Superlubricity of Graphene/C₆₀/Graphene Interface - Experiment and Simulation

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We investigated the nano-scale superlubricity or ultralow friction appeared at the graphene/C₆₀/graphene interface, where the (mean) lateral force becomes nearly zero within the atomic resolution of the frictional force microscopy (FFM). The C₆₀ intercalated graphite film is one of the most successful systems we have developed as the graphene/C₆₀/graphene interface, and it exhibits an excellent friction coefficient, $\mu < 0.001$. Simulated superlubricity of the graphene/C₆₀/graphene interface shows the marked anisotropy with a period of the scan direction of 60°, which reflects the symmetry of the six-membered rings of the C₆₀ molecule and graphene sheet. The physical origins of the maximum peak and near-zero minimum are numerically clarified. Controlling superlubricity of the graphene/C₆₀/graphene interface will contribute to solving the energy and environmental problems.

Keywords: fullerene, graphene, graphite, graphite intercalation compounds, frictional-force microscopy, numerical simulation, friction, superlubricity

1. Introduction

It is the ultimate goal of tribology researchers to realize an ideal friction-free machinery system with zero energy consumption. Since the first observation of the atomic-scale friction [1] and the proposal of the concept of an ideal frictionless sliding [2], fundamental studies on superlubricity have been carried out to date based on mainly two different mechanisms, incommensurate contact [3-16] and weak interfacial interaction [17-21]. Control of the superlubricity leads to the energetically effective control of the motion of nano- or micro-scale objects at the interface.

As efficient solid lubricants, lamellar solids, such as graphite, MoS₂, and boron nitride, are widely used because flakes cleaved from these substrates can contribute to the superlubricity due to the incommensurate stacking of the lattice between the flakes and the substrate surface, such as that between mica flakes on a mica surface [3], MoS₂ flakes on a MoS₂ surface [5,6], MoO₃ nanocrystals on a MoS₂ surface [7], MoS₂/MoO₃/MoS₂ interface [8], and graphite flakes on a graphite surface [9,10].

Although it can be easily expected that the graphite intercalated compounds (GIC) are also lamellar solids suitable for superlubricants, little work has been done to use GIC as practical lubricants. Recently, as a promising artificial superlubric system, we have developed several types of GIC, C₆₀ molecular bearing system, and have studied the superlubric mechanism of the graphene/C₆₀/graphene interface [13-16]. Important point of this system is that the weak chemical- or van der Waals-type bonds between C₆₀ molecules and graphene sheets are not only weak enough to move C₆₀ molecules smoothly but also strong enough to hold the structures of the graphene/C₆₀/graphene interface firmly as illustrated in Fig. 1. This weak and strong physical bonding feature does not appear in the case of the combination of the C₆₀ molecules and the Si substrate surface since the strong chemical bonds are formed between the C₆₀ molecules and the Si surface. We previously showed that the C₆₀ monolayer system confined by graphite walls we have developed have exhibited superlubricity, or ultralow mean lateral force [13,14]. Therefore the graphene/C₆₀/graphene interface can be considered as one of the best candidates of

superlubricant.

Therefore, in this paper, we discuss frictional properties and superlubricity of the graphene/C₆₀/graphene interface both experimentally and theoretically. First, in Sec. 4, the graphene/C₆₀/graphene interface is actually developed by fabricating the C₆₀ intercalated graphite film using chemical and thermal treatments, and the structure and superlubricity of the C₆₀ intercalated graphite film are studied. Next, in Sec. 5, graphene/C₆₀/graphene interface is studied by theoretical simulation. In Sec. 5.1, simulated structure of the graphene/C₆₀/graphene interface is compared with that obtained by our TEM measurements, which gives us a proof of validity of our method of simulation with combined potential model. Then, in Sec. 5.2, the effect of the scan direction of the graphene sheet on the superlubricity at graphene/C₆₀/graphene interface is studied. Marked anisotropy and its load dependence are obtained. The mechanism of the maximum peak and near-zero minimum are discussed in Secs. 5.3 and 5.4, respectively. We anticipate our novel lubrication system to be a start point for developing more practical superlubricant using intercalated graphite, which will contribute to solving the energy and environmental problems.

Fig. 1 Original concept of the “single molecular bearings.” For example, C₆₀ molecule rolls or slides by means of torque produced at the C₆₀/graphene interface.

