Transformation of Amorphous Carbon Clusters to Fullerenes
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Supporting Information

ABSTRACT: Transformation of amorphous carbon clusters into fullerenes under high temperature is studied using molecular dynamics simulations at microsecond times. On the basis of the analysis of both the structure and energy of the system, it is found that fullerene formation occurs in two stages. First, fast transformation of the initial amorphous structure into a hollow sp^2 shell with a few chains attached occurs with a considerable decrease of the potential energy and the number of atoms belonging to chains and to the amorphous domain. Then insertion of the remaining carbon chains into the sp^2 network takes place at the same time as the fullerene shell formation. Two types of defects remaining after the formation of the fullerene shell are revealed: seven-membered rings and single one-coordinated atoms. One of the fullerene structures obtained contains no defects at all, which demonstrates that defect-free carbon cages can be occasionally formed from amorphous precursors directly without defect healing. No structural changes are observed after the fullerene formation, suggesting that defect healing is a slow process in comparison with the fullerene shell formation. The schemes of the performed reactions of chain atom insertion into the fullerene shell just before its completion are presented. The results of the performed simulations are summarized within the paradigm of fullerene formation due to self-organization of the carbon system.

INTRODUCTION

Despite the fact that fullerenes have been known for almost 30 years, the detailed atomic mechanism of fullerene formation still remains a debated topic (see refs 1 and 2 for reviews). The most credible speculation is that the fullerene formation occurs as a spontaneous self-organization of the carbon system as the structural order arises through many local atomic structure changes induced by thermodynamic fluctuations without any certain thermodynamically stable intermediate structures. The detailed arguments which support this hypothesis are adduced in refs 1 and 2 along with the variety of initial systems for which detailed arguments which support this hypothesis are adduced. The transformation of amorphous carbon to an endohedral metallofullerene inside a carbon nanotube have been observed.

As for the stability of fullerenes, calculations based on the density functional theory and second-order Möller–Plesset perturbation method show that the fullerene is the ground state for carbon systems which consist of more than 20 atoms. Theoretical considerations predict the upper limit of the thermodynamic phase stability of fullerenes or multishell fullerenes (carbon onions) to be about 1000 atoms. Thus, fullerene formation should take place with a decrease of the potential energy regardless of the initial structure of the carbon system or the source of energy for bond rearrangement (heat treatment or electron or ion irradiation).

Since the experimental observation of individual bond rearrangement reactions for the chaotic environment of fullerene formation is hardly possible, the methods of atomistic modeling can be helpful. A set of works are devoted to molecular dynamics (MD) simulations of fullerene formation starting from carbon vapor, short carbon nanotubes, a graphene flake, and a small nanodiamond cluster. The simulation of processes similar to the fullerene formation, such as the transformation of amorphous carbon and nanodiamonds to multishell carbon nanoparticles (onions) and graphitization of nanodiamonds of several nanometers in size, should also be mentioned. Here we consider yet...
another possible initial carbon structure which can be used for fullerene synthesis. Namely, the MD simulations performed on the basis of the reactive empirical potential show the transformation of an amorphous carbon cluster into a fullerene under heat treatment. Thus, fullerene formation is possible as self-organization of any pure carbon system with an appropriate number of atoms. This fact supports the paradigm of fullerene formation as a result of self-organization.\textsuperscript{52} The structural characteristics and energetics of the system during the transformation have been analyzed and have allowed the conclusion that the transformation process takes place in two stages.

