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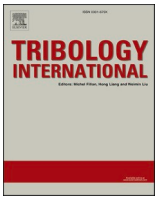

Lubrication of rough copper with few-layer graphene

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ABSTRACT

It has been demonstrated through experiments and simulations that friction decreases significantly when graphene is used as a solid lubricant on various materials. However, the effect of increasing the number of graphene layers on lubrication is controversial. Some studies predict an increase of friction with the number of layers that can be imputed to increased contact area, others a decrease in friction attributed to increased flexural rigidity of the layers. Herein, atomistic simulations are performed to investigate the atomic mechanisms by which few-layers graphene lubricate rough copper surfaces when probed by a smooth tip. The results of the simulations show that increasing the number of graphene layers drastically reduces friction, while the deformation mechanism is found to change from atomic wear to recoverable flattening of surface steps, as the amount of interlocking between the surfaces is reduced.

1. Introduction

Understanding the friction mechanism at the nanoscale is of critical importance to improve the reliability and lifetime of the micro-electro-mechanical systems with moving parts. The large surface-to-volume ratio of nanostructures renders friction and wear deleterious to many existing and potential applications. Owing to structural characteristics, the lubrication of nanodevices often exhibits special requirements, e.g., there can be limited space for the lubricants [1], a high working temperature [2] or a dry environment might be needed. For these reasons solid lubrication with graphene has recently become a valid alternative to other types of lubricants due to its excellent properties in terms of high chemical inertness, high thermal conductivity and thermal stability, and outstanding mechanical strength [3]. Great effort has been devoted to characterize graphene from a tribological viewpoint and it is now established that it presents ultra-low friction, wear reduction capabilities and even super-lubricity [4,5].

At the nanoscale the surfaces of solids are inherently rough, with roughness dictated by the fabrication technique [6]. Friction is known to increase with surface roughness. One of the roles of graphene as a solid lubricant is to mitigate the effect of roughness of the underlying solid and promote easier glide with a counter surface. Carpick and coworkers [7] measured through a silicon AFM tip the friction force exerted by CVD-deposited graphene flakes on polycrystalline copper and found a significant decrease in friction (up to 7 times reduction) when the tip probes the graphene flake compared with when it slides on the bare oxidized copper. From atomistic simulations, Wang *et* al. [8] found that with the aid of graphene, both friction and heat dissipation could be reduced significantly on rough gold surfaces, most significantly if the layer of graphene was stretched.

Adhesion between the graphene layer and the substrate is found to have opposite effects on friction for flat and rough substrates: when the adhesion between graphene and substrate increases, friction on flat substrates decreases, while it increases on rough substrates. This is because adhesion favors the suppression of wrinkles on flat substrates, decreasing the area of contact and thus friction, while on rough substrates it leads to a more intimate contact between the tip and the rough profile, thus increasing friction [9,10].

The lubricating properties of graphene seem to also depend on the number of graphene layers used as lubricant. On atomically flat substrates friction is found to increase with the number of graphene layers [11]. This effect is attributed to the change in contact area: the contact area between the tip and top graphene layer increases with layer number due to thermal effects and lattice mismatch, and leads, as a result, to an increase in friction [11]. An opposite trend is found for rough substrates, where few-layer graphene are found to be better lubricants than single layers. Lee *et al.* [9] exfoliated various graphene layers on a weekly adherent silicon oxide surface, and found that friction would decrease with increasing the number of graphene layers used as coating. Also in the study by Egberts *et al.* [7] the friction between the AFM tip and the

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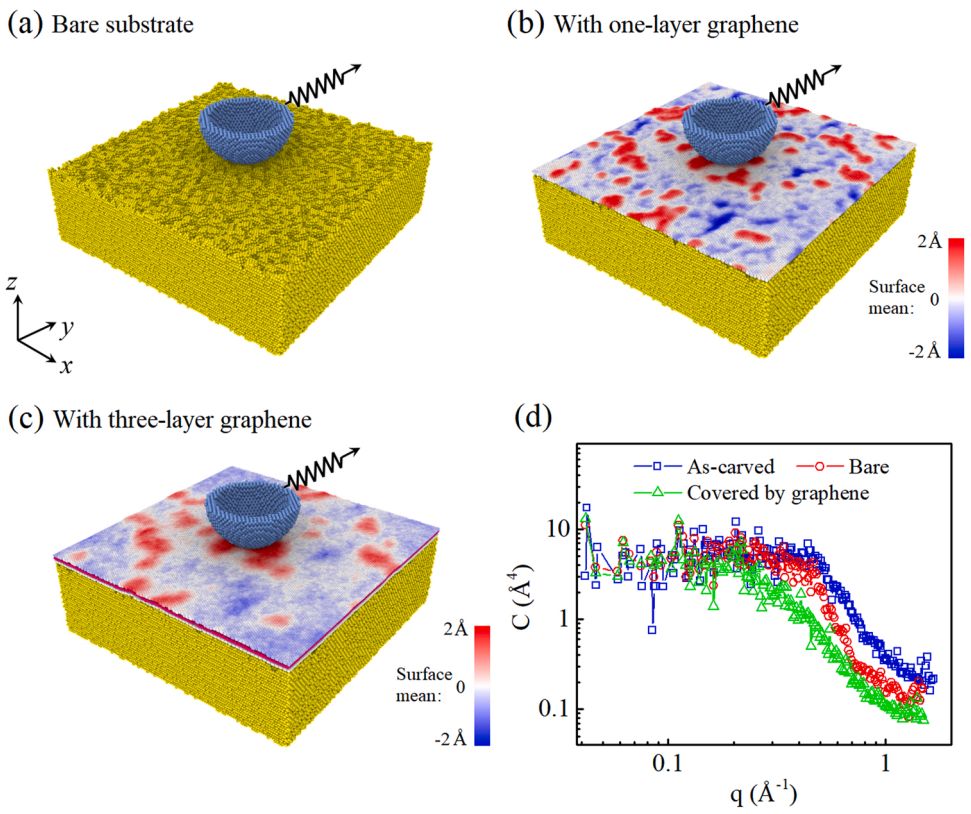

Fig. 1. The atomic models used in present study: (a) a bare substrate with *RMSH* of 2.5Å, (b) substrate with one graphene layer, (c) substrate with three graphene layers (substrates with two or four layers are not shown), and (d) the variation of the PSD of the rough copper substrates in different conditions: 'as-carved', bare, and covered by graphene.

polycrystalline copper would present a layer-dependent reduction in friction when multiple layers of graphene were used. To explain the experimental results, it was postulated that a single graphene layer would pucker ahead of the tip, leading to an increase of the contact area and therefore of friction. When using more layers of graphene as lubricant, instead, their higher stiffness would suppress puckering, decreasing the contact area and thus friction [9]. Atomistic simulations can be used to understand more in detail the lubrication effect of the graphene layers. Li and coworkers [12] studied through atomistic simulations the frictional response of a rough α-silicon substrate covered with graphene layers, they confirmed that lubrication increases with the number of graphene layers, and found additionally that the contact quality contributed to the layer dependence of friction [12], i.e., when a single graphene layer was used as lubricant, the local contact configurations between graphene and tip atoms gradually evolved into more commensurate states, enhancing the local pinning force on the tip atoms, while interfacial commensurability was decreased by the presence of a multilayer with perfect ". ABAB." stacking.

