

A Molecular Dynamics Simulation for the Formation Mechanism of Fullerene*

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Abstract

The formation mechanism of fullerene, a new type of carbon molecule with a hollow caged structure, was studied using a molecular dynamics method. In order to simulate the basic reaction process observed in the arc-discharge or the laser vaporization fullerene generation, we have calculated the clustering process starting from randomly located isolated carbon atoms. Here, an empirical many-body carbon potential proposed by Brenner (1990) was employed. Under a certain condition of the initial density and the temperature control, the simulation yielded the hollow caged carbon network which could be regarded as an imperfect fullerene. Intermediate clusters observed in the clustering process were dimers, trimers, linear chains up to C₁₀, mono-cyclic rings in C₁₀-C₁₅, poly-cyclic rings of about C₂₀, fragments of 2 dimensional network, and the imperfect fullerene. One of the remarkable reactions was a linear chain wrapping a poly-cyclic ring to form a larger fragment of network structure.

KEYWORDS: Fullerene, Molecular Dynamics Method, C₆₀, Cluster, Condensation, Precursor

1 Introduction

Existence of soccer ball structured C₆₀ shown in Figure 1(a) was demonstrated by Kroto *et al.* (1985) through their time-of-flight mass spectra of carbon clusters generated by the laser-vaporization supersonic-nozzle technique. They observed a prominent C₆₀⁺ signal and the complete lack of odd numbered clusters. They named the cluster C₆₀ of truncated icosahedron as Buckminsterfullerene since the beautiful network structure resembled the famous geodesic dome designed by Buckminster Fuller. According to the Euler's rule of geometry, a polyhedron with only pentagonal and hexagonal faces (5/6 polyhedron) must have 12 pentagons and n hexagons ($n = 0, 2, 3, 4, \dots$). Then, the number of vertices (number of atoms) is $2n + 20$. Truncated icosahedron is the case of $n = 20$. Since mass spectra of positive carbon clusters exhibited only even numbered clusters in the range of C₃₀ to at least C₆₀₀ [Rohlfing *et al.* (1984) and Maruyama *et al.* (1991)], we could speculate that all of those clusters had 5/6 polyhedral structure. Carbon clusters with such hollow close-caged structure are called fullerene [Figure 1].

In 1990 discoveries of simple techniques for macroscale generation and isolation of fullerene by Krätschmer *et al.* (1990), Haufler *et al.* (1991) and Taylor *et al.* (1990) made this new material ready for wide areas of applications. The observation of the superconductivity by Hebard *et al.* (1991) at $T_c = 19$ K of potassium-doped C₆₀ crystal further accelerated the research field. Within a few years, macroscale amount of metal containing fullerene [Chai *et al.* (1991), Shinohara *et al.* (1992) and Kikuchi *et al.* (1993)], higher fullerenes [Kikuchi *et al.* (1992) and Achiba & Wakabayashi (1993)] and bucky tube in Figure 1(c) [Iijima (1991) and Ebbesen & Ajayan (1992)] were available.

A common technique of the macroscale generation of fullerene is the arc-discharge method which is simply an arc-discharge of graphite electrodes under certain pressure of helium buffer gas proposed by Haufler *et al.* (1991). The amount of

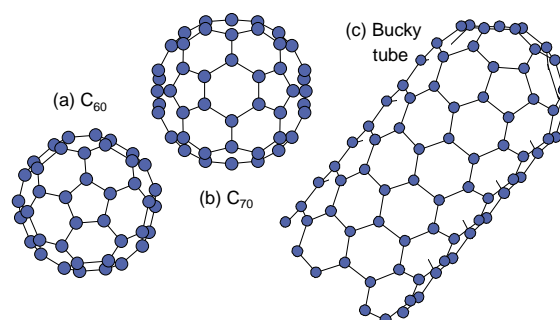


Figure 1 Typical structures of fullerene

extracted fullerene compared to the collected soot can yield up to about 15% under the optimum condition as in Maruyama *et al.* (1994). Usually the generated fullerene consists of 80% of C₆₀, 15% of C₇₀ and a small amount of higher fullerene like C₇₆, C₇₈, C₈₂, C₈₄, ..., quite interesting magic numbers. It is also surprising that once vaporized carbon atoms automatically form such highly symmetric structures like C₆₀ in the clustering process. Besides these theoretical interests, it is required to clarify the generation mechanism in order to find a more efficient generation method of the higher fullerene or the metal doped fullerene.

