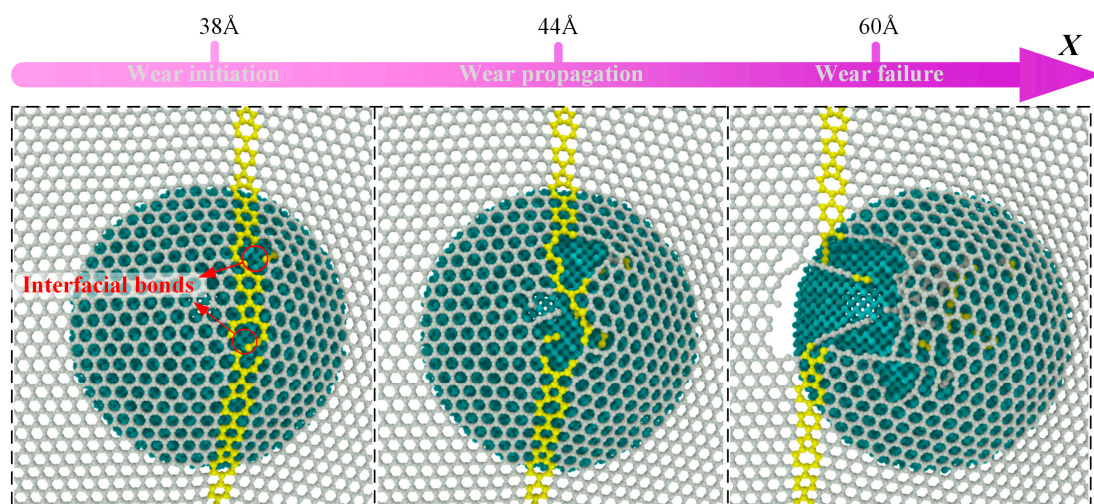


Figure 8. Wear initiation, propagation, and failure of the GB-containing heterostructure film containing bicrystal graphene layers of ZZ-13.2 scratched by a sliding diamond tip under its critical normal load.

The mechanical properties of polycrystalline graphene-based materials are dependent on the GB strength [61,62] as well as the internal stress of the carbon atom [19]. To further study the influence of GB on the wear characteristics of the heterostructure film containing

a bicrystal graphene layer, the initial stress of the single atom in the X-direction of the heterostructure film was also calculated with the virial theorem, the detailed calculation process of which can be found in Ref. [19]. Figure 9a shows the single atom initial stress distribution of the bicrystal graphene layer before exerting a normal load on the diamond tip (i.e., at the moment after energy minimization and relaxation in the simulation). It was obvious that there existed large tensile stress atoms, named as high-energy atoms, distributed on heptagon rings located at the GB. The large stress results from the misorientation angle of the GBs and can lead to a large pre-strain of the covalent bond on high-energy atoms, thus significantly decreasing the wear resistance of the film [63].

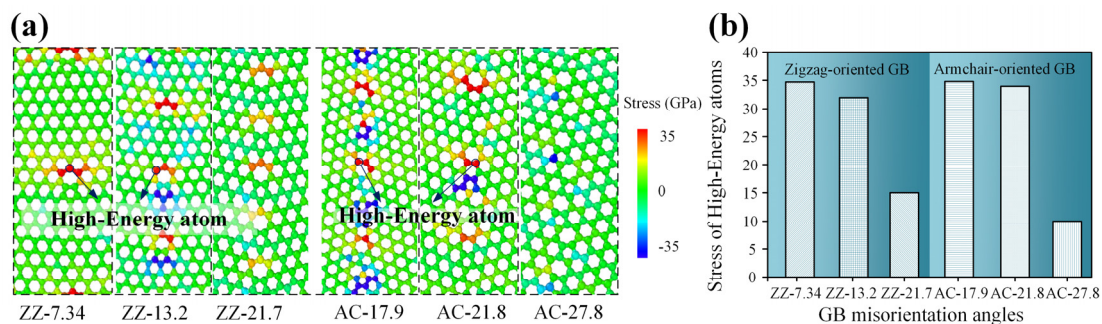


Figure 9. The effect of the GB misorientation angle of the heterostructure film containing bicrystal graphene layers on the initial atom stress distribution: (a) the initial atom stress distribution induced by the misorientation angle of the GBs along the sliding direction before exerting the load on the diamond tip, and (b) the relationship between the GB misorientation angle and the maximum value of the initial single atomic stress.

