

The Quantum Mechanics of Nano-Confined Water: New Cooperative Effects Revealed with Neutron and X-Ray Compton Scattering

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Abstract. Neutron Compton scattering(NCS) measurements of the momentum distribution of light ions using the Vesuvio instrument at ISIS provide a sensitive local probe of the environment of those ions. NCS measurements of the proton momentum distribution in bulk water show only small deviations from the usual picture of water as a collection of molecules, with the protons covalently bonded to an oxygen and interacting weakly, primarily electrostatically, with nearby molecules. However, a series of measurements of the proton momentum distribution in carbon nanotubes, xerogel, and Nafion show that the proton delocalizes over distances of 0.2-0.3Å when water is confined on the scale of 20Å. This delocalization must be the result of changes in the Born-Oppenheimer surface for the protons, which would imply that there are large deviations in the electron distribution from that of a collection of weakly interacting molecules. This has been observed at Spring-8 using x-ray Compton scattering. The observed deviation in the valence electron momentum distribution from that of bulk water is more than an order of magnitude larger than the change observed in bulk water as the water is heated from just above melting to just below boiling. We conclude that the protons and electrons in nano-confined water are in a qualitatively different ground state from that of bulk water. Since the properties of this state persist at room temperature, and the confinement distance necessary to observe it is comparable to the distance between the elements of biological cells, this state presumably plays a role in the functioning of those cells.

1. Introduction

The first indication that the quantum state of the protons in nano-confined water was unusual were measurements of the Debye-Waller factor in water confined in single wall carbon nanotubes(SWNT) at 4K[1]. The Debye-Waller factor was 5 times what it is in bulk ice at the same temperature. This implies a large zero point delocalization of the protons of 0.2-0.3Å. This was confirmed by a neutron Compton scattering measurement[2] of the proton momentum distribution, which revealed a dramatic



narrowing of the momentum distribution at 4K, relative to that of bulk water[3], persisting up to about 230K, with the room temperature distribution being approximately that of the bulk. This was attributed to structural changes in the water in the nanotubes at low temperature. Attempts to reproduce the momentum distribution of the protons at 4K, making use of what was believed to be the structure there and a high quality flexible, polarizeable, empirical potential model, failed. The model produced only small deviations from the momentum distribution of bulk water, and was unable to account for the 30% reduction in the momentum width that had been observed[4].

The next unexpected result was obtained on water confined in double walled carbon nanotubes(DWNT)[5]. The momentum distribution at 4K broadened, rather than narrowed, varied continuously with temperature, and remained anomalous at room temperature. This is particularly extraordinary, as the nominal inner dimensions of the SWNT, 14Å, and the DWNT, 16Å, are so close. The fact that the anomalous behavior persisted at room temperature, led to a new interpretation of an earlier experiment on water confined in xerogel[6], and subsequent experiments on water confined in Nafion, the electrolyte for some commercial fuel cell[5]. It was now conjectured that the changes in the momentum distribution observed were not due to the specifics of the interaction of the water with the confining surfaces, but were the effect of the confinement itself[5], that confinement led to a ground state distinct from the weakly interacting molecular ground state, and that the properties of this state persisted to room temperature. That the ground state of the electrons, oxygen ions and protons was distinct from the usual molecular ground state was confirmed by an x-ray Compton scattering experiment at room temperature in Nafion[7]. The momentum distribution of the valence electrons was measured, and found to be qualitatively different from that of bulk water. The difference at zero momentum is more than an order of magnitude greater than the differences in bulk water due to disordering of the hydrogen bond network as the water is heated from just above melting to just below boiling at atmospheric pressure. We conclude from these measurements, and others, that the state of nano-confined water is not describable by the usual molecular model, and conjecture that it involves the coherent motion of the protons, with a coherence length on the order of 10Å. We review below the experimental evidence and the reasoning behind that conjecture.

