5b

Fullerenes inside Carbon Nanotubes: The Peapods

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5b.1 Introduction

A particularly compelling possibility for filling the inner space of the SWCNTs is that with fullerenes. The existence of such a structure had been long speculated prior to its actual discovery. The speculations were fueled by the capability of fullerenes themselves of retaining atoms or molecules inside [1]. This structure is called endohedral fullerene, referring to the icosahedral \( C_{60} \) symmetry [2]. Such materials are denoted as \( A@C_{x} \) where \( A \) marks the encapsulated atom or molecule and \( x=60, 70… \) is the index of the fullerene.

\( C_{60} \) fullerenes encapsulated inside SWCNTs were discovered by Smith, Monthioux, and Luzzi at the University of Pennsylvania using high resolution transmission electron microscopy [3]. This discovery soon led to the birth of a vivid new field within the nanotube research, the field of the \textit{peapods}, as the structure was baptized. It not only provided a system of inner beauty for the field but it also led to a number of breakthroughs in the study of optical, electronic, and transport properties of the SWCNTs and to a number of applications.

The almost artistic beauty of the peapod structure is shown in Figure 5b.1. The interest in this material originates from the fact that it combines two fundamental carbon molecules: the zero-dimensional fullerene and the one-dimensional SWCNT, which both generate two
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of the carbon allotropes when periodically assembled, namely ‘fullerite’ and ‘SWCNT bundles’, respectively. The latter is sometimes referred to as ‘nanotubulite’. The fate of these two materials is further linked by the discovery that the encapsulated fullerenes merge together to form an inner SWCNT shell upon electron irradiation or heating [4,5].

Here, we review the literature of the peapods covering all aspects from discovery up until applications. Some previous reviews are available in Refs. [6,7]. This chapter is organized as follows: in Section 5b.2, the history and circumstances of the peapod discovery is discussed, followed by a classification of the different peapods in Section 5b.3. In Section 5b.4, the synthesis methods, theory of the synthesis and the peapod stability as well as the behavior of peapods under electron and light radiation and thermal treatment is discussed. The structural, electronic, optical, vibrational, and magnetic properties of peapods are discussed in Section 5b.5, followed by a summary of their realized and expected applications in Section 5b.6.

5b.2 The Discovery of Fullerene Peapods

It is well documented that the point of discovery of carbon nanotubes is a debated issue [8] but it is widely accepted that the discovery of multi-wall carbon nanotubes in the cathode deposit of fullerene synthesis experiments by the electric arc method by Sumio Iijima [9]

Figure 5b.1 Schematics of the C_{60} fullerene peapods from two viewpoints.
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attracted the attention of the scientific community to the topic. In contrast, the discovery of SWCNTs is much clearer as it was reported by two subsequent papers in Nature by Iijima and Ichihashi [10] and by Bethune and coworkers [11]. Similarly, the discovery of the peapod structure is well identified as it was reported in Nature in 1998 by Smith et al. [3].

The possibility for the existence of the peapod structure had been speculated previously but its detection had not been reported. The reason for the speculation came from the fact that $C_{60}$ has a van der Waals diameter of 0.7 nm [2] which could be optimally accommodated inside SWCNTs with diameters of 1.4 nm given an approximately 0.35 nm van der Waals distance (its exact value is 0.335 nm in graphite) between the SWCNT walls and the fullerene cages. An energetic preference for this structure is given by the nature of the molecular orbitals: both the $C_{60}$ exterior and the SWCNT interior has $\pi$ orbitals which are similar (although not identical) to those found in graphite. The second reason why the possible presence of $C_{60}$ fullerenes inside SWCNTs had been speculated was that the SWCNT synthesis was known to produce a sizeable amount of $C_{60}$ as a side product apart from the desired carbon nanotubes. In fact, the original SWCNT synthesis was a modified version of the so-called Krätschmer-Huffman arc-discharge process [12] which was developed to yield fullerenes. Much as the expectations and predictions were put forward, fullerenes inside SWCNT remained elusive.

In Figure 5b.2, we show the first high resolution transmission electron micrograph from Ref. [3] which shows an array of spherical molecules encapsulated inside SWCNTs. The center-to-center separation of the molecules was found to be around 1 nm which is consistent with the van der Waals separation expected for a linear array of $C_{60}$ molecules given the above-discussed 0.7 nm fullerene cage diameter and the van der Waals distance. A similar experimental value is found for a three-dimensional fullerene crystal (fullerite), where the center-to-center separation is 1.00 nm [2]. The samples used in Ref. [3] were purified by the HNO$_3$ acid refluxing method followed by a vacuum annealing up to 1100°C, a method developed by Rinzler and coworkers [13]. The presence of the spherical $C_{60}$ molecules is further corroborated by studying cross-sectional images, which we show.

Figure 5b.2  The first image showing a row of encapsulated fullerenes. The center-to-center spacing of about 1 nm was found to be consistent with the van der Waals separation expected for $C_{60}$. Micrograph reproduced with permission from [3] Copyright (1998) Macmillan Publishers Ltd.
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in Figure 5b.3 from Ref. [3]. Images of this kind show the presence of smaller, circular features inside the SWCNTs which exclude that the structure in Figure 5b.2 would result from a fullerene contamination above or below the studied nanotube. The fact that the circular features are observed in some of the nanotubes only, even though all the tubes are at the same focus depth, excludes that they originate from Fresnel fringes which are common artifacts in HR-TEM. These observations led to the unambiguous identification of this structure which was originally named *nanoscopic peapod* of which later the name *peapod* stuck.

The coalescence of $\text{C}_{60}$ was reported already in Ref. [3] to larger ‘super-fullerenes’ due to the lower binding energy $\text{C}_{60}$, as compared to the SWCNTs. It is discussed next that this observation eventually led to the discovery of the growth of an inner nanotube from the encapsulated fullerenes and to the so-called peapod-based double-wall carbon nanotubes.

The observation in Ref. [3] was first confirmed independently (although on a somewhat different system) by Kwon et al. [14], who studied multi-wall carbon nanotubes synthesized from diamond powder and observed the $\text{C}_{60}^5$ inside the smallest voids. They also proposed a quantum information storage and processing application for the structure, which we discuss further below. The first spectroscopic evidence that the encapsulated molecule is indeed $\text{C}_{60}$ came also from the U-Penn group [15]. They performed a moderate etching of the peapod material in acids in order to ‘liberate’ the encapsulated $\text{C}_{60}$, which were then removed by rinsing in toluene, which is a common fullerene solvent. The resulting solution was studied by UV-vis spectroscopy which showed unambiguous evidence for the presence of $\text{C}_{60}$ and it also allowed quantifying the amount of encapsulated fullerenes.

The mechanism of peapod synthesis was also discussed in Ref. [15]. Two scenarios were considered: production of peapods during the SWCNT synthesis and the production of peapods during the post-treatment purification process. The first scenario was excluded on
the basis that no peapod structure was observed for the as-prepared SWCNT soot. In addition, the catalytic synthesis of SWCNTs, yields a very low amount of tubes and fullerenes per consumed carbon, making the simultaneous synthesis of SWCNTs and fullerenes (the latter being embedded inside the former) very improbable. It was argued that the second possibility is more probable since during the acid refluxing some fullerenes become mobile and have sufficient time to find an opening on a nanotube. The peapod structure itself is energetically favored compared to an isolated fullerene and nanotube, as we discuss next. It is interesting to note here, that this originally suggested mechanism corresponds to peapod formation in solution as compared to the latter developed vapor method. However, the solution method was somewhat forgotten just to be rediscovered latter [16–19].

Another peapod synthesis method was proposed by Smith and Luzzi, who showed [5] that effective peapod formation happens for acid purified SWCNTs if these are heated to 450°C irrespective whether the annealing is performed in a closed or in an open environment. At this temperature, C₆₀, which are stuck to SWCNT walls from the outside, can diffuse along tube walls until an opening is found through which the buckyballs are sucked to the inside. A third synthesis method was described in the work of Kataura and coworkers [20] who heated C₆₀ at 650°C in a closed ampoule together with SWCNTs. At this temperature, C₆₀ molecules contribute to the gas phase and the peapod formation proceeds in this gas or vapor phase.

It is worth discussing in retrospect the circumstances which led to the discovery of the peapod structure:

1) The use of a relatively low electron energy, 100 kV, by the U-Penn group for the HR-TEM microscopy. At that time (1998), state-of-the art HR-TEM instruments used up to 1 MeV electron beam energies. However, beam energies above 100 kV destroy the encapsulated peapods very rapidly, which prevents to acquire high quality micrographs.
2) The synthesis method, using the Co/Ni catalyst process with either arc discharge or laser ablation, which provides fullerenes and the approximately 1.4 nm diameter tubes, which are ideal for the encapsulation. Other methods such as, for example, CVD growth give diameters which are less optimal for encapsulation and provide virtually no fullerenes as side-products.
3) The purified nature of the samples since unpurified samples do not contain peapods, the fullerenes being found outside the tubes in the SWCNT soot.
4) The actual purification protocol, that is, refluxing in acids followed by vacuum annealing up to 1100°C. The acid refluxing induces openings in the nanotube walls, while only moderately oxidizing or destroying the fullerenes. At the same time, it also provides a medium in which fullerenes can travel until an opening in the nanotube walls is found. The temperature and the duration of the annealing is also critical as a long annealing time at temperature above ~1000°C leads to the coalescence of fullerenes and to the formation of inner nanotubes [5].

5b.3 Classification of Peapods

The peapods can be classified according to the variations that are possible for their two constituents, the host nanotubes and the encapsulated fullerenes. Classification is given
**Figure 5b.4** HR-TEM micrograph and a schematic representation (not to scale) of Gd@C$_{82}$ metallofullerene peapods. Dark spots seen on the fullerene cages correspond to the heavy Gd atoms. For a better understanding of the figure, please refer to the colour plate section. Reprinted with permission from [26] Copyright (2000) American Physical Society.

**Figure 5b.5** Two HR-TEM observations for the ‘silo’ arrangement of fullerene peapods inside carbon nanotubes. The arrangement depends on the diameter of the host nanotube. Reprinted with permission from [23] Copyright (2004) American Physical Society.
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according to: (i) the nanotube type; (ii) the fullerene type (with several subclasses) and (iii) the type of arrangement of the fullerenes.

We first give a classification according to the host nanotube:

1) Normal SWCNT peapods such as those reported in 1998 in Ref. [3].
2) Multi-wall CNT peapods [21,22] synthesized first in 2003. As a subcase of this class are double-wall carbon nanotube peapods [23,24].
3) Noncarbon nanotubes, for example, multi-wall boron nitride nanotube peapods, first reported in 2003 [25].

The classification according to the fullerene type is as follows:

1) Pristine fullerenes, for example, C\textsubscript{60}, C\textsubscript{70}, and so on, Ref. [3].
2) Endohedral fullerenes, that is, endohedral metallofullerenes [26,27] and the unique N@C\textsubscript{60} fullerene [28] whose first encapsulation was reported in Ref. [18]. In Figure 5b.4, we show a HR-TEM image of heterofullerene peapods from Ref. [26].
3) Functionalized fullerenes [29].
4) Heterofullerenes, for example, the C\textsubscript{60}N azafullerene [30,31].
5) \textsuperscript{13}C isotope enriched fullerene peapods, reported in Ref. [32].

