Model Simulation of Adhesion and Friction of Nano-Scale Brush

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Model simulation of adhesion and friction of the nano-scale brush interacting with the nano-scale tip is performed by molecular mechanics method. The nanobrush is modeled by a bundle comprised of seven single-walled carbon nanotubes (SWCNTs), and the nanotip is modeled by a diamond [111] cluster cut by (111) lattice plane. During the tip moving process, the nanotip compresses and bends SWCNTs comprising the nanobrush toward the direction reflecting the tip-moving direction and the tip shape. When the bending deflection of each SWCNT goes beyond a critical value, the local structural transition toward another metastable structure of the nanobrush occurs, which results in the discrete signals in the vertical and lateral force curves. The theory of elasticity can qualitatively explain the critical loading force for the buckling of the center SWCNT comprising the nanobrush. [DOI: 10.1380/ejssnt.2011.409]

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I. INTRODUCTION

Recent progress of the fabrication methods of the nanocarbon structures using graphite, graphene sheet, fullerene, and carbon nanotube (CNT), has a great potential of developing various novel mechanical, electronic, magnetic, and optical devices. In the case of the micro- and nano-scale mechanical devices such as Micro Electro Mechanical Systems (MEMS), Surface Force Apparatus (SFA), Quartz Crystal Microbalance (QCM) and Atomic-Force Microscopy (AFM) or Friction-Force Microscopy (FFM), microscopic friction and adhesion can play important roles for their operations and their force-detecting mechanisms.

Considering the future development of the novel mechanical devices using the carbon materials, we have so far investigated friction and adhesion of the following nanocarbon systems: superlubricity of the fullerene intercalated graphite [1–8], peeling and adhesion processes of the single-walled carbon nanotube (SWCNT) [9–13] and the monolayer graphene sheet [14]. Recently we have studied the topic how the nano-scale tip can detect adhesion and friction of the surface, interface and nano-scale object which have characteristic geometries. As an example of the characteristic-shaped structure, the nano-scale lamellar system such as multilayer-stacked graphene sheets was studied [15]. Here the sliding of the external nanotip induces the multilayer slidding of the internal graphene sheet assembling the system. Thus it is clarified that the nanotip can detect the internal degree of freedom of motion of each graphene sheet. This is a system in the lower limit of nano-scale friction.

On the other hand, the nano-scale brush comprised of the SWCNTs is a system in the higher limit of nano-scale friction. Experimentally, the nanobrush such as the vertically aligned CNT film has been successfully fabricated by several groups. Miyake et al. [16] observed tribological properties of the above system depending on the length and diameter of CNTs, which exhibits high friction coefficient of the nanobrush unlike the multilayer graphene system. Studies of not only lower- but also higher-friction system can contribute to the systematic control of nanofriction. Therefore, in this paper, we will discuss the problem how the mechanics of the components (CNT) assembling the nanobrush appears in detecting higher friction force by the tip, and gives influences on adhesion and friction acting between the tip and brush.

II. MODEL AND METHOD OF SIMULATION

As illustrated in Fig. 1, the tip-brush system is prepared as follows. First the nanobrush is modeled by a bundle comprised of seven (3,3) armchair-type single-walled carbon
carbon nanotubes (SWCNTs). Each SWCNT is comprised of 120 carbon atoms and has a diameter of 4.2 Å and a length of 23.9 Å. These seven SWCNTs are structurally optimized by the Polak-Rebiere-type conjugate gradient method (CG method) [17]. Here the Tersoff potential function [18] is used as a chemical bonding interaction potential between SWCNTs, and the modified Lennard-Jones potential function [19, 20] is adopted as a physical nonbonding interaction potential between SWCNTs. The optimized stable distance between the center axes of SWCNTs is 7.3 Å. Next the nanotip is modeled by a diamond [111] cluster comprised of 255 carbon atoms, which is assumed as an atomic force microscopy (AFM) tip. The tip apex is cut by triangular (111) plane, comprised of 10 carbon atoms. Since the diamond tip is hard and chemically inert, it can extract nearly pure information of the nanomechanics of the nanobrush. The length of each side of the tip apex plane and the tip thickness along the z direction obtained using the Tersoff potential [18] are 7.6 Å and 8.6 Å, respectively.

