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Formation of cage-like C_{60} clusters in molecular-dynamics simulations

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Abstract. – We have examined the formation of cage-like C_{60} clusters in helium atmosphere via tight-binding molecular-dynamics simulation. Simulating the laser evaporation experiment, we obtained a C_{60} cage structure containing 11 pentagons, 19 hexagons, one tetragon and one heptagon in the simulation time of 30.8 ps. After examining the stability of the buckminsterfullerene, a pathway is suggested for its formation.

In spite of the fact that there are various methods to produce fullerenes, the underlying process of formation is still poorly understood, and the procedure of industrial production of a given fullerene is not yet found. Here we mention the laser evaporation [1], the arc deposition [2], the pyrolysis [3, 4] and the electrolysis [5, 6] among the most popular methods. Unfortunately they produce a mixture of fullerenes and the separation of individual components is a rather cumbersome work.

Molecular dynamics [7] can provide detailed insight into the formation process, although the simulation time of several ps is small compared to the real time of formation. In the laser evaporation and arc deposition, for example, the average time between collisions of He, C or C_{60} is of the order of nanoseconds [8]. The authors try to avoid this drawback by using higher pressure and increased temperature. In several papers the complicated process of formation is studied with the help of disintegration [9-16], or special routes are supposed in the calculations [17, 18].

In the papers of Ballone and Milani [19], Chelikowsky [20] and Wang *et al.* [9], the process of formation is simulated from a "chaotic" arrangement of carbon atoms, but there are some artificial conditions applied with the aim of obtaining the closed cage-like structure. Ballone and Milani kept the carbon atoms on the surface of a sphere for $T > 4000$ K, Chelikowsky removed and randomly replaced the energetically unfavorable atoms and Wang *et al.* confined them into a sphere and obtained a closed cage only for sphere of radius $R = 3.832$ Å. In the present work we used a natural boundary condition by putting sixty carbon atoms into helium atmosphere. In this way we tried to simulate the original laser evaporation experiment [1] by exploding four different initial arrangements of sixty carbon atoms, as Kroto's four-deck sandwich model 6:24:24:6 [21], and other random structures with amorphous, graphite and diamond densities. The temperature of the helium gas was controlled with Nosé-Hoover molecular dynamics [22, 23].

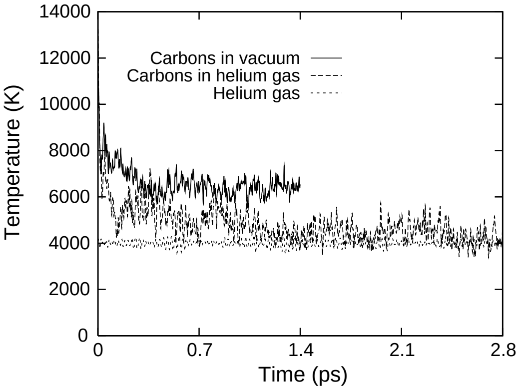


Fig. 1. – Temperatures of the carbon atoms in vacuum and in helium atmosphere with the temperature of the helium gas.

In our simulation the carbon-carbon interaction was calculated with the help of the tight-binding total-energy expression of Xu *et al.* [24],

$$E = \sum_I \frac{P_I^2}{2m} + \sum_n^{\text{occupied}} \langle \psi_n | H_{\text{TB}} | \psi_n \rangle + U_{\text{rep}}\,, \tag{1}$$

where P_I stands for the momentum of atom I. The first term in eq. (1) is the kinetic energy of the ions, the second term is the electronic energy calculated by the parametrized tight-binding Hamiltonian H_{TB}, and the third term is a short-ranged repulsive energy representing the ion-ion repulsion and the correction to the double counting of the electron-electron interaction in the second term.

The helium-helium and carbon-helium interaction was modeled with a pairwise 6-12 Lennard-Jones potential

$$U_{ij} = 4\varepsilon_{ij} \left(\frac{{\sigma_{ij}}^{12}}{r_{ij}^{12}} - \frac{{\sigma_{ij}}^{6}}{r_{ij}^{6}} \right), \tag{2}$$

where $\varepsilon_{\text{HeHe}}/k_{\text{B}} = 10.8$ K, $\sigma_{\text{HeHe}} = 2.57$ Å [25] and $\varepsilon_{\text{CC}}/k_{\text{B}} = 33.25$ K, $\sigma_{\text{CC}} = 3.47$ Å [26,27]. The carbon-helium parameters were calculated with the relations $\varepsilon_{\text{HeC}} = (\varepsilon_{\text{HeHe}}\varepsilon_{\text{CC}})^{0.5}$ and $\sigma_{\text{HeC}} = (\sigma_{\text{HeHe}} + \sigma_{\text{CC}})/2$ [25]. In the actual calculations the van der Waals interaction between the carbon atoms was neglected and the parameters ε_{CC}, σ_{CC} were used only in the helium-carbon interactions.

