Effect of roughness on the layer-dependent friction of few-layer graphene

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Friction on few-layer graphene is known to exhibit unique layer dependence where friction measured via atomic force microscopy (AFM) on the nanometer scale is generally observed to decrease with increasing number of layers. However, this trend is not always observed for AFM probe tips with different sizes and for graphene on different substrates. Within this context, the precise role played by the interface, in particular, the size of the contact and substrate roughness, in the layer dependence of friction on graphene is not yet completely understood. Here, we probe the origins of the roughness dependence of layer-dependent friction on graphene by a combination of AFM measurements and molecular dynamics (MD) simulations. In the experiments, friction is observed to monotonically decrease with increasing number of graphene layers for tips with various apex radii, while the roughness of the sample surface is observed to decrease. In the simulations, two opposite layer-dependence trends for friction are observed on few-layer graphene on substrates with different roughness values. The underlying mechanisms are investigated using atomistic details obtained from the simulations, where the different friction trends are found to originate from an interplay between surface roughness, the trajectory of the tip, and the number of atoms in contact. Finally, the effect of topographical correlation length on the layer dependence of friction on graphene is discussed.

I. INTRODUCTION

Graphene has been at the forefront of research interest in the past decade because of its excellent electrical, mechanical, thermal, optical, and tribological properties. Graphene is especially promising as an extremely thin but effective solid lubricant for nano- and microscale machines [1,2] since traditional lubrication schemes based on fluids are not feasible at such length scales. The frictional behavior of graphene on the nanometer scale is commonly characterized using atomic force microscopy (AFM) and molecular dynamics (MD) simulations. Such studies have revealed an interesting and important phenomenon in which friction varies with the number of graphene layers [3–12]. In most cases, layer dependence is observed as a decrease of friction with increasing number of layers. This trend was initially observed in AFM experiments for one- and two-layer epitaxial graphene samples grown on SiC and the observation was explained via an electron-phonon coupling effect [3,4]. Since then, similar layer dependence has been observed both in experiments [5,6,9–11] and atomistic simulations [7,8,12]. Layer dependence has also been observed on mechanically exfoliated samples of other 2D materials, including molybdenum disulde, niobium diselenide, and hexagonal boron nitride [10]. Often, these observations are explained by a puckering effect that is related to the out-of-plane deformation of the graphene layers [5–10,12].

Although most layer-dependence studies have found that friction decreases monotonically with increasing number of layers, this is not always the case. For example, AFM measurements on suspended graphene showed that friction increased with increasing number of layers at low or negative loads, but decreased with increasing number of layers at high load [13]. This behavior was discussed and correlated to interfacial adhesion between the tip and graphene layers [13]. Another set of recent experiments showed that the layer dependence of friction can be changed by scanning AFM tips with different radii against substrates of controlled nanoscale roughness covered with graphene [14]. In that study, a nonmonotonic layer dependence of friction was observed using a sharp AFM tip and the behavior was explained by the interplay between surface roughness, tip radius, and the relative adhesion between tip and graphene as well as between graphene and substrate [14]. These studies have suggested that layer dependence is sensitive to the roughness characteristics of the substrate supporting the graphene.

In this study, we investigated the layer dependence of friction on few-layer graphene using AFM experiments and MD simulations. Specifically, friction on graphene samples comprised of different numbers of layers was measured via contact mode AFM using calibrated probes and predicted via fully atomistic simulations. The layer dependence of friction was correlated to the roughness of the graphene surface which was found to affect (i) the size of the tip-sample contact and (ii) the vertical trajectory of the tip as it is slid over the graphene surface. The role that the topographical correlation length of substrates plays on the layer dependence of friction was also elucidated via MD simulations. Our study provides atomic insights into the underlying mechanisms of friction on graphene and suggests that roughness, as an alternative or in addition to the puckering and electron-phonon coupling phenomena, plays an important role in determining the experimentally–observed, layer-dependent frictional behavior of this emerging 2D material.

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II. METHODS

A. Experiments

To obtain exfoliated graphene samples, ZYA-quality highly ordered pyrolytic graphite (HOPG) specimens were mechanically cleaved using the Scotch Tape method. Cleaved and thinned down flakes were transferred onto Si wafers covered by 300 nm thick silicon dioxide (SiO_2), and graphene flakes with stairlike structures featuring areas with different numbers of layers were located using optical microscopy. Subsequently, one- and two-layer regions were identified using Raman spectroscopy. The flakes were located and topographically measured using contact-mode AFM with commercial cantilevers (Nanosensors PPP-CONTR). Using height profile data and starting from one- and two-layer regions, other graphene regions containing three and four layers were identified by comparing the height differences to the values reported in previous works [15].