In most of the atomistic studies in the literature, the substrate is either amorphous or taken to be rigid to maintain a constant roughness during the simulations [9–12]. In the present study instead, we intend to focus on a deformable rough copper substrate and keep track on how elastic and plastic deformation influence the lubricating properties of graphene and multilayer graphene. It is expected that rough copper behaves rather different from silicon: the surface consists of many atomic steps, which can serve as strong pinning points during friction [13] but can also deform elastically or plastically, depending on the loads involved. Furthermore, the adhesion between graphene and copper is much higher than that between graphene and α-silicon [9], and adhesion is well-known to affect friction. In the present study, classical atomistic simulations are thus performed on rough deformable copper substrates, bare or covered by graphene layers. The focus of the work is on revealing the atomic scale mechanisms that control the frictional response of rough copper and how those are modified when few-layer graphene are used as a lubricant. As expected the roughness of the copper surface is found to change while the tip slides. When the substrate is bare, wear is found to be the dominant deformation process, which also controls friction. When few-layer graphene are used as lubricant, local wear is reduced or suppressed, and as a consequence friction drops.

2. Model and materials

A spherical and smooth silicon tip was used to probe the rough surface of a copper single crystal, and pristine graphene layers served as dry lubricant. The number of graphene layers was varied from zero to four. Fig. 1 shows the atomic models used in the present study. To analyze the lubrication effect, the response of the bare rough substrate and that of the same rough substrate covered with various graphene layers were compared. The rough copper substrate had a dimension of $30 \times 30 \times 10$ nm^3, with orientations [1$\bar{1}$0], [11$\bar{2}$] and [111] along the *x*-, *y*- and *z*-directions, respectively. The probing hollow silicon tip had an outer radius of 5 nm and a thickness of 1 nm. The size of the graphene layer in the *x*-*y* plane was selected to be the same as that of the copper substrate. Periodic boundary conditions were applied along both the *x*- and *y*-directions. The zigzag orientation of graphene was aligned along the *x*-direction, and the arm-chair orientation along the *y*-direction. The multilayer graphene had a stacking sequence of ". ABAB." when placed on the top of the rough substrate. To prepare the rough substrate, a bulk defect-free copper single crystal was first constructed with a lattice constant of 3.615 Å. An ideal rough surface, with Hurst exponent $H = 0.5$ and root mean square height $RMSH = 3.0$ Å, was used to carve the rough substrate out of the bulk single crystal copper, i.e., when the ideal rough surface was placed at a fixed position, copper atoms above the

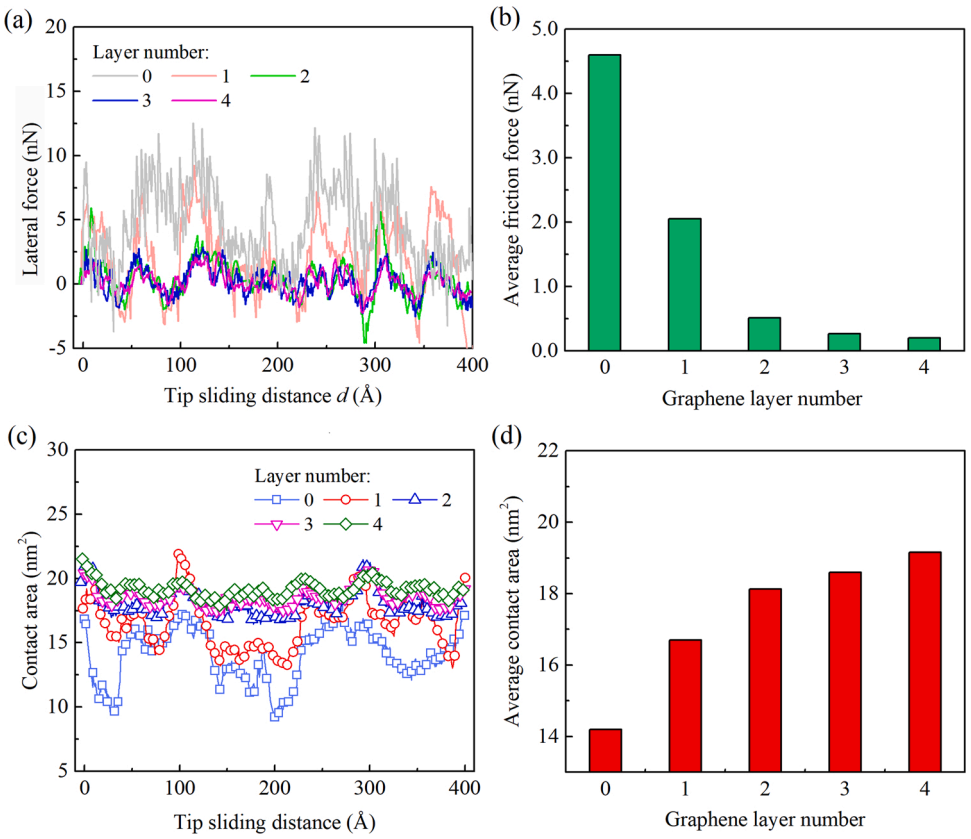

Fig. 2. (a) Variation of lateral force versus tip sliding distance when a different number of graphene layers is used as lubricant. (b) Comparison of the average friction forces. (c) Variation of the contact area versus tip sliding distance. (d) Comparison of the average contact areas.

surface were removed. We will refer to the resulting rough crystal as the 'as-carved' atomic rough substrate. The bottom atoms of the crystal (in a layer of thickness 1.5 nm) were kept fixed in a perfect FCC lattice throughout the simulations. The atoms just above, also in a layer of thickness 1.5 nm, were described in the framework of the canonical ensembles (NVT) and used as a heat-sink, to control the temperature at 300 K by means of a Nosé -Hoover thermostat [14,15]. The other atoms in the substrate and graphene layers were described in the micro-canonical ensembles (NVE), and no thermostat was used to avoid interference with the frictional behavior. A time step of 0.002 fs was employed in the time evolution of the atomic systems.