In our MD simulation we used the Verlet algorithm [28] to integrate the equations of motion over time steps of 7.0×10^{-16} s. The initial arrangement of the atoms was prepared in the following way. We put the initial arrangements of sixty carbon atoms into the center of a cube of side 35.0 Å, and another cube of side 35.0 Å was filled with $4 \times 7^3 = 1372$ helium atoms in fcc lattice. We joined these two boxes side by side and removed the common surfaces. Periodic boundary condition was used when decreasing the side of 70.0 Å from the unit cell $35 \times 35 \times 70$ to 35.0 Å in 1.4 ps. The temperature T_{gas} of the helium gas was controlled with the help of a Nosé-Hoover thermostat. In the next 0.7 ps the side of the cube was decreased to 25.0 Å. In this way we obtained a cubic unit cell of side 25.0 Å containing the initial carbon structure and 1372 helium atoms of temperature T_{gas}. We began the simulation process by giving an initial temperature of $T = 13000$ K to the carbon atoms. During the simulation periodic boundary condition was used for the unit cell of side 25.0 Å and the helium gas was in Nosé-Hoover thermostat of temperature T_{gas}. Trying with different unit cells we found the

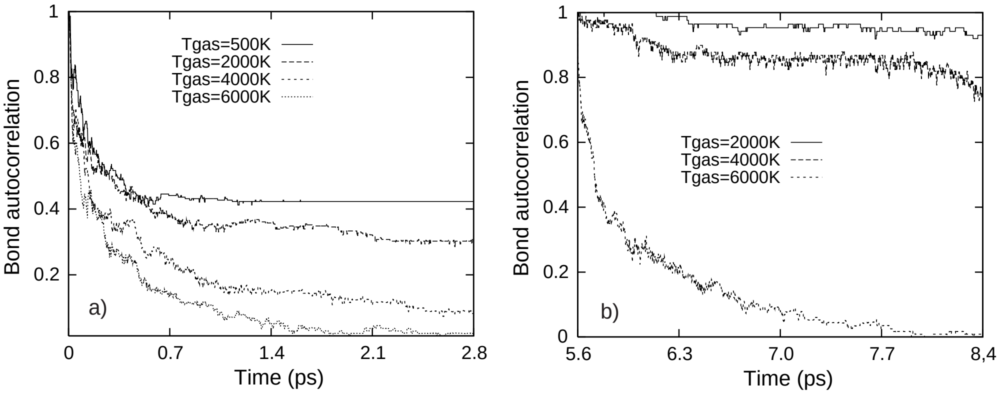


Fig. 2. – Bond autocorrelation functions at helium gas temperatures $T_{\mathrm{gas}} = 500$, 2000, 4000 and 6000 K in the time intervales (a) (0.0 ps, 2.8 ps) and (b) (5.6 ps, 8.4 ps).

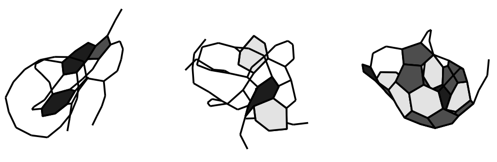
cell of side 25.00 Å to be optimum for a simulation time of few ps. In the following we show our results for the sandwich structure, where the layers were separated by 3.35 Å and the first-neighbor carbon-carbon distance was 1.4 Å, just as in the graphite. Figure 1 shows the temperature of the helium gas and the temperature of the carbon atoms. The temperature of the helium gas fluctuates around $T_{\mathrm{gas}} = 4000$ K, and the temperature of the carbon atoms decreased from 13000 K to 4000 K. This figure also depicts the temperature of the carbon atoms when the helium atmosphere is removed and the simulation is performed in vacuum. In this constant-energy simulation the final temperature of carbon atoms is around 6500 K.

In order to describe the structure transformation we introduced the $Ba(t_2, t_1)$ bond autocorrelation function

$$Ba(t_2, t_1) = \frac{\#(B(t_2) \bigcap B(t_1))}{\#(B(t_2) \bigcup B(t_1))}, \tag{3}$$

where $B(t_2)$ and $B(t_1)$ are the sets of bonds between the carbon atoms at time t_2 and t_1 for $t_2 \geq t_1$. $\#(B(t_2) \bigcap B(t_1))$ is the number of elements in the section of sets $B(t_2)$ and $B(t_1)$ and $\#(B(t_2) \bigcup B(t_1))$ is the number of elements in the union of sets $B(t_2)$ and $B(t_1)$. Bond is defined between two carbon atoms when the interatomic distance is less than 1.8 Å.

