Simulation of Atomic-Scale Wear of Graphite - Nanotip Induced Graphene Formation

Naruo Sasaki,* Hirooki Saitoh, Kazuki Terada, and Noriaki Itamura
Department of Materials and Life Science, Faculty of Science and Technology,
Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan
Kouji Miura
Department of Physics, Aichi University of Education,
Hiroseawa 1, Igayacho, Kariya-shi, Aichi 448-8542, Japan
(Received 6 January 2009; Accepted 5 February 2009; Published 14 March 2009)

The atomic-scale wear, the formation process of the graphene during the lateral line scan process of the nanoscale tip on the multi-layered graphene substrate is studied by using molecular relaxation method. The nanotip is scanned in line forward (along [1230] direction) and backward under the constant-height mode. Analysis of the effect of the tip height on the relative motion of the nanotip, the 1st graphene layer, and the 2nd graphene layer, reveals the transition from the nanotip state to the graphene tip state. During the nanotip state the mean lateral force $<F_z>$ rapidly increases as the mean loading force $<F_z>$ increases. Here the friction between the tip and the surface occurs. However, during the graphene tip state, $<F_z>$ takes nearly the constant value independent of $<F_z>$. Here the internal friction among the 1st, the 2nd and the 3rd graphene layers occurs. The marked scan directional dependence and the increase of $<F_z>$ near the graphene edge appears. The irreversible shift of the graphene layer after all the scan processes can explain the mechanism of the elementary process of the atomic-scale wear.

[DOI: 10.1380/ejssnt.2009.173]

Keywords: Graphite; Friction; Wear; Computer simulations; Atomistic dynamics; Atomic force microscopy; Lubrication; Tribology

I. INTRODUCTION

Since the first measurement of the friction force microscopy (FFM) by Mate et al. [1], the graphite surface has been a standard topic of atomic-scale friction discussed by many researchers [2–16]. However, the interpretations of the FFM measurement have been often complicated in 1990’s. In the previous works the simulated two-dimensional frictional force maps of the graphite surface [7–9] successfully reproduced the observed maps [3–6] qualitatively, which contributed to understanding the mechanism of the stick-slip process. However, the simulated frictional force maps were different from the first one observed by Mate et al. [1]. Furthermore the simulated loading force $F_z$ is two- or three-orders of magnitude smaller than the observed one, $F_z$ [7, 9]. It is thought that these differences between the experiment and theory are due to that the ‘flake tip’ is formed in the experiment, although the single-atom tip is assumed in the simulation. The lamellar solids such as MoS$_2$ graphite and boron nitride are suitable for solid lubricants because the flake cleaved from the substrate can contribute to the superlubricity derived from the incommensurability of the lattice between the flake and the surface, such as mica flakes on mica surface [17], MoS$_2$ flakes on MoS$_2$ surface [18, 19], MoO$_3$ nanocrystals on MoS$_2$ surface [20], and graphite flakes at C$_60$/graphene interfaces [21, 22]. Therefore, in the FFM measurement of the layered substrate, the flake attached to the FFM tip are expected to act as the effective tip - ‘flake tip’. In the FFM measurement of the graphite surface, the graphene plays a crucial role for the flake tip, that’s to say, the ‘graphene tip.’ If the number of atoms included in the graphene tip is on the order of the magnitude of $10^2$ – $10^3$, the difference of the magnitude of $F_z$ mentioned above can be explained with the assumption that the area of the graphene sheet nearly reflects the contact area.

Considering the above backgrounds, the atomic-scale friction of the graphene tip has been studied to reveal the mechanism of the superlubricity as well as to give the quantitative interpretation of the FFM measurement. The direct FFM observation using the graphene-attached FFM tip [10] has successfully reproduced the observed maps by Mate et al. [1] The high-precision FFM observation has successfully observed the anisotropy of the superlubricity of the graphite surface within several tens of pN [11]. These experiments gave a strong proof of the formation of the graphene tip in the FFM measurement. The FFM simulation using the graphene tip has explained the two-dimensional map of the graphite surface [12, 13]. The molecular dynamics simulation of the graphene tip [14] has discussed the origin of the superlubricity using the energy potential surface. The molecular mechanics simulation of the small graphene located on the graphite surface has shown how the dynamics of the graphene tip appears in the two-dimensional maps of the atomic force microscopy [15]. The energy dissipation of the graphene layers and the graphene edge were also reported numerically [16]. However the previous studies have not systematically discussed how the graphene tip is formed during the scanning process yet. Therefore, in this paper, we have numerically investigated the effect of the nanotip on the formation of the graphene tip at the nanotip/graphite interface when the nanotip is pushed onto the graphene substrate by using the molecular relaxation method.