To describe the atomic interactions inside the copper substrate, the Embedded Atom Method (EAM) interatomic potential parameterized by Mishin et al. [16] was adopted. The atomic interactions in the silicon tip were described by the Stillinger-Weber potential [17], while for the graphene layers, the Adaptive Interatomic Reactive Empirical Bond-Order (AIREBO) potential [18] was selected. All other interactions such as those between substrate and graphene, and graphene and tip, were described by the classical 6–12 pairwise Lennard-Jones (LJ) potential. The parameters of the LJ potential were either fitted to the experimental data [12] or calculated according to the universal combination rules for atomic interactions [19,20].

First, atoms were removed from a copper crystal, such as to create the rough surface. The resulting rough copper substrate will be referred to as 'as-carved'. Structural relaxation was then conducted based on a conjugated method, followed by a dynamical equilibration when the substrate was dynamically relaxed at 300 K for about 0.5 ns. After the equilibration, atoms on the 'as-carved' rough surface slightly changed their positions to minimize the energy, and the *RMSH* decreased from 3.0 to 2.5 Å. When graphene layers were used as lubricant, they were placed on top of the rough substrate after the dynamical equilibration, and the atomic system as a whole was equilibrated again. The graphene layers conformed with the rough substrate surface owing to interfacial adhesion and good flexibility. It is noteworthy that the thermal dynamic equilibration and the conformation of the graphene layer with the substrate lead to a variation of the local roughness, and the power spectrum distribution (PSD) after equilibration is different from that of the 'as-carved' one (see Fig. 1d). When the substrates were ready, the silicon tip, treated as a rigid body, was placed on their top in the center. Except for the translation along *y*- and *z*-direction, all the degrees of freedom of the tip were constrained. A normal load of 20.0 nN was applied on the tip, and further relaxation was conducted, before sliding. A harmonic spring with stiffness $k = 25.0$ N/m was used to pull the silicon tip along the *y*-direction. One end of the spring was tethered to the tip, and the other free end moved at constant speed of 0.05 Å/ps. While moving, the tip experienced the force exerted by the spring, which was recorded as the lateral force. The average lateral force corresponds to the friction force when the substrate is flat. Here, we will assume that it is also on average similar to the friction force.

To calculate the contact area between the tip and the substrate, the following method has been adopted [21]: the atoms in the substrate lying in the force range of the tip are counted as being in contact and are then multiplied by the contact area per atom to obtain the real contact area. It should be noted that, when the substrate is bare, the contact area is that between the tip and copper substrate; when the substrate is covered by graphene layers, the contact area is that between the tip and the top-most graphene layer. All the simulations in the present study were carried out by means of the large scale open-source simulator LAMMPS [22]. The atomic configuration was visualized using the open-source package Ovito [23].

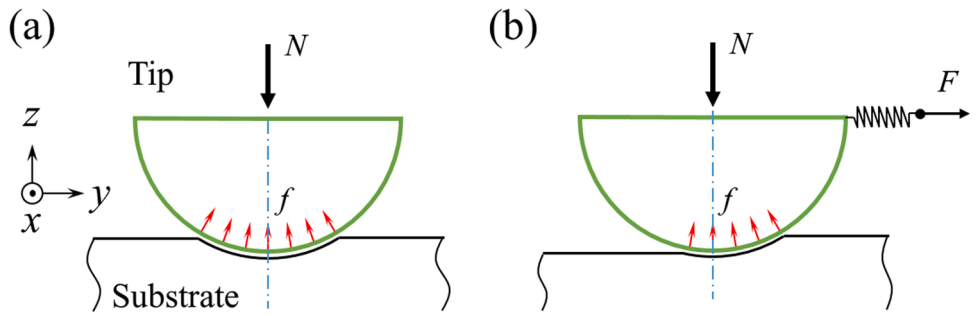

Fig. 3. Schematic representation of the forces exchanged between tip and substrate. (a) The contact is symmetric and loading of the tip is only normal. (b) The contact is asymmetric and loading is both in normal and tangential direction.

3. Frictional response of bare and lubricated substrates

3.1. The effect of graphene layers on friction and contact area

Friction simulations are performed on a rough copper substrate that is either bare or covered by a varying number of graphene layers, ranging from one to four. We sometimes refer to the bare substrate as the zero-layer graphene substrate. The lateral force with respect to the tip sliding distance is calculated for the various cases and presented in Fig. 2a. All the curves representing the lateral force are characterized by fluctuations along the tip sliding distance, due to the typical stick-slip behavior between tip and flat substrates magnified by the surface roughness. However, different characteristics are displayed when the number of graphene layer changes. When the silicon tip slides on the bare substrate, the lateral force curve exhibits irregular peaks with highest frequency and magnitude. When a single layer of graphene is used as lubricant, the frequency and magnitude of some peaks decreases (see, for instance, at the tip sliding distance around 80 $\AA$, the differences between the bare substrate and that with one-layer graphene). As the number of graphene layer increases from two to four, the overall

