Peeling of Graphene Sheet – Simulation Study

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The nanoscale peeling of the graphene sheet is numerically studied by molecular mechanics simulation. In the simulation, a rectangular-shaped monolayer graphene sheet with each side of 38 Å×21 Å, comprised of 310 carbon atoms, is peeled from the rigid graphite surface. The six-membered ring around the center position is lifted. We have first obtained the vertical force-distance curve which reflects the transition of the graphene shape from the surface- to the line-contact during the peeling process. The successive partial peelings of the graphene around the lifting center appear as discrete jumps in the force curve, which induce the arched deformation of the graphene sheet.

Keywords: Peeling; Adhesion; Graphene; Computer simulations; Physical adsorption; Atomic force microscopy; Tribology; Wear

I. INTRODUCTION

Adhesion and peeling phenomena play important roles for connecting two objects regardless of whether they are inorganic, organic or biological materials, which contributes to building up microscopic devices. Recently we have studied the peeling mechanics of the carbon nanotube (CNT) adsorbed on the graphite surface both theoretically [1–3] and experimentally [4]. It is clarified that the transition from the line- to the point-contact between the CNT and the graphite surface appears in the force curve during the peeling process [1–4]. The CNT on the sub-microscale has the same size as the spattucae of the microscopic hairs aligned on the gecko foot [5, 6]. Therefore the study of the peeling process of the nano-scale objects such as CNT is useful for not only developing the gecko-foot-mimic adhesives [7] but also understanding the elementary process of adhesion.

In this paper peeling mechanics of another nano-scale carbon objects, graphene, is focused. Since the success of its experimental isolation [8], the graphene has recently attracted great interests as the components of the electronic devices [9, 10]. The peeling mechanics of the graphene sheet can be regarded as the elementary process of the macroscopic sticky tape or extension of the crack in the fracture. There is also a possibility that its adhesion with the substrate is applied to the adhesive tape at nanoscale. Therefore, in this paper, the peeling mechanics of the graphene sheet is numerically studied as the first step to clarify its adhesive mechanics.

II. MODEL AND METHOD OF SIMULATION

In the simulation, a rectangular-shaped monolayer graphene sheet with each side of 38 Å×21 Å, comprised of 310 carbon atoms, is peeled from the rigid rectangular graphene sheet (which is called ‘graphite surface’ hereafter) with each side of 164 Å×58 Å, comprised of 3536 carbon atoms [Fig. 1(a)]. First, both the above graphene sheets are separately optimized by minimizing the covalent bonding energy described by the Tersoff potential energy [11], $V_{\text{cov}}$, using the Polak-Rebiere-type conjugate gradient (CG) method [12]. Here the convergence criterion is set so that the maximum of absolute value of all the first derivatives of the energy is less than $10^{-5}$ eV/Å. Next, the graphene sheet is put onto the graphite surface, so that the AB stacking registry between the graphene sheets and the graphite surface is conserved [Fig. 1(b)]. Here the green-colored six-membered ring at the center position of the graphene sheet is assumed to be attached to the AFM tip apex [Fig. 1(a)], and then it is gradually moved upward along the z direction, parallel to the [0001] axis, by 0.1 Å. For each lifting position of the graphene sheet, $\Delta z$, the total energy $V_{\text{total}} = V_{\text{cov}} + V_{\text{vdW}}$ is minimized using the CG method, where $V_{\text{vdW}}$ is the non-bonding vdW interaction comprised of the Lennard-Jones (LJ) potential energy [13], acting between the graphene sheet and the graphite surface. Thus the optimized positions of the movable carbon atoms of the graphene sheet, $(x, y, z)$, the vertical peeling force $F_z$, and the lateral sliding forces $F_x$ and $F_y$, acting on the lifting center, are calculated.

