Probing the Adhesion Interactions of Graphene on Silicon Oxide by Nanoindentation

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ABSTRACT

Although a variety of fundamental mechanical properties of graphene have been investigated, the nature of interactions between graphene and other materials is not yet fully understood. Here, we report on adhesive interactions of between diamond indenters and monolayer, bilayer and trilayer graphene on silicon oxide as well as bare silicon oxide and graphite over relatively small spatial domains. Displacement-controlled nanoindentation with an ultralow noise force sensor allowed the complete adhesive responses to be observed without the usual instabilities associated with nanoindenters that operate in force control. It was found that the approach and withdrawal force profiles between diamond and graphene depended on the number of layers of graphene. The unloading response contained very characteristic features, which were attributed to separation between graphene and silicon oxide in subsequent stress analyses of the experiments. The numerical stress analyses accounted for the interactions between the probe and the graphene as well as between graphene and silicon oxide *via* traction-separation relations which included attractive and repulsive interactions. As a result, it was possible to extract the energy, strength and range of the interactions for all cases, thereby providing a much richer measure of the interactions than relying solely on force profiles.

1. Introduction

Due to its extreme thinness and high specific surface area, graphene can be easily deformed by surface forces when the separation between it and a neighboring surface is in the nanometer range [1]. Thus, adhesion is critical in many important applications of graphene such as micro- and nanoelectromechanical systems (MEMS/NEMS) [2, 3], flexible devices

[4, 5], and surface coatings [6]. For example, electromechanical switches, where suspended graphene membranes are actuated by applying an electrical field, cannot operate properly when adhesive interactions prevent the release of the graphene membranes from the electrode after making a contact [3]. In addition to device applications, adhesion is also of importance in manufacturing processes of graphene. One of the most promising methods to synthesize high-quality graphene in large areas is chemical vapor deposition (CVD) on metal seed layers with hydrocarbon sources [7, 8]. However, the graphene grown on metals needs to be transferred to functional target substrates for device applications by using wet/dry transfer techniques [9-13], transfer printing [14], or roll-to-roll transfer techniques [15], where contact and separation events are involved and the detailed adhesion interactions could vary depending on the contact pairs and process environments.

Recently, several research groups have studied the adhesion properties of graphene. Mechanically exfoliated graphene on silicon oxide has been studied for measuring the adhesion energy by applying pressure on the micro-sized suspended graphene membranes and monitoring the surface profile of the deflected membrane [16-19]. This micro-blister test revealed that the adhesion energy between monolayer graphene and silicon oxide was 450 mJ/m^2 [16]. At larger scales, double cantilever beam fracture tests have been used to characterize the adhesion energies of monolayer CVD graphene to silicon [20], copper deposited on silicon [21], and copper foils [13] at 357, 720, and 6000 mJ/m^2 , respectively. Although the adhesion energy can be used to indicate how well surfaces will adhere, the strength and the range of the interactions are required to explain the transient responses associated with approach and separation. The strength of the interaction is the maximum value of the adhesive traction that can be sustained. Traction vector represents the resultant force per unit area on a surface and has the units of stress (Pa). Such continuum descriptions of the interactions between surfaces are known as traction-separation relations and have

recently been determined for interactions of graphene that was wet-transferred to silicon [20]. This approach was also able to distinguish the interactions between graphene and its seed copper foil, and graphene and epoxy [13]. In both cases, the strength of the interactions was lower and their range was longer than those expected for van der Waals forces [20]. However, the adhesion strengths that were determined might have been limited by the resolution of the separation measurements. Thus, we turn to nanoindentation experiments, whose resolution is better by at least two orders of magnitude.

Atomic force microscopy (AFM) has gained widespread use in accurate measurements of adhesion forces at the molecular level because of its superior force sensitivity and spatial resolution [22, 23]. However, the inherent instability of this cantilever-based instrument causes “jump-to-contact” behavior, or a snap in the force-displacement response [24]; when the interaction force gradient between the AFM tip and a sample is larger than the stiffness of the AFM cantilever, the tip crashes onto the surface of the sample and portions of the interaction between the tip and the sample are lost [25]. Thus, high-resolution displacement-controlled measurements are required in order to completely observe adhesive interactions [26, 27].