In bicrystal graphene cases, with the increase in the GB misorientation angle, the maximum value of the initial single atomic stress decreased gradually, as shown in Figure 9b. The reason maybe that the density of the pentagon ring on the GB structures increases with the misorientation angle. The compressive stress in the pentagon rings can offset the tensile stress in the heptagon rings to a certain extent, which can lead to the enhancement in the wear resistance of the heterostructure film. This phenomenon is consistent with the conclusion in Figure 3, and has also been observed in Refs. [60,64]. It can easily be deduced that the cracking of the graphene layer always begins with these high pre-strain bonds when the tip slides across the GB-containing film.

Figure 10 shows the atomic stress distribution of different heterostructure films in the sliding direction at the wear initiation moment of the GB-containing films under corresponding critical loads. The limitation of the stress displayed was set to ± 130 GPa, which corresponded to the breaking strength of the graphene films [65]. As shown in the figure, the stress always concentrated on some atoms. The highly stressed atoms had higher energy (called high-energy atoms) than the other atoms, which made it easier for them to form interfacial bonds with diamond tip and thus initiate wear. However, with the increase in the GB misorientation angle, especially in the cases of ZZ-21.7 and AC-27.8, the stress distribution became more uniform, which made the wear resistance of the film mainly depend on the mechanical strength of the monograins of the graphene layer. It can be concluded that the existence of the GB structure will cause stress concentration at the junction of the hexagon ring and heptagon ring and produce obvious local tensile stress. These high-energy atoms will become dangerous atoms, easily peeled off during the sliding process, resulting in wear and tear.

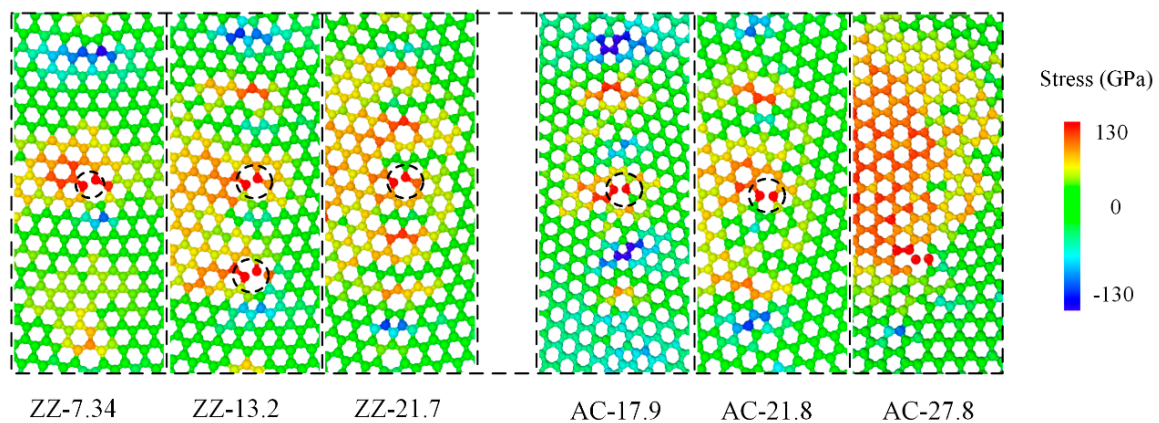


Figure 10. The single atomic stress distribution diagram in the X-direction after the wear initiation on the heterostructure film (the broken bonds are highlighted by the black dotted line).

3.3. The Tribological Performance of the Heterostructure Film with Point Defect on GB Structures

Point defects are inevitable in the manufacturing and application processes for graphene-based two-dimensional materials, which can significantly affect the physical and chemical properties [37–39]. Previous studies on monograin graphene films have proven that the point defect can largely decrease their mechanical and tribological performances [66,67]. For the GB-containing heterostructure film, it is easy to understand that the point defect on each single grain still has a weakening effect on the wear resistance performance.

The GB structure can also be regarded as the defect for the heterostructure film resulting from the manufacturing process, and point defects distributed on the GB structures are also common. As shown in Figures 9 and 10, most atoms occurring on the GB structures had a slight effect on the stress distribution of the film. It can be inferred that the occurrence of point defects on these atoms will also reduce the wear resistance of the film because the pinning-effect and step-effect between the defect and the sliding tip can weaken the strength of the film. However, the high-energy atoms on GB structures have a higher energy than other atoms, which makes it easier for them to initiate wear, as described in Section 3.2. Therefore, the influence of the point defects on the wear resistance performance is more complex when they occur on high-energy atoms.

