Theoretical Simulation of Atomic-Scale Peeling of Single-Walled Carbon Nanotube from Graphite Surface

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Molecular mechanics simulation of atomic-scale peeling of carbon nanotube (CNT) from the graphite substrate surface is performed. We have first obtained the theoretical 'peeling force curve' of the CNT, where the CNT physically adsorbed on the graphite substrate surface is gradually retracted or peeled. In the simulation the single-walled carbon nanotube (SW-CNT) of the (3, 3) armchair type with a length of 40.3 Å comprised of 198 carbon atoms is used. It is clarified that the peeling force curve shows a characteristic behavior mainly dominated by the van der Waals interaction acting between the CNT and the substrate surface. The typical change of the CNT shape during the peeling process, shows a transition from the 'line contact' to the 'point contact', which reflects the covalent bonding interaction. The peeling force curve gives us information of an elementary process of peeling of the CNT. [DOI: 10.1380/ejssnt.2006.133]

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I. INTRODUCTION

The promising mechanical and electronic properties of the carbon nanotubes (CNT's) [1] have attracted our attentions in many research- and industrial areas, which have been discussed so far by many researchers. Recently, experimental studies to use CNT as machinery parts such as CNT tip [2], nano-pinocette [3], and rotational actuators in microelectromechanical systems [4], have been performed. Therefore importance of the study of the CNT's regarded as machinery parts to build up machines and objects in nano- and micrometer scale, have been rapidly increased. First it is important to consider the CNT interacting with the substrate surface. Then the CNT physically adsorbed on the substrate surface must be retracted or peeled from the surface, and moved to a desired position and attached onto the substrate surface again.

In this paper, the former half of the process, 'peeling' process of the CNT from the substrate surface, is numerically studied. Molecular mechanics simulation of atomic peeling of the CNT from the graphite surface is performed. As an example of the substrate surface, graphite is adopted, which is an inert and standard sample. First, it is clarified what interaction gives significant influences on the behavior of the peeling force curve. Here the van der Waals interaction and covalent bonding interaction are considered. We also found characteristic change of the shape of the CNT during the peeling process, the physical origin of which is also discussed by considering the above interactions.

II. MODEL AND METHOD OF SIMULATION

The model used in the simulation is as follows. As a model of the CNT, a single-walled carbon nanotube (SW-CNT) of the (3, 3) armchair type with a length of 40.3 Å and a radius of 2.1 Å, comprised of 198 carbon atoms, is adopted [Fig. 1(a)]. This SW-CNT with open edges is constructed by repeated structures of α and β rings comprised of six carbon atoms as shown in Figs. 1(a) and 1(b). As a model of the substrate surface, the graphene whose shape is an equilateral hexagon with a length of 21.5 Å of each side, comprised of 1176 carbon atoms, is used [Fig. 1(c)].

First covalent bonding structures of both the CNT and graphene are separately optimized by minimizing the total energy described by the Tersoff potential [5], using the Polak-Rebiere-type conjugate gradient (CG) method [6]. Here the convergence criterion is set that the maximum of absolute value of all the forces acting on the movable atoms, is lower than $10^{-4}$ eV/Å, i.e.,

$$ \max_{1 \leq i \leq N} (|F_i|) \leq 10^{-4} \text{ eV/Å}, $$

where $N$ is the total number of movable atoms, and $F_i$ is a force acting on the $i$th movable atom.

Next the CNT is located on the rigid graphene [Fig. 1(d)], so that the AB stacking registry between the bottom part of the CNT and the graphene is conserved [Fig. 2(a)]. Then the optimized structure of the CNT physically adsorbed on the graphene is obtained by minimizing the total energy $V_{total} = V_{vdW} + V_{Tersoff}$, using the CG method. Here, as the interaction potential between the CNT and the graphene, $V_{vdW}$, the L-J type potential
FIG. 1: (a) The model of a single-walled carbon nanotube (SW-CNT) used in the simulation. (b) The $\alpha$ and $\beta$ rings comprised of six carbon atoms which construct the model of SW-CNT. (c) The model of the graphene whose shape is an equilateral hexagon used in the simulation. (d) The CNT located on the rigid graphene. The left edge is lifted along the $z$ direction, parallel to [0001] axis, by 0.1 Å.