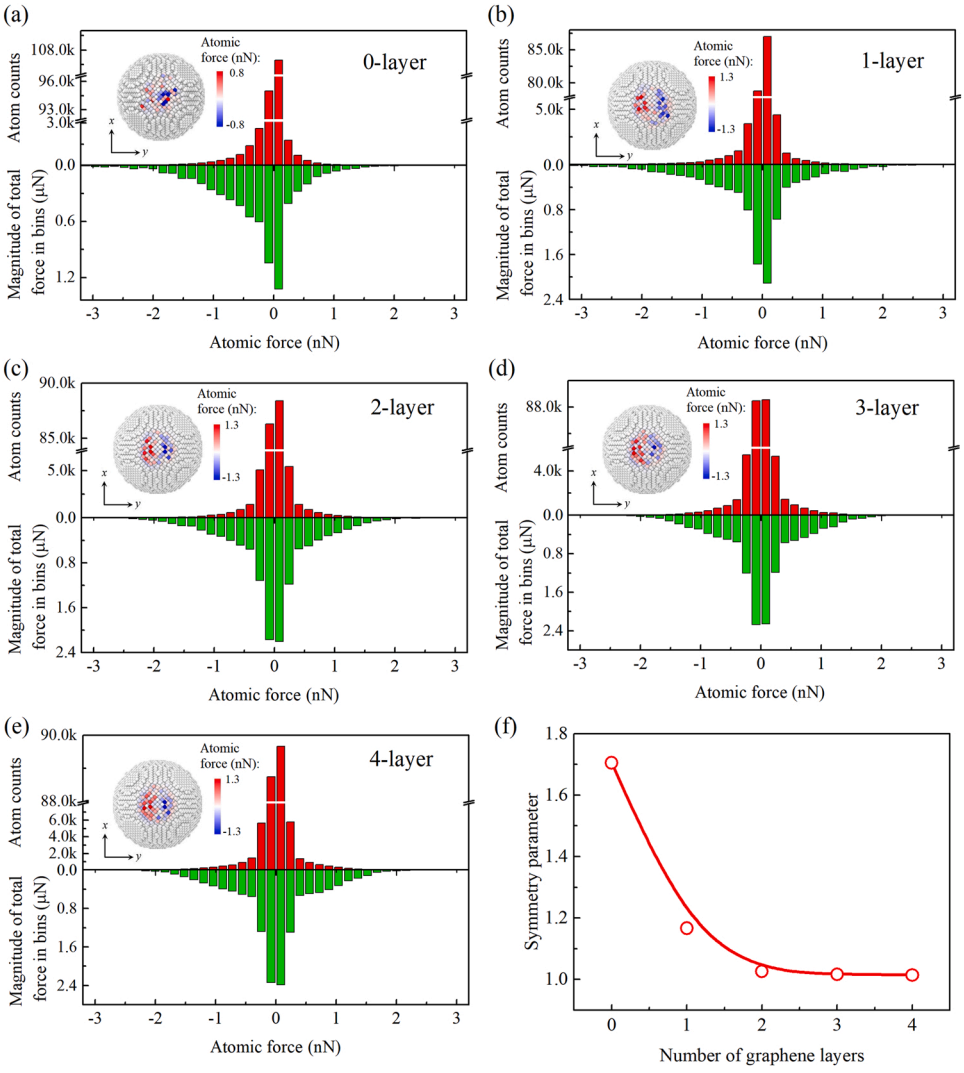

Fig. 4. (a–e) The figures show the distribution of the lateral force acting on the atoms in contact with the tip for the various cases where lubrication is provided by 'n' graphene layers, with n ranging from 0 to 4. On the top panel, the red histogram gives the number of atoms that have a certain lateral force. The lateral atomic force, ranging approximately from −3nN to 3nN is divided in bins. The total lateral force in each bin is given in the bottom panel by the green histogram. The inset shows the atomic interfacial force distribution of the tip atoms at the beginning of tip sliding. (f) Variation of the symmetry parameter of the force distribution in (a–e).

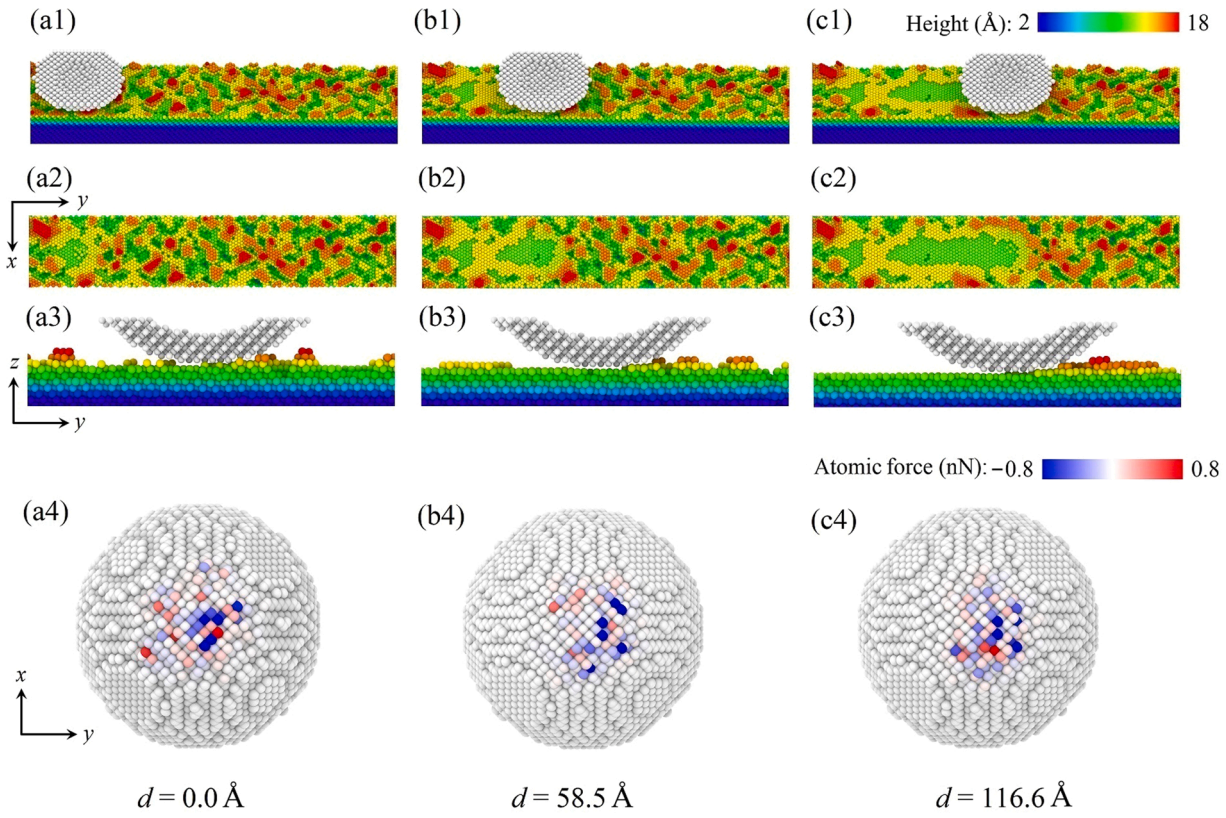

Fig. 5. Bare substrate at the beginning of the simulation, for $d = 0.$ Å, (a1) a top view of the bare substrate showing also the tip; (a2) a top view of the substrate with the tip not shown (a3) a side view of the region around the tip; (a4) the lateral force experienced by the tip atoms. In (b1–b4) and (c1–c4), the same figures are shown at the tip sliding distances $d = 58.5$ Å and $d = 116.6$ Å, respectively.

fluctuation decreases more significantly, while the curves start to converge. This indicates that the increasing number of graphene layers enhances lubrication up to a certain limit (that in this case is 3 or 4 layers), but a further increase in the number of layers does not have a significant effect.

Based on the obtained lateral force curves, the average friction forces are calculated and compared in Fig. 2b. Note that the graphene layers are extremly effective in reducing the friction force: already a single layer decreases the average friction force by more than 50%, while with four layers we reach a decrease by 96%. Our findings are thus qualitatively consistent with those reported in [12] for the case of a rough α-silicon substrate and in [9,11] for the rough silicon dioxide substrates.

