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Properties of small carbon clusters inside the C_{60} fullerene

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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.

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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 onions[2] 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-workers[3,4] using *ab initio* self-consistent field (SCF) Hartree-Fock (HF) methods, by Dunlap and co-workers[5,6] 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 schemes[12] 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 potential[14] 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 growth[19] 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.*[26] 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.[27] 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[28] 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[29,30] while a similar larger structure containing 300 atoms remains relatively stable under thermal treatment at 2700 K,[30] 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[31] 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,[11,32] and for modeling diffusion processes[33] and nanointendation.[34] It has been shown by intense studies of amorphous carbon systems[36–38] 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.*[39] 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)].[31] 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.[31] 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 in depth description of this method one should consult the paper by Briddon and Jones.[35]

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.[20]

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 an 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.

Atoms	Bond lengths (Å) (SCC) (this work)	Bond lengths (Å) (non-SCC, Ref. 32)	Bond lengths (Å) (CCD, Ref. 20)
2	1.241	1.244	1.245
3	1.293	1.288	1.278
4	1.297, 1.324	1.288, 1.321	NA
5	1.279, 1.307	1.256, 1.315	1.271, 1.275
6	1.287, 1.320, 1.286	1.265, 1.324, 1.287	NA
7	1.277, 1.313, 1.292	1.245, 1.337, 1.280	1.270, 1.280, 1.264
8	1.282, 1.321, 1.285 1.312	1.253, 1.335, 1.279 1.308	NA
9	1.276, 1.317, 1.288 1.298	1.240, 1.350, 1.263 1.302	1.269, 1.283, 1.261 1.269
10	1.280, 1.322, 1.284 1.311, 1.286	1.246, 1.345, 1.269 1.311, 1.284	NA

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[11] within the DFTB method to be $\sim$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 neglible 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[40] (1.45, 1.40 Å) and gas-phase electron diffraction[41] (1.46 Å, 1.40 Å) as well as with the results of more sophisticated SCF-LDA calculations[5,42] (1.45, 1.39 Å) and computations at the SCF-HF-MP2 level of theory[4] (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[20] and the previous DFTB results by Porezag *et al.*[32] 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 can not 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 $(E_{N-1}+E_{free}-E_N)/N$ where N is the number of atoms in the cluster under consideration, (E_N is the total energy of the N-atom cluster, E_{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[20,21] 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/at., 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-

TABLE II. The heats of formation per atom for chain and ring structures (including the C_{60} shell atoms). A positive number indicates that the reaction is energetically favorable (exothermic).

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

ergy 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.

C_2 dimers and C_3 trimers inserted into C_{60} 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 C_{60}. 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 C_{60}. 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/at. 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 sp^3-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 III. The binding energies for the structures consisting of C_{60} and a molecule inside. For comparison, the binding energies for the system consisting of the molecule in free space and the empty C_{60} are listed in the fourth column, in the cases when the C molecule is stable in free space.

Atoms in cluster	Seed configuration	Binding energy/ atom (eV) (molecule inside C_{60})	Binding energy/ atom (eV) (free molecule and C_{60})
0	Plain C_{60}	8.91 (TB)	
2	Dimer	8.79 (TB)/8.59 (LDA)	8.78
3	Trimer	8.78/8.64	8.80
4	Four-membered chain	8.73/8.48	8.76
5	Trigonal bipyramid	8.71/8.49	8.74
5	Five-membered chain	8.65/8.47	8.78
5	Five-membered ring	8.70/8.53	8.74
6	Six-membered chain	8.64/8.50	8.75
6	Planar six-membered ring	8.68/8.54	8.73
6	Armchair six-membered ring	8.69 (TB)	8.73
7	Seven-membered ring	8.63/8.47	
7	Eight-membered ring	8.56/8.40	8.68
7	Nine-membered ring	8.43/8.29	8.71
10	Double five-membered ring	8.53/8.30	
12	Double six-membered ring	8.40/8.17	8.62

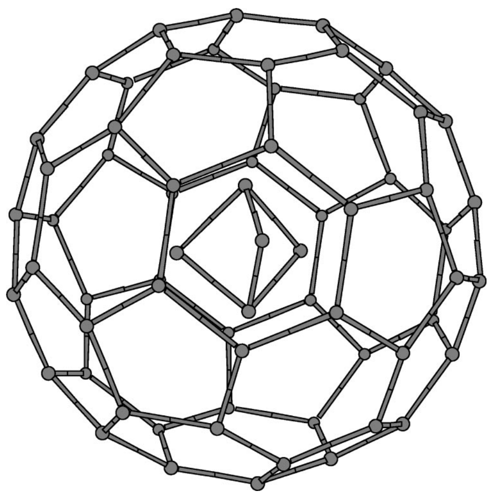

FIG. 1. The C_{60} fullerene containing the trigonal bipyramid cluster.

