

Quantum Mechanics of Liquid Water

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Foreword

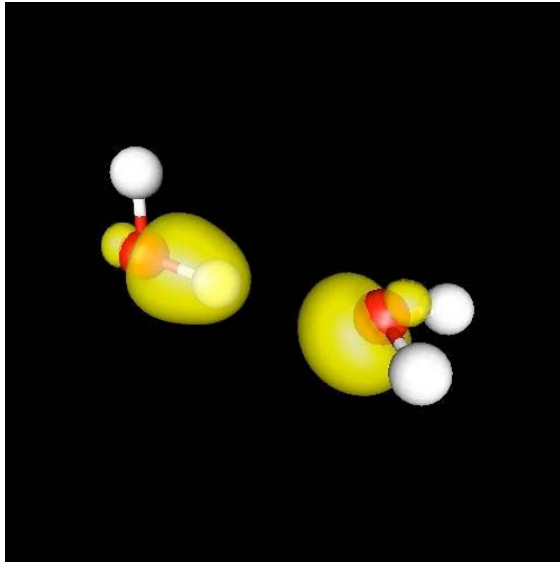
“The fundamental laws necessary to the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved”

P.A.M Dirac, *Proc. Roy. Soc. A* **123**, 714 (1929)

“Don't forget that the reason a physicist can really calculate from first principles is that he chooses only simple problems. He never solves a problem with 42 or even 6 electrons in it. So far, he has been able to calculate reasonably accurately only the hydrogen atom and the helium atom”

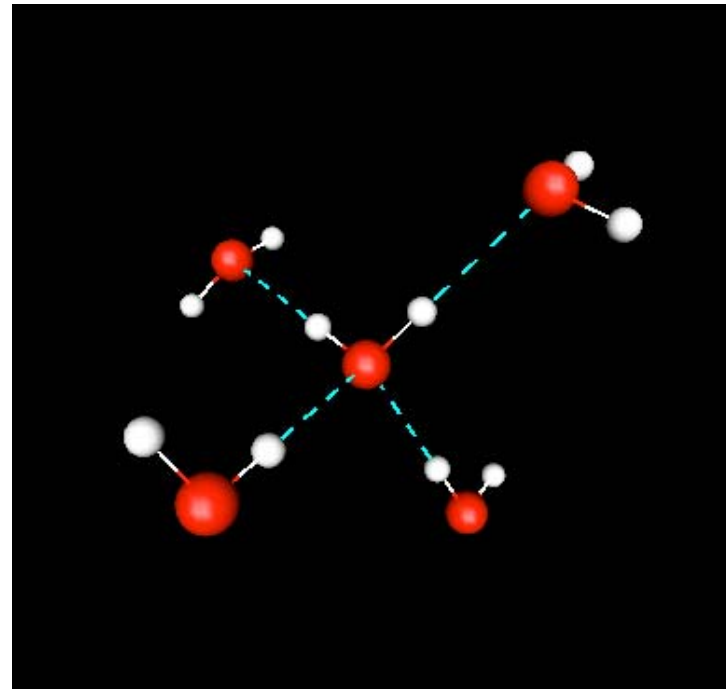
R.P. Feynman, *The Feynman lectures on physics*, 3rd printing (1969)