Here, we report on nanoscale measurements of the adhesion properties of monolayer, bilayer and trilayer graphene on silicon oxide layer as well as graphite. The experiments are conducted under displacement control with a nanoindentation tool with an ultralow noise force sensor under ambient conditions as well as in a nitrogen environment, thereby enabling the transient adhesive interactions between the diamond probe and the samples listed above to be captured in a quantitative manner. The obtained force profiles are first analyzed by the Derjaguin-Muller-Toporov (DMT) contact model. A more detailed numerical analysis is then used to identify some interesting features of the load-displacement response.

2. Experimental

2.1. Preparation of graphene on silicon oxide

To transfer of graphene onto silicon oxide, we used the polymer-assisted transfer technique shown in Fig. S1 (see Supporting Information) [5, 9]. The graphene grown on copper foil was spin-coated with poly(methyl methacrylate) (PMMA, Mw 996,000, Sigma Aldrich) dissolved in chlorobenzene (Sigma Aldrich). The copper was etched away by floating the PMMA/graphene/copper on the surface of an ammonium persulfate solution (0.1 M, Sigma Aldrich). After etching the copper, the PMMA/graphene film was moved to fresh water to clean the surface of graphene. Then, the PMMA/graphene film was picked up by the bare silicon oxide substrate and completely dried. To improve the adhesion of the PMMA/graphene to the silicon oxide surface, the whole substrate was heated at ~ 130 °C for a few hours. The PMMA was removed by putting the substrate into an acetone bath. However, this still leaves some residue of PMMA on the graphene surface. Thus, the graphene on silicon oxide was placed in a furnace and heated at ~ 400 °C in a hydrogen/argon environment to thermally decompose the PMMA residue. To make bi- or trilayer graphene films, the PMMA/graphene film floated on the water surface was picked up with another graphene on copper foil. The adhesion of the PMMA/graphene film to the graphene/copper foil was then increased by heating the sample at ~ 130 °C for a few hours. Once the stacked graphene films were obtained on copper foil, the copper was also etched with the ammonium persulfate. The PMMA/graphene film was then transferred onto silicon oxide.

2.2. Nanoindentation

The nanoindentation tests were performed by a displacement-controlled indentation tool equipped with an ultralow-noise capacitive MEMS force sensor (TI 950 Triboindenter, Hysitron Inc.) to capture the interactions between the target surface and the diamond probe

tip. During the indentation experiments, the tip with a radius of 50 nm approached the surface of the sample at a rate of 2 nm/s and the penetration depth was set to 5 nm. The tip was then withdrawn from the sample at the same rate.

2.3. Analyses

The classical Hertz and DMT contact models were used for an initial examination of the measured force profiles. More detailed finite element analyses were used to provide further insights. All materials were modeled as linearly elastic, isotropic materials and the interactions between the diamond tip and its contact pairs as well as graphene and silicon oxide were accounted for by traction-separation relations. More details are provided in the Supporting Information.

3. Results and discussion

3.1. Preparation of indentation samples

Five types of samples were prepared for the indentation measurements (Fig. 1a): bare silicon oxide (300 nm thick) on silicon, mono-, bi-, trilayer graphene on silicon oxide, and graphite (HOPG, SPI-2 grade, SPI Supplies). Monolayer graphene was grown on copper foils using low pressure CVD with methane as a hydrocarbon source [7]. Then, it was transferred onto silicon oxide by the polymer-assisted wet transfer technique [9]: spin-coating a thin layer of poly(methyl methacrylate) (PMMA), etching the copper foil, transferring the PMMA/graphene film onto silicon oxide, and removing the PMMA with acetone. Any residue of the polymer film, which may affect the adhesion measurements, was removed by thermal decomposition at 400 °C in a hydrogen/argon environment. Bi- and trilayer graphene films were also prepared by sequentially stacking monolayer graphene films in the wet transfer processes (Fig. S1) [5]. Raman spectra (488 nm laser wavelength excitation) after the

transfer exhibited the typical characteristics of high-quality monolayer graphene (Fig. 1b): the minimal D band at $\sim 1350\text{ cm}^{-1}$, a full width at half-maximum of $\sim 27\text{ cm}^{-1}$ for the 2D band at $\sim 2690\text{ cm}^{-1}$, and a high integrated intensity ratio of the 2D band to the G band ($I_{2D}/I_G \approx 3.6$) [28]. A graphite sample was prepared by freshly cleaving HOPG prior to the indentation tests.

