Energetics and packing of fullerenes in nanotube peapods

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We use structure-optimization techniques to study the equilibrium packing of fullerenes in carbon nanotube peapods. Our results for nanotubes containing C_n fullerenes with $60 \leqslant n \leqslant 84$ atoms indicate that the fullerenes are more densely packed in the nanotubes than in the bulk crystal, in agreement with experimental data. We find that the reduction of the interfullerene distance, as well as a structural relaxation of fullerenes and nanotubes, results from a high internal pressure within the peapods, suggesting the use of nanotubes as nanoscale autoclaves for chemical reactions.

Following the discovery of fullerenes[1] and carbon nanotubes[2] (NTs), nanotube peapods emerged as very interesting nanostructures.[3] The first observation of the hierarchical self-assembly of C_{60} molecules and single-walled carbon nanotubes (SWNTs) to peapods by high-resolution transmission electron microscopy[3] (HRTEM) was followed by reports of other fullerenes and metallofullerenes being encapsulated in single-walled carbon nanotubes.[4,5]

Some of the structural aspects of carbon nanotube peapods are intriguing and even appear counterintuitive. In particular, the equilibrium structure of fullerenes in peapods is quantitatively different from that in bulk solids. HRTEM images,[6] electron diffraction,[7] and Raman measurements[4] suggest that the equilibrium spacing between fullerenes in peapods is smaller by 3–4 % than in three-dimensional molecular crystals, but larger than in solids based on polymerized fullerenes. This finding is unexpected, since all interfullerene distances should be equal and independent of dimensionality in close-packed systems with only pairwise nearest-neighbor interactions. Elastic deformations, associated with a fullerene-to-nanotube charge transfer in the peapod, have been offered as a tentative explanation for the reduction of the interfullerene distance.[4,7] Unfortunately, there is no independent evidence for such a charge transfer in these all-carbon systems. Also, like charges on adjacent fullerenes should enhance the interfullerene repulsion, thus increasing the interfullerene distance.

Here we investigate the energetics and packing of fullerenes upon their encapsulation in nanotubes. We find a net energy gain associated with fullerene encapsulation in nanotubes, giving rise to a "capillary force." In nanotube peapods, we find this force to compress encapsulated fullerenes with an effective pressure of the order of GPa, inducing strain in the nanotube wall. Our results indicate that the encapsulation energy of fullerenes depends only on the diameter and not on the chirality of the enclosing nanotube. For a given fullerene, we identify the optimum nanotube radius that maximizes the encapsulation energy. The encapsulation energy is lower in wider nanotubes, and it eventually approaches the adsorption energy of the fullerene on graphite in very wide tubes. Also in narrow nanotubes, encapsulation is energetically less favorable and may even become endothermic. We map our total energy results for specific fullerene-nanotube combinations onto a continuum model,

enabling us to make general predictions for axial separation and off-axis displacement of fullerenes in nanotube peapods.

We calculate the total energy of the fullerene-nanotube system using an electronic Hamiltonian[8] that had been applied successfully to describe the formation of peapods,[9] multiwall nanotubes,[10] the dynamics of the "bucky shuttle,"[11] and the melting of fullerenes.[12] This total energy formalism describes accurately not only the covalent bonding within the graphitic substructures, but also the modification of the fullerene-nanotube interaction due to the interwall interaction. Within this total energy functional, we optimize selected structures using the conjugate gradient technique. In a second step, we map these results onto a continuum model, which provides a better understanding of what causes a change in the packing structure within peapods, and which also yields analytical expressions for the packing geometry of given fullerene-nanotube combinations.

