

分子動力学法による金属内包フラレン生成シミュレーション

Molecular Dynamics Simulations of the Formation of Metal-Containing Fullerene

東京大学大学院 工学系研究科 機械工学専攻 山口康隆, 丸山茂夫

Yasutaka YAMAGUCHI and Shigeo MARUYAMA, Dept. of Mech. Eng., The University of Tokyo

Abstract. The growth process of metallofullerene was studied by using the molecular dynamics method. Based on DFT (density functional theory) calculations of various forms of small clusters MC_n and M_n ($M = La, Sc, Ni$), multi-body classical potential functions for M-C and M-M interactions were constructed with the Morse-type term and the Coulomb term as functions of coordinate number of a metal atom. The clustering process starting from 500 isolated carbon atoms and 5 metal atoms was simulated under the controlled temperature condition at $T_c = 3000$ K. When La atoms were applied, the stable open-cap structure surrounding the La atom resulted in the lanthanum-containing caged cluster. For Sc-C system, the host carbon clusters were not affected so much as the La-C case due to the weaker Coulomb interaction, and the Sc atom was encapsulated in the host cage at the final stage of the growth process. For Ni-C system, the precursor clusters were also similar to those in Sc-C system, although the Ni atom finally stayed on a face of large ring of the caged structure.

1 Introduction

After the discovery of C_{60} by Kroto *et al.* [1], macroscopic amount of empty fullerene[2,3], metallofullerenes [4-7], higher fullerenes [8] and carbon nanotubes [9] were successively produced and isolated. Recently, the high quality generation of single-wall nanotubes (SWNTs) [10,11] has demonstrated new possibilities of applications of this material. Although fullerene is now recognized as an attractive new material, the formation mechanism of these symmetric hollow caged structures is still unknown, because the generation techniques of fullerene [2,3] were discovered almost accidentally.

We have performed molecular dynamics simulations of the clustering process of carbon atoms to investigate the fullerene formation mechanism [12,13], and the temperature dependence of the cluster structures was observed [12]. In addition, we have demonstrated the formation of perfect C_{60} structure by giving sufficient collision-free annealing time, and examined the time and temperature scale of the annealing process through the reaction rate of the network transformations. Based on these results, a new formation model of empty fullerene including the temperature effect was proposed [13].

In this paper, the formation process of metallofullerene was studied using the similar molecular dynamics simulations. In spite of possible interesting applications of metallofullerene, it is still difficult to obtain macroscopic amount of sample because of extremely low yield of generation. In order to find the optimum generation condition, it is inevitable to understand the formation mechanism. According to experimental studies, the metal atoms such as La, Y, Sc, (Ca) and lanthanides can be enclosed inside the carbon cage, and the preferred carbon cage structure depends on the metal. On the other hand, Ni, Co, or Fe, which are not experimentally assigned to be encapsulated in the fullerene cage, are required to generate the SWNTs [10,11]. Here, the effects of these metal atoms on the carbon cluster growth

process are still unknown. In this paper, The difference of the growth processes among La, Sc and Ni containing systems were studied to investigate the effect of metal atoms.

2 Method

The potential function among carbon atoms was the same as our previous reports [12-14]. For the purpose of modeling the metal-carbon and metal-metal potential function appropriate for the MD simulation, the binding energy and charge state of various forms of small clusters MC_n and M_n ($M: La, Sc, Ni$) were calculated. Here the density functional theory based on the Becke's three-parameter exchange functional [15] with the Lee-Yang-Parr correlation [16] (B3LYP) was applied with the effective core potentials derived from the LANL2DZ basis from Gaussian 94 [17]. The semi-empirical calculation results [18] were also used for the Ni-Ni interaction.

