

Nano-Friction of Some Carbon Allotropes

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This paper investigates the mechanisms of the frictional properties of three different forms of carbon—diamond, graphite and carbon nanotube—on contact sliding against a diamond asperity. Molecular dynamics simulations were used to study their behaviour in vacuum. It was found that on the nano scale graphite and carbon nanotubes have low coefficients of friction and that carbon nanotubes can be a better solid lubricant with a friction coefficient of only about 0.03 in vacuum on the nano/micro scales. It concluded that the mechanisms of the difference in frictional properties of the three forms of carbon at different dimensional scales were due to the difference in their atomic structures.

Keywords: Solid Lubricant, Friction, Nano, Molecular Dynamics, Diamond, Graphite, Carbon Nanotube.

1. INTRODUCTION

Diamond, graphite and carbon nanotube are three different forms of carbon, of which diamond is the hardest material where carbon atoms are arranged tetrahedrally. Diamond can be grown in thin-film forms with nearly equivalent mechanical performance as its bulk form¹ and are classified as microcrystalline diamond (MCD), ultrananocrystalline diamond (UNCD) or DLC according to their grain size. In general, sp^2 (graphitic) content and hydrogen concentration increases as the grain size decreases. Although their tribological properties are similar in air at room temperature, their behaviours in vacuum are different and vary with temperature. For example, when sliding against diamond tip in vacuum at room temperature, the coefficient of friction of MCD, UNCD and DLC are about 0.5, 0.05 to 0.15, and 0.03, respectively. As temperature decreases, the coefficient of friction of MCD and DLC increases only slightly whereas that of UNCD can rise up to 0.4.²

Graphite is one of the softest materials having a lamellar sheet structure. The carbon atoms in individual graphite sheets are joined by strong covalent bonds, but in between the sheets there is only weak Van der Waals force. Graphite has been widely used as a solid lubricant. It was thought that lubricity of graphite is entirely due to the weak force in between the sheets. On the other hand, however, it has also been found that graphite is a poor lubricant for use in vacuum (e.g., in space).^{3–4} The friction coefficient of graphite ranges from 0.1 to 0.26 in air⁵ and from 0.5 to 0.8 in vacuum.^{6–7} Such a diverse frictional behaviour

of graphite is attributed to the adsorption of gases on its surfaces during its application in air.

Carbon nanotubes are cylindrical carbon molecules with a nanostructure whose aspect ratio can be extremely large. Similar to graphite, the chemical bonding of nanotubes is composed entirely of sp^2 bonds. They exhibit extraordinary strength and are considered as potentially useful materials in nanotechnological and electronic applications. Measured friction coefficient of CNT films manufactured by depositing CNTs in solvent onto a quartz disk was found to vary from 0.04⁸ to 0.09.⁹ It was considered that this low friction could be due to the rolling of CNTs during contact sliding, because the CNTs in the films were loosely stacked and could roll or slip under lateral sliding forces. Recently, Mylvaganam, Zhang and Xiao¹⁰ investigated the problem in further detail. Theoretically, molecular dynamics analysis is used to explore if the ‘rolling effect’ existed or not. Experimentally, a new deposition technique that minimizes the carbon nanotube rolling/slipping when sliding against a diamond tip in air is developed. The study concluded that a CNT film has an ultra-low coefficient of friction of around 0.01 and is a good solid lubricant.

The above discussion demonstrates that the three forms of carbon, diamond, graphite and carbon nanotube, have rather different frictional properties, even though graphite and nanotube have a very similar atomic structure. The objective of this paper is to examine the mechanisms that cause the different frictional properties of these carbon allotropes using the molecular dynamics simulation.

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2. COMPUTATIONAL METHODOLOGY

Diamond sliding on diamond has been studied extensively.^{11–13} Hence, the results reported in the literature will be used to compare with the other two forms of carbon, graphite and nanotube. Samples of graphite ($20.5 \times 7.8 \times 3.1 \text{ nm}^3$) and nanotube bundle consisting of twenty (17, 0) zigzag single-walled CNTs of about 15 nm in length were generated according to their structural properties. A hemi spherical diamond asperity of about 2.5 nm in radius was placed 0.3 nm above the surface as shown in Figure 1. The asperity was first moved vertically by 0.5 nm in steps of 0.0001 nm to reach a penetration depth of 0.2 nm. It was then slid laterally along the horizontal surface of the sample from right to left as shown in the figure. The penetration depth of the diamond asperity is the depth of the tip measured from the surface of the counterpart material. However, on the atomic scale, a definite surface does not exist because of the discontinuity of the materials. To resolve this, it is assumed that the surfaces of the asperity and the sample are defined by the envelopes at the theoretical radii of their surface atoms.¹⁴ This makes the definition of the penetration depth consistent with the conventional concept in contact mechanics. Both the lateral and normal forces were monitored during the sliding motion.