In this subsection, the tribological behavior was investigated for bicrystal graphene heterostructure films with point defects occurring on high-energy atoms. Given that the dangerous atoms in the four cases of ZZ-7.34, ZZ-13.2, AC-17.9, and AC-21.8 could induce obvious stress concentration and thus largely reduce the wear resistance of the GB-containing heterostructure films (shown in Figures 9 and 10), here, only the above four cases were investigated. Figure 11 shows the point defective MD model of the above four heterostructure films by removing the high-energy atoms. Other conditions were kept the same as the model described in Section 3.1.

Table 3 lists the critical normal loads of four GB-containing heterostructure films with point defects occurring on high-energy atoms. In comparison with Table 2, the point defects obviously increased the corresponding critical normal load, and thus were conducive to improving the wear resistance property of the heterostructure film. In order to account for the beneficial effects of the point defect located at high-energy atoms, Figure 12 compares the single atom initial stress distributions of the bicrystal graphene layer with and without high-energy atom-located point defects before exerting a normal load on the diamond tip (i.e., at the moment after energy minimization and relaxation in the simulation). It was obvious that after the removal of the high-energy atom, the stress concentration had been significantly alleviated, which could reduce the interfacial energy between the graphene atoms and the diamond tip. For this reason, the wear resistance of the heterostructure film will be significantly enhanced, and the critical load will also be increased.

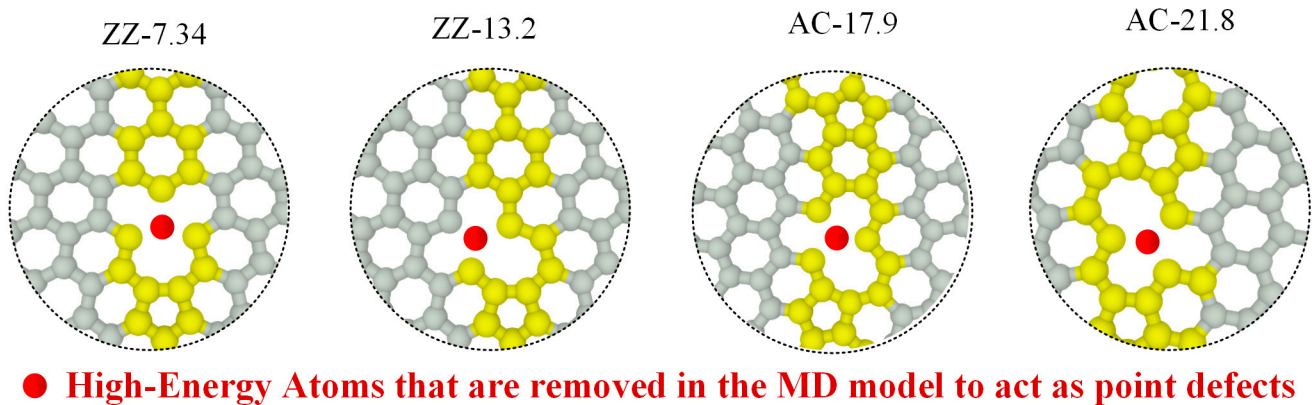


Figure 11. MD structure of GB-containing heterostructure films with single point defect occurring on high-energy atoms.

