Author(s): Astala, R. & Kaukonen, M. & Nieminen, Risto M. & Jungnickel, G. & Frauenheim, T.
Title: Properties of small carbon clusters inside the C60 fullerene
Year: 2002
Version: Final published version

Please cite the original version:

Properties of small carbon clusters inside the C$_{60}$ fullerene

R. Astala,* M. Kaukonen, and R. M. Nieminen
Laboratory of Physics, Helsinki University of Technology, P. O. Box 1100, Helsinki FIN-02015, Finland
G. Jungnickel and T. Frauenheim
Universit"at/Gesamthochschule Paderborn, 33095 Paderborn, Germany

We present the results of an atomic-scale simulation of the confinement of small carbon clusters inside icosahedral C$_{60}$ fullerene. We carefully investigate the incorporation of various clusters into C$_{60}$ including chains, rings, and double ring configurations, and have analyzed both the energetics and the resulting geometries. The calculations have been performed employing the density-functional-based tight-binding methodology within the self-consistent charge representation. We find that certain carbon cluster configurations that are unstable as free molecules become stabilized inside C$_{60}$. By adding single atoms into random positions inside the fullerene shell we establish an upper limit for the filling of C$_{60}$ with carbon. When the number of atoms inside the fullerene exceeds ten we observe bonding to the surrounding shell and, hence, a gradual transition of the fullerene towards an sp$^3$ rich but locally disordered carbon system.

I. INTRODUCTION

The properties of carbon allotropes with closed cage structures have been an active subject of research since the first experimental discovery back in 1985.1 Subsequently, the structure and energetics of fullerene balls, tubes, and nested forms known as carbon onions2 have been studied intensively at different levels of theory. Highest accuracies in calculating the structural properties of single shell fullerenes and fullerene tubes as large as several hundred atoms have been obtained by Scuseria and co-workers3,4 using ab initio self-consistent field (SCF) Hartree-Fock (HF) methods, by Dunlap and co-workers5,6 using a technique based on SCF density-functional theory (DFT), and by Ordejon et al.7 with the linear-scaling SCF-DFT code SIESTA. More recently, Heggie et al.8 using a parallelized SCF-DFT method systematically studied both the single shell isomers and various nested concentric fullerenes up to a size of 840 atoms.

Computationally less demanding, approximate ab initio methods such as the modified neglect of differential overlap within the HF theory scheme of Bakowies et al.9,10 the DFTB (density-functional-based tight-binding) method,11 the empirical tight binding, and the ab initio tight-binding schemes12 have been shown to reproduce quantitatively the results of the more sophisticated methods for this class of materials, with errors of only a few percent.

Maiti et al.13 conducted simulations with the classical Brenner potential14 extended to correctly treat the van der Waals interactions between two consecutive shells. The results are qualitatively in agreement with the self-consistent schemes: both methods predict the shape of larger fullerenes and multishell fullerenes to be faceted at zero temperature, rather than spherical as proposed by Lu et al.15 using a non-self-consistent Harris-functional approach.

Defects in C$_{60}$ fullerene isomers have been studied by Goodwin using semiempirical tight-binding methods.16 Eggen et al.17 based on SCF-DFT calculations of the energetics of a defect known as the Stone-Wales transformation in C$_{60}$, pointed out why the icosahedral isomer is strongly favored in growth experiments. Fullerene fragmentation has been studied by tight-binding molecular dynamics.18 Continuous fullerene growth19 has been simulated, too, by using classical atomic interaction potentials.

Small carbon clusters with atom numbers below 24 have been intensively studied with accurate ab initio methods. Raghavachari et al. have studied the stability of carbon rings and chains with 2–10 atoms.20 More complex structures containing $n = 14–24$ (n even) atoms have also been studied.21 Kent et al. have performed diffusion quantum Monte Carlo simulations of energetics of C$_{24}$, C$_{26}$, C$_{28}$, and C$_{32}$ clusters.22

The unique spherically shaped cage of a C$_{60}$ fullerene contains empty space that is large enough to incorporate atoms of any kind as an endohedral complex.23 The molecule is not very reactive since the carbon atoms are all completely saturated by taking part in an extended π-bonded electron system similar to graphite. The interior of C$_{60}$ is expected to have a good capacity for confining small molecules. C$_{60}$ possesses high stability among the small carbon fullerenes.24 However, the energies of large fullerenes tend towards graphite values, thus making them energetically more stable.8,11

In this work we study the stability and geometries of chain, ring, and double ring structures consisting of 2–15 carbon atoms inside the C$_{60}$ fullerene by optimizing the atomic geometries. The stability of a few selected molecules is further tested by performing molecular-dynamics simulations. We study the packing of carbon atoms into random positions inside the C$_{60}$ and the development of the atomic bonding as the density of particles increases inside the fullerene. The energy landscapes of systems consisting of 60–79 carbon atoms are exceedingly complex and exhibit a large number of metastable configurations. We will concentrate to a low-energy subset of possible structures.