The paradigm of self-organization explains the high yield of abundant isomers of fullerenes (such as C\textsubscript{60} with icosahedral symmetry) by reactions which occur after the fullerene shell formation: emission of C\textsubscript{2} molecules,\textsuperscript{1,2,26,37−39} insertion of C\textsubscript{2} molecules,\textsuperscript{1,26,57−59} and, possibly, Stone–Wales (SW) reactions of bond rearrangement.\textsuperscript{1,40−44} By now, SW reactions\textsuperscript{29,41,45,46} and reactions of insertion of C\textsubscript{2} molecules\textsuperscript{50,47,48} that take place after the shell formation and finally lead to selection of abundant isomers have been carefully investigated. The SW reactions that can lead to defect healing have also been considered.\textsuperscript{29,44,49,50} However, little attention has been paid so far to the contribution of such reactions to the preceding process of shell formation. Up to now, only collapse of large rings giving rise to five-, six-, and seven-membered rings during the fullerene formation in carbon vapor\textsuperscript{23,22,23,77,28} and insertion of five-coordinated atoms attached at the inner surface of the forming sp\textsuperscript{2} shell in the transformation of a small nanodiamond cluster to a fullerene\textsuperscript{51} have been discussed for the last stage of fullerene shell formation. The extensive studies of reactions at the last stage of shell formation are necessary to elucidate the detailed atomic mechanism of fullerene formation and thus to explain the high yield of abundant isomers of fullerenes. Here the schemes of insertion of atoms belonging to carbon chains attached at the outer surface of the forming sp\textsuperscript{2} shell into the hollow sp\textsuperscript{2} network that happens just before the end of the fullerene formation are presented. The types of defects remaining after the fullerene shell formation are also considered.

\section*{COMPUTATIONAL DETAILS}

To study the transformation of amorphous carbon clusters into fullerenes under heat treatment, we have performed reactive MD simulations using the first-generation bond-order Brenner potential\textsuperscript{51} (Brenner I) modified to reproduce graphene edge energies.\textsuperscript{52} While a newer and more sophisticated second-generation Brenner potential\textsuperscript{53} (Brenner II) is currently available, both of the original Brenner potentials are fitted to the experimental data on equilibrium distances, binding energies, and stretching force constants of small hydrocarbons, graphite, and diamond, which means they do not necessarily perform well for carbon nanostructures. With the intention of providing the potential suitable for such condensed carbon phases, the training set of the ReaxFF\textsuperscript{24} force field, originally fitted to the quantum chemistry data on the energetics and reactions of hydrocarbons,\textsuperscript{54} has been recently supplemented by the results of density functional theory (DFT) calculations on equations of state for diamond and graphite, formation energies of defects in graphene, and heats of formation of amorphous carbon clusters.\textsuperscript{55} To choose the adequate potential for our simulations, we have tested these potentials with respect to the quantities relevant for the transformation of an amorphous carbon cluster into a fullerene. In such a process, the energy difference between the initial and final structures, i.e., the driving force, depends on the relation between the energy cost of undercoordinated (e.g., two-coordinated) carbon atoms compared to the three-coordinated ones and the penalty in the elastic energy coming from formation of the fullerene shell. Therefore, it is highly important that the interatomic potential employed is able to describe properly such characteristics as the elastic energy of fullerenes and graphene edge energies.

To compare the performance of different versions of the Brenner potential and the recent C-2013 version of ReaxFF, we have calculated elastic energies of C\textsubscript{60} and C\textsubscript{70} fullerenes, i.e., the energy per atom relative to that in graphene, and graphene edge energies. Armchair, zigzag, and reconstructed zigzag edges are considered, where the latter is obtained from the zigzag edge by transformation of all hexagon pairs at the edge into pairs of heptagons and pentagons.\textsuperscript{57−60} The edge energies per unit edge length are found through calculations for wide graphene ribbons (of more than 4 nm width) with periodic boundary conditions along the ribbon axis as \( E_{\text{edge}} = \frac{1}{L_{\text{edge}}} \sum_{\text{atoms}} E_{\text{atom}} \), where \( L_{\text{edge}} \) is the ribbon energy, \( N_{\text{ribbon}} \) is the number of atoms in the ribbon per unit cell, \( \epsilon_{\text{p}} \) is the energy of bulk graphene per atom, and \( L_{\text{edge}} \) is the total length edge per unit cell. As seen from comparison with the results of spin-polarized DFT calculations in the local density approximation (LDA)\textsuperscript{61} and in the generalized gradient approximation with the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{62} (see Table 1; a more detailed review on DFT calculations of graphene edge energies is available in ref 63), the first-generation Brenner potential describes the characteristics of interest much better than the second-generation Brenner potential, which fails even to describe the correct order of graphene edge energies. ReaxFF is rather accurate in the elastic energies of the fullerenes but also erroneously assigns the lowest energy to the unreconstructed zigzag edge. Setting the parameter \( F(1,2,2) = -0.063 \) in the first-generation Brenner potential (for the second set of parameters from ref 51), as proposed in our previous paper,\textsuperscript{52} further improves the values of the graphene edge energies. Therefore, the modified first-generation Brenner potential able to describe the elastic energies and energies of under-

