TRANSFORMATION OF C\textsubscript{70} PEAPODS INTO DOUBLE WALLED CARBON NANOTUBES

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Abstract

X-ray diffraction studies comparing the transformation of C\textsubscript{60} and C\textsubscript{70} peapods into double-walled carbon nanotubes (DWCNTs) are presented. The structures of the as-formed DWCNTs are strikingly similar, showing that they are not dependent on the nature of the fullerene precursor. High temperature X-ray diffraction measurements of C\textsubscript{70} peapods below the coalescence temperature show that confined C\textsubscript{70} molecules in large tubes undergo an orientational transition to free rotations. Fast reorientations of C\textsubscript{70} molecules allow cyclo-addition between adjacent fullerenes to form, in good agreement with the mechanism of coalescence proposed in the literature for C\textsubscript{60} molecules.
1. Introduction

The filling of single walled carbon nanotubes (SWCNTs) by molecules opens the way towards a new chemistry in confined one-dimensional nanospace. In particular, fullerenes and acenes inside SWCNTs transform into inner-shell tubes after high temperature treatment; a double walled carbon nanotube (DWCNT) is formed. The reader will find in ref. [1] a review discussing the special interest of DWCNTs in terms of stability, transport and mechanical properties, and considering the different routes for their efficient growth.

Here we address the formation of DWCNTs from SWCNTs filled with fullerenes \( C_n \) (the so-called “peapods”), under high temperature treatment; the resulting product will be referred to as “DWn”. DW60 formation has been demonstrated in 2000 [2] and then extensively studied, both experimentally [3-7] and theoretically [8,9]. Two hypotheses have been considered: (i) \( C_{60} \) decomposition into small clusters re-arranging in an inner tube and (ii) molecule coalescence. The first hypothesis has now been ruled out experimentally [6,7]. The most reliable \( C_{60} \) coalescence model is based on two phenomena: cyclo-addition processes (CAp) and Stone-Wales transformations (SWt) [1,6-9].

The formation of DWCNTs from \( C_{70} \) peapods has been reported since 2001 [3,5,10]. But up to now, it has been studied in detail in one article only, using the Raman scattering technique [10]. An anomalous absence of mid diameter inner tubes was noted for DW70 by comparing their Raman spectra with those of DW60. In this article, we present the first X-ray diffraction (XRD) study of DW70 and we compare XRD features of DW70 and DW60. They are strikingly similar. This new result raises questions as the CAp leading to inner tube formation requires convenient orientations of adjacent \( C_{70} \) molecules, which is not likely in
the confined environment of a SWCNT [11]. A key question is the determination of molecular orientations at high temperature, just below the coalescence temperature. We have thus studied the re-orientation of $C_{70}$ molecules as a function of temperature by in situ X-ray diffraction. Our results, which differ from previous ones reported in the literature [12], shed new light on the behaviour of confined $C_{70}$ molecules as a function of temperature.

2. Experimental

Experiments have been made on two different series of samples, having slightly different nanotube diameter distributions. Sample series 1 refers to: (i) a powder of SWCNTs, purchased from NANOCARLAB (Russia), with mean diameter $<D_c> \approx 1.42\text{nm}$, the Full Width at Half Maximum (FWHM) of the diameter distribution being equal to $0.2\text{nm}$ [13]; (ii) powders of $C_{60}$ and $C_{70}$ peapods obtained by heating the open NANOCARLAB nanotubes and a fullerene powder together, so that the powder sublimates and the fullerenes enter into the nanotubes; the procedure is described in detail in ref. [13] and the filling rate $p$ — defined as the amount of fullerenes inside the tube divided by the maximum amount that could enter in it given the interfullerene distance — is of about $90\%$; (iii) powders of DWCNTs obtained by heating the $C_{60}$ or the $C_{70}$ peapods for 48 hours at $1300^\circ\text{C}$. Heating was performed under an argon gas flow of $0.5\ \text{ml/min}$, to avoid sample oxidation during the long heating time. Sample series 2 consists of buckypapers of SWCNTs produced by the laser furnace technique and of peapods obtained by filling these tubes with $C_{70}$ molecules [14]. The SWCNTs exhibit a narrow diameter distribution centred around $13.8\text{Å}$ and the filling rate is high, as for series 1 [4,12,15].
XRD experiments were performed using CuKα radiation, the range of wave-vectors of interest being [0.3-1.6 Å⁻¹]. Room temperature diagrams shown in fig.1 have been obtained on a rotating anode, wave-length selection (λ=1.5418Å) being assured by parabolic confocal W/Si multilayers mirrors. Experiments were performed under vacuum to minimize contamination due to air scattering. The powders were placed inside a home-made aluminium capillary of 1.5 mm diameter, the aluminium width being as thin as possible (10 µm) to limit absorption affects. The diffraction signals from aluminium, above 2.69 Å⁻¹, are outside the region of interest. Diffraction patterns were recorded in transmission on a planar imaging plate. Low temperature diffractograms presented in figure 4 were obtained on a set-up equipped with a closed-cycle cryogenerator mounted on a rotating anode generator. A high intensity monochromatic beam is provided by a doubly-curved graphite monochromator and X-ray detection is ensured by a home-made gas-ionization line detector. The scattering vector detection range was centered around 0.9Å⁻¹, i.e. in the middle of the wave-vector region of interest, to minimize parallax effects. The buckypaper was oriented perpendicular to the incident X-ray beam to maximize the signal characteristic of the periodic arrangement of fullerenes with respect to scattering peaks characteristic of the hexagonal two-dimensional organization of the nanotubes in bundles [11,16,17]. High temperature diffraction diagrams reported in figure 4 were recorded on a ‘D8 Advance’ diffractometer of Bruker-axs using Cu Kα radiation, Göbel mirror and a solid state detector “Sol-X” of Bruker-axs. The XRD system is equipped of a heating chamber with two heaters surrounding one sample carrier in alumina and assuring a homogeneous heating by radiation during the measurements, a thermocouple in Pt / Pt-Rh adjusted in direct contact with the sample and Kapton X-ray windows. This device was used under vacuum. Every diagram was recorded for eight hours, by steps of 0.02° in 2θ (the relation between the scattering angle θ and the wave vector Q - used in this article - is Q=4πsin(θ)/λ).
3. Results and discussion

