Effect of C_{60} Molecular Rotation on Nanotribology

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The effect of C_{60} molecular rotation on the nanotribological properties of C_{60} single crystal surfaces has been studied by atomic/frictional force microscopy. The orientational order-disorder phase transition, in which the high temperature C_{60} free rotation is reduced to a low temperature hindered rotation, is shown to give rise to an abrupt change in friction and adhesion. This change in frictional force is quantitatively consistent with the observed change in adhesion. The similar slopes of the friction versus load curves in both phases indicate that the friction coefficient in the two phases remains about the same. Hence the C_{60} rotation does not provide an additional energy dissipation channel in the friction process.

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C_{60} molecules are near-perfect spheres [1]. Soon after the discovery of C_{60}, there was speculation about the unique lubrication properties of C_{60} films due to the spherical shape of the individual molecules [2–5]. According to classical mechanics, spherical balls between two moving bodies can act as a lubricant by the exploitation of low rolling friction [6]. In analogy, C_{60} molecules were anticipated as nanoscale ball bearings to act as a good lubricant, but this expectation was not borne out by either microscopic or macroscopic experiments [2–5,7–10]. The best friction result between two C_{60} films has a friction coefficient of ~ 0.15, much larger than that of graphite (0.01) [11].

In this Letter, we report the role of C_{60} rotation on nanotribological properties. The rotational degree of freedom of the C_{60} molecules in crystalline C_{60} provides a good system to study the mechanism of energy dissipation during frictional processes, which is the central question for tribological studies [12]. At room temperature, the crystalline C_{60} has a face-centered cubic (fcc) structure [13]. In each cubic unit cell, there are four molecules and each molecule rotates (nearly) freely at a very high frequency ($\sim 10^{11}$ Hz) [13,14]. Since each C_{60} molecule is constantly changing its orientation, all molecules are equivalent when measured over a time period longer than the rotational period. After cooling down to ~ 260 K, the crystal undergoes a first-order orientational order-disorder phase transition from an fcc to a simple cubic (sc) structure [13,15]. In the sc phase, the lattice constant is smaller by $\sim 0.34\%$ [16], which corresponds to a change in molecular orientation [15]. All the C_{60} balls retain their former lattice positions in the newly contracted fcc arrangement, but the four C_{60} molecules associated with the primitive cubic cell are no longer equivalent because they adopt their own specific orientations along different $\langle 111 \rangle$ directions [13]. The C_{60} molecules now execute a hindered rotation (jump reorientation between symmetrically equivalent orientations) at a much slower speed [13,15].

Previous studies on the frictional properties of C_{60} were mostly done with C_{60} thin film samples, prepared by different methods such as vacuum sublimation from C_{60} powder [4,9], magnetron sputtering [7], and molecular beam epitaxy (MBE) [10]. However, for different films or film/substrate systems, the results are quite different and sometimes even contradictory. These could be influenced by sample quality, impurities, lattice mismatch between the C_{60} films and the substrates, etc. In our experiment, we have taken care with the sample preparation and measurement conditions. The sample we used is a C_{60} single crystal with a size ~ 6 mm, grown by a sublimation-condensation technique [17]. Immediately after cleavage to expose the (111) surface, it was put into a high vacuum chamber and baked at 120 °C for more than 1 h to remove adsorbed impurities, e.g., water molecules. The surface remains clean for tribological studies for about 20 h, after which heating at 120 °C for half an hour can recover the surface. The atomic force microscope (AFM) used in our experiments was from Seiko (model SPA 3800), installed in a high vacuum ($< 8 \times 10^{-7}$ torr) and equipped with a cooling stage. By varying the sample temperature through the orientational phase transition, we control the degrees of C_{60} rotational motion, in contrast to previous studies which were done at room temperature [2–5,7–10]. At each temperature, because of the poor heat conductivity of the C_{60} crystal [18], we would wait at least half an hour for thermal equilibrium before taking data. The temperature effect on the piezo scanner has been calibrated and corrected at different temperatures for the data presented in this Letter. To avoid surface wear, we used a soft cantilever with a force constant of 0.1 N/m and limited the externally applied load to 10 nN. Under these conditions no damage was observed (by AFM imaging) at the scan area after each tribological measurement. To avoid accumulative effects in the scan area, a different scan spot was used for each measurement. Before taking the data, the AFM tip was treated by scanning on newly cleaved mica at a relatively high load. This treatment guarantees that during the later measurements, the radius of curvature remains unchanged (50 nm as checked by commercial Nioprobe sample and analyzed by SPIP software [19]). Since the C_{60} molecules adhere easily to the surface of the Si_3N_4 tip, the AFM tip used in our experiment was modified with C_{60} molecules by intentionally scanning the sacrificial areas of the C_{60} crystal surface. Such an AFM tip is then very stable for friction and adhesion measurements. This is also checked by the reproducibility of the room-temperature friction versus load curves of the C_{60} sample before and after the experiment.

