

## Fullerenes, Nanotubes and Carbon Nanostructures

Publication details, including instructions for authors and subscription information:

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C. Bousige <sup>a</sup>, S. Rols <sup>a</sup>, H. Kataura <sup>b</sup> & P. Launois <sup>c</sup>

<sup>a</sup> Institut Laue Langevin (ILL), Grenoble Cedex, France

<sup>b</sup> Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

<sup>c</sup> Laboratoire de Physique des Solides, Univ. Paris Sud, Orsay Cedex, France

Available online: 14 May 2012

To cite this article: C. Bousige, S. Rols, H. Kataura & P. Launois (2012): Translational Dynamics of One-Dimensional Fullerene Chains Encapsulated Inside Single-Walled Carbon Nanotubes, Fullerenes, Nanotubes and Carbon Nanostructures, 20:4-7, 395-400

To link to this article: <http://dx.doi.org/10.1080/1536383X.2012.655209>

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# Translational Dynamics of One-Dimensional Fullerene Chains Encapsulated Inside Single-Walled Carbon Nanotubes

C. BOUSIGE<sup>1</sup>, S. ROLS<sup>1</sup>, H. KATAURA<sup>2</sup> AND P. LAUNOIS<sup>3</sup>

<sup>1</sup>Institut Laue Langevin (ILL), Grenoble Cedex, France

<sup>2</sup>Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

<sup>3</sup>Laboratoire de Physique des Solides, Univ. Paris Sud, Orsay Cedex, France

*Fullerenes inserted in single-walled carbon nanotubes, the so-called “peapods,” provide scientists with an exceptional molecular model system to study one-dimensional physics and confinement. In this communication, we present recent inelastic neutron scattering measurements concerning the translational dynamics of this one-dimensional system. The recent synthesis of a large amount of two-dimensional oriented samples allows us to extract the sole contribution of the inserted C<sub>60</sub> chains. The related quasi-elastic-like peak evolves with the temperature but never shows an additional inelastic contribution when lowering temperature, indicating that carbon peapod is a true one-dimensional system down to low temperatures.*

**Keywords** Fullerene, nanotube, peapod, dynamics

## Introduction

In addition to their exceptional intrinsic physical value, nanotubes offer an inner cavity available to host molecules, providing scientists with a large variety of new nanosystems with novel properties. For instance, water inside nanotubes presents extraordinary transport properties (1) that may pave the way towards a new field in physics—nanofluidics—or lead to major applications in water desalinization. Molecular chains inside single-walled carbon nanotubes (SWCNTs) provide scientists with exceptional model systems in order to study one-dimensional (1D) physics and confinement. This is particularly true when the inner molecules size is comparable to the tubes' diameters, as is the case with C<sub>60</sub> fullerenes inside SWCNTs—such compound being called fullerene “peapods” (2). Regarding the rotational dynamics of the inserted C<sub>60</sub>, it has already been shown that the fullerenes do not present orientational ordering at low temperature (3–5), as is expected in such a 1D system (6). Keeping in mind the exceptional transport of water inside nanotubes, it appeared most interesting to extend our previous studies on rotational dynamics of fullerenes inside nanotubes (3) to the study of their translational dynamics. We present our first results in this article.

Fullerenes inside nanotubes are believed to behave as 1D harmonic system, up to at least room temperature (6,7). The dynamical structure factor of such a system can be

Address correspondence to C. Bousige, Institut Laue Langevin (ILL), 6 rue Jules Horowitz, B.P. 156, F-38042 Grenoble Cedex 9, France. E-mail: bousige@ill.fr

calculated exactly (8–10). Inelastic neutron scattering (INS) experiments were successfully performed with  $\text{Hg}_{3-8}\text{AsF}_6$  single crystals where long 1D mercury chains were shown to be 1D harmonic liquid above the critical temperature of 120 K (11), and the same type of study was also performed on water chains in DNA (12,13). Nevertheless, the common problem of these compounds is that they are not stable at high temperature, and that when lowering the temperature a long range order establishes due to the interaction with the three-dimensional (3D) network (14–16), preventing one from studying 1D properties on a wide temperature range. In the present article, we will discuss the dynamics of fullerenes inside nanotubes down to 10 K.

