Volume 9, Number 8
1009-1963/2000/09(08)/0581-05
CHINESE PHYSICS
August, 2000
© 2000 Chin. Phys. Soc.

TIGHT-BINDING MOLECULAR DYNAMICS STUDY OF C_{60}-GRAPHITE COLLISIONS

FANG YUN-TUAN(方云团), LUO CHENG-LIN(罗成林),
(Department of Physics,Nanjing Normal University, Nanjing 210097, China)

(Received 24 December 1999; revised manuscript received 21 April 2000)

We report the tight-binding molecular dynamics simulations of C_{60} impacting on a graphite (0001) surface with different incident energy. The simulations provide detailed characterizations of the microscopic processes occurring during the collisions and show insight into the deposition mechanisms of C_{60} on semiconductor substrate.

Keywords: tight-binding molecular dynamics, collision, energy, potential barrier
PACC: 3420

I. INTRODUCTION

Since the discovery[1] of the unique stability of C_{60} molecule against surface induced fragmentation, the investigation of fullerene interactions with solid substrates has become an exciting field of research.[1−10] Of particular interest is the case that C_{60} impacts on semiconductor surfaces, which can thus form covalent bonds with the C_{60} cluster. The study of these bonds is an essential prerequisite for the understanding of fullerene deposition on nonmetallic substrates. These deposition processes have been proposed[8] as a way of synthesizing thin films which would retain specific characteristics of the incident cluster.

Studies of C_{60} in collision on a graphite surface have been reported in Refs [9] and [10], in which a model potential (TLHL potential)[11] was employed to describe carbon-carbon interactions. As is well known, potential function plays a central role in the accuracy of the simulation results. The TLHL potential function has a total of nine parameters and it is based on a two-body and an angle-dependent three-body interaction. The parameters for the function were evaluated from fits to various properties of graphite and diamond crystals. Moreover, according to the potential function fullerene C_{60} was found to have the lowest energy. Although those calculated results are in general agreement with the available data, this model is classical in nature and cannot acount for quantum mechanical effects of directional covalent bonding. The tight-binding (TB) potential model allows the quantum mechanical nature of the covalent bonding to enter the potential in a natural way rather than through the addition of *ad hoc* angular terms as in classical potentials. But the usefulness of a TB model in describing the disordered complex system is closely related to its transferability. Xu *et al.*[12] developed a transferable TB potential for carbon after the work of Goodwin *et al.*[13] In this paper we perform molecular dynamics simulations of C_{60} bombardment on graphite (0001) surface by using the TB potential model proposed by Xu *et al.*

II. THE TB POTENTIAL MODEL AND METHOD

In Xu's TB potential model, the total energy of the system is given by

$$E_{\rm tot} = \sum_i \frac{p_i^2}{2m} + \sum \langle \Psi_n | H_{TB} | \Psi_n \rangle + E_{\rm rep}. \qquad (1)$$

The first term is the kinetic energy of the ions, the second term is the electronic energy calculated by summing the eigenvalues of all occupied electronic states from a tight-binding Hamiltonian H_{TB}. The off-diagonal elements of H_{TB} are described by a set of orthogonal Slater-Koster (SK) s-s, s-p two-center hopping parameters ($V_{{\rm ss}\sigma}$, $V_{{\rm sp}\sigma}$, $V_{{\rm pp}\sigma}$, and $V_{{\rm pp}\pi}$) scaled with interatomic separation r as a function $s(r)$, and the on-site elements are the atomic orbital energies, E_s and E_p of the corresponding atom,

$$s(r) = V_\alpha \left(\frac{r_0}{r}\right)^{n_\alpha} \exp\left\{ n_\alpha \left[-\left(\frac{r}{r_{c\alpha}}\right)^{n_{c\alpha}} + \left(\frac{r_0}{r_{c\alpha}}\right)^{n_{c\alpha}} \right] \right\}. \qquad (2)$$

The remainder of $E_{\rm tot}$ is modelled by a short-ranged repulsive term $E_{\rm rep}$ given by

$$E_{\rm rep} = \sum_i f\left(\sum_i \phi(r_{ij}) \right), \qquad (3)$$

$$f(x) = c_1 x + c_2 x^2 + c_3 x^3 + c_4 x^4, \qquad (4)$$

where $\phi(r_{ij})$ is a pairwise potential between atoms i and j. All the needed parameters can be got from

Ref.[12]. Xu *et al.* have checked them extensively, and the resuts are in good agreement with other theoretical calculations and available experimental data.