3.2. Nanoindentation

A series of force profiles taken in an ambient environment (28% relative humidity at 25°C) on bare silicon oxide, monolayer graphene and graphite are compared in Fig. 2a. As the diamond tip approached, the specimens with bare silicon oxide (Fig. 2b) and graphene (Fig. 2c) experienced the largest adhesion forces ($\sim 45\text{ nN}$) with a series of jogs along the way. These are presumably related to the presence of water between the tip and the two surfaces [25, 29, 30]. The maximum adhesion force between the graphite and the diamond tip was about 10 nN . The interaction range was about 8 nm , which was the same as the range for the bare silicon oxide surface. The range for graphene was about 5 nm . Even though transient adhesion responses were successfully measured by means of the stable indentation system, the presence of condensed water on the surfaces [31] and formation of water bridges [29] between the tip and surfaces made quantitative analyses difficult. A higher degree of control of the environment (13% relative humidity at 26°C in a dry nitrogen environment) led to much more consistent behavior and was consequently the focus of this study.

The approach force profiles obtained in a dry nitrogen environment for specimens consisting of silicon oxide, monolayer, bilayer and trilayer graphene and graphite are compared in Fig. 3a. The interactions between diamond and graphite were again quite distinct from all the other cases, but were similar to those observed in the ambient environment. For purposes of clarifying discussion, details of a representative force profile during approach and withdrawal are shown in Fig. 3b-f for each sample. **Note that a number of force profiles**

were obtained at different spots on each substrate. The repeatability of the force profiles was excellent. The bare silicon oxide (Fig. 3b) displayed a much more sudden force drop in dry nitrogen than in ambient. This is most likely due to the formation of a condensed water bridge between the tip and silicon oxide at a relative displacement of ~ 5.5 nm. Even at a relative humidity of 13%, it is likely that a thin layer of water existed on the silicon oxide and diamond surfaces due to their hydrophilic nature. When the surfaces were close enough, the water layers coalesced to form the water bridge in a dynamic event, which exceeded the response time of the feedback circuit to form a snap. Further thickening of the water bridge was more gradual and increased the level of the attractive force which reached a maximum of 25 nN at a relative separation of 2 nm. When specimens with monolayer (Fig. 3c), bilayer (Fig. 3d) and trilayer (Fig. 3e) graphene on silicon oxide were examined, the initial force drops became progressively smaller as the number of layers of graphene increased. The maximum attractive force was the same in all three cases and was slightly lower at ~ 20 nN at separations of ~ 1 nm. There was no evidence of the sudden formation of water bridges when diamond tips approached graphite and the maximum force was ~ 10 nN although the range (~ 6 nm) was slightly longer than any of the other cases. Thus, assuming that the noted interaction between diamond and graphite reflects that of many layers of graphene, increasing the number of layers of graphene on silicon oxide increasingly screens out the intrinsic force field between silicon oxide and the diamond tip. Similar observations were made by Rafiee *et al.* who noted that increasing the number of layers of graphene on copper and glass gradually increased the water contact angle towards that of graphite [32]. In molecular simulations, Shih *et al.* found that substrate-supported graphene can transmit about 30% of van der Waals interactions between water and a substrate [33]. It might be thought that the increasing transparency with decreasing the number of graphene layers reflected the presence of defects, which would be less obscured with fewer layers of graphene. Polycrystalline graphene

synthesized by CVD certainly has point and line defects that may allow the diamond tip to interact with the silicon oxide and might cause variations in the measured force profiles. However, the consistency of repeated measurements on different spots for each sample (Fig. S2) confirms the increased translucency of multilayer graphene.