We report recent inelastic neutron scattering measurements of a  $\text{C}_{60}$  peapods sample using a time-of-flight spectrometer, showing that measurements similar to that performed on the above-cited monocrystals using triple axis spectrometers can be successfully performed for the noncrystalline peapods assemblies. The translational dynamics of the inserted  $\text{C}_{60}$  chains could be observed thanks to the recent synthesis of a large amount of peapods under the form of buckypapers, in which the tubes are mainly oriented along the buckypaper's plane. Using the time-of-flight spectrometer IN5 at the Institut Laue Langevin (ILL), we show that the translational motion of the confined fullerenes can be separated from the inelastic response of the nanotubes.

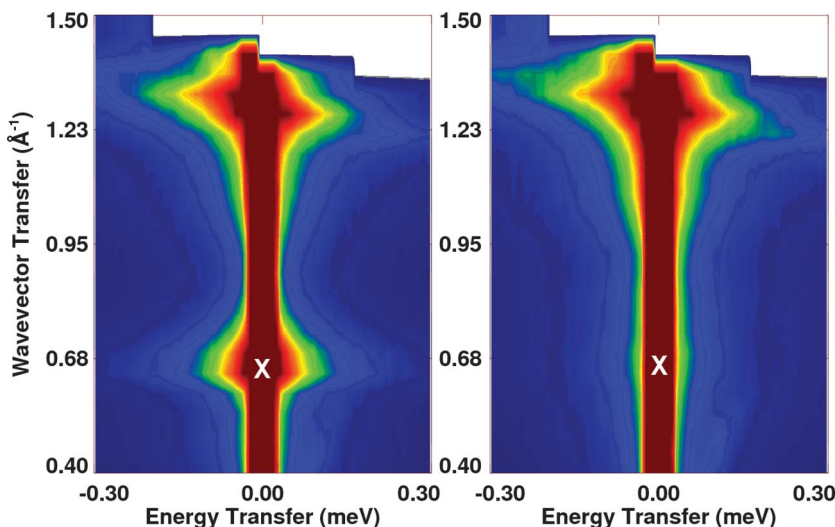
## Experimental

Peapod samples were elaborated to be used for INS measurements. As a consequence, extreme care was taken not to introduce any hydrogenated pollutant during the peapods preparation. Nanotubes of SO type (laser ablation) were purchased from the Meijo Company (Nagoya, Japan), and the fullerenes are MER sublimed  $\text{C}_{60}$  99.9% graded. Following the method developed in Ref. (17), carbon nanotubes under the form of buckypapers were first heated at 600°C under a dynamic vacuum in order to extract any solvent impurities. They were further heated in air at 500°C in order to selectively open them around the reactive sites located at the tips and the defects of the tubes. The tubes and the fullerenes were then sealed in a Pyrex tube under a  $10^{-6}$  mbar vacuum and subsequently heated at 550°C during 8 days. Buckypapers with fullerenes inside nanotubes were then washed in toluene and heated again at 600°C under dynamic vacuum to remove the solvent and the fullerenes that did not enter the tubes. Prior to the neutron experiment, the 1.8 g  $\text{C}_{60}$  peapods buckypapers were compressed in the plane of the aluminum sample holder and heated to 100°C in order to remove water molecules adsorbed post-synthesis.

