Toward a Probe-Based Method for Determining Exfoliation Energies of Lamellar Materials

Zhao Deng, Alex Smolyanitsky, Qunyang Li, Xi-Qiao Feng, and Rachel J. Cannara

***Abstract*—We discuss a potential new measurement application based on nanotribological measurements and simulations of the model lamellar material graphite. While frictional forces always oppose motion, we have observed that friction increases with decreasing load on aged graphite using atomic force microscopy (AFM). This results in an effectively negative nanoscale coefficient of friction. The magnitude of the friction coefficient increases with tip-sample adhesion. Through molecular dynamics and finite element simulations, we have demonstrated that the negative coefficient arises from an increase in out-of-plane deformability of the top layer of graphite with lifting, and is not a result of a variation in atomic corrugation or other material property. Viscoelastic waves which dissipate energy during sliding are more easily generated in the top layer of graphite when it is partially (and reversibly) exfoliated by the AFM tip. As a consequence, the magnitude of the negative friction coefficient is determined by the ratio of the work of adhesion to the exfoliation energy, providing a potential pathway toward the use of friction force microscopy for straightforward determination of the exfoliation energies of lamellar materials.**

I. Introduction

Recently, nanoscale studies of graphite and other lamellar materials have shown that friction can increase with a decreasing number of atomic layers [1]-[3]. Greater electron-phonon coupling was observed for single-layer graphene as versus multilayer graphene grown epitaxially on silicon carbide [1]-[2]; and a greater susceptibility of thinner layers to out-of-plane elastic deformation was determined for graphene supported by a silicon dioxide substrate [3]. Through these atomic force microscopy (AFM) experiments and other previous experimental work [4], it has been established that nanoscale friction is less for graphite than for graphene. Subsequently, we discovered that this behavior has a strong dependence on adhesion between an AFM tip and graphite or graphene surfaces. As an understanding of the impact of adhesive force on friction had been elusive, we performed detailed studies to controllably vary tip-sample adhesion in nanoscale friction force microscopy (FFM) measurements on graphite, using an AFM [5].

Through this discovery, we found that the tip-sample work of adhesion indeed plays a critical role in the frictional behavior of graphite. In certain regimes the deformability of the graphite surface can mimic graphene, leading to effectively negative nanoscale friction coefficients that arise when the tip lifts the topmost graphene layer(s) away from the bulk. Consequently, this effect only occurs during the retraction step, when the tip is being pulled away from the sample in an attempt to separate the materials at the tip-sample interface. Accordingly, through simulation we found that the negative coefficient emerges only when tip-sample adhesion exceeds the exfoliation energy of graphite. Based on this behavior, which we observed for both graphite and molybdenum disulfide, we propose that FFM enables probing of exfoliation energies of lamellar materials through retraction of the tip to low applied loads. If the tip-sample work of adhesion can be accurately tuned to values below and above the exfoliation energy of the material or compound of interest, then FFM may be used as a straightforward technique for determining surface interlayer binding potential. This approach will also require thorough knowledge of the load-dependent distribution of compressive and tensile stresses in the contact zone of these interfaces.

Here we introduce a preliminary idea for a new experimental procedure to interpret the measured dependence of the negative (effective) friction coefficient on adhesive force and extract exfoliation energies of lamellar materials. We also briefly weigh the use of AFM against the alternative use of a displacement-controlled apparatus. This would enable performing the measurement over a range of tip-substrate separations that extends beyond the point of maximum tensile load (to which AFM is limited).

II. Results and Discussion

A. Experiment

Fig. 1 shows an example of friction as a function of applied load for a 30 nm-radius ultrananocrystalline diamond (UNCD) tip sliding on the chemically-modified surface of highly-oriented pyrolitic graphite (HOPG). The

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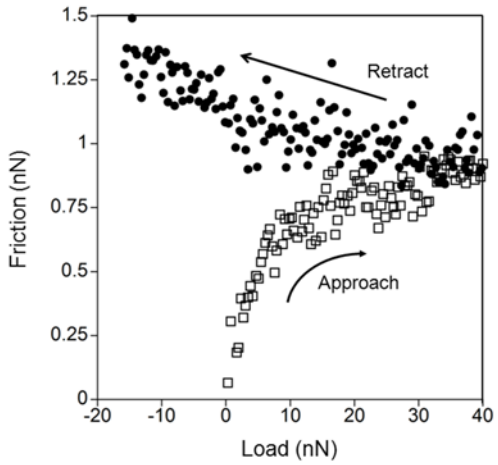

Fig. 1. Friction as a function of applied load for a 30 nm-radius silicon nitride AFM tip sliding on the chemically-modified surface of an HOPG sample. The data for the approach direction (load increasing as the tip presses into the sample) are shown as open squares; data for the retract direction (load decreasing as the tip is pulled away from the sample) are shown as closed circles—both as indicated by the arrows.