According to the arrangement type, the encapsulated fullerenes can form a linear chain [3] or can organize themselves in a ‘silo’ configuration [23,25,33] in larger diameter nanotubes as we show in Figure 5b.5.

5b.4 Synthesis and Behavior of Fullerene Peapods

5b.4.1 Synthesis of Peapods

5b.4.1.1 Mass Scale Synthesis

Clarifying the peapod formation mechanism in Ref. [15] by ascertaining that the fullerenes are originally outside the SWCNT, led to the optimization of the synthesis method. Smith and Luzzi reported [5] that adding a droplet of C\textsubscript{60} suspended in dimethylformamide (DMF) to HR-TEM grids and subsequently heating the samples in vacuum in situ at 450°C leads to an abundant filling of SWCNTs with C\textsubscript{60}, as shown in Figure 5b.6.

The choice of the temperature is very delicate: C\textsubscript{60} is known to sublime, that is, to enter to the gas phase above 350°C with a vapor pressure increasing with the temperature. However, the finding in Ref. [15] shows that C\textsubscript{60}s, which are stuck to SWCNT surface, can travel at this temperature along the tube walls until they find an opening then enter the SWCNT cavity to become encapsulated. However, 450°C is low enough not to remove the fullerenes away from the tubes.

This method of encapsulating additional fullerenes (i.e., which are not present as a side-product in the soot) into the SWCNTs opened the way to prepare other peapods such as of higher fullerenes, metallofullerenes, endohedral fullerenes, and so on. The C\textsubscript{70} fullerenes were also present albeit with a low concentration in the SWCNT soot along with C\textsubscript{60} therefore C\textsubscript{70} peapods were also produced in the original report [3]. This, along with the highly developed nature of the fullerene synthesis and chemistry, opened the way for a new level of SWCNT functionalization.
The Gas Phase Synthesis

A further step toward the mass scale synthesis of peapods, which eventually led to their spectroscopic investigation, was reported by Kataura et al. [20]. They performed the filling on a purified and opened buckypaper of SWCNTs. Opening was a side effect of purification done by refluxing in H₂O₂ and washing in HCl. The buckypaper samples were prepared by filtering and sealed together with an abundant amount of fullerene powder in a quartz ampoule and heated to 650°C for 1–2 h. At this temperature, the fullerenes have a high vapor pressure which enables them to enter through the SWCNT openings. This synthesis method is therefore termed as the gas phase synthesis method. The nonencapsulated fullerenes were removed from the SWCNTs by sonication in toluene (which is an effective solvent for C₆₀). Encapsulated fullerenes are energetically favored inside the SWCNTs and
therefore are not removed meanwhile (exception from this is discussed below for very large diameter nanotubes according to Ref. [33]). The toluene-sonicated samples were again filtered which yielded the final buckypaper peapod sample.

The possibility to synthesize macroscopic amounts of peapod samples in the form of buckypapers opened the way for a variety yet unavailable spectroscopic and structural investigations, which are discussed further below. In Figure 5b.7, we show the first bulk spectroscopic study on the peapods using Raman spectroscopy.

A number of narrow lines, which are originating from the encapsulated fullerenes (C$_{60}$ and C$_{70}$) were observed. Interestingly, the 488 nm laser line used in the study is close to the optical transition energy for the fullerene HOMO-LUMO gap [2], therefore the fullerene

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5b.7}
\caption{Raman spectra of C$_{60}$ and C$_{70}$ peapods with a 488 nm (2.54 eV) laser excitation. The upper panel also shows that the narrow C$_{60}$ appear stronger at lower temperature. Asterisk shows the pentagonal pinch mode (PPM) of the peapod at 1466 cm$^{-1}$. Reprinted with permission from [20] Copyright (2001) Elsevier Ltd.}
\end{figure}
Raman modes are greatly enhanced. Without this resonance condition, the fullerene modes
are unobservable. The Raman spectra provides clear-cut experimental evidence for the
encapsulated nature of the fullerenes as a downshift of the strongest pentagonal pinch
mode (PPM) with the $A_{g}(2)$ symmetry (asterisk in Figure 5b.7) is observed.

A parallel work by the Iijima group clarified the role of and the method for opening the
SWCNTs [26]. They found that a heat treatment at 400–450°C for 10–30 min in air opens
very effectively the tubes, whereas the acid treatment alone does not produce sufficient
number of openings. The treatment in $H_2O_2$ by Kataura et al. essentially provided the same
effect as the nascent oxygen acts similarly to the oxidation in air. There is certainly a balance
between the number of SWCNT openings and the amount of unwanted defects cre-
ated and nanotube material consumed. This optimal treatment (duration, temperature)
depends on the nanotube material and morphology (long or short tubes, highly bundled or
more individual) it therefore has to be optimized for each sample [34].

The removal of nonencapsulated fullerenes from the outside of the nanotubes was sim-
plified as it can be performed directly on the nanotube samples by heating them in dynamic
vacuum in a quartz tube above 650°C for 1–2 h [18]. Then, fullerenes enter the vapor phase
in the middle of the furnace and diffuse to the colder parts of the quartz tube toward the
pump where they deposit.

In summary, the peapod synthesis with the vapor method can be performed in three
steps on the SWCNT soot: (i) heating in air at 400–450°C for 10–30 min; (ii) sealing the
SWCNT material in a quartz (or glass) ampoule with a torch along with 1–2 times
larger mass of fullerenes and heating at 550–650°C for 1–12 h (the short duration applies
to the high temperature); and (iii) placing the resulting material in a quartz tube con-
ected to a vacuum pump (vacuum levels of $10^{-4}$ mbar suffice throughout) and heating
to 650°C for 1 h.

The first step may be omitted when the starting SWCNT material has been previously
purified via oxidizing methods, with purification conditions severe enough to generate
openings in the SWCNT walls.

5b.4.1.3 Low Temperature Synthesis
The vapor synthesis method is applicable to pristine fullerenes such as $C_{60}$, $C_{70}$, and to
metallofullerenes [26] which are stable at the 450–650°C required. However, it cannot be
applied to temperature-sensitive fullerenes derivatives such as the endohedral $N@C_{60}$ (decays
above 200°C [35]) and functionalized fullerene derivatives [36]. The interest in preparing
peapods from such fullerenes emerged in 2002–2003 when four groups independently
described low temperature synthesis methods to obtain high yield peapods [16–19]. The
activity was partly triggered by the suggested use of $N@C_{60}$ peapods for quantum computing
by Harneit [37].

The Iijima group reported a method termed ‘nanoextraction’ [16] in which $C_{60}$ and the
SWCNTs are placed into ethanol for one day. This method was demonstrated for 2 nm
diameter nanotubes, which is larger than the usually considered 1.4 nm nanotubes. 1.4 nm
SWCNTs were considered in a similar method proposed by Monthioux and Noé [17] who
used a saturated solution of $C_{60}$ in toluene in which SWCNTs were soaked upon sonication
at room temperature. They pointed out that optimum filling conditions correspond to mid-
sonication conditions, because of the damaging of SWCNTs induced by the dynamic
shocks of the solvated fullerenes onto the SWCNT walls.
Simon et al. [18] described a method in which the two peapod constituents are placed into refluxing n-hexane (at 69°C). The boiling of n-hexane itself provides a continuous stirring which reduces the required reaction time to 2h. Khlobystov et al. reported the use of supercritical carbon-dioxide as a medium and a reaction time of 10 days. The relative ease, efficiency, and short duration of the n-hexane refluxing method made it more popular than the alternatives and it was also used to encapsulate functionalized fullerenes [38]. Samples prepared with the low temperature (also termed the solvent method) do not differ in any physical properties from those prepared with the vapor method. It is best shown with X-ray diffraction (Figure 5b.8), which provides a bulk structural characterization of the ordered, one-dimensional peapod filling. Were the filling only partial, or the fullerenes not forming a perfect 1D array, the X-ray diffractogram would not be clearly visible.

**Figure 5b.8** X-ray diffractogram (reprinted with permission from [18] Copyright (2004) Elsevier Ltd) showing that $C_{60}$ peapods prepared with the vapor (b) and solvent (c) methods are structurally identical on a macroscopic scale. The diffractogram for the starting, empty SWCNT is shown (a). Note that the Bragg peaks corresponding to the hexagonal lattice of SWCNT bundles are changed upon the fullerene encapsulation as the structure factor of the one-dimensional fullerene lattice modulates these (peak A is reduced, those marked with an asterisk are increased).

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5b.4.1.4 Quantification of Peapod Filling

Characterization of peapod filling efficiency is important to optimize their synthesis routes, to apply bulk spectroscopic methods on them, and also for the applications. In this respect, microscopic methods such as HR-TEM are very time-consuming as a large number of nanotubes have to be sampled. The most straightforward method to estimate the peapod filling ratio is by weight uptake. Raman spectroscopy and X-ray diffractometry are viable candidates for this characterization, and these are macroscopic methods. However, Raman scattering intensity does not directly sense the number of fullerenes or the peapod filling fraction as it depends on a number of factors such as the optical density of the peapod material and the Raman resonance condition [39]. X-ray diffractometry on the other hand requires a peapod material where both the SWCNTs are well ordered in the bundle structure and also the fullerenes form a perfect one-dimensional lattice. However, X-ray diffraction can in principle provide a direct measure of the filling fraction.

Two further methods provide direct counting of carbon atoms on the fullerenes and on the SWCNTs: electron spectroscopy (which measures some characteristic carbon core levels) and nuclear magnetic resonance which is only sensitive to carbon and with which SWCNT and the encapsulated peapod signals can be discriminated.

We discuss the filling characterization methods in this order. An accurate, calibrated measurement was performed by the Luzzi group [40]. It was found that under optimal circumstances, up to 90% filling fraction can be achieved. Here, filling fraction means what amount of the available inner volume of the SWCNTs is occupied by the fullerenes. This was also correlated with the HR-TEM measurements and a good agreement was observed. Kataura and Maniwa studied the X-ray diffractogram of C_{60} peapods. The presence of peapods is to modulate the Bragg peaks of the hexagonal bundle arrangement through the form factor of the one-dimensional C_{60} chain. The effect of this modulation is shown in Figure 5b.8, and the details of the X-ray analysis are discussed in Section 5b.5.1. This analysis allowed for a quantitative determination of the filling fraction in Refs. [41,42].

A more general treatment of the X-ray diffraction for peapods was given by the Launois group [43]. It also considered the effect of the tube diameter distribution, SWCNT alignment, and crystallinity on the determination of the peapod filling. The group of Pichler performed a direct carbon counting of the peapods separately for the carbons on the fullerenes and on the SWCNTs (or on other carbonaceous phases) [44]. Electron energy loss spectroscopy (EELS) was used to study the carbon core level excitation for the peapods. In this method, a core electron is excited to an unoccupied state; for the case of carbon, the 1s electrons are excited to the unoccupied 2p-state-related π* state with an energy onset of 285.4 eV. In Figure 5b.9, we show the EELS data for the peapod as well as for an unfilled SWCNT reference sample. The peapod spectrum contains a shoulder around 284.5 eV and an extra peak at 288.3 eV, which were assigned as spectral features related to the encapsulated fullerenes. The reference spectrum is subtracted from the peapod EELS spectrum after multiplying with a scaling factor such that the difference resembles most to the well-known spectrum of C_{60}s. The difference is also shown in Figure 5b.9.