II. MODEL AND METHODS

In the present simulation, the nanoscale interface between the two sliding surfaces is modeled by the nan-
atomic-scale wear of the graphite surface. However, in
this paper, we would like to discuss the atomic-scale wear
derived from the lamellar structure of the graphite sub-
strate. Therefore, the diamond tip is used as a model
case of the chemically inert hard tip, whose wear can be
completely neglected, in order to extract pure information
of the atomic-scale wear of the multiple layered graphite
structure. Next the graphite substrate is modeled by the
cluster comprised of the three graphene layers. Here the
1st, the 2nd and the 3rd graphene layers comprised of
216, 384 and 600 carbon atoms, have the length of the
diagonal line, $L_1 = 11a = 27.8$ Å, $L_2 = 15a = 38.0$ Å, and
$L_3 = 19a = 48.1$ Å, respectively [Fig. 1(b)]. $a = 2.53$ Å
corresponds to one period of the graphite lattice along [1230]
direction. The lower layers are modeled to become larger
than the higher ones such as $L_T \leq L_1 \leq L_2 \leq L_3$. The
initial orientation among the three graphene layers is set
as the AB-stacking structure [Fig. 1(d)]. Here the Tersoff
potential function $V_{cov}$ [23] is used to describe the
covalent bonding energies of the diamond nanotip and each
graphene layer. The nanotip and each graphene layer are
separately optimized using the Polak-Rebiere-type conju-
gate gradient (CG) method [24] before calculating the
tip-surface system.

Then the tip is located on the surface so that the [111] axis of the diamond crystal becomes parallel to the [0001] axis of the graphite crystal surface [Fig. 1(a)]. The origin
is set as the hollow site P(0,0) of the six-membered car-
bon ring corresponding to the center of the 1st graphene
layer before the relaxation of both the tip and the sub-
strate [Fig. 1(c)]. The tip height $z$ is also defined as the
initial distance between the diamond tip apex (111) sur-
face and the graphite (0001) surface (the 1st graphene
layer) before the relaxation of both the tip and the sub-
strate [Figs. 1(a) and 1(b)]. The Lennard-Jones potential function $V_{vdW}$ [25] is adopted as the
non-bonding energies of the tip-surface interactions and
the graphene-graphene interactions.

In the simulation the diamond nanotip is scanned along
the forward ($+x = [1230]$) and the backward ($-x$) directions
between two hollow sites P(x=0.0 Å) and Q(x=2a= 5.06 Å) on
the graphite surface (the 1st graphene layer) under the constant tip-height mode of $z = 3.0, 2.6, 2.5, 2.4,$ and $1.4$ Å [Figs. 1(a) and 1(b)]. The scan width is set
as 0.1 Å. For each scan position of the nanotip ($x, y, z$),
the metastable structure of the system comprised of the
diamond tip and the graphite substrate is calculated by
minimizing the total energy $V_{total} = V_{cov} + V_{vdW}$ using the
CG method [24]. As a boundary condition, the tip basal
layer (45 carbon atoms) and the 3rd graphene layer (600
carbon atoms) are fixed. This type of structural optimiza-
tion of the tip-surface system in the static limit of temper-
ature $T = 0$ and the scan velocity $v \rightarrow 0$ can reproduce
the scanning process of the FFM system of $v \approx 100$ nm/s
quite well as shown in the previous works [2, 7, 9, 27–32].
Here the convergence criterion is set so that the maxi-
mum of the absolute value of all the forces acting on the
movable atoms becomes lower than $1.6 \times 10^{-6}$ nN. Thus
the lateral force $F_z$ opposite to the scan direction and the
vertical loading force $F_z$ acting on the tip basal position
are calculated together with the relaxed structure of the
tip-surface system [Fig. 1(a)].
FIG. 2: The trajectories for the forward (+x = [1230] direction) scan for (a) the tip-surface (1st graphene layer) contact point \( r_{\text{tip}} \), (b) the 1st-2nd graphene contact point \( r_{\text{sub1}} \), and (c) the 2nd-3rd graphene contact point \( r_{\text{sub2}} \). The tip height corresponds to (1) 3.0 Å, (2) 2.6 Å, (3) 2.5 Å, (4) 2.4 Å, and (5) 1.4 Å. Black circles correspond to the carbon atoms on the (a) 1st, (b) 2nd, and (c) 3rd graphene layers. (a-3) and (b-3) show the red-colored trajectories for 0 Å \( \cdot x \cdot 2 \) Å and the blue-colored ones for 2 Å \( \cdot x \cdot 5 \) Å, respectively. (b-5) and (c-5) show the red-colored trajectories for 0 Å \( \cdot x \cdot 2 \) Å and the blue-colored ones for 2 Å \( \cdot x \cdot 5 \) Å, respectively.