2. Method of Experiment

C₆₀ intercalated graphite films were prepared as illustrated in Fig. 2 [15,16,22-24]. Graphite (highly oriented pyrolytic graphite: HOPG) for frictional force measurement and natural graphite powder for high-resolution transmission electron microscopy (HRTEM) were stirred for 16 hours in a reaction mixture of concentrated sulfuric acid and nitric acid (4:1, v/v). The acid-treated natural graphite was washed with water until neutralized and dried at 100°C to remove any remaining water. The dried graphite particles were heat-treated at 1050 °C for 15 seconds to obtain exfoliated graphite particles, which were then immersed

in 70% alcohol solution in an ultrasonic bath. A C₆₀ powder and the exfoliated graphite enclosed in a vacuum-sealed quartz tube were placed in a furnace at 600°C for 15 days. The structure of the C₆₀ intercalated graphite film was investigated using HRTEM (JEM-2000EX) for very thin sections of an intercalated graphite film prepared from natural graphite powder, which is not representative of the entire sample. Friction forces were measured at room temperature using the same instruments mentioned above for an intercalated graphite block prepared from the HOPG.

Fig. 2 Method of preparation of C₆₀ intercalated graphite film.

3. Method of Simulation

Figures 3(a) and 3(b) show the models of the graphene/C₆₀/graphene interface (C₆₀ molecular bearing) and the graphene/graphene/graphene interface (graphite systems), respectively [25-29]. It is assumed that only the intercalated C₆₀ molecule and graphene sheet sandwiched by the upper and lower rigid monolayer graphene sheets, can deform in the simulation. The periodic boundary condition is applied to the 1 × 1 unit cell of the C₆₀ molecular bearing system [broken parallelogram in Fig. 3(a)], within the (0 0 0 1) plane. The same periodic condition is applied to the graphite system [broken parallelogram in Fig. 3(b)]. As an example, the orientation where six-membered rings of the C₆₀ molecule face parallel to those of the upper and lower graphene sheets is shown in Fig. 3(a). Here, as the covalent bonding and non-bonding energies, Tersoff potential function V_{cov} [30] and modified Lennard-Jones potential function V_{vdw} [31,32] are used respectively. The initial orientation between two graphene sheets is set to be that of AA stacking. In simulation the upper rigid graphene sheet is moved to change the graphene interlayer distance d along the [0 0 0 1] direction. For each fixed d , the upper rigid graphene sheet is scanned to change the lateral position

L . Finally, for each d and L , the metastable structure of the graphene/ C_{60} /graphene interface is calculated by minimizing the total energy $V_{\text{total}} = V_{\text{cov}} + V_{\text{vdW}}$, using the Polak-Rebiere-type conjugate gradient (CG) method [33]. Here, the convergence criterion is set so that the maximum absolute value of all the forces acting on movable atoms is lower than 1.6×10^{-4} nN. Thus the vertical loading force acting on the upper graphene F_z and the lateral force opposite to the scan direction F_L are obtained per 1×1 unit cell. This static simulation has successfully reproduced experimental two-dimensional frictional force maps at a scan velocity of $v \cong 100$ nm/s [9,14,19,20].

Fig. 3 Model of the (a) C_{60} bearing system (graphene/ C_{60} /graphene interface) and (b) graphite system (graphene/graphene/graphene interface). The upper graphene sheet (green) and the intermediate C_{60} molecule (red) or graphene sheet (red) are illustrated. The broken parallelograms show the 1×1 unit cells of the C_{60} bearing system. The initial orientation between the upper and lower graphene sheets is set as the AA-stacking registry.

4. Results of Experiment

4.1. Structure

HRTEM images of the C_{60} intercalated graphite thin film (mean thickness: 500 nm) are shown in Figs. 4(a) and 4(b) within the (0 0 0 1) plane of the graphite and along the (0 0 0 1) axis, c-axis of graphite, respectively, where the indices used are the same as those of graphite [15,16]. These images show the close-packed C_{60}

Fig. 4 TEM images of the C_{60} intercalated graphite (a) parallel and (b) perpendicular to the (0 0 0 1) surface.

monolayers with the nearest neighbour distance of 1 nm between C_{60} molecules within the (0 0 0 1) plane of graphite, and the periodic spacing of 1.3 nm normal to the (0 0 0 1) plane of graphite. This interlayer spacing of 1.3 nm can be reproduced by simulation as discussed in Sec. 5.

