Comparison of frictional forces on graphene and graphite

Hyunsoo Lee¹, Naesung Lee¹, Yongho Seo¹, Jonghwa Eom² and SangWook Lee³

¹ Faculty of Nanotechnology and Advanced Material Engineering and Institute of Fundamental Physics, Sejong University, Seoul 143-747, Korea
² Department of Physics and Institute of Fundamental Physics, Sejong University, Seoul 143-747, Korea
³ Division of Quantum Phases and Devices, School of Physics, Konkuk University, Seoul 143-107, Korea

E-mail: yseo@sejong.ac.kr

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Abstract

We report on the frictional force between an SiN tip and graphene/graphite surfaces using lateral force microscopy. The cantilever we have used was made of an SiN membrane and has a low stiffness of 0.006 N m⁻¹. We prepared graphene flake on a Si wafer covered with silicon oxides. The frictional force on graphene was smaller than that on the Si oxide and larger than that on graphite (multilayer of graphene). Force spectroscopy was also employed to study the van der Waals force between the graphene and the tip. Judging that the van der Waals force was also in graphite–graphene–silicon oxide order, the friction is suspected to be related to the van der Waals interactions. As the normal force acting on the surface was much weaker than the attractive force, such as the van der Waals force, the friction was independent of the normal force strength. The velocity dependency of the friction showed a logarithmic behavior which was attributed to the thermally activated stick-slip effect.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since lateral force microscopy (LFM) was developed by Mate et al in 1987, LFM has been widely used for characterizing surface viscosity and frictional forces [1–3]. In particular, LFM has featured as an atomic scale frictional force measurement and control in air or vacuum [4, 5]. The information which can be obtained from LFM includes friction, adhesive force, and dissipative interactions.

It is well known that frictional force is proportional to the normal force, independent of the apparent contact area and sliding velocity, in classical mechanics. In many lateral force related articles, the proportionality between the frictional force and normal force is considered to be very natural [6]. However, if the tip and sample have a strong attractive force and pull on each other, and frictional contact area is nanoscale, the normal force may not influence the frictional force.

In terms of the velocity dependency, Zwörner et al studied, by means of lateral force microscopy, different carbon compounds (diamond, graphite, amorphous carbon) [7]. The measured frictional force was found to be constant over a wide range of velocities (nm s⁻¹–μm s⁻¹). It was explained by a simple model, where the frictional forces are constant at sliding velocities well below the slip velocity (∼=60 μm s⁻¹). According to their argument, in the case of slow scan the stick-slip behavior [8] is repeated, assuming a multi asperity contact, whereas the tip continuously slides over the specimen in the fast scan case [9]. Bouhacina et al reported a logarithmic dependency of friction with velocity [10]. While mechanical models reveal no velocity dependency, a thermally activated stick-slip behavior should be considered at finite temperature to explain the velocity dependency. Gnecco et al also reported the same logarithmic velocity dependency at room temperature, in an ultra high vacuum condition [11]. On the other hand, there has also been a report on a negative velocity dependency [12]. Surfaces terminated with the hydrogen acceptor and donor...
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Figure 1. Representative topographic (a) and LFM (b) images of multi-layers of graphite measured simultaneously with a SiN cantilever. The image scan size was 5 × 5 μm², the normal force 6 pN and the scan rate 1.5 Hz. (c) The frictional forces were measured as a function of the thickness of the graphite film.

forming hydrogen bonding were suggested to have a friction inversely proportional to the sliding velocity.

It was nearly one hundred years ago when it was found that a graphite surface exhibits a particularly low frictional force [13]. Due to its exceptionally low friction, graphite has been used as a solid lubricant [14]. This superlubricity has been explained by the incommensurability between rotated graphite layers [15]. Recently, single layer of graphite or ‘graphene’ was discovered and has attracted great interest due to its two-dimensional physical properties [16]. Graphene-based composite materials [17] are also studied, because of their mechanical strength and low friction. In this report, we give experimental results and analysis of frictional forces on graphene using LFM technique.

2. Experimental details

A highly oriented pyrolytic graphite (HOPG) and graphite powder were used as starting materials. The graphene sample was formed on a Si wafer covered with a SiO₂ layer 300 nm thick using conventional mechanical exfoliation (the so-called ‘scotch tape’ method) [16]. The locations of large scale graphene layers were determined with an optical microscope.

A commercial AFM (XE-100, PSIA Co.) was used for the lateral force imaging. To achieve a high resolution of the lateral force in this experiment, a low stiffness SiN cantilever (biolever, Olympus) was employed. The cantilever was made from Si₃N₄ with a stiffness \( k = 0.006 \text{ N m}^{-1} \) and a resonance frequency of 13 kHz. Its thickness and length were 180 nm and 100 μm, respectively. This cantilever was particularly developed for force measurement of biological samples, due to its low stiffness. The tip, with \( l = 7 \mu m \) height, formed at the end of the cantilever has a hollow pyramid shape. The contact mode was employed with a feedback scheme to control the vertical bending (A–B signal) of the cantilever. The topographic and lateral force images were taken simultaneously. By changing the scan rate of the fast scan axis motion, the velocity dependence of the frictional force was measured. For the measurement of the normal force dependence, the setpoint of the A–B signal was changed using the proportional integration control algorithm.