III. MECHANICS OF CONTACT FOR FORWARD SCAN

The sliding mechanics of the tip and each graphene layer is discussed. Figure 2 shows the trajectories for the forward (+x = [1230] direction) scan. Here the contact point at the interface is defined. First Fig. 2(a) shows the trajectory of the contact point between the tip and the surface, \( r_{\text{tip}} \),

\[
\mathbf{r}_{\text{tip}} = \mathbf{r}_{\text{tip}}^{\text{in}} + \Delta\mathbf{r}_{\text{tip}}^{\text{ts}},
\]

where \( \mathbf{r}_{\text{tip}}^{\text{in}} = (0, 0) \) and \( \Delta\mathbf{r}_{\text{tip}}^{\text{ts}} \) mean the initial position of the center atom of the diamond-tip apex plane (the red circle located at \( P(0, 0) \) in Fig. 1(c)), and its relative position to the graphite surface (the 1st graphene layer), respectively.

Similarly the trajectories of the contact points between the 1st and the 2nd graphene layers, and between the 2nd and the 3rd graphene layers, \( r_{\text{sub1}} \) and \( r_{\text{sub2}} \), are shown in Figs. 2(b) and 2(c), respectively. Here,

\[
r_{\text{sub1}} = r_{\text{sub1}}^{\text{in}} + \Delta r^{12}_{\text{sub1}}, \quad r_{\text{sub2}} = r_{\text{sub2}}^{\text{in}} + \Delta r^{23}_{\text{sub2}},
\]

where \( r_{\text{sub1}}^{\text{in}} = (0, 1.46) \) and \( \Delta r^{12}_{\text{sub1}} \) are the initial position of the specific carbon atom on the 1st graphene layer (the red circle in Fig. 1(d)), and its relative position to the 2nd graphene layer, respectively. Similarly \( r_{\text{sub2}}^{\text{in}} = (0, 0) \) and \( \Delta r^{23}_{\text{sub2}} \) correspond to the initial position of the specific carbon atom on the 2nd graphene layer (the red circle located at \( P(0, 0) \) in Fig. 1(c)), and its relative position to the 3rd graphene layer, respectively. Figure 2 exhibits the marked transition of the sliding dynamics from the nanotip state to the graphene tip state explained as follows.

A. Nanotip state

For the tip height of \( z = 3.0 \) Å, Fig. 2(a-1) exhibits the trajectory of the continuous line, while Figs. 2(b-1) and 2(c-1) show nearly single spots. Therefore, the tip-surface
FIG. 3: The sliding mechanisms of the nanotip – the multilayer graphene system, corresponding to (a) ‘nanotip state’ for \( z = 3.0 \, \text{Å} \), (b) ‘intermediate state’ for \( z = 2.5 \, \text{Å} \), and (c) ‘graphene tip state’ for \( z = 1.4 \, \text{Å} \). During the nanotip scan of \( x = 5 \, \text{Å} \), the following relative sliding occurs: (a) the nanotip sliding \( \Delta x = 2a \), (b) the nanotip sliding \( \Delta x = a \) and the 1st graphene layer sliding \( \Delta x = a \), and (c) the 1st graphene layer sliding \( \Delta x = \frac{3}{2}a \) and the 2nd graphene layer sliding \( \Delta x = \frac{1}{2}a \).

contact point continuously moves from P to Q, while both the 1st-2nd and the 2nd-3rd graphene contact points are nearly fixed.