In the model of our modecular dynamics simulations, we adopt the constant number, constant volume and constant energy molecular dynomics with a time step of 0.1 fs. The graphite target contains 6 layers of atoms with 240 atoms per layer and the two bottom layers are held rigid throughout the simulations. At first, the whole system is held at a temperature of 300K and the C_{60} molecules are located at a sufficiently large distance above the graphite surface so as to have no interaction with it. Periodic boundary conditions are applied in the directions parallel to the graphite(0001) surface. The nearest C_{60} molecules have no interaction because the large unit cell makes the distance between them large enough. Then we moves the C_{60} molecule in the direction normal to the graphite surface with different kinetic energies, which are 60 eV, 120 eV, 180 eV, 200 eV, 220 eV and 240 eV.

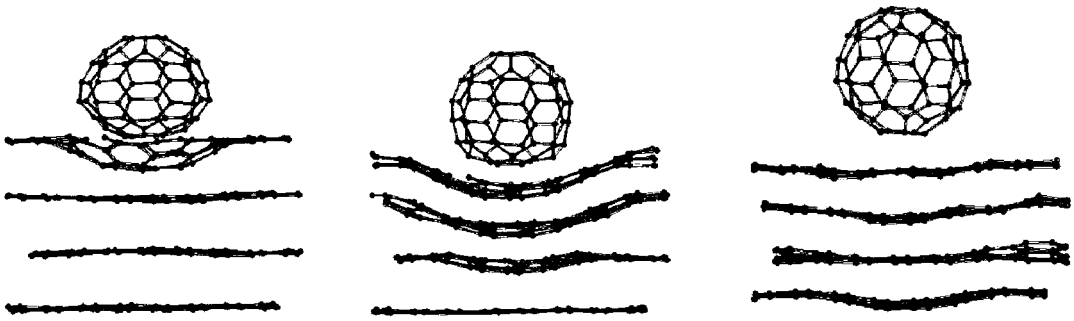
Ⅲ. RESULTS AND DISCUSSION

We take snapshots of atomic positions as a function of the simulation time to characterize general features of the collisions. First, for the lower incident kinetic energies ($E_{\rm in}$) of 60 eV and 120 eV, the C_{60} buckyball is deformed as it approaches the graphite surface (see Figs. 1 and 2, all the lower layers of graphite have not been drawn). But the process of deformation is not fast so that the C_{60} molecule has sufficient time to relax and the five and six-membered ring structure remains intact. During the collisions, all the four graphite layers are compressed in turn. This means that the C_{60} molecule and the target exert repulsive force on each other. Though the repulsive force makes the target deformed, the C_{60} cluster recoils and remains its original shape in the end, with only two bonds broken when $E_{\rm in}$=120 eV (Fig. 2(c)). This ability of buckyball to experience a severe structural distortion and return to its original shape has been referred to as resilience.

Second, when $E_{\rm in} = 180$ eV, the bottom of buckyball is deformed firstly and becomes flat at 100 fs (Fig. 3(a)). The most heavily deformation occurs at 140 fs. Due to large speed of C_{60} molecule the process of deformation is so fast that the C_{60} molecule have not enough relaxation time, which leads to the breaking of some bonds of the C_{60} (Fig. 3(b)). After 140 fs, the C_{60} begin to rebound. Different from Figs. 1 and 2, it cannot recover its original shape and defects are present in its structure. Therefore, we can conclude that the time of relaxation for C_{60} molecule to recover its original shape must be lager than 40 fs. Most interestingly, during the collisions the C_{60} molecule does not form any bond with the graphite substrate, this means that the collision process is still nonreactive. We could think that there may be a potential barrier between the C_{60} molecule and the graphite surface. An incident energe of 180 eV is not large enough for C_{60} to overcome the potential barrier and combine with the graphite. As it moves to the graphite layers, the structure of the substrate are heavily influenced, and some bonds are even broken at first(see Figs. 1-3), but they all recover their initial shape after the C_{60} bounces off. We do not find any broken bonds from them in the end.