III. RESULTS

When the six-membered ring located at the center position of the monolayer graphene sheet is lifted, the graphene sheet exhibits the characteristic transition of its shape during the peeling process within the $x-z$ plane as illustrated in Figs. 2(A)-2(J), corresponding to Figs. 3(A)-3(J), the vertical force acting on the lifting center position $F_z$ plotted as a function of the displacement from the initial position along $z$-direction, $\Delta z$. At first the monolayer graphene sheet takes an initial planar structure parallel to the rigid graphite surface [Fig. 2(A): $\Delta z = 0$ Å]. Here the surface contact is formed between the graphene sheet and the graphite surface. The vertical force $F_z$ is

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FIG. 1: (a) The schematic illustration of the model of the monolayer graphene sheet physically adsorbed onto the rigid graphite surface used in the simulation. The green-colored six-membered ring at the center position of the graphene sheet is assumed to be adsorbed onto the atomic force microscopy tip apex indicated by broken lines, and it is moved upward along the z (or [0001]) direction, by \( \Delta z = 0.1 \) Å. (b) The graphene sheet (red-colored) adsorbed onto the graphite surface (blue-colored) within the \( x - y \) plane.

FIG. 2: The transition of the shape of the monolayer graphene sheet during the peeling process from A to J within the \( x - z \) plane. The red-colored graphene sheet and blue-colored graphite surface are shown. The displacement of the lifting center position from the initial position, \( \Delta z \) [Å], is indicated on the upper-right positions of each picture [14].

Between \( \Delta z = 2.0 \) Å and 2.1 Å, the first discrete partial peeling of the graphene occurs [Figs. 2(B)→2(C)], which produces the 1st discontinuous jump in the force curve [Figs. 3(B)→3(C)]. The partial peeled area around the lifting center of the graphene is shown in Figs. 4(B)→4(C). Then, between \( \Delta z = 2.4 \) Å and 2.5 Å, the second discrete partial peeling of the graphene occurs [Figs. 2(D)→2(E)], which produces the 2nd discontinuous jump in the force curve [Figs. 3(D)→3(E)]. The partial peeled area of the graphene is shown in Figs. 4(D)→4(E). Which of these two areas is peeled first is expected to be actually the stochastic process under the room temperature condition. Now the surface contact region is split into the left and right sections [Fig. 2(E)]. After the two discrete jumps, \( F_z \) increases as the peeling proceeds, since the attractive surface contact region gradually decreases [Fig. 2(F): \( \Delta z = 5.0 \) Å]. Then the surface contact continuously turns into the line contact at \( \Delta z = 7.3 \) Å [Fig. 2(G)]. Here the ‘line contact’ is defined by the following two criteria: 1) The carbon atoms on the left and right outermost arrays of the graphene sheet [Fig. 1(b)] receive the repulsive interaction force from the graphite surface. 2) The carbon atoms on the second arrays [Fig. 1(h)] next to the outermost arrays receive the attractive interaction force. As illustrated in Fig. 5, the average forces acting on one carbon atom on the outermost and the second arrays satisfy the above criteria at \( \Delta z = 7.3 \) Å, which corresponds to Fig. 2(G).

Once the line contacts are formed between the free edges (outermost arrays) of the peeled graphene sheet and the graphite surface, they clearly slide on the graphite surface as indicated by a circle in Figs. 2(G)→2(H)→2(I) with a rapid increase of the bending of the graphene sheet. Within \( x - y \) plane, the right outermost array of the graphene sheet slides nearly straightforward along \(-x\) direction, not so sensitive to the lattice structure of the surface as illustrated in Figs. 6(a) and 6(b), which show the trajectories of the two carbon atoms on the right outer-
FIG. 3: The vertical force, $F_z$, acting on the center six-membered ring, plotted as a function of the lifting displacement $\Delta z$. The positions A–J correspond to those of Fig. 2.