2. Neutron Compton Scattering

We show below a comparison of the neutron Compton profile, as measured on the VESUVIO instrument, for water confined in SWNT and DWNT, at 170K. To a first approximation, the interior of the carbon nanotubes is a smooth cylinder, providing only confinement, with the interaction usually modeled as a 6-12 potential. The diameters, 14Å and 16Å respectively, are sufficiently different to lead to a structure predicted by classical simulations at this temperature to be a cylinder of “square ice” with a chain of either one(SWNT) or three(DWNT) water molecules down the center[8]. Despite the small difference in the diameter, and in the classical structure, there is a great difference in the response of the protons to confinement, manifest in the pronounced narrowing of the momentum distribution in the SWNT case, and broadening in the DWNT case, compared to bulk water. (The momentum distribution for bulk ice at this temperature is similar to that of bulk water) The Compton profiles in both cases correspond to a delocalization of the protons in double well potentials. The potentials can be extracted, if we assume a mean field approximation for the interaction of the protons with themselves, by fitting the data with a simple model of a double well along the bond, and an harmonic well perpendicular to the bond[2]

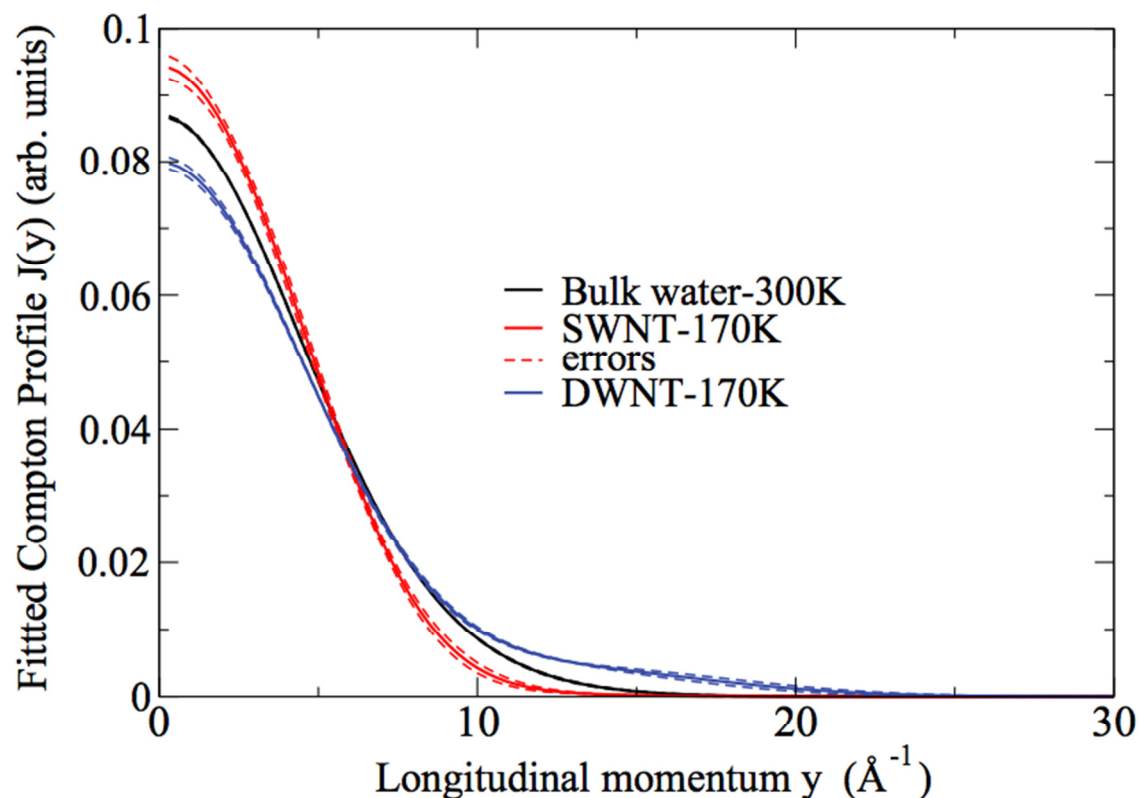


Figure 1. Comparison of the Compton profiles of bulk water, SWNT with diameter 14Å, and DWNT with diameter 16Å.

We show in Fig. 2 the variation with temperature of the effective potential obtained in this way for the DWNT. The increasing delocalization of the proton with temperature is evident from the figure. There is a structural change occurring at about 190K, as observed with the Debye Waller factor, similar to that observed in the SWNT. Particularly significant, from the point of view of the implications for biology, is that in this case, the double well potential is present at room temperature. The flat bottom potential observed at 4.2K is similar to that observed in the SWNT at the same temperature[2], although the overall width is different.

