Energetics and structural characterization of C\textsubscript{60} polymerization in BN and carbon nanopeapods

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As in the case of carbon nanotubes, also boron nitride nanotubes may host arrays of C\textsubscript{60} molecules and form a nanopeapod (NPP). The observed separation between C\textsubscript{60} molecules in BN NPP’s is consistently shorter than in carbon NPP’s, which influences their electronic properties. Here we report on total-energy pseudopotential density functional theory (DFT) calculations for polymerized and nonpolymerized C\textsubscript{60} chains, and optimize their atomic structures to provide a description of their energetic landscape. A fully polymerized C\textsubscript{60} chain and a C\textsubscript{60} dimer are found to be more stable than nonpolymerized C\textsubscript{60}, respectively, by 0.89 and 0.38 eV/C\textsubscript{60}. The geometry and energetics of an encapsulated C\textsubscript{60} chain is not significantly different with respect to the isolated molecule. Encapsulation energies in BN and carbon NPP’s are, respectively, 1.56 and 1.67 eV/C\textsubscript{60}, which are significantly larger than the calculated activation energy for C\textsubscript{60} polymerization, supporting the hypothesis that encapsulated C\textsubscript{60}’s in NPP’s are partially polymerized. Band structure analysis show that polymerization does not affect the gap width of the C\textsubscript{60} chain. BN NPP’s are semiconductors with a gap width determined by the C\textsubscript{60}. The lowest unoccupied C\textsubscript{60} states lie just above the Fermi level in metallic carbon NPP’s and charge transfrt could take place, affecting the C\textsubscript{60} geometry.

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Since their discovery in 1991, carbon nanotubes (CNT) have received a great deal of attention in materials science research. Experimental and theoretical work revealed interesting electronic properties for these materials, making them possible building blocks for technological applications. This is particularly true for electronics, where they may constitute the basic ingredients for the realization of molecular-scale electronic devices. Additionally, the hollow core of CNT’s and their chemical properties may be appropriate for nanometric engineering of novel materials.

High-resolution transmission electron microscopy (HR-TEM) experiments have provided the first observations of nanopeapods (NPP’s), with differing assemblies of fullerences encapsulated within the CNT’s. Depending on the internal diameter of the host nanotubes, the encapsulated molecules are packed in more or less complex arrangements. Experiments, corroborated by theoretical calculations, have shown that nanotubes with diameters of \( \sim 10 \) Å may host a single chain of aligned C\textsubscript{60} molecules. The spacing between C\textsubscript{60} molecules is \( \sim 10 \) Å and the separation between C\textsubscript{60} and the nanotube wall is \( \sim 3 \) Å. These distances are similar, respectively, to the spacing in close-packed C\textsubscript{60} (Ref. 7) and the separation between graphite layers, which are both systems known to be weakly bound by van der Waals forces.

In large-diameter nanotubes, fullerene arrangements appear close-packed and noncrystalline. A NPP can be viewed as a functionalized nanotube, where the electronic structure of the host species is modified and controlled by the encapsulated species, which results in changes to the electronic transport properties. On the other hand, confined arrangements of fullerenes, with different characteristics with respect to crystalline ordering, may become relevant both as proper materials themselves or as precursors for the preparation of coaxial nanotubes.

Another material which may form similar nanotubular structures is boron nitride. Recent experiments have confirmed theoretical predictions\cite{11} of the possibility of embedding C\textsubscript{60} molecules in boron nitride nanotubes (BNNT). Interestingly, it has been noticed in TEM experiments\cite{7} that C\textsubscript{60} molecules in BN NPP’s are 3–10 % more closely spaced than in carbon NPP’s, and this observation is confirmed also in TEM images showing both BN and carbon NPP’s at the same time\cite{12}. This spacing is comparable to that of orthorhombic C\textsubscript{60}\cite{13} which is made of parallel polymerized linear chains of C\textsubscript{60} with a spacing between molecules of 9.12 Å and connected by four-membered rings obtained by joining two hexagon-hexagon bonds on neighboring molecules through a process known as \([2+2]\)-cycloaddition. C\textsubscript{60} polymerization has already been taken into account for the C\textsubscript{60} coalescence under electron beams, but these observations seem to indicate that a certain degree of covalent bonding can be spontaneously present also in undamaged BN peapods, while remaining undetectable in TEM images. Covalently bound C\textsubscript{60} polymers have distinct electronic properties with respect to weakly coordinated solid C\textsubscript{60}. The physical behavior of NPP’s may be similarly affected by the polymerization of the encapsulated molecules.

