The quantum mechanics of nano-confined water: new cooperative effects in the confined ground state revealed with neutron and x-ray Compton scattering

GEORGE REITER, University of Houston, TX
ALEXANDER KOLESNIKOV, Oak Ridge National Laboratory, Oak Ridge, TN
STEPHEN PADDISON, University of Tennessee, Knoxville, TN
JERRY MAYERS, ISIS, RAL, UK
CARLA ANDREANI, Universitat Roma2, Rome, Italy
ROBERTO SENESI, Universitat Roma2, Rome, Italy
ANIRUDDHA DEB, University of Michigan, Ann Arbor, MI
PHIL PLATZMAN

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Weakly electrostatically interacting model of water

R = 2.976 (+0.000, -0.030) Å, α = 6 ± 20°, β = 57 ± 10° [648]; α is the donor angle and β is the acceptor angle. The dimer (with slightly different geometry) dipole moment is 2.6 D [704]. Although β is close to as expected if the lone pair electrons were tetrahedrally placed (= 109.47°/2), the energy minimum (~21 kJ mol⁻¹) is broad and extends towards β = 0°. [Back to Top ▲]
Fit to water $g(r)$ with empirical potential (TTM4-F) based on weakly interacting molecule model

Empirical potentials not able to fit momentum distribution of protons at higher densities.
Comparison of calculated momentum distribution width in water from the supercritical to room temperature phase, using two different methods based on the isolated molecule and electrostatic interactions model. Both fail to soften the potential sufficiently in the higher density phases at room temperature and 150°C, indicating a failure of the weakly electrostatically interacting molecule model.

Proposed structure of nanotube-water. The interior “chain” water molecules have been colored yellow to distinguish them from the exterior “wall” water molecules (colored red).

MD simulations have been performed using the TTM2-F polarizable flexible water model (uses smeared charges and dipoles to model short range electrostatics) [1]. Our MD simulations consist of a rigid carbon nanotube of length 40 Å in periodic boundary conditions that interacts with water through the Lennard-Jones potential [2].

First evidence of something new happening in confined water

To describe $\langle u_H^2 \rangle$ for nanotube-water the calculated curve was vertically shifted by supposed delocalization, $d \sim 0.2$ Å, of the hydrogen atoms due to the flat bottom of its potential (insert).

The momentum distribution of the protons in nanotube-water compared with that in three forms of bulk ice. The inset shows the effect of varying the parameters in an anisotropic harmonic model of the bond. The hda-ice and ice-VI data are displaced vertically for clarity.

\[
n(p) = \frac{e^{-\frac{p^2}{2\sigma^2}}}{(\sqrt{2\pi}\sigma)^3} \cdot \left[1 + \sum_{n=2}^{\infty} a_n (-1)^n L_n^{\frac{1}{2}} \left(\frac{p}{\sqrt{2}\sigma}\right) \right]
\]

where the \( L_n^{1/2}(p^2/2\sigma^2) \) are associated Laguerre polynomials, and the \( a_n \) are coefficients to be determined by the least square fitting process.

\[
\langle E_K \rangle = 3\hbar^2 \sigma^2 / 2M
\]

<table>
<thead>
<tr>
<th>samples</th>
<th>T, K</th>
<th>KE, meV</th>
</tr>
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<tbody>
<tr>
<td>NT-water</td>
<td>5</td>
<td>106</td>
</tr>
<tr>
<td>NT-water</td>
<td>268</td>
<td>146</td>
</tr>
<tr>
<td>Ice-Ih</td>
<td>5</td>
<td>144</td>
</tr>
<tr>
<td>HDA-ice</td>
<td>5</td>
<td>141</td>
</tr>
<tr>
<td>Ice-VI</td>
<td>5</td>
<td>136</td>
</tr>
</tbody>
</table>

Momentum distributions for NT-water at 268 K (green) and 5 K (black), and ice-Ih at 269 K (red). The circles are a fit to a model in which the water proton is delocalized in a double well potential. The potential (red) and wave-function (black) are shown in the inset.

\[ n(p_x, p_y, p_z) = \frac{2\cos^2\left(\frac{p_x d}{2\hbar}\right)}{1 + \exp\left(-\frac{p_i^2}{2\sigma_i^2}\right)} \prod \frac{\exp\left(-\frac{p_i^2}{2\sigma_i^2}\right)}{\sqrt{2\pi\sigma_i}} \]
A Significantly Weaker Hydrogen-Bond Network in Nanotube-Water-
Stretch mode blue shifted

406 meV
$R_{O-O}=2.76 \text{ Å}$

422 meV
$R_{O-O}=2.92 \text{ Å}$
But red shifted in D2O!
**SWNT (dia. 14Å) compared with DWNT (dia. 16Å)**

![Graph showing fitted Compton profile J(y) for different conditions and materials.](image)
The radial momentum distribution, $4\pi p^2 n(p)$, of the water protons in 16 Å DWNT at different temperatures, compared with that of bulk water at room temperatures. The 290 K signal and the bulk water signal have been displaced upward by 0.02 units for clarity.