The sliding simulations on graphite was performed on the (100) plane in vacuum. To eliminate the rigid body motion of the workpiece, layers of boundary atoms which are fixed to the space are arranged to surround the Newtonian atoms except its top surface that is subjected to asperity sliding. Heat generated during sliding is conducted away via thermostat atoms using Berendsen thermostat. All the atoms except the rigid ones were taken as thermostat atoms as pointed out in our previous study on CNTs.¹⁵ The atomic interactions between carbon atoms that are linked through covalent bonds were described by a many-body Tersoff-Brenner potential.¹⁶ The non-bonded interactions between the diamond asperity and the samples as well as the long-range interactions between the atoms that are not linked through covalent bonds were modeled with the Lennard-Jones potential¹⁷ $\phi_{ij} = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ where $\epsilon = 70.69 \times 10^{-23} \text{ J}$ and $\sigma = 0.335 \text{ nm}$. In calculating the forces between the atoms using the Lennard-Jones potential, the cutoff distance r_c is taken as 2.5σ as has been widely adopted. The Newton's equations of motion were integrated using a third order Nordsieck

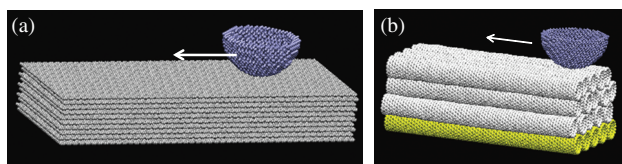


Fig. 1. Initial sliding models of (a) a portion of graphite, and (b) a nanotube bundle.

Predictor Corrector method with a time step of 0.5 fs. The sliding simulations were carried out for a period of 75000 fs.

3. RESULTS AND DISCUSSION

3.1. Observations

Among the three diamond films MCD, UNCD and DLC, the atomic scale order film, DLC contains $\sim 25\%$ hydrogen atoms. Thus the atomic scale sliding between two reconstructed diamond surfaces that are terminated with hydrogen atoms at the interface reported in the literature,^{11–13} would represent the sliding on DLC. At low loads, the results reported by Perry and Harrison showed the stick-slip phenomenon with low friction coefficient. Increasing the normal load resulted in larger values of friction coefficient.¹³ For example, an average normal load of 0.2 nN/atom gave a friction coefficient of 0.002 whereas an applied load of 0.5 nN/atom gave a friction coefficient of 0.37. However, a further increase in normal load to 1.0 nN/atom only increased the friction coefficient slightly to 0.41.

In the atomic scale sliding of diamond on graphite, the carbon atoms of graphite did not adhere to the asperity surface. Figure 2, which shows a portion of graphite during sliding, clearly demonstrates this.

The variation of the normal force and lateral force averaged over every 500 steps with the sliding distance shown in Figures 3(a and b) demonstrates the stick-slip phenomenon. The average coefficient of friction in this case, as shown in Figure 3(c) by the thick line, is about 0.01.

When the diamond asperity slides on the Carbon nanotubes (along their longitudinal axis) under a low load of $\sim 6 \text{ nN}$, the nanotube under the asperity deformed but recovered as the asperity moved away; other carbon nanotubes in the bundle did not show any significant deformation as shown in Figure 4. On increasing the load to $\sim 28 \text{ nN}$, the CNT under the asperity flattened more as well as its neighbouring CNTs deformed to some extent.

The variation of average normal and lateral forces and the friction coefficient when sliding under a load of $\sim 6 \text{ nN}$ are shown in Figure 5.

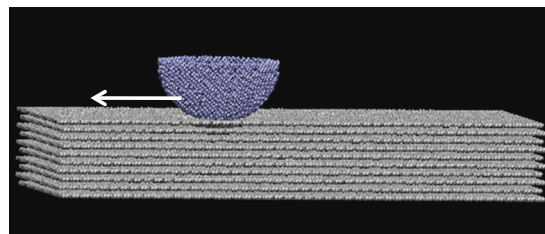


Fig. 2. A portion of graphite during sliding.

