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Analysis of C_{60} Insertion into Single Wall Carbon Nanotube by Molecular Dynamics Simulation

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Classical molecular dynamics is used to simulate the insertion of C_{60} into a (10,10) single wall nano-tube (SWNT). We propose that the insertion process occurs through the open end of the tube. After insertion, the energy exchange between the C_{60} and the nanotube causes the kinetic energy of the former to decrease as it moves inside the tube. This kinetic energy loss is due to a "friction force" which we calculated for several insertion conditions. The binding energy of the C_{60} with the SWNT is due to Van der Waals interaction, and is found to be about 3.5 eV.

Keyword: fullerene, nanotube, insertion, molecular dynamics

1.INTRODUCTION

Encapsulation of C_{60} inside bundles of SWNT was first discovered in 1998 by Smith et al.[1)] by the pulsed laser evaporation method where the laser was shone on a catalyst-containing graphite target. Also, Zhang et al.[2)] and Sloan et al.[3)] have observed fullerenes inside SWNT grown by the arc discharge method. Later, the insertion was also achieved after reaction of C_{60} vapor under 0.1 atmospheric partial pressure with heat-treated and oxygen-treated SWNT at about 700K[2)]. It was found that heat and oxygen treatment improved drastically the insertion yield. Sloan et al.[3)] have proposed that tubes grow on a Ni particle which also contains carbon. A second tube grows inside the former, and a C_{60} (or fullerene) is pinched off of it. On the other hand, Burteaux[4)] et al. has proposed that fullerenes enter into SWNT from the side defect of open side of the SWNT since the walls were seen to have many defects. The mechanism of encapsulation is not precisely known however. Presumably, it could change depending on the type of experiment in which it takes place. The simplest scenario would be of course to assume that C_{60} or other fullerenes enter through the end of the tubes. This is also consistent with the heat treatment at 693K and with the presence of oxygen which would keep the tube end open. A recent experiment in which $Gd@C_{82}$ was inserted in a SWNT also supports this assumption[5)].

We therefore simulated the dynamics of C_{60} insertion from the open end of the nanotube. Our interest in this paper is the dynamics of the fullerene after it is inserted, and the computation of its kinetic energy loss resulting in a "friction force".

2.MODEL and CALCULATION METHOD

We consider a (10,10) armchair nanotube and a C_{60} of diameters 1.4 nm and 0.7 nm respectively. This allows a distance of 0.35 nm between the fullerene and

the tube which is very comparable to the distance between graphene sheets in graphite. One therefore expects an attractive interaction of Van der Waals type between the two. The SWNT is 10 nm long and open ended. The covalent interaction between the carbon atoms is modeled by the Brenner potential[6], and that between atoms of C_{60} and those of the nanotube is of Lennard-Jones form[7]. The Brenner potential is fitted to describe the covalent bonds between the carbon atoms, and the LJ potential, which is successfully used to explain the thermodynamic properties of C_{60} FCC crystal by L. A. Girifalco[8] , is determined to reproduce the correct interlayer distance and binding energy in graphite. Both the fullerene and the nanotube are first relaxed with the Brenner potential. Then C_{60} is placed outside the tube and shot from outside the tube towards the open end of the tube. The given initial kinetic energy is varying between 1.0 and 6.0 eV. The angle between the velocity of the fullerene and the tube axis is also a parameter of the problem, and it is varied from 20 to 40 degrees. The molecular Dynamics (MD) time step is taken to be 1fs.

3. RESULTS AND DISCUSSION

Due to the attractive Van der Waals interaction, C_{60} is more stable inside the SWNT than separate from it by 3.5 eV. This value is larger than what S. Berber et al. describe[9] because they have used the density functional method to compute it. The Girifalco potential, however, is classical but fitted from accurate ab initio calculations.

The Van der Waals interaction between C_{60} and the nanotube would cause an acceleration of the former towards the center of the tube if their distance becomes small enough. In this case, the energy gain by the fullerene is found to be about 3.5 eV. This corresponds to a velocity of 0.969 km/s or 0.969 nm/ps.

There is, however, collision and therefore energy exchange between the tube and the C_{60}, so that the velocity is usually reduced and the energy is transformed to heat. Macroscopically, this is called friction. For large angle insertions, the variations in the Kinetic energy (KE) are large due to strong collisions with the tube walls (See Fig.1).