Since the macroscale generation technique was found accidentally, the formation mechanism of fullerene is not clear. Several models have been proposed based on experimental insights. Haufler *et al.* (1991) described that a growth of a hexagonal network by successive additions of dimers and trimers eventually left pentagons as the defect. They claimed that the pentagons was essential to give the curvature and to decrease the number of dangling bonds. On the other hand, two neighboring pentagons should result too much strain to the network system, so the Isolated Pentagon Rule (IPR) was assumed. It is interesting to

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learn that the smallest fullerene satisfying IPR is C₆₀ and next to the smallest is C₇₀. Quite different precursors of fullerene structure were proposed, such as a piece of graphitic sheet [Robertson *et al.* (1992)] or once grown bucky tube [Dravid *et al.* (1993)]. On the other hand, Heath (1992) proposed a model of clustering sequence from linear chain up to C₁₀, rings in C₁₀-C₂₀ range, fullerene at C₃₀. He explained that successive C₂ additions followed until the satisfaction of IPR. Wakabayashi & Achiba (1992) proposed a special model that fullerene was made of stacking of carbon rings. They could explain magic numbers of higher fullerenes [Kikuchi *et al.* (1992) and Achiba & Wakabayashi (1993)] and isomers of C₇₆, C₈₆ and C₈₄ [Wakabayashi *et al.* (1993)]. Recently, the drift tube ion chromatography experiments of laser vaporized carbon clusters showed the existence of poly-cyclic rings and the possibility of the annealing of such structure to fullerene [Helden *et al.* (1993), Hunter *et al.* (1993), Clemmer *et al.* (1994) and Hunter *et al.* (1994)].

Although each model explains some experimental results, it is difficult to decide which model is more plausible. We have applied a molecular dynamics simulation for the clustering process of carbon atoms in order to speculate the formation mechanism of fullerene from a different point of view.

2 Description of Calculations

We employed the potential function of carbon atoms proposed by Brenner (1990) for his simulation of the chemical vapor deposition of diamond films. This potential could describe variety of small hydrocarbons and graphite and diamond lattices. The basic formulation of the potential was based on the covalent-bonding treatment developed by Tersoff (1986). The total potential energy of the system E_b was expressed as the sum of the bonding energy of each bond between carbon atoms i and j .

$$E_b = \sum_i \sum_{j(i>j)} [V_R(r_{ij}) - B^*_{ij} V_A(r_{ij})], \quad (1)$$

where $V_R(r)$ and $V_A(r)$ were repulsive and attractive force terms, respectively. These terms were expressed by the exponential form with a cut-off function $f(r)$.

$$V_R(r) = f(r) \frac{D_e}{S-1} \exp\{-\beta\sqrt{2S}(r-R_e)\} \quad (2)$$

$$V_A(r) = f(r) \frac{D_e S}{S-1} \exp\{-\beta\sqrt{2/S}(r-R_e)\} \quad (3)$$

$$f(r) = \begin{cases} 1 & (r < R_1) \\ \frac{1}{2} \left(1 + \cos \frac{r-R_1}{R_2-R_1} \pi \right) & (R_1 < r < R_2) \\ 0 & (r > R_2) \end{cases} \quad (4)$$

The effect of the bonding condition of each atom was taken account through B^*_{ij} term which was the function of angle θ_{ijk} between bonds $i-j$ and $i-k$.

$$B^*_{ij} = \frac{B_{ij} + B_{ji}}{2}, B_{ij} = \left(1 + \sum_{k(\neq i,j)} [G_c(\theta_{ijk}) f(r_{ik})] \right)^{-\delta}, \quad (5)$$

where

$$G_c(\theta) = a_0 \left(1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos\theta)^2} \right). \quad (6)$$

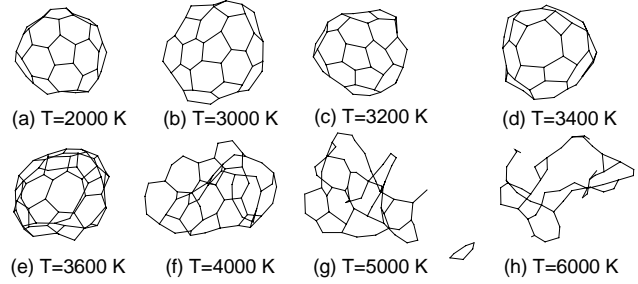


Figure 2 High temperature stability of C₆₀

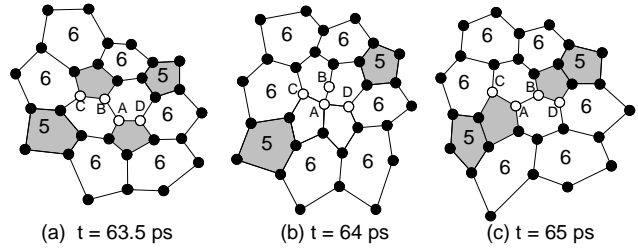


Figure 3 Migration of pentagons observed for $T = 3200$ K

Constants were as follows:

$$\begin{aligned} D_e &= 6.325 \text{ eV} & S &= 1.29 & \beta &= 1.5 \text{ \AA}^{-1} \\ R_e &= 1.315 \text{ \AA} & \delta &= 0.80469 \\ a_0 &= 0.011304 & c_0 &= 19 & d_0 &= 2.5 \\ R_1 &= 1.7 \text{ \AA} & R_2 &= 2.0 \text{ \AA} \end{aligned}$$

Here, we have ignored the term for the compensation of conjugate bonds from original expressions of Brenner (1990).

Verlet method was employed to integrate the classical equation of motion with the time step of 0.5 fs. All calculations were performed in a cubic box with periodic boundary conditions in all 3 directions. When temperature control was enforced, the simple velocity scaling was adopted.

3 High Temperature Stability of C₆₀

In order to determine the characteristics of the potential function when applied to fullerene, we calculated high temperature stability of the structure of C₆₀. Locating 60 carbon atoms at the equilibrium position of truncated icosahedron C₆₀, we gave the vibrational temperature discarding the total translational and rotational energies. With the temperature control at the certain temperature T for initial 15 ps, we calculated the vibration for 100 ps.

Figure 2 summarizes the observed bond-network structure after 100 ps in each temperature. Here, a bond between atoms was defined when two atoms were sitting closer than 1.8 Å. When the temperature was below 3000 K, no change of carbon network was observed within 100 ps [Figure 2(a, b)]. The indication of the deformation of the network structure was observed at $T = 3200$ K. Here, the isomerization of C₆₀ by migrations of pentagons was demonstrated as shown in Figure 3. Until 63.5 ps the structure was perfect C₆₀ with isolated pentagons [Figure 3(a)]. During 63.5 ps to 64 ps, a bond B-C was broken and A-C was formed leaving atom B very unstable position [Figure 3(b)]. Then, at $t = 65$ ps, atom B chose atom D as the new bonding partner [Figure

3(c)]. The whole process can be regarded as a twist of bond A-B and a consequent migration of two pentagons. It's not certain whether this isomerization occurs in practice, however, such a freedom of transformation should be essential for the annealing process of an imperfect fullerene. At $T = 3400$ K the previous transformation occurred one after another, and some heptagons appeared. At $T = 4000$ K, the cage was open as shown in Figure 2(f), and at $T = 6000$ K the dissociation of a part of the cluster was observed. Unfortunately we could not simulate the C_2 loss dissociation observed by O'Brien *et al.* (1988) and Maruyama *et al.* (1991) under a strong laser irradiation.

4 Formation of Fullerene Structure

4.1 Assembly of Fullerene from Random Atoms

The most interesting point of the formation mechanism of fullerene is how such a hollow caged structure can be self-assembled. We first tried the possibility of constructing the caged structure by using the carbon atom potential. As seen in the last section, C_{60} is extraordinarily stable at high temperature, though 3000 K might be an over-estimation since a tiny error in the atomic potential may be amplified in the view of the vibrational temperature. We supposed that this stability at high temperature was the key of the selection of the fullerene structure rather than graphite or diamond lattices.

Locating 200 carbon atoms at random positions in a 80 \AA cubic box with the full periodic boundary condition, we controlled the system temperature at 3000 K for every 0.25 ps. Several snapshots of the simulation are shown in Figure 4. At about 120 ps [Figure 4(a)], most of clusters were smaller than C_3 but several linear chain clusters as large as C_9 were observed. Then, at about 180 ps [Figure 4(b)], some of clusters grew to rings or chains with about 12 atoms and a fragment of flat network with about 30 atoms. Finally at 400 ps [Figure 4(c)], two large clusters of almost closed caged structure were observed. Figure 4(d) shows an enlarged view of the largest cluster (70 carbon atoms). This hollow structure can be regarded as an imperfect fullerene basically made of pentagons and hexagons, though there are 8-membered rings and a small hole. Picking up this cluster with 70 atoms, we continued the simulation more 150 ps after this stage. However, it was not clear whether this cluster was annealing toward the perfect fullerene structure or not.