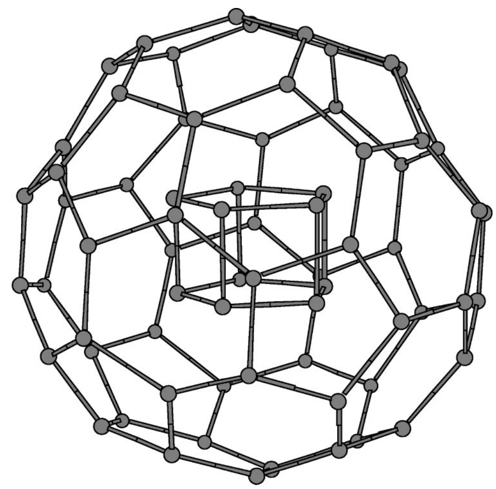

FIG. 2. The C_{60} fullerene containing the double stack of five-membered rings.

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.[20,21] 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 ~ 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 $\sim 25°$ to $\sim 5°$. 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/at. less stable than C_{60} and the bond lengths in the bipyramid are about 1.47 Å long, indicating only partial π 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/at. higher in total energy than C_{60} (see Table III). A seven-membered ring inserted into the fullerene is 0.10 eV/at. more stable than the five-membered ring stack. The seven-membered ring is stabilized, as the strong π 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.[43] A similar double five-membered ring stack in free space has theoretically been found as a metastable minimum for phosphorus.[44]

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 expection is that the planar C_6 ring is the more stable configuration 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 4.2e 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 $\sim 0.2e$ towards the ring, and the system gains an electric dipole moment of ~ 0.09 e Å. The seven-membered ring system is also polarized with an electric dipole moment of $\sim 0.04e$ Å. For an eight-membered ring the total charge flow is 0.3e towards C_{60}. The reduction of valence takes place in the ring atoms forming bonds with C_{60}, amounting to $2\times 0.2e$ and 2×0.1 e, whereas the other cluster atoms gain excess charge. The C_{60} with an eight-membered ring system has a zero 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 AIMPRO to study the electronic properties of $C_{60}+X$ atom clusters.[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.

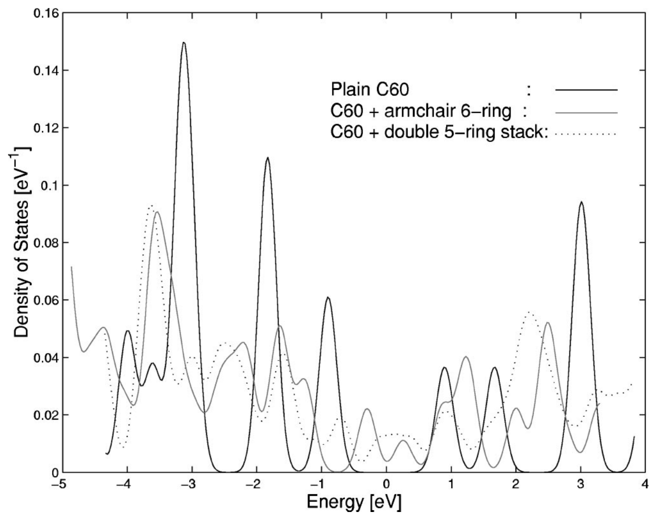

FIG. 3. The total densities of states for the empty C_{60} (dark solid line) and for the C_{60} containing an armchair six-membered ring (light solid line) and double stack of five-membered rings (dotted line). The Fermi energy is at the zero point of the x axis.

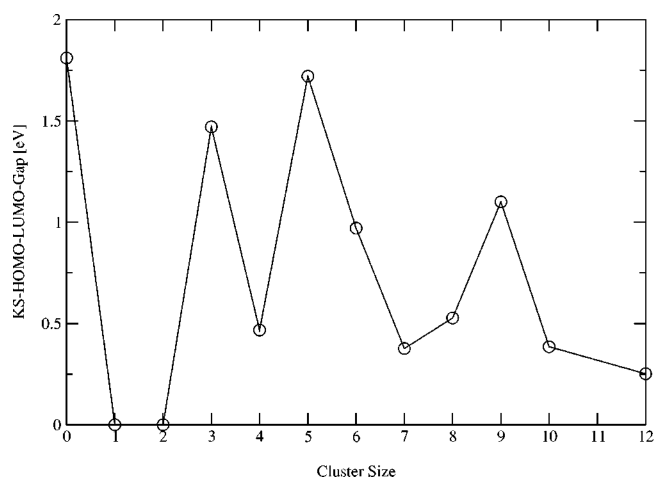

FIG. 4. The size of the electronic HOMO-LUMO gap as the function of the filling of C_{60} fullerene.