Then the nanotip is located above the nanobrush as shown in Figs. 1(a) and 1(b). Here the center axis of the nanobrush is set as parallel to the z-axis, and the origin is set as the center position of the topmost layer of the center SWCNT 1 before the relaxation of the tip-brush system as shown in Fig. 1(c). The tip height z is defined as the initial position of the rigid tip apex (111) plane before the relaxation of the tip-brush system. For each tip position (x, y, z), the total energy of the tip-brush system is minimized by the CG method to obtain the relaxed metastable structure of the system, the vertical loading force \( F_z \), and the lateral force \( F_L = -F_x \) opposite to the scan direction acting on the tip basal plane. The tip-brush interaction is modeled by the modified Lennard-Jones potential function [19, 20]. As a boundary condition, the tip basal plane (45 carbon atoms) and all the bottom layers of the nanobrush at \( z = -23.9 \) Å (6×7=42 carbon atoms) are fixed. The convergence criterion is set so that the maximum of the absolute value of all the forces acting on the movable carbon atoms becomes lower than \( 1.6 \times 10^{-5} \) nN. It is noted that this type of structural optimization of the tip-brush system in the static limit of temperature \( T \to 0 \) K and the scan velocity \( v \to 0 \) can reproduce the tip-moving and scanning processes of AFM and FFM for \( v \approx 100 \) nm/s very well as already shown in our previous works [21–24].

III. RESULTS

A. Adhesion Process

The nanotip is initially located at \( x = y = 0 \) Å corresponding to the center axis of the nanobrush and at the height of \( z = 2.8 \) Å (\( \Delta z = 0 \) Å) [Fig. 2A]. Then the nanotip is approached and indented into the SWCNT nanobrush [Figs. 2B-2D] and retracted again [Figs. 2D-2F] along the z direction within the tip height of \( 2.8 \) Å \( \geq \Delta z \geq -7.2 \) Å corresponding to the tip displacement of \( 0.0 \) Å \( \leq \Delta z \leq 10.0 \) Å. Each moving width of the nanotip is set as \( 0.1 \) Å. As shown in Fig. 3, a single hysteresis appears in the vertical force curve, \( z - F_z \) and \( \Delta z - F_z \) relations.

First the tip slightly compresses the center SWCNT 1 just below the tip downward along the \( z \) direction and slightly bends the surrounding SWCNTs 2-7 outward within the \( x-y \) plane as shown in Fig. 2B. The surrounding CNTs’ bending direction clearly reflects the nanotip shape, and is nearly perpendicular to each side of the triangular tip-apex plane, PQ, QR and RP. For A→B the vertical force \( F_z \) increases approximately proportional to the tip displacement \( \Delta z \) as shown in Fig. 3. This nearly linear relation means that the nanobrush interacting with the nanotip acts as an approximately linear spring along the \( z \)-direction for the region A→B. Effective spring con-
and 3 are largely bent by the penetration of SWCNT 1 outerward largely [Fig 2D]. Particularly, SWCNTs 2 from the tip apex layer PQR, goes just below the top nearly linear relation between SWCNT 1 and 3 bend nearly parallel to the side PQ. As a result, between SWCNTs 2 and 3 to split them. Both SWCNTs 2 and 3 bend nearly parallel to the side PQ. As a result, the discrete jump occurs from B to C in SWCNTs 2 and 3 as shown in Figs. 3 and 4(b), respectively. Therefore it can be said that the discrete jump in Fig. 3 is induced by the structural transition from the compressing- to the bending-mode of the center SWCNT 1.

Then, for C→D the nanotip further penetrates into the nanobrush. When the tip plane P’Q’R’, the eighth layer from the tip apex layer PQR, goes just below the top layer of the nanobrush, the tip bends all the SWCNTs 1-7 outerward largely [Fig 2D]. Particularly, SWCNTs 2 and 3 are largely bent by the penetration of SWCNT 1 and at the same time are pushed outerward by the facet PQQ’P’ of the tip. The inset of Fig. 4(b) exhibits 0.16 ≤ Fz=center/Fz ≤ 0.23 for C→D, that’s to say, Fz is nearly equivalently divided into all the SWCNTs 1-7. Therefore the bending of the SWCNTs 1-7 plays a major role for the elasticity of the tip-brush system for the region C→D. Thus Fig. 3C→3D reflects mainly the ‘bending’ mode of the SWCNTs 1-7.

For the retracting cycle, the structural transition from the bending- to the stretching- mode of the SWCNTs 1 occurs, which is followed by the equivalent structural transition of SWCNTs 2 and 3 [Figs. 2E→2F]. This produces the discrete jump from E to F in Fz as shown in Fig. 3. Thus, during the approaching and retracting cycles, the structural bistability of the SWCNT 1 located just below the tip center position between the compressing (A→B)- or stretching (F→A)-mode and the bending-mode (C→D→C→E) produces the hysteresis in the vertical force curve. If the center position of the tip is located at a position a little deviated from the center of the SWCNT 1, the force curve whose shape is different from

FIG. 3: Vertical force curve, Fz plotted as a function of the tip displacement Δz and the tip height z during the approaching (A→B→C→D) and retracting (D→C→E→F) cycles of the nanotip. Single hysteresis reflects the structural bistability of the nanobrush, particularly the center SWCNT 1.

