Experimental Report

17/07/2014

Proposal:	**6-02-514**	**Council:**	10/2012
Title:	Unusual dynamics of water entrapped in the core of carbon nanotubes		

This proposal is continuation of: 6-02-486

Researh Area: Physics

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Samples: C12

Instrument	**Req. Days**	**All. Days**	**From**	**To**
IN6	6	4	05/08/2013	09/08/2013
IN16	6	4	01/08/2013	09/08/2013

Abstract:

Strong confinement of polar liquids into hydrophobic nanopores is a topic of great scientific interest due to potential spin-offs in a variety of fields, from biology to geology, to nanoscale fluids engineering. In spite of the large amount of computational works produced about this subject in the past decade, experimental confirmations to simulated data are still largely skimped on because of objective difficulties in direct manipulation of nanometer-sized systems, so causing a real epistemological gap to grow between theory and experiment. The present study proposal aims to investigate the unusual dynamics of a ubiquitous solvent, water, confined both on the outer surface and in the inner core of a system of single-wall carbon nanotubes over a motional characteristic-time range from ps to ns as a function of temperature. Consequently, beamtime on a combination of BS and ToF instruments is applied for, in order to support predictions from simulation literature and scanty results from experimental investigations about a possible unexpected behavior of water in a quasi-1D geometry.

We performed measurements on carbon nanotubes (NT) of 1.4 nm diameter using IN6 and IN16 inelastic scan set-up. The main goal of experiments concerned the study of water dynamics inside nanotubes which has been shown to be anomalous (faster diffusion inside NT than in bulk water, see ref. 5 of proposal) by MD data. The samples were provided in powder form. Two procedure were used for samples preparation: i) dry NT (taken in an oven at about 50 °C for 12 hours), used in the analysis as reference system; ii) partially hydrated NT containing both H_2O and D_2O for IN16, just H_2O for IN6. The partially hydrated NT contained water molecules only inside the NT. The procedure to reach this condition has been based on a first step in which samples were fully hydrated in a saturated water steam environment for 2 hours at 120 °C and 2 atm. Afterward, the samples were put in a dry over at 40 °C for 4 hours, during which only external water evaporates while the internal one is retained because its dipper free energy minimum (J. Burnham et all J. Chem. Phys. 124, 194703-1 (2006)).

Data from IN6 were taken at 2,10, 100, 150, 200, 250, 280, 300 K. After the standard data reduction, a preliminary data fit has been performed by using a linear combination of gaussian and lorentzian functions to take into account both the scattering resolution window and the water diffusion dynamics. The loretzian width as a function of Q^2 is reported in Fig. 1.

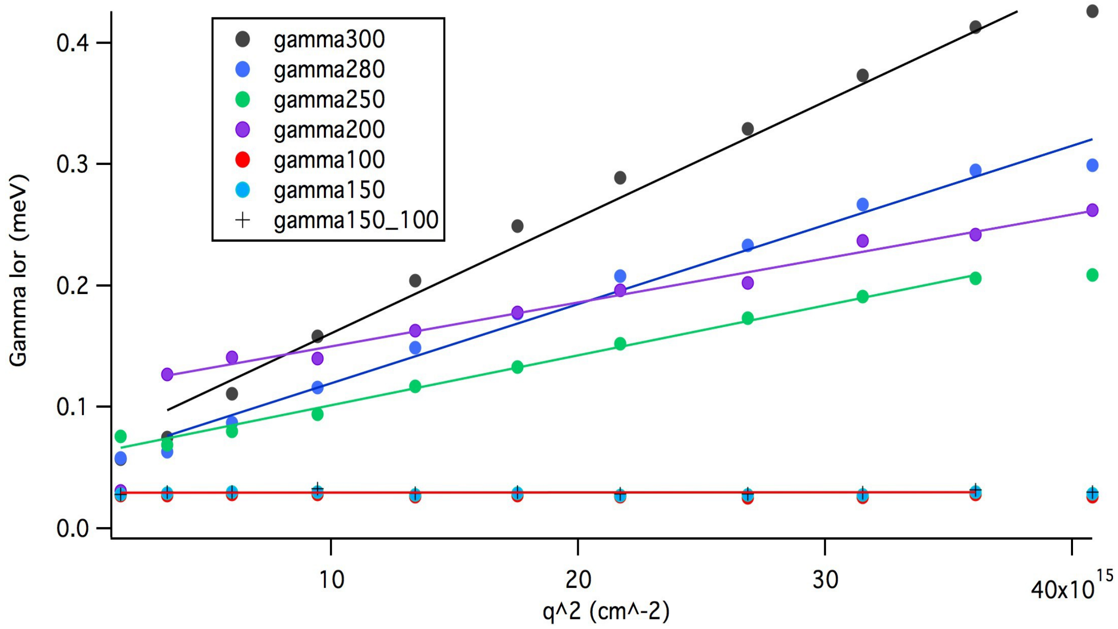

Fig. 1 Loretzian width as a funtion of Q^2.