Metal-carbon multi-body potential functions were constructed as functions of carbon coordinate number of a metal atom. The total potential energy was expressed as the sum of binding energy E_b as follows.

$$E_b = V_R + V_A + V_C \quad (1)$$

$$V_R = f(r_{ij}) \frac{D_e}{S-1} \exp\left\{-b\sqrt{2S}(r_{ij} - R_e)\right\} \quad (2)$$

$$V_A = -f(r_{ij}) \cdot B^* \frac{D_e S}{S-1} \exp\left\{-b\sqrt{2/S}(r_{ij} - R_e)\right\} \quad (3)$$

$$V_C = -f(r_{ij}) \frac{e^2}{4\pi\epsilon_0} \frac{c_C c_M}{r_{ij}} \quad (4)$$

Here, r_{ij} , V_R and V_A denote the distance between metal i and carbon j , Morse-type repulsive and attractive terms, respectively. The Coulomb term V_C is applied only to the La-C and Sc-C interactions that were calculated to be strongly

Table 1. Potential parameters for metal-carbon interactions.

	D_e (eV)	S	b (1/Å)	R_e (Å)	R_1 (Å)	R_2 (Å)	b	d	k_1	k_2
La-C	4.53	1.3	1.5	2.08	3.2	3.5	0.0854	-0.8	0.0469	1.032
Sc-C	3.82	1.3	1.7	1.80	2.7	3.0	0.0936	-0.8	0.0300	1.020
Ni-C	3.02	1.3	1.8	1.70	2.7	3.0	0.0330	-0.8	-	-

Table 2. Potential parameters for metal-metal interactions.

	S	b (1/Å)	D_{e1} (eV)	D_{e2} (eV)	C_D	R_{e1} (Å)	R_{e2} (Å)	C_R	R_1 (Å)	R_2 (Å)
La-La	1.3	1.05	0.740	2.64	0.570	3.735	0.777	0.459	4.0	4.5
Sc-Sc	1.3	1.4	0.645	1.77	0.534	3.251	0.919	0.620	3.5	4.0
Ni-Ni	1.3	1.55	0.74	1.423	0.365	2.520	0.304	0.200	2.7	3.2

ionic due to the electron transfer from the metal to carbon atoms.

The coordinate number of the metal atom N^C is defined using the cut-off function $f(r)$, and both the additional term B^*_{ij} and electric charge c are expressed as functions of the coordinate number. Here, the effect of the angle among bonds is ignored.

$$f(r) = \begin{cases} 1 & (r < R_1) \\ \left(1 + \cos \frac{r - R_1}{R_2 - R_1}\right) / 2 & (R_1 < r < R_2) \\ 0 & (r > R_2) \end{cases} \quad (5)$$

$$N^C = 1 + \sum_{\text{carbon } k (\neq j)} f(r_{ik}) \quad (6)$$

$$B^* = \{1 + b(N^C - 1)\}^d \quad (7)$$

$$c_M = 3 - \exp(-k_1 N^C + k_2), \quad c_C = c_M / N^C \quad (8)$$

The potential parameters are shown in Table 1, and the total potential E_b and Coulomb term V_C of La, Sc and Ni for $N^C=5$ and $N^C=15$ are demonstrated in Fig. 1. The Coulomb interaction of La-C is much stronger than that for Sc-C.

Metal-metal interactions were constructed in the same formula as in eq. (1). In this case, the equilibrium binding energy D_e and the bond length R_e are expressed as direct functions of the metal coordinate number N_{ij} instead of using the additional term B^* in eq. (3).

$$N^M_i = 1 + \sum_{\text{metal } k (\neq j)} f(r_{ik}), \quad N_{ij} = (N^M_i + N^M_j) / 2 \quad (9)$$