The time history of the bonding characteristics is compared with the snapshots in Figure 4. Here, we counted the number of bonds N_B (a bond was defined when two atoms were closer than 1.8 \AA). We also plotted the number of carbon atoms N_{N_x} having a coordination number x . Hence, N_{N_0} represents the number of isolated atoms and N_{N_3} the atoms with sp^2 bondings. The number of isolated atoms N_{N_0} decreased monotonously whereas N_B and N_{N_3} increased monotonously. On the other hand, N_{N_1} and N_{N_2} had the maxima at certain time. Atoms contributing N_{N_1} and N_{N_2} were atoms at the ends of chains and atoms inside of chains or rings, respectively.

4.2 Precursors in the Reaction Process

Figure 5 shows the outline of the clustering process yielding the imperfect fullerene C_{70} shown in Figure 4(d). One of the major pieces was irregular three dimensional cluster C_{43} which had grown rather irregularly by additions of small clusters into the irregular poly-cyclic ring C_{26} . This irregular feature was almost kept after growing to C_{70} . Another piece was the fragment of flat network C_{25} which had been regularly grown by successive

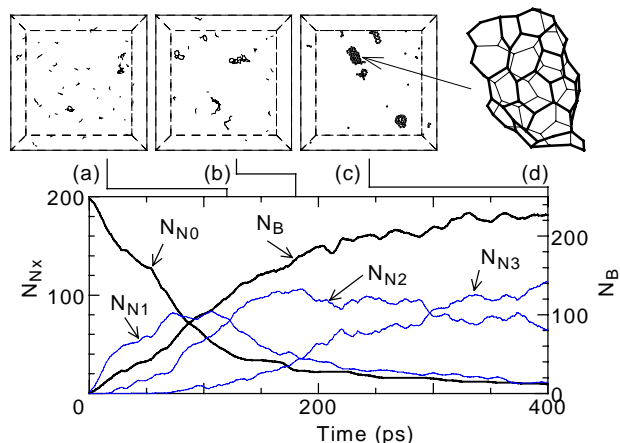


Figure 4 Assemble of fullerene structure from randomly distributed 200 carbon atoms

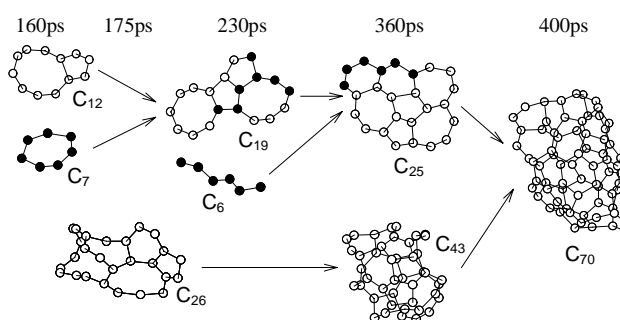


Figure 5 Clustering process yielding to the imperfect fullerene

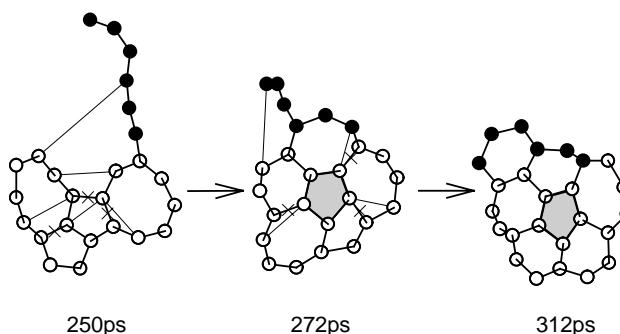


Figure 6 Chain wrapping transformation

additions of a poly-cyclic ring C_{12} , a mono-cyclic ring C_7 and a linear chain C_6 . Seven solid atoms in C_{19} represent atoms originally from the C_7 ring structure. It should be noticed that no original ring structure was kept after the merge of C_7 and C_{12} . On the other hand, 6 solid atoms in C_{25} cluster originally from C_6 linear chain kept the original bondings, suggesting a rather organized process of the addition.

The details of this organized process are shown in Figure 6. The C_{19} poly-cyclic cluster captured the C_6 chain and the chain wrapped the poly-cyclic cluster to add two hexagons. However, there were considerable number of bond alternations during this process. The thin lines in Figure 6 mark the newly forming bonds and the crosses mark breaking bonds. Anyway, it is clear that a chain cluster is a very convenient source of the organized growth of a network structure. This process is quite similar to the part of

the model proposed by Hunter *et al.* (1994). The key precursor in their model consisted of two hexagons and a long chain whose each end was connected to each hexagons. They proposed that the chain would spirally wrap the fragment until completely closed to the fullerene. Though our chain is short and one end is open, this similarity is remarkable.