In all cases, the approach and withdrawal portions of the force profiles provided evidence of adhesion hysteresis (Fig. 3b-f). This usually means that some irreversible transformations occurred during contact [34] possibly due to chemical effects, humidity and surface roughness [35]. However, in comparing the unloading response of the diamond indenter from the silicon oxide (Fig. 3b) and transferred graphene samples (Fig. 3c-e), it can be seen that the peak separation force was higher in the latter and was followed by a much larger and sharper drop before settling into a nearly linear withdrawal response. The peak separation force and drop in the adhesive interaction was even more apparent when the diamond indenter was withdrawn from the graphite sample (Fig. 3f). This suggests that additional mechanisms such as delamination between graphene and silicon oxide or graphite interlayers were at play. This possibility will be explored later.

3.3. Analyses

3.3.1 DMT Analysis

Several theories have been developed for describing the contact regime. The classic Hertz model [36] assumes a hemispherical contact pressure inside the contact area, but does not include adhesive forces between contact pairs. However, adhesive interactions were apparent in all cases (Fig. 2 and 3). Thus, the Hertz model does not apply here. Adhesive contact has been addressed analytically by Johnson-Kendall-Roberts (JKR) [37], DMT [38] and Maugis [39] models. The Tabor parameters (see Methods section) for each contact pair are listed in Table 1. They were all within the 0.1 upper bound for applicability of the DMT model. The

adhesion energies for approach (ω_a) and withdrawal (ω_w) extracted on the basis of the DMT model are also shown in Table 1 and Fig. 4. In all cases, $\omega_a < \omega_w$ as expected from the force profiles. The slight differences in the force profiles (Fig. 3) for diamond indenting silicon oxide and mono-, bi- and trilayer graphene on silicon oxide were mainly reflected in the value of ω_a for the trilayer graphene on silicon oxide, which was $61.9 \pm 2.2 \text{ mJ/m}^2$ compared with a nearly constant value of 75 mJ/m^2 for the other three cases. The corresponding adhesion energy for graphite was considerably lower at $25.9 \pm 5.8 \text{ mJ/m}^2$. The situation was reversed for the adhesion energies on withdrawal (Fig. 4), where the diamond-graphite interaction yielded an adhesion energy of $187.1 \pm 12 \text{ mJ/m}^2$. Mono-, bi- and trilayer graphene on silicon oxide came in next at $\sim 120 \text{ mJ/m}^2$, followed by bare silicon oxide at $91.5 \pm 2.9 \text{ mJ/m}^2$. Thus, in terms of the adhesion energy derived from the DMT model, the adhesive hysteresis appeared to be greatest for HOPG and least for bare silicon oxide. However, the force profiles obtained from the DMT analyses were unable to capture some of the characteristics of the measured ones (Fig. S5), which suggested that more complex numerical analyses of the experiments might be warranted.

3.3.2 Simple Interactions

Such numerical analyses should incorporate traction-separation relations as the continuum representation of the interactions between the tip and contact surface. The closed form analysis by Maugis [39] was able to accomplish this by assuming the simplest possible traction-separation relation; a constant traction over the full interaction range. The bilinear form was used to extract the traction-separation relations between the tungsten tip of an interfacial force microscope and a self-assembled monolayer [40]. This approach was attempted for the experiments that were conducted in the present study, but was unsuccessful. A series of bilinear traction-separation relations were selected to demonstrate this for the indentation of silicon oxide. They all had the same adhesion energy (80 mJ/m^2) and strength

(20 MPa) but became progressively stiffer (Fig. S6a). The resulting force profiles are compared in Fig. S6b. In all cases, the maximum adhesion force and repulsive response were captured quite well. However, the sudden increase in the adhesive response could not be captured by even the stiffest traction-separation relation. Furthermore, the measured gradual transition from adhesion to repulsion could not be captured by these bilinear traction-separation relations, most likely due to the lack of a repulsive component.

