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Abstract
We investigate the nanoscale frictional behaviors and characteristics of mono-, bi-, and tri-layer graphene/Cu (1 1 1) systems using molecular dynamics simulations. The existence of graphene layers significantly enhances the load carrying capacity, extends the low friction range, and effectively decreases the friction. The friction coefficient depends on the normal force, which is very distinctive in contrast to classic friction laws and shows the nanoscale effect. The stable friction coefficients are 0.24, 0.18, and 0.11 for monolayer, bilayer, and trilayer graphene, respectively. Such distinguishable nanofriction behaviors suggest an experimental routine to characterize the number of graphene layers on copper foil or other substrates through nanoscratching as an alternative approach to Raman spectroscopy.

1. Introduction
Since its first exfoliation from graphite crystals in 2004 [1], graphene, with its distinctive band structure and fascinating combination of extraordinary properties, has attracted enormous attention in scientific and industrial communities because of its potential for various applications in graphene-based composites [2], nano-devices [3], energy storage materials [4], and so on. As the strongest ever measured [5], gas-impermeable [6], chemically and thermally stable [7,8], and atomically thick material [1], graphene is an excellent candidate as a protective coating or solid lubricant for enhancing surfaces, reducing adhesion, friction, and wear when coated on various surfaces so as to extend the longevity of graphene-based devices [9–13].

The microscale and nanoscale friction characteristics of micro-electro-mechanical-systems (MEMS) and nano-electro-mechanical-systems (NEMS) devices play an important role in determining performance, reliability, and lifetime of the overall system [14,15]. As such, controlling and minimizing friction and wear-related mechanical failures remains one of the greatest challenges for contemporary moving assemblies. Nanoscale friction on graphene exhibits different behaviors from its 3D counterpart [16,17] because of its large surface-to-volume ratio, super-high mechanical stiffness, and strength [5]; all are highly desirable for wear protection. Most experimental studies have reported ultralow friction [18], or even superlubricity [19] sometimes accompanied by wear reduction [20]. The coefficient of friction for SiO2 reduces from 0.68 to 0.12–0.22 after coating it with monolayer graphene [12]. Suspended graphene exhibits distinctive behavior in which nanoscale friction first increases and then decreases with increasing loads [21]. Deng et al. reported an adhesion-dependent negative friction coefficient on chemically modified graphite at the nanoscale [22]. Zhang et al. experimentally studied the nanoscale friction characteristics of graphene exfoliated onto weakly adherent silica substrates, and found that surface fluctuations are the main reason behind the suppression of thermal lubrication, which leads to an increase in friction force with temperature [23,24]. A scanning probe technique provides a clearer picture of friction at the nanometer scale, and an understanding of friction in layered materials [25]. The friction is attributable to the interaction between the incommensurate interface lattices [26], and is dominated by the so-called mechanism of “puckering” in front of the scanning tip, which increases the contact area and, therefore, the amount of friction [17]. Smolyanitsky et al. demonstrated that the experimentally observed reduction of friction with an increasing number of graphene layers in case of a narrow scanning tip can be a result of decreased sample deformation energy due to increased local contact stiffness under the scanning tip [27], and an increase of friction when the scanning tip is retracted away from the sample [28]. The JKR model [29] and DMT [30] model are generally successful in explaining friction behavior between smooth surfaces of various geometries, however, there is a lack of atomistic insight into the tip-sample interactions. So, detailed atomistic simulation has emerged as important...
method to describe the nanoscale friction characteristics [16,27]. In brief, the factors including load [21], properties and roughness of substrate [31], scratch velocity [32,33], adhesion strength between contact surfaces [34], tip sizes [28] and temperature [35] significantly affect the friction properties of graphene or graphene-coated materials.