The energetics of fullerene encapsulation is described in Fig. 1. A static "capillary" force F [depicted in Fig. 1(a) and associated with the energy gain across a finite distance Δ_z during fullerene encapsulation] compresses other fullerenes in the peapod. The encapsulation energy[13] ΔE of isolated C_{60} and C_{84} fullerenes in single-walled nanotubes with radii in the range $0.6 \text{ nm} \lesssim R_{NT} \lesssim 0.8 \text{ nm}$ is shown in Fig. 1(b). The results of our atomistic calculations, given by the data points, also reflect the relaxations in the nanotube peapod system. These data indicate how energetically favorable the encapsulation process is for a particular fullerene-nanotube combination. Following our expectations, only nanotubes with a radius R_{NT} beyond a threshold value may encapsulate a particular fullerene with an energy gain. We find that the encapsulation energy ΔE depends primarily on the nanotube radius and does not depend significantly on the chiral index (n, m) of a particular nanotube. We find the minimum of the $\Delta E(R_{NT})$ curve, reflecting the favorable fullerene and nanotube combination, at $\approx 0.4 \text{ eV}$ for $C_{60}@(10,10)$ and $C_{84}@(11,11)$. This value agrees with the *ab initio* calculations,[14] but is lower than the empirical fits to experimental data.[15] In general, we find the optimum snug fit to occur at $R_{NT} \approx R_F + 0.3 \text{ nm}$, where R_F is the fullerene radius. Increasing the nanotube radius reduces the snug fit and the fullerene-nanotube attraction. For very large tube radii, the encapsulation energy should approach the fullerene adsorp-
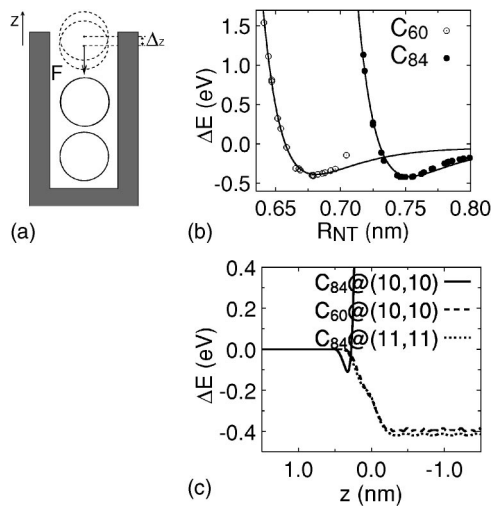
FIG. 1. Energetics of fullerene encapsulation. (a) During its insertion into a nanotube, a fullerene is pulled in by a "capillary" force F, which is linked to the energy gain upon axial displacement Δz. (b) The encapsulation energy ΔE of isolated C_{60} ($\bigcirc$) and C_{84} ($\bullet$) fullerenes in single-walled carbon nanotubes with radii ranging from $0.6 \text{ nm} \lesssim R_{NT} \lesssim 0.8 \text{ nm}$. (c) The energy change during the fullerene insertion process along the tube axis z, with $z=0$ denoting the tube end. C_{60} and C_{84} are pulled into the best fitting $(10, 10)$ and $(11, 11)$ nanotubes by a force $F=-\Delta E/\Delta z \gtrsim 0.1$ nN close to the tube end. The high energy cost prevents spontaneous entry of the C_{84} fullerene into the narrow $(10, 10)$ nanotube.

tion energy on planar graphite. As expected, fullerene encapsulation is energetically less favorable and eventually turns endothermic with a decreasing tube radius.

Close inspection of the structural relaxations in optimized peapods, both in the absence and the presence of an external force F, reveals that the major modifications occur in the interfullerene and fullerene-nanotube distances, with only a minor shape deformation of the fullerenes and the enclosing nanotube. Furthermore, we have found that the continuum approximation,[16] which ignores discrete atomic positions, provides a good estimate of the packing geometry. Indeed, our data in Fig. 1(b) for near-spherical C_{60} and C_{84} fullerenes in various (n, m) nanotubes lie very close to the model predictions for perfect spheres inside smooth tubes, given by the solid lines.