The number of carbon atoms on the encapsulated C_{60}s relative to the host nanotubes is obtained by integrating the C 1s spectrum of the difference normalized by the integral of the reference sample. This allowed essentially counting the carbon atoms which make the encapsulated fullerenes. The carbon counting provided by EELS was used to calibrate the Raman spectra [45], which is a more available method for the peapod filling efficiency.
characterization. Benchmarks were provided for the filling efficiency as a function of the observed Raman modes at well-defined laser energies. For instance, for a SWCNT sample with 1.4 nm mean diameter and 0.1 nm Gaussian diameter variance, the maximum volume that could be filled with C$_{60}$s is 94% of the total inner volume of the tubes (SWCNTs smaller than 1.2 nm cannot be filled). Considering the best visible C$_{60}$ A$_{(2)}$ mode and the SWCNT G modes, the Raman intensity ratio is $A_{(2)}/G=4.6\cdot10^{-3}$ at 488 nm laser excitation for such a sample if all the available volume is occupied by fullerenes.

Another, bulk carbon counting method is based on encapsulating $^{13}$C enriched fullerenes inside the SWCNTs, and performing nuclear magnetic resonance, NMR, on them [32]. Since NMR is only sensitive to the $^{13}$C isotope, the encapsulated isotope-enriched fullerenes (with enrichments up to 90%) are detected with a large contrast as compared to the host nanotubes, which contain $^{13}$C with a natural, 1.1%, abundance only. The NMR signal intensity provides an absolute measurement of the detected number of $^{13}$C nuclei, therefore calibrating it with a NMR standard with known number of $^{13}$C nuclei directly yields the number of carbon atoms encapsulated inside the SWCNTs.

5b.4.1.5 Theory of Peapod Synthesis, Stability and Arrangement
The theoretical understanding of the peapod formation and energetic stability is important for the successful synthesis and to explore similar systems. In addition, the description of the peapod stability is an interesting test-bed for the theoretical methods in a true nanosized environment. It is a well-known problem in the first principles based calculation methods that the van der Waals interaction is difficult to handle accurately. Therefore the description
of the peapod system, which is controlled by the van der Waals interaction, led to the development of the theoretical methods as well.

The first theoretical description for the peapod synthesis was reported by the Tomanek group [46]. Molecular dynamics calculations were performed using a parameterized interaction Hamiltonian which had been developed to describe the wall-wall interaction in MWCNTs. The authors found that the fullerene encapsulation happens in two steps: first a fullerene outside the SWCNTs is physisorbed on the surface with an energy gain of about 0.07 eV. Then, at the elevated temperatures of the encapsulation (above 400°C), the fullerene can freely diffuse along the nanotube until an opening is found through which it can enter the nanotube with a further energy gain (discussed next). It was found that the openings themselves do not form an activation barrier for the encapsulation. Of the two possible scenarios, that is tube-wall or tube-end openings, it was found that the encapsulation is more probable through the tube-wall opening. The two scenarios are shown schematically in Figure 5b.10. A simple explanation of this difference is that, for a tube-end encapsulation, the fullerene is required to make a ‘U-turn’, which is a less probable trajectory at the synthesis temperature.

The energetic stability of the peapod structure motivated a number of theoretical studies to calculate the binding energy (Figure 5b.11).
It was observed experimentally [5] that the encapsulated peapods cannot escape the host nanotubes even at elevated temperatures (above 1000°C) and they form an inner nanotube, which leads to the double-wall carbon nanotube structure. Therefore the encapsulation is essentially an irreversible process with a relatively large binding energy, yet it was found that releasing encapsulated C$_{60}$s was as easier as the host tube diameter is larger [33,48].

In Table 5b.1, we summarize the theoretical reports on this matter. The applied calculation method, the largest binding energy observed, and the diameter of the smallest outer tube.

**Table 5b.1** Summary of the available theoretical results on the energetics of peapod encapsulation. The calculation method, the binding energy for the (10,10) host outer tube, $E_b$, and the minimal host tube diameter $d_{\text{min}}$ for which the encapsulation is exothermal are given. DFT-LDA stands for the Density Functional Theory method with the Local Density Approximation.

<table>
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</table>

Figure 5b.11 Binding energy of C$_{60}$ in various peapods as a function of the host outer tube diameter, $d$. The calculation was performed with the density functional theory in the local density approximation. The negative binding energy corresponds to the energetically stable, exothermic encapsulation. Reprinted with permission from [47] Copyright (2004) American Physical Society.
where the encapsulation is still energetically preferred, are given. Although the parameters scatter somewhat, some general conclusions can be drawn from these works. First, the encapsulation is energetically preferred if the host outer tube has a diameter above $\sim 1.2$ nm, but the incorporability of $C_{60}$s inside SWCNTs decreases for diameters beyond $\sim 2$ nm [48]. Next, the typical binding energy observed for a $(10,10)$ outer tube is $1–2$ eV per $C_{60}$ molecule. This corresponds to a binding energy of about $5$ meV per carbon atom (considering the carbon atoms of the host tube as well) [49]. This is much smaller than that found in graphite ($23$ meV per atom) which reflects the trivial fact that the coordination of most of the carbon atoms on the fullerene is such that they do not face optimally the surrounding outer tube, thus the van der Waals energy gain is not optimal.

Once the energetic stability of $C_{60}$ upon encapsulation was understood theoretically, interest turned toward understanding configuration as a function of the host tube diameter, $d$, and also for other fullerenes. We discuss the related results in this order in the following. The encapsulated fullerenes occupy a high symmetry position inside the host nanotubes and the relative orientation of the fullerenes with respect to outer tube is incommensurable, that is, it is ill-defined except for some special cases (e.g., $C_{60}$ inside a $(10,10)$ nanotube) when a commensurable structure can be achieved. As it is discussed below, this results in a low energy barrier for the $C_{60}$ rotation [50]. Provided the fullerenes are situated perfectly along the nanotube axis (which is realized for $d \leq 1.5$ nm), their mutual arrangement of the neighboring $C_{60}$s can take several well-defined arrangements; facing pentagons, facing hexagons, or facing double bonds, which were studied by Michel et al. [51]. It was found that for $d \leq 1.4$ nm the facing pentagon structure is energetically preferred. For $d \geq 1.5$ nm, the fullerenes are displaced from the tube axis thus no mutually ordered structure of the $C_{60}$ can be identified and the structure takes the so-called silo arrangement such as that shown in Figure 5b.5 after Ref. [23].

It is worth noting that considering SWCNTs with diameters above $d \sim 7$ nm cannot compare to other SWCNTs as such large nanotubes are flattened. Due to this specific morphology that those nanotubes are enforced to adopt upon energetical constraints, encapsulated fullerenes are found to align along the nanotube edges, revealing that they are actually trapped in the tube-like channels left on both sides of the flattened part [48]. We show this situation in Figure 5b.12.

![Figure 5b.12](image-url) HR-TEM micrograph of a flattened large diameter SWCNT containing encapsulated $C_{60}$ chains along the tube-like channels on both sides. Reprinted with permission from [48] Copyright (2007) Elsevier Ltd.
There exists a transition region, for $-1.4 \text{nm} < d \leq 1.5 \text{nm}$ where the facing hexagons and facing double bond configurations occur. These are energetically so close that no distinction could be made for the preferred alignment. The silo structure in larger diameter nanotubes was understood on the basis of the arrangement taken by fullerenes for the optimal van der Waals energy [47,52]. It is energetically preferred for the fullerenes to displace themselves from the middle of the nanotube, so that the fullerene-tube wall separation is the optimal van der Waals distance. Since all fullerenes prefer to stick to the host nanotube walls on different sides, they are essentially located around the tube center, giving rise to the structure shown in Figure 5b.5. We discuss below that apart from the local HR-TEM evidence, X-ray diffractometry shows a smaller fullerene lattice constant along the tube axis for the silo arrangement [33].

Okada et al. studied the configuration for C_{70} as a function of the host diameter nanotubes [53]. It was found that a lying configuration (i.e., when the longer axis of C_{70} is parallel with the nanotube axis) is realized for tube diameters below 1.41 nm and the standing configuration (i.e., when the shorter C_{70} axis is parallel to the tube axis) is realized for larger diameter host nanotubes. Verberck and Michel [54] found that the lying structure is realized for $d < -1.4 \text{nm}$ and the standing for $d > 1.44 \text{nm}$ and a transition region in between with a mixture of the two configurations. It is discussed next that this structure is indeed observed experimentally [55,56]. The Launois group found in X-ray studies [56] that structural change from the lying to standing configuration happens for $d = 1.42 \text{nm}$ in good agreement with the theoretical prediction [54].

### 5b.4.2 Behavior of Peapods under Various Treatments

#### 5b.4.2.1 Behavior under Electron Irradiation

The behavior of encapsulated peapods under the electron beam of the HR-TEM was already studied in the first report on peapods [3]. It was found that exposure to the 100kV electron beam causes the encapsulated fullerenes to coalesce into smaller tubular structures with a capped ends. This behavior was interpreted with the energy per carbon atom which is higher for a fullerene than for a carbon nanotube. Obviously, the lieu where the \( \pi \)-electrons are shared with the outer tube that results in the so-called van der Waals interaction is limited to a single circle per fullerene molecule, while it corresponds to a genuine cylindrical surface for coalesced fullerenes. In this sense, coalescence into the smaller tubular structure is energetically preferred and the electron beam irradiation provides sufficient energy to overcome an activation barrier. The exposure effect has an important technical implication: the peapod structure can be best studied for relatively low electron beam energies in HR-TEM. Many state-of-the-art HR-TEM instruments operate with beam energy above 200keV, which cannot be exploited when studying peapods.

The electron beam-induced coalescence of the encapsulated fullerenes was subsequently studied in more detail [4]. The resulting structure was termed ‘coaxial tubes’ (CATs) and was found to be the smallest multi-wall carbon nanotubes for a while. It was shown that the diameter of an inner nanotube is 0.7 nm, which is inside a 1.4 nm outer tube. Therefore the wall-wall separation is close to the ideal van der Waals distance, which is 0.335 nm in graphite. It is more common to call this structure ‘double-wall carbon nanotubes’ (DWCNTs), a structure which had been described prior to the discovery of peapods [57]. However, electron irradiation also goes with a ballistic interaction with electrons, inducing atom displacements and ultimately, knocking off of carbon atoms from the lattices (yet in
an extent that depends on the electron energy). The resulting coalesced structure is highly
defective, and barely long enough for being called a genuine ‘inner nanotube’. Hence, the
destructive and constructive effects of the interacting electrons compete, ultimately possibly
resulting in the amorphization of the whole irradiated material.

5b.4.2.2 Behavior upon Annealing: The Double-Wall Carbon Nanotubes
The ability to obtain the inner nanotubes under the electron beam exposure motivated to
study their temperature-induced formation. For this purpose, Smith and Luzzi developed
the method of preparing a macroscopic amount of peapods as we described earlier [5]. This
sample was subjected to a 1200°C annealing in dynamic vacuum for 24 h. In the resulting
material, an abundant occurrence of double-wall carbon nanotubes was observed, which
confirmed that the temperature excitation can be also used to overcome the activation
barrier for the inner tube formation.