A quadrant photodiode was used to measure both the normal force (cantilever deflection) and frictional force (cantilever torsion) simultaneously. The friction was measured from the friction loop signals at each given external load [11]. By varying the external load, a friction versus load curve was constructed. The adhesion force between the AFM tip and C_{60} surface was measured from normal force-distance curves. Both the normal force constant and the lateral force constant of the AFM tip were calibrated by well-established methods [20].

Figure 1 shows a frictional image of the C_{60} (111) surface with molecular resolution. This image demonstrates the high quality of the crystal sample. Shown in Fig. 2 are the frictional force versus external load data at a sliding speed of 1.5 μm/sec obtained at various temperatures between 250 K and room temperature, both below (solid symbols) and above (open symbols) the phase transition temperature. An abrupt jump in the frictional force is apparent as the temperature is decreased across the phase transition temperature ($T_C \sim 260$–265 K, in good agreement with previous results [15]), with little difference among data on either side of the transition. The friction in the sc phase is increased by about 50% from that in the fcc phase. This change is mostly reflected through the offset at zero external load. The slopes of the friction versus external load curves (i.e., the friction coefficient) remain basically the same. The above observation has been checked to carry no artifact from the instrument since the control experiment with a clean Si_3N_4 tip on the oxidized Si(100) wafer surface shows no change in the relevant temperature range. Furthermore, when the sliding speed varies from 100 to 2000 nm/sec, in a range far lower than the C_{60} rotation frequency in both phases, the above result of friction abrupt change remains unaffected.

To understand the abrupt changes in the friction force across the phase transition temperature, we have measured the adhesion force between the (C_{60} modified) AFM tip and the C_{60}(111) surface via the normal force-distance curves. The pullout forces (adhesion) at different temperatures are plotted in Fig. 3. It is seen that while the adhesion force below the transition is ~18 nN, it decreases abruptly to ~9 nN above the transition. To check the reversibility of this jump, we have switched the temperature of the sample between 260 and 270 K a number of times and measured the resulting adhesion at each temperature at different positions. The results verifying the reversibility are shown in the inset of Fig. 3. The adhesion force value at room temperature is consistent with several previously reported measurements for C_{60} films on GeS [5], and C_{60} monolayer on self-assembled monolayers (SAM) [21]. The control experiment of

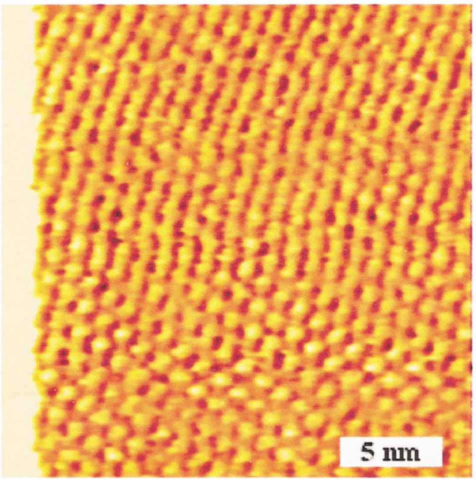

FIG. 1 (color). A frictional image of the C_{60}(111) surface at 2 nN external load.

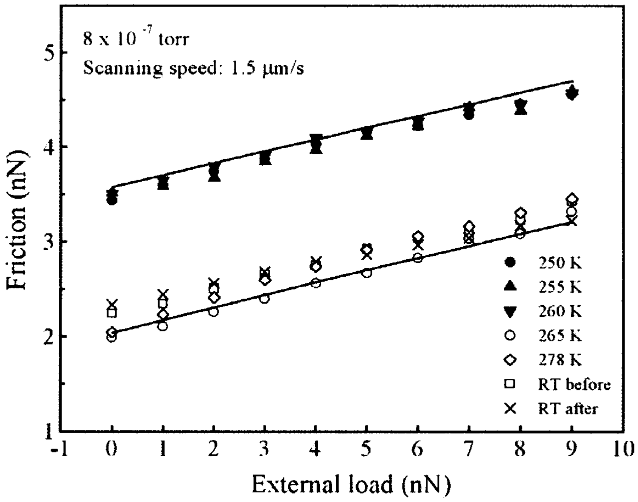

FIG. 2. Friction versus external load curves at a number of different temperatures both above (open symbols) and below (solid symbols) the orientational order-disorder phase transition. The sliding speed is 1.5 μm/sec. The solid curves are calculations based on Eq. (2)