The number of graphene layers may be another important factor affecting the friction behaviors and characteristics of the overall system. Once more graphene layers are present, the interlayer van der Waals interaction can minimize the puckering effect and thereby reduce the friction. FFM (friction force microscopy) measurements found that monolayer epitaxial graphene on SiC exhibits higher friction than bilayer graphene [36]. Solution-processed graphene layers reduce friction and wear on steel surfaces in air [20]. However, there are few reports on the layer-dependent nanofriction of graphene coated systems [37]. The atomic characteristics are as of yet unexplored. Furthermore, it is especially interesting to investigate the friction properties of metal foils coated with graphene. Graphene grown on copper foils using the chemical vapor deposition method supplies the perfect test sample which shows great merit as a surface coating because of its excellent scalability and transferability [38]. In addition, there is no contamination and damage existing as there is no complex transfer process of graphene, such as PMMA (polymethyl methacrylate), which is typically used for the transfer process, that may have a significant effect on the results. The fundamental understanding of the atomistic process governing the friction behaviors and characteristics of multi-layer graphene/copper systems is still lacking.

In this study, we employ a faithful atomistic modeling to elucidate the friction behavior of graphene coated copper films, as well as the characteristics. The graphene/Cu system is selected because graphene on Cu (111) has a higher quality than that grown on other crystal orientations of copper [39]. We conduct atomic nano-indentation and scratching simulations of monolayer, bilayer, and trilayer graphene supported by a single crystal Cu (111) substrate. We have found that the friction reduces as the number of graphene layers increases. The corresponding behaviors and characteristics are explored in atomistic detail and excellent agreement with experiment is achieved.

2. Modeling and method

Our molecular dynamics (MD) calculations in this study are performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [40]. We have used a rigid hemispherical diamond tip with a 2.5 nm radius to indent graphene layers grown on a Cu (111) substrate as shown in Fig. 1. Our model is smaller than that used in recent nano-indentation experiments, which has a size of 15.37 nm × 16.24 nm × 14.81 nm. However, our model dimension sizes are sufficiently large to simulate a semi-infinite boundary since the Cu (111) substrate block is cubic with a side length of around 5 times the tip radius [41] and the stress is localized and not impacted by the boundaries. In addition, the periodic boundaries are also employed in both lateral directions to avoid spurious edge effects. The choice above represents a compromise that minimizes finite-size effects while keeping the simulations affordable.

The quality of the MD simulation results significantly depends on the accuracy of the potential function used. The adaptive inter-molecular reactive empirical bond order (AIREBO) potential [42] is used to describe the interatomic interaction for the tip and graphene, because it has been shown to accurately capture the bond-bond interaction between carbon and hydrogen atoms as well as bond breaking and bond reforming. Therefore, the AIREBO potential is also reliable for the studies of friction on graphene. The interaction cutoff distance in the switching function of the AIREBO potential must be selected carefully to avoid the known spurious post-hardening behavior arising from an improper cutoff distance. We set the cutoff distance to be 2.0 Å as suggested in [43]. Interatomic forces within the Cu (111) substrate are derived from an embedded atom method potential [44]. The interactions between tip and graphene, tip and copper, and graphene and copper are described by the van der Waals interaction as a 12–6 Lennard–Jones (LJ) potential. The parameters of the LJ potentials in our model are as follows: $\epsilon_{C–C} = 2.86$ meV, $\sigma_{C–C} = 0.347$ nm, $\epsilon_{C–Cu} = 11.7$ meV, $\sigma_{C–Cu} = 0.300$ nm [45], which actually indicates the adhesion strength between the tip, graphene, and substrate, a key factor in determining the frictional characteristics of the system.

The time increment of simulations is fixed at 1.0 fs, and a Langevin thermostat is applied to the whole system to maintain a stable temperature of 300 K. Firstly, the system is relaxed to minimum energy state for 15 ps. Then, the tip moves down and penetrates into the graphene/Cu (111) system at the speed of 0.05 nm/ps while the bottom copper atoms with thickness of 0.55 nm are fixed. Finally, the tip scratches laterally at a speed of 0.015 nm/ps while the normal ($F_N$) and lateral forces ($F_L$) acting on the rigid tip are recorded, which gives us much information of the scratch process of the tip on monolayer, bilayer, and trilayer graphene/Cu (111). Using the three procedures above, we can study the nanoscale friction behaviors and characteristics of different layers of graphene/Cu (111) systems by gradually changing the nano-indentation depth. In order to assess graphene’s protective potential, analogous indentation and scratch simulations with a bare Cu (111) substrate are also performed.