But after a few collisions, the motion is more smooth and the KE decreases uniformly as a function of the fullerene coordinate. The friction force is defined as the average slope of KE versus fullerene coordinate along the tube axis. A typical MD run of insertion with initial kinetic energy of 2.0 eV and incidence angle of 4.5 degree is shown in Fig.2. In Fig.2, the horizontal axis indicates the coordinate of the center of the fullerene parallel to the axis of the nano-tube which is 10 nm long. The upper dot line indicates the kinetic energy of C_{60} and down solid line indicates the potential energy of the system. C_{60} goes into SWNT from the left side and the potential energy of the system goes down. Due to the collision between C_{60} and wall of SWNT, C_{60} loses its kinetic energy. In this case, because of its low kinetic energy, C_{60} can not get over the potential at the opposite side of SWNT and therefore is pulled back into it. According to our calculation, potential inside the tube is almost flat. From the oscillation between 0 and 10 nm one can clearly see the energy exchange and loss in this figure.

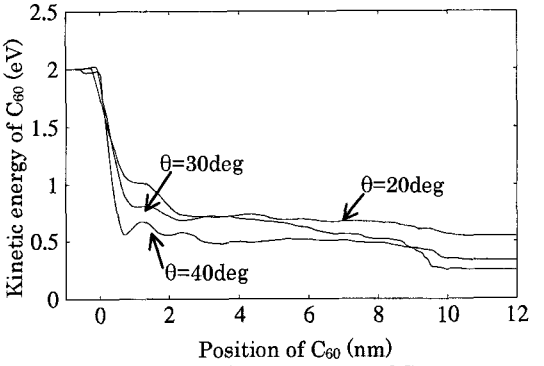

Fig. 1 Variation of kinetic energy of C_{60}. For large insertion angle against nanotube axis, kinetic energy loss is large.

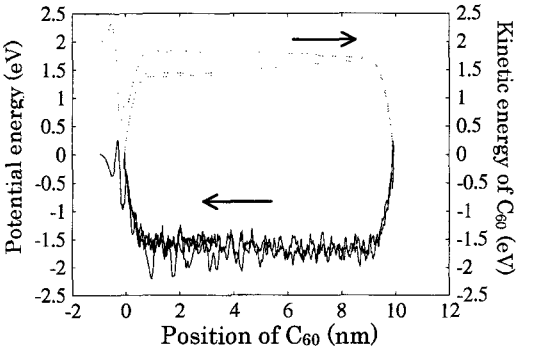

Fig. 2 Variation of potential energy of the system. Energy fluctuations in 1~9 nm range indicate that the kinetic energy of C_{60} is transferred to SWNT.

Fig.3 shows the relation between the friction force

and the average KE of C_{60} after it has suffered enough collisions and just before exiting the tube, for incidence angles varying from 20 to 40 degrees. In this case, there is no dependence on the angle since the memory of initial angle has been erased during

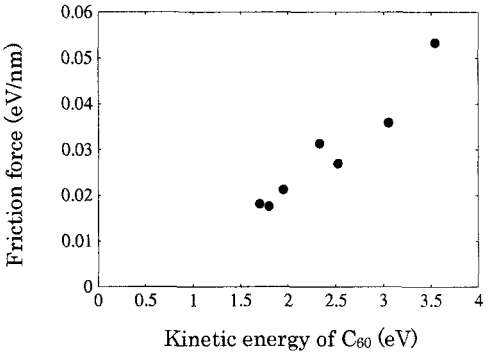

Fig. 3 Friction force increases against the kinetic energy of C_{60} along the axis of SWNT. After many collisions, the friction force does not depend on the insertion angle anymore.

continuing collision. To know the relation between friction force and kinetic energy, we need more sample points, but if we simply assume that the friction force linearly increases with the kinetic energy , the slope is found to be 0.0125 nm^{-1}.

4. CONCLUSIONS

In summary, the dynamics of C_{60} insertion into a SWNT has been studied. Based on experimental evidence and molecular dynamics and statistical considerations, we proposed that the insertion is very likely to take place from the open end of the tube in the case where peapods were synthesized from heating up the mixture of C_{60} and SWNT[5]. This is also supported by the fact that in bundles peapods are formed as well. If the insertion was to take place from wall defects as suggested by Berber et. al.[9] , only the outermost tubes of the bundles should be filled and not the inner ones as well.

The energy exchange between the tube and the fullerene causes the motion of the latter to dampen and results in encapsulation in the tube. The corresponding friction force was found to increase with the average kinetic energy during the period over which the force was computed.

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