3.1. Structure of DW60 and of DW70

Room temperature XRD patterns of reference SWCNTs (series 1) are shown in fig.1a. They consist of broad peaks characteristic of the two-dimensional arrangement of the tubes in hexagonal bundles, which are slightly displaced from the hk peaks of an infinite lattice due to form factor effects [18].

The intensity diffracted by a powder of SWCNT bundles formed of N nanotubes of diameter D is [19]

\[
I_{SW,D}(Q) \propto \frac{\sigma^2 f_c(Q)^2}{Q} \left[ DJ_0\left(\frac{QD}{2}\right)\right]^2 \sum_{j,k=1}^{N} J_0(QR_{j,k}) \tag{1}
\]

where \(Q\) is the wave-vector modulus, \(f_c(Q)\) is the carbon atomic factor, \(\sigma\) is the density of carbon atoms on a nanotube (\(\sigma \approx 37 \text{ at/nm}^2\)), \(J_0\) is the cylindrical Bessel function of order zero, \(R_{j,k}\) is the modulus of the vector joining the centers of tubes \(j\) and \(k\) within a bundle, in the plane perpendicular to the bundle axis, as is drawn in fig. 1a, and \(N\) is the number of tubes per bundle. In equation (1), the term \(\sum_{j,k=1}^{N} J_0(QR_{j,k})\) is an interference term. For large \(N\) values, it gives the Bragg peaks indexed by hk integers in the reciprocal hexagonal lattice; for smaller values of \(N\), it gives larger peaks around these positions. The term \(A = \sigma DJ_0\left(\frac{QD}{2}\right)\) (which appears to the square in equation (1)) comes from the Fourier transform of the nanotube atomic density projected along its long axis, in the plane perpendicular to it. Equation (1) is
obtained under the assumption that discrete carbon atoms at the surface of a nanotube can be replaced by a homogeneous atomic density, which limits its validity to Q values under 2Å⁻¹. Our experimental data, limited to 1.6Å⁻¹, can be well interpreted using this simple formula. The distribution of nanotube diameters between different bundles, in real samples, can be accounted for by considering a Gaussian distribution of diameters \( p(D) \) characterized by its FWHM \([19]\). Simulation of experimental data is thus performed by integrating expression (1) weighted by such a distribution, and taking into account standard geometrical and polarization factors \( G \) and \( P \) \( (G(\theta) = \cos^3(2\theta)) \) for the planar geometry of the imaging plate detector, \( P(\theta) = \frac{1 + \cos^2(2\theta)}{2} \), \( \theta \) being the scattering angle defined by \( Q = \frac{4\pi \sin(\theta)}{\lambda} \).

Convolution to the resolution function can be omitted because it is sufficiently narrow compared to the measured peaks (FWHM~0.02Å⁻¹ for the resolution). Intensity is thus calculated as

\[
I(Q) \propto GP \int_0^\infty I_{SW,D}(Q) p(D) dD
\]  

The best fit of the SWCNT powder pattern (see fig. 1a) is obtained for \( \langle D\rangle = (1.42 \pm 0.02)\text{nm}, \) \( FWHM = 0.2\text{nm}, \) \( N = 31, \) the inter-tube distance being \( g = (0.32 \pm 0.01)\text{nm}. \) Aiming at determining the structural parameters for which our simulation is the closest to the experimental diffraction profile, we adopted a trial & error procedure, in which each structural parameter is varied successively and the corresponding diffraction profile is calculated. The matching degree of each calculated pattern is evaluated by a naked-eye comparison with the experimental data, and finally a “best fit” can be selected. Contrarily to classical crystals, it is not possible in the case of nanotube-based materials to achieve a formal statistical analysis of the fit accuracy. For example, the use of the reliability factor (R factor) commonly used in powder diffraction pattern fitting is not relevant here. Indeed, the diffraction features to be considered are rather large and of low in intensity with regards to the background. The R
factor would therefore become over-dependent on the background correction, considerably limiting its relevance. Rietveld analysis of a SWCNT sample has only been published by one team [20] but it did not give more information than qualitative comparison of profile matching. We have also attempted to perform reliability factor minimization and we reached the same conclusion. However, we managed to estimate error bars of our fittings. The error bars given here and in the following are determined by the parameter values, around the ones corresponding to best profile matching, for which simulations are still in good agreement with experiments. Such “error bar” determination is illustrated in fig.2(b) and (c) for DW60 (see below).

Room temperature X-ray diffraction patterns of DWCNTs obtained by heating C_{60} and C_{70} peapods from series 1 are drawn in fig.1b. We report here the first measurement of the XRD pattern of DW70, and it looks, as shown in fig. 1b as well as in its inset, very similar to that of DW60.

