Unique Near-Zero Friction Regime of C\textsubscript{60} Molecular Bearings Along [12¯30] Direction

Noriaki Itamura\textsuperscript{1}, Hiroko Asawa\textsuperscript{1}, Kouji Miura\textsuperscript{2} and Naruo Sasaki\textsuperscript{1}

\textsuperscript{1} Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino-shi, Tokyo 180-8633, Japan
\textsuperscript{2} Department of Physics, Aichi University of Education, Hirosawa 1, Igayacho, Kariya-shi, Aichi 448-8542, Japan
E-mail: naru@st.seikei.ac.jp

Abstract. We numerically analyzed unique near-zero friction regime of the C\textsubscript{60} molecular bearings, graphite/C\textsubscript{60}/graphite interface, for the lateral scan along the [12¯30] direction under the relatively low loading condition. Here the C\textsubscript{60} molecule slides, facing its six-membered ring nearly parallel to both the upper and lower graphene sheets. The sinusoidal motion of the C\textsubscript{60} molecule along the carbon bond is continuous and reversible during the forward and backward scans. As a result, the hysteresis loop of the lateral force curve nearly disappears, which leads to a mean frictional force of nearly zero, \(\langle F_L \rangle \approx 0\). The mechanism of this conservative motion is clarified by comparing the structural optimization of the C\textsubscript{60} molecular bearing system with the direct calculation of the local minimum position located on the total potential energy surface \(V_{\text{total}}\). The energy barrier between the neighboring minimum positions always exists, which prevents the C\textsubscript{60} molecule from taking stick-slip motion.

1. Introduction
Control of the superlubricity leads to the energetically effective control of the movement of objects at the interface at from micro- to macroscopic scale. As a first step to control superlubricity, we have paid attentions to the combination of the fullerene and graphene, and developed several types of the fullerene molecular bearing system, where the fullerene/graphene interface plays a dominant role in superlubricity [1, 2, 3, 4, 5]. Next we numerically studied the anisotropy of the superlubricity of the C\textsubscript{60} bearing system by molecular mechanics simulation [6]. It is clarified that, under the low average loading force of \(\langle F_L \rangle = 0.27\) nN corresponding to the graphene interlayer distance \(d = 1.3\) nm, the simulated mean lateral force \(\langle F_L \rangle\) takes a maximum peak value along the [10¯10] scan direction, and a minimum value of nearly zero less than 1 pN along the [1230] scan direction. The peak of \(\langle F_L \rangle\) along the [10¯10] scan direction is derived from the stick-slip motion of the C\textsubscript{60} molecule due to the commensurate stacking of the six-membered rings between the C\textsubscript{60} molecule and the graphene sheet [7, 8, 9]. Then we clarified that, at the peak region, the tilting motion of the C\textsubscript{60} molecule and the elastic contact at the C\textsubscript{60}/graphene interface contribute to the superlubricity of the C\textsubscript{60} molecular bearings [9]. However, the mechanism of the minimum value of \(\langle F_L \rangle\) along the [1230] scan direction is not discussed in detail yet. Therefore, in this work, we studied the unique near-zero friction regime along the [1230] direction, and analyzed the mechanism of the conservative continuous motion of the C\textsubscript{60} molecule by calculating the total potential energy surface.
Figure 1. Model of the C\(_{60}\) bearing system (graphene/C\(_{60}\)/graphene interface). The blue upper graphene sheet and the red intermediate C\(_{60}\) molecule are illustrated with the broken parallelogram of the 1\(\times\)1 unit cell. The x direction corresponds to the [12\(\bar{3}0\)] scanning direction.

2. Model and Method of Simulation

In the simulation, we adopted the same model and method of simulation as those used in our previous works [4, 5, 6, 7, 8, 9]. Fig. 1 shows the model of the C\(_{60}\) bearing system with the closely packed structure of the C\(_{60}\) molecules [1, 2, 3, 4, 5, 10]. Only the intercalated C\(_{60}\) molecule sandwiched by the upper and lower rigid graphene sheets is assumed to relax. The periodic boundary condition is applied not to the z-direction but to the 1\(\times\)1 unit cell of the C\(_{60}\) bearing system within the (0001) plane [Fig. 1]. The Tersoff potential \(V_{\text{cov}}\) [11] and the modified Lennard-Jones potential \(V_{\text{vdW}}\) [12, 13] are used as the covalent bonding and nonbonding interaction energies, respectively. Then, the lateral position \(L\) of the upper rigid graphene sheet is varied along the [12\(\bar{3}0\)] and its backward directions, with a fixed interlayer distance \(d = 1.3\) nm between the upper and lower rigid graphene sheets, which results in the mean vertical loading force of \(\langle F_z \rangle = 0.27\) nN. Here the initial structure is set so that the AB-stacking registry of the six-membered ring between the graphene sheets and the intermediate C\(_{60}\) molecule is satisfied. For each scanning position \(L\), the metastable structure of the C\(_{60}\) molecular bearing system is obtained by minimizing the total energy \(V_{\text{total}} = V_{\text{cov}} + V_{\text{vdW}}\) using the Polak-Rebiere-type conjugate gradient (CG) method [14] under the convergence criterion that the maximum absolute force acting on all the relaxed atoms should become lower than \(1.6 \times 10^{-2}\) pN. Thus the lateral force opposite to the scan direction \(F_L\) acting on the upper graphene sheet for each 1\(\times\)1 unit cell is obtained for \(0 \leq L \leq 0.506\) nm during the forward and backward scans.