$$D_e(N_{ij}) = D_{e1} + D_{e2} \exp\{-C_D(N_{ij} - 1)\} \quad (10)$$

$$R_e(N_{ij}) = R_{e1} - R_{e2} \exp\{-C_R(N_{ij} - 1)\} \quad (11)$$

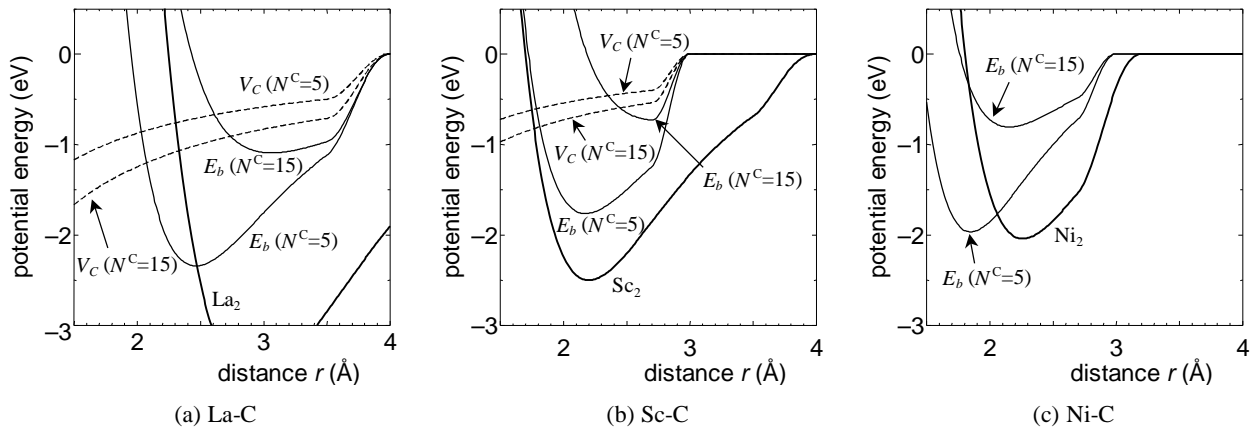
Thus, the Coulomb term V_C always gives repulsive force. The potential parameters are shown in Table 2, and the shapes for dimers are shown in Fig. 1.

The temperature control method is also the same as our previous report [12], where the translational, rotational and vibrational temperatures of the system were independently controlled every 0.1 ps by simple velocity scaling so that the difference between the control temperature T_c and each temperature was reduced to 60 %. Verlet's method was adopted to integrate the differential equation of motion.

3 Results and Discussions

3.1 Lanthanum containing system

Five hundred carbon atoms and 5 La atoms in gas phase with random positions and velocities were distributed in a 342 Å cubic box with full periodic boundary condition. The system was controlled toward a control temperature T_c of 3000 K. These parameters correspond to the condition in which C_{60} and C_{70} caged clusters were obtained in the simulation without including metal atoms [12].


Fig. 1. Metal-carbon potential function E_b , Coulomb term V_C and potential function of M_2 for: (a) La-C, (b) Sc-C and (c) Ni-C.