Extended analyses of the electronic properties of semiconducting and metallic carbon NPP’s have been performed, while recent works have focused on possible mechanisms of formation of carbon\cite{18} and BN NPP’s.\cite{19,5,6,11,20} Okada et al.\cite{5,6,11,20} have reported on a series of first-principles calculations comparing atomic and electronic structures of BN and carbon NPP’s. However, none of the mentioned works has taken into consideration the effects of polymerization on the encapsulated species, and consistently treated all these structures with an \textit{ab initio} approach. In this paper we consider various possible structures of C\textsubscript{60} chains, with molecules either weakly interacting or polymerized, isolated or encapsulated in BN and carbon nanopeapods. We analyze the modifications to the atomic and electronic struc-
tures caused by encapsulation and polymerization using first-principles total-energy calculations. On the basis of our results, similarities and differences between structural and electronic properties of BN and carbon nanopeapods are examined.

Our calculations are performed using density functional theory within the local density approximation (LDA) for the exchange-correlation functional. It has been pointed out that DFT-LDA calculations of graphitic structures, in which van der Waals interactions play a major role, give inaccurate results when intermolecular distances exceed typical van der Waals distances by more than ~15%. We take care that our simulations are limited to structures within this range, while making use of the reliability of DFT in consistently calculating configurations with different levels of covalent bonding. Norm-conserving pseudopotentials in the Kleinman-Bylander form are used for all atomic species. The electronic wave functions are expanded in a basis of localized atomic orbitals, and are calculated on a cell multiple of the simulation cell, to improve the sampling of the reciprocal space. Because of the possible presence of delocalized electronic states in the systems under study, a careful choice of additional orbitals augmenting the atom-centered ones is required to obtain accurate results. This requires particular attention to maintain consistency between calculations performed on systems with different atomic configurations, particularly with respect to energetics and geometries. For our calculations, we choose a double-zeta polarized basis set augmented by floating atomic orbitals to improve the description of regions far away from where the atoms are located.

To test the accuracy of our approach, the optimized structures for an isolated C\(_{60}\) molecule and for empty boron nitride and carbon (10,10) nanotubes have been obtained. The C\(_{60}\) structure has two characteristic bonds: one shared by two hexagonal faces, and the other by a pentagon and a hexagon. Our calculated values for these two bond lengths are, respectively, 1.403 Å and 1.450 Å, in excellent agreement with those obtained from electron diffraction experiments on gas-phase C\(_{60}\), which are respectively 1.401 Å and 1.458 Å. The relaxed structure of a carbon (10,10) nanotube is univocally defined by two independent parameters, corresponding to two possible bond lengths, \(d_\perp\) for the bond perpendicular to the nanotube axis, and \(d_\parallel\) for the one with a component parallel to the axis. A BN (10,10) nanotube has an additional buckling parameter \(\rho\), which corresponds to the difference between the distance of a nitrogen and a boron atom from the tube axis. Our calculated values are compared with previous calculations for BNNT’s (Ref. 27) and experimental results for CNT’s (Ref. 28) in Table I.

The accuracy of our choice for the localized orbital basis has been tested also by comparing electronic band structures and densities of states obtained with this approach and with results from similar pseudopotential total-energy DFT calculations, where a plane wave basis set defined by a cutoff energy of 70 Ry is used to expand the electronic wave functions. All features of the electronic structure are in good agreement, both qualitatively and quantitatively, between the two calculations.

Before proceeding to investigate nanopeapods, we have to consider an important limitation to our approach, which uses a finite simulation cell repeated in space with periodic boundary conditions. The periodicity of an encapsulated C\(_{60}\) chain may be incommensurate with the nanotube periodicity because of the very weak potential barriers against sliding or rotations of the C\(_{60}\) inside the nanotube. For this reason, it would not be possible to continuously relax the spacing between the encapsulated molecules and preserving the periodicity of the system at the same time to fully optimize the atomic structure.