FIG. 4: The atomic structures of the graphene sheet just before and after the discrete change, B→C, D→E, and I→J. The regions surrounded by dotted ellipses show the partial peeled areas.

most array illustrated in Fig. 1(b). The sliding of the outermost arrays during G and I appears much more clearly than that during A and G. During H and I, the decrease of $F_z$ [Figs. 3(H) and 3(I)] can be explained by the decrease of the repulsive force acting on the carbon atoms on the left and right edges of the graphene sheet as shown in Fig. 5, that’s to say, the relative increase of the effect of the attractive interaction force [2].

When the bending of the graphene sheet becomes larger than a certain range, both the left and right line contacts break and the graphene sheet is completely peeled from the surface [Figs. 2(1)→2(J); $\Delta z = 14.8 \rightarrow 14.9$ Å], which produces the 3rd discontinuous jump in the force curve [Figs. 3(I)→3(J)]. As illustrated in Figs. 2(I)–2(J), and Figs. 4(I)–4(J), the graphene sheet exhibits the transition from the arched shape to the planer shape.

Thus the vertical peeling force $F_z$ exhibits the characteristic shape as shown in Fig. 3, which reflects the transition from the surface to the line contact between the graphene sheet and the graphite surface. On the other hand, the lateral sliding force $F_x$ is zero due to the structural symmetry of the system. However, the lateral sliding force $F_y$ shows a finite value with an oscillation whose period and amplitude decreases as $\Delta z$ increases. This os-

FIG. 5: The averaged forces acting on one atom on the left and right outermost arrays (red-colored) and those on the left and right second arrays (blue-colored), as a function of the displacement of the lifting center position from the initial position, $\Delta z$ [Å].

FIG. 6: The trajectory of the two carbon atoms on the right free edge (outermost array) indicated by white circles in Fig. 1(b). (a) The whole trajectory A→I, and (b) the part of the trajectory A→E, including the discrete jumps, B→C and D→E, are indicated. White circles mean carbon atoms of the graphite surface. The indices A–I correspond to those in Fig. 2.
The positions A-J correspond to those of Fig. 2.

oscillation of Fig. 7 reflects the trajectory of the graphene edges illustrated in Fig. 6 at the graphene-substrate interface during the peeling process. The maximum lateral force \( F_0 \approx 0.1 \text{ eV/Å} \) which is only about 3% of the absolute value of the maximum adhesion force \( |F_z| \approx 3.1 \text{ eV/Å} \).

**IV. CONCLUSION**

In this work molecular mechanics study of the nanoscale peeling of the monolayer graphene sheet has been performed. The peeling force curve clearly exhibits the change of the graphene shape from the surface-to-the-line-contact. It is noted that the maximum lateral sliding force \( F_y \approx 0.1 \text{ eV/Å} \) is only about 3% of the absolute value of the maximum adhesion force \( |F_z| \approx 3.1 \text{ eV/Å} \). This small sliding force \( F_y \) is derived from the superlubricity at the interface between the graphene sheet and the graphite surface [15, 16] and atomic-scale wear [17]. There is possibility that such anisotropy between the vertical force \( F_z \) and the lateral sliding force \( F_y \) can be applied to the adhesives, which can be strongly adhered to the substrate but can be easily slid on it.

In our preliminary experiments, we have already succeeded in peeling the graphene plate with a thickness of several \( \mu \text{m} \), comprised of the multilayered graphene sheets by using atomic-force microscopy tip. Here the standard Si3N4 tip for the contact AFM experiment is used. Then the two-component epoxy resin adhesive is adopted to bond the graphene sheets to the AFM tip. Our measurement exhibits that the maximum pull-off force is about several hundreds of nN, which is clearly much larger than the binding force, \( 3.1 \text{ eV/Å} \approx 5 \text{ nN} \), assumed in our simulation. Here it is noted that the junction formed between the AFM tip and the graphene should be mechanically rigid enough to measure the elasticity of the graphene sheet during the peeling process. The two-component epoxy resin adhesive satisfies the above condition. If the thickness of the peeled graphene plate is reduced, the comparison between the present simulation and the experiment will become possible in the near future.

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