The contact area during sliding is calculated and presented as a function of tip sliding distance in Fig. 2c. When the substrate is bare, the contact area changes drastically in the range between 10.0 and 17.5 nm^2 as the tip slides. The variation of contact area indicates that the atomic morphology in the contact region changes markedly when the tip slides over. When a single graphene layer is used as lubricant, the magnitude of the contact area still fluctuates visibly, and on average is larger than that between the tip and the bare substrate. With multiple graphene layers the variation of the contact area is smaller, but its average is larger, as can be better seen in Fig. 2d where the average contact areas are reported for the various numbers of graphene layers. It is evident that the average contact area between tip and graphene increases with the number of graphene layers. Therefore, our findings demonstrate that friction decreases with the number of layers, despite contact area increases. This seems to be at odds with the usual macroscale dependency of friction on contact area and also on the similar nanoscale dependency shown, for instance, on an atomically flat substrate by Mo and co-authors [24]. When considering the literature on multi-layer graphene, our findings are consistent with those reported for rough silicon dioxide (SiO_2) substrates [11], where contact area increases with the number of graphene layers, but opposite to the results obtained for rough amorphous silicon. For both substrates, however, the friction force decreases with the number of graphene layers. This indicates that the decrease in contact area is not the dominant factor in the lubricating effect of multilayer graphene. A more detailed analysis of the origin of friction in our simulations will be conducted in the following sections.

3.2. *Distribution of the interfacial force on the tip atoms*

As shown schematically in Fig. 3a, when a spherical tip indents a solid substrate, the substrate responds through a distributed force along the contact area with normal and tangential component. While the net normal component equals the applied load the net tangential component is zero. When the tip is also pulled in y-direction by the spring, the substrate resists the tangential loading with a net tangential force different from zero, the friction force (see Fig. 3b). The deeper the tip enters the substrate, the larger the resistance to the pulling force. In general, on a rough substrate the contact between the tip and the substrate is not nicely symmetric as in Fig. 3a, owing to the original roughness and also to the roughening caused by deformation. Every 'hill' or 'bump' that the indenter finds in its path, opposes tangential loading and acts as an additional resistance to the pulling force.

The distribution of the lateral force in the simulations for the various graphene layers presented in the previous section, is here analyzed. The inertial component of the force acting on the moving tip is found to be very small, about ~ 0.1 nN, smaller than one percent of the maximum lateral force of the tip, and is therefore neglected. First, the interfacial tangential forces on the tip atoms are calculated. Then, the values, which range approximately from -3nN to 3nN are distributed in 40 bins, and the number of tip atoms with lateral interfacial force lying in each bin is counted. The red histogram in Fig. 4 gives the number of atoms that lie in each bin. The green histogram, instead, gives the total atomic force

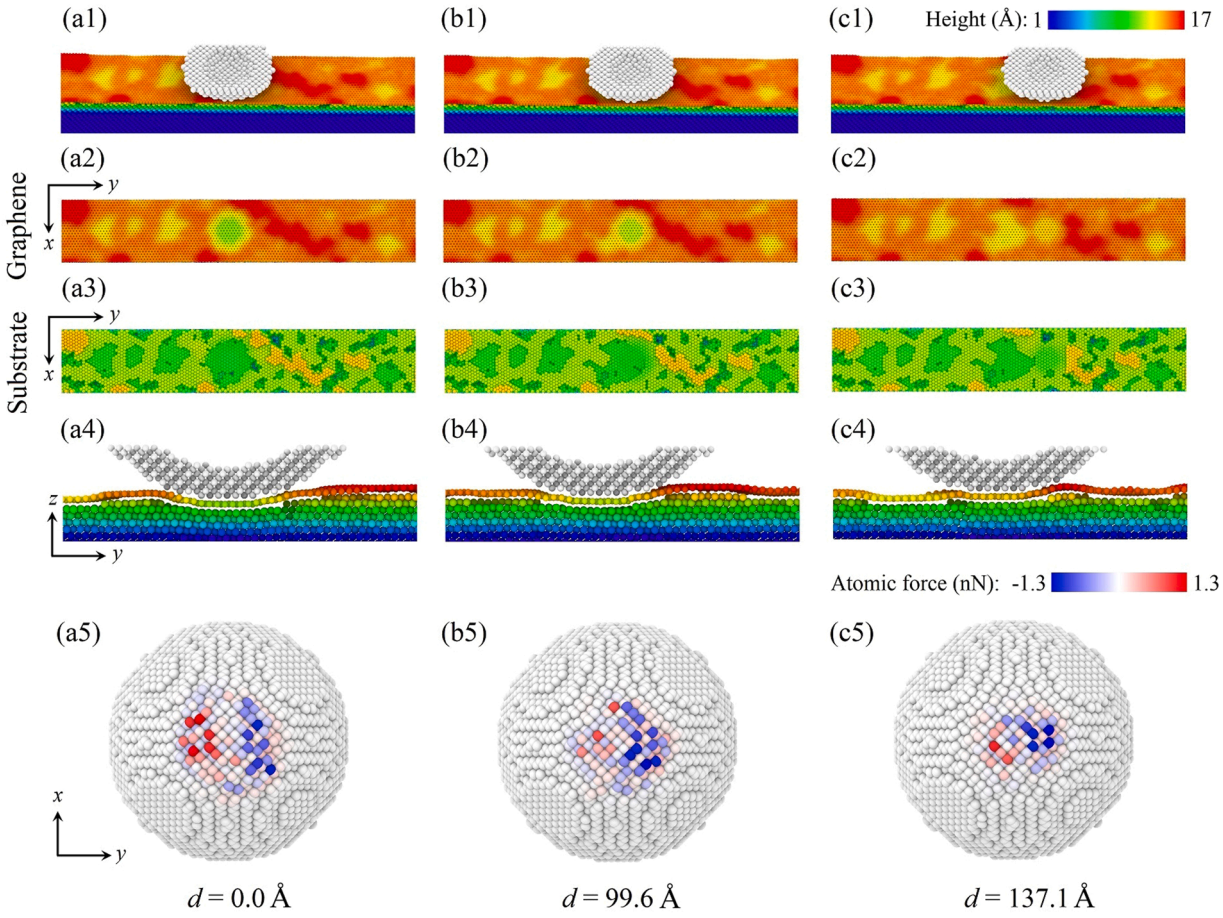

Fig. 6. Substrate covered by a single graphene layer at the beginning of the simulation, for $d = 0.0$ Å, (a1) a top view of the covered substrate showing also the tip; (a2) a top view of the graphene layer with the tip not shown: (a3) a top view of the substrate with the tip not shown (a) a side view of the region around the tip; (a) the lateral force experienced by the tip atoms. In (b1–b) and (c1–c), the same figures are shown at the tip sliding distances $d = 58.5$ Å and $d = 116.6$ Å, respectively.

per bin. The insets to the figure show the atomic interfacial force distribution of the tip atoms at the beginning of tip sliding.