The annealing-induced coalescence is potentially capable of producing double-wall
carbon nanotubes in macroscopic amounts. The attention to study this material with
macroscopic spectroscopy methods was drawn by the report of Bandow et al. [58], who
showed that Raman spectroscopy can be performed on the DWCNTs and that the

![Raman spectra of empty nanotubes, C₆₀ peapods, and annealed peapods (at 1200°C) with a 515 nm laser excitation. A deconvolution into different components is shown with dashed curves. Note the peaks which appear for the annealed peapod sample in the 230–370 cm⁻¹ spectral range, which correspond to the RBMs of the inner tubes. Reprinted with permission from [58] Copyright (2001) Elsevier Ltd.](image)

Figure 5b.13  Raman spectra of empty nanotubes, C₆₀ peapods, and annealed peapods (at 1200°C) with a 515 nm laser excitation. A deconvolution into different components is shown with dashed curves. Note the peaks which appear for the annealed peapod sample in the 230–370 cm⁻¹ spectral range, which correspond to the RBMs of the inner tubes. Reprinted with permission from [58] Copyright (2001) Elsevier Ltd.
characteristic Raman modes, which correspond to the inner tubes, are observed. We show the Raman spectra for empty nanotubes, $C_{60}$ peapods, and for annealed peapods in Figure 5b.13. The annealing was performed at 1200°C, which is sufficient to induce the coalescence of all the encapsulated fullerenes and to form the inner tubes.

Raman spectroscopy is particularly useful to characterize the growth of carbon nanotubes in a diameter-selective manner, as the so-called radial breathing mode (RBM), which is unique to SWCNTs (and DWCNTs), is sensitive to the nanotube diameter. There is a reciprocal relation between the energy of Raman mode and the diameter: $\nu_{\text{RBM}} \approx C_1/d$ [59]. The value of the $C_1$ constant depends on the environment of the tubes and $C_1 = 235 \text{ cm}^{-1} \text{ nm}^{-1}$ is an accepted value. Clearly, new Raman modes in the 230–370 cm$^{-1}$ range arise upon annealing the peapod material which correspond to small diameter nanotubes with $d = 1$ to 0.65 nm and these modes were identified as the radial breathing modes of the small diameter inner tubes.

5b.4.2.3 Alternatives to Mere Electron Irradiation or Annealing

An interesting alternative to the thermally induced coalescence is the local heating using a high power focused laser. Kramberger et al. [60] found that peapods suspended on TEM grids can be made white glowing in vacuum using a 1064 nm laser of an FT-Raman spectrometer if it is focused onto a 1 $\mu$m$^2$ spot with 500 mW power. This in situ heating also allowed for Raman monitoring of the inner tube growth process. The widespread transformation of the peapods into genuine DWCNTs was, however, not confirmed by clear TEM images.

A similar approach was used by Kalbac et al. [61]. They also claimed the successful formation of DWCNTs, yet with a higher yield when starting from $C_{70}@$SWCNT than from $C_{60}@$SWCNT due to the higher sensitivity to photolysis of the former. Since the irradiation was carried out with a pulsed laser in order to prevent thermal load of the material, the coalescence mechanism is explained via multiphoton photolysis of the encapsulated fullerenes, without passing via the intermediate event of $[2+2]$ cycloaddition-driven fullerene polymerization (see Section 5b.4.2.2). The outer tubes of the resulting DWCNTs are found larger and less defective than upon coalescence by thermal annealing. This might be surprising as temperature is always a structuring process for graphene-based materials, provided the atmosphere is nonreactive. However, it is worth noting that no TEM image of the resulting DWCNTs was shown in the paper.

Puech et al. [62] also carried out UV light laser irradiation experiments, yet with a different goal as above since the purpose was to induce local heating (i.e., convenient for temperature-sensitive substrates such as Si-doped wafer-supported devices) and check whether reaching temperatures high enough for inducing the formation of DWCNTs was possible. Using nonpulsed UV-light laser made possible to record the Raman spectrum evolution simultaneously. Starting from empty SWCNTs or CVD-prepared DWCNTs as reference materials [63] and using the downshift of the $G^+$ and $G^-$ bands as local temperature probe, it was shown that temperatures as high as 800–1000°C could be reached for a laser power of 280 mW, that is, able to initiate the fullerene coalescence mechanisms. However, deep changes (merging of the $G^+$ and $G^-$ bands, and sudden upshift of the resulting G band) occurred on irradiated peapods as early as for a laser power of 140 mW (corresponding to a temperature of −480°C), which was explained by oxidation phenomena locally promoted by the contained-fullerenes, thanks to a some partial pressure of oxygen as an impurity in the low pressure argon atmosphere.
Achieving the peapod-to-DWCNT transformation via laser irradiation seems to be possible both photo-induced mechanisms, that is, photolysis or thermal annealing, but further work is still needed to support this statement further.

Another alternative was proposed by Monthioux et al. who studied the coalescence process combining electron beam irradiation with in situ heating [64,65]. First, the two extremal handling was studied, that is, no heating and long 200 keV electron beam irradiation time and 1200°C heating without exposure to irradiation. The heating alone produced structurally perfect double-wall carbon nanotubes, whereas the elongated irradiation alone produced a large number of defects on the outer and inner walls in addition to promoting the coalescence of the encapsulated fullerenes. It was found that the combination of the two methods, that is annealing at 200°C while irradiating produced inner wall to outer wall distances of 0.5–0.55 nm which is far beyond of that anticipated from the van der Waals distance of −0.35 nm.

Then, by applying various couples of temperature (in the range 480–700°C) and electron irradiation (energy in the range 150–300 kV, in addition to various electron dose and flow values) conditions, it was found that some were able to successfully achieve the peapod-to-DWCNT transformation whereas others were resulting in the peapod destruction, with all the intermediate features also obtained depending on the conditions. The most interesting observation was that, based on TEM investigation statistics, the diameter of the resulting inner tube or capsules as well as the inner-outer shell distance were also depending on the temperature/irradiation condition couple used. The leading parameter was found to be the host (outer) nanotube diameter, whose increase relates linearly to an increase of both the inter-tube distance (see Figure 5b.14) and the inner tube diameter.

This indicates that, in such conditions, the coalescence mechanisms are driven by a compromise between two contradictory energetic requirements, that is, tentatively enforcing the regular 0.34 nm van der Waals distance between the inner and outer graphenes, and tentatively maintaining the initial 0.7 nm diameter originating from the starting fullerenes. With respect to this overall mechanism, temperature appeared to be an important parameter to control the dimensional features of DWCNTs. Typically, for a given electron energy, both the resulting inner tube and outer tube diameters appeared smaller (and the intertube distance larger) after 490°C than after 700°C heat-treatment (see Figure 5b.14), and both resulting inner tube and outer tube diameters were larger after 700°C heat treatment than for the starting peapods. On the other hand, none of the electron beam features were found to have a significant influence on the DWCNT features, but possibly on the electron dose. This suggested distinct coalescence regimes according to the temperature range. At high temperature (700°C), thermal effects may prevail, resulting in larger (inner and outer) tube diameters possibly via a tube fattening mechanism which involves the creation of Stone-Wales defects, their subsequent splitting into two 5–7 ring pairs, and the migration of the two 5–7 pairs apart from each other [66]. At low temperature (490°C), irradiation effects such as knocking-off of atoms and hindering of the fattening mechanism just mentioned may prevail, resulting in a relative shrinkage of both inner and outer tube diameter. This effect is more pronounced for inner tubes than for outer tubes, which probably relates to the fact that the former are building-up whereas the latter pre-exist.

5b.4.2.4 Coalescence Mechanisms

The possibility to form single-wall carbon nanotube inside another nanotube is interesting for both the fundamental understanding of the coalescence process and also for practical
To date, the growth of SWCNTs requires the use of metal catalysts which results in inevitable contaminations and defects. In contrast, the peapod-derived SWCNTs are formed in a catalyst-free ‘nano clean-room’ where the outer wall as a template enforces the building of a highly curved tubular structure. As we mentioned above, the clear preference of the $sp^2$-like bonds on the carbon nanotube and the absence of any pentagons (which are energetically not preferred) make them energetically more stable than the peapods. However, the details of the coalescence process are somewhat subtle.

The first attempt to describe the formation of the inner tubes was made by the Tomanek’s group [67]. They found a particularly low energy route (which is therefore a very probable growth channel), which starts with a $(2+2)$ cycloaddition bond on neighboring $C_{60}$s. This requires that the fullerences can take a position where their doubly bonded carbon atoms are facing each other as the cycloadditional bond is only possible upon breaking up this bond. Once the $(2+2)$ bond is formed a series of transformations can take place where the bonds are rotating but bond breaking is avoided. This process is the so-called Stone-Wales transformations [68], which were first proposed to describe the evolution of nonoptimal fullerene cages toward the energetically stable ones. The series of such transformations, which can lead to cycloadditionally bonded fullerences to a fully merged $C_{120}$ molecule, is shown in Figure 5b.15 from Ref. [67].

This mechanism has the advantage that it only involves the relatively low energy Stone-Wales transformations. In principle it predicts that the inner tube formation results in
perfect (5,5) inner tubes. However, it is observed experimentally that not only there is more than one type of inner tube that is formed, it is also observed that the inner tube diameter increases until that of the outer tube until the van der Waals separation between the walls is attained. Therefore, additional (probably also Stone-Wales related) transformations are required to produce all the inner tubes which are observed experimentally. Nevertheless, this growth model suggests that the relatively small diameter (5,5) tube is formed first which is followed by its enlargement toward larger diameter tubes.

This mechanism found experimental support in the Raman studies of Bandow et al. [69] who monitored the development of the inner tube spectra during a careful, relatively low temperature annealing process. Annealing temperatures as low as 800°C were used, making that the inner tube formation proceeded over weeks. As mentioned above, the Raman spectra are directly sensitive to the diameter of the grown inner tubes. It was observed that the small diameter inner tubes grow earlier which is followed by their enlargement to the larger tubes that have diameters which is optimal inside the outer tube.

A proposed alternative mechanism for the growth of inner tubes from peapods suggests the complete decay into small carbon fragments which then join to form the inner tubes. This was based on the information that the source of carbon is unimportant for the growth of inner tubes: it can also proceed from, for example, toluene [70] and ferrocene [71]. At present it is believed that both kinds of mechanisms are at play: for fullerene peapods probably the Stone-Wales route prevails. For the encapsulated non-fullerenes, the molecules decay into small carbon fragments which readily combine to form the inner tube and there is no substantial diffusion along the carbon axis.
It was shown experimentally with the help of $^{13}\text{C}$ isotope labeling that, for C$_{60}$ peapods, there is no diffusion of the carbon atoms [72]. A mixture of $^{13}\text{C}$ labeled and natural C$_{60}$ (1.1% $^{13}\text{C}$ content) was encapsulated into SWCNTs and transformed to DWCNTs. It was found that the Raman RBM lines of the inner tubes are substantially broadened due to the inhomogeneous distribution of the $^{13}\text{C}$ nuclei. This could be explained by assuming that the $^{13}\text{C}$ and the $^{12}\text{C}$ do not mix with each other thus $^{13}\text{C}$ rich and poor regions alternate along the inner tube axis. This experimental result also supports the inner tube formation model proposed in Ref. [67].