Motivation for this work comes from the recent observation of the nucleation of diamond in the core region of a carbon onion by Banhart et al.25 Such a nucleation process...
clearly involves a transition of a curved two-dimensional system to a three dimensionally connected structure. The transformation requires the hybridization of the carbon atoms to change from $sp^2$ to $sp^3$. In order to understand this phase transition from graphite-like structures to diamond, we investigate the bonding behavior of carbon clusters confined in the most natural cage $C_{60}$. It is essential to understand the structure formation inside such a fullerene as the initial step of the diamond nucleation process. In a recent complementary paper by Fugaciu et al., this problem has been discussed from the opposite point of view by investigating the transition from diamond particles to concentric fullerene shells during molecular dynamics initiated by stochastic energy fluctuations to simulate irradiation. Alternatively, the effects of irradiation have been modeled by randomly filling a large nested $C_{60}$@$C_{240}$ fullerene, as presented in our earlier paper. In that study we used DFTB method and a combination of molecular dynamics (MD) and conjugate-gradient (CG) techniques and observed a formation of diamondlike regions in the onion core.

In an interesting work by Zeger and Kaxiras, dense icosahedral carbon clusters made of fourfold coordinated atoms have been investigated using a classical potential. The authors observed that spherically shaped molecules consisting of 100 or more fourfold coordinated carbon atoms can be stabilized by surface hydrogenation. Subsequent studies with quantum-mechanical potentials showed that an unsaturated cluster with 100 atoms spontaneously delaminates into concentric fullerenes while a similar larger structure containing 300 atoms remains relatively stable under thermal treatment at 2700 K, indicating a size threshold for the graphitization of such diamondlike particles.

In the present paper, we systematically study carbon cluster incorporation into the prototype fullerene $C_{60}$ and discuss the implications of the results for the diamond nucleation observed experimentally. For this, we briefly introduce the theoretical methodology in Sec. II, describe the carbon systems under consideration in Sec. III, and present our results in Sec. IV. This includes energetics, optimized geometries, and hybrid statistics of the models. Finally, we put the results into perspective in Sec. V and can conclude in Sec. VI that the confinement of carbon clusters inside the strongly bonded and very rigid fullerene cage clearly promotes the transition of graphitic toward diamondlike local geometries.

II. THE SCC-DFTB METHOD

The DFTB method is a quantum-mechanical computer-simulation method that represents the total energy of a many-particle system by the sum of a one electron contribution and a repulsive term as is usual for a tight-binding scheme. Unlike traditional empirical tight-binding methods, however, the interatomic potentials are generated by self-consistent DFT calculations for two atom centers within the local-density approximation (LDA). This leads to highly transferable potentials. The method is faster than true ab initio methods, because the atomic forces can be evaluated more rapidly and the Hamiltonian matrix elements can be tabulated and reused many times. The DFTB method has been tested for a number of elements such as C, Si, N, O, B, and H, for systems including small carbon molecules, hydrocarbons and fullerenes, and for modeling diffusion processes and nanointeraction. It has been shown by intense studies of amorphous carbon systems that the DFTB method can describe the varying hybridization of carbon systems very accurately. An extensive description of the DFTB methodology can be found in a review by Goringe et al. To account for charge fluctuations between atoms in systems with a delicate charge balance such as heteropolar structures or with defects, DFTB has recently been extended to treat charge-transfer self-consistently [SCC–DFTB (self-consistent charge DFTB)]. This method has been found to increase the overall accuracy of the original scheme in organic molecules such as hydrocarbons, for biological systems, and for III-V semiconductor surfaces. We apply the SCC method throughout this work to precisely account for any charge-transfer effects that might occur between nonbonded fragments such as the confining fullerene shell and its filling and at cluster ends such as in atomic chains. The method can be used to extract the Mulliken charges of individual atoms. One should note, however, that their absolute values depend on the basis functions while the differences in Mulliken charges are more physically relevant.

Additional checks after the DFTB relaxations were carried out using a cluster DFT-LDA program (AIMPRO). For an in-depth description of this method one should consult the paper by Briddon and Jones.

III. SIMULATED SYSTEMS

We have performed four different simulations. At first, small carbon clusters in free space with simple geometries were CG relaxed with respect to all degrees of freedom and without additional constraints and/or confinement, as a reference. The structures investigated include chains of atoms (2–15 atoms long), ring structures (5–15 atoms long), and fused five-, six-, and seven-membered rings. The results have been compared to true ab initio calculations.

Second, some of the above carbon clusters were inserted into $C_{60}$. These include chains with 2–6 atoms, rings with 5–9 atoms, and fused five- and six-membered rings, consisting of two five- or two six-membered rings located on top of each other. The energy of the full structures consisting of both the fullerene and the inner cluster was then minimized again using the CG algorithm with no additional constraints. The relaxation was always terminated when maximum rms force was below $10^{-4}$ eV/Å, which corresponds to a numerical accuracy of few meV for the total energy.