3. Results

In this section, the lateral force curve and the C\(_{60}\) dynamics are shown, which are explained by analyzing the total potential energy \(V_{\text{total}}\) for each scan position \(L\) of the upper graphene sheet.

3.1. Lateral force curve

Fig. 2 shows the lateral force \(F_L\) curve plotted as a function of the scan position \(L\) for the forward ([12\(\bar{3}0\)] direction) and backward scans. \(F_L\) clearly exhibits a sinusoidal behavior with a lattice period of \(a = 0.253\) nm along the [12\(\bar{3}0\)] scan direction, and \(F_L\) curves for both the forward and backward scans are completely the same as each other. Therefore the hysteresis loop does not appear in the force curve, where the average lateral force \(\langle F_L \rangle\) exhibits nearly zero, \(\langle F_L \rangle \simeq 0\).
Figure 2. Lateral force curve of the C$_{60}$ bearing system along [12\,\bar{3}\,0] ( = x) direction for 0 nm \(\leq\) \(L\) \(\leq\) 0.506 nm for \(\langle F_z \rangle\) = 0.27 nN. The forward (red) and backward (blue) scans are completely the same as each other.

Figure 3. Tilting angles of the C$_{60}$ molecule within the \(z-x\), \(x-y\), and \(y-z\) planes, \(\theta_{zx}\) (red), \(\theta_{xy}\) (green), and \(\theta_{yz}\) (blue), respectively, plotted as a function of the scan position \(L\) of the upper graphene sheet along the [12\,\bar{3}\,0] ( = x) direction for \(\langle F_z \rangle\) = 0.27 nN.
3.2. Dynamics $C_{60}$ molecule

The mechanism of the nearly zero friction can be ascribed to the motion of the $C_{60}$ molecule during the scanning process. Since the interlayer distance $d = 1.30$ nm considered in the present work is near an equilibrium distance $d = 1.32$ nm of the graphite/$C_{60}$/graphite interface as discussed in refs. 7 and 8, $C_{60}$ molecule deforms quite little even during the scanning process. Therefore the tilting angles of the $C_{60}$ molecule within the $x-y, y-z$ and $z-x$ planes, $\theta_{xy}, \theta_{yz}$ and $\theta_{zx}$, are very small, respectively, as shown in Fig. 3. The maximum tilting angles are at most $|\theta_{xy}| \approx 0.002^\circ$, $|\theta_{yz}| \approx 0.007^\circ$ and $|\theta_{zx}| \approx 0.25^\circ$. This means that the $C_{60}$ molecule slides facing its six-membered ring nearly parallel to the upper and lower graphene sheets during the scanning process. Therefore motion of the upper six-membered ring is equivalent to that of the $C_{60}$ molecule itself.