INS measurements were performed on the cold neutron time-of-flight spectrometer IN5 at the ILL. Incident neutrons with wavelength of 8 Å were used, which allowed us to probe the [0, 1] meV energy range (Stokes side) with 25 µeV resolution, for transfer vectors  $\mathbf{Q}$  within the [0.4, 1.4] Å<sup>-1</sup> range. The measurements were performed at several temperatures between 10 K and 420 K, and the data were subsequently background corrected and normalized to vanadium. At each temperature, two configurations of the sample holder were used. They are referred as “para” and “ortho,” corresponding to the configurations in which the plane of the sample holder is set either parallel or orthogonal to the transfer vector  $\mathbf{Q}$  corresponding to the elastic scattering of the inter  $\text{C}_{60}$  distance.

## Results and Discussion

Using these two configurations allows us to separate the response of the  $\text{C}_{60}$  chains from the one of the nanotubes. Indeed, the dynamical structure factor  $S(\mathbf{Q}, \omega)$  is proportional to

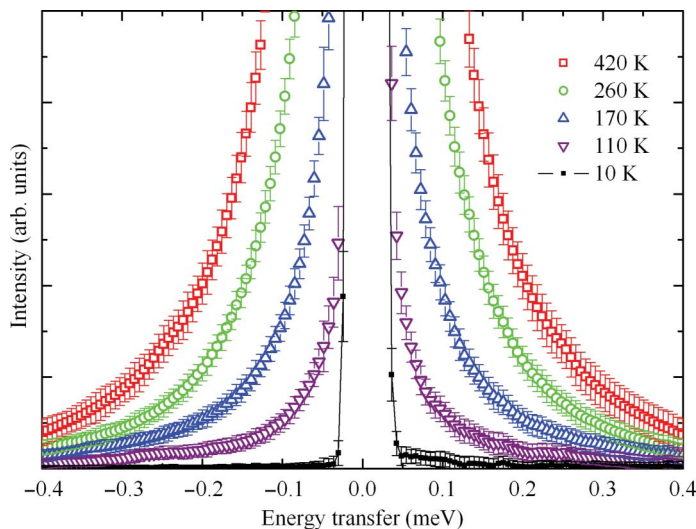


**Figure 1.**  $S(Q, \omega)$  maps taken at 420 K, for incident wave-length of 8 Å, in the para (left) and ortho (right) configurations. Maximum intensity is saturated for the sake of clarity. The white cross indicates the location of the signal from fullerene translational motions, around the wave-vector position corresponding to the first diffraction peak from fullerene chain at  $0.64 \text{ Å}^{-1}$  (color figure available online).

$(\mathbf{Q} \cdot \mathbf{e}_p)^2$ , where  $\mathbf{Q}$  is the neutron transfer vector and  $\mathbf{e}_p$  is the direction of the motion of the molecules induced by the phonon  $p$ . This means that the longitudinal  $C_{60}$  1D phonons contribution is maximum in the para configuration and extinguished in the ortho one, as can clearly be seen in Figure 1, showing the  $S(Q, \omega)$  maps at 420 K in both configurations. In para configuration, the signal from fullerene translational motions is located around the wave-vector position corresponding to the first diffraction peak from fullerene chain at  $0.64 \text{ Å}^{-1}$  (18). On the contrary, the inelastic contribution of the tubes is much less sensitive to the orientation in this  $[Q, \omega]$  range. In this area it consists mainly of soft radial modes, and since the motion of the atoms is perpendicular to the axes of the tubes, atomic displacements occur in all three directions of space, and thus their contribution is similar in both configurations. The above considerations allow us to determine the inelastic contribution of the fullerenes chains by a simple subtraction of the para and ortho data.