<table>
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<th>method</th>
<th>( E_{\text{ZZ}(57)} )</th>
<th>( E_{\text{AC}} )</th>
<th>( E_{\text{EZ}} )</th>
<th>( E_{\text{C60}} )</th>
<th>( E_{\text{C70}} )</th>
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<tr>
<td>original Brenner I \textsuperscript{(ref 51)}</td>
<td>0.937</td>
<td>1.000</td>
<td>1.035</td>
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<td>1.247</td>
<td>1.494</td>
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<td>0.34</td>
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<tr>
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<td>1.091</td>
<td>1.041</td>
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<td>0.49</td>
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<tr>
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<td>1.110</td>
<td>1.207</td>
<td>1.089</td>
<td>0.37</td>
<td>0.33</td>
</tr>
<tr>
<td>DFT (LDA) \textsuperscript{(ref 57)}</td>
<td>1.147\textsuperscript{a}</td>
<td>1.09\textsuperscript{b}</td>
<td>1.202\textsuperscript{a}</td>
<td>1.10\textsuperscript{b}</td>
<td>1.391\textsuperscript{a}</td>
</tr>
<tr>
<td>DFT (PBE) \textsuperscript{(ref 58)}</td>
<td>0.98\textsuperscript{c}</td>
<td>1.02\textsuperscript{c}</td>
<td>1.15\textsuperscript{c}</td>
<td>0.36\textsuperscript{d}</td>
<td>0.32\textsuperscript{e}</td>
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\textsuperscript{a}Reference 57. \textsuperscript{b}Reference 58. \textsuperscript{c}Reference 59. \textsuperscript{d}Reference 60. \textsuperscript{e}Reference 52.
coordinated atoms at the same level of accuracy seems to be the optimal choice for simulations of transformations of carbon clusters.

The adequacy of the modified first-generation Brenner potential used in the present paper has already been checked by simulations of the transformation of graphene flakes with nickel clusters attached to nickel heterofullerenes under electron irradiation. The potential was also previously applied for modeling of carbon nanotube cutting catalyzed by nickel under electron irradiation, showing the qualitative agreement of structure evolution with the experimental observations and correctly predicting the key stages of the cutting.

MD simulations have been carried out using the in-house MD-kMC (Molecular Dynamics–Kinetic Monte Carlo) code. The periodic boundary conditions are applied to the simulation cell of 20 nm × 20 nm × 20 nm size with a single amorphous cluster. The procedure for generation of the initial structures of amorphous carbon clusters is described in the Supporting Information. The velocity Verlet integration algorithm is used, and the integration time step is 0.6 fs. The temperature is maintained at T = 2500 K by the Berendsen thermostat with a relaxation time of 0.3 ps. Since the Berendsen thermostat can transfer the kinetic energy from the internal degrees of freedom to the global motion and rotation of the cluster, the linear and angular momenta of the system are set to 0 every 0.3 ps.

Thermodynamic fluctuations have a considerable influence on nonequilibrium processes in nanoscale systems that can lead to different behaviors for similar starting conditions. For example, MD simulations show that different metal–carbon nano-objects form from a graphene flake with a metal cluster attached under electron irradiation or from a metal cluster surrounded by amorphous carbon under both heating and electron irradiation starting from the same initial structure. Only a minor part of the MD simulation runs starting from carbon vapor at certain conditions lead to fullerene formation. Thus, at least several tens of simulation runs are necessary to obtain statistically significant results for the nonequilibrium behavior of a nanoscale system. In total, we have performed 47 MD simulation runs of about 1 μs duration for slightly different initial structures of amorphous carbon clusters with an even number of atoms ranging from C₆₈ to C₇₄ and 25 MD simulation runs of about 400 ns duration for the same initial structure of amorphous carbon cluster C₆₀.

To describe the evolution of the system structure during the simulation runs, we use the following definitions. We define a fullerene as a hollow closed carbon shell with the sp² structure without any carbon chains attached to the shell at one or both ends. Chains are defined as two or more connected two-coordinated and one-coordinated atoms. We assume that the fullerene shell may contain defects of the atomic structure such as single one-coordinated carbon atoms and rings not only of five or six atoms but also of seven atoms (hereafter referred to as 5-rings, 6-rings, and 7-rings, respectively). To identify chains and rings, the topology of the carbon bond network is analyzed on the basis of the "shortest path" algorithm. Two carbon atoms are considered as bonded if the distance between them does not exceed 1.8 Å.