When the tip height is decreased to \( z = 2.6 \, \text{Å} \), the tip-surface contact point exhibits continuous lines with discrete jumps [Fig. 2(a-2)] corresponding to the stick-slip motion. The 1st-2nd graphene contact point oscillates a little around the equilibrium position [Fig. 2(b-2)]. This is because the 1st graphene layer is dragged along the scan direction by the tip for the sticking part, then it comes back to the position around the equilibrium for the slipping part. The 2nd-3rd graphene contact point is nearly fixed [Fig. 2(c-2)].

To summarize, for the cases of \( z = 3.0 \, \text{Å} \) and \( z = 2.6 \, \text{Å} \), the sliding occurs mainly between the nanotip and the graphite surface (the 1st graphene layer) as illustrated in Fig. 3(a). This can be said the ‘nanotip state’ where the friction mainly between the tip and the graphite surface (the 1st graphene layer) occurs.

B. Intermediate state

For the tip height of \( z = 2.5 \, \text{Å} \), when the tip is approached toward the graphite surface further, the intermediate state appears. First Fig. 2(a-3) exhibits nearly the single spot for the scan position of \( 0 \, \text{Å} \leq x \leq 2.2 \, \text{Å} \) [red-colored spot], then it shows the continuous lines with discrete jumps for \( 2.3 \, \text{Å} \leq x \leq 5.0 \, \text{Å} \) [blue-colored line and spot]. On the other hand, Fig. 2(b-3) and Fig. 2(c-3) show the sinusoidal curve and nearly a single spot, respectively. Therefore, for the first half of the scan (\( 0 \, \text{Å} \leq x \leq 2.2 \, \text{Å} \)), the 1st graphene layer is attached to the nanotip to form the ‘graphene tip’, and then takes the zigzag motion to conserve AB stacking registry with the 2nd graphene layer. However, for the last half of the scan (\( 2.3 \, \text{Å} \leq x \leq 5.0 \, \text{Å} \)), the 1st graphene layer takes the discontinuous jump one half of the lattice toward \(-x\) direction. On the other hand the 2nd-3rd graphene contact point is nearly fixed.

Thus, for the case of \( z = 2.5 \, \text{Å} \), the sliding occurs not only between the nanotip and the graphite surface but also between the 1st and the 2nd graphene layers as illustrated in Fig. 3(b). This can be said the ‘intermediate state’ where both the surface friction and the internal friction occurs.

C. Graphene tip state

As the tip is pushed onto the graphite surface further, the marked transition occurs. For the tip height of \( z = 2.4 \, \text{Å} \), Fig. 2(a-4) exhibits nearly a single spot, which means that the nanotip and the 1st graphene layer are completely stuck to each other, and the ‘graphene tip’ appears. The graphene tip whose trajectory is represented by that of the 1st-2nd graphene contact point [Fig. 2(b-4)], takes the zigzag motion to conserve the AB stacking registry with the 2nd graphene layer, while the 2nd-3rd graphene contact point is nearly fixed [Fig. 2(c-4)]. Thus the sliding occurs only between the 1st and the 2nd graphene layers. This can be said the ‘graphene tip state’ where the internal friction between the 1st and the 2nd graphene layers occurs.

