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Structure and Dynamics of Hydrogen-Bonded Systems

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Nuclear quantum effects in water: A study in position and momentum space

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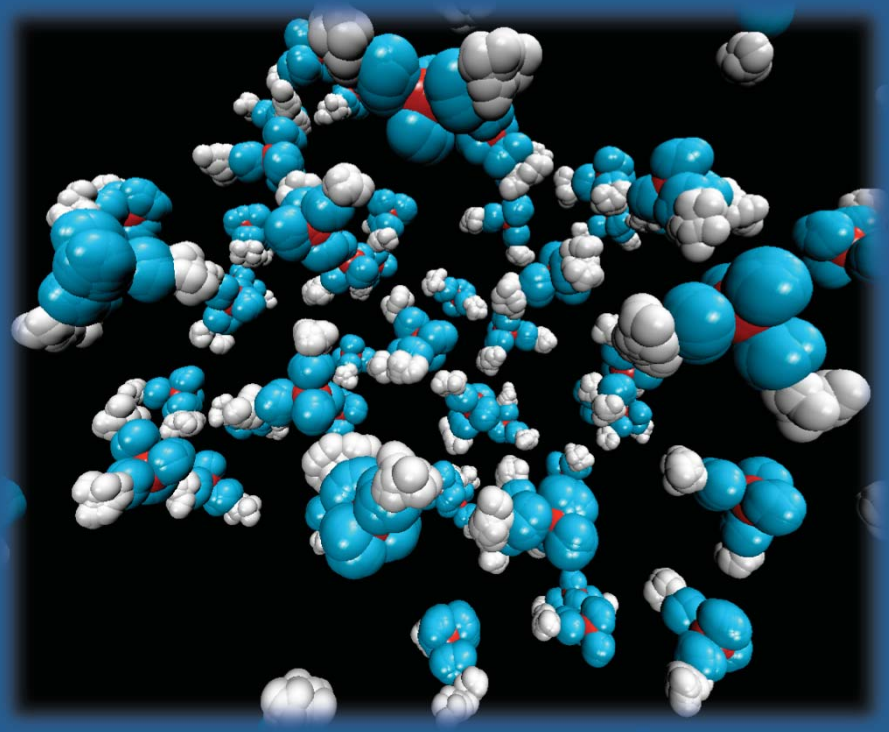

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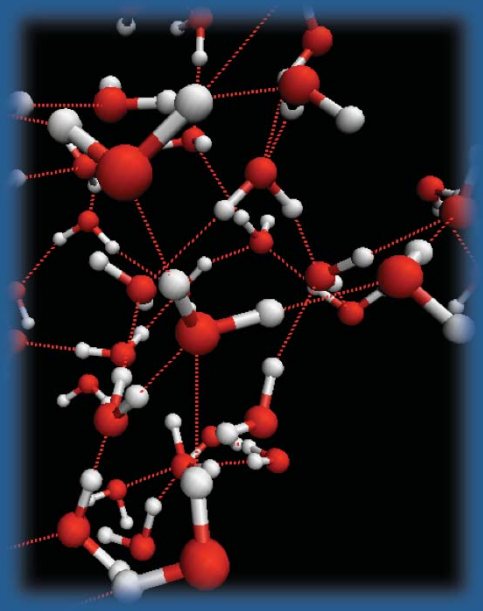
A ubiquitous and unique substance

> Water is one of the most important of all chemical substances. It is a major constituent of our bodies and of the environment in which we live. Its physical properties are strikingly different from those of other substances, in ways that determine the nature of the physical and biological world.
>
> –*Linus Pauling*

- Ubiquitous:
  - Environment
  - Biological systems
- Unique:
  - Hydrogen Bonding
  - Nuclear quantum effects