However it should be noted again that, HRTEM images were taken on very thin regions, and may not be representative of the entire sample. Therefore in the newly developed sample, close-packed C_{60} monolayers and graphite layers are not necessarily periodically repeated. Furthermore, HRTEM images of the C_{60} intercalated graphite film quite often have moiré patterns, which exhibits that the fullerene close-packed monolayers rotate by a finite angle slightly different from each other around the c-axis of the graphite. If the close-packed C_{60} monolayers distribute randomly around the c-axis of the film, ultralow friction is expected to be observed in all the scan directions. Essentially the same mechanism - friction-induced reorientation of the (0 0 0 1) basal planes of the MoS_2 grains has been already pointed out by Martin et al. [5].

4.2. Superlubricity

Fig. 5 shows the lateral force maps and the lateral force loops for the C_{60} intercalated graphite film (2.3 mm $\times$ 2.3 mm $\times$ 0.2 mm) using a frictional force microscope [15,16]. When the loading force is lower than 100 nN, the friction force becomes ultralow with less than the order of 0.1 nN. Furthermore, this feature of the ultralow friction force was observed in all the scan directions, which is confirmed by rotating the scanner underneath the C_{60} intercalated graphite film. The load dependence of the mean lateral force $\langle F_L \rangle$ exhibits the friction coefficient $\mu < 0.001$ which is smaller than $\mu < 0.002$ for MoS_2 observed by Martin et al. [5] and $\mu \cong 0.001$ for graphite previously observed by our group [9].

However, when the loading force increases up to nearly 100 nN, which we call the critical loading force, the stripe pattern with a period of 1 nm appears, which corresponds to the nearest neighbor spacing between the C_{60} molecules within a C_{60} close-packed monolayer

surface. This critical loading force ranges from 80 nN to 120 nN on the entire surface of the film. This result indicates the possibility that the motion of C₆₀ molecules is inhibited by the squeezing action of the graphite walls and/or by the formation of chemical bonds between C₆₀ molecules and those between C₆₀ molecules and graphite [34]. This speculation also indicates a possibility that an existence of fluid layers confined by solid surface would be important for smooth sliding of the graphite sheet. Simulations by other groups [35,36] have shown that dynamics of C₆₀ molecule exhibit complicated feature derived from the effect of the lattice stacking. Therefore, in the following sections, simulated structure and superlubricity of graphene/C₆₀/graphene interface will be discussed.

Fig. 5 Measurement of superlubricity of C₆₀ intercalated graphite films. Load dependence of two-dimensional frictional maps (left) and lateral force loops (right). Load dependence of friction exhibits friction coefficient is less than 0.001. For less than 100 nN, both static and dynamic frictional forces are nearly zero within the measurement accuracy of FFM.

5. Results of Simulation

5.1. Structure

If the structures of graphene/C₆₀/graphene interface with various initial orientations of C₆₀ molecules for $d = 1.3$ nm are optimized assuming that the upper and lower graphite sheets are located as AA stacking, three different types of metastable orientations of C₆₀ molecule are obtained [25,26]. As illustrated in Fig. 6(a), each type where six-membered rings, single carbon bonds, and single carbon atoms of C₆₀ molecules face to the upper and lower graphene sheets, is called 'AB stacking type (AB)', 'Bond stacking type (B)', and 'On top stacking type (OT)', respectively. For B type, C₆₀ molecule tilts by several degrees from [0 0 1] axis. OT type is the same as 'frustrated AB stacking' obtained by Legoas et al. [35] using structural optimization. Although the most stable interface is OT type as shown in Fig. 6(b), AB type is also a local metastable structure. AB, B and OT types give the stable graphene interlayer distances $d = 1.314$, 1.321 and 1.320 nm, respectively, any of which reproduces well $d \approx 1.3$ nm observed in our previous TEM measurements [15,16]. This result gives us a proof of the validity of our method of

Fig. 6 (a) Three different kinds of metastable orientations of C₆₀ molecules: AB stacking (AB), Bond stacking (B), and On top stacking (OT) types. (b) Total energy as a function of the graphene interlayer distance d for AB, B and OT types. Observed TEM image indicates interlayer distance of 1.3 nm.

simulation with an adopted potential model mentioned in Sec. 3. Our simulation shows that the graphene/C₆₀/graphene interface is stable only for $d \leq 1.4$ nm. It is also noted that the stable interlayer distance of graphene/graphene/graphene interface is calculated as $d = 0.68$ nm.