The intensity diffracted by a powder of DWCNT bundles [4, 6, 21-23] formed of N nanotubes of external diameter D and of internal diameter D_{i} writes

\[ I_{DW,D,D_{i}}(Q) \propto \frac{\sigma^2 f^2}{Q} \left[ DJ_{0}\left(\frac{OD}{2}\right) + \alpha D_{i} J_{0}\left(\frac{OD_{i}}{2}\right) \right]^2 \sum_{j,k=1}^{N} J_{0}(QR_{j,k}) \]

where \( \alpha \) is the ratio between the lengths of the internal and external tubes. Indeed, one easily shows that the Fourier transform of the projected atomic density, which gave \( A = \sigma D J_{0}\left(\frac{OD}{2}\right) \) for SWCNT, now leads to

\[ A = \sigma \left[ DJ_{0}\left(\frac{OD}{2}\right) + \alpha D_{i} J_{0}\left(\frac{OD_{i}}{2}\right) \right] \]

In DWCNT produced directly, by chemical vapor deposition methods [24,25], the lengths of the inner and of the outer tubes are the same and \( \alpha=1 \) [21]. In DWCNTs resulting from C_{n}
peapods conversion (n=60, 70, etc), conservation of the number of atoms inside the outer tube gives

$$\alpha = \frac{np}{\sigma \pi D_i L}$$

(5)

where L is the distance between the centers of two adjacent fullerenes, i.e. the 1D lattice parameter of the fullerene chain, and p the filling rate of the initial peapod.

Let us first discuss the DW60 diffraction diagram. It consists of broad peaks located close to the hk positions of the hexagonal bundle lattice like that of SWCNTs: DW60 tubes are organized in bundles. However the relative intensities of the diffraction peaks are very different from those of SWCNTs because of the modification of the form factor term A (they are similar to those obtained by Abe and co-workers for DW60 also [4]). Fitting of the experimental data is reported in fig. 1b and leads to the following parameters: $<D>=(1.42\pm0.02)\text{nm}$, $\text{FWHM}=0.2\text{nm}$, $N=31$, $g=(0.335\pm0.01)\text{nm}$, $p=0.9$ (for $L=0.98\text{nm}$) and $D_t=D-0.72\text{nm}$. Calculation of the intensity was made, using eq. (3), as follows

$$I(Q) \propto GP \int_{0}^{\pi} I_{DW,D,D,D-0.72\text{nm}}(Q) p(D)dD$$

(6)

The mean-value of the external diameter as well as its distribution and the number of tubes within a bundle are the same as in the reference SWCNTs. The lower value of the filling rate p determined on DW60 diffraction pattern can be estimated to about 0.8, as shown in fig.2b, since the increase of the intensity of the 10 and 21 peaks becomes too important to allow good fitting of experimental data for $p=0.7$. The filling rate p and the inter-fullerene distance are in accordance with values deduced from XRD data obtained on C$_{60}$ peapods before heating, as is shown in fig.2a (the reader may refer to [15] for a detailed discussion on C$_{60}$ peapods diffraction pattern). The value of the gap g appears to have increased from $(0.32\pm0.01)$ nm in SWCNT bundles to $(0.335\pm0.01)$ nm in DWCNT bundles. Error bars allow some
overlapping, however this gap increase, if meaningful, may be related to change in inter-tube interactions, which can in some cases be more dramatically modified for DWCNT, as compared to SWCNTs [26]. Let us discuss in more details the structure of the DW60 tubes deduced from XRD data. We find that the distance between inner and outer tubes is $(0.36\pm0.01)$ nm ($D_i=D-2\times0.36\text{nm}$), this result being stable over small variations of the other fitting parameters. Error bars of 0.01 nm on this distance can be evaluated as follows from fig.2(c): for values of $(0.36\pm0.02)$ nm, simulated diffraction patterns would clearly be in poorer agreement with experimental data. It is consistent with the conclusions of Abe and co-workers, based on XRD experiments on DW60 with slightly smaller external diameters [4], or with that from Raman and electron diffraction studies [3,27]. Our result corroborate, on larger nanotubes, the conclusion of Abe and collaborators: the intertube spacing between inner and outer tubes is determined by the interlayer distance of turbostratic graphite at the synthesis temperature. The inner tube, during its formation, adapts its diameter to minimize van der Waals interactions with the outer tube. Note that studied samples were annealed at 1300°C for 48 hours and have thus reached the final stage of the DWCNT formation; discussion about intermediate stages is not within the scope of this paper but interesting results can be found in ref. [5,6]. However, we stress that the high filling factor we used to fit DW60 data ($p=0.9$) implies that there is no fullerene depletion inside nanotubes during heating, in agreement with Abe XRD results [4] but in contradiction with those of Pfeiffer and collaborators [6].
Figure 1. Full symbols: Room temperature X-ray diffraction patterns of (a) SWCNTs and (b) DWCNTs obtained after heating of C\textsubscript{60} peapods (squares) and of C\textsubscript{70} peapods (triangles); samples are from series 1. Curves are translated for clarity. Inset in (b): magnification of the [0.6-1.6Å\textsuperscript{-1}] range. Open symbols: simulations for \langle D\rangle=1.42\text{nm}, FWHM=0.2\text{nm}, 31 tubes per bundles, (a) g=0.32\text{nm}, (b) \text{D}_{i}=D-0.72\text{nm} \text{ g}=0.335\text{nm}, \text{ p}=0.9, \text{ D}_{\text{enc}}, the diameter below which the tubes are empty, is taken equal to 1.2\text{nm for C}_{70} molecules (see the text). Vertical lines indicate hk peak positions in the reciprocal hexagonal lattice. Views of the hexagonal arrangement of SWCNTs and DWCNTs are schematically drawn in (a) and (b), respectively, in the plane perpendicular to the tubes axes.
Figure 2. (a): full circles: room temperature X-ray diffraction patterns of C$_{60}$ peapods used to synthesize DW60, solid line: simulation for $<D>$=1.42nm, FWHM=0.2nm, 31 tubes per bundle, $p$=0.9 and $L$=0.98nm, dashed dotted line: $p$=0.8. Arrow points toward the asymmetric peak characteristic of the C$_{60}$ periodicity $L$. (b) and (c): open squares: simulations for $<D>$=1.42nm, FWHM=0.2nm, 31 tubes per bundle, $D_i$=D-0.72nm, $g$=0.335nm, $p$=0.9, as in fig.1 (b); in (b), dotted dashed line: same parameters except for $p$ which is taken equal to 0.8, solid line : $p$=0.7. In (c), dotted dashed line: same parameters as for open squares except for $D$, which is taken equal to D-0.76nm, solid line : $D_i$= D-0.68nm. Vertical lines indicate $hk$ peak positions in the reciprocal hexagonal lattice.