plot demonstrates the significant approach-retract hysteresis characteristic of this surface when adhesion is enhanced relative to the surface binding potential. Here, the enhancement is achieved through exposure to oxygen, as described elsewhere [5]. Fig. 2a shows further examples for a different sized tip and HOPG surfaces that are identical, except they have undergone longer exposure times to mild amounts of oxygen. Thus, they exhibit varying adhesion, as manifested by the different pull-off forces (L_C) as a function of oxygen content indicated in the legend of Fig. 2a. Fig. 2b is a plot of the different slopes (friction coefficients, α) of such data, but for the smaller tip, as a function of the magnitude of the pull-off (or adhesive) force. The lower limit of $|L_C|$ represents the range of values typically measured for this tip (30 nm-radius UNCD) on freshly cleaved HOPG.

Also shown in Fig. 2b is a second order polynomial fit to the data that we have employed simply as a guide to the eye; however, it also shows that $|\alpha|$ tends to increase faster as the work of adhesion (W, upper abscissa) approaches the exfoliation energy for graphite. A range of values for the exfoliation energy is shown to include both measured and calculated values that have been reported in the literature [6]-[8]. This range spans approximately 50 meV/atom to 60 meV/atom depending on the method, and corresponds to adhesion values ranging from approximately 300 mJ/m^2 to 370 mJ/m^2, as shown in the plot. We note that W was estimated by applying a standard continuum mechanical model [9]. From the simulations we have performed (discussed in Section II*B*), it is expected that this represents a significant underestimate for the tip-sample adhesion. Accordingly, the onset of the negative coefficient is expected to occur for the same L_C (a measured quantity), but those L_C values realistically correspond to smaller

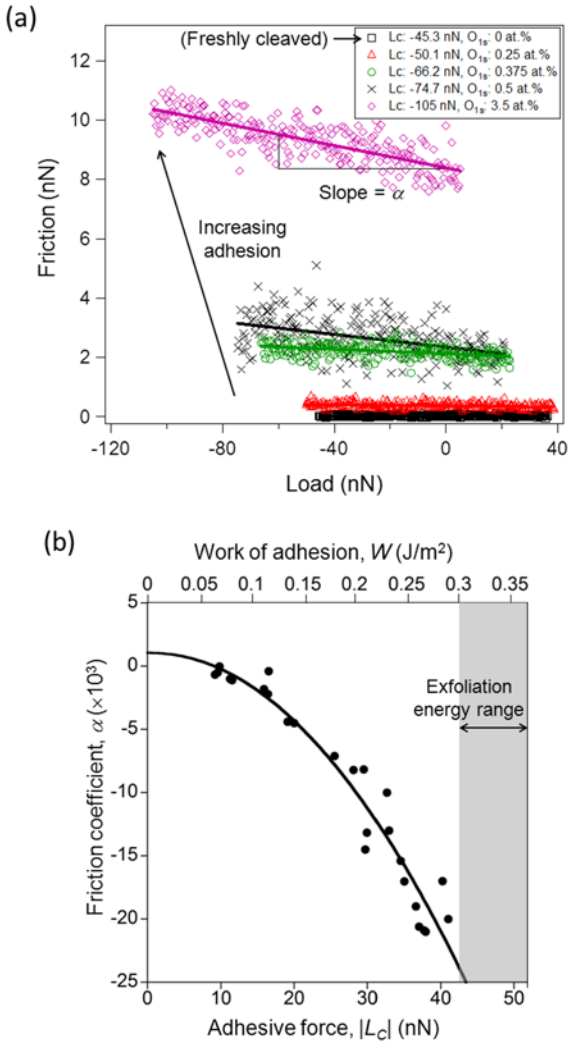

Fig. 2. (a) Friction as a function of applied load for a 75 nm-radius UNCD tip sliding on HOPG surfaces that have different amounts of adsorbed oxygen (measured by x-ray photoemission spectroscopy), leading to varying adhesive forces (L_C). (b) Effective friction coefficient (α) data as a function of the magnitude of the pull-off (or adhesive) force and estimated work of adhesion, W, for the 30 nm-radius UNCD tip sliding on chemically-modified graphite surfaces. A second order polynomial fit to the data is included as a guide to the eye, but it also indicates that $|\alpha|$ increases faster as W approaches the exfoliation energy of graphite (range shown in gray).

compressive contact areas than established methods predict. This leads to a dramatic increase in W for a given L_C.

Fig. 3 shows a schematic representation of the phenomenon, where the AFM tip lifts the topmost graphene layer of the graphite surface and deforms it asymmetrically during sliding. Both the atomistic and continuum-based simulations that we have performed confirm the general property that lifting leads to a negative coefficient; however, the asymmetric profile is reproduced only in the AFM tip-sized simulation.