As shown in Figs. 4(a)-4(g), the six-membered ring slides along the path $C_1 \rightarrow C_2 \rightarrow C_3$, when the upper graphene sheet is scanned forward along the [1230] direction within $0 \leq L \leq 0.506$ nm as follows: First the upper and lower graphene sheets take the AA-stacking registry for $L = 0$ nm and the six-membered ring of the $C_{60}$ molecule is initially located above the AB stacking site, $C_1$ (Fig. 4(a)). As the upper graphene sheet is scanned forward along the [1230] direction, the six-membered ring of the $C_{60}$ molecule slides nearly along the carbon bond $C_1-C_2$ of the lower graphene sheet (Figs. 4(b)-4(d)). When the upper graphene sheet slides for $L = 0.253$ nm, one period of lattice along the [1230] direction, the upper and lower graphene sheets take the AA-stacking registry again, and the six-membered ring of the $C_{60}$ molecule becomes located above the AB stacking site, $C_2$ (Fig. 4(e)). Considering the symmetry, the structure of Fig. 4(e) is essentially equivalent to that of Fig. 4(a). Then, for $0.253 \leq L \leq 0.506$ nm, the six-membered ring of the $C_{60}$ molecule takes a sliding motion nearly along the carbon bond $C_2-C_3$ (Figs. 4(e)-4(g)) similar to that nearly along $C_1-C_2$ for $0 \leq L \leq 0.253$ nm (Figs. 4(a)-4(e)). Finally, for $L = 0.506$ nm, two periods of lattice along the [1230] direction, the upper and lower graphene sheets take the AA-stacking registry again, and the six-membered ring of the $C_{60}$ molecule becomes located above the AB stacking site, $C_3$ (Fig. 4(g)). The structure of Fig. 4(g) is completely equivalent to that of Fig. 4(a). For the backward scan along $-x$ direction, the six-membered ring of the $C_{60}$ molecule takes a sliding motion $C_3 \rightarrow C_2 \rightarrow C_1$ just opposite to that for the forward scan. As shown in Fig. 4(h), trajectories for the forward and backward scans are completely the same as each other. This means the $C_{60}$ motion is reversible and continuous for the forward and backward scans of the upper graphene sheet along [1230] direction. Thus the $C_{60}$ molecule slides nearly along the carbon bonds and exhibits sinusoidal zigzag motion among $C_1$, $C_2$ and $C_3$.

3.3. Total potential energy surface

Figs. 5(a)-5(g) show the total potential energy surface $V_{\text{total}}(x, y; L) = V_{\text{conv}} + V_{\text{vdW}}$ plotted as a function of the center position $(x, y)$ of the $C_{60}$ molecule within $x-y$ plane, for each upper graphene position $L$. The simulation procedure is as follows: For each scan position $L$ of the upper graphene sheet, the $C_{60}$ molecule is scanned within the square region ($0 \text{ nm} \leq x \leq 0.6 \text{ nm}, 0 \leq y \leq 0.6 \text{ nm}$) to calculate $V_{\text{total}}$. Here it is noted that all the optimized coordinates of the $60$ carbon atoms of the $C_{60}$ molecule for each scan position $L$ are used to calculate $V_{\text{total}}$. As a result the $C_{60}$ molecule (or the center position of the $C_{60}$ molecule) is located at the local minimum point $P$ indicated by the larger circle as illustrated in Fig. 5.

As shown in Fig. 5(a), $V_{\text{total}}(x, y; L)$ initially exhibits the two-dimensional pattern reflecting the honeycomb network of the graphene sheet. The $C_{60}$ position $P$ corresponds to the AB-stacking site $C_1$ between the $C_{60}$ molecule and the upper graphene sheet, located on the vertices of the hexagon. The blue regions around the carbon bond correspond to the low-energy regions. On the other hand, the local maximum points are the A-A stacking sites. These maximum points are located on the center positions of the hexagon (hollow sites) and are surrounded by
Figure 4. During the scanning process of the blue upper graphene sheet, red upper six-membered ring of the $C_{60}$ molecule slides nearly along the green carbon bond of the lower graphene sheet or the blue carbon bond of the upper graphene sheet. The red center position of the six-membered ring is located nearly on the carbon bonds of the lower and upper graphene sheets, for the scan position $L = (a) 0, (b) 0.067, (c) 0.127, (d) 0.186, (e) 0.253, (f) 0.380$, and $\text{(g) } 0.506 \text{ nm}$. (h) Trajectories of the center position of the $C_{60}$ molecule on the carbon bonds $C_1$-$C_2$-$C_3$ of the green lower graphene lattice for the forward (red) and backward (blue) scans for $0 \text{ nm} \leq L \leq 0.506 \text{ nm}$. The trajectories for the forward and backward scans are completely the same as each other. The $C_{60}$ molecule takes a sinusoidal motion along the zigzag carbon bonds $C_1$-$C_2$-$C_3$. 
Figure 5. Total energy $V_{\text{total}}$ plotted as a function of the center position of the C$_{60}$ molecule $(x, y)$ for the scan position of the upper graphene sheet, $L = (a)~0$, (b) 0.067, (c) 0.127, (d) 0.186, (e) 0.253, (f) 0.380, and (g) 0.506 nm. Red honeycomb network (upper graphene sheet) is scanned and the violet one (lower graphene sheet) is fixed. Circles P and Q denote the nearest neighboring local minima. The larger circle P corresponds to the center position of the C$_{60}$ molecule. The cross sections along the broken line connecting P and Q are illustrated in Fig. 6. (h) Trajectories of P obtained by directly checking the total potential energy $V_{\text{total}}$, and the center position of the C$_{60}$ molecule calculated by the CG method, which are completely the same as each other.
red round regions as shown in Fig. 5(a). Furthermore the saddle points of \( V_{\text{total}} \) appear at the center position of the carbon bond.