We continued by running MD simulations for the obtained structures exposing them to a heat pulse of 3000 K for 145 fs. Two structures were selected for this type of simulations, the relaxed armchair six-membered ring and the double five-membered-ring cluster inside the $C_{60}$. The coupling to the heat bath was simulated by velocity scaling. Finally, the system was equilibrated in a microcanonical simulation for another 300 fs and frozen in by a sub-
TABLE I. The bond lengths of various small carbon chains with 2–10 atoms in free space. SCC denotes the inclusion of charge transfer in the DFTB scheme. CCD denotes the coupled-cluster Hartree-Fock approach. NA denotes not available.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bond lengths (Å) (SCC)</th>
<th>Bond lengths (Å) (non-SCC, Ref. 32)</th>
<th>Bond lengths (Å) (CCD, Ref. 20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.241, 1.293</td>
<td>1.244, 1.288</td>
<td>1.245</td>
</tr>
<tr>
<td>3</td>
<td>1.297, 1.307</td>
<td>1.288, 1.321</td>
<td>1.278</td>
</tr>
<tr>
<td>4</td>
<td>1.279, 1.312</td>
<td>1.256, 1.315</td>
<td>NA</td>
</tr>
<tr>
<td>5</td>
<td>1.287, 1.320, 1.286</td>
<td>1.265, 1.324, 1.287</td>
<td>NA</td>
</tr>
<tr>
<td>6</td>
<td>1.277, 1.313, 1.292</td>
<td>1.245, 1.337, 1.280</td>
<td>1.270, 1.280, 1.264</td>
</tr>
<tr>
<td>7</td>
<td>1.282, 1.321, 1.285</td>
<td>1.253, 1.335, 1.279</td>
<td>1.269, 1.283, 1.261</td>
</tr>
<tr>
<td>8</td>
<td>1.276, 1.317, 1.288</td>
<td>1.240, 1.350, 1.263</td>
<td>NA</td>
</tr>
<tr>
<td>9</td>
<td>1.298</td>
<td>1.302</td>
<td>1.269</td>
</tr>
<tr>
<td>10</td>
<td>1.280, 1.322, 1.284</td>
<td>1.246, 1.345, 1.269</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>1.311, 1.286</td>
<td>1.311, 1.284</td>
<td>NA</td>
</tr>
</tbody>
</table>

sequent CG relaxation to reveal the possible changes in the configuration.

The fourth type of simulations is characterized by adding carbon atoms into random positions inside the C_{60}. At the beginning, a set of five C atoms was inserted and the resulting system was CG relaxed. Further, C atoms were added one after another, CG relaxing the structure after each addition. This was continued until the number of additional atoms inside the fullerene reached 18. The insertion of the carbon atoms was subject to the constraints that the random position of new atoms was not further away from the fullerene center than 1.9 Å and at least 1.2 Å apart from the already existing atoms.

IV. RESULTS

The radius of a relaxed empty C_{60} fullerene shell has been determined previously within the DFTB method to be ~3.54 Å. The characteristic two different bond lengths were determined to be 1.40 Å and 1.45 Å for the bonds joining two six-membered rings, and the bonds joining one five-membered ring and one six-membered ring, respectively. The charge transfer between associated atoms is negligible and the application of the SCC-DFTB does not alter the geometries nor the energetics. Note that the bond lengths are in excellent agreement with experimental results obtained by nuclear magnetic resonance (1.45, 1.40 Å) and gas-phase electron diffraction (1.46 Å, 1.40 Å) as well as with the results of more sophisticated SCF-LDA calculations (1.45, 1.39 Å) and computations at the SCF-HF-MP2 level of theory (1.45, 1.41 Å).

A. Small carbon molecules in free space

When simulating small free carbon molecules we find that seven-membered rings and a stack of two five-membered rings are very unstable configurations. The six-membered ring is stable, and chains prefer a linear conformation. In Table I we list the bond lengths of some of the investigated chains for reference along with the results from coupled-cluster Hartree-Fock (CCD) calculations by Raghavachari and Binkley and the previous DFTB results by Porezag et al. The bond lengths determined with SCC-DFTB are in better agreement with the CCD results due to charge-transfer effects along the chain body, initiated by the unsaturated orbitals at the chain ends. The average error with respect to the CCD calculation is only 1.6% while the standard DFTB technique deviates by about 2.1%. The binding energies of the structures are strongly overestimated as the DFTB methods cannot properly treat the strong electron correlation effects in the small carbon clusters.

B. Small carbon molecules inside C_{60}

1. CG relaxations

In Table III we summarize the total and the binding energies for the clean fullerene and the one loaded with various clusters. The heats of formation given in Table II have been obtained from \((E_{N-1} + E_{\text{free}} - E_{N})/N\) where N is the number of atoms in the cluster under consideration, \(E_{N}\) is the total energy of the N-atom cluster, \(E_{\text{free}}\) is the energy of a free carbon atom, and \(E_{N-1}\) is the energy of the \(N-1\)-atom cluster.