To analyse the DW60 XRD further than already done in the literature [4,6], we consider two hypotheses: corrugated inner tube and inner tube off-centering.

One of the first theoretical papers devoted to the formation of DWCNT from peapods [8] pointed out that the structure of the inner tube could be very defective, containing pentagons, heptagons and octagons. How sensitive would XRD experiments be to such an effect of corrugation of the inner tube? Within the homogeneous approximation, valid in the
studied Q range, one may consider an annulus instead of a circle to schematize the inner tube projection. Let us note $D_{i,1}$ and $D_{i,2}$ the internal and external diameter of this annulus ($D_{i,1}=D_r - \Delta$ and $D_{i,2}=D_r + \Delta$, $\Delta$ being equal to zero for a non corrugated inner tube). The Fourier transform of the annulus is easily calculated in terms of the cylindrical Bessel function of order 1, $J_1$, using the well-known property $\frac{d}{dx}(xJ_1(x)) = xJ_0(x)$, and one finds that $A$ (equation (4)) transforms into $A_{corr}$ given by

$$A_{corr} = \sigma \left[ DJ_0 \left( \frac{QD}{2} \right) + \alpha \frac{2}{D_{i,2} - D_{i,1}} \frac{D_{i,2}J_1 \left( \frac{QD_{i,2}}{2} \right) - D_{i,1}J_1 \left( \frac{QD_{i,1}}{2} \right)}{Q} \right] \quad (7)$$

The scattered intensity is thus given by

$$I_{corr}(Q) \propto GP \int_0^\infty A_{corr}^2 \sum_{j,k=1}^\infty J_0(QR_{j,k}) p(D) dD \quad (8)$$

Comparison between calculations for standard DWCNTs and DWCNTs with corrugated inner tubes shows that corrugation effects cannot be easily measured using XRD: even for a rather important value of $\Delta=0.05\text{nm}$, the curves calculated from eq. (6) and (8), drawn in fig. 3, present too subtle differences to be observed experimentally [43].

Let us now turn towards the second hypothesis. The inner tube is considered to be at the center of the outer tube at high temperature. Its diameter equals that of the outer tube minus twice the van der Waals distance in turbostratic graphite at the synthesis temperature ($D_r=2 \times 0.36\text{nm}$). When temperature is lowered, the inner tube may take an off-center position because its diameter is 0.04 nm too small with respect to the energetically optimized one at room temperature (the van der Waals distance at room temperature is 0.34 nm to be
compared to 0.36 nm at 1300°C; variation of nanotube diameter with temperature are not
taken into account because they are negligible [42]). The effective off-centering of the inner
tube is expected to be lower than 0.02 nm, since a displacement of the inner tube towards the
outer tube wall in a given direction should involve a competing attraction of the inner tube
towards the outer wall in the opposite direction. We have calculated the potential energy of a
DWCNT with $D_i = D_e - 2 \times 0.36 \text{nm}$ as a function of the distance $d$ between the inner and outer
tube centers for different outer tube diameters, within the continuum approximation and using
van der Waals parameters at room temperature [28]. Off-centering occurs only for very large
diameter tubes. It follows that in our sample the inner tube positions fluctuates around $d=0$,
fluctuations being of course larger than for the case $D_i = D_e - 2 \times 0.34 \text{nm}$. We nevertheless
calculated the XRD profile resulting from a sample where all inner tubes would be 0.02 nm
off-centered, as an “extreme case” for the XRD pattern. The scattered intensity of a powder of
bundles of DWCNT with outer diameter $D$, inner tube diameter $D_i$ and out-of center position
$d$ is given by

$$I_{D,D_i,d}(Q) \propto \frac{\sigma^2 f_e^2}{Q} \left[ D J_0 \left(\frac{QD}{2}\right) + \alpha D_i J_0 \left(\frac{QD_i}{2}\right) J_0(Qd) \right]^2 \sum_{j,\ell}^N J_0(QR_{j,\ell}) + N \left[ \alpha D_i J_0 \left(\frac{QD_i}{2}\right) \right]^2 \left(1 - J_0(Qd)^2\right) \right\}$$

(9)

Averaging over all possible directions of translation by the distance $d$ in the plane
perpendicular to the tube axis leads to the additional contribution $J_0(Qd)$ in the first term of
eq (9). The second term is a diffuse scattering term of the Laue form [29], characterizing the
random disorder from one tube to another (different directions for off-center translations).
Integrating equation (9) over the experimentally determined distribution of tube diameter
$p(D)$, we have calculated the scattered intensity with $d=0.02 \text{ nm}$ (fig. 3) and we show that it is
so similar to that calculated in the case $d=0$ that experimental discrimination between the two
hypotheses $d=0$ and $d=0.02\text{nm}$ is impossible. It follows that XRD experiments will not be sensitive to the thermal fluctuations around $d=0$.