As mentioned above and shown in Fig. 1(c), the maximum energy gain upon encapsulation is close to 0.4 eV in the case of the snug fit of $C_{60}@(10, 10)$ or $C_{84}@(11, 11)$. This energy gain near the tube end at $z=0$ occurs across a short distance of $\Delta z \approx R_F \approx 0.5$ nm, resulting in a typical capillary force of $F \gtrsim 0.1$ nN. Even though the insertion of C_{84} inside the narrow $(10, 10)$ nanotube is strongly energetically unfavorable, the potential well near the tube end may be used to manipulate a fullerene, which would adhere to a carbon nanotube tip of a scanning probe microscope (SPM).[17,18]

At nonzero temperatures, the interfullerene distance is affected by "dynamic" forces, which are especially important in partly filled peapods, where the static capillary force vanishes. In that case, we need to consider the vibrations of the nanotube wall and the thermal motion of the encapsulated fullerenes, described by the Maxwell-Boltzmann velocity
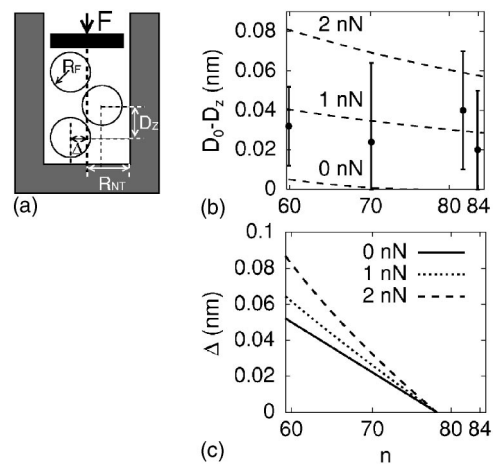

FIG. 2. Equilibrium packing structure of fullerenes in peapods. (a) An external capillary force F reduces the axial interfullerene distance D_z. An off-axis fullerene displacement Δ is expected especially if the fullerene radius R_F is much smaller than the nanotube radius R_{NT}. (b) The reduction of the axial interfullerene distance D_z in peapods with respect to the equilibrium separation D_0 in bulk crystals of C_n fullerenes with 60–84 atoms. The observations for different fullerenes inside a 1.4-nm-wide nanotube, reported in Ref. 7 and given by the data points with error bars, are compared to our analytical results for various applied forces F, shown by the dashed lines. (c) The predicted off-axis displacement Δ inside a 1.4-nm-wide nanotube as a function of the fullerene size, for various applied forces F.

distribution. Independent of the filling fraction, the time-averaged dynamic force exerted during a central collision between a fullerene and a one-dimensional (1D) fullerene chain amounts to ≈ 0.5 nN at room temperature, tending to decrease the interfullerene distance. Finally, the volume contraction in the fullerene-free nanotube segments at nonzero temperature,[19] caused primarily by a low-frequency pinch mode of the wall, is expected to further compress the fullerene arrays in the partly filled peapods. In view of the small cross section of the nanotube, the effective compressive force in the nN range translates into an effective pressure in the sub-GPa range. This effective pressure modifies the packing geometry, in particular reducing the interfullerene distance.[4,7] In view of this high effective pressure, the nanotube may be considered a nanoscale pressure container or autoclave.

The equilibrium geometry of the encapsulated fullerenes, which are subject to an external force F, is discussed in Fig. 2. This force can be thought of as being mediated by a "piston," shown schematically in Fig. 2(a). The main effect of the effective pressure is to reduce the axial interfullerene distance D_z and to increase the off-axis displacement Δ. We focus our investigation on peapods based on 1.4-nm-wide nanotubes, which are most abundant among the single-walled nanotubes, and which have been used in Ref. 7. In our atomistic calculations, we consider the most stable fullerene isomers with 60–84 atoms, select the $(18, 0)$ nanotube to represent the 1.4-nm-wide nanotubes of Ref. 7, and perform a global structure optimization for a given applied force. We find also that these results can be reproduced well

by a continuum model, which considers rigid spheres contained in a rigid tube.