Also, due to the geometry of a neutron time-of-flight instrument, the sample will only be parallel (resp. orthogonal) to the wave vector  $\mathbf{Q}$  for  $Q_0 = 0.64 \text{ Å}^{-1}$ , and  $\omega = 0$  – where  $Q_0 = 0.64 \text{ Å}^{-1} = 2\pi/L$  is the first diffraction peak from the fullerene chain,  $L$  being the mean inter-fullerene distance. For the second diffraction order,  $\mathbf{Q}$  and the sample make similar angles (about  $15^\circ$  difference) in both configurations, resulting in an almost unchanged feature around  $Q = 2Q_0 = 1.28 \text{ Å}^{-1}$ . In the following, we will consider only the region where  $Q$  belongs to  $[0.5, 0.8] \text{ Å}^{-1}$  and  $\omega$  stays within  $[-0.5, 0.5] \text{ meV}$  in order to monitor the most parallel and the most orthogonal configurations.

In the para configuration, the additional signal around  $0.68 \text{ Å}^{-1}$  that comprises a quasi-elastic-like part is due to the fullerene chains. It is moreover obvious from Figure 1 that integrating this signal in energy leads to a curve with an asymmetric  $Q$  shape. Such an asymmetric shape is characteristic of 1D long range—or quasi-long range order for a strongly correlated liquid as the  $C_{60}$  chain (6)—after orientational average. It holds for



**Figure 2.**  $S(\omega)$  for several temperatures after extraction of the sole  $C_{60}$  chains contribution. The integration is done over  $Q$  vectors within the  $[0.5, 0.8] \text{ \AA}^{-1}$  range (color figure available online).

3D powder average (18) and also for 2D powder average (19). Our system, with preferential in-plane orientation of the peapods, is intermediate between 3D and 2D powder, which explains the asymmetric shape of the integrated peak.

Figure 2 shows the temperature evolution of  $S(\omega)$  of the sole  $C_{60}$  chain after data treatment and integration over  $Q$  vectors within  $[0.5, 0.8] \text{ \AA}^{-1}$ . There is a clear temperature evolution of the signal, which is more and more intense as the temperature increases. Discussion of the precise shape of the peapod spectra and possible determination of the speed of sound along a  $C_{60}$  chain are beyond the scope of this article, but one can underline the absence of any inelastic peak at any temperature, indicating that the system remains truly one-dimensional down to very low temperatures.

Indeed, such inelastic peaks have been observed when studying long 1D mercury chains in  $\text{Hg}_{3.8}\text{AsF}_6$  at low temperature (11). In this system, the mercury chains behave as 1D liquid at high temperatures and undergo a low temperature phase transition due to interchain coupling. The emergence of this interchain coupling results in a modulation of the acoustic phonons dispersion and hence in the creation of a gap, giving rise to a characteristic peak in the density of states. As a consequence, the absence of such a peak down to 10 K indicates that  $C_{60}$  peapods remain a 1D model system even down to low temperatures. Indeed, the  $C_{60}$  chains, separated by nanotubes walls, are too distant from one another to interact by van der Waals forces.

## Conclusion

Inelastic neutron scattering, when performed on an oriented sample in para or ortho configuration, has proven to be an efficient method in order to study the translational motion of the  $C_{60}$  molecules inserted inside nanotubes. The ability to separate the signal from the sole  $C_{60}$  chains from the one of the hosting nanotubes is of high importance and paves the way to further detailed analysis of the translational dynamics of fullerenes inside nanotubes.

Measurements were performed at several temperatures and the sole  $C_{60}$  chains contribution could be extracted. The temperature evolution of the dynamical structure factor shows no appearance of any inelastic peak even at such a low temperature as 10 K, showing that  $C_{60}$  peapods remain a one-dimensional model system down to low temperatures.

These first results motivate the incoming detailed study of the dynamics of carbon peapods, down to temperatures that could not be achieved in other systems where 3D character is predominant at low temperature. Moreover, the exceptional stability of peapods up to high temperature (1100 K) should allow us to investigate the dynamical behavior of fullerenes upon heating, where an interesting “transition” from a correlated liquid to a hard sphere can occur based on Monte Carlo simulations (7).

## Acknowledgments

The authors would like to thank Jacques Ollivier who was of great help during the experiment on IN5 at the ILL as well as Julien Cambedouzou for interesting discussions.

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