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Role of wrinkle height in friction variation with number of graphene layers

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Molecular dynamics simulations are performed to study the frictional behavior of graphene. It is found that the friction between a diamond tip and graphene decreases with increasing number of graphene layers. This behavior is also affected by the graphene sheet size; specifically, the effect of the number of layers on friction becomes significant only when the modeled graphene sheets exceed a critical length. We further show that the frictional behavior can be directly correlated to the height of near-contact wrinkles that resist sliding. These observations are rationalized in terms of the ability of multiple sheets to act as a single material as they resist wrinkle formation.
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Graphite is widely used in lubricated systems because its weak interlayer interaction strength leads to low friction. To understand the mechanisms underlying its friction behavior, researchers have used friction force microscopy (FFM) to study it at a nanoscale. Recent measurements have revealed a novel trend where the frictional resistance to sliding is smaller on bilayer graphene than on single layer graphene.[1,2] This trend was confirmed through another set of experiments that included graphene up to four layers and other layered materials.[3,4] The latter experimental measurements were explained by a puckering effect where a wrinkle in front of the FFM tip that resists sliding is more dominant with fewer layers.

Since the FFM studies cannot provide direct evidence as to what is happening in the interface buried between the probe and graphene, molecular dynamics simulations have been introduced to help explain the observed behaviors. In two cases the experimental trend was reproduced, i.e., friction decreased with the number of graphene layers,[5,6] while in another case the opposite trend was observed.[7] However, none of them proved or disproved the puckering mechanism proposed based on the experimental measurements.

In this communication, we report physically representative atomistic simulations of friction on variable-layered graphene, which (a) reproduce the experimentally observed trends, (b) support the theory that wrinkles resist sliding, (c) show the behavior is affected by model sheet size, and (d) illustrate the connections between number of layers, sheet size, and wrinkle height through flexural rigidity and binding energy.

The atomistic model, illustrated in Fig. 1, described the apex of an FFM tip scanning over graphene. The graphene sheets were initially 8 nm wide and their lengths were varied from 8 to 52 nm; all were in the zig-zag configuration relative to the sliding direction. The atoms in the bottom most layer of graphene were fixed to model a supporting substrate. Simulations were performed with one, two, and three layers of graphene above the fixed layer (i.e., subsequent mention of number of layers does not include the fixed layer) with an initial interlayer distance of 0.335 nm. The atoms at one end (in the scan direction) of all the layers were fixed to prevent relative sliding. The model tip had a hemispherical geometry and consisted of carbon atoms in a diamond structure. The topmost layers of atoms in the tip were treated as a rigid body. A constant external normal load was maintained on the rigid body and it was connected by a harmonic spring to the support that moved with a constant speed of 4 m/s in the x-direction. The spring had stiffness of 8 N/m in the x- and y-directions, but did not resist motion in the z-direction (normal to the graphene surface). A Langevin thermostat was applied to the free atoms in the system to maintain a temperature of 10 K; all trends reported were also exhibited at 300 K, but the lower temperature enabled more clear illustration of the subtle relationships between friction and structure. The boundaries were non-periodic in the x–y plane, and the boundary in the z-direction was formed by the fixed bottom layer of graphene and the rigid body of atoms at the top of the tip. The root mean square (RMS) roughness of the graphene surface was calculated to be 0.01-0.03 nm which is reasonably compared to the range of values measured experimentally (0.002–0.017 nm) for graphene on a boron nitride substrate.[8] The inter-atomic interactions within the tip and substrate were described via the adaptive intermolecular reactive empirical bond order (AIREBO) potential,[9] and the long range interactions between tip and substrate were modeled using the Lennard-Jones potential (energy minimum 0.016 eV, zero-crossing distance 0.28 nm). The simulations were performed using LAMMPS simulation software.