Electrons and Hydrogen Bonds



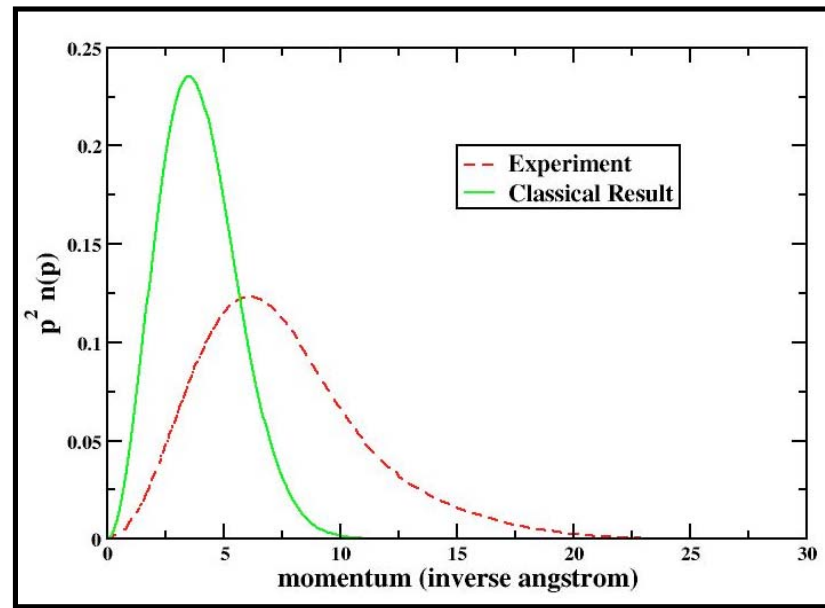
Water molecules interact via H-bonds

Each liquid molecule is in a local “tetrahedral” cage in the H-bond network



Nuclear Quantum Effects

Not only the electrons but also the protons need a quantum mechanical description

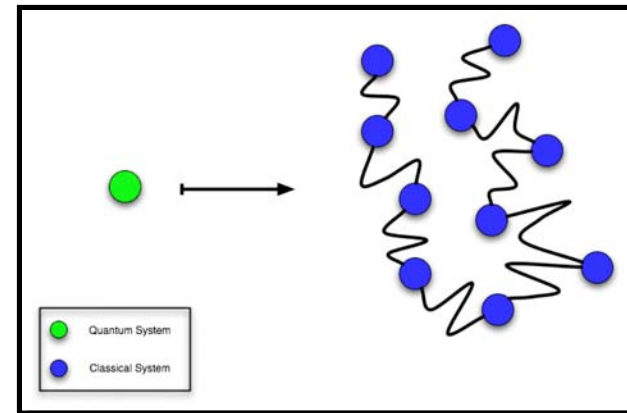
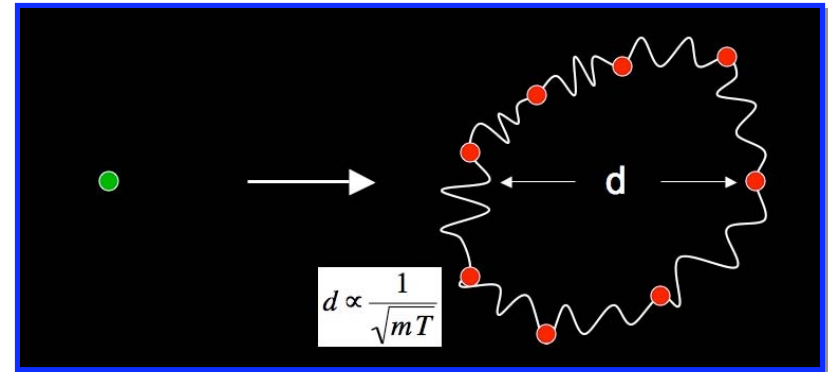


The Proton Momentum distribution in water probed by neutron Compton scattering displays importance of nuclear quantum effects

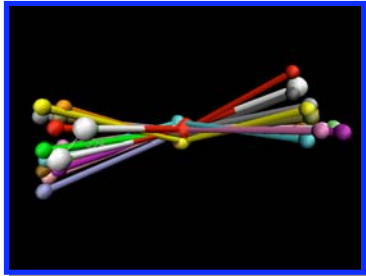
Simulating Nuclear Quantum Effects

Feynman Path Integral Methodology:

- Quantum system is mapped onto system of classical replicas (the beads of a polymer).
- Thermal equilibrium properties of a quantum system are calculated by performing Molecular Dynamics or Monte Carlo simulations on the system of classical replicas
- Depending on properties closed or open paths are needed