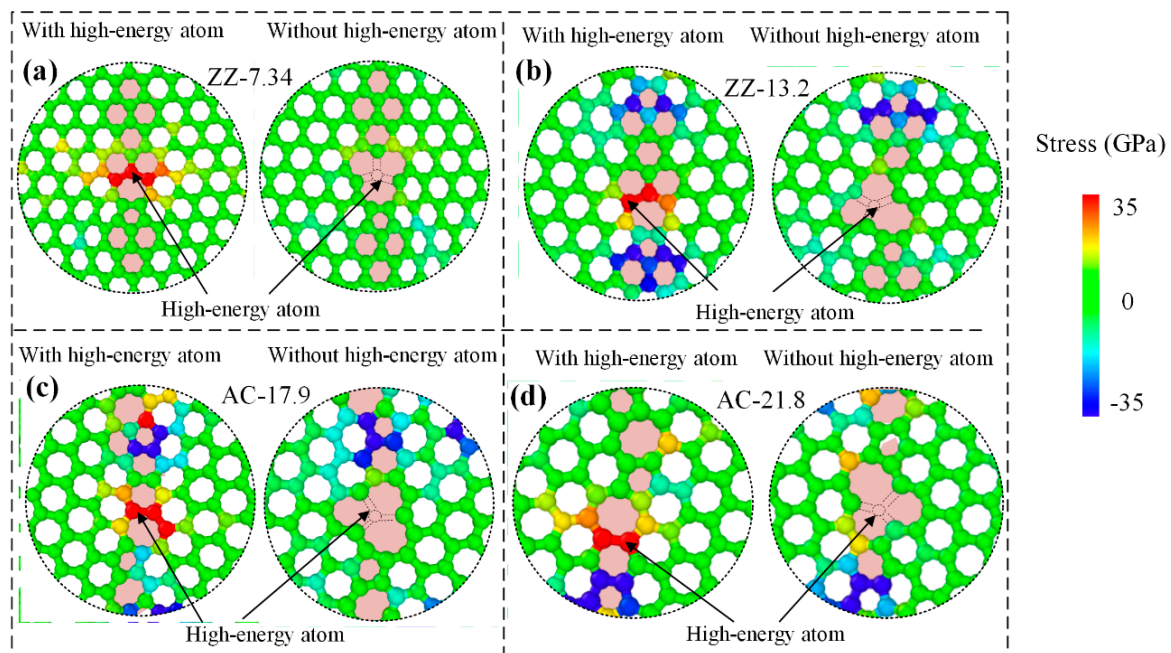


Figure 12. Comparisons of the single atom initial stress distributions on the bicrystal graphene layer with and without high-energy atom-located point defects before exerting a normal load on the diamond tip in the cases of: (a) ZZ-7.34, (b) ZZ-13.2, (c) AC-17.9, and (d) AC-21.8.

Table 3. The critical normal load of the heterostructure film with point defects occurring on high-energy atoms.

	Zigzag-Oriented		Armchair-Oriented	
	ZZ-7.34	ZZ-13.2	AC-17.9	AC-21.8
F_{cn} (nN)	300	370	300	310

In order to evaluate the effects of the scratching path on the results, another three different paths for the scratching contact between the tip and the heterostructure film were simulated for the cases of ZZ-7.34 and AC-17.9, as shown in Figure S1, Supplementary Materials. The critical normal loads for both the intact bicrystal film and the film with point defects occurring on the high-energy atoms are listed in Table S1, Supplementary Materials. Comparing Table S1 with Tables 2 and 3, it can be seen that the path had little impact on the critical normal load of the film. In addition, as stated in Refs. [36,51], the researchers

also found that the sliding path of the diamond had little influence on the critical normal load of the film with the misorientation angle of the grain boundary.

In order to reveal the influence of the high-energy atom on the friction resistance, Figure 13 compares the variations in the lateral forces experienced by the tip during the sliding on the film with and without high-energy atoms under the critical normal loads of the cases with high-energy atoms. In this figure, the bottom image refers to the initial atomic height distribution of the film with point defects on high-energy atoms before exerting a load on the MD contact system. It was obvious that the friction was almost the same for both cases (with and without high-energy atoms) and had the same stick-slip phenomenon before the tip reached the GBs. Because the existence of high-energy atoms can significantly decrease the wear resistance of the film (as shown in Figure 9), the graphene layer can be cracked when the tip slides across the GB-containing film. Therefore, the lubrication ability of the heterostructure film decreases rapidly due to the wear after the tip slides across the GBs.

