

## Quantum coherence and temperature dependence of the anomalous state of nanoconfined water in carbon nanotubes

There has been considerable interest in water confined in carbon nanotubes as a model for the flow of water in biological channels and, in its own right, as a filtration system due to the super-rapid (compared to Poiseuille) flow observed in tubes of the same diameter. Water is usually thought of as a collection of weakly interacting molecules, held together by hydrogen bonds. Just like a school of fish in an ocean can move independently, but yet responds to its group simultaneously as a whole, similarly for water in the smallest level (quantum), there is unity and cooperation between them (coherence), which allows them to respond together as a larger unit. Neutron Compton scattering measurements [1] in the last few years have shown that the proton momentum distribution in nanoconfined water, with water confined on the scale of 20 Å, differs greatly from that expected of a water molecule in bulk water. The proton delocalizes over distances of 0.2–0.3 Å, and the confining potential appears to be a double well, rather than the covalent bond of the water molecule.

It has been shown recently by X-ray Compton scattering that water confined in Nafion is in a new state, not describable by the usual picture, with the protons delocalized over distances on the order of 0.2–0.3 Å and the electron momentum distribution strongly perturbed from its value in bulk water [2]. Also in the simplest system for which this has been observed are single wall (SWNT) and double wall (DWNT) carbon nanotubes, where the momentum distribution of the proton is sensitive to the size of the confinement. The momentum distribution narrows in the case of SWNTs, and broadens in the DWNTs, with very different temperature dependencies in the two cases. A classical simulation of the low temperature structure of water confined in a SWNT, with inner diameter 14 Å is shown in Fig. 1. For this system, the momentum distribution of the protons is temperature independent up to 230 K, where the structure changes to one resembling bulk water, whereas for the DWNT, inner diameter 16 Å, the momentum distribution, and hence the confining potential, varies continuously with temperature.

The confining potential for the protons is provided by the valence electrons. Changes in that potential must therefore reflect changes in the distribution of the valence electrons. These can be observed in the changes in the momentum distribution of the electrons with X-ray Compton scattering. Measurement of the changes in the Compton profiles (CP) of water was

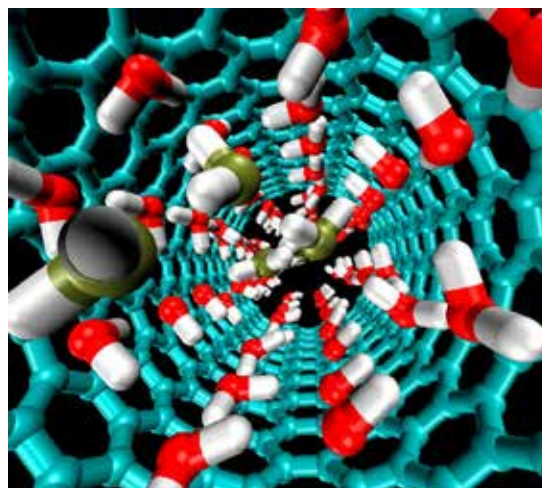


Fig. 1. MD (molecular-dynamics) simulated structure of water in 14 Å SWNT (cyan). The confined square ice sheet of water molecules (red and white) surrounds a chain of water molecules (green and white).

performed at the High Energy Inelastic Scattering beamline **BL08W**, SPing-8. The study for the first time was performed by confining water in both SWNTs (14 Å) and DWNTs (16 Å) and have shown that this temperature and size dependence is observable in the CP, demonstrating that the quantum ground state of the electron-proton system in nanoconfined water is a new state of water, qualitatively different from the bulk molecular state. The carbon nanotubes have been taken as a model system for the study of water flow through protein channels in cell membranes. This model is very useful as it resembles the confinement similar to the distance between the elements of our cells which is typically 20 Å. This state of water, and its properties, is the state that is relevant for the biological functioning of our cells [3].