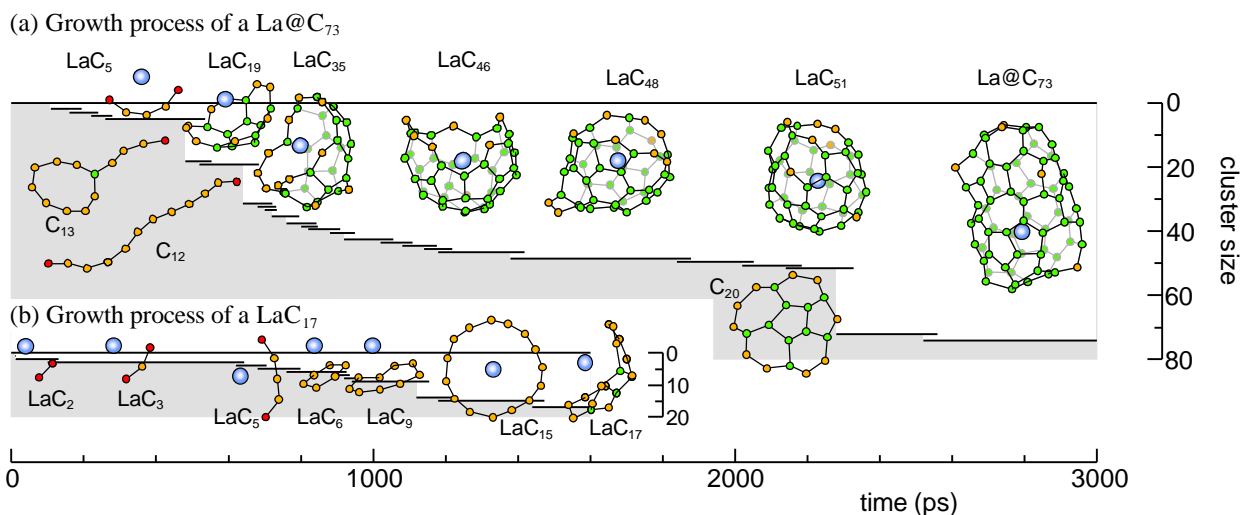


Fig. 2. Growth process of La attached clusters: (a) La@C_{73} and (b) La@C_{17} .

Fig. 2 shows the growth process of typical La attached clusters in the simulation; (a) a La containing caged cluster La@C_{73} observed at $t = 3000$ ps, and (b) a La attached cluster LaC_{17} observed at $t = 1600$ ps. The vertical width and horizontal length denote the cluster size and time, respectively. For example, in Fig. 2(a), the LaC_5 and C_{13} cluster independently existed each other, coalesced at about 530 ps, and the LaC_{19} was formed after the addition of a carbon atom at about 550 ps.

When the cluster was smaller than LaC_5 , short carbon chains surrounded the lanthanum atom (fan-type structure [19,20]) as shown in Fig. 2(b). When it grew larger than LaC_6 , the lanthanum atom attached on the monocyclic carbon ring, and positioned in the center of the monocyclic ring at LaC_{15} . The host monocyclic ring changed to a polycyclic ring and the lanthanum atom attached on it around LaC_{17} , where the Coulomb attractive force induced curvature to the host poly-cyclic ring. The host annealed to a curved graphitic sheet when it grew as large as LaC_{19} as shown in Fig. 2(a), and extended the structure until about LaC_{35} , resulted in the formation of a stable open-cap structure. The cluster grew larger with closing the open-cap structure, however, the number of carbon atoms was not enough to close the open-cap at about LaC_{50} . In this case, a collision with a large cluster of C_{20} prevented gradual growth and resulted in the formation of a caged cluster larger than La@C_{71} , and the La atom was almost encapsulated in the carbon cage.

Considering the difference of time and temperature scale between the real phenomena and simulation [13], these hollow caged structures could have sufficient collision free annealing interval to form more sophisticated structures.

Fig. 3 shows the collision process of other two La attached clusters. In this case, two lanthanum atoms could not attach on the same face of the flat structure during the coalescence process due to the Coulomb repulsion, and that resulted in the encapsulation of only one La atom.

3.2 Scandium containing system

Another clustering process using Sc atoms was simulated under the same condition as the previous section. Fig. 4

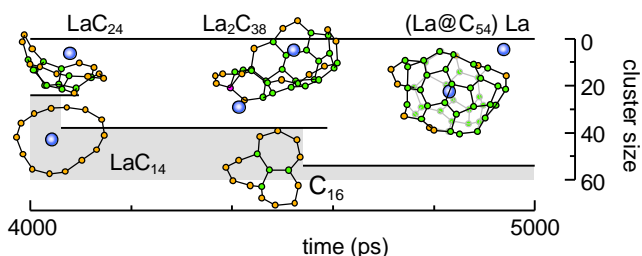


Fig. 3. Collision of La attached clusters.

shows the growth process of a ScC_{55} observed at $t = 4000$ ps. A first remarkable difference of the process from La-C system is apparent for the structures of MC_n ($20 < n < 40$) because of the weaker Coulomb force. The cluster annealed to the 3-dimensional open cage structure around ScC_{43} , where the scandium atom moved around open edge. The Sc atom slipped into the caged structure just before closing at around Sc@C_{54} .