5b.4.2.5 Behavior upon Alkali Doping or Pressure: The Polymerization of the Peas

The C$_{60}$ fullerenes possess a number of different polymer phases, such as that induced by charging [73] and two-dimensional [74], and three-dimensional [75] polymers induced by pressure. This motivated the search for similar polymers inside the host outer tubes. The motivation arose from the rich nature of the physics encountered for the fullerene polymers which includes, for example, low-dimensional correlated states [76] or superionic conductivity [77]. First principles calculations showed [78] that the structures of the different C$_{60}$ polymer phases are dictated by the charging. For instance C$_{60}^-$ gives rise to a one-dimensional (2+2) cycloaddition polymer, C$_{60}^{4-}$ prefers a single-bonded one-dimensional polymer, C$_{60}^{6-}$ results in a single bonded two-dimensional polymer structure, and for C$_{60}^{6-}$ a single bonded one-dimensional polymer is preferred. The three-dimensional polymer structure is formed in neutral C$_{60}$ upon high pressure and temperature treatment.

For peapods, the C$_{60}$-C$_{60}$ coordination can take positions [51] which allow the (2+2) bond formation and also a single bonded polymer structure (when single carbon atoms are facing each other). In contrast, the (2+2) configuration is hindered for C$_{70}$ in the lying configuration since the pentagons are facing each other with no double bonds [54]. Pichler et al. studied the behavior of C$_{60}$ peapods upon alkali doping [79]. It was found that a one-dimensional, single-bonded, metallic polymer structure is formed from the peapods when the encapsulated fullerenes are charged to C$_{60}^{6-}$. This structure is consistent with the theoretical prediction by Pekker et al. [78].

The pressure induced polymerization of peapods was studied using X-ray scattering [80] and it was shown that 25 GPa (250 kbar) causes an irreversible polymerization. The C$_{60}$-C$_{60}$ distance was reduced from 0.956 nm to 0.845 nm. The role of the temperature in promoting the polymerization was also studied [81]. It was shown that a simultaneous annealing at 1000°C reduces the pressure required for the polymerization down to 4 GPa. In contrast, for C$_{70}$ no polymerization was observed [82] using a pressure of 2.5 GPa and annealing at 550°C, even though crystalline C$_{70}$ polymerizes with the application of 2 GPa and 300°C [83]. This was interpreted that as the confinement inside the nanotubes prevents the C$_{70}$ molecules from taking positions which is required for the bond formation.

5b.5 Properties of Peapods

5b.5.1 Structural Properties

The compelling one-dimensional structure of the peapods was recognized immediately in the first publication [3] and is shown in Figure 5b.2. It indicated a perfect linear chain arrangement with an approximate C$_{60}$ center-to-center separation of 1 nm. More detailed
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structural information was provided by electron an X-ray diffraction (XRD), upon the availability of peapods with a large fullerene filling [5]. The advantage of electron diffraction is that it can be performed within the TEM and also on microscopic amounts of sample. The first report on the peapod structure using electron diffraction was performed on the Gd@C\textsubscript{82} metallофullerene peapod [26]. While we do not intend to consider any priority question, we are aware that the Luzzi group also performed electron diffraction studies on the peapods around the same time.

XRD performed on pristine peapods was mentioned by Kataura \textit{et al.} in [41], but the details of the measurement and a careful analysis of the XRD data were actually published first in Ref. [42]. In Figure 5b.16, we show the measured XRD profile for C\textsubscript{60} peapods along with a simulation from Ref. [84].

The XRD profile for peapods is a product of the Bragg peaks for the hexagonal bundle structure of SWCNTs and the form factor of the one-dimensional C\textsubscript{60} chain. The effect of the encapsulated C\textsubscript{60}s is most apparent for the first two Bragg peaks of the unfilled SWCNT around $Q=4.5$ and 7.5 nm\textsuperscript{-1} ($Q$ is the scattering wave-vector); the first peak is larger in the unfilled material whereas it is smaller in the filled one. This change is due to the multiplying effect of the form factor of the fullerene chain, which is small below $Q=6$ nm\textsuperscript{-1} with a strong peak around 6.5 nm\textsuperscript{-1}.

The good agreement between the experimental and simulated XRD profiles means that the encapsulated fullerenes indeed form a perfect one-dimensional lattice with a long range structural coherence, that is, there is not a significant number of chain breaking defects or voids. On the other hand, the validity of the simulated one-dimensional C\textsubscript{60} form factor means that there is no correlation between fullerene chains in neighboring tubes due to the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5b16.png}
\caption{Observed and simulated XRD profiles of C\textsubscript{60} peapods. The lower panel shows the diffraction pattern for the hexagonal bundle structure of empty SWCNT and the form factor of the one-dimensional C\textsubscript{60} chain. Reprinted with permission from [84] Copyright (2003) American Physical Society.}
\end{figure}
Fullerenes inside CNTs: Peapods

The fullerene center-to-center distance was found to be 0.96(1) nm, in good agreement with the earlier TEM observations. This also confirms that the encapsulated fullerenes form a one-dimensional van der Waals crystal as this separation agrees with that in crystalline fullerite and is significantly larger than the lattice constant of a fullerene polymer (0.92 nm) [2].

The most rigorous treatment of the description of the peapod XRD profile was given by the group of Launois [43]. The influences of tube diameter distribution, different filling rates, and bundles with various sizes on the XRD profile were considered. We discussed above that the encapsulated fullerenes form a perfect one-dimensional chain only in nanotubes with sufficiently small diameter whereas, for larger diameter nanotubes, the so-called silo crystal arrangement is preferred. As a first approximation, the one-dimensional lattice constant of the fullerenes is reduced. This effect was reported using XRD in Ref. [33], that is, as an observed upshift of the C_{60} related peak at 6.5 nm\(^{-1}\).

The structure of C_{70} peapods was first studied by Kataura et al. using electron diffraction and XRD in Refs. [41,42]. Clear signatures of a double peak was observed with both techniques corresponding to lattice constants of 1.0 and 1.1 nm. This observation evidences that two types of arrangements are observed for the C_{70} peas, the so-called standing and lying. The energetic stability for both structures was shown (also discussed in Section 5b.4.1.5) to depend on the host tube diameter, a value of \(-1.45\) nm being a boundary between the two [53].

In Figure 5b.17, we show the XRD image for C_{70} peapods from Ref. [56] along with a simulated diffractogram assuming a superposition of the two different configurations. Two peaks can be identified at 5.7 and 6.3 nm\(^{-1}\) which correspond to one-dimensional lattices with lattice constants of 1.1 and 1.0 nm, respectively. The presence of separated

**Figure 5b.17** X-ray diffraction profile for C_{70} peapods (large circles) along with a simulated diffractogram (solid curve) and the diffuse background (small circles). Miller indices indicate the Bragg peaks of the SWCNT lattice and L and S indicate the diffraction positions of the lying and standing configurations, respectively. Inset shows the schematics of the two configurations. Reprinted with permission from [56] Copyright (2007) American Physical Society.
peaks is the evidence that the two configurations exist in separate nanotubes and no experimental signature for the presence of a mixed configuration was found. The relative intensity (i.e., the structural abundance) of the two kinds of configuration is about 1:1. The host SWCNTs used in Ref. [56] had a mean diameter of 1.4 nm which corresponds to the earlier mentioned boundary between the two configurations, which results in the equal abundance of the two types of $C_{70}$ arrangements.

5b.5.2 Peapod Band Structure from Theory and Experiment

Before going into the details, we will summarize in short the present knowledge on the electronic structure of the $C_{60}$ peapods. There is little interaction between the encapsulated fullerenes and the host SWCNT. The fullerene LUMO (lowest unoccupied molecular orbital) and the band derived from the LUMO is situated about 0.5 eV above the Fermi energy of metallic or semiconducting nanotubes (the mid-gap energy is understood as Fermi energy for the latter). This meets accidentally the first Van Hove singularity of the semiconducting nanotubes but, for neutral SWCNTs, this state is unfilled therefore the encapsulated fullerenes remain neutral. The early literature on the peapod electronic properties is reviewed in Ref. [85].

Describing the peapod band structure starts with the brief introduction to the band structure of pristine SWCNTs given in Chapter 1. Then we discuss the molecular orbitals of $C_{60}$ and the molecular bands in the solid molecular crystal, that is, the fullerite. The HOMO (highest occupied molecular orbital) of $C_{60}$ has an $h_{1u}$ symmetry and is five-fold degenerated thus it is fully occupied by 10 electrons. This is separated by a gap of about 2.5 eV from the triply degenerated LUMO with the $t_{1u}$ symmetry.

The first theoretical work addressing the band structure of $C_{60}$ peapods appeared in 2001 [86]. Using DFT-LDA calculations, it was found that for the $C_{60}$ peapods with a (10,10) armchair host tube, the fullerene $t_{1u}$ level is located near the Fermi energy of the SWCNTs. This would cause that the fullerene chain becomes a metal. Instead of the usual two linear bands, this material was claimed to have four conduction bands, two of which are fullerene related with a smaller Fermi velocity due to the weaker metallicity of this component. This result was reproduced later in another DFT-LDA calculation by Dubay and Kresse [47] and was extended to semiconducting SWCNTs. For the latter, the fullerene $t_{1u}$ state was claimed to be near the middle of the gap.

However, our present knowledge and in particular the experimental results do not support the first principles results. This in fact shows that for such a delicate van der Waals system as the peapods, otherwise powerful methods fail. Liu et al. performed electron energy loss spectroscopy (EELS) studies on $C_{60}$ peapods [44]. They found that the electronic and optical properties of the encapsulated $C_{60}$s are very similar to those of solid fcc fullerite. This excludes the possibility that the $t_{1u}$ of the encapsulated $C_{60}$s is occupied in contrast to the prediction of the first principles result. This means that the fullerene $t_{1u}$ band is located above the Fermi energy (or mid-gap for semiconducting tubes) level of the SWCNTs and is thus unfilled.

The EELS result, which is a spectroscopic method on the bulk scale, was clearly confirmed by a local, microscopic method, scanning tunneling spectroscopy (STS). Hornbaker et al. performed STM and STS on the $C_{60}$ peapods [87]. For usual metals with broad conduction bands, this method provides a topographic information on the studied surface
irrespective of the applied bias voltage. For peapods, a strong sensitivity on the bias was observed. For negative sample bias, that is, when the occupied states are monitored, no signature of the embedded fullerenes is observed. This drastically changes for positive sample bias, that is, when the unoccupied states are monitored, when a periodic modulation of the apparent sample height is observed along the nanotube axis for constant current operation. We show this result in Figure 5b.18. The topographically higher surface translates to larger density of states for the unoccupied states in the positive bias measurement. This means that the unoccupied fullerene $t_{1u}$ band is located near the unoccupied SWCNT states, which confirms the result of the EELS and also contradicts the first principles prediction. We note that the STS measurement was performed on a semiconducting host SWCNT and to our knowledge no data for metallic host tubes were reported.

In a similar STS study, the effect of encapsulated metallofullerenes was investigated [88]. It was found that the encapsulation of Gd@C$_{82}$ reduces the band gap in semiconducting SWCNTs from about 0.5 eV to 0.1 eV. This is mainly the result of the additional charges transferred from Gd (Gd$^{3+}$ when ionized).