It is evident that the linear trend as a function of Q^2 is not fulfilled. This may occur because of multiple scattering effect or because of poor data fitting approximation. Nevertheless, using the lower Q values which fit linear approximation, the diffusion activation energy as a function of temperature may be evaluated. The results are reported in Fig. 2, together data from MD.

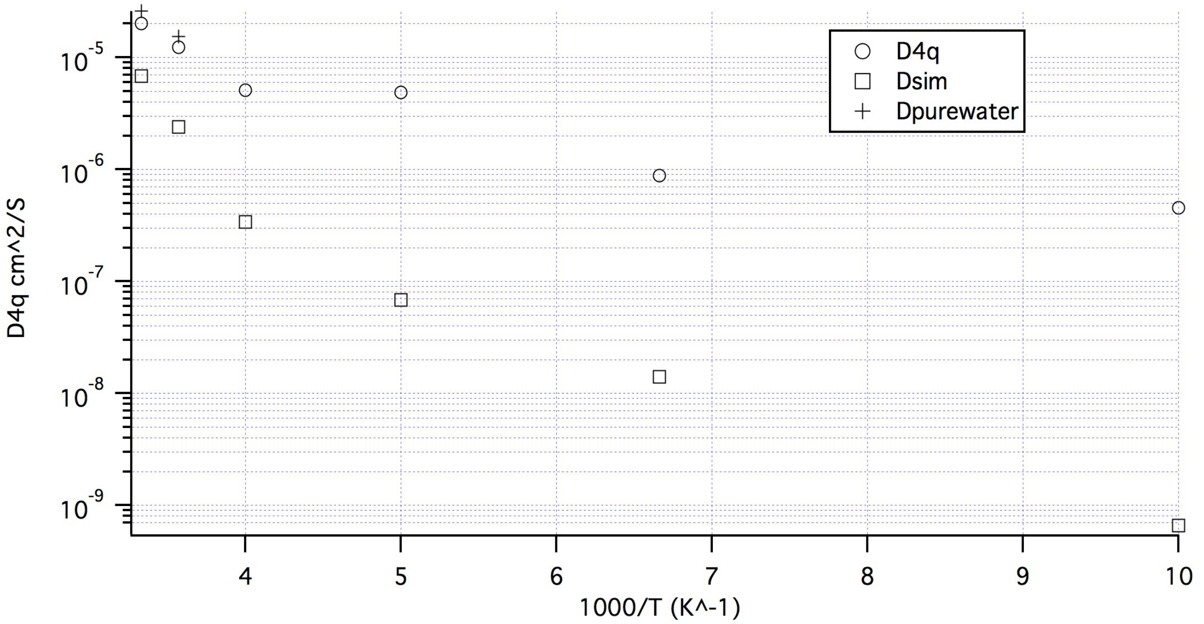

Fig. 2 Diffusion coefficients as a function of 1000/T, circle experimental fit of D vs Q^2; square MD.

The two sets of data, experimental and MD, differ in the absolute values. This may mainly be attributed to MD model choice as it results from comparison between MD results and diffusion coefficient for pure water. Nevertheless, MD and experiment results show a very similar behavior characterized by two different slopes, whose intersection is at about 200 K. At this temperature a change in water dynamic was already observed (see ref. 4 and 5 of proposal). But, in our knowledge, the two-slopes behavior has been observed in water as a function of pressure and not of temperature (S. Klotz et all App. Phys. Lett 103, 193504, 2013). However, in such a confined geometry, the reduction of activation energy for diffusion at decreasing temperature may indicate a special geometry of hydrogen bonding within water molecules. This aspect have to be confirmed by an increased data handling procedure.
We are now working on a more accurate fitting procedure using deconvolution integral, defining a more accurate zero energy of each data and taking into account multiple scattering reduction.

For IN16 experiments the previously observed dynamics at low temperature (10-100 K) was not confirmed, the results were taken at 2, 10, 200 K in dry and H_2O/D_2O partially hydrate samples.