In addition to this final stage of encapsulation, the flat structures around ScC_{35} maybe related to the possibility of catching another Sc atom, which is in good agreement with experimentally observed prominence of di-metallofullerene for Sc-C system.

3.3 Nickel containing system

Nickel atom, which is not experimentally assigned to be encapsulated in the fullerene cage so far, is also examined. As shown in Fig. 5, the growth process is very similar to that for Sc attached cluster. However, at the final stage, the Ni atom preferred to attach at the large defect of the caged structure such as large rings of more than 7 or 8 membered rings, and frequently moved in and out of the carbon cage. Fig. 6 shows the similar motion also observed for the larger caged cluster of NiC_{78} obtained for another Ni atom.

Moreover, when two Ni atoms were enclosed in the host cage as shown in Fig. 6 (b), the Ni atoms remained inside the cage more stably than the case of single Ni atom, and that can be a hint of a new endohedral metallofullerene.

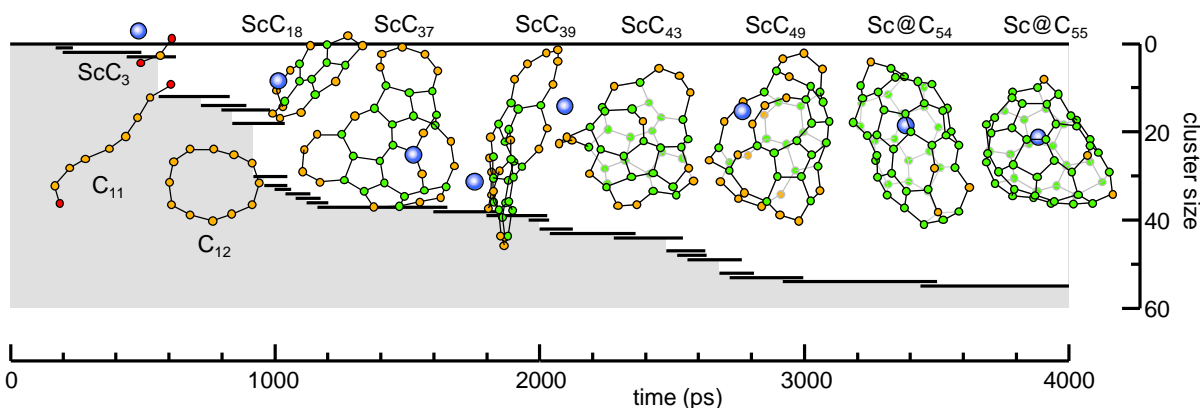


Fig. 4. Growth process of a Sc attached cluster Sc@C₅₅.

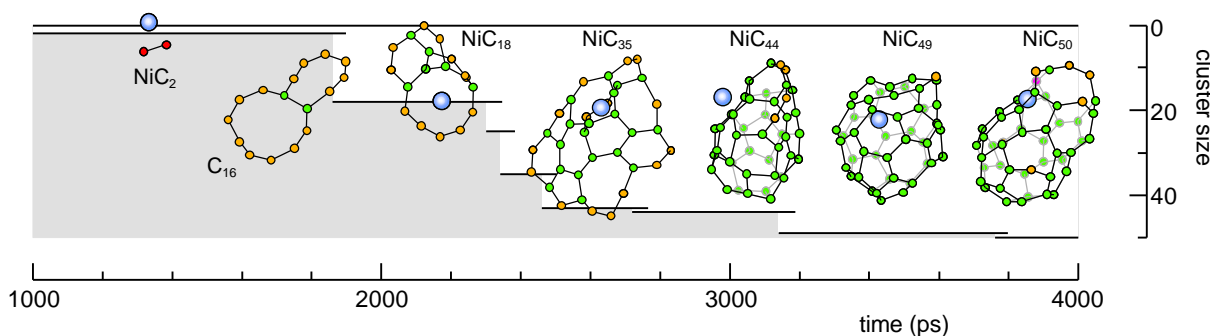


Fig. 5. Growth process of a Ni attached cluster NiC₅₀.