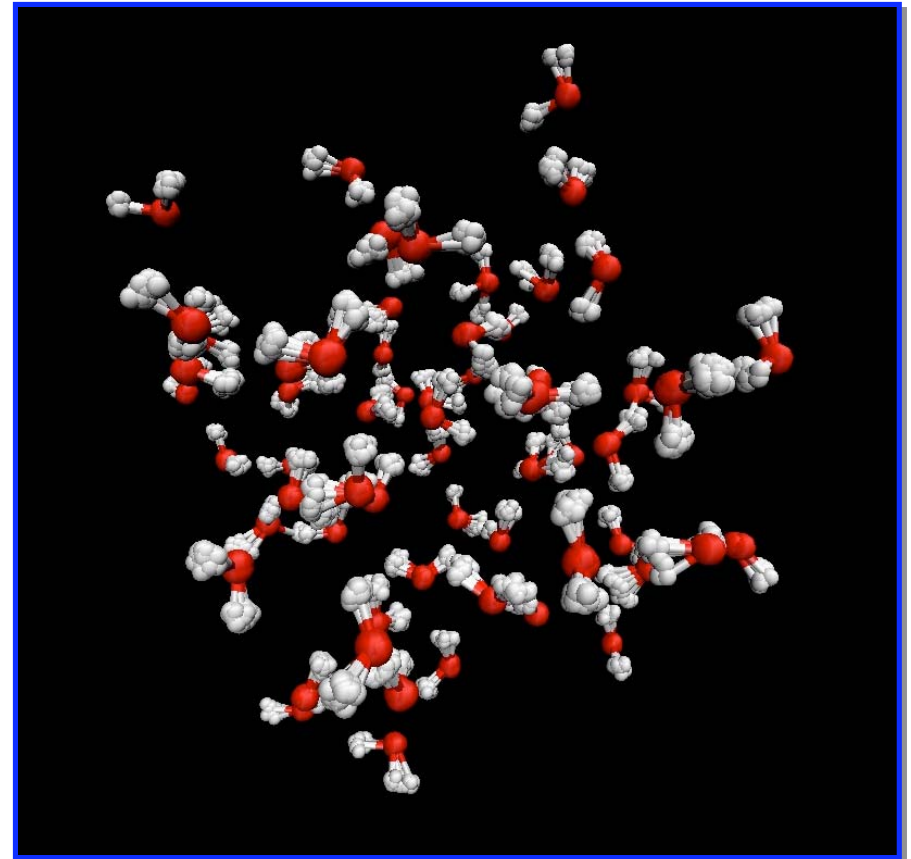
PIMD Simulation



Representation of 1 water molecule

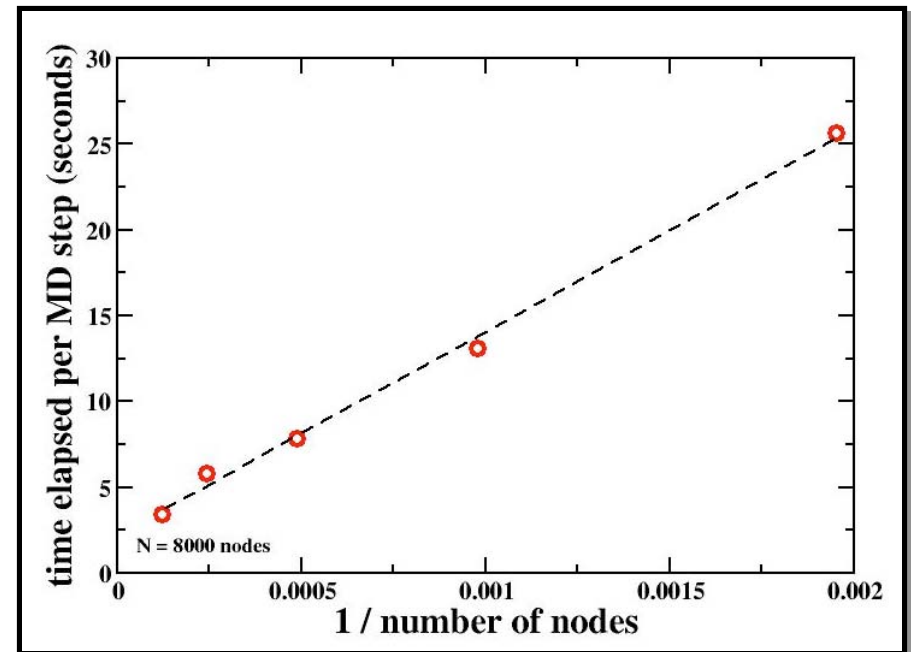
Quantitative Details:

- 32 beads
- 64 molecules
- 8 (valence) electrons per molecule
- isomorphic classical system: $32 \times 64 \times 3 = \mathbf{6144}$ atoms
 $32 \times 64 \times 8 = \mathbf{16384}$ electrons
- Car-Parrinello MD