Although the effective potentials provide a convenient way of representing the momentum distribution data, it is clear that the delocalization of the proton is not an independent particle effect. As pointed out in references [1, 2], the vibrational band associated with the stretch mode is blue shifted in the SWNT, which cannot be accounted for with a single particle potential which softens to the extent observed. We take the pronounced difference shown in figure 1 to be additional indication of cooperative effects between the protons. If the momentum distribution was affected only by the ions in the immediate neighborhood of the proton, the momentum distribution would not be qualitatively different when the diameter of the nanotube changed by 13%. For this to happen, the change in the boundary conditions must be communicated throughout the material. While commensurability effects could account for this in the low temperature, ordered, structure, it would not be expected to do so in the room temperature phase, which is, if classical simulations are qualitatively correct, disordered in a way that is similar to bulk water.

The delocalization of the protons of water at room temperature has been observed in two other nano-confining systems, xerogel[9] and Nafion[5]. Variation of the pore size in the xerogel, allowed the conclusion that the effects of confinement were limited to scales on the order of 20Å.

Whatever the origin of the delocalization of the protons, the fact that they are delocalized implies that the many body Born-Oppenheimer potential that they are contained by is quite different from that of bulk water, where the proton is localized to about 0.1\AA in the covalent bond with the oxygen. For this to be true, the spatial distribution of the valence electrons in the nano-confined water must be significantly different from that of bulk water. If that is the case, then the momentum distribution of the valence electrons must also be significantly different from that of bulk water.

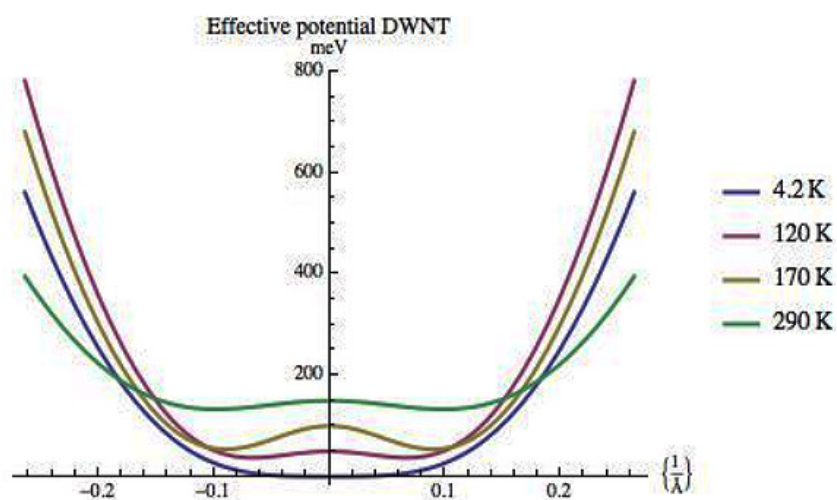


Figure 2. Temperature dependence of the effective potential for the protons in DWNT. The 120K, 170K, and 290K curves have been shifted up by 50, 100 and 150 meV respectively from the 4.2K curve.

3. X-Ray Compton Scattering

The momentum distribution of the electrons in the samples can be measured using X-ray Compton scattering. Measurements done at Spring-8 of water in Nafion at room temperature[7] show clearly that the changes in the valence electron distribution is large, far greater than can be accommodated within model for water that is based on a weakly interacting hydrogen bonded network of molecules. The technique measures the average momentum distribution of all the electrons in the system. Measurements on dry Nafion are used to subtract out the contribution from the electrons of the Nafion, and standard calculations for the momentum distribution for the core electrons of oxygen are used to obtain the contribution from the valence electrons. The resulting distribution was then subtracted from the measured distribution of bulk water to obtain the effects of confinement on the valence electrons. The results for two structurally different variants of Nafion are shown in figure 3.