Small carbon chains appear to be the most likely candidates for an incorporation into a fullerene cage. Chains have been shown in the past to be the most stable carbon configurations for free clusters with less than ten atoms. We find here that chains containing two, three, or four atoms introduced into a fullerene decrease the stability of the system by only 0.12–0.18 eV/atom, which accounts for less than 2% of the SCC-DFTB binding energy of C_{60}. In Table III we have listed the binding energies for both C_{60} with various seeded clusters, and for plain C_{60} with the seed in free volume conditions. The trend is that the binding energy decreases by the seeding. However, the differences in the en-
Energy are small and likely to be quantitatively incorrect due to strong electron correlation effects in small clusters, which the SCC-DFTB computations cannot properly capture.

C₂ dimers and C₃ trimers inserted into C₆₀ remain disconnected from the fullerene. Instead of a linear configuration, though, the trimer develops a bond angle of 117.1°. In contrast, the chain end atoms of the four- and five-membered chains form bonds with the fullerene shell. The chains are nonlinear, too, with bond angles of 166.4°, 157.5°, 157.4°, and 166.4° for the four-membered chain, where the larger angles belong to the atoms at the ends bonded to C₆₀. For the five-membered chain the angles found are 140.7°, 120.2°, and 140.8° for the three atoms in the middle of the chain. The end-standing atoms of this chain have two bonds each with C₆₀. Associated with the relative stabilization is a charge transfer between the small chains and the surrounding fullerene determined by a Mulliken analysis. In the case of the dimer ~0.2 e/atom flow towards the dimer atoms. For the three-atomic and four-membered chains we observe that the same amount of extra charge accumulates at the central chain atoms. In a Mulliken charge analysis bond charges are detected indirectly by projecting them likewise onto the atoms making the bond. Hence, we interpret the observed charge flow as a partial saturation of the dangling orbitals at the chain ends by the occupation of π states along the chain that would be antibonding without confinement in the cage.

A six-membered chain does not fit nicely into the fullerene. The edge atoms of the chain push the fullerene atoms away from their natural positions. As a result four seven-membered rings are created inside the fullerene shell. Again, the inserted six-atomic chain becomes nonlinear. Each edge atom transforms into a fourfold coordinated sp³-like geometry by forming three bonds with nearby fullerene atoms. Here we observe almost no charge transfer between the cluster atoms and the ball due to the formation of strong bonds such that the occupation of antibonding

---

**TABLE II.** The heats of formation per atom for chain and ring structures (including the C₆₀ shell atoms). A positive number indicates that the reaction is energetically favorable (exothermic).

<table>
<thead>
<tr>
<th>Configurations, old→new</th>
<th>Heat of formation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer→trimer</td>
<td>0.134 (TB)/0.112 (LDA)</td>
</tr>
<tr>
<td>Trimer→four-membered chain</td>
<td>0.084/0.098</td>
</tr>
<tr>
<td>Four-membered chain→five-membered chain</td>
<td>0.053/0.061</td>
</tr>
<tr>
<td>Five-membered chain→six-membered chain</td>
<td>0.121/0.098</td>
</tr>
<tr>
<td>Five-membered ring→armchair six-membered ring</td>
<td>0.121 (TB)</td>
</tr>
<tr>
<td>Armchair six-membered ring→seven-membered ring</td>
<td>0.076 (TB)</td>
</tr>
<tr>
<td>Seven-membered ring→eight-membered ring</td>
<td>0.052/0.051</td>
</tr>
<tr>
<td>Eight-membered ring→nine-membered ring</td>
<td>−0.009/0.008</td>
</tr>
</tbody>
</table>

---

**TABLE III.** The binding energies for the structures consisting of C₆₀ and a molecule inside. For comparison, the binding energies for the system consisting of the molecule in free space and the empty C₆₀ are listed in the fourth column, in the cases when the C molecule is stable in free space.

<table>
<thead>
<tr>
<th>Atoms in cluster</th>
<th>Seed configuration</th>
<th>Binding energy/atom (eV)</th>
<th>Binding energy/atom (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(molecule inside C₆₀)</td>
<td>(free molecule and C₆₀)</td>
</tr>
<tr>
<td>0</td>
<td>Plain C₆₀</td>
<td>8.91 (TB)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Dimer</td>
<td>8.79 (TB)/8.59 (LDA)</td>
<td>8.78</td>
</tr>
<tr>
<td>3</td>
<td>Trimer</td>
<td>8.78/8.64</td>
<td>8.80</td>
</tr>
<tr>
<td>4</td>
<td>Four-membered chain</td>
<td>8.73/8.48</td>
<td>8.76</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramid</td>
<td>8.71/8.49</td>
<td>8.74</td>
</tr>
<tr>
<td>5</td>
<td>Five-membered chain</td>
<td>8.65/8.47</td>
<td>8.78</td>
</tr>
<tr>
<td>5</td>
<td>Five-membered ring</td>
<td>8.70/8.53</td>
<td>8.74</td>
</tr>
<tr>
<td>6</td>
<td>Six-membered chain</td>
<td>8.64/8.50</td>
<td>8.75</td>
</tr>
<tr>
<td>6</td>
<td>Planar six-membered ring</td>
<td>8.68/8.54</td>
<td>8.73</td>
</tr>
<tr>
<td>6</td>
<td>Armchair six-membered ring</td>
<td>8.69 (TB)</td>
<td>8.73</td>
</tr>
<tr>
<td>7</td>
<td>Seven-membered ring</td>
<td>8.63/8.47</td>
<td>8.68</td>
</tr>
<tr>
<td>7</td>
<td>Eight-membered ring</td>
<td>8.56/8.40</td>
<td>8.68</td>
</tr>
<tr>
<td>7</td>
<td>Nine-membered ring</td>
<td>8.43/8.29</td>
<td>8.71</td>
</tr>
<tr>
<td>10</td>
<td>Double five-membered ring</td>
<td>8.53/8.30</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Double six-membered ring</td>
<td>8.40/8.17</td>
<td>8.62</td>
</tr>
</tbody>
</table>
states along the chain is inhibited. However, this structure is 0.27 eV/atom less stable than the empty fullerene but also less stable than \( C_{60} \) seeded with chains of 2–5 atoms, five-membered rings, and a trigonal bipyramid, all of which do not form strong bonds to the fullerene. This indicates the importance of the charge balance and is due to a loss in binding energy as a result of the bond distortions inside the fullerene shell.