4 Conclusions

Multi-body potential functions of metal-carbon and metal-metal system were constructed based on the MO calculations of small MC_n and M_n (M: La, Sc, Ni) using the density functional theory. By applying the potential function to the molecular dynamics simulation, the clustering processes starting from randomly distributed carbon and metal atoms were simulated and the formation process of metal attached caged carbon clusters were examined. When La atoms were applied, the stable open-cap structure surrounding the La atom resulted in the lanthanum-containing caged cluster. For Sc-C system, the Sc atom was encapsulated in the host cage at the final stage of the growth process. For Ni-C system, the Ni atom finally stayed on a face of large ring of the caged structure.

Acknowledgements

This work was supported by Grant-in-Aid for JSPS Fellows (No. 08004746) and Grant-in-Aid for Scientific Research (No. 09450085) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. H. W. Kroto, *et al.*, *Nature* **318**, 162 (1985).
2. W. Krätschmer, *et al.*, *Nature* **347**, 354 (1990).
3. R. E. Haufler, *et al.*, *Proc. Mat. Res. Soc. Symp.* **206**, 627 (1991).

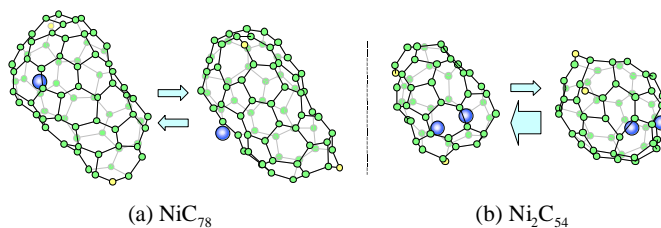


Fig. 6. Structures of Ni attached cage clusters: (a) NiC₇₈ and (b) Ni₂C₅₄.

4. Y. Chai, *et al.*, *J. Phys. Chem.* **95**, 7564 (1991).
5. H. Shinohara, *et al.*, *J. Phys. Chem.* **96**, 3571 (1992).
6. K. Kikuchi, *et al.*, *Chem. Phys. Lett.* **216**, 23 (1993).
7. M. Takata, *et al.*, *Nature* **377**, 46 (1995).
8. K. Kikuchi, *et al.*, *Chem. Phys. Lett.* **188**, 177 (1992).
9. S. Iijima, *Nature* **354**, 56 (1991).
10. S. Iijima, T. Ichihara, *Nature* **363**, 603 (1993).
11. A. Thess, *et al.*, *Science* **273**, 483 (1996).
12. Y. Yamaguchi, S. Maruyama, *Chem. Phys. Lett.* **286**, 336 (1998).
13. S. Maruyama, Y. Yamaguchi, *Chem. Phys. Lett.* **286**, 343 (1998).
14. D. W. Brenner, *Phys. Rev. B* **42**, 9458 (1990).
15. A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
16. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
17. M. J. Frisch, *et al.*, *Gaussian 94 Revision E.1*, (Gaussian, Inc., Pittsburgh PA, 1995).
18. E. Curotto, *et al.*, *J. Chem. Phys.* **108**, 729 (1998).
19. A. Ayuela, *et al.*, *Z. Phys. D* **41**, 69 (1997).
20. D. L. Strout, B. M. Hall, *J. Phys. Chem.* **100**, 18007 (1996).

連絡先 :

〒113-8656 東京都文京区本郷 7-3-1
 東京大学大学院 工学系研究科 機械工学専攻 丸山茂夫
 TEL: 03-3812-2111 (内線 7697) FAX: 03-5800-6823
 E-Mail: maruyama@photon.t.u-tokyo.ac.jp