Fig. 2 presents a typical friction vs. scanning displacement result from our simulations with 0 nN external normal load. For this sheet size (42 nm long), we can clearly see that the peak friction (and also the average friction although not as clearly visible from the figure) decreases as the number of layers increases from 1 to 3. This trend is in agreement with experimental observations.[3] To verify the robustness of this behavior, we performed simulations on graphene with different sizes. The variation of peak friction with number of layers and sheet length is summarized in Fig. 3. The results show that, for longer graphene systems, friction decreased with number of layers, consistent with experiment. However,

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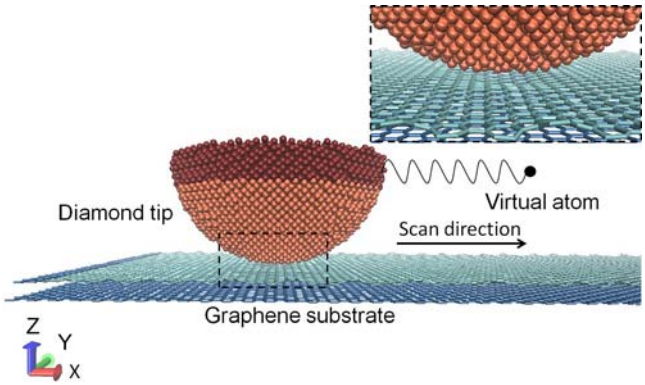

FIG. 1. Snapshot of the model system where a hemispherical diamond tip is connected to a harmonic spring which pulls it over graphene layers.

this trend is not observed when the graphene is 24 nm or shorter which suggests that graphene size affects the mechanism underlying layer-dependent friction.

As mentioned previously, one theory used to explain layer-dependence is the formation of a wrinkle in front of the tip that resists friction, called puckering,[3,4] whose effect decreases as the number of layers increases. To explore this possibility, we tracked the x-direction profiles of the graphene layers near the contact region as they evolved during sliding. An illustration of these profiles is shown in Fig. 4. In this example, we can clearly see that the upper graphene layer conforms locally to the tip such that there is a wrinkle in front and back of the tip; a similar pattern can be observed in the second layer but with much smaller amplitude. It is reasonable to expect that these wrinkles might resist sliding and therefore increase friction. To determine if they can also explain the layer-dependence, we calculated the time-averaged height of the wrinkle in front of the tip for the various model sizes. The results, shown in Fig. 5, reveal that the size of the wrinkle decreases with increasing number of layers for long graphene sheets, but not for the shorter systems. This is exactly consistent with the friction trends observed in Fig. 3, i.e., friction decreases and wrinkle height

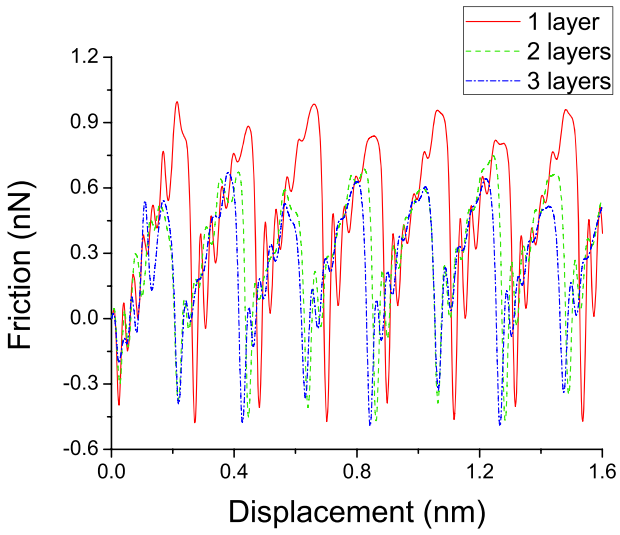

FIG. 2. Effect of number of graphene layers on friction for 42 nm long sheets.