All the tested ring configurations are metastable inside the fullerene. It is obvious from Table III that small rings of 3–4 atoms are less stable than equivalent chain structures inside \( C_{60} \), which is the same trend as observed for free molecules. Energetically favorable five-, six-, and seven-membered rings do not prefer to form bonds with the fullerene shell. Instead in the ground state geometry the ring is still intact and clearly separated from the shell. In the case of the six-atom ring we find the planar and the armchair configuration to be identical in the binding energy within the error bars. The planar ring is characterized by a charge transfer of \( \approx 0.2 \) e/at. to the two atoms at the opposite ends of the ring. In the armchair six-membered ring the charge transfer is considerably smaller. However, with the \( C_{60} \) confinement the armchair torsion angle decreases from the free-space value of \( \approx 25^\circ \) to \( \approx 5^\circ \). The planar six-membered ring induces the contraction of \( C_{60} \). There is an inward movement of the order of 0.2 Å of four \( C_{60} \) atoms. An interesting alternative for the fivefold ring inside the \( C_{60} \) is a trigonal bipyramid consisting of three carbon atoms in one equilateral triangular plane and two atoms above and below the center of the triangle. The relaxed \( C_{3h} \) geometry inside \( C_{60} \) is shown in Fig. 1. This structure is only 0.20 eV/atom less stable than \( C_{60} \) and the bond lengths in the bipyramid are about 1.47 Å long, indicating only partial \( \pi \) bonding.

A double stack of five-membered rings does not bond to the surrounding shell. The relaxed configuration is shown in Fig. 2. This cluster is only 0.37 eV/atom higher in total energy than \( C_{60} \) (see Table III). A seven-membered ring inserted into the fullerene is 0.10 eV/atom more stable than the five-membered ring stack. The seven-membered ring is stabilized, as the strong \( \pi \) bonds of the \( C_{60} \) shell prevent relaxation towards more open structure. In free volume conditions we observe the seven-membered ring to relax towards a curved chain structure. The point group symmetry for the five-membered ring stack is \( C_{5h} \). We note that a free stack of five-membered rings is a molecule that can be stabilized by hydrogenation resulting in pentaprismane \((CH)_{10}\) that has been synthesized. A similar double five-membered ring stack in free space has theoretically been found as a metastable minimum for phosphorus.

A double stack of six-membered rings is less symmetrical than the five-membered ring double stack, as four cluster atoms bond with \( C_{60} \) causing deviation from ideal \( C_{6h}\)-symmetric geometry for the cluster.

The eight-membered ring forms bonds with four \( C_{60} \) shell atoms, resulting in \( sp^3 \) hybridization of these atoms. The two six-membered rings of \( C_{60} \) to which these atoms belong, are located symmetrically on the opposite hemispheres of the fullerene, and are transformed into an armchair configuration as known from diamond. The four atoms of the eight-membered ring making bonds to the fullerene appear to be in an \( sp^2\)-like graphitic local geometry. The inserted eight-membered ring becomes elliptically shaped during relaxation indicating that a filling threshold is almost reached. A ring containing nine atoms makes multiple bonds with the surrounding \( C_{60} \) shell inducing \( sp^3 \) hybridization of a total of 12 carbon atoms. Atoms, both from the \( C_{60} \) shell and the nine-membered ring, are \( sp^3 \) hybridized. What remains of the eight- and nine-membered rings is a relatively distorted non-planar geometry.

2. Ab initio calculations

We performed DFT-LDA calculations on a set of clusters inside \( C_{60} \) to confirm the accuracy of the calculations and to gain a more detailed picture of the electron structure. The binding energies of the clusters follow similar trends as with the DFTB calculations; the energies per atom are systematically lower by about 0.1-0.2 eV (Table III). The most notable exception is that the planar \( C_6 \) ring is the more stable con-
figuration in DFT calculations. Among the five-atom clusters, the bipyramidal arrangement is more stable than the simple chain.

3. MD relaxations

After the static calculations we performed MD simulations for the C_{60} containing a six-membered ring and a double stack of five-membered ring.