3.3.3 Lennard-Jones Interactions

Lennard-Jones (L-J) type potentials with their adhesive and repulsive components have been used to model adhesive contacts [41]. The standard 6-12 L-J potential was considered for modeling the interactions between the diamond tip indenting graphite. This case was chosen because there was no jump to contact (Fig. 3f) to complicate matters on approach. The finite element analysis was conducted by using the commercial code ABAQUS with an axisymmetric model (Fig. S4) which captured the linearly elastic, isotropic response of diamond and graphite. However, it was found that it was necessary to use the form $\sigma = (9\Gamma_a / 2\delta_0) \left[(\delta_0 / \delta)^4 - (\delta_0 / \delta)^{10} \right]$ for the traction-separation relation for approach and $\sigma = (9\Gamma_w / \delta_0) \left[(\delta_0 / \delta)^4 - (\delta_0 / \delta)^{10} \right]$ for withdrawal (Fig. S7a). In these expressions, Γ_a and Γ_w were the adhesion energies associated with approach and withdrawal, respectively, and δ_0 was the equilibrium separation (Table S3). While the initial approach was successfully modeled up to the maximum adhesive force (Fig. S7b), the selected traction-separation relation was unable to capture the transition to higher repulsive loads, where the simulation and data were quite close. The transition is governed by the repulsive stiffness of the traction-separation relation. The differences in the unloading response were more noticeable. Because the adhesion energy in withdrawal was chosen on the basis of the maximum adhesive force during withdrawal, the simulation and data were in reasonable

agreement, but the separation at which it occurred was not. A smaller value of δ_0 would have had to have been selected for the traction-separation relation for withdrawal. Finally, the simulated decay of the adhesive force was much more rapid than the measured one. The long, nearly linear tail of the measured response is due to capillary forces, which cannot be captured in L-J type potentials. The hypothesis that is explored next is that the sharp peak during withdrawal could be a reflection of solid/solid van der Waals interactions between the tip and graphite. It could also be caused by interlayer delamination in the graphite. The long tail is due to capillary effects, which were also present during withdrawal of the diamond tip from mono-, bi- and trilayer graphene. However, in those cases, the sharp peak was likely due to delamination between graphene and silicon oxide.

In order to define the interfacial response between the graphene and silicon oxide, 420 mJ/m² was used as the steady-state adhesion energy with a maximum strength of 100 MPa at 0.5 nm (Table S2). The energy level and the exponential decay were motivated by results of previous work [20].

3.3.4 Complex Interactions

The procedure that was adopted to determine the traction-separation relations that provided the best fit to the measured force profiles was as follows. All the force profiles exhibited hysteresis. This was not due to any permanent deformation of the target substrates as neither scanning electron nor atomic force microscopy revealed any signs of this. Instead, it was due to changes in conditions during contact, which required different traction-separation relations for approach and withdrawal as described below.

For approach, in all cases, the measured force profiles were subtracted (Fig. S4d) from the Hertz force profile. The difference was taken to be due to the interactions between the contact pairs. The traction-separation relations that provided the best fit to this difference in force profiles were determined iteratively. For withdrawal, different mechanisms had to be

accounted for: a) for silicon oxide, capillary effects were dominant and were modeled by a constant traction over the interaction range; b) for single layer graphene, delamination between the graphene and silicon oxide and capillary interactions between graphene and the diamond tip were considered; c) for graphite, the initial part of the traction-separation relation for interactions between the tip and graphite during withdrawal was obtained using the same fitting process that was used for approach (comparison with Hertz force profile) until capillary interactions became dominant. It is possible that there may also have been interlayer delamination in the graphite, but this was beyond the scope of the present study. The details of all the modeling are provided in supplementary materials.

3.3.5 Diamond/Silicon Oxide

The traction-separation relation that was used to model the approach of the diamond tip to the silicon oxide is shown in Fig. 5a. As indicated above, it was obtained by comparing the measured and Hertz force profiles. The repulsive traction at zero separation was 200 MPa, the equilibrium separation was 1.2 nm and the maximum adhesion strength was 70 MPa at 5.3 nm with an adhesion energy of 84.2 mJ/m². The drop in traction from the maximum to zero reflected the jump to contact that was seen in the measured force profile (Fig. 5b). The use of a finite repulsive traction (200 MPa) was required to ensure convergence and provided a smooth transition from attraction to repulsion in the force profile. The traction-separation relation for withdrawal (Fig. 5a) had a small peak (see arrow) before dropping to the constant traction of 10 MPa, which taken to represent the effect of capillary forces, whose range was 10 nm. This provided the observed slope for the long linear response during withdrawal and essentially provided a means of accounting for the thinning of the water bridge. The adhesion energy was 98 mJ/m².