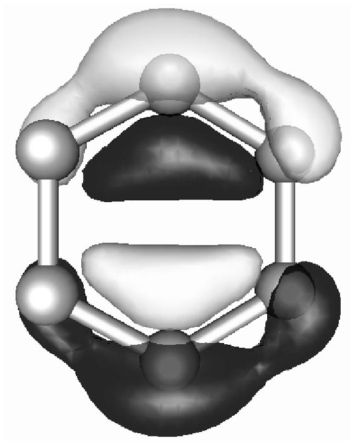

FIG. 5. The DFT-LDA HOMO level of $C_{60}+C_6$. This type of bonding-antibonding combination of wave functions is not present with C_6 in free space. Only the C_6 molecule inside the fullerene cage is shown.

C. Random filling

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_{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/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 two three-membered rings, and bonded to C_{60}. Up to 17 additional carbon atoms inside the outer C_{60} fullerene shell, though heavily distorted, is still reminiscent of the original C_{60} ball. We were not able to introduce 18 atoms or more without severely damaging the outer shell thus establishing the filling threshold accordingly.

TABLE IV. The binding energies for random structures inside the C_{60} fullerene.

Atoms in cluster	Binding energy/atom (eV) (including C_{60} atoms)
5	8.70
6	8.64
7	8.60
8	8.57
9	8.52
10	8.50
11	8.47
12	8.43
13	8.40
14	8.37
15	8.35
16	8.30
17	8.27
18	8.28

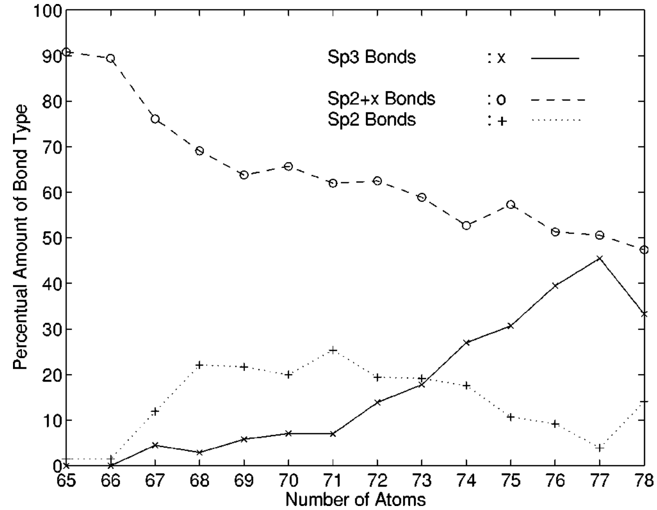

FIG. 6. The development of the atomic bonding during the random filling of the C_{60} fullerene. The sp^{2+x}'s bonded atoms have nonplanar threefold coordinated bonds. The fractions of atoms with sp^1 bonds, unbonded atoms, or unidentifiable bond geometries are not displayed.

During the random filling the amount of sp^3 bonded atoms in the total structure increases significantly. A considerable amount of the former C_{60} atoms are transformed from their original sp^2-like state to an sp^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.[36] We 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_{60} are classified as sp^{2+x}, indicating trigonally bonded atoms with a nonplanar local geometry with a hybridization somewhere between graphite (sp^2) and diamond (sp^3). Most atoms prefer three-fold or fourfold coordination indicating that the formation of numerous single bonds is preferred during subsequent addition of atoms over the formation of π bonds within separated ring structures inside the fullerene that would make the atoms in the C_{60} twofold coordinated. Also, it is not expected that the atoms rearrange at a later step into rings since this would require breaking many of the formerly established single bonds and would thus require overcoming large energy barriers. When reaching the filling threshold the carbon sp^3 fraction decreases due to the breakdown of C_{60}, revealing the importance of the confinement of the fullerene. As soon as this constraint for the inner atoms is lifted the structure suddenly has more freedom to relax towards a more graphitic material.

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 C_{60}. 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 C_{60} 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 C_{60}, while in larger ring systems the situation is reversed.

The C_{60} 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 C_{60} 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.

C_{60} possesses enough rigidity to confine internal carbon atoms into a relatively small stressed region that cannot fully relax. Short chains can be accommodated into C_{60} and all of them (apart from the dimer) have geometries with bond angles below 180°, in contrast to the unconstrainted 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 C_{60} shell. Initial defects in the shell may reduce its capacity of 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 sp^3-rich structure is further supported by the formation of bonds between the confined cluster and its surrounding C_{60} 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 C_{60} 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 C_{60}. A strong increase of the sp^3 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 C_{60} is below 20.

C_{60} 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 C_{60} breaks when the number of added atoms inside the C_{60} approaches 20. However, the stability of C_{60} may be increased considerably if the C_{60} is nested inside bigger carbon shells.[2]

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