In summary, our XRD experiments performed on DW60 allow us to determine the diameters of the inner and outer tubes. In addition, we have shown that possible off-centering or corrugation effects result in changes in the diffraction profile too small to be resolved experimentally. We point out that off-centering and corrugation effects had not yet been considered in the literature before, and that the results presented in this section nicely show what information can be deduced from XRD with no ambiguity, as well as the method’s limitations.
Figure 3. Bottom: calculated intensity from eq. (6) for ‘standard’ DWCNTs (squares) and eq. (8) for DWCNTs with corrugated inner tube (solid line), a tiny difference between two curves is underlined; up: intensity from eq. (6) repeated (squares), and from eq. (9) for DWCNT with inner tube off-centering (solid lines). Curves have been translated vertically for clarity. Calculation parameters are $<D>=1.42nm$, FWHM=0.2nm, $N=31$, $g=0.335nm$, $p=0.9$ (for $L=0.98nm$) and $D_i=D-0.72nm$, $D_{i,2}=D_i+0.01nm$, $D_{i,1}=D_i-0.01nm$, $d=0.02nm$, $\Delta=0.05nm$. Schematics are shown on the right to explicit hypothesis of the calculations described in the text.

The new experimental result presented in fig. 1 is the DW70 diagram. The diffraction diagram of DW70 appears very similar to that of DW60. It follows that DWCNT made from C$_{70}$ peapods present the same structure as those made from C$_{60}$ peapods. In particular, the difference between their internal and external diameters is determined by the van der Waals distance in turbostratic graphite at high temperature: $D_i=D_f-2 \times 0.36nm$. Calculation of the DW70 diffraction pattern is however a little bit more complicated than that of DW60 because
one has to consider two different orientations of the C\textsubscript{70} ovoid molecules for the reference peapods at room temperature [30], whose parameters are used to determined the \( \alpha \) coefficient (eq. (5)): the lying orientation, where the long axis of C\textsubscript{70} molecules is parallel to the nanotube axis and the standing one, where it is perpendicular. Lying and standing orientations occur for tube diameters smaller and larger than \( D_c=1.42 \) nm, respectively [13]. They correspond to different inter-fullerene distances: \( L_{\text{ly}}\approx1.1\)nm and \( L_{\text{st}}\approx0.98\)nm, giving different values, \( \alpha_{\text{ly}} \) and \( \alpha_{\text{st}} \), of the coefficient \( \alpha \) used in eq. (3). Moreover, one should also consider an encapsulation diameter \( D_{\text{enc}} \) below which the tubes are empty [13]. In C\textsubscript{60} peapods, it was not necessary to consider such a diameter. One explanation might be that the value of the encapsulation diameter is smaller for C\textsubscript{60} than for C\textsubscript{70}. Indeed, when heating together a powder of nanotubes and of fullerenes, which sublimate, nanotube filling occurs spontaneously in tubes with larger diameter that the insertion diameter. It corresponds to the diameter for which the energy of a molecule inside the nanotube is equal to \( T \) times the difference in entropy between a free and an encapsulated molecule

\[
E_{\text{tube,full}} = -T\Delta S
\]  

(10)

\( \Delta S \) is larger for C\textsubscript{70} than for C\textsubscript{60} (the ovoid molecule loses some rotational degrees of freedom when confined, being in lying orientation in relatively small diameter tubes, see also section 3.2). It implies that insertion occurs for higher energies \( E_{\text{tube,full}} \) for C\textsubscript{60} than for C\textsubscript{70} and thus that the insertion diameter should be larger for C\textsubscript{70} (see e.g. fig. 8 in ref. [13]). Intensity scattered by a powder of DWCNTs synthesized by heating C\textsubscript{70} peapods writes:

\[
I(Q) \propto G \frac{\sigma^2 J^2}{Q} \left\{ \frac{\alpha_{\text{ly}}}{\alpha_{\text{st}}} \sum_{j,k} J_{\alpha}((QR)_{j,k})p(D)\,dD + \frac{\alpha_{\text{ly}}}{\alpha_{\text{st}}} \sum_{j,k} J_{\alpha}((OD)_{j,k})\,dD \right\} 
\]

(11)
The calculated curve in fig. 1(b), in good agreement with the experimental one, is obtained for the following parameters: \( <D> = 1.42 \text{nm}, \ \text{FWHM}=0.2\text{nm}, \ \text{31 tubes per bundle}, \ D_i=De-0.72\text{nm}, \ g=0.335\text{nm}, \ p=0.9, \ D_{enc}=1.2\text{nm}, \ p=0.9 \ \text{for} \ \geq D_{enc}, \ \text{De}=1.42\text{nm}, \ L_{ly}=1.1\text{nm}, \ L_{st}=0.98\text{nm}. \) Error bars on values of \( <D> \), \( g \) and of the inter-tube distance are the same as those given above for DW60; the high filling rate value is in good agreement with the one found in C\(_{70}\) peapods, as was shown in fig.2 in ref. [13].

