ESRF	**Experiment title:** C_{60} and C_{70} peapods: Temperature evolution and influence of the inserted molecules' shape on the structure of 1D compounds.	**Experiment number**: HS-4360
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Names and affiliations of applicants (* indicates experimentalists):

Colin BOUSIGE*, ILL, Grenoble – Laboratoire de Physique des Solides (LPS), Orsay

Erwan-Nicolas PAINEAU*, LPS Orsay

Pascale LAUNOIS, LPS Orsay

Stéphane ROLS, ILL Grenoble

I. Introduction – Goal of the experiment

The filling of single-walled carbon nanotubes (SWNT) with fullerenes C_n (n = 60 or n = 70) leads to new nanohybrids – called 'peapods' – allowing one to study the physics of one-dimensional confined molecular chains. Such nanohybrids can reach rather high temperatures without desorbing fullerenes, which allows studies over a wide temperature range. The concern of the present proposal was the study of their liquid properties as a function of temperature. Indeed, Monte-Carlo simulations [1] showed that the translational order in the 1D fullerene chains evolves strongly with temperature, from that of a highly correlated Gaussian liquid at low temperature to a hard-core liquid at ~ 700 °C.

For this experiment, we monitored the structural evolution of fullerenes chains with temperature as well as the impact of the fullerenes shape on this evolution. It is to our knowledge the first experimental evidence of a transition from a correlated harmonic liquid towards a hard rod liquid in a 1D system.

II. Experimental results

XRD measurements were performed on ID11, using a Linkam oven under 5 mbar pressure of N_2 – continuous pumping and flux of N_2 – and incoming wave length of 0.3439 Å. Measurements on 3 samples could be performed, 1 on peapods C_{60}, 1 on peapods C_{70}, and one on bulk C_{60} for reference on intermolecular thermal expansion. XRD patterns of 1 min were taken continuously during the temperature cycle shown on the inset Fig. 2.

In figure 1 is plotted the diffracted pattern of C_{60} peapods at two different temperatures. One can see different peaks, which are attributed to the nanotubes hexagonal bundles or to the one-dimensional chains of C_{60} [2].

A fine monitoring of the mean inter-fullerene distance as a function of the temperature and time is plotted on the figure 2.

The progressive increase of the distance is correlated with the lowering of the slope at the inflexion point (increase of the width of the Gaussian function in the inset in figure 1). This is characteristic of the progressive evolution from an highly correlated 1D liquid towards a rigid rod 1D liquid, in agreement with Monte Carlo simulations.