A six-membered ring inside C_{60} distorts strongly during molecular-dynamics simulations starting with a 3000 K heat pulse but does not become fragmented. We observe preference for the armchair configuration when quenching the final MD snapshot structure. Six-membered rings and double stack of five-membered rings behave alike. They deform under a MD simulation but the original conformation is still apparent after a quench. For the latter clusters, we observe bond formation between the clusters and the surrounding shell during the MD simulation, thereby inducing some damage into C_{60} which, however, is removed after the quench.

4. Electronic structure

Due to the charge transfer mentioned earlier, two opposite atoms in the planar six-membered ring have the electron count of 4.2 e each. Furthermore, about 0.1 e/at. is transferred away from the four shifted C_{60} fullerene atoms on the six-membered ring plane. The system has a zero electric dipole moment. On the other hand, with the armchair six-membered ring, there is a total charge flow of ~0.2e towards the ring, and the system gains an electric dipole moment of ~0.09 e Å. The seven-membered ring system has both considerable charge transfer and electric dipole moment. The nine-membered ring system has both considerable charge transfer and electric dipole moment. The nine-membered ring becomes positively charged with a value of 0.3e. The electric dipole moment is as large as 0.30 e Å, and it is directed parallel to the plane roughly defined by the nine-membered ring. The system consisting of C_{60} and the double stack of five-membered rings is polarized with an electric dipole moment of 0.14 e Å. The double stack of six-membered rings has zero electric dipole moment, but the total charge flow away from the cluster to the C_{60} shell is 0.1e. The DFTB electron densities of states for some low-energy structures have been presented in the Fig. 3.

In the following we have applied the DFT-LDA code AM-PRO to study the electronic properties of C_{60}+X atom clusters.\textsuperscript{35} The Kohn-Sham electronic gaps of C_{60}+X atoms in the interior cluster are shown in Fig. 4. With C_{1} both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are degenerate p orbitals with 2/3 e occupancy of the C atom, resulting in a zero HOMO-LUMO gap. Already with C_{1}, the orbitals of the molecule have some overlap with the fullerene. With C_{2} and C_{3} the HOMO level is a delocalized state at the fullerene shell (as with the pure C_{60}) and the LUMO is localized in the inner molecule. For the C_{4} chain and C_{5} bipyramid both the HOMO and LUMO are spread over the fullerene. C_{6} is a special case, its HOMO being a bonding p-type orbital in the C_{6} ring but the LUMO spreads all over the fullerene shell. Perhaps the confinement begins to affect here pushing the bonding orbitals of the inner molecule upwards into the gap. The Kohn-Sham HOMO for C_{60}+C_{6} is shown in Fig. 5. This type of bonding-antibonding mixture is not observed in C_{6} in free space. From C_{7} on towards bigger inner clusters, neither the HOMO nor LUMO are localized only to the inner cluster. Generally, if there are bonds between the inner cluster and the fullerene, the HOMO and LUMO are spread over the whole system (C_{8} and C_{9}) whereas in the case where the inner molecule is disconnected from the fullerene (C_{10} and C_{12}) the HOMO and LUMO are localized only to the fullerene.

In the following we have applied the DFT-LDA code AM-PRO to study the electronic properties of C_{60}+X atom clusters.\textsuperscript{35} The Kohn-Sham electronic gaps of C_{60}+X atoms in the interior cluster are shown in Fig. 4. With C_{1} both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are degenerate p orbitals with 2/3 e occupancy of the C atom, resulting in a zero HOMO-LUMO gap. Already with C_{1}, the orbitals of the molecule have some overlap with the fullerene. With C_{2} and C_{3} the HOMO level is a delocalized state at the fullerene shell (as with the pure C_{60}) and the LUMO is localized in the inner molecule. For the C_{4} chain and C_{5} bipyramid both the HOMO and LUMO are spread over the fullerene. C_{6} is a special case, its HOMO being a bonding p-type orbital in the C_{6} ring but the LUMO spreads all over the fullerene shell. Perhaps the confinement begins to affect here pushing the bonding orbitals of the inner molecule upwards into the gap. The Kohn-Sham HOMO for C_{60}+C_{6} is shown in Fig. 5. This type of bonding-antibonding mixture is not observed in C_{6} in free space. From C_{7} on towards bigger inner clusters, neither the HOMO nor LUMO are localized only to the inner cluster. Generally, if there are bonds between the inner cluster and the fullerene, the HOMO and LUMO are spread over the whole system (C_{8} and C_{9}) whereas in the case where the inner molecule is disconnected from the fullerene (C_{10} and C_{12}) the HOMO and LUMO are localized only to the fullerene.