Figure 5b.18 Structural and STM image of a C$_{60}$ peapod. A representative HR-TEM image (a), STM image with 1.5 V bias and 700 pA (b) and -1.5 V and 700 pA (c). Bright areas indicate a topographically higher surface, the amplitude of the height modulation is 0.04 nm. Note that only the positively biased STM image indicates the presence of the fullerenes. Reproduced from [87] Copyright (2002) AAAS.
In an improved first principles calculation, Louie's group [89] qualitatively confirmed the validity of the above description. Using ab initio pseudopotential density functional approach with a linear combination of localized orbitals basis, it was found that the Fermi energy of SWCNTs lies indeed between the HOMO and LUMO levels of the encapsulated C$_{60}$s, thus the latter molecules are neutral and do not contribute to the conduction.

Another way of studying the unoccupied states is to dope them with donor atoms and to monitor the changes to the density of states. The Pichler group studied [90] the electronic structure of C$_{60}$ peapods by means of shifting the Fermi energy upon K-doping using photoemission spectroscopy. Previously, the method was successfully used to evidence a crossover from the Tomonaga-Luttinger liquid (TLL) phase [91] to the Fermi liquid (FL) [92]. It was shown for pristine metallic SWCNTs using photoelectron-spectroscopy (PES) [93], that strong electron-electron correlations combined with the one-dimensionality gives rise to the TLL state. This is observable as a power law behavior in the density of states near the Fermi level (DOS $\propto (E_F - E)^\alpha$, where $E_F$ is the Fermi energy), rather than the Fermi-edge behavior, which characterizes usual metals. However, the Fermi edge and thus the FL state is recovered upon K-doping when all the SWCNTs are rendered metallic due to the electron doping [92], and the system loses its one-dimensional character. The TLL to FL crossover happens when the dopant electrons start occupying the valence band of the otherwise semiconducting nanotubes.

For C$_{60}$ peapods, the situation is different and is a fingerprint of the presence of the encapsulated fullerenes [90]. In Figure 5b.19, we show the power law scaling factor, $\alpha$, for

**Figure 5b.19** The power law scaling factor of the DOS, $\alpha$, as a function of K-doping for pristine SWCNTs and peapods (left panel) and schematic band dispersion and DOS (right panel). Numbers in the panels show the doping stages. Grey and black lines denote the DOS for metallic and semiconducting SWCNTs, respectively. Note that for C$_{60}$ peapods, the TLL state is preserved for higher doping level as the exponent remains finite, however, its value indicates a two-channel TLL state. Reprinted with permission from [90] Copyright (2005) American Physical Society.
the pristine SWCNT and for the peapod material as a function of the K-doping [92]. For the pristine material, the FL state (i.e., $\alpha = 0$) is recovered for a K/C ratio of $8 \times 10^{-4}$. This point corresponds to the charging of the valence band of the semiconducting nanotubes. For peapods, the fullerene $t_{1u}$ level is situated around the valence band of the semiconducting SWCNTs (see the right panel in Figure 5b.19). In real space, this band corresponds to the states on the one-dimensional chain of the fullerenes. Therefore, upon doping, this lower lying band gets doped earlier, forming a perfect one-dimensional conductor. Inside metallic SWCNTs, the presence of a one-dimensional metal inside gives rise to an additional channel of TLL, thus their ensemble appears to be a two-channel TLL, which results in a reduced (but non-zero) $\alpha$. Therefore, the phase diagram of the K-doped peapods is such that for low doping it is a TLL, for high doping it is a FL, and for intermediate doping it is a two-channel TLL.

5b.5.3 Transport Properties

The first transport studies were performed on metallofullerene (Gd@C$_{82}$) peapods, the sample being in the form of a buckypaper [26]. The temperature dependent resistance for a metallofullerene and C$_{60}$ peapods, and for an empty SWCNT is shown in Figure 5b.20.

It was found that the resistance follows a $\ln R \propto T^{-1/4}$ temperature dependence in the 5–300 K range, which is characteristic for a three-dimensional variable range hopping behavior [94]. The peapod films were found to have a higher resistance than the empty SWCNT sample, which was assigned to the electrostatic scattering or due to disorder.
induced by the presence of the fullerenes. This temperature dependence was confirmed for a thin film of C_{60} peapods [95], which confirms the presence of disorder.

Transport measurements on individual SWCNT peapods were also performed [96,97]. The advantage of such studies is that the individual behavior can be better studied and the measurements are not influenced by the tube-tube contacts which are inevitable for the bucky-paper measurements. The power low-like nature of the low temperature conductivity was confirmed in the individual peapod measurements [96]. Below 30 K, it was found that the peapods behave as a regular array of individual quantum dots [97]. This was assigned to the local changes induced by the presence of the encapsulated fullerenes.

5b.5.4 Optical Properties

The optical properties of SWCNTs are clearly unique among the common materials. First, the optical transitions are extremely well defined and intense due to the presence of van Hove singularities in the density of states for both the occupied and unoccupied states. Second, the optical transition energies strongly depend on the nanotube type (metallic or semiconducting) and helicity (or diameter). Depending the SWCNT helicity, optical transition energies ranging from the near infrared (1 eV) to UV (3 eV or higher) can be found. For a given SWCNT helicity, the optical transition energies form almost a mathematical series. The important question related to the peapods is whether the optical properties are significantly affected by the encapsulation. The answer in brief is no, although some minor changes specific to peapods were observed.

The optical properties were studied by the Pichler group using optical absorption spectroscopy and EELS [44]. In Figure 5b.21, we show the optical absorption spectra for empty SWCNTs and for the peapod sample. A small downshift of 14 meV was observed, which can be thought of as a fingerprint for the presence of the fullerenes. It was suggested that the downshift is either due to a small increase of the SWCNT diameter, or due to a change in the intertube interaction. The earlier possibility is related to the fact that the

![Figure 5b.21](image-url)
optical transition energy is inversely proportional to the tube diameter. The second possibility is related to the fact that upon encapsulating fullerenes, the inner van der Waals interaction could make the tube-tube interaction weaker on the outside.

The present understanding of the optical properties is more complicated than a single electron picture with a band-band transition. It is known that the optical excitations are of excitonic nature, that is, the excited electron and hole pair forms a bound state with a sizeable binding energy [98]. It is also known that the dielectric environment plays an important role in the exciton binding energy due to dielectric screening effects [99], which could also account for the observed shift. Our conclusion is that it cannot be decided at present what the real source of the observed optical transition energy downshift is.

Concluding the optical properties, we mention another yet unsolved problem. It is known (although being a negative result, it is unpublished) that the infrared vibrations of the encapsulated $C_{60}$ has not been observed. $C_{60}$ has four infrared active vibrations in the mid-infrared (IR) range below 1429 cm$^{-1}$ [2]. It was suggested that these are invisible since, for a SWCNT assembly, these lie below the plasma edge thus they are screened. However, optical measurements did not show a clear plasma edge for SWCNTs and rather show the evidence for a low energy (10 cm$^{-1}$) gap instead [100].

5b.5.5 Vibrational Properties

Studying the vibrational properties of peapods is restricted to Raman spectroscopy due to the above mentioned anomalous absence of the IR lines of the encapsulated fullerenes. We discussed the first Raman study in Section 5b.4.1.2. and in Figure 5b.7. from Ref. [20]. It was shortly followed by a detailed Raman study by Pichler et al. involving several laser energies and low temperatures [79]. $C_{60}$ has four IR and 10 Raman active modes [2]. Of the latter two are totally symmetric, the $A_{g}(1)$ and the $A_{g}(2)$ at 496 and 1469 cm$^{-1}$, respectively. The totally symmetric nature means that these modes are nondegenerate, that is, they cannot split even upon lowering the icosahedral symmetry of $C_{60}$. The other nonsymmetric modes are the $H_{g}(1)$ (272 cm$^{-1}$), $H_{g}(2)$ (433 cm$^{-1}$), $H_{g}(3)$ (709 cm$^{-1}$), $H_{g}(4)$ (772 cm$^{-1}$), $H_{g}(5)$ (1099 cm$^{-1}$), $H_{g}(6)$ (1252 cm$^{-1}$), $H_{g}(7)$ (1425 cm$^{-1}$), $H_{g}(8)$ (1575 cm$^{-1}$). Among all the Raman modes, the $A_{g}(2)$ (also called pentagonal pinch mode, or PPM) is the strongest.

Two properties prove that the $C_{60}$ vibrations are indeed observed in the peapod Raman spectra. First, most of the modes can be identified, even though the SWCNT modes are also present and overlap with the $C_{60}$ modes. As we show in Figure 5b.22, the $H_{g}(2)$, $A_{g}(1)$, and the $A_{g}(2)$ can be undoubtedly identified. The other property is the Raman resonance behavior. It is known that the Raman signal is enhanced by several orders of magnitude when the exciting laser energy matches an optical transition of the studied molecule [101]. $C_{60}$ has a HOMO-LUMO gap of around 2.5 eV where a relatively strong optical transition takes place. In the Raman spectra, a clear enhancement of the fullerene vibrational mode intensity (best seen for the PPM) is observed.

The $C_{60}$ PPM shows a characteristic splitting for the peapods. The two components are at 1466 and 1474 cm$^{-1}$. In fact, the splitting itself is very surprising. As mentioned above, the totally symmetric $A_{g}(2)$ mode should not be split even upon symmetry lowering. This means that the observed splitting is an inhomogeneous effect, that is, the two components come from different fullerene molecules, which are located in different areas of the sample. The optical transition energy seems to be different for the two components, as the stronger,
low frequency one is in resonance with the 2.54 eV laser, whereas the weaker, high frequency component is stronger with the 2.47 eV laser. Two further Raman experiments led to the clarification of the origin of the split components.

Pfeiffer et al. [102] studied the temperature dependence of the split $A_g(2)$ components. It was found that the high frequency one reversibly disappears with increasing temperature (above 500 K). This suggests that the high frequency mode vanishes due to the activated rotation of the molecule. Simon et al. [33] studied the Raman spectra of the PPM when $C_{60}$ is encapsulated inside SWCNTs with different diameters and the result is shown in Figure 5b.23. The Raman spectrum of molecular $C_{60}$ is shown for reference. For a host SWCNT with a mean diameter of 1.34 nm, the characteristic double PPM peaks are found with the Raman shifts discussed above. For a somewhat larger diameter host SWCNT sample (1.4 nm) the higher PPM peak is absent but the lower frequency component remains at the original position (1466 cm$^{-1}$). For even larger diameter host SWCNTs (for which the so-called silo arrangement occurs), the single PPM mode is found at the position where it appears in crystalline $C_{60}$.

These observations can be interpreted in conjunction with the theoretical work of Michel et al. [51], who found that two different $C_{60}$ configurations are realized depending on the diameter of the host tube. For $d \leq 1.4$ nm, $C_{60}$'s form a structure with facing pentagons whereas the fullerenes rotate freely for larger diameter host SWCNTs. This leads to the conclusion that the mode with the higher Raman shift originates from the fullerenes with facing pentagons and the mode with the low Raman shift originates from the rotating $C_{60}$. This explains the observation in Ref. [102] that the high frequency mode disappears at higher temperatures as fullerenes formerly arranged with facing pentagons start to rotate. The 3 cm$^{-1}$ downshift of the low frequency mode with respect to the mode in crystalline fullerenes disappears for the very large diameter host tubes as the tube-fullerene interaction therein is smaller.