Therefore, we start our simulations with an isolated C\(_{60}\) chain [Fig. 1(a)]. Each simulation cell contains one molecule, with its transverse sizes fixed, to maintain a 15 Å center-to-center distance between neighboring chains. The chain axis is aligned along the \(z\) direction and crosses the middle points of two opposite hexagon-hexagon bonds of the molecule. With this choice, molecules are correctly oriented to polymerize by [2+2]-cycloaddition or, in the case of single bonded chains, stabilized only by doping anions. We define \(d\) as the center-to-center distance between two adjacent molecules in a chain, and \(l\) as the shortest distance between atoms on two adjacent molecules. Two series of calculations are performed. One starts with \(d=15\) Å, corresponding to approximately isolated molecules, and the other one with \(d=9\) Å, which is close to the configuration of a polymerized chain. In

![FIG. 1. Atomic structures of (a) a polymerized chain of C\(_{60}\) molecules; (b) a (C\(_{60}\))\(_2\) dimer. The center-to-center distance in the polymer is \(d\), the intermolecular bond length or shortest intermolecular distance is \(l\), and the dimer length is \(L\).](https://example.com/figure.png)
energetic dependence on \( d \) is realized. The polymerized and nonpolymerized minimums differ by small amounts for each run, we ensure that the starting configurations do not get out of the basin of stability of either polymerized or nonpolymerized configurations. In this way, we obtain the energy dependence on \( d \) for both chain structures and determine their respective lowest energy configurations.

The results of the calculations are reported in the inset of Fig. 2. Fitting the data with cubic splines, we find that the weakly interacting chain reaches its lowest energy at \( d = 9.96 \) Å, with \( l = 3.015 \) Å, which can be compared to \( l = 2.98 \) Å calculated from data in Ref. 7. Up to \( d \approx 9.6 \) Å the molecule preserves the structure of an isolated \( C_{60} \) with nearly spherical symmetry. At shorter distances, a repulsive barrier between molecules builds up and the resulting compression along the chain axis flattens the molecule, giving rise to an increase in the transverse diameter by 2−3% when \( d \) changes from 9.6 to 8.4 Å. The shortening of \( d \) is realized in equal parts by a reduction of the \( C_{60} \) diameter along the axis and of the intermolecular distance. The polymerized structure reaches its minimum energy at \( d = 9.03 \) Å, with the formation of two pairs of bonds connecting each molecule to its two neighbors with a length \( l = 1.568 \) Å (estimated value 1.57 Å from fitting experimental data)\(^3\). The polymerized structure is energetically more stable, with a polymerization energy (given by the total energy difference between polymerized and nonpolymerized minimums) \( \Delta E_{\text{poly}} = 0.89 \) eV/\( C_{60} \). Previous first-principles calculations\(^3\) have obtained a value of 0.44 eV/\( C_{60} \), with a 9.127 Å separation between molecules and a 1.600 Å intermolecular bond length. The equilibrium structure of a molecule in the polymerized chain is a cylindrically symmetrical ellipsoid with eccentricity 0.933. Most of the change (86%) in the period-
FIG. 3. Energetic landscape of a dimer (C₆₀)₂, representing the dependence of the total energy of two possible configurations with respect to the dimer length L and shortest intermolecular distance l: dotted, nonpolymerized chain; dashed, polymerized chain. The solid curves represent the profile of the potential barrier between the two configurations for various values of L. In the inset details of the total energy dependence on L are given.

distant bonds defines the dimer total length L. All the configurations are described on the basis of these two parameters. Minimum-energy configurations are obtained by fully relaxing all atoms. For nonequilibrium configurations, we fixed L by constraining the positions of the four atoms of the two most distant hexagon-hexagon bonds. In this way we avoid having the system spontaneously relax to the equilibrium structure. Since in the optimized bonded dimer the atomic positions at opposite ends of the dimer are not significantly distorted with respect to an isolated C₆₀ molecule, the constraints are not expected to significantly affect the energetics of the dimer.

The inset of Fig. 3 shows the results of these calculations. The equilibrium structure of the nonbonded dimer is the same as in the case of the nonpolymerized chain. The optimized bound dimer has a lower total energy than the nonbonded dimer, with a difference ∆E = 0.38 eV/C₆₀. As expected, this energy is approximately half of that obtained for the full polymerization since now each molecule forms only one pair of bonds with its only neighbor. We mention that a polymerization energy of 0.35 eV/C₆₀, in excellent agreement with ours, while calculated fullerenes and nanotube walls are not expected to extend longer than the typical van der Waals distance (3–4 Å).