FIG. 4: (a) Schematic illustration of Fz=center and Fz=sup. (b) Fz=center and Fz=sup plotted as a function of the tip displacement Δz and the tip height z during the approaching (A→B→C→D) cycle of the nanotip. Inset shows Fz=center/Fz plotted as a function of Δz and z.
that of Fig. 3 will be obtained, where the ratio between $F_{\text{center}}$ and $F_{\text{sur}}$ also becomes different from that of the inset of Fig. 4(b).

**B. Friction Process**

Next the nanotip is initially located at the lateral-positions, $(x, y) = (-20.0 \, \text{Å}, 0.0 \, \text{Å})$ ($\Delta x = 0 \, \text{Å}$), and the vertical-positions, $z = -2.2 \, \text{Å}$ ($\Delta z = 5.0 \, \text{Å}$), to calculate the lateral and vertical forces acting on the tip indented a little into the nanobrush [Fig. 5A]. Here the triangular tip apex is denoted as PQR, and the 3rd triangular layer of the tip located just below the top layer of the nanobrush is denoted as P'Q'R' [Fig. 5A]. Now the tip is scanned along the +x direction within the lateral region of $-20.0 \, \text{Å} \leq x \leq 20.0 \, \text{Å}$, corresponding to $0 \, \text{Å} \leq \Delta x \leq 40.0 \, \text{Å}$, at the constant height of $z = -2.2 \, \text{Å}$ [Figs. 5A-5J]. Then the tip is scanned backward along the $-x$ direction. The scan width of the nanotip is set as 0.1 Å. As shown in Fig. 6, the several sawtooth behaviors of the discrete jumps appear in the frictional force $F_L = -F_x$ and vertical force $F_z$ curves, which means the stick-slip motion followed by the discrete local structural changes of the SWCNTs comprising the nanobrush by the lateral tip scan.

At the first stage of the scan, due to the repulsive interaction, the facet of the tip, PQQ' pushes both SWCNTs 5 and 6 to bend toward the direction perpendicular to the facet PQQ' [Fig. 5B]. Then, for B→C, part of the side QQ' splits SWCNTs 5 and 6 along the $+y$ and $-y$ direction, respectively. Here other SWCNTs' deflections also change discretely [Figs. 5B→5C]. As a result, the small discrete jump appears from B to C in $F_L$ and $F_z$ as shown in Fig. 6.

As the nanotip is scanned further, the facet PQQ' P'
pushes both SWCNTs 1 and 6 to bend their neighboring SWCNTs 2, 3 and 7 [Fig. 5D]. On the other hand, SWCNTs 4 and 5 bend toward +y direction perpendicular to the facet QRR P ′. Then, for D→E [Figs. 5D→5E], SWCNT 6 slips away from the facet PQQ P ′, and is finally pushed by the facet RPP R ′ toward its perpendicular direction. Thus all the SWCNTs 1-7 bend outward due to the small indentation of the tip [Fig. 5E]. The discrete jump occurs from D to E in $F_L$ and $F_z$ as shown in Fig. 6. Here it is noted that the structure of the tip-indentated nanobrush for $(x, y, z) = (-1.7, 0.0, -2.2)$ [Fig. 5E] seems similar to the intermediate structure between $(x, y, z) = (0.0, 0.0, -0.3)$ [Fig 2C] and $(0.0, 0.0, -7.2)$ [Fig 2D].

At the scan position F [Fig. 5F], the facet PQQ P ′ strongly bends both SWCNTs 1 and 3 toward +x direction. Then, for F→G [Figs. 5F→5G], SWCNT 1 slips away from the facet PQQ P ′ to take its nearly original shape, and bending of SWCNT 2 also vanishes. Nevertheless the facet PQQ P ′ still pushes SWCNT 3 along its perpendicular direction [Fig. 5G]. As a result, $F_L$ curve exhibits a cusp where the first derivative of $F_L$ is discontinuous for F→G as shown in Fig. 6F→6G. On the other hand, $F_z$ curve shows a larger discrete jump for F→G, since all the deflections of SWCNT 1, 2, and 4, together with SWCNT 3, along z direction vanish. Finally, for H→I [Figs. 5H→5I], SWCNT 3 slips away from the facet PQQ P ′ to RPP R ′, which makes a discrete jump from H to I in $F_L$ and $F_z$ as shown in Fig. 6.

The lateral force curve for the forward scan is nearly reversed with respect to $x$-axis to become that for the backward scan. As a result, clear frictional hysteresis loop appears in $F_L$ as shown in Fig. 6, which shows high friction occurs during the forward and backward scans. On the other hand, $F_z$ is not reversed. Thus the elasticity of the SWCNTs induces the large bending of the SWCNTs together with the buckling of the SWCNTs toward the tip-scanning direction, which contributes to the friction. It is noted that tip displacements $\Delta x$ corresponding to discrete changes for $F_L$ completely correspond to those for $F_z$. On the other hand, the relative magnitude of the amplitude of the discrete jump in $F_L$ is not the same as that in $F_z$.