5.2. Superlubricity

In this section, frictional properties are discussed by scanning the graphite sheet. Anisotropy of superlubricity of the C₆₀ bearing system (graphene/C₆₀/graphene interface) [Fig. 3(a)] is simulated and is compared with that of a graphite system (graphene/graphene/graphene interface) [Fig. 3(b)] [27]. In simulation, the lateral position L of the upper rigid graphene sheet is varied along the scan direction, $-30 \leq \theta \leq 90^\circ$, and the direction opposite to it, with a fixed distance $d = 1.3$ nm maintained between the upper and lower rigid graphene sheets. Here the initial structure is set so that the AB-stacking registry between the upper graphene sheet and the intermediate C₆₀ molecule or graphene sheet is conserved. The mean loading force $\langle F_z \rangle$ and the lateral force $\langle F_L \rangle$ are calculated for the scan position of $0 \leq L \leq 5$ nm for the forward and backward scans. Here the interlayer distance between the upper and lower graphene sheets is set so that $\langle F_z \rangle = 0.27$ nN is obtained.

Figure 7 shows the mean lateral force $\langle F_L \rangle$ plotted as a function of the scan angle θ of the upper graphene sheet for the mean loading force $\langle F_z \rangle = 0.27$ nN. Here, $\theta = -30, 30$, and 90° are equivalent to the commensurate $\langle 1\bar{1}00 \rangle$ direction of the six-membered rings among the intercalated C₆₀ molecule (graphene sheet) and the upper and lower graphene sheets. Similarly, $\theta = 0$ and 60° are also equivalent to the commensurate $\langle 11\bar{2}0 \rangle$ direction. Figure 7 clearly shows a periodicity of 60° , which is quite similar to that obtained by Dienwiebel et al. [10] $\langle F_L \rangle$ of both the C₆₀ bearing and graphite systems

Fig. 7 Mean lateral force $\langle F_L \rangle$ as a function of the scan angle θ ($-30^\circ \leq \theta \leq 90^\circ$) of the upper graphene sheet under the condition of $\langle F_z \rangle = 0.27$ nN for the C₆₀ bearing (red) and graphite (blue) systems. Magnification of the region $29.5^\circ \leq \theta \leq 30.5^\circ$ is shown in the inset.

has a minimum value of nearly zero at $\theta = 0$ and 60° , and a maximum value at $\theta = -30, 30$, and 90° . $\langle F_L \rangle$ has an almost constant value of about less than 1 pN except for a narrow region of $\theta \approx 30^\circ \pm 0.5^\circ$, as shown in the inset of Fig. 7. The maximum peak value at $\theta = 30^\circ$ of the C₆₀ bearing system, 6.4 pN, is about 40% of that of the graphite system, 15 pN. This difference in peak value can be explained by the effects of the rolling and elastic contact of the C₆₀ molecule at the C₆₀/graphene interface, which will be discussed in Sec. 5.3. Within the region of $\theta \approx 30^\circ \pm 0.1^\circ$, $\langle F_L \rangle$ is very sensitive to θ , and the peak rapidly decreases to about 60 and 30% for the C₆₀ bearing and graphite systems, respectively, as illustrated in the inset of Fig. 7.

The scan-directional dependence shown in Fig. 7 reflects the difference of the atomic-scale motion of the intermediate C₆₀ molecule and the graphene sheet. Since the intermediate graphene sheet exhibits a similar behavior to the C₆₀ molecule, only the case of the C₆₀ bearing system is discussed. The frictional loops of F_L and the types of C₆₀ motion are shown in the left and center panels of Figs. 8(a)-8(c). Right panels of Fig. 8 are the Fourier spectra of the left panels. First, for $\theta = 30^\circ$, the frictional loop exhibits sawtooth behavior with a lattice periodicity of $a_1 = 3a_0 = 0.44$ nm along the $\langle 1\bar{1}00 \rangle$ direction [Fig. 8(a)]. Here, $a_0 = 0.146$ nm is the carbon-carbon bond length. In this case, the C₆₀ molecule slides above the carbon bond along the $\langle 1\bar{1}00 \rangle$ direction (P→Q) and discretely slips to the neighboring AB stacking position (Q→R), as illustrated in the center panel of Fig. 8(a). Since F_L has a large hysteresis due to this periodic stick-slip motion derived from the commensurate scan, the maximum peak of $\langle F_L \rangle$ appears in Fig. 7. Next, for $\theta = 15^\circ$, the frictional loop shows a nonperiodic shape with a small hysteresis due to the incommensurate scan [Fig. 8(b)]. As shown in the center panel of Fig. 8(b), the C₆₀ molecule exhibits essentially the same motion as that for $\theta = 30^\circ$, with sliding along the carbon bond (not necessarily along the $\langle 1\bar{1}00 \rangle$ direction) (R→S) and a discrete slip to the neighboring AB-stacking position (P→Q). Lastly, for $\theta = 0^\circ$, the frictional loop exhibits sinusoidal behavior with a lattice period of $a_2 = \sqrt{3}a_0 = 0.25$ nm along the $\langle 11\bar{2}0 \rangle$ direction. As shown in the center panel of Fig. 8(c), the C₆₀ molecule slides almost exclusively along the carbon bonds and exhibits zigzag motion (P→Q→R). The important feature of this zigzag motion is that it is nearly continuous and reversible. Therefore, the hysteresis loop nearly disappears, which leads to a mean frictional force of nearly zero, $\langle F_L \rangle \approx 0$, the mechanism of which will be discussed in Sec. 5.4.