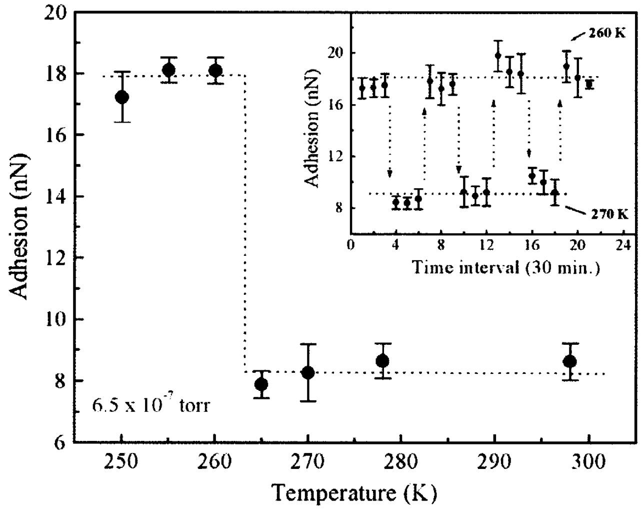

FIG. 3. Adhesion force between a C_{60} modified AFM tip and the $C_{60}(111)$ surface as a function of temperature. The inset shows the reversibility of the adhesion measurement for over 10 h.

adhesion force between a clean Si_3N_4 tip and the oxidized Si(100) wafer surface, showing a constant adhesion from 250 K to room temperature, indicates the observed effect on C_{60} is very specific to the phase transition.

We show that the abrupt change in adhesion can induce an abrupt change in friction. Assuming that the contact area is A and the shear strength τ takes the form $\tau = \tau_0 + \alpha P$, the frictional force F_f is given by

$$F_f = (\tau_0 + \alpha P)A, \tag{1}$$

where τ_0 and α are constants, and$P$ is the pressure. By using the JKR model [22] to calculate A, we can derive the frictional force in terms of the adhesion force L_a and the external load L as [5]

$$F_f = \alpha(L + L_a) + \tau_1(\sqrt{L + L_a} + \sqrt{L_a})^{4/3}, \tag{2}$$

where τ_1 is a constant that is proportional to τ_0. Using the adhesion force L_a as measured and setting either $\alpha = 0$ or $\tau_1 = 0$, Eq. (2) cannot fit the data in Fig. 2. This indicates that the shear strength of the contact must be pressure dependent ($\alpha \neq 0$) and a simple Amonton law, even with a modification in the total load, does not apply ($\tau_1 \neq 0$). The two solid curves in Fig. 2 are fittings with $\alpha = 0.092$ and $\tau_1 = 0.11\ \text{nN}^{1/3}$. The fact that the same set of parameters can reasonably fit the friction data both below and above the phase transition temperature implies that our observed difference in the abrupt friction change is mainly induced by the adhesion force change, that is, due to the change in contact area. Only minor effects, if any, originate from the shear strength change across the phase transition. This leads to a conclusion that the rotational degree of freedom of C_{60} molecules does not significantly participate in the energy dissipation in the friction process.

As there must be no capillary force contribution to the adhesion under high vacuum conditions, the C_{60}-C_{60} interaction between molecules on the AFM tip and in the C_{60} crystal, including van der Waals and short-range Coulomb interactions [23,24], must be responsible for the observed abrupt change in adhesion. The C_{60}-C_{60} interaction consists of an isotropic (orientation-independent) part and an orientation-dependent part [23,24]. The latter is due to the icosahedral structure of C_{60} and the nonuniform charge distribution over the C_{60} cage [24]. In the sc phase, the double bonds in one C_{60} molecule were found to preferentially face the centers of pentagons of its neighbor C_{60} molecules [16,24]. This preferential orientation ("bonds") increases the attractive interaction energy and thus the adhesion if the C_{60} molecules on both the tip and sample adopt this optimally oriented configuration upon contact. In the fcc phase, the free rotation of C_{60} breaks such bonds and smooths out the orientation-dependent part of the interaction, resulting in a reduction of adhesion. The orientation-dependent interaction energy was found from various model calculations to be ~0.2–0.4 eV/molecule for crystalline C_{60}, quite significant as compared to the orientation-independent interaction energy (~ 1.5–1.7 eV). Under the Derjaguin approximation [25], which states that the adhesion force for a sphere-plane geometry is proportional to the interaction energy per unit area of two flat surfaces at contact (surface energy), the preferential orientation between C_{60} molecules in the sc phase can account for an abrupt increase of the adhesion force by as much as ~25%.