First, the simulation for the bare substrate is considered in Fig. 4a. It is noted that the distribution of forces is strongly non symmetric, and while many atoms experience a lateral force that is nearly zero, there is a significant number of atoms on which a negative force is exerted. This is an indication that much interlocking took place. When the substrate is covered by graphene with increasing layer number, Fig. 4b–e, the distribution of the interfacial force becomes progressively more symmetric, indicating that the net friction force became smaller and smaller. In order to quantify the variation in the symmetry characteristics of the interfacial force distribution, a symmetry parameter S is defined as

$$S = -F_N/F_P \tag{1}$$

where F_N is the sum of the negative bin forces, and F_P is the sum of the positive bin forces. In Fig. 4f, the symmetry parameter is found to monotonically decrease as the graphene layer number increases, indicating a decreasing friction. The decrease in the symmetry parameter is fast when passing from the bare substrate to one and two graphene layers, then it becomes slow. This indicates that while interlocking was the driving mechanism in the bare substrate, it was suppressed by the few-layers graphene.

3.3. The frictional mechanisms at the atomic scale

The rough copper surface consists of surface steps, atomic 'valleys' and 'hills'. When the silicon tip slides on a rough surface, interlocking between the tip and surface steps often occurs. With the progressing of tip sliding, the atoms composing the surface steps are pushed forward and the atomic 'ridges' are worn away. Meanwhile, the atomic 'valleys' in front of the tip are filled up by the removed atoms (Fig. 5). A similar wear mechanism has been reported in our previous study with a quasi-3D atomistic model [21] where the phenomenon was even more evident due to the two-dimensional nature of the body. Also in three dimensions, after the tip moves away, a flattened slip path is left behind the tip. The accumulation of atoms in front of the tip, caused by the wear mechanism, leads to a larger intimate contact between the front half of the tip and the substrate and a greater asymmetry in the contact shape, as can be seen in the snapshots of Fig. 5. For three sliding distances of the friction simulation, the distribution of the atomic interfacial tangential force experienced by the tip atoms is depicted in Fig. 5 in subfigures a4, b4 and c4. It is shown that the tip atoms involved in interlocking undergo a strong interfacial force.

When a single graphene layer is used as lubricant the frictional mechanism changes from atomic wear to recoverable flattening of the surface 'hills'. It is important to notice, however, that the substrate roughness, even before the tip is positioned on the graphene layer, is not as pronounced as it is in the case of a bare substrate. As previously mentioned, although we started from the same 'as-carved' rough surface, relaxation with and without the graphene layer leads to different roughness (see Fig. 1(d)). This entails that the covered copper surface has, already before being loaded, less protruding 'hills' and is therefore less prone to interlocking. The deformation mechanism can be observed in Fig. 6: after indentation, the tip is located in a valley. When the tip moves forward, it first approaches the hill, which has more the shape of a surface step, at the edge of the valley. As it moves further, instead of

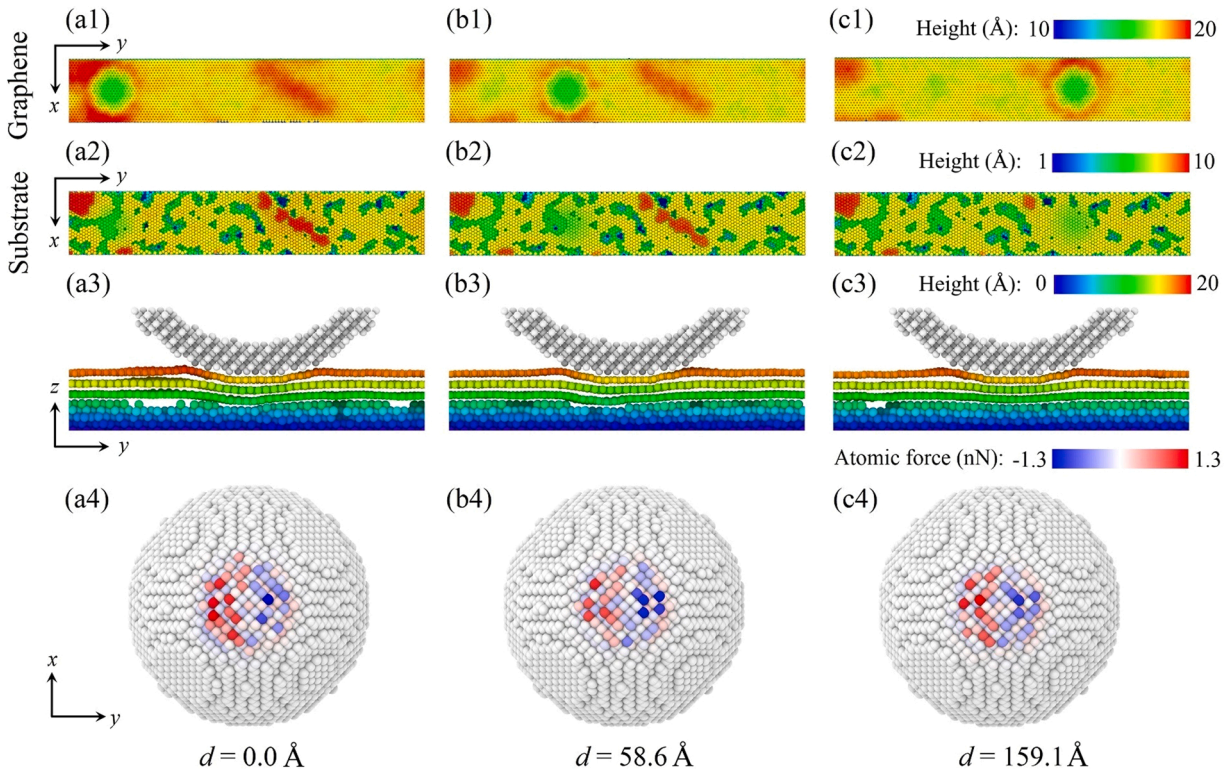

Fig. 7. Substrate covered by three graphene layers at the beginning of the simulation, for $d = 0.0$ Å, (a1) a top view of the covered substrate; (a2) a top view of the substrate with the tip not shown: (a3) a side view of the region around the tip; (a4) the lateral force experienced by the tip atoms. In (b1–b4) and (c1–c4), the same figures are shown at the tip sliding distances $d = 58.5$ Å and $d = 116.6$ Å, respectively.