Simulation needs massively parallel computer

- CPMD* optimized for IBM Blue Gene/L ideal for this computation
- On 512 nodes on Orangena it takes ~1 month to get converged statistical distributions

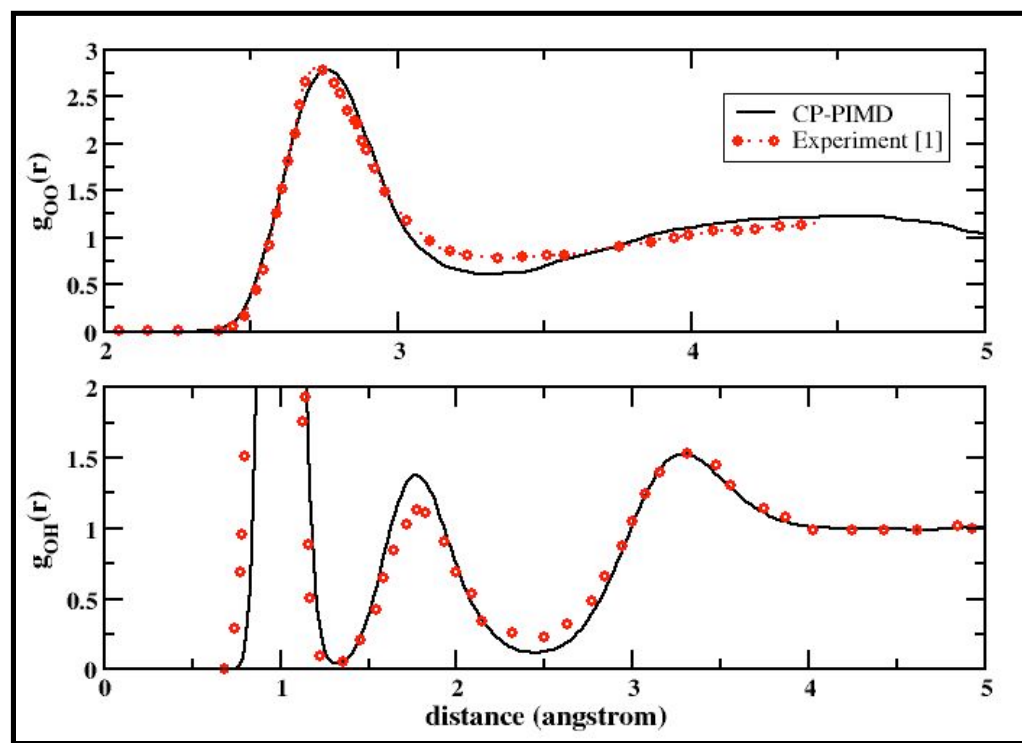


Linear scaling to larger number of nodes is possible

• <http://www.cpmc.org>

Scaling results from our system run on BG at IBM Watson facility in Yorktown, NY

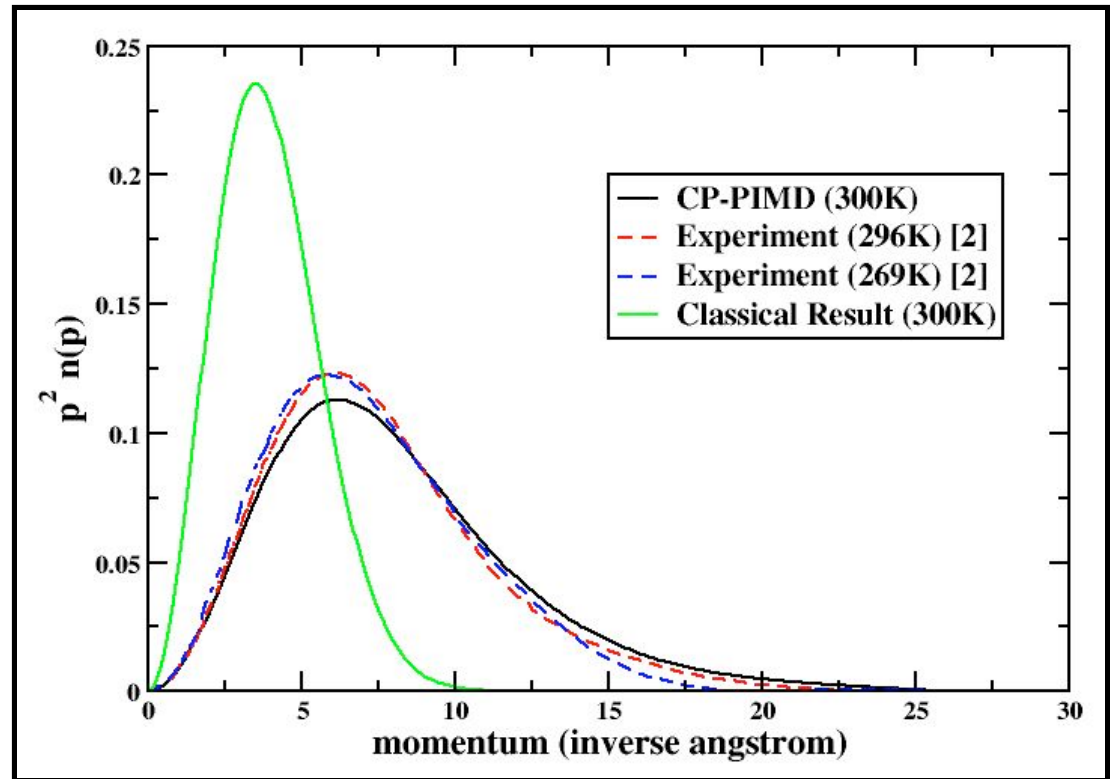
Radial Distribution Functions



- Simulation data are compared to neutron elastic scattering data
- Slight over structuring compared to experiment points to remaining deficiencies in the description of the nuclear potential energy surface, i.e. in the approximate treatment of the electronic ground-state

Proton Momentum Distribution

- CP-PIMD results broader than experiment.
- Consistent with more structured radial distribution functions



[2] Reiter et al., Brazilian J. Phys., 34, (2004).

Perspectives

- Quantum effects on the protons provide a signature of the water structure.