The lateral tilting signal \( (V_{\text{C–D}}) \) of the cantilever was converted into the lateral force \( L \) by using a simple calibration method [18]. The conversion coefficient \( \alpha = (L/V_{\text{C–D}}) \) was estimated by fitting results of the preliminary data with a normal force \( N = 0.2 \text{ nN} \), and the coefficient \( \alpha \) obtained was found to be \( \approx 0.013 \text{ nN V}^{-1} \).

3. Results and discussion

Figure 1 shows representative topographic (a) and LFM (b) images of multi-layers of graphite measured simultaneously with a SiN cantilever. The image scan size was 5 × 5 μm²,
Figure 2. The topographic (a) and LFM (b) images at a boundary of a graphene layer were measured with a 500 × 500 nm² scan area. The normal force was 6 pN and the scan rate was 1.5 Hz. The line profiles are shown in the lower part. At the boundary, one can see a trench in the topography and a peak in LFM.

the normal force 6 pN, and the scan rate 1.5 Hz. The contact mode was employed and the scan direction was left-to-right. The left-top corner shows the SiO₂ substrate and successive higher layers corresponding to multi-layers of graphite with 1–4 nm gaps. As the graphite (thick layer) exhibits a particularly low friction, the area covered with graphite are shown in dark contrast in the LFM image [19]. One can see the contrast difference of the lateral force image between graphite layers with different thicknesses, though some impurities make the image blurred. If the frictional force is determined by physical properties of the surface only, the frictional coefficient on graphite layers with different thicknesses should have the same value. However, this image implies that the surface properties are not the only factor determining the friction.

The friction forces were measured as a function of the thickness of the graphite film, as shown in figure 1(c). The first data point in this graph indicates the friction on the SiO₂ substrate. These data points were measured on several different samples and different cantilevers and average values were taken. It is noticeable that the thinnest graphite film or graphene is measured to have a 1.5 nm thickness, which is much larger than the typical thickness of graphene. This discrepancy can be attributed to the exceptionally low stiffness of our cantilever. According to the literature, the thickness of graphene measured by AFM could be exaggerated by the difference of the attractive forces between graphene and the substrate [20, 21]. In order to check the influence of the adsorbed water in ambient conditions, the same sample was measured in distilled water. Qualitatively the same result was achieved (not shown in figure) except for the poor signal to noise ratio due to water fluctuation.

To study the difference of the frictional force in detail, a boundary area with different thicknesses was scanned, as shown in figure 2. The topographic (a) and LFM (b) images of the layer boundary of graphite of a few monolayer’s thickness were measured with a 500 × 500 nm² scan area. The normal force was 6 pN, and the scan rate was 1.5 Hz. The line profiles shown in the lower part indicate the average value across the width of the red areas in the images. In the topographic image (a), the layer height difference is about 0.5 nm from the line profile. This means that the boundary has a single atomic layer difference. However, one could see a trench at the boundary interface, which may be an artifact, because the graphene layer has a strong binding force in-plane and is not expected to be torn and separated with a small gap. We attribute this artifact to an excessive attractive force at the graphene boundary. This explanation is supported by the LFM image (b), which has a peak at the boundary. The LFM image shows also the contrast difference between the higher and lower terraces. It is plausible that the tip feels a large lateral force at the edge as it moves from lower to higher terraces. However, the tip motion direction was from left to right and it cannot be explained unless the additional attractive force at the boundary is considered.

The additional attractive force could be van der Waals or chemical forces induced at the graphene edge. The attractive forces can be considered to be isotropic and irrelevant to the direction moved. The increment of the attractive force at the graphene edge can be attributed to a Hamaker summation [22] of the van der Waals interaction, which could be increased if the substrate has complicated structures rather than a two-dimensional plane. However, considering the single atomic layer difference of the step, the Hamaker summation is not expected to be that different. The possible reason for the attractive force could be a chemical bonding force between the atoms of the tip and the graphene edge, but the detailed discussion is beyond the scope of this paper.
forces are independent of the normal forces.

In our experimental condition, the isotropic attractive force can be assumed to be much stronger than the normal force. The scanning velocity was slow so that a simply static mechanical force balance can be considered. Assuming that the cantilever is a mass suspended on a spring with a spring constant \( k \), the normal force can be ignored and the attractive force and the force dragging the cantilever need to be considered. The attractive force \( F_{\text{att}} \) should be equal to the restoring force of the spring, that is, \( F_{\text{att}} = k \Delta l \), where \( \Delta l \) is the expansion of an effective length of the cantilever. If \( \theta \) is the tilt angle of the cantilever, \( \theta \) can be considered to be approximately proportional to \( V_{\text{C-D}} \). \( \Delta l \) is given by the tilt of the cantilever from \( \cos \theta = l/(l + \Delta l) \). As a result,

\[
\cos \theta = \frac{l}{l + F_{\text{att}}/k}.
\]

Also, \( \theta \) describes an angle between the tilted attractive force \( F_{\text{att}} \) and horizontal lateral force \( L \).

\[
\sin \theta = L/F_{\text{att}}.
\]

By combining equations (1) and (2) with \( \sin^2 \theta + \cos^2 \theta = 1 \) and with \( \theta \ll 1 \), \( F_{\text{att}} \) can be approximated as

\[
F_{\text{att}} \simeq \left(\frac{1}{\alpha} \frac{\lambda \alpha^2 V_{\text{C-D}}^2}{2}\right)^{1/3},
\]

where \( \alpha = L/V_{\text{C-D}} \). By using this equation, the attractive (chemical) force can be estimated. With this calibration, the chemical force at the graphene edge was obtained as being 110 pN, which is a value much larger than the normal force 6 pN.