Frictional force loops include information of the periodicity of the dynamics. The right panels of Fig. 8 show Fourier spectra of the left panels, frictional loops. For the commensurate scan, the lattice period of the graphene sheet along the scan direction appears in the

Fourier spectra. For $\theta = 0^\circ$, single peak appears at $f_2 = 3.9 \cong 1/a_2$. For $\theta = 30^\circ$, several peaks appear at $f_1 = 2.3 \cong 1/a_1$, $2f_1$, $3f_1$, $4f_1$, $\dots$. However, for the incommensurate scan, the spectrum becomes noisy and reflects the periodic feature of both $\theta = 0$ and 30° corresponding to $f'_1 = 2.0$ and $f'_2 = 4.1$, respectively, as shown in the inset of the right panel of Fig. 8(b), and f_3 seems to exhibit the quasiperiodic feature, details of which will be discussed elsewhere.

Fig. 8 The left panel shows frictional loops of the C₆₀ bearing system for $\langle F_z \rangle = 0.27$ nN. The scan angles correspond to $\theta =$ (a) 30, (b) 15, and (c) 0° . The red and blue lines correspond to the forward and backward scans for each scan direction, respectively. The center panel shows the trajectories of the six-membered ring of the C₆₀ molecule in red on the lower graphene lattice for the forward scan shown in grey. Some periodic trajectories [(a) and (c)] and all the nonperiodic trajectories [(b)] are shown. The right panel shows Fourier spectra of the left panel, frictional loops.

The scan-directional dependence has a characteristic load dependence, as shown in Fig. 9. The friction coefficients obtained by linear fitting for all the cases are presented in Table 1. Here, $\mu < 10^{-4}$ is assumed to be $\mu = 0$. For $\theta = 30^\circ$, $\langle F_L \rangle$ shows a clear load dependence for both C₆₀ bearing and graphite systems, and is proportional to $\langle F_z \rangle$, where the relation $\mu_G(\theta = 30^\circ) > \mu_{C_{60}}(\theta = 30^\circ)$ is satisfied. For $\theta = 0$ and 15° , $\langle F_L \rangle$ is nearly zero for the graphite system. On the other hand, for the C₆₀ bearing system, $\langle F_L \rangle$ slightly increases as $\langle F_z \rangle$ increases. Thus the relation $\mu_{C_{60}}(\theta = 0^\circ(15^\circ)) > \mu_G(\theta = 0^\circ(15^\circ)) \cong 0$ is satisfied for larger $\langle F_z \rangle$ condition. Thus, for larger loading condition, superlubricity is enhanced by C₆₀ bearing for $\theta = 30^\circ$, but not for $\theta = 0^\circ$.

5.3. Maximum peak along $\langle 1\bar{1}00 \rangle$ direction ($\theta = 30^\circ$)

The mean lateral force $\langle F_L \rangle$ takes the maximum peak value at $\theta = 30^\circ$ as shown in Fig. 7. In this section, lateral stiffness of the C₆₀ molecular bearing system along the $\langle 1\bar{1}00 \rangle$ direction is evaluated compared with that of the graphite system [28]. In simulation the lateral position L of the upper rigid graphene sheet is moved along the $\langle 1\bar{1}00 \rangle$ direction with a fixed distance d between the upper and lower rigid graphene sheets. Here ΔL is chosen as the displacement from the starting position of the sticking part of the C₆₀ molecule. For each ΔL and d , the metastable structures of the C₆₀ bearing and graphite systems, the vertical loading force acting on the upper graphene sheet F_z , and the lateral force applied opposite the scan direction F_L are obtained per 1×1 unit cell by structural optimization. The mean loading force $\langle F_z \rangle = 1/\Delta L \int F_z dL$ is calculated in the stick region ($0 \leq \Delta L \leq 0.11$ nm). Here d is varied within the

Table 1 Friction coefficients of the C₆₀ bearing and graphite systems for the scan directions $\theta = 0, 15$, and 30° for $\langle F_z \rangle = 0.27$ nN.