We performed calculations at four different helium gas temperatures $T_{\mathrm{gas}} = 500$, 2000, 4000 and 6000 K. Figures 2a and b show the bond autocorrelation functions $Ba(t, 0)$ and $Ba(t, 5.6)$. At $T_{\mathrm{gas}} = 500$ K the topological structure of the carbon cluster was frozen for $t > 1.4$ ps. Its constant value was of 0.42 and the corresponding connected structure

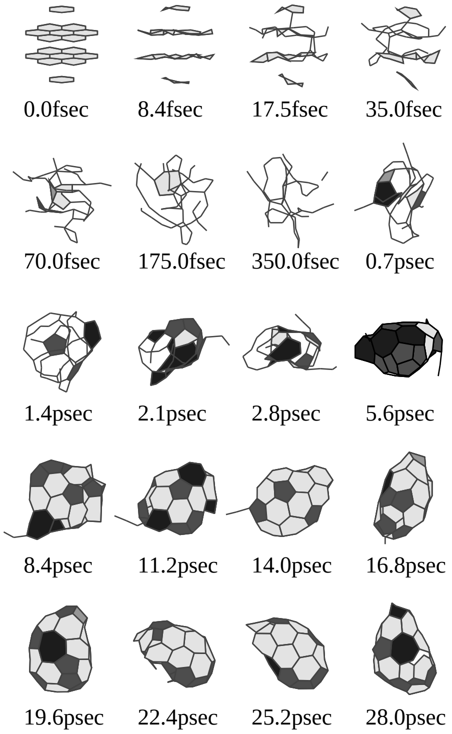


500K 1.4psec

6000K 14.0psec

2000K 14.0psec

Fig. 3. – Final structures of the carbon atoms at helium gas temperatures $T_{\mathrm{gas}} = 500$, 6000, and 2000 K with the corresponding times of simulations.



0.0fsec 8.4fsec 17.5fsec 35.0fsec

70.0fsec 175.0fsec 350.0fsec 0.7psec

1.4psec 2.1psec 2.8psec 5.6psec

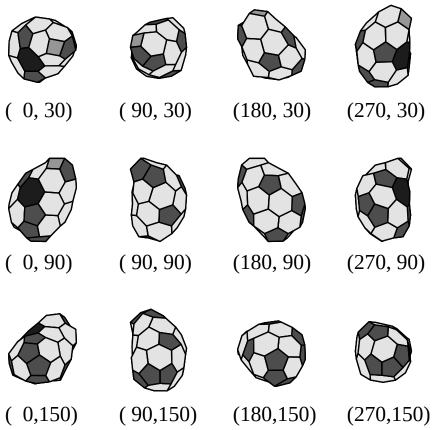
8.4psec 11.2psec 14.0psec 16.8psec

19.6psec 22.4psec 25.2psec 28.0psec

Fig. 4. – Snapshots of the formation process of the C_{60} structure at helium gas temperature $T_{\rm gas} =$ 4000 K. At 0.0 fs the initial four-deck sandwich model 6:24:24:5 is depicted.

contained a pentagon, two heptagons, some rings and chains formed by a dozen of carbon atoms (fig. 3). As the transformation was very slow we stopped the simulation at 2.8 ps. The situation was just the opposite for $T_{\rm gas} = 6000$ K, where $Ba(t, 0)$ and $Ba(t, 5.6)$ presented practically exponential decay to 0 in 2.8 ps (fig. 2a and b). We stopped the simulation at 14.0 ps because $Ba(t, 11.2)$ had the same exponential structure as $Ba(t, 0)$. This means that at $T_{\rm gas} = 6000$ K the topological transformation was very fast and we could not obtain a stable structure in our time of simulation. The general form of this changing structure was a chain-like structure with accidental five-, six- and seven-fold rings (fig. 3). Let us turn to the case of $T_{\rm gas} = 2000$ K. Now $Ba(2.8, 0)$ was equal to 0.3 and $Ba(8.4, 5.6)$ had the value of 0.94. There was a considerable slowing-down in the transformation process. As fig. 3 shows, we obtained a semi-closed cage-like structure in the simulation time of 14.0 ps. In the next 2.8 ps the changing of this structure was very slow ($Ba(16.8, 14.0) = 0.95$) and we rejected the continuation of the simulation process.