The following set of parameters is monitored in time to study the details of the transformation process: the potential energy of the system per atom, E, the numbers of 5-rings, N₅, 6-rings, N₆, 7-rings, N₇, and other rings (3-, 4-, 8-, or 9-rings), Nᵣ, the number of one-coordinated and two-coordinated atoms in the chains, N, and the numbers of three-coordinated atoms which belong to the sp² network and to the amorphous domain, N₁ and N₃, respectively. The latter two types of three-coordinated atoms are introduced to follow the build-up of the smooth and nearly spherical sp² shell from the disordered structure. To distinguish the sp² and amorphous domains, the local normal to the shell around each three-coordinated atom (i.e., to the plane going through the three neighbors of the atom) is analyzed. While in the ordered sp² domain this local normal changes its orientation continuously from one atom to another, in the amorphous domain there is little correlation in the orientation of the local normal for the adjacent atoms. Therefore, to calculate the numbers N₁ and N₃ each three-coordinated atom is assigned with a unit vector that describes the normal to the plane passing through three neighbors of the considered atom. If the angle α between these vectors at two bonded three-coordinated atoms is such that cos(α) < 0.7, i.e., the atoms do not lie on a smooth surface, both of these atoms are supposed to belong to the amorphous domain.

### RESULTS AND DISCUSSION

The main result of the performed MD simulations is that in all simulation runs initial amorphous carbon clusters transform into hollow shells with sp² structure. The complete transformation of amorphous carbon clusters into fullerenes within 1 μs is revealed for 8 simulation runs out of 47. Examples of the structure evolution of an amorphous carbon cluster into a fullerene are presented in Figure 1a–h and Figures S2a–h in the Supporting Information. As for the rest of the simulation runs, the same transformation process is observed, although one or a few chains remain attached to the hollow shell with the sp² structure after 1 μs of the simulation time.

Examples of the time dependences describing evolution of the numbers of different atomic types, numbers of rings, and potential energy for several simulation runs in which fullerenes are formed are shown in Figure 1i–k and Figures S2i–k and S3i–k in the Supporting Information. On the basis of these dependences, consecutive modifications of the initially amorphous structure can be followed. The initial cluster cut from the bulk amorphous carbon (as described in the Supporting Information) contains many dangling bonds and chains attached to the core of the structure (see Figure 1a). These dangling bonds and chains close into polycyclic rings within several nanoseconds (see Figure 1b). Then polycyclic rings rearrange into sp² fragments which consist mainly of 5-, 6-, and 7-rings. Finally, as a result of this first transformation stage, a hollow shell with the sp² structure and several chains attached (usually at both ends) is formed within several tens of nanoseconds (see Figure 1c). The number N₅ of three-coordinated atoms which belong to the amorphous domain, the total number N₁ of 3-, 4-, 8-, and 9-rings, and the potential energy E of the system per atom decrease drastically during this stage as shown in Figure 1i–k and Figures S2i–k and S3i–k in the Supporting Information. Clusters with the sp² structure and chains attached typically at both ends or at one end were revealed also in classical MD simulations of fullerene formation starting from carbon vapor. Therefore, the results obtained here and discussed below, including the information on the last events of chain atom insertion into the forming sp² shell and defects remaining after the shell formation, may also be applicable to fullerene formation in arc discharge and by laser ablation of carbon material. It should
be noted that a similar stage of fast formation of the sp² structure (with the portion of three-coordinated atoms in the system about 80–90%) was observed also in MD simulations for large carbon systems of several thousands of atoms in the processes of transformation of amorphous carbon and nanodiamonds to multishell carbon nanoparticles (onions) and graphitization of nanodiamonds several nanometers in size.