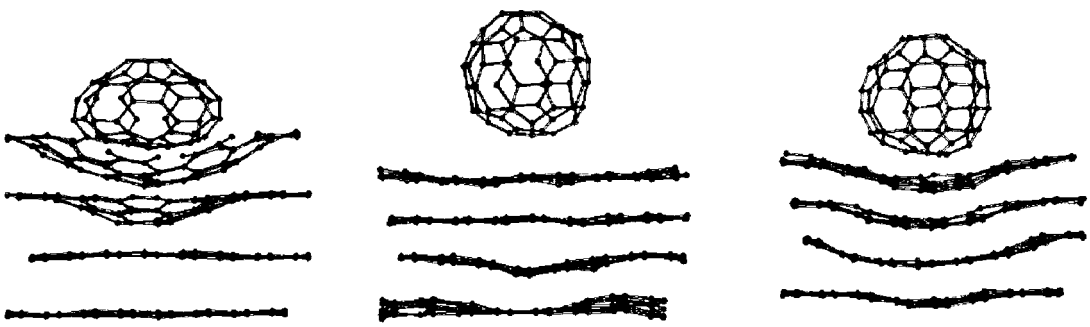
Finally, when the C_{60} impacts on the graphite with higher incident kinetic energies ($E_{\rm in}$) of 200 eV, 220 eV and 240 eV, the result of 200 eV is similar to that of 180 eV. As for the impacts with energies 220 eV and 240 eV, not only many bonds of the C_{60} molecule are broken but also many bonds are formed between the cluster and the substrate (Fig.4). Such a result indicates that the C_{60} molecule has an enough energy to overcome the potential barrier, and the presence of defects in the C_{60} structure can cause the molecule to react with the surface more easily. The high incident energy and the bonds forming between the C_{60} molecule and the graphite surface make the graphite surface structure destroyed and unable to recover. As we see in Figs. 4(b) and 4(c), many bonds of the graphite surface are still broken in the end.

All our simulation results are close to the experimental observations. First, Beck *et al.*[1] detected a negligible yield of charged fragments resulting from the impact of C_{60}^{+} with graphite(0001) surface with collision energies in the rang 0–170 eV, which corresponds to Figs. 1–3 and Fig. 4(a). Second, in other experiments by Busmann *et al.*, there is evidence for transient chemisorption of C_{60}^{+} on graphite surface when C_{60}^{+} with larger energies above 275 eV collide with graphite surface,[2] which just verify the result of the simulation corresponding to Fig. 4. Obviously, we can easily get the imformation about the chemisorption process (see Fig. 4) which could not be derived from experiments yet. For example, the incident energy threshold for chemisorption and the height of potential barrier between C_{60} and the graphite surface could be considered to be in the range 200-220 eV.



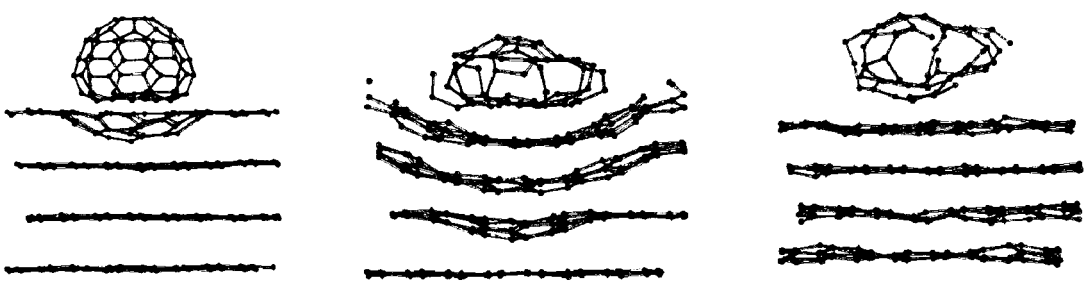
(a) 90 fs (b) 200 fs (c) 300 fs

Fig.1. Snapshots of the atomic positions at various times for E_{in}=60eV.