We see from Fig. 2 for SWNT, that there is no change in the CP of the electrons between 10 K and 170 K, and a large change between 170 K and 300 K, consistent with the observations of the temperature variation of the proton momentum distribution. The results are compared with the fits with changes in the CP of bulk water due to substitution of D for H (Nygård *et al.* [4]) and increasing the O-H distance by 0.003 Å (Juurinen *et al.* [5]). The changes due to confinement are about 30 times those calculated by Juurinen *et al.* [5] In contrast with the SWNT case, Fig. 3 shows that the CP in the DWNT's vary continuously, consistent with the neutron Compton results. They are

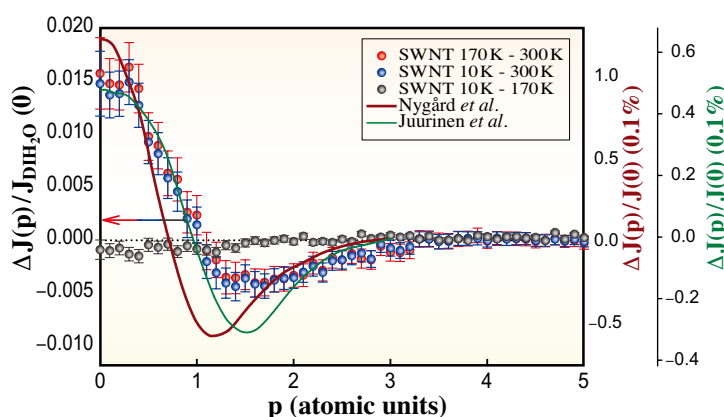


Fig. 2. Difference of X-ray Compton profiles for SWNT and temperatures shown in the inset. Amplitude given by axis on left. Solid curves are comparisons with calculations for D replacing H in bulk water [4] and varying O-H distance in alcohol water mixtures [5]. The amplitudes are represented by the axes on right (which are in parts per thousand).

larger by about a factor of 60 than the simulated results that assumed a small displacement of the protons from their position in the hydrogen bonded bulk liquid.

These results, together with the neutron Compton scattering results, demonstrate that nanoconfined water is not the weakly hydrogen bonded molecular network of bulk water, but is in a unique quantum state of the electrons and protons. Earlier work measuring the X-ray CP of water in Nafion at room temperature, [2] and an experiment on water confined in xerogel at room temperature, demonstrate that this state is still

present at room temperatures. The flow of water through carbon nanotubes with diameters on the order of 20 Å is anomalous, being both much faster than continuum mechanics would predict, and much slower than classical simulations of molecular water would predict. It is the momentum carrying excitations of this state that determine the flow rate through the nanotubes. Since the elements of our cells are separated by a characteristic distance of 20 Å, it is the properties of this state, not that of bulk water, that determine the functioning of the cells of our bodies.

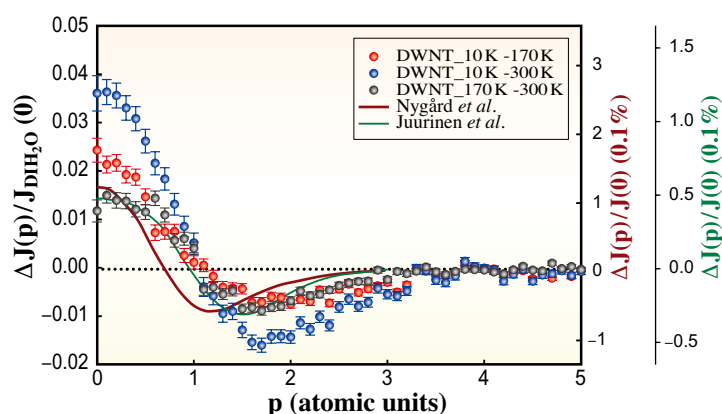


Fig. 3. Difference of X-ray Compton profiles for DWNT and temperatures shown in the inset. Amplitude given by axis on left. Comparison with calculations for D replacing H in bulk water [4] and varying O-H distance in alcohol water mixtures [5]. The amplitudes are represented by the axes on right (which are in parts per thousand).

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