At the next transformation stage, carbon atoms at the ends of the chains insert into the sp² structure of the shell. As a result of these atom insertions followed by structure rearrangements, the number and length of the chains decrease. The decrease in the number \( N_6 \) of two-coordinated and one-coordinated carbon atoms in the chains during this transformation stage is shown in Figures 1i and 2 and Figures S2i and S3i in the Supporting Information. The forming shell tends to be more and more smooth, which corresponds to the increase in the number \( N_3 \) of three-coordinated atoms belonging to the sp² network during this transformation stage (see Figure 1i and Figures S2i and S3i). The simultaneous decrease in the number \( N_6 \) of one-coordinated and two-coordinated atoms in the chains and the number \( N_7 \) of three-coordinated atoms which belong to the amorphous domain averaged over the simulation runs (see Figure 2) implies an increase in the number \( N_3 \) of three-coordinated atoms which belong to the sp² network averaged over the simulation runs. This confirms formation and smoothing of the sp² shell in the majority of the simulation runs.

We do not consider here in detail different reactions of atom insertion from long chains into the sp² structure of the shell. However, we should note that two atoms at both ends of the long chain usually insert at the same time. An example of such a simultaneous two-atom insertion is shown in Figure 4a. Evidently, the suggested division of the transformation process into two stages, formation of the hollow shell of the sp² structure with chains attached to it and chain insertion into the shell, is rather speculative because it is difficult to unambiguously determine the moment of cavity formation inside the initial amorphous cluster. Thus, we can only roughly estimate that the binding energy increase during the stage of chain insertion ranges from 4 to 11 eV.

In all eight simulation runs in which all chains got inserted into the shell with sp² structure, the obtained shell structures contain only 5-, 6-, and 7-rings. Thus, according to the definition given above, fullerenes are formed in these eight simulation runs. One of these fullerenes consists only of three-coordinated atoms and contains only 5- and 6-rings; i.e., it has no defects at all (see Figure 1h). As far as we know, this is the
The majority, seven out of eight, of the fullerenes formed contain structural defects such as single one-coordinated atoms and 7-rings. The presence of multiple defects in the structure of fullerenes formed is in agreement with other MD simulations of fullerene formation from carbon vapor,\textsuperscript{17,23,26} graphene flakes,\textsuperscript{29,30} a short carbon nanotube with open ends,\textsuperscript{27,28} and a small nanodiamond cluster.\textsuperscript{31} Figure 3 shows the defects of the fullerene structure at the moment of fullerene shell formation. Only one fullerene has no defects, whereas the other seven fullerenes have from one to five 7-rings. In addition to 7-rings, two fullerenes have a single one-coordinated atom located outside the shell and attached to atoms belonging to two 6-rings. The list of all remaining defects is given in Table 2.

To study possible changes of the local structure after the fullerene formation, the molecular dynamic simulations of the transformation of amorphous carbon clusters. Single one-coordinated atoms and atoms which belong to 7-rings are colored in yellow and light blue, respectively. The list of the defects for each fullerene is given in Table 2. The list of the defects remaining at the end of each simulation run, transformation time, \( \tau \), and additional simulation time after the end of the transformation, \( \tau_{\text{add}} \), is given in Table 2.

![Figure 3](image-url)  
**Figure 3.** Calculated structure and defects remaining for all fullerenes formed in the molecular dynamic simulations of the transformation of amorphous carbon clusters. Single one-coordinated atoms and atoms which belong to 7-rings are colored in yellow and light blue, respectively. The list of the defects for each fullerene is given in Table 2.
defects in the fullerene structure. However, neither defect healing nor any other bond rearrangements occur in these fullerenes within the net time of all simulations after the shell formation on the order of 10 μs. Thus, defect healing in an isolated fullerene (without the influence of the buffer gas or reactions with carbon vapor) is a slow process at a temperature of 2500 K, with the characteristic time exceeding 10 μs. This result of our simulations is consistent with the quantum chemical calculations that give a high value of the SW reaction activation barrier, 4.8–6.9 eV, even in the case where 7-rings are present in the fullerene structure. The opposite result was obtained in previous MD simulations, where a lot of SW reactions were observed at the same temperature of 2500 K for the fullerene with defects, and the activation barrier of these SW reactions was estimated to be about 2.5 eV. This difference in the simulation results is related to the use of different versions of the Brenner potential. Whereas the simplified version of the Brenner potential was used in ref 43, we use the full version of the Brenner potential with the new set of parameters fitted recently to reproduce the energies of fullerenes and graphene edges. Contrary to the high activation barrier of SW reactions, the barrier of C₂ insertion is only 1.0–2.5 eV. Thus, studies of the reactions of C₂ insertion and emission resulting in healing of 7-rings and single two-coordinated atoms and formation of the sp² structure consisting only of 5- and 6-rings are necessary to understand the last stage of the fullerene formation and the high yield of abundant isomers such as the C₆₀ fullerene with icosahedral symmetry.