The structure of DW70 has also been compared to that of DW60 using Raman scattering [10]. Simon and co-workers [10] pointed out an anomalous absence of middiameter inner tubes (\( D_i \approx 0.67\text{nm} \)) for outer tubes with diameter around 1.39\text{nm} and they argued that it should be caused by the absence of C\(_{70}\) molecules inside nanotubes in the transition region between standing and lying configurations. Calculations estimate the width of the transition region to be of 0.04 to 0.06\text{nm} [13, 31]. We show in fig. 4 what would be the contribution of empty tubes with diameters between 1.4 and 1.44\text{nm} to the diffraction pattern. Arrows point towards Q values where obviously one should have observed more scattered intensity if the hypothesis put forward in ref. [10] was right. The non-observation of such a feature tends to infirm the hypothesis of unfilled middiameter nanotubes. Another striking point may be underlined here concerning Raman data. After publication of ref. [10], Pfeiffer and co-workers [32] presented a detailed analysis of the Raman scattering cross section of the radial breathing modes (RBM) of DWCNT and showed that the observed clusters of RBM modes (mode width\( \sim 3 \text{ cm}^{-1}, \ \text{cluster width} \sim 30 \text{ cm}^{-1} \)) represent one inner tube inside different outer tubes, one mode representing a well-defined pair of inner and outer tubes. Re-examining results of ref. [10] in the light of this analysis, it follows that only one well-defined pair of inner and outer tube would be missing in DW70. This result is puzzling when one recalls that the only constraint between inner and outer tubes concerns their diameter (\( D_i \approx De-0.72\text{nm} \)) but
not their helicity, as shown by electron diffraction [27]. If the latter result was confirmed, the understanding of the absence of one given helicity in these DWCNT would be of great interest.

In the case of C$_{60}$, the route to inner tube growth is the formation of precursor cycloadditionally bonded C$_{60}$ dimers [6-9]. One question still remains for C$_{70}$ peapods, which has already been raised by Simon and co-workers [10]: reactive double bonds being located around the C$_{70}$ tips only [33,34], how could dimers form between standing C$_{70}$ molecules? To

Figure 4. Room temperature X-ray diffraction patterns of DWCNT obtained after heating of C$_{70}$ peapods (filled squares); sample series 1. Open squares: corresponding calculations for <$D$> =1.42nm, FWHM=0.2nm, 31 tubes per bundles, for $D_i$=$D_e$-0.72nm, $g$=0.335nm, $p$=0.9, $D_{enc}$=1.2nm and $D_e$=1.42nm (like in fig.1). Solid line: calculated contribution of empty tubes with diameters between 1.4 and 1.44nm. Curves are translated for clarity. Arrows point to empty tube contribution incompatible with experimental data.
try to answer to this question, we have studied the structural evolution of C$_{70}$ peapods as a function of temperature.

### 3.2. C$_{70}$ reorientation as a function of temperature

Experiments were performed between 30K and 1073K (below DW70 formation temperature) and they are reported in fig. 5 (a) [35]. The two peaks located at $Q_1 \approx 0.57\AA^{-1}$ and $Q_2 \approx 0.63\AA^{-1}$ at room temperature are characteristic of the periodic ordering of C$_{70}$ molecules in lying and in standing orientations, respectively: $Q_1 \approx \frac{2\pi}{L_1}$ with $L_1=L_{\text{ly}}\approx 1.1\text{nm}, Q_2 \approx \frac{2\pi}{L_2}$, $L_2=L_{\text{st}}\approx 1.0\text{ nm}$.

The position $Q_1$ of the first peak does not change with increasing temperature between 30K and 673K, but its intensity diminishes at 573K and 673K, which indicates an increase of disorder with temperature. One may speculate that the orientation of the long axis of lying molecules fluctuates noticeably, at high temperature, around its average position along the tube axis, inducing large fluctuations of the interfullerene distances. Confinement by the nanotube wall however does not allow the molecule to rotate in nanotubes with diameter smaller than the ‘critical’ diameter $D_c$. The evolution of $L_1$, renormalized to its value at room temperature, is shown in fig.5(b). Within experimental error bars, it is constant but the dotted curve, calculated using the thermal expansion of crystalline C$_{60}$ [36], could also fit experimental data. One thus concludes that molecules in lying orientation, confined in small diameter nanotubes, stay in average in the same orientation at high temperature, with possible larger thermal fluctuations in orientations, and that thermal expansion of the lying lattice parameter is weak but compatible with normal expansion in a fullerene based-crystal.
The position $Q_2$ of the second peak is constant between 20K and 300K, but diminishes from 373 to 573K, reaching a constant value of about $0.61\text{Å}^{-1}$ above 673K. The inter-fullerene distance, which is equal to about 1.00 nm at room temperature and below, increases to 1.03 nm at high temperature. In three-dimensional crystalline C$_{70}$, there is an orientational phase transition from a phase where nearest-neighbour long axes are parallel (in analogy with the standing configuration [37]) towards a high temperature one in which molecules rotate freely [38] (or nearly freely [39]). The transition occurs around 345K and inter-fullerene distance changes from 1.01nm for parallel molecules to 1.06nm for rotating molecules. Such an increase in interfullerene distance is similar to our experimental result in C$_{70}$ peapods. We also present here calculated interaction energies between two molecules in standing orientation, two molecules in lying orientation and two rotating molecules. Calculations were performed within the homogeneous approximation, i.e. approximating standing and lying molecules by nine circles on an ellipsoidal (see fig. 4 in ref. [13]) and approximating the rotating C$_{70}$ molecules by spheres. Calculations are detailed in ref. [13] for standing ($\psi=0^\circ$ [37]) and lying molecules; corresponding energies are drawn in fig. 6 (or in fig. 7 in ref. [13]).