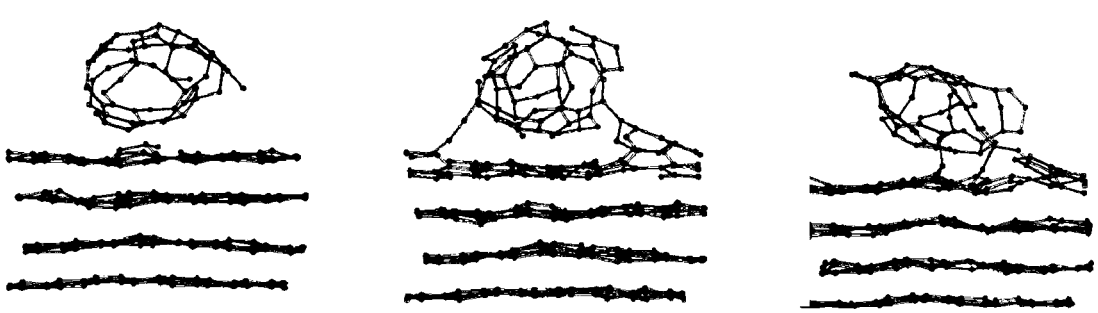
(a) 100 fs (b) 200 fs (c) 300 fs

Fig.2. Snapshots of the atomic positions at various times for E_{in}=120eV.



(a) 100 fs (b) 140 fs (c) 280 fs

Fig.3. Snapshots of the atomic positions at various times for E_{in}=180eV.



(a) 200 eV (b) 220 eV (c) 240 eV

Fig.4. Snapshots of the atomic positions for diffrent E_{in} at 300fs.

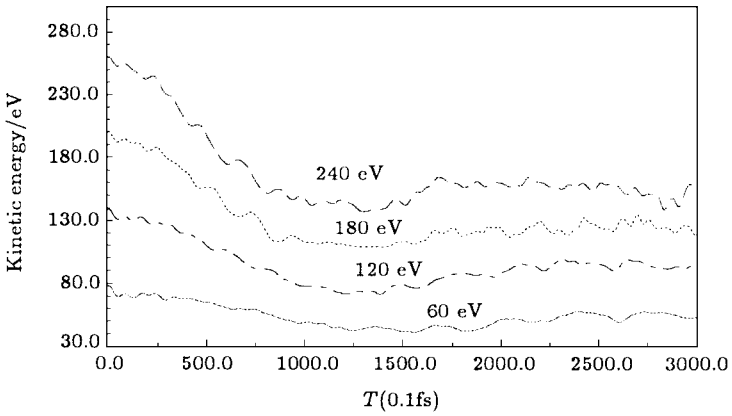


Fig.5. Total kinetic energy $E_{\rm kin}$ of the system as a function of time

Figure 5 shows the total kinetic energy $E_{\rm kin}$ as a function of time for different incident energies. Most part of $E_{\rm kin}$ is the C_{60}'s center-of-mass kinetic energy and the rest is the internal kinetic energies of the C_{60} molecule and the graphite. So the change of $E_{\rm kin}$ mainly reflects the change of the C_{60}'s center-of-mass kinetic energy. Considering the energy changes in Fig. 5 and the atomic trajectories pictured in Figs. 1–4, the collision could be regarded as a two-stage process. The first stage is characterized by severe deformations. At the same time the center-of-mass kinetic energy of the C_{60} is transferred into the internal kinetic energy and repulsive potential energy of both the C_{60} and the substrate, which are referred to as the decreasing process of $E_{\rm kin}$ at first. The second stage is characterized by the resilience, bond breaking and chemisorption, during which the deformation potential energy is released, becoming the cluster center-of-mass kinetic energy and the internal kinetic energies of both the cluster and the substrate. This corresponds to the latter part of the $E_{\rm kin}$ curves. The turning point of the process just corresponds to the time when the C_{60} molecule deforms most severely (see Table 1). During the first stage, $D = \dfrac{E_0 - E_{\rm min}}{t}$ denotes the average decreasing rate of $E_{\rm kin}$(E_0 and $E_{\rm min}$ are the beginning value and the minimum of $E_{\rm kin}$ respectively and t is the time at which the $E_{\rm kin}$ is at its lowest point). From Fig. 5, we obtain the values of t and D, as listed in the Table 1. It shows that D increases with increasing $E_{\rm in}$. Every final $E_{\rm kin}(E_{\rm end})$ is less than the corresponding beginning $E_{\rm kin}(E_0)$, which means all processes of the collisions are inelastic. In this study, the inelastic extent of all collisions can be measured by calculating $e = \dfrac{E_0 - E_{\rm end}}{E_0}$, whose values are also shown in Table 1. The bigger the value of e , the severer the inelastic degree of the collision. Moreover, we also find that the value of e increases with increasing $E_{\rm in}$.