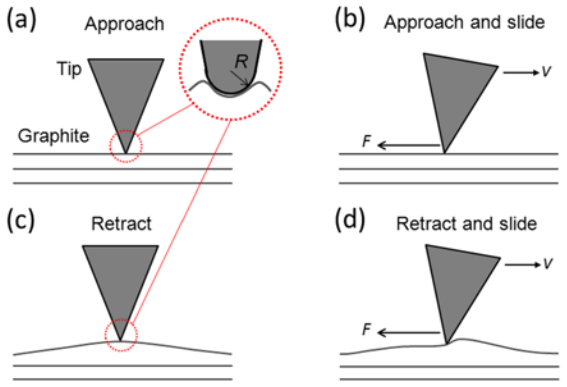

Fig. 3. Schematic representation of the lifting and sliding process that occurs at the onset of the effectively negative coefficient of friction. (a) shows the conformation of the topmost layer(s) of the graphite surface to an AFM tip of radius, *R*, under positive loading (pressing into the sample) without sliding; and (c) shows the corresponding retraction profile post loading. (b) and (d) are the respective cases while sliding.

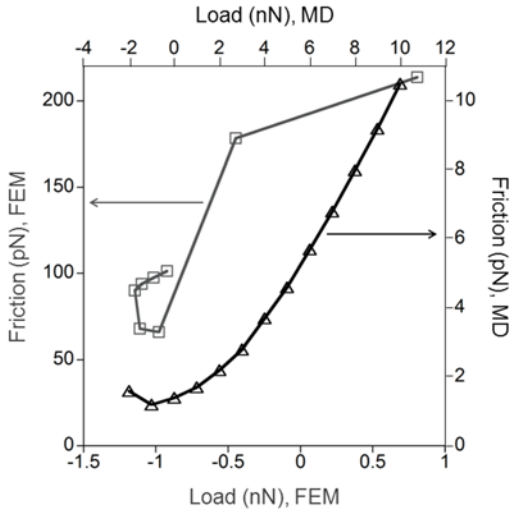

Fig. 4. Friction as a function of applied load for a two-fold tip-sample interaction enhancement relative to the interlayer binding energy as calculated from the FEM (dark gray, open squares) and MD (black, open triangles) simulations. The FEM load data are calculated from a displacement-controlled simulation based on the sum of compressive and tensile stresses in the contact zone; whereas, the MD load data are imposed directly in the simulation.

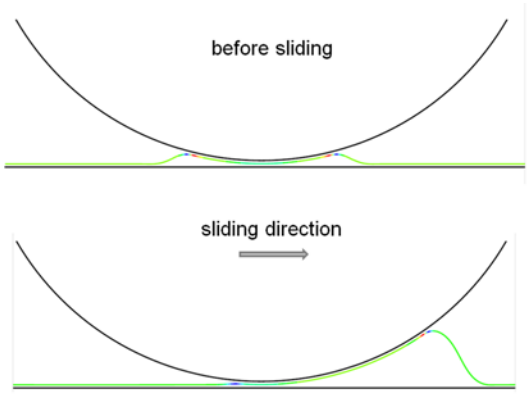

Fig. 5. 2-D FEM simulation of a rigid 30 nm-radius tip before (top) and during (bottom) sliding on a graphene layer with rigid substrate with the tip-sample interaction enhanced two-fold relative to the layer-substrate interaction energy.

B. Simulations

We modeled the AFM tip-graphite system using both molecular dynamics (MD) and finite element method (FEM) simulations. Respectively, these two techniques have allowed us to view this system from both atomistic and continuum perspectives to reveal the various dissipation mechanisms at play. Although MD and FEM simulations span a different range of probe tip diameters and scan velocities, both techniques have established that the topmost layer of graphite can be lifted by the AFM tip when the tip-sample interaction energy is enhanced relative to the surface interlayer binding (exfoliation) energy of the layered substrate, as indicated by the experimental results.

MD simulations of a 0.6 nm-radius carbon nanotube tip sliding on five layers of ABAB-stacked graphene predicted an increase in frictional energy dissipation at increasingly negative applied loads through additional phonon losses in the lifted layer(s). An example of friction data as a function of applied normal load for a two-fold enhancement of the tip-surface interaction relative to the graphene-graphene binding energy is shown in Fig. 4 (black data). Pull-off occurs at the maximum tensile load, as it does in an AFM experiment.

Using an AFM-sized tip, the two-dimensional (2-D) FEM simulation provided a snapshot of the realistic asymmetry of the contact profile due to bunching of the topmost layer during sliding. There, as discussed above, the relative distribution of tensile and compressive stresses varied differently than for typical continuum mechanical contacts, with compression occurring at the perimeter of the contact during retraction. This variation arose alongside a slight increase in the physical height of the lifted layer, and together these effects lead to an effectively negative friction coefficient. Fig. 4 also shows data from the FEM simulation of a two-fold enhanced tip-graphene layer interaction relative to the graphene-substrate interaction energy. As the simulation models a displacement-controlled experiment, pull-off does not take place at the maximum tensile load, and we have included several points beyond this load to demonstrate continuation of the negative coefficient.