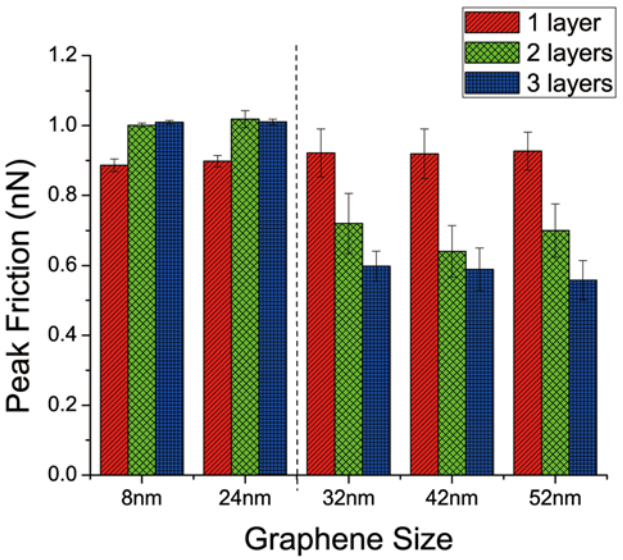

FIG. 3. The effect of graphene length on frictional layer-dependence.

increases with increasing layers only for graphene of 32 nm or longer.

We also performed simulations at external normal loads of 5 and 10 nN (values comparable to the experimental work[4]). We observed that, as expected, both the average friction and the wrinkle heights increased with increasing load. In addition, the same variations of friction and wrinkle height with number of layers and graphene length observed at 0 nN were observed at 5 and 10 nN.

The results shown so far indicate that the dependence of friction on layers and size can be correlated to the formation of wrinkles at the three loads studied. This leads to the question of why wrinkle formation is affected by the number of layers or sheet size. We propose a mechanism based on the ability of the sheets to resist wrinkle formation.

For longer graphene sheets, we suggest that the multiple graphene layers act together to resist wrinkle formation. In this case, the graphene can be considered to be an elastic body whose flexural rigidity is $D = \frac{Eh^3}{12(1-\nu^2)}$, where E is the Young's modulus, ν is Poisson's Ratio, and h is an effective

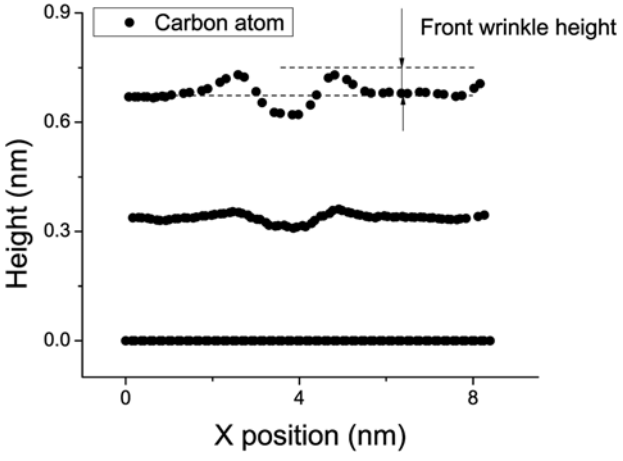

FIG. 4. Local profiles of the graphene layers during the scanning process.

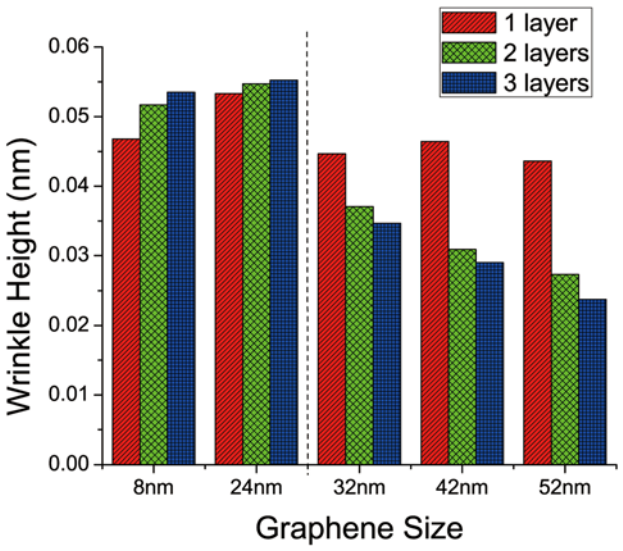

FIG. 5. Height of the wrinkle in front of the tip varying with number of graphene sheets and their length.