Normal spring constants (k) of AFM probes which were used to measure friction forces on graphene were determined using Sader's method [16]. Subsequently, using Ogletree's method [17], the AFM probes were calibrated to obtain friction force values from lateral deflection signals. With calibrated cantilevers, friction force maps were obtained on samples containing one-, two-, three-, and four-layer graphene. Friction results obtained on three- and four-layer graphene were almost identical in the majority of experiments (in accordance with results in the literature [10,11]) and, as such, friction results from one, two, and three layers of graphene are reported here. The fast scan speed was 10 μm/s and the applied normal load values ranged from 0 to 16 nN. Friction force data were obtained using friction loop half-width values [18].

To obtain AFM tips with different apex sizes, calibrated AFM probes were coated with gold using thermal evaporation or a precision etching coating system (PECS). AFM probe tip apex radii were increased via gold deposition and the radii were quantified via scanning electron microscopy (SEM) after every deposition step. Additionally, the cantilevers were recalibrated to adjust for the changes in cantilever thickness caused by gold deposition. Simultaneous with the acquisition of friction forces, topographical maps were also recorded from which root-mean-square (rms) roughness values on the SiO_2 substrate as well as one-, two-, three-, four-layer graphene were obtained.

B. Simulations

The atomistic model is illustrated in Fig. 1. In this model, the apex of an AFM tip was scanned over one, two, or three layers of graphene having in-plane dimensions of 20×20 nm.

The graphene layers were placed either on a smooth or rough surface. The smooth substrate was modeled as atomically flat crystalline silicon and the rough substrates were modeled as amorphous silicon [12] with rms roughnesses of 0.1, 0.2, 0.3, or 0.4 nm. The atoms in the model substrates were fixed in place throughout the simulation. A model tip was constructed of gold in the shape of a hollowed hemispherical tip apex with a 10 nm outer radius and 8.5 nm inner radius. The topmost atoms in the tip were treated as a rigid body. A constant external normal load of 16 nN was maintained on the rigid body at the top of the tip. The rigid body was connected by a harmonic spring to the support that moved at 1 m/s in the sliding direction. The spring had stiffness of 8 N/m in the horizontal directions, but did not resist motion in the vertical direction (normal to the graphene surface) [19]. A Langevin thermostat was applied to the free atoms in the system to maintain a temperature of 300 K. The interatomic interactions within the tip and graphene layers were described via embedded-atom method (EAM) potentials [20] and the adaptive intermolecular reactive empirical bond order (AIREBO) potential [21], respectively. The long range interactions between tip and substrate were modeled using the Lennard-Jones (LJ) potential with parameters obtained from the standard mixing rules [22,23]. The simulations were performed using the LAMMPS simulation software [24].

III. RESULTS AND DISCUSSION

Friction on different graphene samples was measured using AFM tips with various radii (up to 80 nm) in our experiments. Figure 2(a) shows the topographical AFM image of a graphene flake on a silicon dioxide substrate where one-, two-, three-, and four-layer regions are identified. Figure 2(b) shows that the friction force decreases with increasing number of graphene layers as measured by tips with apex radii of 40 nm, 60 nm, and 80 nm. This layer dependence trend is consistent with previous experiments and simulations [5–12]. On the other hand, somewhat counterintuitively, the friction is slightly higher for the smallest tip than the other two tips. We performed pull-off tests and confirmed that the pull-off force increased from an average of 6.3 nN with the 40 nm tip to an average of 11.5 nN with the 80 nN tip, which suggests that the adhesion increases with larger tip size. The overall decrease in friction with increasing tip radius thus cannot be explained by a decrease in adhesion. On the other hand, AFM-based topographical studies of thermal evaporation of gold on SiO_2 have revealed that gold coating at low thickness values ($<$20 nm) leads to the formation of globular structures on the surface and, therefore, a rough topography when compared with thicker coatings
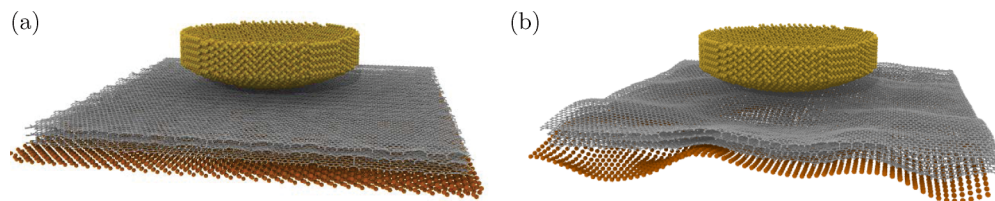