As \( L \) is varied, the two-dimensional pattern of \( V_{\text{total}}(x, y; L) \) markedly changes as follows. For \( L = 0.067 \) nm, the minimum position \( P \) moves nearly along the carbon bond and the red regions surrounding the maximum points extend along the scan direction to become elliptic shape as shown in Fig. 5(b). Then, for \( L = 0.127 \) nm, half of the period along \([12\overline{3}0](=x)\) direction, \( P \) is located on the center position of the carbon bond as shown in Fig. 5(c). Here the red elliptic regions vanish, which results in the formation of the green and blue stripe patterns (Fig. 5(c)). For \( L = 0.186 \) nm, \( P \) moves further nearly along the carbon bond, and the red regions take elliptic shape the same as that for \( L = 0.067 \) nm (Fig. 5(b)) again as shown in Fig. 5(d). Then, as shown in Fig. 5(e), for \( L = 0.253 \) nm, the red round regions just the same as the initial one for \( L = 0 \) nm (Fig. 5(a)) appear again. Here \( P \) is located on the carbon atom \( C_2 \). For \( 0.253 \leq L \leq 0.506 \) nm (Figs. 5(e)-5(g)), the movement of the minimum position \( P \) and the variation of the two-dimensional patterns of \( V_{\text{total}}(x, y; L) \) are just the opposite to those for \( 0 \leq L \leq 0.253 \) nm. Thus the initial minimum position \( P \) for \( L = 0 \) nm becomes completely equivalent to \( P \) for \( L = 0.506 \) nm.

Fig. 5(h) shows two kinds of trajectories. One is the point \( P \) obtained by directly checking the local minimum position located on the total potential energy surface \( V_{\text{total}} \). The other is the center position of the \( C_{60} \) molecule obtained by the structural optimization, CG method, which is the same as Fig. 4(h) for the forward scan. As shown in Fig. 5(h), the minimum position \( P \) and the center position of the \( C_{60} \) molecule are completely the same as each other. This means analysis of the total potential energy gives the same results of the \( C_{60} \) motion as the CG method.

### 3.4. Energy barrier

Figs. 6(a)-6(g) shows the cross sections along the yellow-dotted line in Figs. 5(a)-5(g) connecting the nearest neighboring minimum positions, \( P \) and \( Q \). During all the scan processes, there exists an energy barrier between \( P \) and \( Q \), which prevents the \( C_{60} \) molecule from jumping from \( P \) to \( Q \) under \( T \rightarrow 0 \) K from the static point of view. Therefore the \( C_{60} \) molecule can continuously slide kept to be located on the local minimum position \( P \). Fig. 6(h) shows the activation energy barrier \( \Delta V_{\text{total}} \) between \( P \) and \( Q \) plotted as a function of the scan position of the upper graphene sheet, \( L \). \( \Delta V_{\text{total}} \) takes the maximum value of 3.8 meV for \( L = 0.245 \) and 0.498 nm, and takes the minimum value of 0.83-0.84 meV for \( L = 0.110 \) and 0.371 nm. At the room temperature, even the maximum energy barrier of 3.8 meV is low enough to be jumped due to the thermal activation where various types of translation, rotation and oscillation of the \( C_{60} \) molecule are expected to occur easily. Nevertheless the effect of the energy barrier of 3.8 meV on the \( C_{60} \) dynamics clearly appears under the ultralow temperature condition of \( T \rightarrow 0 \) K.

### 4. Conclusions and Discussions

In this paper we numerically studied the unique near-zero friction regime along the \([12\overline{3}0]\) direction of the \( C_{60} \) molecular bearings. The mechanism of the conservative and reversible motion of the \( C_{60} \) molecule can be understood by the structural optimization based on the CG method and direct analysis of the minimum position of the total potential energy \( V_{\text{total}} \) as follows:

1. The lateral force curve shows the sinusoidal behavior with a period of the graphite lattice along \([12\overline{3}0]\) direction, 0.253 nm. The lateral force curves are completely the same as each other between the forward and backward scans.