3. Results and discussion

3.1. Scratching

A qualitatively distinct scratch behavior for a 2.06 nm nano-indentation depth on a monolayer graphene/Cu (111) system is presented in Fig. 2. After a nano-indentation depth of 2.06 nm,
the tip scratch laterally (Fig. 2(a)) above the surface, and the \( F_L \) and \( F_N \) on it are shown in Fig. 2(b). Initially, \( F_L \) increases while the \( F_N \) decreases with fluctuations, and both of them become stable after scratching about 2.40 nm laterally. The phenomenon is also present in that of tip scratching laterally on graphene/Pt system [41] because of periodic lattices of graphene and the underlying substrate. We consider the values after \( L = 2.40 \) nm as \( F_L = 142.57 \pm 8.56 \) nN, \( F_N = 494.45 \pm 14.45 \) nN.

Similarly, the \( F_L \) and \( F_N \) at different nano-indentation depths are calculated at the state before the rupture of graphene, as shown in Fig. 3. We choose some critical value point and insert its corresponding state of nano-indentation and scratching laterally. The state after the rupture of graphene is shown in the bottom right.

From Fig. 3, we can see that both \( F_L \) and \( F_N \) increase as the nano-indentation depth increases before the rupture of graphene. However, the relationship is not linear which is in contrast to classical friction laws.

At small nano-indentation depths, monolayer graphene/Cu (1 1 1) mainly deforms elastically under the sliding of the tip. The lateral force is small and shows a modulation of \( -0.25 \) nm lattice constant of graphene as shown in Fig. S1 in the Supplementary Information, a behavior reminiscent of stick-slip which requires dragging springs [46]. The characteristics at very small nano-indentation depths are consistent with a previous study [41] and experiments on SiO\(_2\) [12]. The lateral force \( F_L \) always fluctuates around 0 nN before \( F_N \) increases to 74.21 nN. These results indicate that when the system deforms in the elastic regime, there can be very low and even negligible friction for sliding on the tip, which is more pronounced for graphene-covered Cu than for the bare Cu.

When the penetration depth reaches deep enough to induce plastic deformation in the Cu (1 1 1) substrate, \( F_L \) becomes finite as shown in Fig. S2 in the Supplementary Information. As the tip has penetrated into the substrate deep enough to induce fracture of monolayer graphene, the graphene ruptures further during the scratch and the lateral force increases suddenly and significantly while the normal force drops down to that of bare Cu (1 1 1), which is in agreement with that of graphene/Pt system [41]. This jump means that graphene has little or no effect on indentation and scratch behaviors, indicating that graphene layers wear out and lose their effectiveness on the mechanical behaviors of the Cu (1 1 1) substrate. Similar to the monolayer graphene/Cu (1 1 1) system above, the \( F_L–F_N \) relationship of bilayer and trilayer graphene/Cu (1 1 1) systems are shown in Figs. S3 and S4 in the Supplementary Information, respectively.

\[ \text{Fig. 3. } F_L–F_N \text{ relationship of monolayer graphene/Cu (1 1 1) with inserted figures of critical nano-indentation.} \]

3.2. \( F_L–F_N \) and \( \mu–F_N \)

In order to quantitatively evaluate how different the friction characteristics of the three graphene/Cu (1 1 1) systems and the protective effect of graphene, their \( F_L–F_N \) relationships are shown in Fig. 4(a) considering bare Cu (1 1 1). The coefficient of friction is defined as \( \mu = \frac{F_L}{F_N} \), and the corresponding \( \mu–F_N \) relationship is shown in Fig. 4(b).

It can be seen from Fig. 4 that the lateral force changes nonlinearly with relatively high normal force, which are different from the results at significantly lower normal loads as shown in Fig. S5 in the Supplementary Information predicting sub-linear dependence of lateral force on the normal load. The nonlinearity comes from the large plastic deformation of underlying copper substrate at relatively high normal loads.