As suggested by our results in Fig. 1(b), the packing geometry inside an (n, m) nanotube depends primarily on its radius, given by $R_{NT} = 3.92 \times 10^{-2}$ nm $(m^2 + mn + n^2)^{1/2}$, and not on the chiral index. For general trends, we neglect deviations from sphericity for encapsulated fullerenes, and assume their mean radius to be given by $R_F = 4.58 \times 10^{-2}$ nm $n^{1/2}$. We also assume $d_{vdW} = 0.3$ nm as the equilibrium separation between the walls of fullerenes and nanotubes in the absence of external forces. We find that near the equilibrium distance, the interaction energy between two C_n fullerenes can be expressed by a harmonic potential with the force constant $c_{FF} = (0.41n)$ N/m. In the limit of very wide nanotubes, the fullerene-nanotube interaction resembles the fullerene-graphite interaction, which also can be represented by a harmonic potential with the force constant $c_{FG} = (0.36n)$ N/m. With these values, the optimum packing structure within any peapod, consisting of fullerenes with radius R_F encapsulated inside a nanotube of radius R_{NT} and subject to an external force F, can be determined analytically from the total energy minimization.

Our quantitative results for the reduction of the axial separation between fullerenes inside a 1.4-nm-wide nanotube are presented in Fig. 2(b). A comparison between our predictions and the experimental data of Ref. 7, suggesting an interfullerene distance reduction of 3–4 %, is displayed by the data points. These data suggest that encapsulated fullerenes are likely subject to an axial compressive force in the nN range, in agreement with our estimates above.

For peapods containing fullerenes with a radius below the optimum value $R_F = R_{NT} - d_{vdW}$, a nonzero off-axis displacement[20,21] Δ of the encapsulated fullerenes is expected even for small external forces $F \rightarrow 0$. Increasing the fullerene radius leads to a more snug fit and reduces Δ, as seen in Fig. 2(c). Furthermore, in the presence of an axial compressive force, we also find a significantly larger off-axis displacement, which has been observed by HRTEM.[7] The ability of fullerenes to undergo such off-axis displacements should result in zigzag arrangements, or even more complex chiral packing structures, which have been proposed for spheres contained in a cylinder[20,22] and recently observed experimentally.[23]

In Fig. 3 we depict the strain distribution on the wall of nanotube peapods by displaying the reduction of the atomic binding energy. The schematic packing geometry of peapods containing too small and too large fullerenes is shown in Figs. 3(a) and 3(c), respectively. Our results in Fig. 3(b) suggest that the strain on the (10, 10) nanotube, induced by the C_{60} molecules, is localized near the fullerenes. When subject to an axial compressive force of 0.5 nN, the encapsulated fullerenes press towards the nanotube wall, thus locally reducing the binding energy of wall atoms by as much as 1 meV from the initial value of ≈ 7 eV/atom.

In Fig. 3(d) we display the strain on the (10, 10) nanotube wall containing the C_{84} molecules. According to our results presented in Fig. 1, the insertion of this large fullerene into the (10, 10) nanotube is energetically highly unfavorable. In this case, the fullerene is centered on the nanotube axis. Even in the absence of an external force, the larger C_{84} molecules
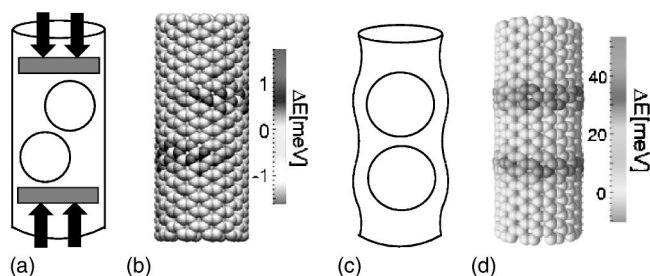