FIG. 6: Lateral force curve $F_L = - F_z$ and vertical force curve $F_z$, plotted as a function of the tip displacement $\Delta x$ and the tip position $x$ during the lateral scan of the nanotip along the forward +x direction (red) from A to J illustrated in Fig. 5 and its backward direction (blue). Several sawtooth behaviors reflect the discrete structural changes of the nanobrush due to the bending or buckling of the SWCNTs. Hysteresis loop in $F_L$ shows high friction occurs during the forward and backward scans. Tip displacements $\Delta x$ corresponding to discrete changes for $F_L$ completely correspond to those for $F_z$. On the other hand, the relative magnitude of the amplitude of the discrete jump in $F_L$ is not the same as that in $F_z$.

IV. CONCLUSIONS AND DISCUSSIONS

In this paper molecular mechanics simulation of the atomic-scale adhesion and friction of the SWCNT
nanobrush interacting with the diamond nanotip is performed. During the tip moving process, the nanotip compresses and bends SWCNTs comprising the nanobrush toward the direction reflecting the tip-moving direction and the tip shape. When the bending deflection of each SWCNT goes beyond a critical value, the local structural transitions toward another metastable structures of the nanobrush occurs, which results in the discrete signals in the vertical and lateral force curves.

In our previous work, we pointed out that the theory of elasticity can qualitatively explain the nanoscale mechanics of the SWCNT spring using macroscopic elastic and structural parameters such as Young modulus \( E \), geometric moment of inertia \( I \), and the SWCNT length \( l \) [10]. In approaching process of the tip, the transition from the compressing- to the bending-mode for \( B \rightarrow C \) occurs as illustrated in Fig. 4(b), which exhibits the buckling of the center SWCNT 1. The critical compressing load for the buckling of the SWCNT 1 at \( B \) is

\[
F_{z,c}^{\text{center}} = 27.5 \, \text{eV/Å} \quad \text{[Fig. 4]}
\]

corresponding to the total loading force \( F_z = 28.4 \, \text{eV/Å} \) [Fig. 3]. Here, if the SWCNT 1 is regarded as the hollow circular cylinder with the boundary condition of one fixed edge based on the theory of elasticity as illustrated in Fig. 7, the critical compressing load for the buckling can be evaluated as

\[
F_{z,c}^{\text{ela.free}} = \frac{2.045\pi^2}{l^2} EI \simeq 4.7 \, \text{eV/Å}, \quad \text{(the other free edge)},
\]

\[
F_{z,c}^{\text{ela.rot}} = \frac{\pi^2}{4l^2} EI \simeq 38 \, \text{eV/Å}, \quad \text{(the other rotational edge)},
\]

where \( l = 23.9 \, \text{Å} \), \( E \simeq 3.5 \, \text{TPa} \) [27] and \( I = \pi (R^4 - r^4)/4 = \pi (3.8^4 - 0.4^4)/4 \, \text{Å}^4 \).

In the present simulation, since the free edge of the center SWCNT 1 is stucked to the tip due to the tip-SWCNT interaction force, the assumption of the completely free edge based on theory of elasticity (Fig. 7(a)) gives smaller critical loading force \( F_{z,c}^{\text{ela.free}} \) than the simulated one \( F_{z,c}^{\text{center}} \). On the other hand, the assumption of the rotational edge (Fig. 7(b)) gives larger critical loading force \( F_{z,c}^{\text{ela.free}} \) than \( F_{z,c}^{\text{center}} \). This can explain the following relation,

\[
F_{z,c}^{\text{ela.free}} \leq F_{z,c}^{\text{center}} \leq F_{z,c}^{\text{ela.rot}}.
\]

Thus the theory of elasticity can explain the buckling of the SWCNT 1 appeared in Figs. 3 and 4 to a certain extent.

Miyake et al. [16] experimentally clarified that shorter and thicker CNTs induce higher friction. Although the systematic simulation of the tip-height \( z \) dependence of the friction has not been performed yet, our preliminary simulation for the several different indentation depths \( \Delta z \) shows the similar frictional properties of those obtained by Miyake et al., which will be reported elsewhere.

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[26] It is noted that, in actual experimental condition, toward which directions SWCNT 1 bends, is a stochastic problem. Since the bending directions toward between SWCNTs 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, 6 and 7, and 7 and 1, are structurally or energetically equivalent, SWCNT 1 stochastically bends toward one direction among the above possible directions.
[27] Single SWCNT is compressed along the long axis, and then the Young modulus $E = \sigma/\varepsilon$ is evaluated for the condition, $\varepsilon = 0.1 \text{ Å}/l$ and $\sigma = F_2/\pi R^2$. 