FIG. 2: (a) The bottom part of the CNT (red balls and sticks) and the graphene (grey balls and sticks). The carbon atoms surrounded by blue-lined box are located on A sites below which graphene atoms exist. (b) Initial position of CNT and graphene atoms seen from $x$ axis, corresponding to the cross section indicated by dotted line in (a). Due to the larger repulsive interaction force, A-site atoms are located a little higher than B-site atoms.

obtained by Lu, Li and Martin [7], is used, which was parameterized in order to reproduce the interlayer distance 3.354 Å and elastic modulus $c_{33} = 4.08$ GPa of AB stack- ing graphite crystal structure.

As shown in Fig. 2(a), there are two series of arrays of carbon atoms at the bottom part of the CNT. All carbon atoms of one array surrounded by blue-lined box are located on A sites below which graphene atoms exist, and
FIG. 3: Change of shapes of the CNT on the graphene during the peeling process seen from the y axis. The blue and red colors correspond to the low and high van der Waals interaction energies, $V_{vdW}$, respectively. A-D show the transition from the line contact to the point contact.

III. RESULTS AND DISCUSSION

A. Peeling process of CNT

Figures 3A-3F show the shapes of CNT on the graphene during the peeling process seen from the y axis. The colors allotted to each atom correspond to the van der Waals interaction energies, $V_{vdW}$, where blue and red colors correspond to the low and high energies, respectively. First the CNT takes an initial structure parallel to the substrate surface just before the peeling starts [Fig. 3A: $\Delta z = 0 \text{ Å}$]. Here the blue region where the effect of the van der Waals interaction energy is the largest, covers all the bottom parts of CNT, that’s to say, the 'line contact' between the CNT and graphene occurs. However, as the CNT is peeled from the surface little by little, the line contact gradually vanishes, the bending of the CNT increases more [Fig. 3B: $\Delta z = 1.1 \text{ Å}$ $\rightarrow$ Fig. 3C: $\Delta z = 3.0 \text{ Å}$], and the 'point contact' appears [Fig. 3D: $\Delta z = 7.5 \text{ Å}$]. Finally when the bending of the CNT becomes larger than a certain range, the point contact breaks and the CNT is completely peeled from the surface, although the CNT sill bends a little towards the surface due to the attractive vdW interaction force [Fig. 3E: $\Delta z = 7.6 \text{ Å}$]. After the CNT is moved upward further, the CNT takes an original line shape parallel to the graphene surface because the effect of vDW interaction becomes negligibly small [Fig. 3F: $\Delta z = 15 \text{ Å}$].

B. Peeling force curve of $F_z$

The vertical peeling force, $F_z$, acting on the lifting edge, is plotted as a function of the displacement $\Delta z$, as shown in Fig. 4. The positions A-F correspond to those of Fig. 3. The peeling force $F_z$ is initially a small positive value [Fig. 4A: $\Delta z = 0 \text{ Å}$], because the CNT is slightly pushed onto the graphene at first. Just after the beginning of the peeling, $F_z$ rapidly decreases to the minimum [Fig. 4B: $\Delta z = 1.1 \text{ Å}$]. However, as the peeling process is proceeded, $F_z$ rapidly increases [Fig. 4C: $\Delta z = 3.0 \text{ Å}$] and then gradually increases until it discretely changes [Fig. 4D: $\Delta z = 7.5 \text{ Å}$ $\rightarrow$ Fig. 4E: $\Delta z = 7.6 \text{ Å}$], corresponding to the complete peeling from graphene. After that vertical force $F_z$ gradually increases to zero [Fig. 4F: $\Delta z = 15.0 \text{ Å}$]. Figure 4 shows a basic feature of the peeling force curve for much longer and larger CNT’s.
FIG. 4: Peeling force curve: the vertical peeling force, $F_z$, acting on the lifting edge, plotted as a function of the displacement $\Delta z$. The positions A-F correspond to those of Fig. 3.