In the following we have applied the DFT-LDA code AM-PRO to study the electronic properties of C_{60}+X atom clusters.\textsuperscript{35} The Kohn-Sham electronic gaps of C_{60}+X atoms in the interior cluster are shown in Fig. 4. With C_{1} both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are degenerate p orbitals with 2/3 e occupancy of the C atom, resulting in a zero HOMO-LUMO gap. Already with C_{1}, the orbitals of the molecule have some overlap with the fullerene. With C_{2} and C_{3} the HOMO level is a delocalized state at the fullerene shell (as with the pure C_{60}) and the LUMO is localized in the inner molecule. For the C_{4} chain and C_{5} bipyramid both the HOMO and LUMO are spread over the fullerene. C_{6} is a special case, its HOMO being a bonding p-type orbital in the C_{6} ring but the LUMO spreads all over the fullerene shell. Perhaps the confinement begins to affect here pushing the bonding orbitals of the inner molecule upwards into the gap. The Kohn-Sham HOMO for C_{60}+C_{6} is shown in Fig. 5. This type of bonding-antibonding mixture is not observed in C_{6} in free space. From C_{7} on towards bigger inner clusters, neither the HOMO nor LUMO are localized only to the inner cluster. Generally, if there are bonds between the inner cluster and the fullerene, the HOMO and LUMO are spread over the whole system (C_{8} and C_{9}) whereas in the case where the inner molecule is disconnected from the fullerene (C_{10} and C_{12}) the HOMO and LUMO are localized only to the fullerene.
We proceeded by randomly filling the fullerene with additional atoms as mentioned in Sec. III. Typically, the structures after random filling have higher binding energies than the systems with the cluster seeds discussed previously. The initial randomly generated configuration contained five atoms and relaxed towards a distorted five-membered ring.

When two more atoms are added bonds are established between the C\textsubscript{60} shell and the interior cluster. The fullerene becomes increasingly distorted when the number of extra atoms exceeds 10. The energetics of the random clusters are presented in Table IV. Interestingly, for 12 randomly added atoms we find a structure that is higher in binding energy by only 0.037 eV/\text{at.} than the comparable double stack of six-membered rings. Also the eight- and nine-atomic random clusters have higher binding energies than comparable eight- and nine-membered rings. The strain in the large random clusters is probably lower. This 12-atom structure is shell-like, consisting of a six-membered ring, four five-membered rings, one four-membered ring, and bonded to C\textsubscript{60}. Up to 17 additional carbon atoms inside the outer C\textsubscript{60} fullerene shell, though heavily distorted, is still reminiscent of the original C\textsubscript{60} ball. We were not able to introduce 18 atoms or more without severely damaging the outer shell thus establishing the filling threshold accordingly.

The evolution of the hybrid fractions during the filling process is shown in Fig. 6. The sp\textsuperscript{2} atoms in the total structure increases significantly. A considerable amount of the former C\textsubscript{60} atoms are transformed from their original sp\textsuperscript{2}-like state to an sp\textsuperscript{3}-like geometry as a result of bond formation between the inner extra and the outer shell atoms. This can be best described by a gradual transition towards an amorphous diamond structure. We were also able to detect tiny regions resembling a local geometry typical for crystalline diamond.

The binding energies for random structures inside the C\textsubscript{60} fullerene are shown in Table IV.

### Table IV. The binding energies for random structures inside the C\textsubscript{60} fullerene.

<table>
<thead>
<tr>
<th>Atoms in cluster</th>
<th>Binding energy/atom (eV) (including C\textsubscript{60} atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.70</td>
</tr>
<tr>
<td>6</td>
<td>8.64</td>
</tr>
<tr>
<td>7</td>
<td>8.60</td>
</tr>
<tr>
<td>8</td>
<td>8.57</td>
</tr>
<tr>
<td>9</td>
<td>8.52</td>
</tr>
<tr>
<td>10</td>
<td>8.50</td>
</tr>
<tr>
<td>11</td>
<td>8.47</td>
</tr>
<tr>
<td>12</td>
<td>8.43</td>
</tr>
<tr>
<td>13</td>
<td>8.40</td>
</tr>
<tr>
<td>14</td>
<td>8.37</td>
</tr>
<tr>
<td>15</td>
<td>8.35</td>
</tr>
<tr>
<td>16</td>
<td>8.30</td>
</tr>
<tr>
<td>17</td>
<td>8.27</td>
</tr>
<tr>
<td>18</td>
<td>8.28</td>
</tr>
</tbody>
</table>

During the random filling the amount of sp\textsuperscript{3} bonded atoms in the total structure increases significantly. A considerable amount of the former C\textsubscript{60} atoms are transformed from their original sp\textsuperscript{2}-like state to an sp\textsuperscript{3}-like geometry as a result of bond formation between the inner extra and the outer shell atoms. This can be best described by a gradual transition towards an amorphous diamond structure. Were also able to detect tiny regions resembling a local geometry typical for crystalline diamond.

The evolution of the hybrid fractions during the filling process is shown in Fig. 6. Due to the curvature of the fullerene the bonds of C\textsubscript{60} are classified as sp\textsuperscript{2} \(2+1\)'s bonded atoms have nonplanar threefold coordinated bonds. The fractions of atoms with sp\textsuperscript{1} bonds, unbonded atoms, or unidentifiable bond geometries are not displayed.

FIG. 5. The DFT-LDA HOMO level of C\textsubscript{60}+C\textsubscript{6}. This type of bonding-antibonding combination of wave functions is not present with C\textsubscript{6} in free space. Only the C\textsubscript{6} molecule inside the fullerene cage is shown.