4.3 Artificial Precursors

Learning the chain-wrapping transformation in Figure 6, we speculated that this might be the key mechanism of the network growth. Then, we tried a simulation which could enhance this feature. We prepared a seed fragment made of 2 hexagons [see top left C_{10} in Figure 7] and five C_{10} linear chains as the initial condition. This configuration of the fragment C_{10} is the same as the initial cup precursor used in the ring-stacking model by Wakabayashi & Achiba (1992). Keeping the temperature at 3000 K, the same simulation as the case of the random initial position was performed. Observed clustering process outlined in Figure 7 shows that the final structure of C_{60} was the flat graphitic sheet. The growth of the network fragment was systematic and organized as seen in Figure 7. Chains or small rings worked as nice feed stocks of the network growth. However, we should notice that the initial configuration of the C_{10} was completely lost when it was grown to C_{30} . The solid atoms in Figure 7 represent 10 atoms initially located as the precursor C_{10} . Probably this result implies that the systematic organized growth of the network fragment is not a good choice to formulate a fullerene.

4.4 Thinner System

In order to reduce the computational time, the density of initial carbon atoms used in the previous calculations was a few orders larger than the practical condition of the experimental fullerene generation. The largest discrepancy from the physical phenomena such as the arc-discharge generation is in the collisional frequency. With such a simulation of compressed time scale, it is expected that small clusters collided each other before they were fully annealed. So, we tried about 30 times thinner density system with 100 carbon atoms in a 200 Å cubic box. As a result, the clustering process shown in Figure 8 was obtained. Clustering process was very systematic and yielded the graphitic sheet structure. Again the organized growth of the network fragment did not yield the fullerene structure. This result raises a serious question about the previous seemingly successful formation of the imperfect fullerene.

5 Conclusions

A molecular dynamics simulation of the clustering process starting from randomly located carbon atoms yielded the imperfect fullerene at certain temperature and density conditions. The simplified potential function of the carbon atoms and the unrealistic density for the sake of the computational limitations, make it difficult to compare the calculational condition with the actual physical phenomena. However, since we could calculate the some imperfect fullerene structures from the completely random configuration, we could imagine that the self assembly of carbon atoms might be calculated by simulations. Though some of the transformations observed in the simulations were remarkably similar to a proposed model by Hunter *et al.* (1994), we could not verify the validity of our simulation at this stage.

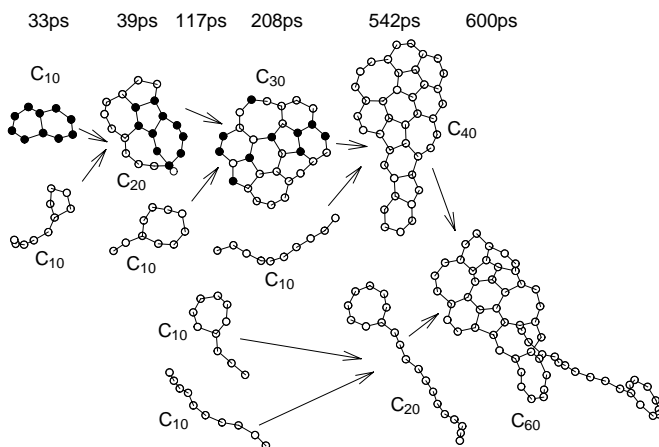


Figure 7 Simulation from artificial precursors

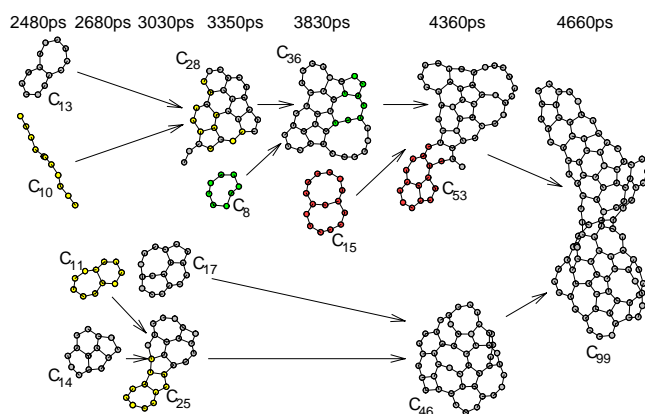


Figure 8 Clustering process observed for thinner density system

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