Experimental report

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Title: Dynamics of water under hydrophobic ultra-confinement

Research area: Physics

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Samples: H2O
D2O
C

Instrument	Requested days	Allocated days	From	To
IN11	7	7	08/02/2017	15/02/2017
IN6	6	0		
IN5	5	0		

Abstract:

Known structural and dynamic peculiarities of bulk water get even enhanced when this substance is confined within geometries that make the H-bond network undergo severe distortion with respect to the more common tetrahedral arrangement. For example, hydrophobic confinement at the nanoscale allows for appreciating very low-T molecular motions flagged by a significant amount of quantum behavior.
After having experimentally assessed by QENS the formation of a shell+chain structure for water entrapped in small-size CNTs (d around 1.4 nm), and witnessed the persistence of a rotational dynamics even at temperatures as low as 1.5 K, a new batch of measurements designed to extend the lower range of both tube diameter and operational temperature at longer diffusional timescales would be desirable in order to more exhaustively characterize the influence of strict axial confinement on dynamic properties of the scatterers, also probing D2O to get a taste of quantum isotope effects under the same conditions.

Dynamics of water under hydrophobic ultra-confinement

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Motivation. The bulk structure of the most ubiquitous of liquids – water – is dominated by the marked capacity of this substance to establish large networks of hydrogen bonds. Despite this feature persists even under strict confinement, strong stereochemical distortions caused by the host cavity – especially when hydrophobic – can induce pronounced modifications in the physical properties of the encapsulated material in comparison to the bulk case [1]. Single-wall carbon nanotubes (SWCNTs) can be used as a prototypical example of hydrophobic quasi-1D containers, and can induce an extreme confinement to water molecules.

In this context we performed a series of quasi-elastic neutron scattering experiments to study the translational and orientational dynamics of water in SWCNTs from 300 down to 10 K. Results showed that, reducing temperature below 200 K, part of this water behaves as a quasi-free rotor, that is, the orientational energy of such molecules becomes comparable to the rotational energy of water in the gas phase. This novel and unique dynamic behaviour is related to the appearance of water molecules characterized by a coordination number of about two, which is promoted by sub-nanometre axial confinement. This peculiar molecular arrangement allows water to show an active rotational dynamics even at temperatures as low as 10 K. The translational mobility shows a behaviour compatible with the rotational one. To our knowledge, this is knowledge the first experimental determination of this dynamical behaviour of water and the details of this study can be found in an article that was recently published [2].

Experimental Results.

We have just completed an experiment at the spin echo spectrometer IN11C to probe the dynamics of axially-confined water at longer timescales, in the ns region. The same SWCNT system was used as for the above-mentioned QENS study, which was hydrated following the same procedure. NSE measurements were conducted on a couple of samples - one dry, one H_2O-hydrated - in a range of temperatures between 2 and 300K, and at two detector angles of 20 and 50 deg, so exploring two Q-ranges, from 0.15 to 0.62 $Å^{-1}$ (low-Q region) and from 0.83 to 1.26 $Å^{-1}$(high-Q region). In the low-Q region a flat S(Q,t)/S(Q,0) curve is found in the whole range of explored temperatures. Conversely, in the high-Q region, the trend of S(Q,t)/S(Q,0) highlights the onset of one or more dynamical processes at temperature higher than 180K (Figure 1). We are now in the process of finding a link between the observed dynamics and the physical processes that might trigger them[3]. The control scan performed on the dry SWCNT system did not

show any dynamic feature in the explored range of Q and temperatures.

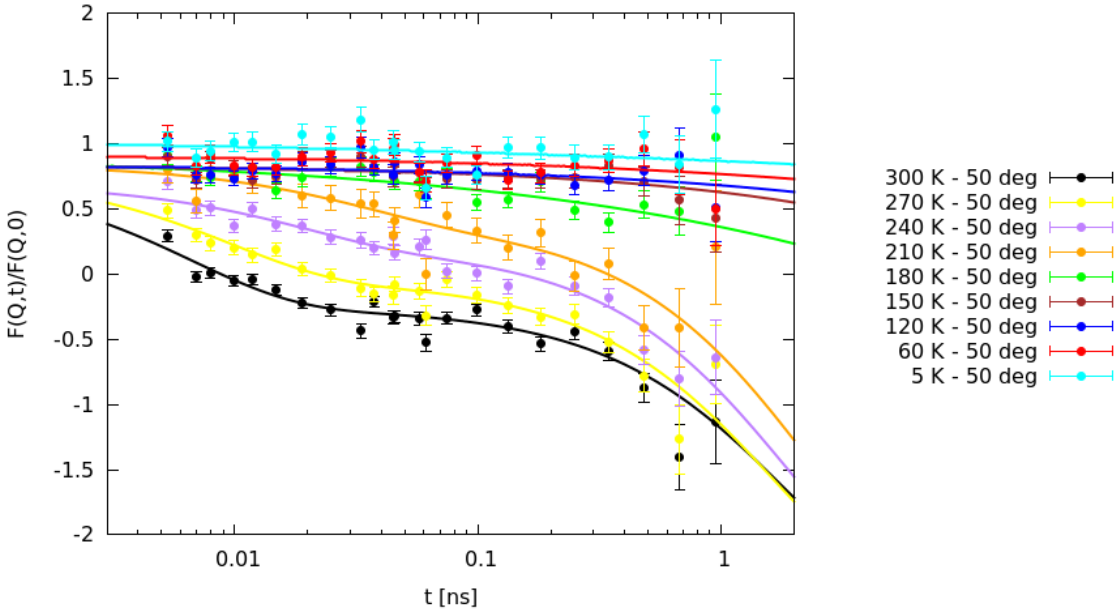

Figure 1. *The intermediate scattering functions measured for a hydrated sample of SWCNTs at different temperatures. The curves correspond to an average of the multidetector set at 50 deg. The fits were performed by setting a baseline to -2.43 the value predicted for the elastic contribution of the coherent/incoherent scattering of the confining system.*

[1] B. Mukherjee *et al.*, *ACS Nano* **2**, 1189 (2008)
[2] G. Briganti, G. Rogati, A. Parmentier, M. Maccarini, F. De Luca, Sci. Rep. (2017) 7, 45021
[3] P. Gallo, M. Rovere, S.-H. Chen, J. Phys. Chem. Lett. 1, 729-733 (2010)