pushing the atomic step forward, it climbs over it and flattens it (Fig. 6b3 and b4). After the tip moves away, the surface step recovers (Fig. 6c3 and c4), demonstating that the defomration was reversible and thus only elastic. With the aid of the graphene layer, less atoms are worn away except some small atomic hill on the top, and the surface morphology does not change much compared to the variations in morphology observed in the bare substrate. Also, for the covered substrate, fewer copper atoms are accumulated in front of the tip compared with the bare substrate. Since the cohesive energy between graphene and copper is higher than that between graphene and α-silicon [12], the graphene layer conforms well with the copper substrate and the puckering of graphene observed in that study is here barely observed. Because of less wear, the intimate contact could occur both in the rear and front of the tip as shown in Fig. 6a4, b4 and c4. Therefore, the contact is rather symmetric with respect to the middle x-z plane of the tip.

When multiple graphene layers are placed on top of the rough substrate, atomic wear is restricted even further, interlocking is absent, and even the flattening of surface steps is prohibited. Fig. 7 shows snapshots of the simulations for the substrate covered with three layers of graphene. While the single graphene layer has a high out-of-plane flexibility, and conforms rather well with the substrate; the bending stiffness of a multilayer of graphene is larger [12,25], and prevents it from conforming to the rough substrate. This can be seen in Fig. 7a3, where the graphene layers are suspended on an atomic 'valley', rather than

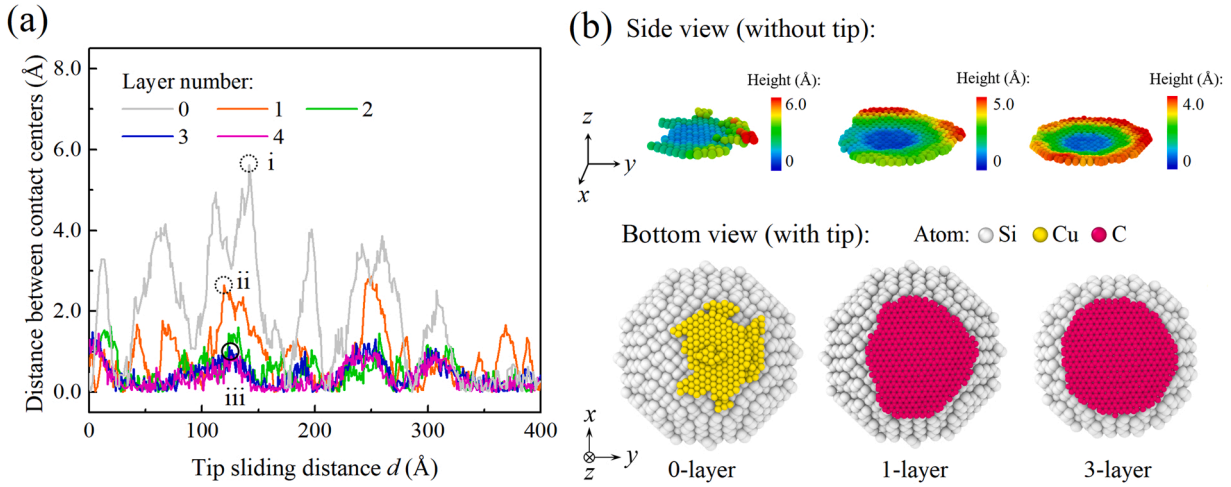

Fig. 8. (a) The variation of the distance between mass centers of the tip and the substrate contact atoms during tip sliding. (b) The atomic morphologies of the tip and contact atoms corresponding to the three points marked in (a).

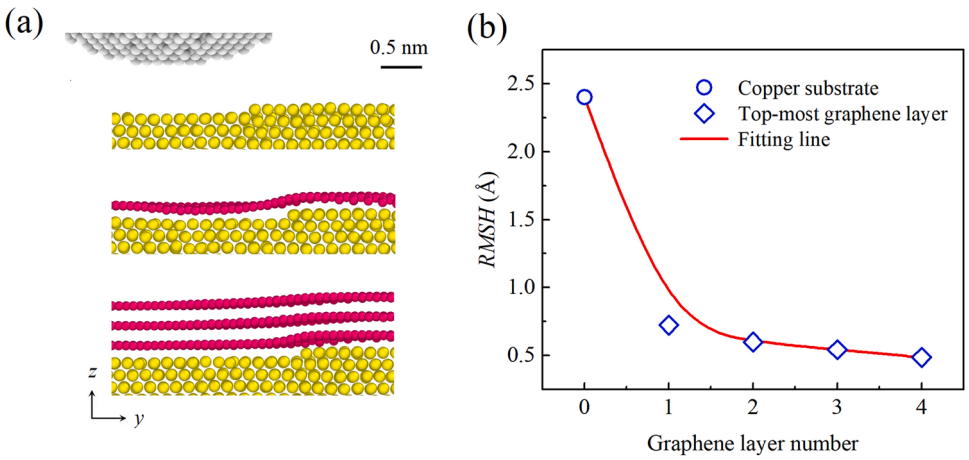

Fig. 9. (a) Atomic configurations around a unit surface step of a bare substrate, a substrate covered with a single layer of graphene, and a substrate with three layers of graphene. (b) *RMSH* of the top-most graphene layer varies with layer number.

intimately making contact with the bottom of the 'valley'. The layers thus decrease the effective roughness of the substrate such that the *RMSH* of the top-most graphene layer, which is in contact with the tip is significantly decreased [11] and the interlocking fully suppressed. The top-most graphene layer experiences weak adhesion forces from the tip and the graphene layers below, and is also sheltered from the stronger adhesion forces from the copper substrate. As a result, the top-most graphene layer tends to pucker locally towards the tip around the contact fringe, both at the front and at the rear, such that the contact is nicely symmetric irrespective of the underlying surface roughness. At the beginning of simulation, the tip is located right on top of a surface step, which does not flatten (Fig. 7a1–a3). As the tip moves forward the atomic steps withstand wear (Fig. 7b1–b3) and the original rough copper surface is well preserved except for very small atomic islands that are worn and fill up atomic 'valleys'. It is mostly the lack of interlocking, inhibited by the larger bending stiffness of the multilayer which shelters the tip from the rough surface, that gives rise to optimal lubrication.