We found that at the gas temperature $T_{\rm gas} = 4000$ K the sandwich C_{60} transformed into a cage C_{60} structure (fig. 4 and 5). During the simulation we obtained the following bond autocorrelation functions: $Ba(2.8, 0) = 0.08$, $Ba(5.6, 2.8) = 0.54$, $Ba(8.4, 5.6) = 0.74$, $Ba(11.2, 8.4) = 0.72$, $Ba(14.0, 11.2) = 0.65$, $Ba(16.8, 14.0) = 0.97$, $Ba(19.6, 16.8) = 0.88$, $Ba(22.4, 19.6) = 0.74$, $Ba(25.2, 22.4) = 0.86$, $Ba(28.0, 25.2) = 0.98$, $Ba(30.8, 28.0) = 0.97$. In the time interval (28.0 ps, 30.8 ps) the carbon structure was relaxed at $T_{\rm gas} = 300$ K. Under 70.0 fs we obtained practically the same structures independently of the gas temperature $T_{\rm gas}$. At the beginning of the simulation the influence of the helium gas on the motion of carbon atoms can be neglected. For 350.0 fs the sandwich structure of C_{60} was totally destructed



(0, 30) (90, 30) (180, 30) (270, 30)

(0, 90) (90, 90) (180, 90) (270, 90)

(0,150) (90,150) (180,150) (270,150)

Fig. 5. – Different views of the final C_{60} structure after the simulation time of 30.8 ps at helium gas temperature $T_{\text{gas}} = 4000$ K. The (Φ, Θ) values are the polar coordinates of the views.

but at 0.7 ps we found that the number of pentagons, hexagons and heptagons was in order 1, 2, 2 and 2. The first cage-like structure with a wandering C_2 on the surface was found at 5.6 ps. This structure contained 12 pentagons, 6 hexagons and 8 heptagons. The first closed cage was obtained at 19.6 ps with one tetragon, 11 pentagons, 19 hexagons and 1 heptagon. In the following this structure was destructed or reconstructed from time to time depending on the number of broken bonds. Figure 5 shows the relaxed final structure from different views. During the last 2.8 ps only two new bonds were appearing and the obtained cage structure has the same topological arrangement as that of 19.6 ps. We call such kind of structures dynamically stable structure. In the buckminsterfullerene each of the carbon atoms is bonded to 3 neighbors and they form 12 isolated pentagons and 20 hexagons. We obtained 11 pentagons, 19 hexagons, one tetragon and one heptagon. All of the atoms have three neighbors but unfortunately only 3 pentagons are isolated. One of the isolated pentagons has a common bond with the heptagon and there are two pairs of neighboring pentagons. A chain of 3 pentagons is connected to the heptagon. We suppose that after 19.6 ps accidental bond breakings can lead to Stone-Wales transformations [29] or other transformations that produce the icosahedral buckminsterfullerene, however, the changing of the structure is rather slow. It is interesting that the bond autocorrelation function $Ba(8.4, 5.6)$ equals $Ba(22.4, 19.6)$, but there is a great difference between the two values. The first one is due to forming new structure of bonds but the second one is due to temporary bond breaking

In order to check our results, we performed calculations with other initial carbon structures where the 60 carbon atoms were arranged randomly in graphite or diamond densities. At $T_{\text{gas}} = 4000$ K the original structures were destructed around 350 fs and for 5.6 ps we obtained structures that were very similar to the corresponding structures of fig. 4. In some cases the "wandering" atoms were inside the cage or they were separated from the others.

We studied, as well, the stability of the buckminsterfullerene by taking it as initial structure for the 60 carbon atoms. In this case, however, the initial carbon temperature was 0 K. The following bond autocorrelation functions were obtained: $Ba(2.8, 0) = Ba(5.6, 2.8) = Ba(8.4, 5.6) \sim 1.0$ at $T_{\text{gas}} = 4000$ K and $Ba(2.8, 0) = 0.93$ at $T_{\text{gas}} = 6000$ K. Practically the same values were produced for the C_{60} of C_{2v} symmetry obtained by one Stone-Wales transformation from the buckminsterfullerene.

In conclusion, our molecular-dynamics simulations suggest the following pathway for the formation of the buckminsterfullerene. In the first 350 fs there is a destruction of the initial structure by obtaining a chain-like structure. Around 0.7–1.4 ps the first dynamically stable pentagons and hexagons appear. The first cage-like structures with the "wandering" carbon atoms are developed around 5.6 ps, and the first dynamically stable cage structures appear around 19.6 ps. In the following there is a slowing-down in the formation of new bonds. As the structure nears the buckminsterfullerene the dynamical stability increases. The abovementioned points of times are valid only if the density of the helium gas corresponds to the one of the present molecular-dynamics simulation. In the case of the real laser vaporization experiment these points of time are much greater because of the lower helium gas density.

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