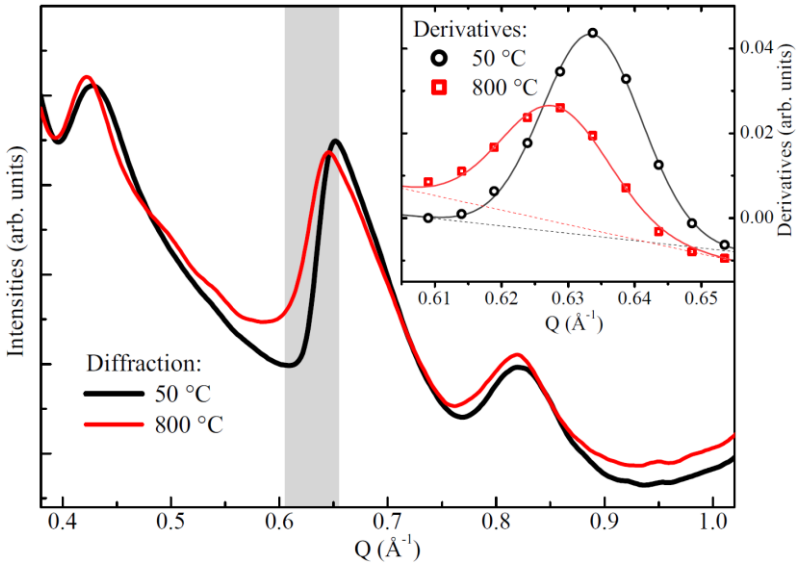

Figure 1 – X-ray diffraction patterns of C_{60} peapods at 50 and 800 °C. The Q-asymmetric peak at 0.64 Å^{-1} is characteristic of the 1D chains of C_{60}, the other peaks are due to the bundle organisation of the nanotubes. The inset shows the evolution of the derivative of the diffraction pattern within the shaded area (scatters) and its fit by a gaussian and a linear background (lines). The local maximum in the derivative gives the position of the inflexion point of the XRD pattern, whose position is $2\pi/\langle L\rangle$ where $\langle L\rangle$ is the mean inter-fullerene distance. The width of the Gaussian function gives precious information on the interfullerene correlation function.

Additional orientational effects are observed for ovoid C_{70}. At room temperature, depending on their diameter, nanotubes contain one-dimensional chains of C_{70} in 'lying' or 'standing' orientation, resp. referring to C_{70} with the long axis parallel or orthogonal to the tube axis [3]. Up to 800°C, one can see a dramatic change in the correlations of the fullerenes, but also that the C_{70} standing molecules start to rotate freely, which increases the mean distance between two molecules [3]. This effect is purely dynamic, and it is coupled to the transformation from a highly correlated harmonic 1D liquid towards a rigid rods 1D liquid.

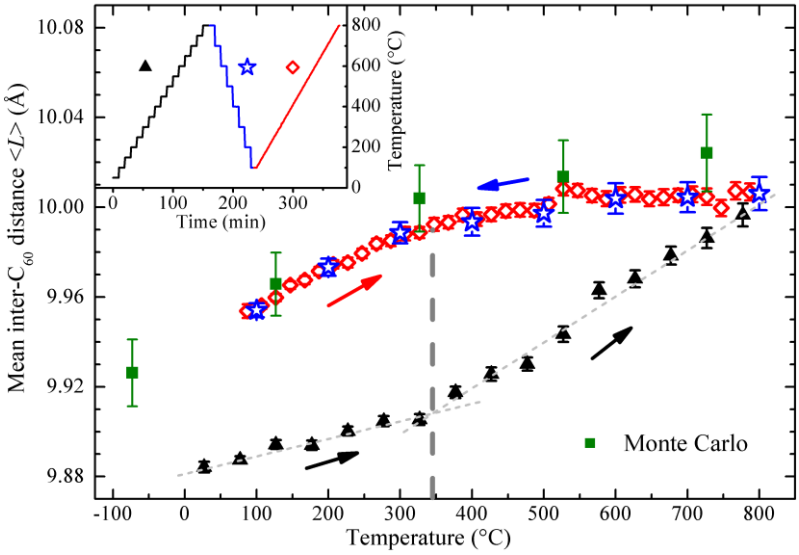

Figure 2 – Temperature evolution of the mean inter-C_{60} distance $\langle L\rangle$. The experimental data are compared to Monte Carlo simulations [4] (green full squares). The inset shows the temperature cycle used during the measurements as well as the correspondance of plotting symbols with the different ramps. The dashed grey lines are linear fits of $\langle L\rangle$ for temperatures under and above 330 °C, their intersection at 345 °C being marked by the dashed vertical line.

Coming back to C_{60} peapods in fig.2, one should underline that the existence of an hysteresis and of a sharp change in dL/dT below and above 345 °C are extremely astonishing since no phase transition is usually expected in a 1D system. Further investigation are being performed in order to fully understand this phenomenon.

This experiment brought us many useful information that will soon be gathered in an article dealing with the evolution from the correlated liquid to the rigid rods one.

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[3] P. Launois, M. Chorro, B. Verberck, P.-A. Albouy, S. Rouzière, D. Colson, A. Forget, L. Noé, H. Kataura, M. Monthioux and J. Cambedouzou, Carbon, 48, **2010**, 89
[4] Article in preparation