$\theta(\text{deg})$	C ₆₀ bearing system: $\mu_{C_{60}}(\theta)$	Graphite system: $\mu_G(\theta)$
0	0.2×10^{-3}	0
15	0.6×10^{-3}	0
30	1.8×10^{-3}	8.5×10^{-3}

Fig. 9 Mean lateral force $\langle F_L \rangle$ as a function of the mean loading force $\langle F_z \rangle$ for the C₆₀ bearing (red) and graphite (blue) systems for $\theta = 0, 15$, and 30° .

region of $1.3 \text{ nm} \geq d \geq 1.2 \text{ nm}$, corresponding to $\langle F_z \rangle = 0.26$ and 5.8 nN , respectively.

5.3.1 Effect of C_{60} tilting

Fig. 10(a) shows effective lateral spring constants of the C_{60} bearing and graphite systems, $k_{C_{60}}$ and k_G , respectively, plotted as a function of the mean loading force $\langle F_z \rangle$ along the commensurate scan direction of $\theta = 30^\circ$. For the loading region of $\langle F_z \rangle$ shown in Fig. 10(a), $k_{C_{60}} < k_G$ clearly holds, which means that the superlubricity of the C_{60} bearing system is more excellent than that of the graphite system. If the tilting (rotation) of the C_{60} molecule derived from the sliding of the graphene sheet is prohibited in the simulation, the lateral spring constant without the tilting of the C_{60} molecule, $k'_{C_{60}}$, can be evaluated. Comparison of $k'_{C_{60}}$ with $k_{C_{60}}$ gives us information of the effect of C_{60} tilting on the superlubricity.

For the lower loading region, $k_{C_{60}} \leq k'_{C_{60}} < k_G$ holds, where the effect of C_{60} tilting is relatively small.

Fig. 10 Simulated superlubricity along $\theta = 0^\circ$ ($\langle 1\bar{1}00 \rangle$) direction of the C_{60} molecular bearings. (a) Effective lateral stiffness $k_{C_{60}}$, k_G and $k'_{C_{60}}$, and (b) rotational angle of C_{60} molecule ϕ , plotted as a function of the mean loading force $\langle F_z \rangle$. $k'_{C_{60}}$ denotes the lateral stiffness without tilting of C_{60} molecule.

However, as the loading force $\langle F_z \rangle$ increases, $k'_{C_{60}}$ increases more rapidly than $k_{C_{60}}$, which results in $k_{C_{60}} < k_G < k'_{C_{60}}$, and the effect of C_{60} tilting is enhanced. The tilting angle of the C_{60} molecule ϕ along the scan direction of the graphene sheet is nearly proportional to the loading force $\langle F_z \rangle$ as shown in Fig. 10(b). Thus it is clarified that the effect of C_{60} tilting contributes to the decrease of the lateral spring constant.

5.3.2 Effect of elastic contact

There still remains a difference between $k'_{C_{60}}$ and k_G , which is ascribed to the difference in elastic properties between the C_{60} /graphene and graphene/graphene interfaces explained as follows. First, the normalized mean loading force and the lateral stiffness per six carbon atoms (single six-membered ring), $\langle F'_{z,C_{60}} \rangle$ and k^* , are defined. It should be noted that the $k'_{C_{60}} - \langle F'_{z,C_{60}} \rangle$ relation of the C_{60} bearing system without tilting becomes the same as the $k_G - \langle F'_{z,G} \rangle$ relation of the graphite system. However, we actually observe the $k - \langle F_z \rangle$ relation per unit cell, not the $k^* - \langle F_z \rangle$ relation per six-membered ring. Therefore, owing to the elastic spherical shape of the C_{60} molecule, the mean loading force per unit cell $\langle F'_{z,C_{60}} \rangle$ is different from that per six-membered ring $\langle F'_{z,C_{60}} \rangle^*$ such as $\langle F'_{z,C_{60}} \rangle = \langle F'_{z,C_{60}} \rangle^* + \langle F'_{z,C_{60}} \rangle^{\text{attr}}$, where $\langle F'_{z,C_{60}} \rangle^{\text{attr}}$ is the mean attractive interaction force acting from the region except for the six-membered ring of the C_{60} molecule shown in Fig. 11(a). Thus, in the case of the C_{60} bearing system without tilting, the conversion of the variables such as $k'_{C_{60}}^* = k'_{C_{60}}$ [37]