To study the influence of the initial amorphous cluster structure on the fullerene formation, 25 additional simulation runs of 400 ns duration have been performed at a temperature of 2500 K for the same initial structure. In these simulations the

Figure 4. Calculated structures and schemes of the insertion of atoms into the sp² network. (a) Insertion of two atoms from a six-atom chain (red atoms) at the intermediate stage of fullerene shell formation. (b−g) Events of the last insertion of atoms. The characteristics and description of these events are listed in Table 2. Scheme f corresponds to structures e−g shown in Figure 1. Scheme e shows only a part of the shell area involved in the last insertion event; the complete scheme of this last insertion event is shown in Figure S5a in the Supporting Information. To clarify the correspondence between atoms of the structures and in the schemes, atoms corresponding to chains, rings of sp² atoms which contain ≥7 atoms, and other atoms in the schemes before the insertion events are colored in red, light blue, and dark blue, respectively. The time periods between subsequent structures of the same event are indicated. Forming and breaking bonds are indicated by dashed green lines and X's, respectively.
initial structure is the amorphous cluster \( \text{C}_{66} \) (see Figure 1a), and the difference between the calculations is only in the initial random Maxwell velocity distribution. The \( \text{C}_{66} \) cluster is the one which transformed into the fullerene without defects during 230 ns in one of the 47 main simulation runs discussed above. The time dependences of the numbers \( N_{16} \) and \( N_{e} \) for the 47 main simulation runs starting from different initial structures and 25 additional simulation runs starting from the same initial structure are compared in Figure 4S in the Supporting Information. Figure 4S shows that the main and additional simulation runs are characterized by similar decrease rates of the number \( N_{16} \) of three-coordinated atoms which belong to the amorphous domain and the number \( N_{e} \) of atoms in the chains. However, in none of the additional simulation runs is a fullerene formed. Therefore, the transformation of the amorphous cluster into a fullerene is a totally stochastic process, which does not depend on the initial structure of the amorphous cluster. It should be noted that although the duration of the additional simulation runs is about 2 times greater than the transformation time of \( \sim 230 \) ns for the fullerene without defects, this time is more than 2 times less than the duration of the 47 main simulation runs of about 1 \( \mu \)s. Thus, a direct comparison of the fullerene yield for the sets of simulation runs with the same and different initial structures is not possible.

Not only reactions of defect healing after the fullerene shell completion but also reactions at the last stage of the formation of the \( \text{sp}^{2} \) structure of the fullerene are important to understand the atomistic mechanisms of fullerene formation and the origin of the defects remaining after the shell formation. Here the last events of chain insertion into the hollow shell with the \( \text{sp}^{2} \) structure are studied in detail. We consider as the last insertion events not only reactions that take place immediately at insertion of chain atoms but also subsequent rearrangement of the structure around the place of insertion if this rearrangement is encouraged by the insertion and occurs within a few tens of nanoseconds after insertion. Table 2 presents the description of the last insertion events, the binding energy increase, \( \Delta E \), and the number of bonds formed and broken during the last insertion event for all the fullerenes formed. Seven different schemes of chain insertion are revealed for eight fullerenes formed. Such a variety of the insertion schemes is in agreement with the paradigm that the fullerene formation occurs as a stochastic process of the structure self-organization and contradicts fullerene formation mechanisms on the basis of the existence of fullerene precursors of a certain structure at intermediate stages of the fullerene formation (see reviews in refs 1 and 2 devoted to fullerene formation mechanisms). The schemes of the observed last insertion events are given in Figure 4 and Figure 5S in the Supporting Information.

The number of fullerenes formed is insufficient to draw quantitative conclusions related to the last insertion events at the fullerene shell formation. However, we can find some common features in the characteristics of these events. All observed last insertion events are exothermic, with the energy release ranging from 3.8 to 7.4 eV (see Table 2). This energy release corresponds to a considerable part (\( \sim 30-80\%) \) of the total increase of the binding energy during the chain insertion stage of the transformation.