The normal force dependences of the friction on surfaces of (a) SiO_2, (b) graphene, and (c) graphite were measured, as shown in figure 3. The friction on SiO_2 was the greatest, that on graphene was next, and that on graphite was the least. These data were measured with a constant scanning velocity (10 \( \mu \text{m s}^{-1} \)) in air and at room temperature. As it is shown, the frictional forces are not dependent on the normal force. Independence of the normal force is plausible, considering that the attractive force was much stronger than the normal force.

The mean frictional force between the tip and the surfaces of samples was measured as a function of the scanning velocity \( v \), as shown in figure 4. These were measured at room temperature and in air, and the normal force was 6 pN. Three different data sets on (a) silicon oxide, (b) graphene, and (c) graphite are shown in a graph with semi-log plot. This kind of velocity dependence has been explained by the thermally activated stick-slip effect [10, 11]. The data were fitted to [11]

\[
F_L = F_{L0} + F_{L1} \ln \frac{v}{v_1},
\]

and the slopes \( F_{L1} \) were obtained to be (a) 0.83, (b) 0.48, and (c) 0.23, respectively. According to Gnecco, et al’s argument, the energy barrier \( \Delta E^+ \) vanishes near a critical point \( F_{L1}^* \),

\[
\Delta E^+ = \lambda (F_{L1}^* - F_{L1}),
\]

where \( \lambda = k_B T/F_{L1} \). From our experimental data, \( F_{L1} \) looks proportional to the average frictional force. In other words, the energy barrier \( \Delta E^+ \) is lower as the surface has higher friction, if the surfaces have a similar critical frictional force \( F_{L1}^* \).

The force–distance curve measurements were performed to investigate the attractive force for different sample heights, as shown in figure 5. Figure 5(a) shows the measured topographic image, with the line profile shown in red, where the last part corresponds to the SiO_2 substrate. The approach curves as a function of tip–sample distance were measured in water and in air as shown in figures 5(b) and (c), respectively. As the tip approaches the seven points numbered in figure 5(a), the cantilever deflections were measured and converted into a force using Hooke’s law. These curves show the typical shape of force spectroscopic data including slight decreases (attractive), jump-to-contact, and rapid increases (repulsive force) [23]. The sample and the tip were biased to ground and no static charge was involved in this measurement. Therefore,
these attractive forces are supposed to be van der Waals interactions judging from their long range. (A chemical force would be much shorter range.) As is expected, the data on SiO$_2$, numbered 1 and 2 involve large decreases and deep jump-to-contacts. The other data numbered 3–7 show that the jump-to-contact depths are decreased as the thickness at the contact points are increased. That is, the attractive force on SiO$_2$ was strongest and thicker graphite has a weaker attractive force. This could be indirect evidence that the friction is closely related to the van der Waals interaction, rather than the surface property.

In the water measurement, five different height points were selected and the approach curves were measured, as shown in figure 5(c), where the label shows the height differences. Except for one data set (▼), most data show the tendency that a thinner layer exerts a stronger attractive force. One can see that the force curves incline upward as they approach their jump-to-contact points. We attribute this repulsive force to the double layer force. The double layer force is supposed to exist for a charged tip or surface in an electrolyte solution. Although we used pure water, some ionic impurity could still be present in the water container, and a static charge could also exist at the Si$_3$N$_4$ tip. Regarding the attractive forces, the same qualitative result was obtained in the water experiment.

In order to confirm that the film 1.5 nm thick is indeed graphene, a Raman spectroscopy measurement was performed. The Raman spectroscopy results are shown in figure 6, where the data measured on the graphene (1.5 nm) layer are shown in black. The data on graphite, a thick flake on the same substrate, are measured and shown in red for comparison. It is well
known that the 2D peak at 2700 cm\(^{-1}\) is down-shifted and the height of the G peak at 1580 cm\(^{-1}\) is lowered in graphene [24].

4. Conclusions

We have studied frictional behavior as an SiN tip slides on three different surfaces: SiO\(_2\), graphene and graphite. It was found that the values of friction on graphite and graphene are quite different, even though they have the same surface in terms of morphology and chemical structure. By measuring the force–distance spectroscopy, the difference of friction between graphene and graphite was suspected to be related to the van der Waals forces. The friction as a function of velocity was measured, and a logarithmic dependency was found, which could be explained by thermally activated stick-slip behavior.

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