When the nanotip is approached toward the graphite surface further, for \( z \leq 2.3 \, \text{Å} \), the 2nd-3rd graphene contact point begins to move. One of the typical cases is shown in Figs. 2(a-5), 2(b-5) and 2(c-5). Figure 2(c-5) shows the trajectory of the part of the sinusoidal curve, which means the 2nd graphene layer moves to conserve AB stacking registry between the 1st- and the 3rd graphene layers. On the other hand, the length of the trajectory of the 1st-2nd graphene contact point becomes shorter than that for \( z = 2.4 \, \text{Å} \). Fig. 2(b-4). Therefore the 1st and 2nd graphene layers are stuck to each other stronger than in the case for \( z = 2.4 \, \text{Å} \). Here it should be noted that both the 1st-2nd and the 2nd-3rd graphene contact points move nearly the same distance along the scan (+\( x \)) direction at the same time within \( 0 \, \text{Å} \leq x \leq 2.5 \, \text{Å} \) [red-colored curves in Figs. 2(b-5) and 2(c-5)]. Therefore, for the first half of the scan (\( 0 \, \text{Å} \leq x \leq 2.5 \, \text{Å} \)), the uniform deformation of the 1st and the 2nd graphene layers along the scan (+\( x \)) direction occurs. Then, for the last half of the scan (\( 2.6 \, \text{Å} \leq x \leq 5.0 \, \text{Å} \)), the 2nd graphene layer is nearly fixed at the point one half of the lattice along the +\( x \) direction (blue-colored spot in Fig. 2(c-5)), and the monolayer graphene tip slides on it (blue-colored curve in Fig. 2(b-5)).

Thus, for the case of \( z = 1.4 \, \text{Å} \), the multilayer sliding occurs among the 1st-, 2nd- and 3rd graphene layers in-
chuding the lateral uniform deformation as illustrated in Fig. 3(c). In this case the internal friction among the 1st, the 2nd and the 3rd graphene layers occurs.

D. Load dependence

As shown in Fig. 4(a), the mean loading force $<F_z>$ 1/L \int F_z dz$ monotonically increases as the tip height $z$ decreases. Here $L = 5 \text{ Å}$. On the other hand, the behavior of the mean lateral force $<F_x> = 1/L \int F_x dz$ as a function of $<F_z>$ for the $+x$ scan clearly exhibits the transition from the nanotip state to the graphene tip state as shown in Fig. 4(b). For the nanotip state, $<F_z>$ rapidly increases from nearly zero, as $<F_z>$ increases ($z$ decreases) [Figs. 4(b)-(1) and (2)]. However, after the intermediate region [Figs. 4(b)-(3)], the graphene tip is formed and the monolayer graphene sliding occurs [Fig. 4(b)-(4)], where the mean lateral force $<F_x>$ takes the maximum value due to the finite size effect of the graphene layer as follows: As the monolayer graphene tip slides along $+x$ direction further, the edge of the 1st graphene layer comes nearer the edge of the 2nd graphene layer. Therefore asymmetric summation of the van der Waals interaction force along the $\pm x$ direction induces the larger lateral force $F_x$ due to the finite-size effect, which results in the larger friction, or the mean lateral force $<F_x>$. Therefore $<F_x>$ has a peak just when the graphene tip appears. However, when $<F_z>$ increases further, the edge effect decreases for the same scan position $x$ because the 2nd layer graphene moves one half period of lattice along $+x$ direction. Thus $<F_x>$ decreases to nearly a constant value. For the larger $<F_z>$, the double-layer sliding apperas, and the uniform deformation along $+x$ direction occurs [Fig. 4(b)-(5)].

Thus the nanotip state is limited to the low and narrow loading region compared to the graphene tip state. Although $<F_z>$ rapidly increases as $<F_z>$ increases for the nanotip region, $<F_z>$ is nearly constant for the graphene tip region.

IV. MECHANICS OF CONTACT FOR BACKWARD SCAN

In order to study the effect of the scan direction, the sliding mechanics for the backward ($-x$) scan is discussed. Similarly to the case of the forward ($+x$) scan, Fig. 5 shows the trajectories of the contact points, $r_{tip}$, $r_{sub1}$, and $r_{sub2}$, for the backward scan. Figs. 6(a) and 6(b) show $z - <F_z>$ and $<F_z> - z$ relations for the backward scan, respectively. As shown in Fig. 6(a), $z < F_z>$ for the backward scan is just the same as that for the forward scan. However the effect of the backward scan on $<F_z>$ clearly appears in Fig. 6(b), which exhibits a behavior rather different from Fig. 4(b).