All last insertion events are represented by the insertion of two- or three-atom chains attached outside the fullerene shell into the \( \text{sp}^{2} \) structure of the shell (see Figure 4 and Figure 5S in the Supporting Information). These events occur with rearrangement of the \( \text{sp}^{2} \) structure of the shell. For most of the last insertion events (seven out of eight), the inserted chains are attached to atoms of the shell which are members of rings with more than six atoms. In these events, the rearrangement of the \( \text{sp}^{2} \) structure of the shell occurs with transformation of 8-, 9-, and 10-rings into 5-, 6-, and 7-rings, and 4-, 7-, and 8-rings into 5- and 6-rings (see Figure 4 and Figure 5S in the Supporting Information).

Five last insertion events take place with only local rearrangement of the shell structure near the atoms to which the chain is attached before the insertion. These events include breaking and formation of 1–4 bonds and last up to 1 ns. Three other last insertion events are accompanied by defect healing (namely, healing of the single two-coordinated atom) located rather far from the area of the last insertion event. These events occur with a considerable binding energy increase (more than 6 eV) and breaking and formation of up to 20 bonds and last up to several tens of nanoseconds.

For five out of eight last insertion events (including three events with healing of single two-coordinated atoms), the \( \text{sp}^{2} \) structure which is involved in the event has no local defects after the event. A single one-coordinated atom attached to the atom which is a member of two 7-rings is observed at the last insertion event only as an intermediate state, and this one-coordinated atom is incorporated into the \( \text{sp}^{2} \) structure with formation of 5- and 6-rings after 5 ns (see Figure 4d and Figure 5S in the Supporting Information). In contrast to this case, single one-coordinated atoms attached to atoms which are members of two 6-rings (mentioned above among the defects remaining) are considerably more stable and exist at the same temperature of 2500 K for times that are at least 3 orders of magnitude longer. We believe that reactions related to the last insertion of chains are of interest for further studies, for example, by ab initio methods.

**CONCLUSIONS**

In summary, atomistic modeling of the transformation of amorphous carbon clusters to fullerenes at a temperature of 2500 K has been performed on the basis of the reactive empirical potential and molecular dynamics method. Two stages of the transformation with different time scales are revealed: (1) formation of a hollow shell with \( \text{sp}^{2} \) structure and attached chains with a characteristic time of \( \sim 100 \) ns, (2) formation of a fullerene as a result of chain insertion into this hollow shell with \( \text{sp}^{2} \) structure with a characteristic time of \( \sim 1 \) \( \mu \)s. The schemes of reactions of bond rearrangement during the last events of chain insertion into the shell structure, which occur just before the fullerene shell completion, are studied in detail. A considerable variety of these reactions is observed, which means that the performed simulations confirm the paradigm of fullerene formation as a result of self-organization. It should be noted that this conclusion is made only for pure carbon systems (or for the systems with the inert buffer gas), and we do not consider here chemical synthesis from a polycyclic aromatic hydrocarbon precursor. One of the fullerenes formed consists entirely of three-coordinated atoms arranged in 5- and 6-rings. This example shows that once in a while defect-free carbon cages can be formed from purely amorphous precursors directly without defect healing. The rest of the fullerenes obtained, however, contain local defects of the structure such as 7-rings and single one-coordinated atoms. To observe possible defect healing,
structural changes have been tracked after the fullerene shell completion at the same time scale as the shell formation. Neither defect healing nor any other events of bond rearrangement have been observed within the net time of all simulations after formation of the fullerene shell on the order of 10 μs. Therefore, processes which lead to selection of abundant isomers (such as C60 with icosahedral symmetry) are slow in comparison with the processes of fullerene shell formation.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04030.

Scheme of the generation of the amorphous carbon clusters (Figure S1), examples of the structure evolution of amorphous carbon clusters into fullerenes (Figures S2 and S3), comparison of the calculated time dependences for 47 simulation runs starting from different initial structures and 25 simulation runs starting from the same initial structure (Figure S4), analysis of the last chain insertion events (Figure S5), and calculated characteristics for all simulation runs (Table S1) (PDF)

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**REFERENCES**

Selective Growth of Fullerenes from C₆₀ to C₇₀: Inherent Geometrical
Irregularities of Their Isomers. The Journal of Physical Chemistry C