FIG. 5: $V_{total}$ and $V_{Tersoff}$ plotted as a function of displacement $\Delta z$. The red and blue curves correspond to $V_{total}$ and $V_{Tersoff}$, respectively, where $V_{total} = V_{vdW} + V_{Tersoff}$.

C. Discussion

The physical origin of the shape of the peeling force curve [Fig. 4] can be understood by dividing $F_z$ into the van der Waals part $F_{vdW}$ and the covalent bonding one $F_{Tersoff}$, where $F_z = F_{vdW} + F_{Tersoff}$. First Fig. 5 shows $V_{total}$ and $V_{Tersoff}$ plotted as a function of the displacement $\Delta z$. The red and blue curves correspond to $V_{total}$ and $V_{Tersoff}$, respectively, where $V_{total} = V_{vdW} + V_{Tersoff}$. Both $V_{total}$ and $V_{Tersoff}$ increase just before the complete peeling of the CNT. Then they discretely change at the complete peeling position ($\Delta z = 7.6$ Å).

Then calculated $F_{vdW}(\Delta z) = -dV_{vdW}/d(\Delta z)$ and $F_{Tersoff}(\Delta z) = -dV_{Tersoff}/d(\Delta z)$, are plotted as shown in Fig. 6. It is clearly shown that the attractive van der Waals interaction force $F_{vdW}(\Delta z)$ [green curve in Fig. 6] plays a dominant role in the shape of the peeling force curve $F_z(\Delta z)$ [Fig. 4] including the minimum position around $\Delta z = 1.2$ Å. However, as the CNT is gradually peeled, the magnitude of attractive force $|F_{vdW}(\Delta z)|$ gradually decreases, and finally $F_{vdW}(\Delta z)$ and $F_{Tersoff}(\Delta z)$ [blue curve in Fig. 6] become approximately equal to each other, around the position just before the complete peeling ($\Delta z = 6.8$ Å), which means the relative increase of the effect of the covalent bonding interaction force $F_{Tersoff}(\Delta z)$.

$F_{Tersoff}(\Delta z)$ reflects the change of the shape of the CNT during the peeling process. The schematic illustrations of the typical CNT shape are shown in the insets (1)-(4) of Fig. 6. First $|F_{Tersoff}|$ increases to a maximum value around $\Delta z = 0.8$ Å, where the CNT shape opens upwards [inset (1) of Fig. 6]. Next $|F_{Tersoff}|$ reduces to a minimum value about zero around $\Delta z = 3.0$ Å, where the CNT shape takes a ‘reverse S character’ [inset (2) of Fig. 6]. Then $|F_{Tersoff}|$ increases to a maximum value again around $\Delta z = 6.8$ Å, where the CNT shape opens downwards [inset (3) of Fig. 6]. Finally, when $|F_{Tersoff}|$ reduces to nearly zero after the complete peeling, the CNT
takes a line shape again [inset (4) of Fig. 6].

IV. CONCLUSIONS

We investigate a peeling process of the single-walled carbon nanotube (SW-CNT) of the (3, 3) armchair type with a length of 40.3 Å. It is clarified that the van der Waals interaction plays a dominant role in the shape of the peeling force curve, and the covalent bonding interaction contribute to the shape of the CNT during peeling process. The changes of the CNT shape show a transition from a ‘line contact’ to a ‘point contact’.

The calculated peeling process can be regarded as an elementary process of that for much longer CNT, which is also useful for understanding the low-friction system comprised of carbon materials [8, 9]. Especially dynamics along the lateral direction is closely related to the effect of friction, which requires detailed studies. Furthermore extended studies of peeling of longer CNT with larger radius from the substrate and attaching to the substrate, will give us more realistic and profound feature of the peeling. Such simulations are being performed and will be reported in the near future.

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APPENDIX

Movies of the peeling process of the CNT discussed in Section III.A: 'Peeling process of CNT', are added as Electronic Appendices.

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