- Proton momentum distribution in confined water reveals structural transitions that suggest proton tunneling structures (quantum phase transitions)
- Confined water important in nanoscience and in biology
- Modern supercomputers make possible to simulate subtle quantum phenomena in highly complex situations (...quite a long way from H or He atoms!)

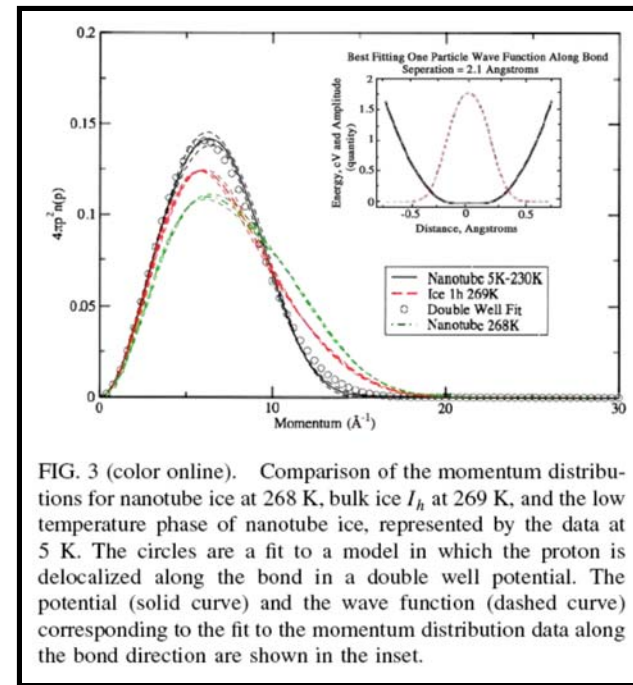


FIG. 3 (color online). Comparison of the momentum distributions for nanotube ice at 268 K, bulk ice I_h at 269 K, and the low temperature phase of nanotube ice, represented by the data at 5 K. The circles are a fit to a model in which the proton is delocalized along the bond in a double well potential. The potential (solid curve) and the wave function (dashed curve) corresponding to the fit to the momentum distribution data along the bond direction are shown in the inset.

Burnham et al., PRL **97** 247801 (2006).

Acknowledgement

- The work presented is part of the PhD thesis project of Joe Morrone, a Hertz Foundation fellow at the Chemistry Department