FIG. 1. Snapshots of the initial configurations of the molecular dynamics simulations of a 10 nm gold tip (yellow) sliding on three-layer graphene (gray) on (a) atomically flat and (b) rough model substrates (brown).
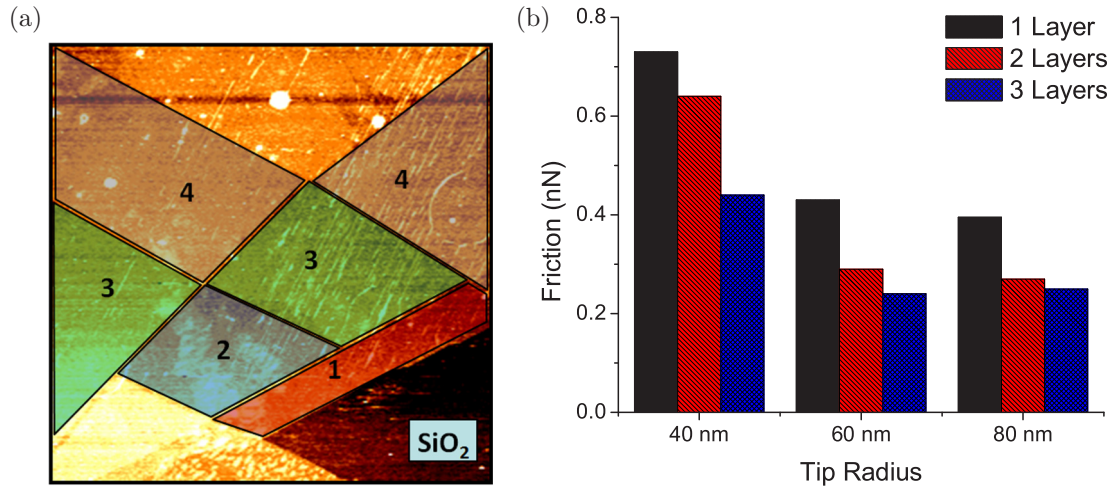
FIG. 2. (a) Topographical AFM image of a graphene flake on silicon dioxide substrate (image size is 10 μm×10 μm), where regions with different numbers of layers are marked. (b) Experimentally–measured friction forces on different numbers of graphene layers, acquired by AFM tips with apex radii of 40, 60, and 80 nm at an applied normal load of 16 nN.

($>$30 nm), which have more uniform and smoother distribution of gold over the surface [25]. As a smoother tip surface on the nanometer scale would contribute to a reduction in the overall roughness of the tip-sample interface, we tentatively attribute the observation of decreasing overall friction with increasing tip size in our experiments to this effect. Regardless, for all tip sizes, the friction decreases with increasing number of graphene layers.

To investigate the origin of the layer dependence of friction, fully atomistic simulations were performed. The first model consisted of graphene with one, two, or three layers on an atomically smooth silicon substrate. The results are shown in Fig. 3(a) where we observe that friction monotonically increases with number of layers, a trend opposite to that observed in the experiments. This figure also reveals that there is a relatively small increase in the roughness of the topmost graphene layer as the number of total layers increases. This observation can be presumably understood in the context of out-of-plane deformations of the first graphene layer above the atomically smooth substrate, which are induced by both thermodynamic effects and the lattice mismatch between the first graphene layer and the substrate, and lead to a finite roughness, meaning that the first graphene layer acts as a rough substrate for the second and so on. As a control simulation, the atomically smooth silicon substrate was replaced by a rigid graphene layer and the results were nearly identical to those shown in Fig. 3(a).

The stark difference between the friction trends in the simulations and the experiments can be likely attributed to the difference in the roughness of the employed substrates. In fact, several previous studies have focused on the influence of substrate roughness on the frictional behavior of graphene [9,14,26]. In our experiments, the rms roughness of the substrate was measured to be 0.275 ± 0.05 nm. Therefore, the simulations were repeated on model, amorphous silicon substrates with rms roughness values varying from 0.1 nm to 0.4 nm. As shown in Figs. 3(c)–3(e), friction on the rougher substrates, i.e., rms 0.2 nm or greater, decreases with increasing number of graphene layers, consistent with the experimental

results. For these cases, we also observe a decrease of the rms roughness of the topmost layer of graphene with increasing number of layers, a trend which is again consistent with our experiments (where the rms roughness of the topmost layer decreases from 0.410 ± 0.05 nm to 0.210 ± 0.03 nm when going from one- to three-layer graphene) and existing literature [14,27]. This trend is attributed to the decreasing conformity to the structural features of the rough substrate with increasing number of layers [14]. It is to be noted that the relative decrease in the friction values, as well as the roughness of the topmost graphene layer with increasing number of layers, becomes more pronounced with increasing substrate roughness.