Fig. 11 Simulated superlubricity along $\theta = 0^\circ$ ($\langle 1\bar{1}00 \rangle$) direction of the C_{60} molecular bearings. Elastic contact for the (a) C_{60} bearing system without tilting and the (b) graphite systems, where 6 and 32 carbon atoms (red circles) are involved per unit cell, respectively. The numbers of pairs of A and B sites, N^{AB} , are (a) 3 and (b) 16.

and $\langle F'_{z,C_{60}} \rangle^* = \langle F'_{z,C_{60}} \rangle - \langle F'_{z,C_{60}} \rangle^{\text{attr}}$ is well established.

Next, in the case of the graphite system [Fig. 11(b)], the contact area per unit cell is different from that of the C₆₀ bearing system without rotation [Fig. 11(a)]. Considering that 32 carbon atoms are involved within the unit cell, the conversion of the variables such as $k_G^* = 6/32 k_G = 3/16 k_G$ and $\langle F_{z,G} \rangle^* = 6/32 \langle F_{z,G} \rangle = 3/16 \langle F_{z,G} \rangle$ is well established. Here, the $\langle F_z \rangle \propto N^{\text{AB}}$ and $k \propto N^{\text{AB}}$ relations [38], are used, where N^{AB} is assumed to be the number of pairs of A and B sites. An A or B site means an atomic site that has and has no carbon atoms above or beneath, respectively.

The effects of the elastic spherical shape of the C₆₀ molecule and the contact area per unit cell mentioned above can be summarized as the effect of the 'elastic

contact' at the interface. Thus, the elastic contact contributes to the conversion from the relation $k^* - \langle F_z \rangle^*$ per six-membered ring to the $k - \langle F_z \rangle$ relation per unit cell. Therefore, the difference between $k'_{C_{60}}$ and k_G appears to be due to the effect of the elastic contact at the interface. It should be noted that $k'_{C_{60}}$ (k_G) is also determined by the lateral motion of the six-membered ring corresponding to the sliding distance of the upper graphene sheet, ΔL . Therefore, it can be said that the effect of the elastic contact includes the effect of the lateral motion of the intercalated C₆₀ (graphene).

5.4. Near-zero minimum along $\langle 11\bar{2}0 \rangle$ direction ($\theta = 0^\circ$)

The mean lateral force $\langle F_L \rangle$ takes the minimum

Fig. 12 Simulated superlubricity along $\theta = 0^\circ$ ($\langle 11\bar{2}0 \rangle$) direction of the C₆₀ molecular bearings. The total potential energy surface V_{total} for the scan position of the graphene sheet $L =$ (a) 0, (b) 0.067, (c) 0.127, (d) 0.186, and (e) 0.253 nm. C₆₀ molecule is always located at the minimum position P.

Fig. 13 Simulated superlubricity along $\theta = 0^\circ$ ($\langle 11\bar{2}0 \rangle$) direction of the C₆₀ molecular bearings. The cross section of the total energy surface V_{total} along the broken line connecting the minimum positions P (center position of the C₆₀ 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, ΔV_{total} , illustrated in (a)-(g), plotted as a function of L , the scan position of the upper graphene sheet.

value of nearly zero at $\theta = 0^\circ$ as shown in Fig. 7. Particularly, for the lower loading region, this tendency is enhanced. This can be explained as follows: C_{60} molecule does not tilt (rotate) along the scan direction and takes a translational motion along the carbon bond on the graphite substrate, facing one of its six-membered rings nearly parallel to the upper and lower graphene sheets. For the forward and backward scans of the graphene sheet, the C_{60} molecule moves on the same sinusoidal trajectory. Therefore C_{60} molecule continuously moves and the lateral force curve has no hysteresis. As a result, the mean lateral force becomes nearly zero, $\langle F_L \rangle \cong 0$ [29]. The mechanism of this conservative motion of the C_{60} molecule is clarified by the analysis of the total potential energy surface, V_{total} . The two-dimensional map of V_{total} markedly changes during the scan process of the graphene sheet as illustrated in Figs. 12(a)-12(e).