FIG. 6. The development of the atomic bonding during the random filling of the C\textsubscript{60} fullerene. The sp\textsuperscript{2} \(2+1\)'s bonded atoms have nonplanar threefold coordinated bonds. The fractions of atoms with sp\textsuperscript{1} bonds, unbonded atoms, or unidentifiable bond geometries are not displayed.
V. DISCUSSION

The first interesting observation from this study is the ability of a fullerene to help stabilizing certain carbon molecules inside the cage which otherwise would not have a chance to exist. This refers, for example, to the investigated seven-membered ring and the double stack of five-membered rings as shown in Fig. 2 inside C₆₀. Note that the latter configuration that represents the backbone of pentaprismane,⁴³ can accommodate a large number of atoms without forming bonds to the surrounding shell.

In the free volume conditions the binding energies typically increase with the ring size or the chain length. This is not the case, apart from the five and six atom inner molecules, for these structures inside the C₆₀ shell as the increasing size of the inner cluster leads to a growing distortion of both the cluster and the fullerene.

The heats of formation (Table II) for the chains and rings are positive, which indicates that there is a bias to incorporate small clusters into the fullerene. However, the larger the inner clusters the lower is the energy gain. This is due to the strong distortions of the clusters and the ball, although the probability of creating single bonds with the shell increases.

The small difference in the armchair and planar six-membered ring configurations leads to a completely different charge distribution picture, while the energies of these structures are close to each other. The smallest clusters with 2–5 carbon atoms have a tendency to become negatively charged when inside C₆₀, while in larger ring systems the situation is reversed.

The C₆₀ fullerene shell can stabilize the inner structures by either directly terminating dangling orbitals or by transferring charge and thereby (partially) satisfying molecular orbitals. This first process involves changes of the hybridization of atoms belonging to the C₆₀ shell causing them to convert from the native graphitic to a diamondlike state. This results in a dentlike distortion in the fullerene shell, in which a carbon atom in the diamondlike state moves towards the center of the fullerene relative to its neighboring atoms.

C₆₀ possesses enough rigidity to confine internal carbon atoms into a relatively small stressed region that cannot fully relax. Short chains can be accommodated into C₆₀ and all of them (apart from the dimer) have geometries with bond angles below 180°, in contrast to the unconstrained situation. The stability of the surrounding cage is so high that the inner carbon atoms cannot easily escape from the confined region. This blocking is effective until the fullerene structure becomes severely damaged. The filling threshold is at about 17 atoms inside the fullerene. During our simulations we could not observe migration of atoms through the shell which indicates a large barrier for such an event. Note that in this study we have studied the confinement by undefected C₆₀ shell. Initial defects in the shell may reduce its capacity to confine interior atoms.

The simulations imply that the armchair six-membered ring and the double stack of five-membered rings are not just metastable configurations in terms of a static total energy calculation. They survive a heat pulse of 3000 K in a molecular-dynamics simulation without a transformation into some other geometry. In addition they do not stimulate the fullerene to disrupt.

During random filling, internal structures rapidly evolve into three-dimensional networks thereby occupying the whole volume. This is accompanied by high coordination numbers of the inner carbon atoms. The transition towards an sp³-rich structure is further supported by the formation of bonds between the confined cluster and its surrounding C₆₀ shell. It is interesting that the shell due to strong π-bonding effects is very rigid on one hand, but on the other hand has some flexibility to rehybridize in order to accommodate any internal carbon atoms most effectively. Clearly, there is a competition between the energy loss due to any disturbances of the extended π-electron system typical for the pure fullerene and the energy gain due to the generation of single inner bonds.

VI. CONCLUSIONS

We have studied the incorporation of carbon atoms into the C₆₀ fullerene by tight-binding simulations based upon density-functional theory. At first, binding and total energies for systems where small carbon clusters were seeded into fullerene have been investigated. We observe that the confinement due to the fullerene can stabilize internal clusters which would not exist as free molecules, such as a double stack of five-membered rings. It appears that the number of metastable atomic configurations of a cluster with a given number of atoms is higher when being confined by an external cage.

We have investigated systematically the evolution of the carbon structure when randomly adding carbon atoms one after another to C₆₀. A strong increase of the sp³ hybrid fraction has been observed for the composite system. Structures with a fraction of fourfold coordinated carbon atoms as high as 45% can support themselves as metastable states, even when the number of atoms added in C₆₀ is below 20.

C₆₀ possesses enough rigidity to act as a constraining cage that promotes the nucleation of fourfold coordinated atoms due to the relatively high local stress. In our simulations the C₆₀ breaks when the number of added atoms inside the C₆₀ approaches 20. However, the stability of C₆₀ may be increased considerably if the C₆₀ is nested inside bigger carbon shells.²

ACKNOWLEDGMENT

This work has been supported by the Academy of Finland.

---

*Present address: Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK.


PROPERTIES OF SMALL CARBON CLUSTERS INSIDE . . .


PHYSICAL REVIEW B 65 245423


245423-9