Another possible explanation comes from different minimum separations between the tip and the C_{60} surface for the two phases. Across the interface, the separation between the C_{60} molecules need not maintain that of the crystalline bulk. While a full microscopic calculation is beyond the scope of the present Letter, we here illustrate our point by computing the interaction energy between two C_{60} molecules using the Lennard-Jones potential $W(r) = 4\varepsilon[(\sigma/r)^{1/2} - (\sigma/r)^6]$ with carbon atoms as the interaction centers [23]. The results are shown in Fig. 4. In the fcc phase, because of the free rotation we model the tip-sample interaction by a C_{60} vertex-to-vertex geometry [model (a)]. With the cessation of the molecular free rotation in the sc phase, the C_{60} molecules on the surfaces might have their hexagonal facets facing outwards (an assumption). We thus model the tip-sample interaction by a C_{60} hexagon-to-hexagon geometry [model (b)]. Such a geometry allows the AFM tip to get closer to the sample surface. With $\sigma = 3.407$ Å [23], we found an increased attractive interaction energy by ~25% and a shorter tip-sample distance by ~0.3 Å for model (b) as compared to those of model (a). If the C_{60} molecules on the surfaces take the same orientation as in the bulk, i.e., with the double bonds of a C_{60} facing the centers of the pentagons

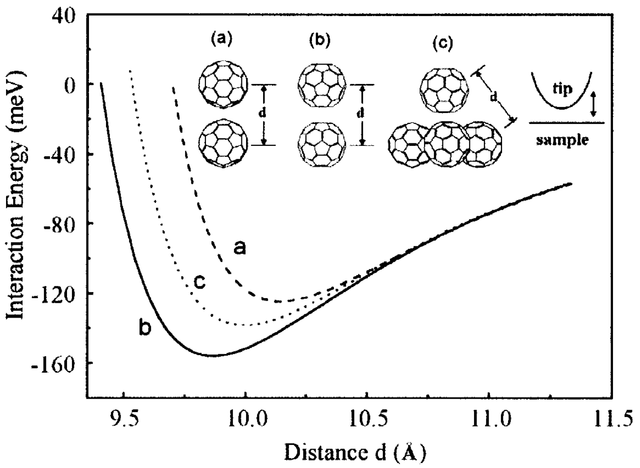

FIG. 4. Calculated van der Waals interaction energy vs distance between two C_{60} molecules for a number of different models. The interaction energy minima are assumed to correspond to the tip-sample contact. The inset shows models for (a) vertex-to-vertex, (b) hexagon-to-hexagon, and (c) double bond to pentagon center geometries.

of its neighbors in the sc phase [model (c)], we only found an interaction energy increase of ~11% and a tip-sample distance shortening of ~0.087 Å. Using the Derjaguin approximation [25], the adhesion force is expected to increase by the same amount as the interaction energy in the sc phase. We must note, however, the calculation results above are only of qualitative value. Detailed calculations must include the other C_{60} molecules in both the tip and the sample, the appropriate C_{60} configurations, a better model for the van der Waals interaction (e.g., bonds as the interaction centers), and the short-ranged Coulomb interaction.

In summary, we have studied the nanotribological properties of C_{60} single crystals around the phase transition temperature, ~260 K, by AFM/FFM in high vacuum. The results show that there is an abrupt change in both friction and adhesion across the phase transition. The frictional force jump is quantitatively consistent with the associated adhesion force increase. In both the fcc and sc phases, the shear strength (and therefore the friction coefficient) exhibits no obvious change, indicating that the rotational degree of freedom does not provide an additional channel for energy dissipation in the friction process. The effect of C_{60} free rotation is mainly to cause an abrupt change in adhesion. We have provided two possible explanations for the adhesion increase in the sc phase. While both of them give correct trend, the estimates do not fully account for the experimental observation. This remains a challenge for further theoretical study.

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