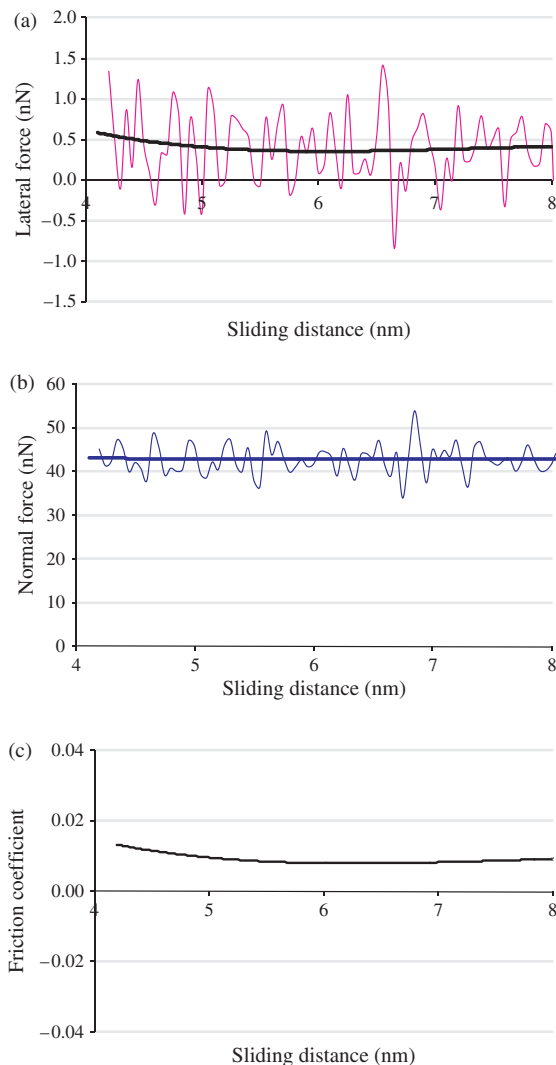


Fig. 3. Variation of average (a) lateral force, (b) normal force, and (c) coefficient of friction when sliding a diamond asperity on graphite.

3.2. Discussion

Throughout the sliding process, both the lateral and normal force fluctuated due to the changes in tool-work piece contacts as shown in Figures 3 and 5. This type of fluctuation of frictional and normal forces on the atomic scale is expected, of which the mechanism has been clearly explained by Zhang and Tanaka.¹⁸

Atoms in crystal diamond are in tetrahedral coordination and this arrangement leaves the surface atoms with dangling bonds. Reconstructing the surface with hydrogen atoms would saturate the atoms with dangling bonds and thereby eliminating the adhesion effect which in turn reduce the coefficient of friction. At low load, the hydrogen atoms at the interface interact repulsively and cause them to revolve around each other. When the load is increased, the rotation of the interface hydrogen atoms would be restricted. The hydrogen atoms take up a direction that reduces the interactions between

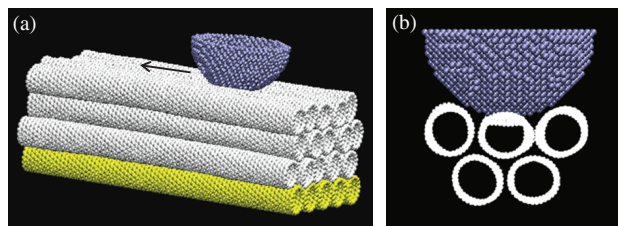


Fig. 4. (a) CNT bundle after sliding for 15000 fs under a load of ~6 nN, (b) Cross-sectional view of deformed CNT and its neighbours.