Figure 5b.22 Energy dependent Raman spectra at 20 K for $C_{60}$ peapod samples. The spectra are scaled relative to the Raman G mode. The lines between 360 and 390 cm$^{-1}$ originate from the overtone of the SWCNT RBMs. Reprinted with permission from [79] Copyright (2001) American Physical Society.
The behavior of the PPM mode upon charge transfer was studied using K vapor [79,103] and electrochemical doping [104]. It was found that the PPM downshifts of 6 cm$^{-1}$ per transferred electron. This charging-induced downshift is identical to that found for the crystalline fullerenes [2].

### 5b.5.6 Magnetic Properties

The magnetism of peapods originates from encapsulated magnetic fullerenes. Among the available experimental methods, we discuss magnetic resonance only, that is, electron spin resonance (ESR) and nuclear magnetic resonance (NMR). Other magnetism related experiments such as, for example, bulk magnetometry, are not usable for SWCNTs due to the inevitable presence of magnetic catalyst particles which gives a nonseparable contribution to the net magnetism [105]. In contrast, magnetic resonance spectroscopy enables to separate the magnetism of the catalytic particles from the encapsulated fullerenes due to its spectroscopic nature.
Two different kinds of magnetic fullerenes could be encapsulated, those carrying electron magnetism such as, for example, N@C₆₀, C₅₉N, and other fullerene nitoxide radicals, and those carrying a nuclear spin on the ¹³C nuclei. We discuss below (Section 5b.6), that efforts to encapsulate magnetic fullerenes into SWCNTs is motivated by a proposal from Harneit [37] that this system would be suitable for quantum computing.

The first encapsulation of a magnetic fullerene was performed in 2001 [26] in a now seminal paper, which is discussed herein in many aspects (HR-TEM on metallofullerenes and transport). To our knowledge the magnetic properties of the encapsulated Gd@C₈₂ metallofullerene has not been studied in its peapod form, although the electron spin resonance for the pristine metallofullerene was investigated [106].

The first encapsulation of a C₆₀-derived magnetic fullerene inside SWCNTs was reported by Simon et al. [18]. The endohedral N@C₆₀ was encapsulated with the low temperature peapod synthesis method, which is discussed in Section 5b.4. In N@C₆₀ [28], the nitrogen is in an atomic state with an S=3/2 high spin state due to Hund’s rules. The I=1 nuclear spin state of the most abundant ¹⁴N nuclei gives rise to a characteristic hyperfine splitting into three components with a uniquely large hyperfine coupling constant. This is the result of the compressed nitrogen orbitals inside the fullerene cage, which thus increases the overlap of the electron wave functions with the nucleus. The unique magnitude of the splitting allowed the unambiguous identification of the encapsulated molecule. However, an inhomogeneous broadening was observed whose origin remains unclear.

The major limitation related to the N@C₆₀ magnetic fullerene is that it is prepared with N ion bombardment of C₆₀ fullerenes with a very low yield (tens to hundreds of ppm in C₆₀) and concentrating it requires a costly repetition of high-performance liquid chromatography [107] which relies on the longer retention time of the heavier N@C₆₀ for achieving 100% concentration.

Another magnetic fullerene is the azafullerene C₅₉N. In this molecule, nitrogen replaces a carbon atom whose extra electron is unpaired and the monomer form of the molecule is a free radical. The material can be chemically prepared [108,109], however the unpaired electrons readily form a bond and the material occurs as (C₅₉N)₂ dimers which can be converted to C₅₉N−X (where X denotes a side-group). However, both of these azafullerene compounds are ESR silent as the extra electron is located in the bond. This also means that encapsulating (C₅₉N)₂ dimers into the SWCNTs does not result in a magnetic peapod.

C₅₉N could be only temporarily produced in light [110] or thermally excited [111] conditions. It was shown that the C₅₉N free radical could be also stabilized if it is embedded in the C₆₀ matrix, that is, when it forms a solid solution [112] and is denoted as C₅₉N:C₆₀. This motivated to attempt a similar stabilization inside SWCNTs. First, C₅₉N−X was encapsulated inside the SWCNTs along with C₆₀ [30]. The C₆₀ was intended to separate the azafullerene molecules from each other. Then, a heat treatment around 600°C removes the −X side-group leaving behind the azafullerene free radical with high concentration [31]. This material is denoted as C₅₉N:C₆₀@SWCNT.

In Figure 5b.24, we show the ESR spectrum for the azafullerene peapod from Ref. [31]. For reference, the ESR spectrum for the crystalline C₅₉N:C₆₀ solid solution is also shown. It was recognized previously that the latter ESR spectrum consists of a triplet component and a singlet line component [113]. The triplet signal corresponds to electron spins which reside on the C₅₉N molecule and interact strongly with the ¹⁴N nucleus. However, the singlet component comes from electron spins which are transferred nominally to a neighboring C₆₀ when a
A $C_{59}N:C_{60}$ heterodimer molecule is formed. The latter is the ground state of the $C_{59}N:C_{60}$ system and the excited state is the rotating $C_{59}N$ monomer, surrounded by neutral $C_{60}$s.

For the azafullerene peapod, several properties of the encapsulated azafullerene change with respect to the crystalline form. These changes are all characteristic for the encapsulation. First, the rotation of the $C_{59}N$ inside the SWCNT is strongly anisotropic with a preferred axis of rotation parallel to the nanotube axis. Second, the binding energy of the heterodimer is larger, probably due to the more compact fullerene-azafullerene arrangement. Third, a reversible charge transfer from the azafullerene towards the host nanotube was observed above $\sim 350$ K. Measurement of the spin-lattice relaxation time on the heterodimer at low temperatures allowed measuring the density of states on the host nanotubes.

Following the azafullerene peapod synthesis, nitroxide spin-labeled fullerenes were also prepared [114,115]. The advantage of the nitroxide spin labels is that these are (i) air stable, and (ii) do not tend to dimerize, thus these are stable as a peapod even without being separated, as a fully linear spin chain.

Nuclear magnetism of fullerenes is sizeable for highly $^{13}$C enrichment only since natural abundance of $^{13}$C in carbon is only 1.1%. The first encapsulation of $^{13}$C enriched $C_{60}$ inside SWCNTs was reported in Ref. [32]. NMR spectroscopy was also performed but the attention was focused on the properties of the peapod derived inner tube. These NMR investigations led to an evidence for the Tomonaga-Luttinger liquid phase for the inner

Figure 5b.24 Room temperature ESR spectra of the azafullerene peapod (upmost panel) and of the azafullerene-fullerene solid solution (lowest panel). The middle panel shows deconvolution into a triplet and a single line components. The latter is indicated with an arrow. Reprinted with permission from [31] Copyright (2006) American Physical Society.
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The rotational dynamics of the encapsulated C$_{60}$s was studied by Maniwa et al. [50]. It was found that C$_{60}$ rotates quasi-freely with rotational correlation times of 5–10 ps at 300 K. Down to 30 K, the large angle molecular jumps persist but there is no phase transition in the rotational behavior which is related to the one-dimensional nature of the arrangement.

5b.6 Applications of Peapods

We split the discussion of peapod applications into already existing (or demonstrated) on the one hand and expected (or theoretically envisioned) on the other hand. We note that ‘existing’ or ‘demonstrated’ does not mean a device functioning on an industrial scale but rather an application which is demonstrated already at least in laboratory conditions. To our knowledge, there is no application of peapods which has gone to the real industrial use level yet. The expected applications are those which have been only theoretically speculated.

5b.6.1 Demonstrated Applications

5b.6.1.1 Transistor

SWCNTs are ideal building blocks for nanoelectronics given their small size and their high current-carrying capability. There are three obstacles for the applicability though: (i) the inability of patterned growth and contacting; (ii) the random chirality (and thus conductivity) distribution of the tubes; (iii) the relatively large, above 1 eV, direct gap of the semiconducting tubes. Modern electronics tends to use small gap semiconductors for increased speed and reduced dissipation. The band gap problem was overcome using fullerenes. The Shinohara group showed that the band gap can be reduced to 0.1 eV by means of encapsulating charge donor metallofullerenes inside the SWCNTs [88].

Later, the transistor behavior of this metallofullerene peapod system was also proven. In Figure 5b.25, we show the HR-TEM image of such a peapod material along with the transistor characteristics, from Ref. [118]. The device (shown in the Figure 5b.25 inset) shows conduction for both polarities of the gate bias (gate-source voltage), $V_{GS}$. For comparison, a C$_{60}$-peapod-based transistor device was also investigated and a unipolar p-type behaviour was found. This is related to the strong electron acceptor nature of C$_{60}$ and the behavior of the metallofullerene peapod is related to the fact that the metallofullerene can behave either as an acceptor or as a donor. The latter is due to the three valence electrons of Gd which are removed with relative ease. This experiment showed the potential of peapods in enabling a control of the electronic properties of the SWCNT hosts which can lead to a variety of applications.

Evidence for single-electron transistor behavior was found for C$_{60}$ peapods by the group of Roth [119]. The conductance through a gate-biased peapod was studied as a function of temperature. At room temperature, the result of the Shinohara group was reproduced, that is, that the conductance is p-type, being finite for negative bias and vanishing for positive bias. At 1.8 K, however, the conductance is reduced for both polarities, but surprisingly the positive bias conductance shows (random) oscillations as a function of the gate potential. This oscillatory behavior was associated with the presence of the C$_{60}^-$. Indeed, the molecule modifies the Fermi surface in its vicinity [87,88] and when some fullerenes are separated...
from each other by empty tube segments, a quantum dot is created. Transport in the nanotube thus proceeds through the quantum dots in the form of single electrons.

5b.6.1.2 Solar Cell

Solar cells are in the focus of applied research as these could enable sustainable development for the energy industry. Solar cells consist of an active medium which provides an electron-hole pair upon light excitation which are separated from each other with an electrode. The electrode has to be transparent and highly conducting. A well-known problem is that the most common electrode material, ITO (indium tin oxide), is expensive and it has a limited supply of indium (projected to run out in 20 years). Viable and promising alternatives to ITO are conducting thin films of SWCNTs as proposed by the Rinzler group [120]. The use of SWCNTs for solar cell purposes received another boost by the observation of Li et al. [121] that fullerenes encapsulated inside SWCNTs act as the active electron-hole producing medium. This means that peapods alone can act as solar cells as they have the active

Figure 5b.25 HR-TEM micrograph of Gd@C₈₂ metallofullerene peapods (upper panel) and the current voltage characteristics of the device shown in the inset. Note the darker spots in the HR-TEM image which are the heavy Gd ions. Also note the finite current for both positive and negative V GS which is characteristic for an ambipolar transistor behavior. Reprinted with permission from [118] Copyright (2002) American Institute of Physics.
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medium as well as the electrode naturally integrated. Although this effect requires further studies and in particular benchmarks for the quantum efficiency for the light induced electron transfer, it shows a high application potential of peapods for solar cell purposes.

5b.6.1.3 Drug Delivery

Drug delivery is one of the promising areas of application of carbon nanotubes, the activities being reviewed in [122]. This application potential stems from (i) the biocompatibility of the carbonaceous materials, (ii) the possibility to attach the active molecules to the nanotubes, as the SWCNTs have a high specific surface area, and (iii) the possibility to track the carbon nanotubes in vivo, for example, by fluorescence spectroscopy [123]. In addition to functionalization, the inner space of the SWCNTs provides another possibility for drug delivery, either using functionalized fullerenes or other nonfullerene peapods.