A rotating molecule is approximated by concentric spheres with radii $R_\nu=0.3565$, 0.3663, 0.3876, 0.4029 and 0.4172 nm, and with corresponding atomic density $\sigma_\nu=6.3$, 11.9, 10.6, 4.9 and 4.6 at/nm$^2$ ($\nu=1$-5). Sphere radii and atomic density are deduced from carbon atomic coordinates of a C$_{70}$ molecule, by performing a rotational average. The interaction energy between two rotating molecules, numbered 1 and 2, writes, within the homogeneous approximation,

$$E_{1,2} = \sum_{\nu_1,\nu_2=1}^{5} \sigma_{\nu_1} \sigma_{\nu_2} \iiint u(r) d\Sigma_1 d\Sigma_2$$  \hspace{1cm} (12)
where $r$ is the distance between two points $M$ and $P$ on the spheres $\nu_1$ and $\nu_2$ of the two molecules. The van der Waals potential is

$$u(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$  \hspace{1cm} (13)

with $A = 20 \text{ eVÅ}^6$ and $B = 34.8 \times 10^3 \text{ eV Å}^{12}$ [13, 28]. Integration over sphere $\Sigma_1$ can be performed in a referential frame where the $z$ axis is parallel to the distance $O_2P$, $O_2$ being the center of sphere $\Sigma_2$. One thus shows that the integral over $\Sigma_1$ gives

$$\int u(r)d\Sigma_1 = 2\pi R_{\nu_1}^2 \left[ \frac{A}{2\alpha^6} \left( \frac{1}{(\beta+1)^2} - \frac{1}{(\beta-1)^2} \right) - \frac{B}{5\alpha^{12}} \left( \frac{1}{(\beta+1)^{12}} - \frac{1}{(\beta-1)^{12}} \right) \right]$$

with $\alpha(O_2P) = 2R_{\nu_1}\sqrt{R_{\nu_1}^2 + d^2 - 2dO_2P}$ and $\beta(O_2P) = \frac{R_{\nu_1}^2 + R_{\nu_2}^2 + d^2 - 2dO_2P}{\alpha^2}$, $d$ being the distance between the centers $O_1$ and $O_2$ of the two fullerenes. Using $O_2P = R_{\nu_1}\cos(\theta_2)$ in a fixed referential where the $z$ axis is now parallel to $O_1O_2$ for instance, one easily shows that integral over $\Sigma_2$ can be reduced to a one-dimensional integral and that

$$E_{\nu_{12}} = 4\pi^2 \sum_{\nu_1,\nu_2} \sigma_{\nu_1,\nu_2} R_{\nu_1}^2 R_{\nu_2}^2 \int \frac{A}{2\alpha(xR_{\nu_1})^6} \left( \frac{1}{(\beta(xR_{\nu_1})+1)^{12}} - \frac{1}{(\beta(xR_{\nu_1})-1)^{12}} \right) - \frac{B}{5\alpha(xR_{\nu_1})^{12}} \left( \frac{1}{(\beta(xR_{\nu_1})+1)^{18}} - \frac{1}{(\beta(xR_{\nu_1})-1)^{18}} \right) dx$$  \hspace{1cm} (14)

Numerical integration of equation (14) leads to the calculated energy curve for rotating molecules in fig.6. Equilibrium distances are found to be 1.13, 1.08 and 1.02nm for lying, rotating and standing molecules, respectively. It confirms that the expected inter-fullerene distance for rotating $C_{70}$ molecules in peapods is situated in-between the distances between lying molecules and between standing ones. We thus infer that the observed increase from 0.98-1nm to 1.03 nm in interfullerene distance in large tubes ($D>D_c$), where molecules are in standing orientation at room temperature, corresponds to a transition from standing to rotating molecules at high temperature. The increase appears progressively from 373 to 573K; this may correspond to a progressive increase of the fluctuations around the standing orientation.
until free rotation is reached and/or to different transition temperatures between standing and rotating molecules phases, the transition temperature $T_{\text{standing-rotation}}$ depending on the diameter. The increase of the transition temperature towards free rotations of C$_{70}$ fullerenes in peapods with regards to bulk C$_{70}$ (373-573K compared to 345K) illustrates an effect of the lateral confinement of the molecules in nanotubes. Another effect of confinement had already been evidenced in the case of C$_{70}$ peapods, where C$_{70}$ molecules were not able to polymerize under high pressure and high temperature conditions [11].
Figure 5. (a) X-ray diffraction pattern of C$_{70}$ peapods, as a function of temperature (lines identified as “Oven”: sample series 1, lines identified as “Cryostat”: sample series 2). The solid lines indicate the position of the peaks originating from molecules in lying and standing orientation at room temperature. (b) Thermal expansion of the C$_{70}$ intermolecular distance for molecules in parallel orientation at room temperature (filled circles) and for molecules in perpendicular orientation at room temperature (open triangles). Solid lines are guides for the eye; the dotted line illustrates the linear thermal expansion in bulk C$_{60}$. 
Figure 6. Interaction between two C\textsubscript{70} molecules as a function of the distance L between their centers of mass. Optimal L values are found to be equal to 1.015\textit{nm}, 1.08\textit{nm} and 1.134\textit{nm} for standing, rotating and lying molecules, respectively.