3.3.6 Diamond/Monolayer Graphene

The traction-separation relation that was used to model the approach of the diamond tip to single layer graphene on silicon oxide is shown in Fig. 5c. The overall shape of the traction-separation relation was the same as the one used for diamond and silicon oxide. However the critical parameters were as follows: The repulsive traction at zero separation was 2.9 GPa, the equilibrium separation was 2.35 nm and the maximum adhesion strength was 50 MPa at 6.0 nm with an adhesion energy of 55 mJ/m². The lower strength accommodated the smaller load snap (Fig. 5d) that was observed. The 2.9 GPa repulsive traction was selected for a smooth transition from attraction to repulsion in the force profile. The traction-separation relation for withdrawal (Fig. 5c) had a maximum strength of 100 MPa at a separation of 0.8 nm and transitioned to 10 MPa at 1.2 nm in order to follow the same capillary force that was used for diamond and silicon oxide. The adhesion energy was 149 mJ/m². This choice of parameters provided the observed peak force and linear pull off. The peak tensile force was much higher than the one for diamond interacting with silicon oxide and reflected the possibility of separation between graphene and silicon oxide as will be explored later.

3.3.7 Diamond/Graphite

The traction-separation relation that was used to model the approach of the diamond tip to graphite is shown in Fig. 5e. Because there was no snap in this case, the shape was somewhat different from the other two. The repulsive traction at zero separation was 532 MPa, the equilibrium separation was 2.3 nm and the maximum adhesion strength was 4.2 MPa at 5.6 nm with an adhesion energy of 21.5 mJ/m². This choice of parameters provided a good fit to the observed force profile (Fig. 5f) for approach. The traction-separation relation for withdrawal (Fig. 5e) had a maximum strength of 230 MPa at a separation of 0.8 nm and transitioned to 10 MPa at 1.2 nm in order to follow the same capillary force that was used for

the previous two cases. The adhesion energy was 227 mJ/m^2 . While this was sufficient to capture the peak withdrawal force and the interaction range (Fig. 5f), there were some notable differences. First, the initial unloading slope was stiffer than the loading one. This portion of the response is controlled by the elastic stiffness of the contact pair, but since it is unlikely that the diamond stiffness changed, it appears that the graphite had become stiffer ($\sim 25 \text{ GPa}$) during indentation. It is not clear what the mechanism for this might be. Second, the steepness of the decrease in the tensile load following the peak was not captured by the simulation, which also predicted a linear response for the remainder of the interaction. The sharper drop in tensile force could have been due to interlayer delamination in the graphite. The lack of a subsequent linear decay, which had been attributed to thinning of the water bridge in the previous two cases, suggests a different mechanism in this case. This may be related to the lack of the formation of a water bridge during approach as evidenced by the lack of a snap for the more hydrophobic graphite surface. Thus while some water was likely present during withdrawal, there was much less than in the previous two cases, which may then have altered the manner in which any thin water layers separated.

3.3.8 Diamond/Graphene

The most interesting case was the indentation of single layer graphene on silicon oxide, where the possibility of delamination between the two was considered while the diamond tip and graphene were still interacting. The details of the stress histories and distributions during the approach of the diamond tip are shown in Fig. 6. The simulated force profile indicates (Fig. 6a) that the interaction between the graphene layer and the tip initiated at the point ① at a relative displacement of $\sim 5 \text{ nm}$. The radial distribution of normal stress between the diamond and graphene at ① (Fig. 6b) was attractive up to 5 nm from the center and zero beyond that, as the separation was beyond the interaction range of the two. The corresponding stress contours in the tip, graphene and silicon oxide at ① are shown in Fig. 6c.