2. The evaluation of the tilting angles of the \( C_{60} \) molecule gives us information that, for the interlayer distance \( d = 1.3 \) nm, the \( C_{60} \) molecule slides with its six-membered ring faced nearly parallel to both the upper and lower graphene sheets during the scan.
Figure 6. The cross section of the total energy surface $V_{\text{total}}$ along the broken line connecting the minimum positions P (center position of the C$_{60}$ molecule) and Q (nearest neighboring minimum to P), for $L =$ (a) 0, (b) 0.067, (c) 0.127, (d) 0.186, (e) 0.253, (f) 0.380, and (g) 0.506 nm. (h) The energy barrier between the neighboring minima P and Q, $\Delta V_{\text{total}}$, illustrated in Figs. 6(a)-6(g), plotted as a function of $L$, the scan position of the upper graphene sheet.
The six-membered ring of the C\textsubscript{60} molecule slides along the path C\textsubscript{1} → C\textsubscript{2} → C\textsubscript{3} for the forward scan along the [12\overline{3}0] (\(= x\)) direction within 0 \(\leq L \leq 0.506\) nm. For the backward scan along \(-x\) direction, the six-membered ring of the C\textsubscript{60} molecule takes a sliding motion C\textsubscript{3} → C\textsubscript{2} → C\textsubscript{1} just opposite to that for the forward scan. The trajectories of the C\textsubscript{60} molecule with a sinusoidal shape for the forward and backward scans are completely the same as each other. This means the C\textsubscript{60} motion is reversible and continuous for the forward and backward scans of the upper graphene sheet along [12\overline{3}0] (\(= x\)) direction. It should be noted that the physical origin of the sinusoidal shape of the trajectory can be understood by considering the shape of the energy potential surface \(V_{\text{total}}\) for each \(L\).

The C\textsubscript{60} motion mentioned in (3) can be understood by calculating the minimum position \(P\) of the total potential energy surface \(V_{\text{total}}(x, y; L)\) during the scanning process. It is confirmed that the trajectories of \(P\) obtained by directly checking \(V_{\text{total}}\), and the center position of the C\textsubscript{60} molecule obtained by the structural optimization, CG method, are completely the same as each other.

It is clarified that, during all the scanning processes, there exists an energy barrier between the nearest neighboring minimum positions, which prevents the C\textsubscript{60} molecule from jumping toward the nearest neighboring minimum position under \(T \rightarrow 0\) K from the static point of view. Therefore C\textsubscript{60} molecule can slide continuously kept to be located on the local minimum position.

In this paper, we discuss the low loading condition corresponding to the graphene interlayer distance of 1.3 nm. For the smaller interlayer distance corresponding to the higher loading condition, effect of the C\textsubscript{60} tilting or rotation can give marked influences on the superlubricity similar to the case of the scan along the [10\overline{1}0] direction [7, 8, 9]. Therefore the superlubricity of the C\textsubscript{60} molecular bearings, graphene/C\textsubscript{60}/graphene interface, for the [12\overline{3}0] scan under the low loading and low temperature conditions is very unique. If this system including the loading and temperature conditions is realized, there is a possibility of energy-conserved transportation of the nanoscale objects by using the stacking registry of the carbon-network. This condition can be achieved more easily in the system of graphene/graphene/graphene stacking interface, which will be reported elsewhere.

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References
[1] Miura K, Kamiya S and Sasaki N 2003 Phys. Rev. Lett. 90 055509
[2] Sasaki N and Miura K 2004 Jpn. J. Appl. Phys. 43 4486
[3] Miura K, Tsuda D and Sasaki N 2005 e-J. Surf. Sci. Nanotech. 3 21
[4] Miura K, Tsuda D and Sasaki N 2005 Tribologist 49 553
[5] Miura K, Tsuda D, Itamura N and Sasaki N 2007 Jpn. J. Appl. Phys. 46 5269
[6] Itamura N, Miura K and Sasaki N 2009 Jpn. J. of Appl. Phys. 48 060207
[7] Sasaki N, Itamura N and Miura K 2007 J. Phys.: Conf. Ser. 89 012001
[8] Sasaki N, Itamura N and Miura K 2007 Jpn. J. Appl. Phys. 46 L1237
[9] Itamura N, Miura K and Sasaki N 2009 Jpn. J. of Appl. Phys. 48 030214
[10] Miura K and Kamiya S 2002 Europhys. Lett. 58 610
[11] Tersoff J 1988 Phys. Rev. Lett. 61 2879
[12] Lu Jian Ping, Li X -P and Martin Richard M 1992 Phys. Rev. Lett. 68 1551
[13] Stoddard S D and Ford J 1973 Phys. Rev. A8 1504
[14] Press W H, Teukolsky S A, Vetterling W T and Flannery B P 1992 Numerical Recipes: The Art of Scientific Computing, 2nd ed (New York: Cambridge Univ. Press) pp 413-418