The results presented here suggest that there may be two mechanisms affecting friction, one that is dominant when the substrate roughness is small and one that is dominant for larger substrate roughness values. To analyze this proposition, we first calculated the rms values of the vertical position/trajectory of the tip during sliding, whereby a large value would indicate that the tip has to move up and down over more corrugated surface features and thus experience more friction while laterally sliding over the surface due to geometric resistance. The results are shown as a function of substrate roughness in Fig. 4(a). We observe that the tip's rms vertical trajectory increases with increasing substrate roughness for all graphene samples. In addition, the difference in vertical trajectories between graphene samples of different numbers of layers is most pronounced for large substrate roughness values, whereby rms vertical trajectories decrease with increasing number of layers, consistent with the observed trend in friction for rough substrates. In contrast, for ideally smooth substrates, a very slight increase in trajectories is observed with increasing number of graphene layers.

We also quantified the size of the contact between tip and graphene as the number of tip atoms "in contact" with the surface. Atoms in contact were identified as those within 0.4 nm distance of a substrate atom. As shown in Fig. 4(b), the size of the real contact, quantified by the time averaged number of contact atoms, decreases with increasing substrate
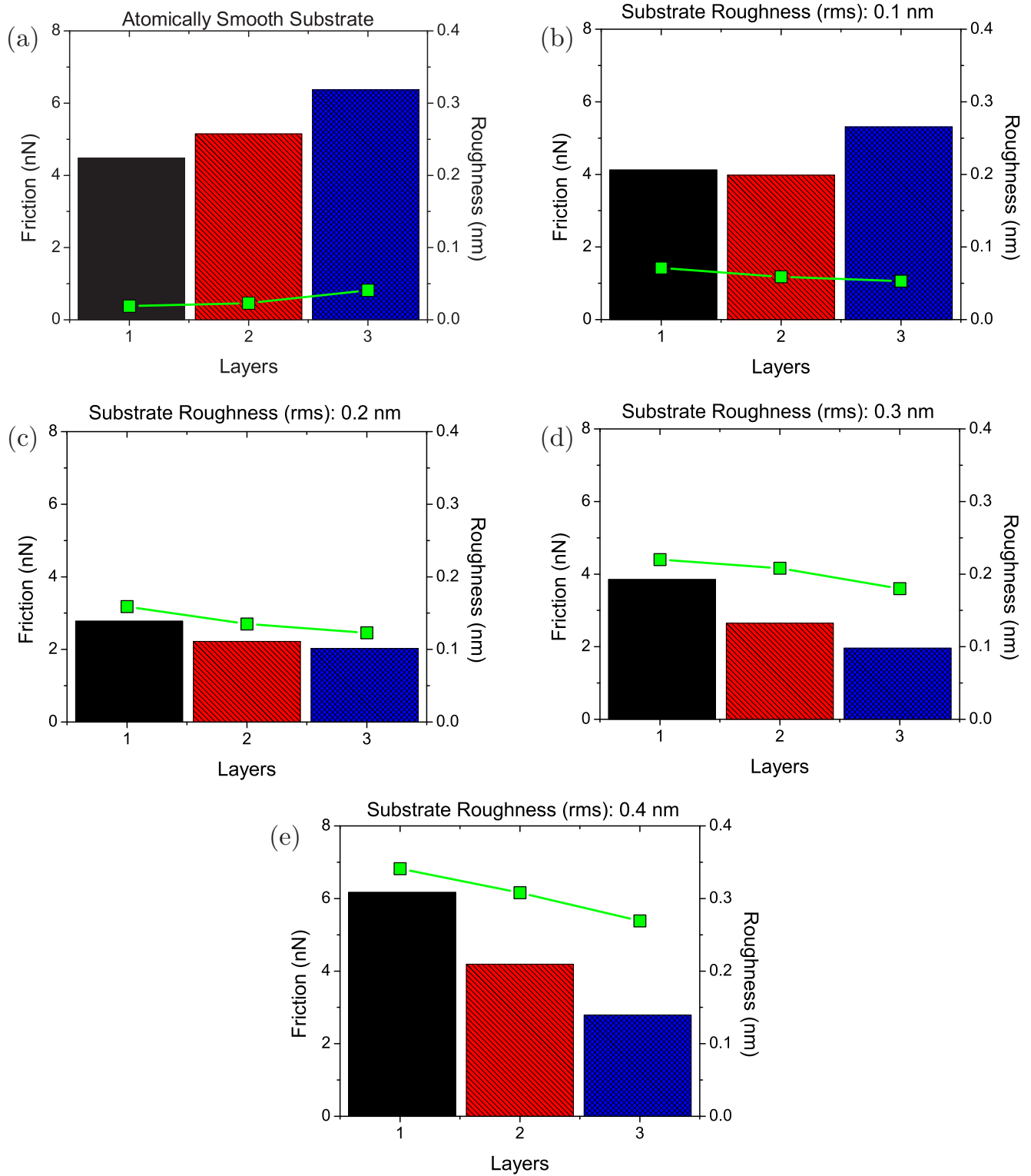
FIG. 3. Friction (bars) and roughness of the topmost graphene layer (symbols) from simulations with (a) atomically smooth and rough substrates with (b) 0.1 nm, (c) 0.2 nm, (d) 0.3 nm, and (e) 0.4 nm root-mean-square roughness.