The tensile zone in the tip had the highest stresses at about 65 MPa and there were signs of **separation** between graphene and silicon oxide (see insert to Fig. 6c). States ② and ③ mark the transition from adhesion to repulsion. Thus it can be seen that the distribution (Fig. 6b) of the normal stress at ② is zero at the center and reaches its maximum at about 20 nm from the center, before returning sharply to zero due to the sudden drop in the traction-separation relation (Fig. 5c). The corresponding normal stress contours (Fig. 6d) are slightly tensile and the **separation** between the graphene and silicon oxide is no longer apparent. The normal stress distribution for ③ captures part of the repulsive portion of the traction-separation relation at the center and all of its attractive part. The contours (Fig. 6e) are compressive near the center with some tensile stresses beyond that.

The force profile during the withdrawal is shown in Fig. 7a and the states ④, ⑤, and ⑥ are identified for further discussion. State ④ was at the peak attractive force, so the normal stress distribution along the graphene surface (Fig. 7b) from the center first reflects large tensile interaction (Fig. 5c) in the traction-separation relation for graphene and the diamond tip. This then transitions to the capillary interaction at about 12 nm from the center, which itself ends at about 30 nm. At the same time, the normal stress contours in the graphene and silicon oxide indicate that the separation between the two was sufficient to cause some damage but not complete separation. This was due to the low bending stiffness of the one-atom-thick graphene layer [1] and the relative strengths of the interactions between the diamond tip and graphene and silicon oxide and graphene. At state ⑤, there was more separation (Fig. 7d) between the graphene and silicon oxide, but this subsided (Fig. 7 e) by the time State ⑥ was reached and capillary forces became dominant.

Further insight into the separation between graphene and silicon oxide is provided in Figure 8, where the variation of crack radius with the relative position of the indenter is plotted. There was a 5-nm jump in the crack radius at an approximate relative tip separation

of 7 nm. This coincides with the formation of the water bridge between the probe and monolayer graphene. The crack then grew more and more slowly until the direction of the probe was reversed. Nevertheless, this means it was growing while the overall load was compressive. This was due to the tensile interactions outside the compressive zone (Fig. 6e). There was some growth (~3 nm) associated with the switch to the diamond/graphene traction-separation relation for withdrawal. The crack healed as the probe was withdrawn, but the healing was incomplete due to some residual damage to the graphene/silicon oxide interface.

4. Conclusion

The displacement-controlled indentation experiment, with ultralow-noise force measurements, allowed the complete nonlinear adhesive interactions between a diamond indenter and mono-, bi- and trilayer graphene on silicon oxide to be observed. Bare silicon oxide and HOPG surfaces were also considered as controls. As the number of graphene layers was increased, there was a transition in the adhesive interactions between the tip and the surfaces that ranged from that of bare silicon oxide to that of graphite. On approach, there was a snap which was associated with water bridge formation. The extent of this snap was greatest for bare silicon oxide, which is hydrophilic; it diminished as the number of graphene layers increased and was completely absent for graphite, which is hydrophobic. These observations suggest that graphene partially screened the force field between the diamond tip and the silicon oxide.

In the traction-separation relations for approach, the snap was represented by a sharp tensile interaction with a strength of 70, 50 and 4.2 MPa and a range of 5.3, 6 and 5.6 nm for diamond/silicon oxide, diamond graphene and diamond graphite interactions, respectively. The first two are commensurate with expectations for long-range van der Waals interactions,

with high enough strengths and slightly long ranges. The strength of the diamond/graphite interaction is so low that any van der Waals interaction is somehow being modulated. An interesting feature of all the interactions for approach was that repulsive ones were required in order to bring the compressive portions the measured and predicted force profiles into registration. Hard wall (rigid repulsive) interactions would have been much too stiff. Diamond interactions with silicon oxide and graphene required compressive strengths of 200 GPa and equilibrium interaction ranges of 1.2 to 2.35 nm, respectively. The diamond/graphite interaction was also much weaker in repulsion. The higher attractive and repulsive strengths given here certainly suggest the presence of van der Waals forces, while the snaps that occurred at about 6 nm suggest the formation of water bridges was an additional factor.