III. Pairing a Model with Experiment

A. Experimental Apparatus

To develop a working procedure for determining exfoliation energies of lamellar materials from FFM experiments, a new model describing the contact mechanical properties of isotropic solid probes sliding on (anistropic) layered materials or compounds is needed. Further, the

experiment should be compatible with and enable precise comparisons with an analytical model.

In Section II*B*, we mentioned that the MD and FEM simulations employ load and displacement control, respectively. The AFM and interfacial force microscope (IFM) [10]-[11] also differ in this respect. As a consequence of the relatively low cantilever spring constants used, the load range in an AFM is limited by the snap-in and snap-off instabilities. Although the AFM is a more commonly used instrument, the IFM is also capable of performing sliding experiments, with the additional ability to continuously balance displacement at an interface by tracking and feeind back on interfacial forces and force gradients. Therefore, as with the FEM simulations discussed above, IFM can extend the experimental load range into the tensile regime [12]. This ability may be particularly important for contacts where the negative coefficient may emerge near pull-off. In general, it is appealing for obtaining a more comprehensive range of data.

B. Modeling

Where the turnaround in the calculated normal load occurred in the FEM simulation, standard continuum models for elastic contacts [9], friction should continue to decrease to zero as the contact evolves from this turnaround point toward zero load. Full separation occurs when the contact area vanishes (at zero normal load). Instead, we observed that, after an initial negatively-sloped trajectory just prior to the maximum tensile load, friction continues to increase (Fig. 4). If plotted as a function of displacement, we found that this trend is linear from the onset of the negative coefficient to the last simulated tip-substrate separation value [5].

The linearity of the experimental friction-load data under retraction (Fig. 1) motivated us to add a pressure-dependent term to the shear strength. Typically, the shear strength used in standard continuum representations of nanoscale single-asperity contacts is a constant, with the variation in friction with load a result of the load-dependence of the contact area. However, previous work on Langmuir-Blodgett layers revealed an additional pressure-dependence that was attributed to plowing [13]. This property contributes a friction term that is linear in load. As our experimental data reveal that friction is fairly linear with load under retraction, and the effect we observed may also be considered plowing, the following equation from [13] may be useful for modeling friction on lamellar surfaces:

$$F_f = \tau_0 A + \alpha F_n , \qquad (1)$$

where F_f and F_n are the force of friction and normal load, respectively; τ_0 is the interfacial shear strength, and A is the contact area (typically a function of F_n). As we have observed that α is negative (this is particularly apparent when $F_n < 0$), the second term in (1) serves to increase F_f while the first term is typically decreasing. Based on the FEM simulations, this increase in F_f arises from the compressive stresses that emerge at the perimeter of the contact during tip retraction, lifting, and bunching of the surface while sliding.

We propose that α is a function of the ratio of W to the exfoliation energy. If this is the case, a model that can be used to independently calculate W from measured L_C values and accurately describe the functional form of α would enable identification of exfoliation energies from direct analysis of α-L_C plots (*e.g.*, Fig. 2b).

IV. Conclusion

We hope that this work represents the initiation of a new approach for experimentally determining the exfoliation energies of lamellar (or layered) materials. We expect this technique to extend to new and existing engineered materials in this category. In fact, we have also observed the negative coefficient effect for the more complicated layered material, molybdenum disulfide.

Exfoliation energies of layered materials are of interest, for example, for producing particulate inclusions for high strength polymer-based nanocomposites, for creating atomically thin membranes for switches and gas or pressure sensing, and for understanding the properties and performance of various intercalation compounds. The latter have applications in a wide range of areas, including battery and electrode materials, heat shields, optical filters, and material storage and recovery (*e.g.*, in the energy sector). In addition to the benefit of providing quantitative values for potentially tunable material properties, knowledge of the interlayer binding properties can help assess costs for manufacturing engineered materials and compounds that rely on exfoliation as a processing step.

We emphasize that the opportunity for direct measurement of these properties here depends on the ability to develop an accurate, physics-based model describing the contact mechanics between the probe and measured surface. As is true for existing continuum models that describe contact mechanics for isotropic material interfaces, a model should also yield reliable work of adhesion values. Accordingly, in the ideal case these values would be extracted directly from model fits to the friction-load data. Further, an apparatus with displacement control, such as an IFM, may be the more appropriate tool for this measurement, as it could provide data beyond the maximum tensile load and into the tensile regime. This would allow for greater precision (statistics) in fitting data to the relevant model.

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