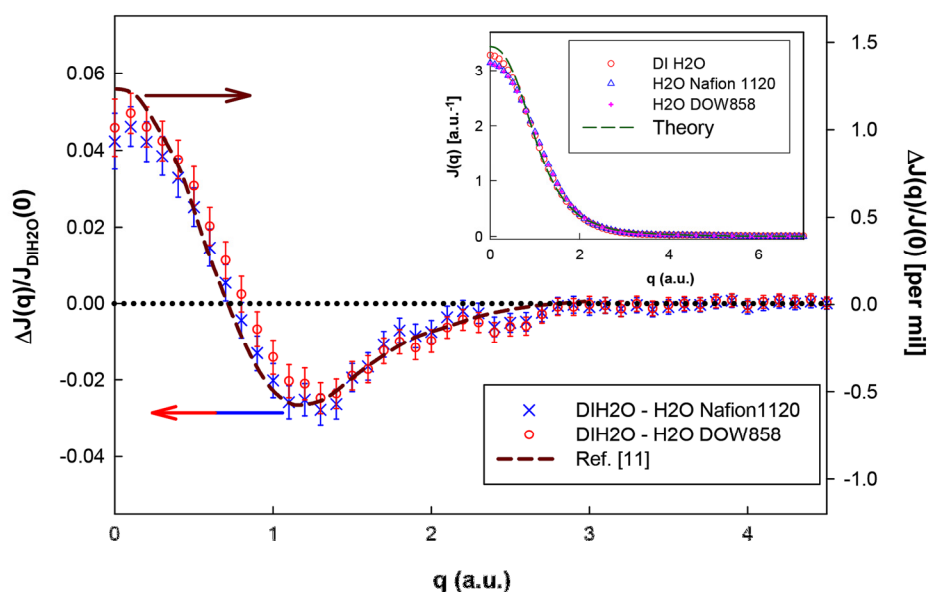


Figure 3. Comparison of the electron momentum distribution, measured with x-ray Compton scattering, of de-ionized bulk water (DIH₂O) with that of water confined in two forms of Nafion. The main figure shows the difference between the Compton profile of the valence electrons in bulk water with that of the water confined in the Nafion samples. The fit is an empirical one. The shape of the fitted curve is that of the measured difference of the Compton profiles between deuterated and hydrogenated bulk water. The amplitude of the fitted curve is 46 times larger than that difference. The inset gives the un-subtracted measurements compared with a theoretical calculation for bulk water. The amplitude of the difference at $q=0$ is 17 times greater than the amplitude of the difference in bulk water between 5°C and 95°C

Calculations based on the molecular model, in which the variation with temperature of the electron momentum distribution are due to changes in the distribution of lengths and angles for the hydrogen bond[10], agree well with variation in the measured x-ray Compton scattering results on bulk water from just above freezing to just below boiling at room temperature. The variation in figure 3 between bulk and confined water at $q=0$ is 17 times the variation with temperature in bulk water at $q=0$, and cannot be explained within the molecular model. The phenomenological fit to the difference data shown in Fig. 3 is obtained by using the shape of the Compton profile from the difference between deuterated and hydrogenated bulk water[11], and fitting the amplitude to our data. The amplitude is 46 times larger, emphasizing again the large scale of the changes in the momentum distribution of the protons.

The disruption of the hydrogen bond network by confinement is far more profound than can be accounted for by varying the lengths and angles of the bonds. Together with the neutron measurements, the x-ray data demonstrates that the electron ion system in water is in a qualitatively different ground state from that of bulk water. We conjecture that is the correlated, cooperative motion of the protons, needed to explain the neutron data, that leads to the large changes in the electron distributions, and that these self consistently determine a Born-Oppenheimer potential that allows for the correlated motion.

4. Conclusions

There is a self consistent ground state of the electron proton-oxygen ion system, in which the protons are delocalized by 0.2-0.3Å, that is close in energy to the molecular ground state of bulk water. When the preferred structure of the hydrogen bonded network, a tetragonal arrangement of the water molecules, is sufficiently frustrated by confinement, this self-consistent delocalized state becomes the preferred ground state. The properties of this ground state are markedly different from that of bulk water. Measurements of the motion of free protons in the Nafion system, and the related system of reverse micelles[12], demonstrate that motion of the protons is so dramatically modified that it can no longer be called diffusive. Measurements of the decay of photo-excited marker ions in the water confined in Nafion[13] show the possibility of decay to states that would be in the band gap of bulk water.

In as much as the distance between the elements of biological cells is about 20Å, it seems likely that evolution has made use of the properties of this state in the functioning of our cells.

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