Table 1. The values of t, D and e for different $E_{\rm in}$

$E_{\rm in}$(eV)	t(fs)	D(eV/fs)	e
60	180	0.205	0.346
120	150	0.5	0.357
180	140	0.657	0.425
240	130	0.89	0.458

IV.CONCLUSIONS

We have conducted TB molecular simulations to study the bombardment of C_{60} cluster on graphite surface (0001) with impact energies ranging from 60 to 240 eV. For lower incident energies (60 eV and 120 eV), the molecule bounces off the surface and can recover its original shape after severe distortions. For intermediate incident energies (180 eV and 200 eV), the molecule rebounces off the substrate with some broken bonds. But it does not form any covalent bonds with the surface. For higher collision energies (220 eV and 240 eV), we get pieces of the broken cage, and stable bonds with the substrate are formed. The relaxation time for C_{60} molecule to gain its original shape must be larger than 40 fs. The incident energy threshold for C_{60} chemisorption on graphite surface and the height of potential barrier between the C_{60} molecule and the graphite surface are in the range 200–220 eV. All our results are in qualitative agreement with experimental results.

REFERENCES

[1] R. Beck, P. St. John, M. Alvarez, F. Diederich and R. L. Whetten, *J. Phys. Chem.,* **95**(1991),8042.

[2] H. G. Busman, T. Lill, B. Reif and I. Hertel and H. G. Maguire, *J. Chem. Phys.*,**98**(1993),7574.

[3] T. Lill, H. G. Busman and I. Hertel, *Appl. Phys.,* **A55** (1992),461.

[4] C. Yeretzian and R. L. Whetten, *Z. Phys.,* **D24**(1992),199.

[5] R. Mowrey, D. W. Brenner, B. I. Dunlap, J. W. Mintmire and C. T. White, *J. Phys. Chem.,* **95**(1991),7138.

[6] P. Blaudeck, T. Frauenheim, H. G. Busman and T. Lill, *Phys. Rev.,* **B49**(1994),11409.

[7] Y. Z. Li, M. Chander, J. C. Patrin, J. H. Weaver, L. P. F. Chibante and R. E. Smalley, *Phys. Rev.,* **B45**(1992), 13837.

[8] V. Paillard, P. Melinon, V. Dupuis, J. P. Perez and B. Champagnon, *Phys. Rev. Lett.,* **71**(1993),4170.

[9] Z. Y. Pan, Z. Y. Man, Y. K. Ho, J. Xie and Y. Yue, *J. Appl. Phys.,* **83**(1998),4963.

[10] Z. Y. Man, Z. Y. Pan, L. Liu and R. W. Li, Chinese *Phys.Lett.,* **12** (1995),751.

[11] T. Takai, C. Lee, T. Halicioglu and W. A. Tiller, *J. Phys. Chem.,* **94**(1990),4480.

[12] C. H. Xu, C. Z. Wang and K. M. Ho, *J. Phys. Condens Matter,* **4**(1992),6047.

[13] L. Goodwin, A. J. Scinner and D. G. Pettifor, *Europhys. Lett.,* **9**(1989),701.