One should mention that our experimental results concerning the evolution of inter-C\textsubscript{70} distances as a function of temperature are not compatible with those presented in ref. [12], where for the standing orientation, the authors reported a progressive increase of the interfullerene distance between 100K and 1000K, with a specially strong variation between 100 and 300K. We have thus performed another low temperature experiment than the one shown in this article, between 30 and 300K, using another cryostat and an Image Plate instead of a linear detector. It confirmed the data shown in fig. 5. Two models have been developed from the experimental data of ref. [12]: a model of thermal activation allowing molecules to stumble from standing to lying orientations [12] and a related one-dimensional Ising model [40] where spins $\sigma=1$ and $\sigma=-1$ represented standing and lying orientations, respectively. Both models were very attractive, however, in our opinion, the new results presented here show that one should also take into account free rotation of the molecules at high temperature.

To summarize, we conclude from our XRD experiments as a function of temperature that (i) in small diameter tubes (diameter smaller than $D_c\approx1.42\text{nm}$), molecules stay in lying
orientations from low to high temperatures, with possibly larger librations at high
temperature, and (ii) in larger tubes, molecules in standing orientation at room temperature
perform free rotations above 673K.

The latter result is an important clue to understand the formation of the inner tube
from C\textsubscript{70} molecules within a mechanism implying - like for C\textsubscript{60} molecules - first,
cycloaddition processes (CAp) and second, Stone-Wales transformations (SWt). We propose
here two possible CAp’s: (1) head-to-head coalescence, as described in ref. [41] for facing
(5,5) nanotubes, which are rigorously analogous, geometrically, to facing lying C\textsubscript{70} molecules,
or (2) formation of dimers through active double-bonds close to the molecules tips\textsuperscript{1}. Head-to-
head coalescence would be geometrically possible in all tubes, since the lying orientation is
the mean molecular orientation in narrow tubes and since it can be adopted instantaneously in
large tubes where molecules rotate freely at high temperature. Instantaneous formation of
dimers is also possible in large tubes because of the rotation of the molecules and of
fluctuations in positions around their mean position along the tube axis: their reactive double
bonds face each other at different times. It can occur in smaller tubes because of thermal
fluctuations of lying molecules around their mean orientation. It was shown in ref [11] that
tubes with diameter larger than 1.35 nm can accommodate dimers into their hollow cores. The
demonstration was simply made by considering the van der Waals distance of equilibrium
between the dimer parts facing the tube wall and the tube wall. This condition is a sort of
equilibrium condition: thus, at high temperature, instantaneous dimer formation may be
possible in all tubes of our samples, even for the smallest. After Cap (’s), SWt would ensure
rearrangments towards a more tubular structure, and the succession of CAp and SWt would

\textsuperscript{1} Van Lier G, private discussion
lead to an internal tube with its diameter determined by that of the outer one minus two times the van der Waals distance in turbostratic graphite at high temperature.

3. Conclusion

This article reports the first XRD study of DWCNT synthesized from C\textsubscript{70} peapods, after heating 48 hours at 1300°C. Two main results concerning their formation mechanism and their structure are obtained. The diameter of the inner wall is determined by that of the outer wall and by the synthesis temperature: \( D_i = D_o - 2 \times 0.36 \text{nm} \), the inter-wall distance being the optimum van der Waals distance in turbostratic graphite at 1300°C. The formation of the inner tubes can be explained by re-orientation and coalescence of the C\textsubscript{70} molecules. We have shown that C\textsubscript{70} molecules in standing orientation at room temperature start rotating at high temperature, allowing cyclo-addition processes to occur between adjacent molecules. Like in C\textsubscript{60} peapods, Stone-Wales re-arrangements will then allow the formation of the inner tubular structure.

Our XRD results on peapods and DWCNT obtained after heating peapods contribute substantially to the understanding of different mechanisms of DWCNT formation, essential for the control of their structure and their physical properties. As a next step, we are currently planning in situ XRD experiments capturing the evolution of the coalescence process itself. The analysis of the resulting XRD patterns will rely crucially on the structural information of the begin and end products obtained in the present paper.

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[35] The intensities of the peaks coming from nanotube two-dimensional organization and from periodic arrangement of fullerenes in the low and high temperature data shown in figure 4 cannot be compared directly since the low temperature experiments were performed on a buckypaper, where nanotubes have preferential orientation in the paper plane, while high temperature experiments were performed on powders. Moreover, low temperature experiments and high temperature experiments were performed on samples series 2 and 1, respectively, where mean tube diameters, and thus proportions of lying and standing molecules, differ. However, it has no incidence on the discussion developed in this article where we consider peak positions only.


[37] In the standing configuration, molecules long axes are perpendicular to the tube axis but in fact they are not necessarily parallel, their relative orientations being characterized by the angle $\psi$ between their long axis viewed in a plane perpendicular to the tube axis. However,
the $\psi$ dependence of the energy is very weak [13] and analogy between standing configuration inside nanotube and parallel molecules in the crystal is thus valuable.


[43] No Debye-Waller (DW) temperature factor is considered in equations giving nanotube diffracted intensities in the article. First, it should be underlined that X-ray diffraction data are taken at room temperature, where, to the best of our knowledge, a DW factor was introduced only in one article [19] in the literature. No Debye factor was used in refs [4, 6, 13, 15, 17, 18, 21] for instance. Second, one can notice that thermal fluctuations along the tube direction have no influence in the Q-range studied here, where homogeneous approximation is valid, and that our calculations based on equation (7) illustrate that thermal fluctuations perpendicular to the tube are negligible.