The graphene layers significantly change the friction characteristics of bare Cu (1 1 1), and the monolayer, bilayer, and trilayer graphene/Cu (1 1 1) also show very different characteristics. Furthermore, the friction force of Cu (1 1 1) covered with more layers is reduced. Compared to bare Cu (1 1 1), graphene coated Cu (1 1 1) can hold larger normal force. As to bare Cu (1 1 1), the normal force remains stable while the lateral force monotonically increases with the increase of nano-indentation depth, which is consistent with that of bare Pt substrate [41].

Furthermore, the \( F_L–F_N \) curves of graphene/Cu (1 1 1) systems mainly consist of four regimes [41]: the elastic regime, the small plastic regime, the large plastic regime, and the regime after rupture of graphene layers. In the first regime, the lateral force
remains small and relatively stable while the normal force increases, which means negligible friction and super lubricity. This elastic regime holds until the normal force reaches 74.22, 98.97, and 192.30 nN for the monolayer, bilayer, and trilayer graphene/Cu (111) systems, respectively. In the next regime, the lateral force increases monotonically rather than linearly with the normal load ranging from 74.22 nN to 378.36 nN for the monolayer graphene/Cu (111) system (from 98.97 nN to 589.26 nN for the bilayer graphene/Cu (111) system, and from 179.50 nN to 715.43 nN for the trilayer graphene/Cu (111) system). In the large plastic regime, the lateral force increases almost linearly with the normal force from 589.26 nN to 946.93 nN for the bilayer graphene/Cu (111) system (from 715.43 nN to 1018.56 nN for the trilayer graphene/Cu (111) system). However, the lateral force increases in fluctuations with the normal force from 378.36 nN to 627.82 nN for the monolayer graphene/Cu (111) system because the tip interacts with the Cu (111) substrate more strongly than that in the other two systems. Finally, the normal force drops down to 112.70 nN while the lateral force increases significantly and steadily with the nano-indentation depth, which means graphene layers crack and rupture, and then lose their protective effects. In the last regime, the scratch characteristics are the same as that of bare Cu (111), which is not shown in Fig. 4(a).

In order to reveal the physical mechanism of the characteristics observed above, we obtain the relationship between the lateral force, the normal force and the nano-indentation depth shown as in Fig. 5.

From Fig. 5(a), we find that the normal force strongly differs between bare Cu (111), monolayer graphene/Cu (111), bilayer graphene/Cu (111) and trilayer graphene/Cu (111) systems. For a given h, graphene/Cu (111) systems can carry more load than bare Cu (111), and the system with more graphene layers can carry more load than the system with less graphene layers. Graphene changes the indentation hardness of the overall graphene/Cu (111) system, acting as an elastic high-stiffness coating with a high Young’s modulus.

In contrast to the normal force, the lateral force mainly depends on the nano-indentation depth and changes less when the bare Cu (111) is covered with graphene, as well as with increasing number of layers, as shown in Fig. 5(b). Graphene does not change the work that is necessary to scratch the copper substrate.

At the same normal load, the indentation depth decreases from bare Cu (111), monolayer graphene/Cu (111), bilayer graphene/Cu (111) to trilayer graphene/Cu (111) which indicates that it is the indentation depth reduction responsible for the reduction of friction.

The characteristics of graphene/Cu (111) above come from that graphene should only change the indentation hardness of the overall graphene/Cu (111) system but not the work that is necessary to scratch it, which are in excellent agreement with that of graphene coated Pt substrate [41] indicating that our results are reasonable. What’s more, different number of graphene layers shows different nanofriction characteristics that is also in agreement with simulations and experiments of suspended graphene and supported graphene by other substrates [12,36].