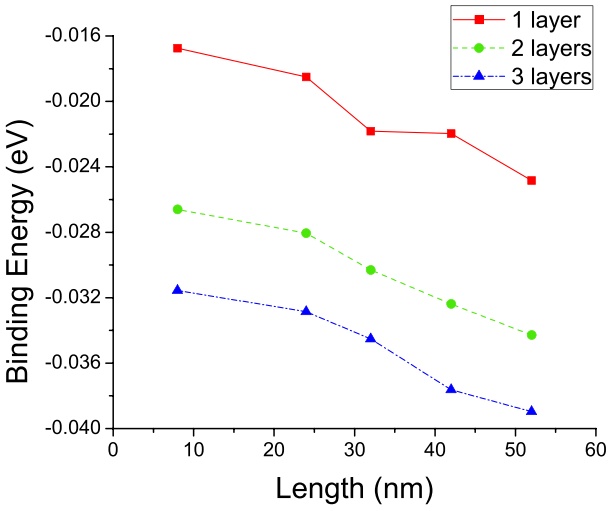

FIG. 6. Binding energy of multi-layer graphene decrease monotonically with sheet length.

thickness that can be correlated to the number of graphene layers. This expression tells us that, as its thickness increases, the flexural rigidity of the material will increase and it will be harder to bend. Although flexural rigidity is typically used to describe the resistance of a material to global bending, it was recently shown to also be related to local out-of-plane deformation; specifically, the square of the out-of-plane displacement was found to be inversely proportional to the flexural rigidity.[10] Since flexural rigidity increases with thickness and local deformation decreases with flexural rigidity, this analysis is consistent with our observation that the height of wrinkles decreases with the number of long graphene layers (see the results in Fig. 5 to the right of the dashed line).

This trend is not observed in the shorter graphene sheets. For these cases, we propose that the sheets do not behave as a single material, and the uppermost sheet does not have the support of those below it to resist the formation of wrinkles. This supposition is supported by the binding energy where, for this system, binding energy is defined as the difference between the per atom configurational energy of the multilayer materials and that of the layers separated from one another: $E_B = (E_{total} - \sum_{i=1}^{n} E_i)/N$, where E_{total} is the energy for the layered material, n is the number of layers, E_i is the energy of individual ith layer, and N is the number of atoms. Fig. 6 shows that binding energy decreases with sheet size for one, two, and three layer systems; this is consistent with size effects reported in previous studies.[11,12] The effect in our research is that the structural stability, and therefore the ability of multiple layers to act together to resist near-contact wrinkles, increases with length. The concept of length-induced stability is further supported by a calculation of the average distance between graphene layers which decreased with increasing sheet length; the average distance decreased from 0.340 to 0.337 nm as length increased from 8 to 52 nm. Therefore, in smaller graphene systems, the uppermost layer is less tightly bound to the layer beneath and less able to resist wrinkle formation. This is consistent with our observation that increasing the number of short graphene layers does not result in smaller wrinkles (see the results in Fig. 5 to the left of the dashed line).

In conclusion, we have used molecular dynamics simulation to explore the mechanisms underlying experimentally observed frictional layer-dependence. Results support the previously suggested puckering effect by showing that the height of the wrinkle that resists sliding is affected by the number of layers. Further, we show that this effect is dependent on the size of the system such that it is only observed with sufficiently long model sheets. This behavior is rationalized in terms of the ability of multiple sheets to act as a single material as they resist wrinkle formation.

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