roughness. Moreover, it is observed that the number of atoms in contact increases with increasing number of layers, at all substrate roughness values.

The two complementary trends discussed above, i.e., the predicted increase in rms trajectory values with increasing substrate roughness accompanied by a decrease in atomic-scale contact area, can explain the trends observed in Fig. 3. Specifically, if the substrate roughness is very small, the atomic-scale contact area will dominate frictional behavior and, since contact area increases with number of layers [Fig. 4(b)], friction also increases with number of layers. On the other hand, for cases with larger substrate roughness, the
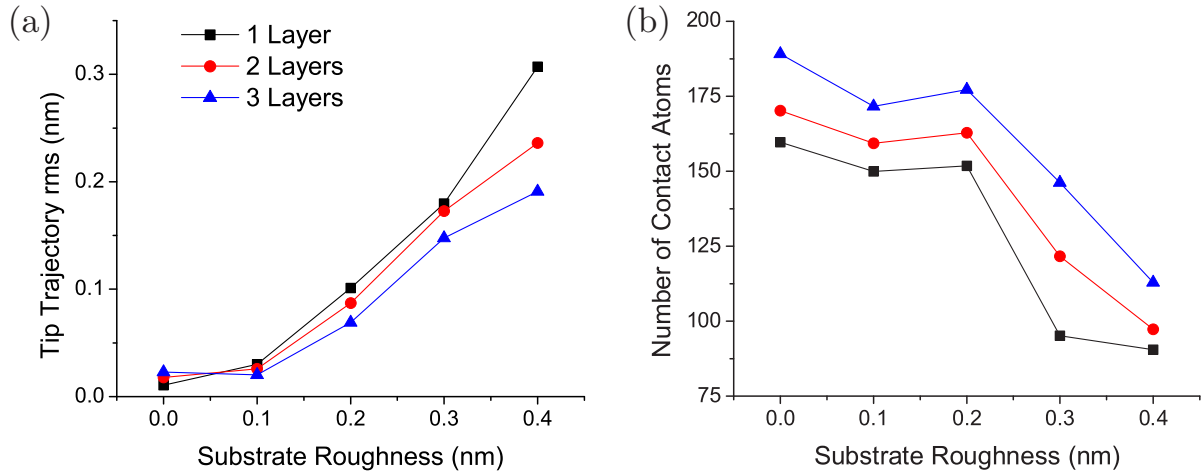
FIG. 4. (a) Root-mean-square values of the model tip's vertical position/trajectory during sliding motion and (b) the average number of tip atoms "in contact" with graphene as functions of the rms roughness of the substrate for one-, two-, and three-layer graphene. The atomically smooth substrate case is represented by zero rms roughness.

geometric effect associated with the vertical trajectory of the tip is seen to dominate over the reduction in contact area. Thus, since rms trajectory values decrease with increasing number of layers [Fig. 4(a)], friction also decreases.