A potential hindrance to use encapsulated materials for drug delivery purposes is how to control the removal at the target. As we discussed above, the encapsulated fullerenes are energetically stable inside the host SWCNTs allowing the largest binding energy, typically the SWCNTs with \( d \sim 1.4 \text{nm} \) such as the (10,10). The encapsulation is so stable, that the fullerenes do not escape at any temperature and rather form an inner tube. Clearly, the removal of the fullerenes could be attempted for larger diameter host nanotubes. In Ref. [33] the controlled removal of encapsulated fullerenes was presented. First, \( \text{C}_{60} \)s were encapsulated inside larger diameter SWCNTs, where the so-called silo (i.e., a non-linear, zigzag like) arrangement is realized. The encapsulation was performed in methanol and the removal proceeded in dichlorobenzene. Although the mechanism of this observation is not fully clear yet it is probably related to the different solubility of fullerenes in these two solvents: \( \text{C}_{60} \) has a three orders of magnitude lower solubility in methanol than in dichlorobenzene in units of mg ml\(^{-1}\) [2]. This suggests that the fullerenes prefer entering the nanotubes when in methanol and prefer leaving the tubes when the latter are surrounded by the dichlorobenzene. Although neither of these solvents is biocompatible, it was speculated that, for example, water-soluble fullerenes (with an attached bioactive group) would enable drug-delivery.

A promising alternative to the fullerene peapods was presented recently by the group of Borowiak-Palen [124]. Instead of the fullerene, an anticancer drug was directly encapsulated inside SWCNTs. Its effect was verified for an in vitro environment. We suggest herein, that a combination of external functionalization of the SWCNTs and encapsulated drugs could be a viable route. The external functionalization would be responsible for the targeted nature of the delivery, whereas the encapsulated molecule would be the drug itself.

5b.6.2 Expected Applications

5b.6.2.1 Photonic Crystals

Photonic crystals refer to materials where the periodic array of their constituents give rise to a periodic modulation of the dielectric constant. This results in unique optical properties such as, for example, well-defined gaps in the transmittance in a manner analogous to the band gap behavior of solids. Peapods were suggested to be used as photonic crystals [125] thanks to the periodicity of the encapsulated fullerenes which is well-defined. It was found that the periodicity and the dielectric properties of \( \text{C}_{60} \) fullerenes give rise to an optical gap around 7 nm which means that soft X-rays with this wavelength could be trapped inside the peapods. This means that if an effective medium, which emits radiation with this wavelength,
is placed within the peapod structure, the emitted radiation would be amplified such as in a laser, which could provide a way to construct a soft X-ray laser.

5b.6.2.2 ‘Nanogun’

The effect of charging the outer walls of the host SWCNT on the motion of a neutral \( \text{C}_{60} \) was studied in Ref. [126]. It was found that the motion of the inner \( \text{C}_{60} \) is different depending on the sign of the outer tube charging. If the outer tube is positively charged, it drives out the molecule with speeds over 1 km s\(^{-1}\), just like a ‘nanogun’, while a negatively charged tube can drive the molecule into oscillation inside it and can absorb inwards a neutral molecule in the vicinity of its open end, like a ‘nanomanipulator’. This asymmetric behavior is related to the different affinity of \( \text{C}_{60} \) toward charging: it is an effective electron acceptor but it is a bad electron donor. The validity of this proposal lies in the ability to charge the host outer tube almost independently from the encapsulated fullerenes. Pichler \textit{et al.} [103] observed that upon intercalating K (electron doping) or FeCl\(_3\) (hole doping) into peapods, the host SWCNT walls are charged at low intercalation levels and that there is no charge transfer to the encapsulated fullerenes.

5b.6.2.3 Peapod ‘Shuttle’ Memory

Early dynamic observations of the behavior of encapsulated fullerenes by TEM showed that they were able to move back-and-forth in the SWCNT cavity, presumably upon random ionization effects due to electron irradiation in the TEM [4] (see Figure 5a.11 in Chapter 5a). The first paper confirming the existence of \( \text{C}_{60} \) inside carbon shells via modeling by Kwon \textit{et al.} discussed the possibility to use these as ‘shuttle’ memories. It was shown that \( \text{C}_{60} \) can move relatively easily inside a carbon shell while retaining energy minima around the ends of the outer shell. The small but well defined energy minima would enable to use the \( \text{C}_{60} \) as an information carrier, the position being the different bit values. The name ‘shuttle’ describes the fact that the encapsulated \( \text{C}_{60} \) switches between the different bit values by a rapid shuttling.

In Figure 5b.26, we show the schematics of the proposed device from Ref. [14] along with a HRTEM observation of a peapod-like structure which motivated the shuttle memory concept.

In addition to the issue of actually making such a short single-wall capsules deliberately (which could possibly be solved by, e.g., considering nanohorns) a potential problem of the shuttle memory device is to provide the driving force for the memory switch. Charging the \( \text{C}_{60} \) with K atoms was proposed [14,127], which would enable electrostatic control, but another possibility (to our knowledge proposed herein for the first time) is to encapsulate \( \text{C}_{59} \)N azafullerenes, which can be ionized with ease [109].

Alternative shuttle memory devices were proposed such as those based on small, encapsulated K ion clusters [128] and also using BN nanotubes as host material for the fullerenes [129]. Another interesting proposal is to form a short inner tube segment from the encapsulated fullerenes and to use this as information carrier unit inside a host nanotube [130]. Whereas these suggestions are definitely interesting, we are not aware of any experimental realization of a similar device, neither of any attempt to achieve control of a single encapsulated fullerene.

5b.6.2.4 High Frequency Oscillator

Quartz crystal oscillators are common in information technology to provide synchronizing pulses. However, typical crystal sizes are millimeters, which prevent their direct integration. In addition, energy dissipation becomes an increasing problem for such crystals at the
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required high frequencies (several 10 GHz for state-of-the-art computing). Recently, interest turned toward utilizing carbonaceous structures for oscillator purposes motivated by the demonstration of very low friction in coaxial multiwall carbon nanotubes by the Zettl group [131]. First, double-wall carbon nanotube structures were considered [132] and studied using molecular dynamics calculations. It was shown that a (9,0) nanotube inside an (18,0) would behave as a 38 GHz nanooscillator. A peapod-based oscillator was proposed in Ref. [133] and a fundamental eigenfrequency of 50 GHz was found for the C_{60} motion inside a 5 nm long section of a (10,10) SWCNT. In a recent work, the evidence for nanoelectromechanical coupling in peapods has suggested them as NEMS resonators, with an operation frequency set by the vibrational motion of the encapsulated fullerenes in the 100 GHz range. The condition for the encapsulated fullerenes is not to be closely packed so that they can arrange into short (e.g., involving 10 C_{60}s) chains [134]. The major obstacle for such a resonator is how to provide the continuous driving force for the motion. It is difficult to control externally the motion of C_{60} thus the C_{60}N^+ ion was suggested as a better candidate for such a purpose [133,135]. This molecule has a sizeable electric dipole moment which allows initiating its motion with an electric field impulse. It was also shown that the tube length allows controlling the frequency of the proposed oscillator [135].

Figure 5b.26  (a) HR-TEM micrograph of a fullerene encapsulated inside a multiple-wall shell of sp² carbons. (b) The schematics of the proposed ‘shuttle memory’ device. (c) The energetics of the C_{60} for different configurations. Reprinted with permission from [14] Copyright (1999) American Physical Society.
We note, that neutral C\textsubscript{59}N monomers were successfully encapsulated inside the SWCNTs [30,31]. Preparation of a sample containing short SWCNT segments filled with single C\textsubscript{59}Ns could be the next step toward the realization of such an oscillator. Ionization could be achieved by UV light or soft X-ray irradiation as the extra electron on the C\textsubscript{59}N is relatively weakly bound [109].

5b.6.2.5 Quantum Computing
Quantum information processing can be divided into quantum computing (QC) and quantum information storage [136]. Both areas require the availability of a true quantum variable or qubit (such as, e.g., an atomic state, a supercurrent, photon polarization, or a spin). For information storage, a high level of decoupling of the quantum variable from the environment is desired. For information processing, a number of the quantum variables has to interact in order to form an entangled state on which the calculation proceeds. There are two potential challenges in quantum computing: upscalability and decoherence. Practical calculations require a large number of qubits, which however increases complexity and also the decoherence due to the increased level of interactions, thus these two objectives are somewhat exclusive. QC has been demonstrated on a 7 qubit system using nuclear magnetic resonance [137] with already an enormous complexity. A possible alternative for an upscalable solid state qubit system with reasonable complexity was proposed by Kane [138], which relies on Si nuclei arranged in a linear fashion.

Building upon this suggestion, Harneit [37] suggested to prepare a linear chain of spin qubits for QC. It was proposed that a single qubit would contain a N@C\textsubscript{60} endohedral fullerene [28] and the concept of the proposal is shown in Figure 5b.27. In this molecule, the atomic nitrogen is remarkably decoupled from its environment due to the protecting shielding of the fullerene cage. The utility of this molecule for quantum computing has been demonstrated by Mehring et al. [139].

Although not suggested explicitly in the original paper, it became evident that the peapod structure would be an ideal realization for the linear arrangement of the endohedral fullerenes. This motivated the low temperature peapod synthesis efforts (described in Section 5b.4.1.3) as the N@C\textsubscript{60} molecule is unstable above 200°C [35]. Although, the QC field itself is continuously progressing, there is a long way until practical application, nevertheless the proposal to use peapods for this purpose remains an interesting and compelling suggestion.
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Overall Conclusion for Chapter 5

Regarding filled CNTs, most of the expectations for the discovery of unprecedented properties—and subsequent promises for a variety of applications—involves SWCNTs instead of MWCNTs as the containing nanotubes. In contrast with pessimistic early predictions, the narrow cavity of SWCNTs can actually be filled with liquid and gaseous materials with high filling rate efficiency. For filling methods involving liquids, this means that, in first approximation, wetting nanosized capillaries obeys the same laws (such as Laplace-Young’s laws) as wetting of submillimeter capillaries. However, it is now ascertained that the surface tension of the filling materials at liquid state is not the only relevant parameter to consider in nanowetting when the latter involves narrow (∼1 nm and below) nanotubes. A large panel of methods is now available to fill SWCNTs with a large variety of materials (elements or compounds) with an efficiency that unfortunately still largely depends on empirically determined filling conditions. Filled SWCNTs are now currently investigated worldwide with respect to a variety of properties and behaviors, with the reasonable hope that breakthrough reports may be anticipated in the close future, as it has started to happen.

In this broad picture, although they are the first example, evidenced as early as in 1998 of a hybrid structure involving SWCNTs filled with individual molecules, fullerene-filled single-wall carbon nanotubes; peapods are still the most studied filled nanotubes. This is because they are: (i) fascinating materials, built from the combination of two of the most recently discovered carbon molecular structures; (ii) easy to prepare, with large yield if
necessary; (iii) beautiful model objects for revealing unprecedented physical behaviors and
new properties; (iv) useful training objects for practicing nanoengineering; and (v) full of
promise for the synthesis of a variety of novel materials. It is not ascertained yet whether
practical applications will actually come out once, as those aspects are still investigated at
a point where cost issues are not yet considered. If they will, however, the first application
area will probably be electronics. The next decade will tell.