The coefficients of friction of the bare Cu (111), monolayer, bilayer, and trilayer graphene/Cu (111) systems are a function of the normal force, as shown in Fig 4(b). For the graphene/Cu (111) systems, the nanofriction curve can be divided into four
parts correspondingly. In part I, the coefficient of friction are below 0.01. This is a sliding regime. In part II, the coefficient of friction mono-tonotonically increases to 0.30 with normal forces ranging from 74.22 nN to 378.36 nN for the monolayer graphene/Cu (111) system (to 0.18 from 98.97 nN to 589.26 nN for the bilayer graphene/Cu (111) system, and to 0.11 from 192.30 nN to 715.43 nN for the trilayer graphene/Cu (111) system), which means a large amount of elastic and little plastic deformation. In part III, the coefficient of friction drops down to a stable 0.24 ranging from 378.36 nN to 627.82 nN for the monolayer graphene/Cu (111) system while it holds stably at about 0.18 ranging from 589.26 nN to 946.93 nN for the bilayer graphene/Cu (111) system, and about 0.11 ranging from 715.43 nN to 1018.56 nN for the trilayer graphene/Cu (111) system, indicating a large amount of plastic and little elastic deformation. In the part IV, the rupture of graphene layers occurs. The friction coefficient increases beyond 1.00 and increasing monotonically with the nano-indentation depth thereafter.

The same behavior is observed in bare Cu (111). However, the coefficient of friction of bare Cu (111) significantly increases with greater nano-indentation depth while the normal force holds stably around 112.70 nN, which is not shown in Fig. 4(b).

The results above indicate that the existence of graphene layers enhances the load carrying capacity, extends the low friction range, and effectively decreases the frictional force of Cu (111). In addition, the bilayer graphene reduces friction more than the monolayer graphene while the trilayer graphene reduces friction more than the bilayer graphene.

The normal force is large enough to stabilize the friction coefficient before the rupture of the graphene layers, and the relationship between the friction coefficient and the number of layers of graphene (N) is shown in Table 1.

Table 1 shows the distinctive nanofriction characteristics of monolayer, bilayer, trilayer graphene/Cu (111), and bare copper foil. Such a relationship can be used to determine the existence, and the number of layers of graphene, which suggests a routine to characterize the number of graphene layers on a substrate, as an alternative approach to Raman spectroscopy.

There are few studies about the friction coefficient of graphene coated copper foil. As the friction coefficient of SiO2 substrate reduces from 0.68 to 0.12–0.22 after coating it with graphene [12], our results about the friction coefficients of different graphene layers are reasonable. The differences are caused by the different surface interaction forces between the underlying substrate and graphene.

There are differences in the nanoscale friction characteristics of monolayer graphene/Cu (111), bilayer graphene/Cu (111), trilayer graphene/Cu (111), and the bare Cu (111). Graphene, due to its ultra-strong mechanical properties, significantly improves the normal load bearing capacity of a copper substrate through effectively constraining dislocation motion and providing increased resistance against dislocation propagation across the graphene-metal interface [47].

4. Conclusions

We have employed MD modeling of nano-indentation simulations to study the nanoscale frictional characteristics of monolayer, bilayer, and trilayer graphene/Cu (111) systems. Under different nano-indentation depths, F1 and F2 were recorded when the tip scratches laterally on the surface of graphene/Cu (111) systems. We found that Cu (111) covered with more graphene layers has less friction at the same normal force before the rupture of graphene layers. The lateral forces for every system changes nonlinearly rather than linearly with increasing normal force, and the coefficient of friction increases to a stable 0.24, 0.18, and 0.11 for monolayer, bilayer, and trilayer graphene/Cu (111) systems respectively before the rupture of graphene. The different coefficients of friction are related to their lower bending stiffness of different layers. Finally, the coefficients of friction of the systems increase suddenly to beyond 1.00, which is the same as that of bare Cu (111) when the graphene layers break up.

Our results show that graphene layers can effectively reduce the friction and extend the normal force range of low friction. This study provides insights into the nanoscale frictional characteristics and behaviors of monolayer, bilayer, and trilayer graphene/Cu (111). We quantify the dependence of the coefficient of friction on the normal force, which could help in studying nanoscale friction of systems and applications of graphene in nano-devices. Our findings suggest a routine to characterize the number of graphene layers on copper foil or other substrates, as an alternative approach to Raman spectroscopy.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.commatsci.2016.01.007.

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