The above arguments could be further validated by simulations of model substrates with the same rms roughness, but different correlation lengths. As the correlation length determines the average spacing of topographical features on a given surface, a small ratio of tip apex size with respect to correlation length would be expected to give similar results to a flat substrate since; in this case, the tip would smoothly follow the contours of surface topography, as if it were moving on a flat surface. On the other hand, a large ratio of tip apex size with respect to correlation length would result in the tip continuously having to overcome the rough topographical features of the surface as it is moved laterally.

To confirm these expectations, several model rough substrates with the same rms roughness value of 0.3 nm (consistent
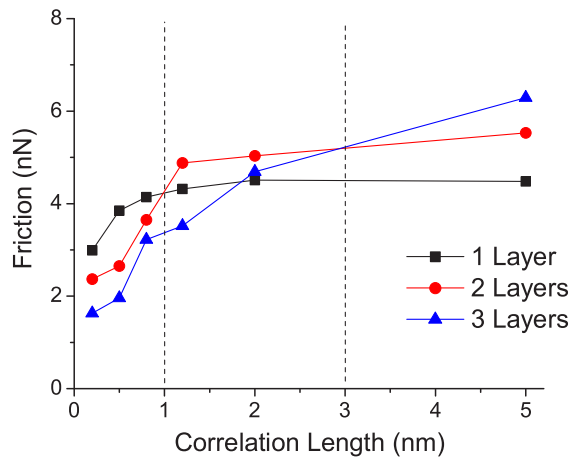

FIG. 5. Results from MD simulations of friction on few-layer graphene on rough substrates with varying correlation lengths. Small, medium, and large correlation length regimes (see text) are separated by vertical dashed lines.

with the rms roughness value measured in the experiments), but different correlation lengths in the range of 0 to 5 nm, were created and one to three layers of graphene placed on top. The model tip was slid across these surfaces. The calculated friction forces are shown in Fig. 5. For small correlation lengths (<1 nm), we observe that friction decreases with increasing number of layers, as expected from a rough substrate. On the other hand, for large correlation lengths (>3 nm) which should exhibit friction similar to that observed on atomically smooth substrates, we observe that friction indeed increases with increasing number of layers. In the transition regime represented by medium correlation lengths (between 1 and 3 nm), we observe a nonmonotonic layer dependence trend for friction. Our results confirm and shed light on the experimental results of Spear *et al.* [14], where the typical layer dependence of graphene (decreasing friction with increasing number of layers) was only observed with large tip apices, on graphene samples deposited on a rough substrate consisting of silica nanoparticles. With such tips, the ratio of the tip size to the correlation length of the surface would be high, which, according to the results presented in Fig. 5, would correspond to the regime where friction forces decrease with increasing number of layers. Overall, the results discussed here emphasize that rms roughness is not the only parameter affecting the layer-dependent frictional behavior of graphene and that it needs to be considered together with the correlation length and tip apex size.

IV. CONCLUSION

In summary, we presented AFM experiments and MD simulations aimed at investigating the influence of roughness on the layer-dependent friction of few-layer graphene. Our experiments, conducted with tips of various apex size, confirmed that friction decreases with increasing number of layers. On the other hand, only simulations with realistically rough substrates were able to reproduce the same trend, while simulations employing atomically smooth substrates

resulted in the opposite behavior. These observations have been explained by an interplay of surface roughness and the number of atoms in contact during sliding. Specifically, the roughness of the topmost graphene layer decreases with increasing number of layers for graphene on rough substrates, resulting in smaller topographical corrugation that needs to be surmounted by the tip and, thus, smaller friction forces. On the other hand, on atomically smooth substrates, the increase in the number of atoms "in contact" with increasing number of graphene layers dominates frictional behavior, resulting in an increase of friction with increasing number of layers. Moreover, our results demonstrate that topographical correlation length and tip apex size need to be considered in addition to rms roughness values to explain the layer-dependent frictional behavior of few-layer graphene. In particular, for small ratios of tip apex size to correlation length, the layer-dependence trend follows that of an atomically smooth substrate. For large ratios of tip apex size to correlation length, the opposite (and experimentally verified) trend is observed. Our study shows that the layer dependence of friction on graphene as measured by AFM is a complex phenomenon that is affected by a variety of factors involving the structure of the interface (its roughness, correlation length, as well as its size), in addition to effects such as puckering [5–10,12] and electron-phonon coupling [3,4] that have been suggested previously. Future work could be performed in which additional parameters are varied, including tip and substrate materials, to understand the sensitivity of the trends observed here to other conditions which would then enable the development of a general analytical model to predict the effect of roughness on the layer dependence of atomic friction on 2D materials.

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