First, for $z = 3.0 \text{ Å}$, the tip-surface contact point for the backward scan [Fig. 5(a-1)] takes the continuous motion between P and Q just the same as that for the forward scan [Fig. 2(a-1)]. Second, for $z = 2.6 \text{ Å}$, the tip-surface contact point for the backward scan [Fig. 5(a-2)] takes the stick-slip motion between P and Q similar to that for the forward scan [Fig. 2(a-2)]. Therefore $<F_z> - <F_z>$ relations of the nanotip state, (1) $z = 3.0 \text{ Å}$ and (2) $z = 2.6 \text{ Å}$ for the backward scan, are nearly the same as those for the forward scan [Figs. 6(b)-(1) and (2)]. However, for $z = 2.5 \text{ Å}$, the monolayer graphene tip state appears in place of the intermediate state. It should be noted that the 1st graphene layer slips one half period of the lattice toward the $+x$ direction at $x = 4.0 \text{ Å}$ during the forward scan [Fig. 2(a-3)]. The 1st graphene layer remains slipped even after the backward scan. The 1st graphene layer takes the zigzag motion to conserve AB stacking registry with the tip apex plane and the 2nd graphene layer. As a result the 1st graphene layer becomes located one period of the lattice toward the $-x$ direction [Figs. 5(a-3) and 5(b-3)]. Thus the final structure becomes different from the initial structure such as $r_{tip}^{fin} \neq r_{tip}^{inf}$ and $r_{sub1}^{fin} \neq r_{sub1}^{inf}$, which means the plastic deformation due to the irreversible shift of the 1st graphene layer.

For $z = 2.4 \text{ Å}$, the monolayer graphene tip state for the backward scan [Figs. 5(a-4) and 5(b-4)] is just the same as that for the forward scan [Figs. 2(a-4) and 2(b-4)]. However the negative peak of $<F_x>$ appears as shown in Fig. 6(b)-(4), which is due to the finite size effect mentioned in Sec. III. D. On the contrary to the forward scan, the 1st graphene layer is pushed toward the $-x$ direction by the repulsive interaction from the 2nd graphene layer.

Lastly, for $z = 1.4 \text{ Å}$, the monolayer graphene tip state
appears [Figs. 5(a-5), 5(b-5) and 5(c-5)] although the multilayer sliding including the uniform deformation occurs for the forward scan. The stable monolayer graphene tip sliding along \(-x\) direction occurs for the tip height of 1.4 Å \(\leq z \leq 2.5\) Å [Fig. 6(b)]. Therefore \(< F_z >\) for the backward scan becomes smaller than that for the forward scan. Furthermore it should be noted that the 2nd graphene layer shifts a half period of lattice during the forward scan of 0 Å \(\leq x \leq 2.5\) Å. Even after the backward scan, the 2nd graphene layer is nearly fixed at the above position. Thus the final structure becomes different from the initial structure such as \(r_{\text{fin}}^{\text{sub}_{1}} \neq r_{\text{sub}_{1}}\) and \(r_{\text{fin}}^{\text{sub}_{2}} \neq r_{\text{sub}_{2}}\), which means the plastic deformation due to the irreversible shift of the 2nd graphene layer. It can be expected that such a plastic deformation often occurs in the actual experimental condition depending on the scan direction, initial scan position, scan length, and loading condition. The irreversible movements of the 1st graphene layer [Fig. 5(b-3)] and the 2nd graphene layer [Fig. 5(c-5)] exhibit the elementary process of the atomic-scale wear.

**V. CONCLUSIONS AND DISCUSSIONS**

In this paper, it is numerically clarified that, as the nanotip is pushed onto the substrate and dragged on it, the transition from the nanotip friction to the graphene tip friction occurs along [12\(\bar{3}0\)] direction. The nanotip state is restricted to the low and narrow loading region where \(< F_z >\) is less than several nN. On the other hand the graphene tip state is too flat to determine the friction coefficient \(\mu\). These simulated features are in good agreement with the previous experiments of the quite small friction coefficient \(\mu \approx 0.001\) observed by Miura et al. [10], and those saying the typical increase in graphene-tip friction between the load of 0 and 25nN was as low as 0.05% – 0.4%, observed by Dienwiebel et al. [11].