4. Pile-ups and interlocking

To quantify the variation of contact symmetry during sliding, i.e., the varying pile-up of material in front of the contact due to deformation and wear, we calculate the distance between the mass center of the tip and that of the substrate atoms in contact with the tip. When the contact between the tip and the substrate is symmetric with respect to the middle *x-z* plane of the tip, the mass centers overlap in the *x-y* plane, and the in-plane distance is zero. When there is an asymmetry due to more material piling up at the front of the contact, the distance is larger than zero. As shown in Fig. 8a, the curve representing the distance between mass centers during tip sliding for the bare substrate has the largest variations, the multilayers have the smallest variations. On a bare substrate, atomic wear changes the contact morphology drastically. When the removed atoms are accumulated in front of the tip, the frontal part the of the tip has a larger contact area than the other part and the in-plane distance between mass centers increases. When the removed atoms fill up the atomic 'valleys', less atoms are accumulated ahead of the tip, and contact becomes more symmetric, leading to a decrease of the in-plane distance. As more graphene layers are used as lubricants, less atomic wear occurs, the curves exhibit lower fluctuation, and the overall average values decrease. Fig. 8b shows the atomic morphologies of the contact regions at the three points marked in Fig. 8a with Roman numbers. It is evident that the more graphene layers serve as lubricants, the more regular and symmetric the contact becomes.

Besides pile-ups causing significant contact asymmetry and providing evident resistance to sliding, the lateral interfacial force distribution is also affected by local interlocking around surface steps. To demonstrate the decreasing interlocking effect with more graphene layers, the simple scenario of a unit step is considered in Fig. 9a for a

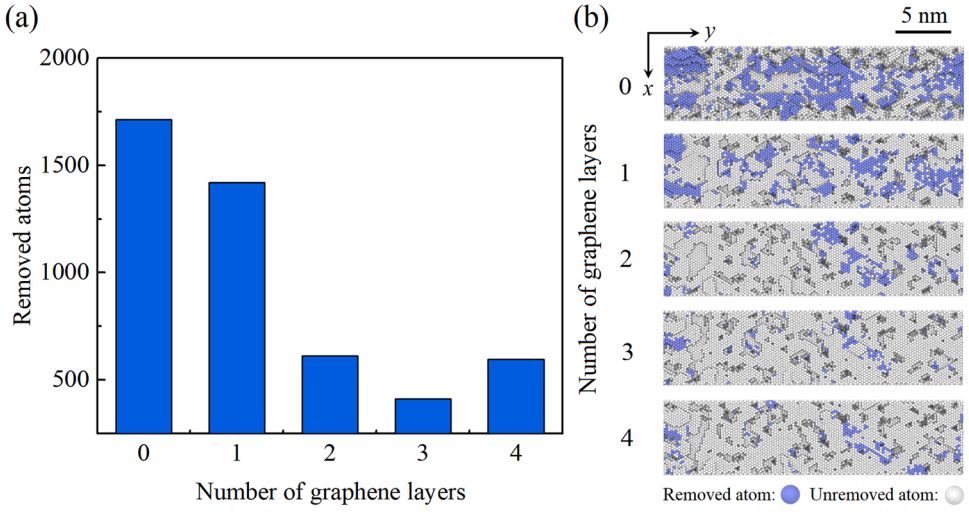

Fig. 10. (a) Worn atoms for the various simulation cases. (b) The distribution of the worn atoms of the rough substrate in different cases.

varying number of graphene layers. Clearly, the bare substrate has a sharp height change due to the surface step, which is prone to interlocking with the sharp atomic steps that are also present in the silicon tip. When the substrate step is instead covered by graphene layers, the height of the coating smoothly varies from the lower to the higher side of the step.

For the actual rough substrates used in the previous sections, the reduction in the sharpness of the surface steps reflects in a reduction of the *RMSH* of the top-most graphene layer (Fig. 9b), and a consequent reduction of the friction force with increasing number of graphene layers. The reduced roughness of the top most graphene layer is also the reason for the increase in contact area with the number of graphene layers. The puckering of the graphene layer is not particularly pronounced, contrary to what observed in the study on α-silicon [12] because the adhesive interaction between copper and graphene is rather strong.

4.1. Wear

In this section we measure the amount of wear that occurs with different layers of graphene. We assume that if the displacement of an atom with respect to its initial position is larger than the magnitude of the Burger's vector of a <111>/2 perfect dislocation, the atom can be considered worn away. As shown in Fig. 10(a), the number of the removed atoms is largest on the bare substrate where atomic wear dominates. When more graphene layers are used, fewer atoms are removed by the tip. However, when only one layer of graphene is used as lubricant, the number of removed atoms is close to that of the bare substrate and larger than that when multiple graphene layers are used. This happens because the single graphene layer conforms with the substrate better than the multiple graphene layers and the tip can still experience the morphology variation of the rough substrate. When the tip moves forward, it only flattens the step in the sliding direction, while the steps along the *x*-axis are pushed away. Therefore, the number of removed atoms is still significant. When two or more graphene layers are used, the multilayer has a higher bending stiffness, which decreases the interlocking effect of the surface steps in any direction, therefore, there is less wear.

5. Conclusions

In the present study, atomistic simulations are performed to investigate the lubrication effect of few-layers graphene on a copper rough substrate. The study is motivated by the controversial results in the literature related to the effect on lubrication of more than a single sheet of solid lubricant. Some studies report a reduction in friction with increasing number of layers of lubricant sheet [11,12,26], others a reduction in friction [5,4,3]. Here, we are interested in understanding whether few-layers graphene can effectively be used as solid lubricant on rough metal surfaces, and how the presence of the various layers of graphene affects the way in which the metal surface deforms, while a tip slides on it.

Results of the simulations have demonstrated that friction reduces by about 50% when a rough metal crystal is covered by a single graphene sheet. Increasing the number of graphene layers further improves lubrication, at the point that with four layers of graphene, friction is reduced by 95%. Although the contact area increases with increasing the number of graphene layers the friction force decreases, because the tip is more and more isolated from the roughness of the copper substrate. The first graphene layer protects the rough surface from wear, by preventing the tip from interlocking with the rough surface. With an additional layer of graphene the leading deformation mechanism is flattening of the surface steps by means of the tip, which is sufficiently sheltered from the roughness to be able to climb on the steps instead of shearing them away. With the small normal force used in the simulations, the steps recover after the tip moves away, demonstrating that the deformation is predominantly elastic. Finally with many sheets the tip does no longer interact with the roughness and slides on an almost flat top-graphene layer. The contact area, despite larger than for a single layer, is very symmetric, and provides very small resistance to the advancement of the tip.

Declaration of Competing Interest

There are no competing financial interests.

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