Figs. 13(a)-13(g) shows the cross sections along the yellow-dotted line in Figs. 12(a)-12(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. 13(h) shows the activation energy barrier ΔV_{total} between P and Q plotted as a function of the scan position of the upper graphene sheet, L . ΔV_{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.

6. Conclusions and Discussions

In this paper, superlubricity of the graphene/ C_{60} /graphene interface is investigated experimentally and theoretically. The C_{60} intercalated graphite film we have developed by chemical and thermal treatments have shown excellent superlubricity with quite an excellent friction coefficient $\mu < 0.001$, which is smaller than $\mu < 0.002$, for MoS_2 [6] and $\mu \cong 0.001$, for graphite [9]. The magnitude of the (mean) lateral force becomes smaller than the atomic resolution of FFM. This novel system gives us a key to developing more practical and effective superlubricant using GIC. Controlling superlubricity of graphene/ C_{60} /graphene interface leads to the reduction of the energy loss, the increase of durability, and solution of the energy and environmental problems. Simulated graphite interlayer distance of

graphene/ C_{60} /graphene interface reproduces well $d \cong 1.3$ nm observed in our previous TEM measurements. This result gives us a proof of the validity of our method of simulation with an adopted potential model. Then simulated superlubricity of the graphene/ C_{60} /graphene interface shows the marked anisotropy, which reflects a lattice periodicity of the graphene/ C_{60} /graphene interface. For $\theta = 30^\circ$, along the $\langle 1\bar{1}00 \rangle$ direction, the simulated $\langle F_L \rangle$ has a maximum peak, where the C_{60} bearing system has a lower friction coefficient and a lower lateral stiffness than the graphite system. This can be explained by the C_{60} tilting and the elastic contact at the C_{60} /graphene interface. On the other hand, for $\theta = 0^\circ$, along the $\langle 11\bar{2}0 \rangle$ direction, $\langle F_L \rangle$ has a near-zero minimum because of the small hysteresis derived from the nearly reversible sliding above the carbon bond of the C_{60} molecule. This can be explained by the finite energy barrier during all the scan process.

Now simulated spike-like peak region of $\langle F_L \rangle$ around $\theta = 30^\circ$ is considered. In actual experiments, the peak width observed by FFM tip is expected to broaden, because the scanned graphene sheet tends to slide along the commensurate $\langle 1\bar{1}00 \rangle$ direction even if the sliding direction of the FFM tip deviates slightly from the $\langle 1\bar{1}00 \rangle$ direction. This peak width broadening is also expected to be induced by the thermal effect. Furthermore the difference between the C_{60} bearing and graphite systems clearly appears in this peak region, because the effect of the intercalated C_{60} tilting and the difference in elastic contact between the intercalated C_{60} and graphene are most enhanced in this region owing to the commensurate (AB-stacking) contact.

However, outside of this narrow peak region, $\langle F_L \rangle$ is not sensitive to the scan angle θ and has a nearly constant small value of about less than 1 pN. Here, the C_{60} bearing and graphite systems exhibit nearly the same superlubricity owing to the incommensurate contact at the interface for the low loading condition, as illustrated in Fig. 7. Furthermore, the anisotropy of the C_{60} bearing system can be explained by the contact of its six-membered ring with the upper and lower graphene sheets, which causes a qualitatively similar effect to that of the graphite system.

The load dependence of the superlubricity also exhibits a marked scan-directional dependence. From previous experiments of the graphite and C_{60} bearing systems, we showed that $\mu_G \cong 10^{-3}$ and $\mu_{C_{60}} < 10^{-3}$, respectively. Considering the average of the simulated μ values for $\theta = 0, 15$, and 30° [Table 1], the orders of magnitude of the simulated μ is comparable to those of experimental μ . For the actual multilayered system, (graphite) $_n$ / C_{60} /(graphite) $_n$ ($n \geq 2$), the deformation of the graphene sheets, the slight rotation of the graphene sheet within (0 0 0 1) plane around the [0 0 0 1] axis, and the effect of the tip [12] can markedly affect the

superlubricity. The deformed graphene and C₆₀ molecules are expected to stick to each other like 'nano-gears', which can increase friction. On the other hand, C₆₀ rotation that occurs below the room temperature will decrease friction. The effect of the sliding velocity on the superlubricity is also important. Systematic studies of the above effects are our future problems.

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