The withdrawal portion of the force profiles contained two main features; the first was a relatively sharp drop from the maximum adhesive force, particularly for the graphene and graphite surfaces. The second was the gradual decay to zero force without the snap that had been observed on approach. The possibility that the sharp drop was caused by delamination between the graphene and silicon oxide was explored by assigning different traction-separation relations to the diamond/graphene and graphene/silicon oxide interactions in simulations of the experiment. It was found that the graphene separated during approach and withdrawal, but never to the point of complete separation. For the bare silicon oxide and all three graphene surfaces, the long linear decay prior to complete separation between the indenter and the surfaces was attributed to the thinning of the capillary bridge, which was captured by a constant traction within the remaining interaction range.

The traction-separation relations for withdrawal were initially characteristic of van der Waals interactions with strengths of 100 and 230 MPa with range of 0.8 nm for interactions diamond and graphene and graphite, respectively. This initial portion of the attractive response during withdrawal was followed by a thinning of the water bridges that formed

during approach, with an essentially linear response that was captured by capillary forces with a strength of 10 MPa and interaction range of 10 nm. Note that attractive portion of the diamond/silicon oxide force profile during withdrawal was completely captured by capillary effects, which is consistent with the hydrophilic nature of silicon oxide.

Note that graphene/silicon interactions were also manifest in the attractive portions of the force profiles during both approach and withdrawal. This was accomplished via a traction-separation relation for interactions between graphene and silicon oxide, with a strength of 100 MPa and range of 9.6 nm. This strength level matched that of the diamond/graphene interaction and ensured that the graphene was not completely stripped from the silicon oxide. Thus while the strength value suggests van der Waals forces, the range of the interaction also suggests the possibility of the presence of a very thin layer of water between the graphene and silicon oxide. This combination of parameters was quite different from the strength and range of 8 MPa and 250 nm that were extracted in fracture experiments [20]. The contact areas in the fracture experiments were much larger than those experienced in the indentation experiments reported here, which suggests the potential for interesting scale effects.

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Fig. 1. (a) Schematic illustration of nanoindentation on monolayer graphene on silicon oxide.
(b) Raman spectra of monolayer graphene on silicon oxide and graphite.

Fig. 2. Force profiles obtained under ambient conditions: (a) comparison of all responses and individual responses for (b) bare silicon oxide, (c) monolayer graphene, and (d) graphite.

Fig. 3. Force profiles obtained in nitrogen: (a) comparison of all responses and individual responses for (b) bare silicon oxide, (c) monolayer graphene, (d) bilayer graphene, (e) trilayer graphene and (f) graphite.

Fig. 4. Adhesion energies for all surfaces obtained from DMT analyses of approach and withdrawal.

Fig. 5. Traction-separation relations for and comparison between simulated and measured force profiles during approach and withdrawal: (a and b) bare silicon oxide, (c and d) monolayer graphene and (e and f) graphite.

Fig. 6. Normal stress distributions as a diamond tip approached monolayer graphene on silicon oxide: (a) force profile identifies states ①, ② and ③, (b) normal stress distribution along the graphene surface from the center of the model and (c-e) normal stress contours at (c) state ①, (d) state ② and (e) state ③.

Fig. 7. Normal stress distributions as a diamond probe withdrew from monolayer graphene on silicon oxide: (a) force profile identifies states ④, ⑤, and ⑥, (b) normal stress distribution along the graphene surface from the center of the model and (c-e) normal stress contours at (c) state ④, (d) state ⑤ and (e) state ⑥.

Fig. 8. The crack radius as the diamond probe approached to and withdrew from monolayer graphene on silicon oxide

Table 1. Tabor parameters and adhesion energy (DMT) under a dry nitrogen environment

DMT					
	SiO ₂	Monolayer	Bilayer	Trilayer	Graphite
μ_T	0.0836	0.0649	0.0603	0.057	0.0622
ω_a (mJ/m ²)	76.9±4.6	74.4±2.7	76.6±2.9	61.9±2.2	25.9±5.8
ω_w (mJ/m ²)	91.5±2.9	121±10.3	119.4±10.4	119.9±6.4	187.1±12
FEM					
ω_a (mJ/m ²)	84.2	55.5	-		21.57
ω_w (mJ/m ²)	98	149			227

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