FIG. 3. Fullerene-induced strain in the nanotube walls of peapods for different packing geometries. (a) In peapods containing fullerenes equal to or smaller than the optimum size, the strain in the nanotube wall is induced by an axial force. (b) The strain distribution on the wall of a (10, 10) nanotube containing C_{60} fullerenes, subject to the axial force of 0.5 nN. (c) In peapods containing fullerenes exceeding the optimum size, the strain is induced even in the absence of an axial force. (d) The strain distribution on the wall of a (10, 10) nanotube containing C_{84} fullerenes. The strain energy is represented by the reduction of the atomic binding energy on a gray scale in (b) and (d).

locally reduce the binding energy of the atoms on the nanotube wall by as much as ≈ 50 meV. The resulting bulge on the wall is still very small, and it preserves the cylindrical symmetry of the initial nanotube.

Our results suggest two unusual applications of nanotube peapods. The first application is a possible way to separate nanotubes by diameter, due to the energetic preference of particular fullerenes to enter nanotubes within a narrow diameter range. The currently known synthesis techniques produce fullerenes and nanotubes in a wide diameter range. Whereas separation of fullerenes by isomer is possible using high-pressure liquid chromatography, there is no analogous technique allowing us to separate nanotubes by diameter. Exposing nanotubes with a wide diameter distribution to a particular fullerene should lead to a preferential formation of peapods with an optimum nanotube diameter. The fact that nanotube peapods should have a higher gravimetric density than their empty nanotube counterparts could be utilized for a physical separation of peapods with a specific diameter from other nanotubes in a sample.

A second possible application is related to the high effective pressure inside the nanotube, caused by the motion of the encapsulated fullerenes. In view of the small nanotube cross section, even forces in the nN range give rise to GPa pressures, suggesting a possible use of nanotubes as nanoscale autoclaves to facilitate chemical reactions. As a matter of fact, HRTEM observations of peapods subject to electron irradiation[24] or elevated temperatures[25] suggest a spontaneous fusion of fullerenes to long nanocapsules, in contrast to the more inert two-dimensional (2D) and three-dimensional (3D) fullerene structures.[26,27]

New phenomena may occur in nanotubes containing other systems than spherical fullerenes, which have been discussed so far. In peapods containing nonspherical fullerenes, the thermal activation of rotational degrees of freedom tends to increase the interfullerene distance with respect to the most tightly packed geometry at low temperatures.[28] Also, selected diamondoid molecules[29] are expected to enter car-

bon nanotubes spontaneously.[30] Taking advantage of the physical confinement within the nanotube template, these diamondoids may fuse to one-dimensional diamond wires at nominal pressure.

In summary, we have studied the energetics and equilibrium-packing geometry of fullerenes encapsulated in nanotubes. We found that each fullerene has an energetic preference for a narrow range of nanotube diameters for peapod formation. The resulting selective filling of particular nanotubes could be utilized to separate nanotubes according to diameter. Nanotubes, which are too narrow to encapsulate a particular fullerene, may still bind it at the open end and manipulate it when attached to a scanning probe microscope tip. We found that the insertion of a fullerene inside an optimum nanotube host is associated with an energy gain of $\gtrsim 0.4$ eV. The capillary force produced by the entering fullerene may be augmented by an average force caused by interfullerence collisions at nonzero temperatures to a value in the nN range. In view of the small nanotube cross section, this force should be equivalent to a pressure of the order of GPa. We found the observed reduction of the axial interfullerene distance to show evidence of this effective pressure. This large nominal pressure may become beneficial when using nanotube peapods as nanoscale pressure containers. The equilibrium packing geometry of smaller-thanoptimum fullerenes inside nanotubes is a zigzag arrangement, with an expected increase in the off-axis displacement with increasing pressure. The strain in the nanotube wall, associated with closely packed fullerenes, may locally modify the reactivity of the tube wall, which could be used for chemical functionalization.

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