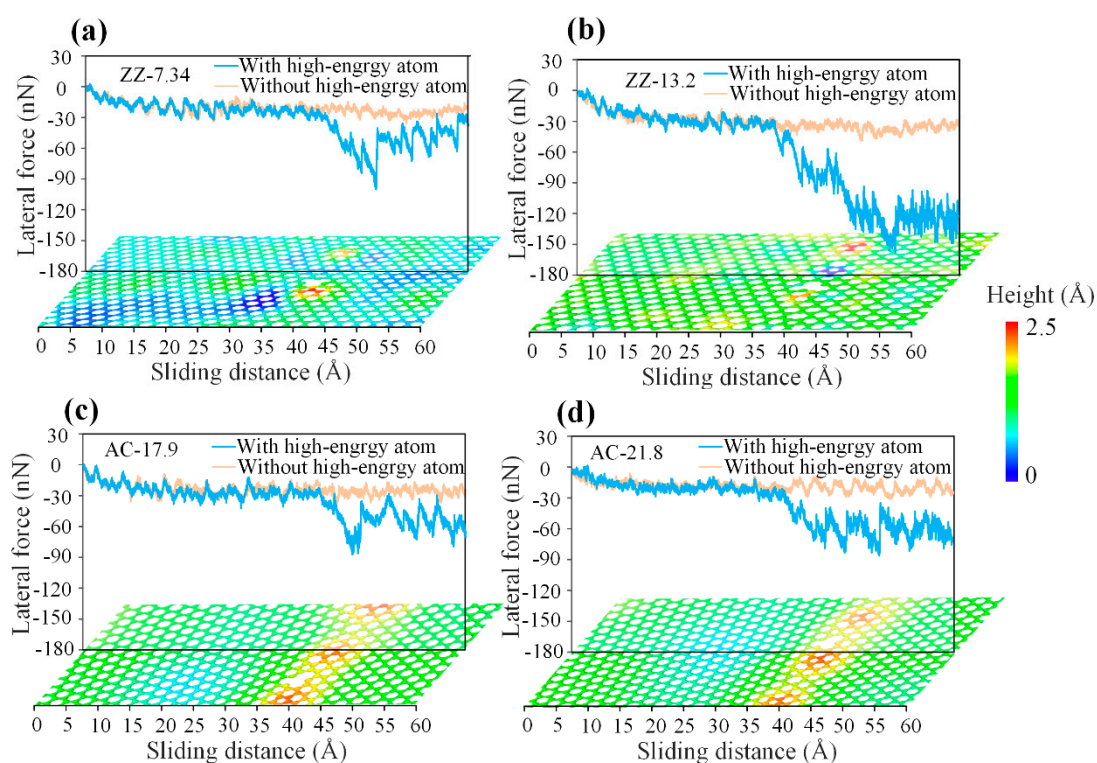


Figure 13. Variations in the lateral forces experienced by the tip during sliding on the film with and without high-energy atoms in cases where the GB-containing heterostructure films had different misorientation angles of: (a) ZZ-7.34, (b) ZZ-13.2, (c) AC-17.9, and (d) AC-21.8. The bottom image refers to the initial atomic height distribution of the film with point defects on the high-energy atoms before exerting a load on the MD contact system.

While the point defect located at high-energy atoms can alleviate the stress concentration, as shown in the figure, for the film with point defects located at high-energy atoms, although there was also a strain-induced hillock, the GB structure had little effect on the friction. Moreover, the wear resistance of the film was also improved, which could also be inferred from the fact that the friction experienced by the tip showed little change when the tip slid over the GBs. Therefore, high-energy atoms can pose a significant impact on the tribological characteristics of the polycrystalline heterostructure film. The point defect located at high-energy atoms can alleviate the stress concentration, thus improving the tribological performance of GB-containing films.

4. Conclusions

The graphene/*h*-BN heterostructure film showed excellent performance in friction reduction, wear resistance, and long-term corrosion resistance, especially in marine surroundings. Graphene tends to exist in a polycrystalline structure, and the existence of GB structures can significantly affect the physical and chemical properties of the film. In this study, the tribological properties of the GB-containing heterostructure films scratched by a diamond tip were studied with the molecular dynamics method. The GB misorientation angle of the bicrystal graphene film as well as the point defects occurring on GB structures were investigated to reveal their influence on the tribological characteristics of heterostructure films. The results led to a few major conclusions, as specified in the following:

- (1) The bicrystal structure has little influence on the friction resistance, but can reduce the mechanical strength and weaken the wear resistance performance of the heterostructure film. Furthermore, with the increase in GB misorientation angle, this weakening effect gradually decreases.
- (2) There exist high-energy atoms shared by heptagon and hexagon rings on the GBs, which can easily form interfacial bonds with the diamond tip. These atoms result from the misorientation angle of the GBs and can lead to stress concentration and large pre-strain of the covalent bond, thus significantly decreasing the wear resistance of the film.
- (3) The occurrence of point defects on the bicrystal graphene layer can reduce the strength and wear resistance of the heterostructure film. While the point defects occurring on high-energy atoms can significantly alleviate the stress concentration at GBs, this can obviously increase the mechanical strength of the heterostructure film, and thus is conducive to improving the wear resistance property of the film.