The encapsulation energy is calculated as ∆E_encaps = E[C₆₀@NT] − E[NT] − E[C₆₀]. Since ∆E_encaps is obtained by comparing calculations for different systems, we must ensure that all results are obtained with a consistent atomic basis set. For this reason, the same basis set used to calculate the combined system is also used for the calculations on the single components. To describe accurately the near-free-electron-like states in the conduction band of the nanotubes, the basis set is augmented with 1s-like atomic orbitals evenly distributed at 1 Å distance inside and outside the nanotube.

The resulting encapsulation energies for a boron nitride and a carbon (10,10) NPP are, respectively, 1.56 and 1.67 eV/C₆₀. These results are fairly consistent, within the accuracy of these calculations, with previous estimates of ∆E_encaps similarly based on a local-density DFT approach, which gave ∆E_encaps = 1.267 and 1.73 eV/C₆₀, respectively, for a BN and a carbon (10,10) NPP. The result for an all-carbon NPP is in particularly good agreement with ours, if we consider the wide range of values (between 0.4 and 3.0 eV/C₆₀) provided by other calculations using empirical potentials. The relaxed geometry of the encapsulated fullerenes show no significant change with respect to isolated molecules. Relative changes in geometric parameters are of the order of 10⁻³, smaller than the expected accuracy of the calculations. In particular, no significant difference is noticeable between structures of BN- or carbon-encapsulated molecules. No covalent bonds are formed between C₆₀ and the nanotube walls, which interact only with weak van der Waals forces.

To compare values for the dimerization energy and potential barriers previously obtained for the isolated systems with those in the corresponding encapsulated species, calculations...
were performed on systems consisting of a \((\text{C}_{60})_2\) dimer (either weakly or covalently bonded) in an 8-unit-cell (10,10) boron nitride or carbon nanotube, obtaining their fully relaxed configurations. The energy gain from the encapsulation of a dimer is not significantly different from that of an isolated molecule. The calculated dimerization energy in the BN nanopeapod is 0.37 eV/\text{C}_{60}, with an activation energy of 0.58 eV/\text{C}_{60} with respect to the nonbonded dimer. Similar results have been obtained for the dimerization energy in carbon nanopeapods. Comparison of these values with those previously calculated for an isolated dimer shows the negligible effects that encapsulation has on the geometry and energetics of a fullerene dimer. Strong interactions with the nanotube have been initially considered to explain the shorter \text{C}_{60} separation in BN versus. carbon NPP’s,\(^{10}\) but this is not confirmed by our results. The energetic landscape of isolated \text{C}_{60} configurations can be considered to accurately represent the energetics of polymerized and nonpolymerized nanopeapods.

The calculated potential barriers are too high for thermally induced dimerization in NPP’s even at the high temperatures \((\sim 1000 \text{ K})\) at which they are usually synthesized. However, comparing the calculated values for \(\Delta E_{\text{encaps}}\) with the activation energy for dimerization, we observe that a \text{C}_{60} molecule entering the nanotube gains enough kinetic energy to overcome the potential barrier and spontaneously dimerize, given the absence of strong energy loss mechanisms, as confirmed by MD calculations on relative motions of fullerenes in nanotubes\(^{18}\) or of coaxial nanotubes.\(^{19}\) Therefore, partial or full polymerization of \text{C}_{60} molecules in NPP’s could indeed take place in experimental samples, as it appears to be proven at least in BN NPP’s by the observed shorter separation between encapsulated molecules. Such a speculation was already proposed based on electron energy loss spectroscopy experiments, which measured the separation of \text{C}_{60} molecules encapsulated in single-walled carbon nanotubes to be 9.77 Å.\(^{41}\)

Because of the exothermicity of the encapsulation process, the spacing of the \text{C}_{60} molecules must be adjusted to account for the effective compression given by their favorable closer packing in a fixed volume. Given the dependence of the \text{C}_{60} chain energy with respect to the molecule separation \(d\) as \(E(d)\), and defining \(d_0\) as the value of \(d\) that minimizes \(E(d)\), the effective enthalpy to minimize is \(H(d)=E(d)−\Delta E_{\text{encaps}}(d_0−d)/d_0\). Taking \(E(d)\) from our calculations (Fig. 2), and considering \(\Delta E_{\text{encaps}}\) a constant (on the basis of our previous results), the value of \(d\) which minimizes \(H(d)\) for the weakly interacting polymer is \(\sim 9.8\) Å, 2\% shorter than \(d_0\). The effect of compression on the covalently bonded polymer is negligible.