If the wave function is

Then the momentum distribution $n(p)$ is

More generally, the momentum distribution is the diffraction pattern generated by the wave function thought of as a transmission amplitude
Water in xerogel-room temperature

Water in xerogel 23 Å pores (T=300 K). The dashed red line is a fit to the data with a single particle in a double-well model (top figure) [1].


The radial momentum distribution, $4\pi p^2 n(p)$, of the protons in Nafion1120 (blue) and Dow 858 (magenta) compared with that of bulk water (black), all at room temperature.

<table>
<thead>
<tr>
<th>Water Sample</th>
<th>$\sigma(\text{Å}^{-1})$</th>
<th>K.E.-meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk-300K</td>
<td>4.72 ± .03</td>
<td>138</td>
</tr>
<tr>
<td>DWNT-4.2K</td>
<td>5.40 ± .36</td>
<td>181</td>
</tr>
<tr>
<td>DWNT-120K</td>
<td>5.65 ± .06</td>
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<tr>
<td>DWNT-170K</td>
<td>5.97 ± .15</td>
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<tr>
<td>DWNT-290K</td>
<td>5.26 ± .08</td>
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<tr>
<td>SWNT-170K</td>
<td>4.09 ± .07</td>
<td>104</td>
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<tr>
<td>Nafion1120-300K</td>
<td>6.28 ± .40</td>
<td>245</td>
</tr>
<tr>
<td>Dow858-300K</td>
<td>6.50 ± .27</td>
<td>262</td>
</tr>
</tbody>
</table>
X-ray Compton profiles from Nafion and Dow 858
Difference profiles: Bulk water-water in Nafion, Dow 858

Direct electronic de-excitation of excited state possible in nano-confined water

Figure 3. A) The signal as a function of pump-probe delay time at a wavelength of 440 and 520 nm for large reverse micelles ($w = 15$). The lines are obtained by fitting the data to Equation (1). B) The signal as a function of pump-probe delay time at a wavelength of 440 and 520 nm for medium size reverse micelles ($w = 8$). The lines are obtained by fitting the data to Equation (2).

Changes in the kinetic energy (almost all zero point motion) are biologically significant.

Changes in the zero point energy of protons completely accounts for enthalpy change in A to B phase for 6 mol/bp of water.

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Changes in coherence also observed for protons in water on Lysozyme

Variation of kinetic energy of the protons in a dilute lysozyme solution as the protein unfolds with temperature. Red line is what is to be expected if there are no changes in the proton quantum state.

The making and breaking of hydrogen bonds as a protein unfolds with temperature.
Summary

- The momentum distribution of water confined to distances of the order of 20 Å is sensitive to the global nature of the confinement.

- The quantum ground state of the electrons and protons in nano-confined water is qualitatively different from that of bulk water. The usual model of molecules interacting weakly electrostatically does not apply.

- Free proton transport in the nano-confined state is qualitatively different from that of bulk water, as are the electronic excitations.

- The changes in zero point energy of the protons are thermodynamically significant in the transformations in shape of biological molecules, and hence, most biological processes.

- It is necessary to understand the origin and properties of the nanoconfined state to understand the role that quantum mechanics has played in the origins of life.
FIG. 1 (color online). The experimental neutron Compton profile $J(y)$ at 5 and 268 K, constructed by binning the time of flight data for each of the 28 detectors in $\Delta y$ bins assuming that the data satisfies $y$ scaling [Eq. (1)]. The solid and dashed curves are fits to the entire data set and include the instrumental resolution and final state effects.
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The temperature dependences of the residence time for water in SWNT (left) and DWNT (right), and their fits with a Vogel-Fulcher-Tamman (VFT) law, \( \tau = \tau_0 \exp\left(\frac{DQ^2}{T-T_0}\right) \), above and an Arrhenius law, \( \tau = \tau_0 \exp\left(\frac{E_A}{RT}\right) \), below the crossover temperatures \( T_L = 218 \text{ K} \) for SWNT [1] and 190 K for DWNT [2].

Water Enters the Nanotubes by Exposing SWNT to Water Vapor at 110 °C

Low-angle neutron diffraction: \( I(Q) \sim S(Q) \cdot F(Q) \). Here, \( S(Q) \) consists of a Bragg reflection at 0.41 Å\(^{-1}\) from the (01) planes of the 2D hexagonal lattice of SWNT crystalline bundles.

SWNT sample with \( D \approx 14 \pm 1 \) Å, \( l \approx 10 \) μm was characterized by HRTEM, TEM, SEM, Raman and ND.

To fill the SWNT with water, the dry SWNT sample was first exposed to water vapor at 110° C in an enclosed environment. The excess water adsorbed in the exterior of the nanotubes was then evaporated at 35° C. An optimal filling, in terms of H\(_2\)O/SWNT mass ratio, was found to be 11%.