In addition, it should be highlighted that compared to bicrystal grains, the influence of multi-crystals on the frictional behavior of 2D materials is more complex due to the fact that the grain size and misorientation angle of grain boundaries can significantly affect the property of the film. The bicrystal case investigated in this study can be regarded as the foundation for tri-crystal and more complex scenarios. Furthermore, this study only considered single vacancy defects occurring on GB structures. Other typical point defects as well as line- and surface-like defects in the film will have different impacts on its physical and chemical properties. Tri-crystal and more complex multi-crystal structures, different defects as well as experimental verification will be further investigated in our future work.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants12080296/s1>, Movie S1: The initiation and propagation of the wear failure in the GB-containing heterostructure films (MP4). Figure S1: Schematic of scratch lines (SL) of the diamond tip (the red atoms represent the high-energy atoms in the corresponding path). Table S1: The critical normal load of the heterostructure film with different scratching paths.

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Data Availability Statement: The authors declare that all the relevant data are available within the paper and its Supporting Information file or from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

AIREBO: The AIREBO potential consists of three terms:

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} E_{ijkl}^{\text{TORSION}} \right] \quad (\text{A1})$$

E_{REBO} = REBO energy; E_{LJ} = Lennard-Jones energy; E_{TORSION} = Torsion energy.

Lennard-Jones potential:

$$r_c E = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r < r_c \quad (\text{A2})$$

where r_c is the cutoff.

EAM: EAM computes pairwise interactions for metals and metal alloys using the embedded-atom method (EAM) potentials (Daw). The total energy E_i of an atom i is given by

$$E_i = F_\alpha \left(\sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \quad (\text{A3})$$

where F is the embedding energy, which is a function of the atomic electron density ρ , ϕ is a pair potential interaction, and α and β are the element types of atoms i and j . The multi-body nature of the EAM potential is a result of the embedding energy term. Both summations in the formula are over all neighbors j of atom i within the cutoff distance.

Tersoff: The Tersoff style computes a 3-body Tersoff potential (Tersoff_1) for the energy E of a system of atoms as

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij} \quad (\text{A4})$$

where

$$\left\{ \begin{array}{l} V_{ij} = f_c(r_{ij}) [f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \\ f_c(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{r - R}{D}\right), & R - D < r < R + D \\ 0, & r > R + D \end{cases} \\ f_R(r) = A \exp(-\lambda_1 r) \\ f_A(r) = -B \exp(-\lambda_2 r) \\ b_{ij} = \left(1 + \beta^n \zeta_{ij}^n\right)^{-\frac{1}{2n}} \\ \zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) \exp\left[\lambda_3^m (r_{ij} - r_{ik})^m\right] \\ g(\theta) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (\cos \theta - \cos \theta_0)^2]}\right) \end{array} \right. \quad (\text{A5})$$

Lennard-Jones (LJ): The Lennard-Jones potential, also known as the L-J potential, or 6–12 potential, was first proposed by John Edward Lennard-Jones in 1924 to describe the interaction between two neutral atoms (molecules). It is the earliest two-body potential model proposed. The formula for the L-J potential is as follows:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r < r_c \quad (\text{A6})$$

where variable r is the distance between atom pairs; ϵ and σ are potential energy parameters depending on the type of atoms.

Minimize: Perform an energy minimization of the system by iteratively adjusting the atom coordinates. The objective function being minimized is the total potential energy of the system as a function of the N atom coordinates:

$$E(r_1, r_2, \dots, r_N) = \sum_{i,j} E_{pair}(r_i, r_j) + \sum_{ij} E_{bond}(r_i, r_j) + \sum_{ijk} E_{angle}(r_i, r_j, r_k) + \sum_{ijkl} E_{dihedral}(r_i, r_j, r_k, r_l) + \sum_{ijkl} E_{improper}(r_i, r_j, r_k, r_l) + \sum_i E_{fix}(r_i) \quad (A7)$$

where the first term is the sum of all non-bonded pairwise interactions including long-range Coulombic interactions, the second through fifth terms are the bond, angle, dihedral, and improper interactions, respectively, and the last term is energy due to fixes that can act as constraints or apply force to atoms.

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