The electronic structure of an isolated fullerene molecule is well known:\(^{42}\) the highest occupied \(h_u\) state is fivefold degenerate, with a 1.7 eV gap separating it from the lowest unoccupied \(t_{1u}\) state, threefold degenerate; a second-lowest unoccupied \(t_{2g}\) state, also threefold degenerate, lies 0.66 eV above the LU state. This structure is still recognizable in the nonbonded \text{C}_{60} chain polymer, as shown in Fig. 4(a). The degeneracy of the states is lost, but there is no mixing between bands coming from states of different symmetry. The calculated direct gap at \(\Gamma\) is 1.15 eV, close to the gap of fcc solid-phase \text{C}_{60}. Figure 4(b) shows the band structure around the Fermi level for the polymerized chain. Strong mixing occurs between the molecular states, which cannot be distinguished anymore with respect to the symmetries of the isolated molecules. The calculated gap width is 1.14 eV, in excellent agreement with previous tight-binding calculations,\(^{43}\) and it is interesting to notice how the gap width hardly changes at all upon polymerization.

After encapsulation of a fullerene nonbonded chain or of a bonded dimer in a BN nanotube, we find that the resulting band structures close to the gap region may be described as a simple overlap of the bands of the single constituents. This is easily explained in terms of the wide-gap (\(\sim 5\) eV) semiconducting nature of BNNT’s and the weak interactions between encapsulated molecules and the nanotube wall. The resulting BN nanopeapods are semiconductors with a \(\sim 1\) eV gap width, determined by the encapsulated \text{C}_{60}. The bands of the bonded dimer have very small dispersion, because of the wide (\(>4\) Å) separation between dimers, and the stronger localization of the wave functions. On the other side, as shown by Fig. 5, encapsulation in a metallic carbon (10,10) nanotube produces interesting effects in the band structure of the resulting nanopeapods. Both for a nonbonded \text{C}_{60} chain or a \text{C}_{60} double-bonded dimer, there appears to be a small hybridization between fullerene and nanotube states. The Fermi level is still determined by the two crossing bands of the nanotube, but, in both configurations, the lowest conduction bands coming from the \text{C}_{60} molecules are only slightly above the Fermi level. Previous works\(^6\) have already proposed similar band structures for metallic nanopeapods, describing their electronic transport properties in terms of multielectrons even distributed between nanotube and fullerenes. Because of the proximity of the \text{C}_{60} states to the Fermi level, charge transfer can be expected to happen from the nanotube to the encapsulated species, which could lead to stabilizing other configurations, such as single-bonded polymers, as is known to happen in the presence of alkaline metals as electron donors.\(^{32,44,45}\)
FIG. 5. Band structures in the region close to the electronic gap for the equilibrium configurations of: (a) a nonbonded C$_{60}$ dimer encapsulated in a (10,10) carbon nanotube; (b) a double-bonded C$_{60}$ dimer encapsulated in a (10,10) carbon nanotube. The position of the Fermi level is indicated by a dashed line.

In conclusion, optimized geometries for various conformations of a chain of C$_{60}$ molecules (nonpolymerized, dimerized, and fully polymerized) have been calculated. Encapsulation in a BN or carbon nanopeapod does not change either the geometries or the relative energies of the various conformers with respect to the isolated species. On the basis of these results, we predict that encapsulated C$_{60}$ is likely to be at least partially polymerized, and the calculated geometries for such structure agrees well with experimental data on BN nanopeapods. Kinetic energy gained after encapsulation may provide C$_{60}$ molecules with the activation energy needed for the formation of polymers. Differences in encapsulation energies or geometric distortions can be discounted as possible reasons for the observed closer packing of fullerenes in BN versus carbon nanopeapods, nor is C$_{60}$ polymerization in itself a sufficient factor to explain them. As regards the electronic properties of the systems under analysis, polymerization in a C$_{60}$ chain does not change the gap width. In particular, no significant difference is seen in the relative alignment of bands arising from fullerene and nanotube states. However, while BNNT’s remain semiconductors after C$_{60}$ encapsulation, with no charge transfer between nanotube and fullerenes, in carbon NPP’s conduction states located on the C$_{60}$ lie only slightly above the Fermi level, and charge transfer could occur, stabilizing configurations with different geometries that may correspond to the experimental observations.

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