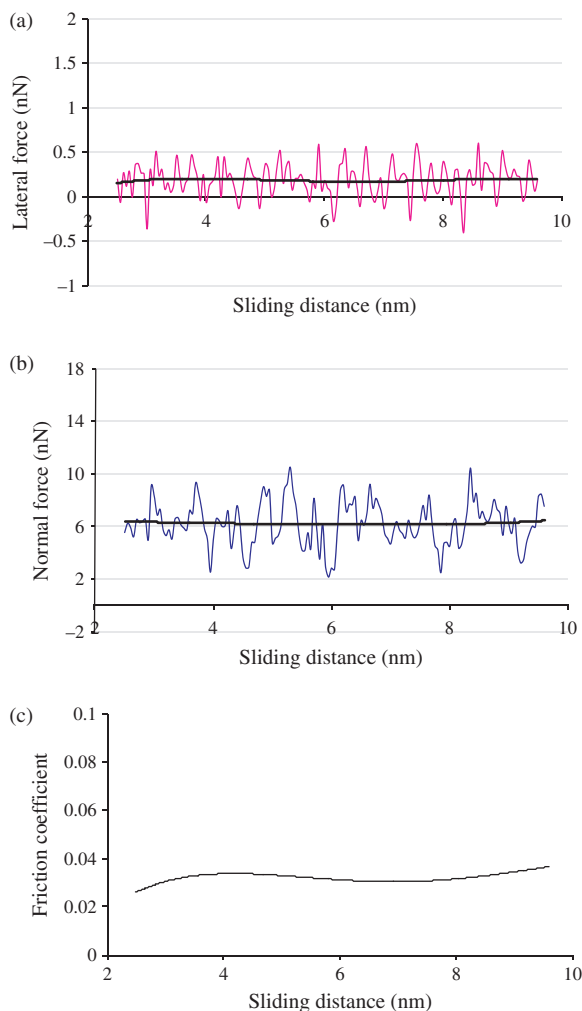


Fig. 5. Variation of average (a) lateral force, (b) normal force, and (c) friction coefficient when sliding a diamond asperity on a bundle of CNTs at a penetration depth of 0.2 nm.

them. Experimentally, Feng et al. had demonstrated that the passivation of diamond surface with atomic hydrogen/oxygen or with molecular oxygen would reduce the friction coefficient.¹⁹ According to them, the friction coefficient in ultra-high vacuum was between 0.6 and 1.0 which is about ten times that measured in air.

In graphite and nanotube, the atoms are sp^2 hybridized and this gives a planar structure. As such both graphite and nanotube have surfaces with no dangling bonds; the only

difference is that the nanotube has a closed shell structure whereas graphite has a planar sheet structure, which can be considered to have a link with their friction properties. Although graphite is a well known solid lubricant and is being used in a number of applications, it was found that it does not function in the absence of assisting agents such as water vapor and oxygen. Recently Dienwiebel et al.²⁰ developed a novel frictional force microscope and measured the atomic scale friction when sliding a tungsten tip over a graphite surface in dry contact. According to their measurements the coefficient of friction is in the order of 0.01–0.02. Our molecular dynamics calculation for diamond sliding on graphite also gives an average value of ~ 0.01 . These show that on the micro/nano scale, graphite can be a good lubricant even in vacuum. On the other hand, according to Hirata,⁷ the sliding of steel ball on graphite in vacuum gives a value between 0.5 and 0.6 for the coefficient of friction. This poses an interesting question: What happens at the macro level? In addition to the fact that macroscopic-scale friction is accompanied with wear and involves multiple microcontacts with different sizes and orientations as stated by Dienwiebel et al.,²⁰ it is possible to have the edges of different layers of graphite exposed to the surface at different positions during fabrication. Thus a sample of graphite surface would have atoms with dangling bonds which would have high adhesion with asperity and as such the coefficient of friction in vacuum would be high at the macro level. In a non-vacuum environment, for example in air, adhesion would be reduced due to surface passivation. At the micro/nano level, sliding occurs with a single layer of graphite and hence these problems disappear.

In the case of carbon nanotubes, as identified in our previous work on CNTs,²¹ the origin of low friction is the atomically smooth surface of CNTs. Because of their cylindrical shell structure and large aspect ratio of length to diameter, the surface of a nanotube bundle will not have atoms with dangling bonds. Hence adhesion with the asperity would be low and so as the coefficient of friction. This low frictional property of CNT films can be maintained across any dimensional scales. Moreover the full recovery of CNTs after sliding shows that they maintain good durability. This means that nanotubes could function as a good solid lubricant both at the nano and micro scales in vacuum. Unlike DLC film, where the coefficient of friction increased up to a certain load, for CNTs, the coefficient of friction did not change significantly on increasing the normal load from 6 nN to 28 nN, and from 9.8 mN to 98 mN according to experimental tests.¹⁰

4. CONCLUSIONS

Among the carbon allotropes (diamond, graphite and nanotube), nanotubes are the best solid lubricant as it has a low coefficient of friction that can be maintained across any dimensional scales from nano to macro scales due to the large aspect ratio of length to diameter. Graphite, though a well known solid lubricant, cannot function well in vacuum at the macro scale. Diamond (the atomic scale order film DLC studied in this paper) can be a good solid lubricant only at very low loads.

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