In our simulation, the \(< F_z >\) \(-\) \(< F_z >\) relations are
rather different between the forward and the backward
scans because the friction is a nonconservative process
sensitive to the initial condition and the scan direction,
including the plastic deformation which induces an irre-
versible structural change. This corresponds to the ele-
mentary process of the atomic-scale wear. As the nanotip
or the upper graphene layer approaches the edge of the
lower graphene layer, the larger lateral force \( F_z \) is induced
due to the finite-size effect, asymmetric summation of the
van der Waals interaction force along the \( \pm x \) direction,
which results in the larger friction, or the mean lateral
force \( < F_z > \). Such an increase of the energy dissipation
at the edge of the graphite surface was reported by the
previous studies of dynamic force microscopy [16, 33].

Here, the origin of the irreversible and the reversible
motions of the graphene layer is discussed. When the
graphene tip is dragged toward \( +x \) direction, the 1st
graphene layer receives the repulsive interaction force
along \( -x \) direction from the 2nd graphene layer. There-
fore, for \( z = 2.5 \) Å, when the slip occurs, the 1st graphene
layer is discretely pushed toward \( -x \) direction due to the
above repulsive force. This movement of the 1st graphene
layer is energetically metastable because the repulsive in-
teraction between the 1st and the 2nd graphene layers
decreases. Therefore the 1st graphene layer remains to
be moved even after the backward scan. Similarly, for
\( z = 1.4 \) Å, \( < F_z > \) is so large that both the 1st- and
2nd graphene layers are moved together toward \( +x \) direc-
tion. This movement of the 2nd graphene layer is also
energetically metastable because the repulsive interaction
between the 1st and the 2nd graphene layer decreases.
Therefore the 2nd graphene layer remains to be moved
after the backward scan. Thus the scanning processes
in the cases of \( z = 2.5 \) Å and \( z = 1.4 \) Å exhibit ir-
reversible motions because of the local stability derived
from the decrease of the repulsive interaction. However,
for \( z = 2.4 \) Å, the following two conditions are satis-
fied. (1) \( < F_z > \) is too strong to induce the slip as in
the case of \( z = 2.5 \) Å. (2) \( < F_z > \) is too weak to push the
2nd graphene layer toward \( +x \) direction as in the case of
\( z = 1.5 \) Å. Therefore the irreversible motion of the 1st
and 2nd layers does not occur in the case of \( z = 2.4 \) Å for
the scan region of \( 0 \leq x \leq 2a \). For \( z < 2.4 \) Å, the above
conditions are not satisfied and the irreversible motion
occurs. Furthermore it should be noted that, even for
\( z = 2.4 \) Å, the atomic-scale wear occurs due to the size
effect for the wider scan region of \( 0 \leq x \leq 4a \). Thus the
atomic-scale wear, that’s to say, the irreversible structural
change, is quite sensitive to the loading condition and the
scanning path.

Recently the development of the method how to make
the monolayer graphene has become one of the most im-
portant and attractive problems in the electronic and the
optical engineering. Therefore the graphene formation
using the atomic-scale wear will become important as one
of the methods how to controll not only superlubricity but
also electronic properties at the interface. Thus it can
be expected that the graphene formation simulated by
the present paper can contribute to such an interdiscipli-
ary theme of the application of the graphene to various
nanoscale devices.

Lastly it is noted the transition from the nanotip state
to the graphene tip state predicted in the present work has
been experimentally observed by our group [34], where
the two-dimensional frictional force maps dependent on
the load can give the direct proof of the simulated tran-
sition. Detailed comparison between this experiment and
the FFM simulation will be reported elsewhere in the near
future.

Acknowledgments

This research was supported by a Grant-in-Aid for Sci-
cientific Research (B) from the Japan Society for the Pro-
motion of Science (Nos. 18340087 and 20360022) and
Grant-in-Aid for Building Strategic Research Infrastruc-
tures from MEXT.

APPENDIX

Movies of Figs. 3(a) nanotip state, 3(b) intermediate
state, and 3(c) graphene tip state, are added as Electronic
Appendices.

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