Experimental Evidence

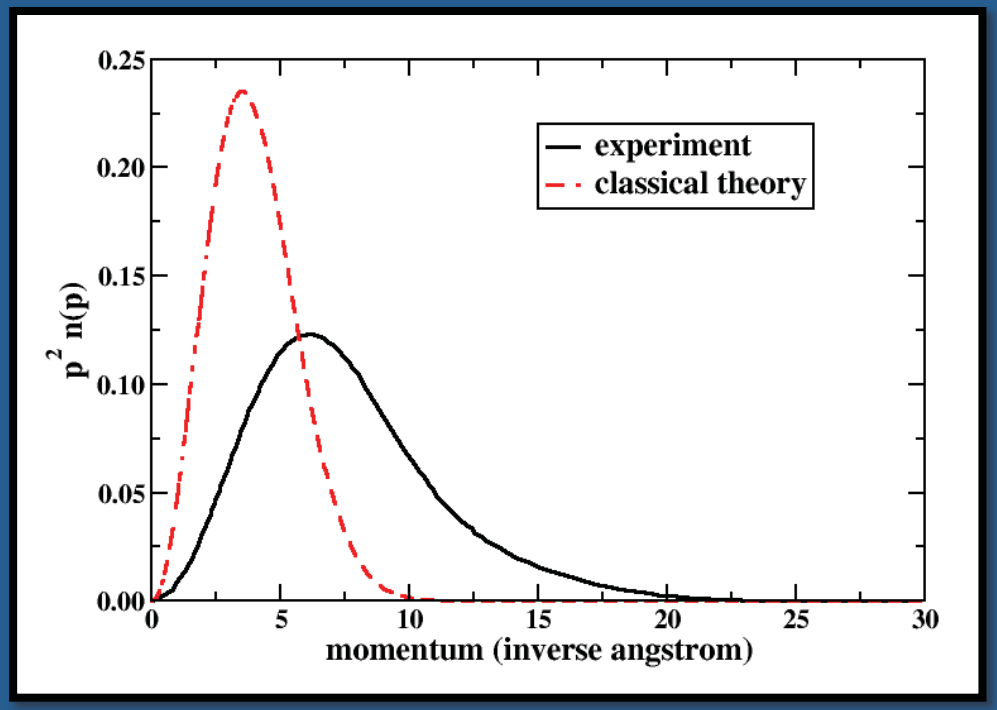
- Experimental properties differ between light and heavy water.
- Average, equilibrium properties should not depend on mass unless nuclear quantum effects are significant.
- Data indicates that heavy water exhibits relative preference for bonding.

	Melting point[1]	Boiling point[1]	Enthalpy of formation[1]	Enthalpy of fusion[2]	Dielectric Constant[1]
H_2O	0.0°C	100.0°C	-285.9 kJ/mol	6.01 kJ/mol	87.9 (T=0°C) 78.4 (T=25°C)
D_2O	3.8°C	101.4°C	-294.6 kJ/mol	6.28 kJ/mol	85.8 (T=5°C) 78.1 (T=25°C)

[1] N. N. Greenwood, et al. Chemistry of the elements, 2nd Ed. Butterworth Heinemann, Oxford (1997).
[2] D. Eisenberg et al. The structure and properties of water, Clarendon, Oxford (1969).

The proton momentum distribution

- Neutron Compton scattering experiments have uncovered proton momentum distribution in a variety of hydrogen bonded systems.[1]
- Large difference between experiment and classical theory.



[1] J. Mayers et al. J. Mol. Struct, 615 275 (2002).
G.F. Reiter et al. Phys. Rev. B 645, 104305 (2002).
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G.F. Reiter et al. Braz. J. Phys. 34 142 (2004).
C. Andreani et al. Adv. Phys. 54 377 (2005).
G.F. Reiter et al. Phys. Rev. Lett. 97 247801 (2006).
V. Garbuio et al. J. Chem. Phys. 127 154501 (2007).
D. Homouz et al. Phys. Rev. Lett. 98 115502 (2007).
R. Senesi et al. Phys. Rev. Lett. 98 138102 (2007).
A. Pietropaolo et al. Phys. Rev. Lett 100, 127802 (2008).
C. Pantalei et al. Phys. Rev. Lett. 100, 177801 (2008).
S.E. Pagnotta et al. Biophys. J. 96 1939 (2009).
D. Flammini et al. J. Chem. Phys. 130 236101 (2009).

Quantum momentum distribution

- Classical: momentum distribution completely separate from configurational partition function.

$$Q = \int \mathrm{d}p\, e^{-T(p)/kT} \times \int \mathrm{d}x\, e^{-V(x)/kT}$$

- Quantum: potential energy surface is intertwined with the momentum due to the uncertainty principle.

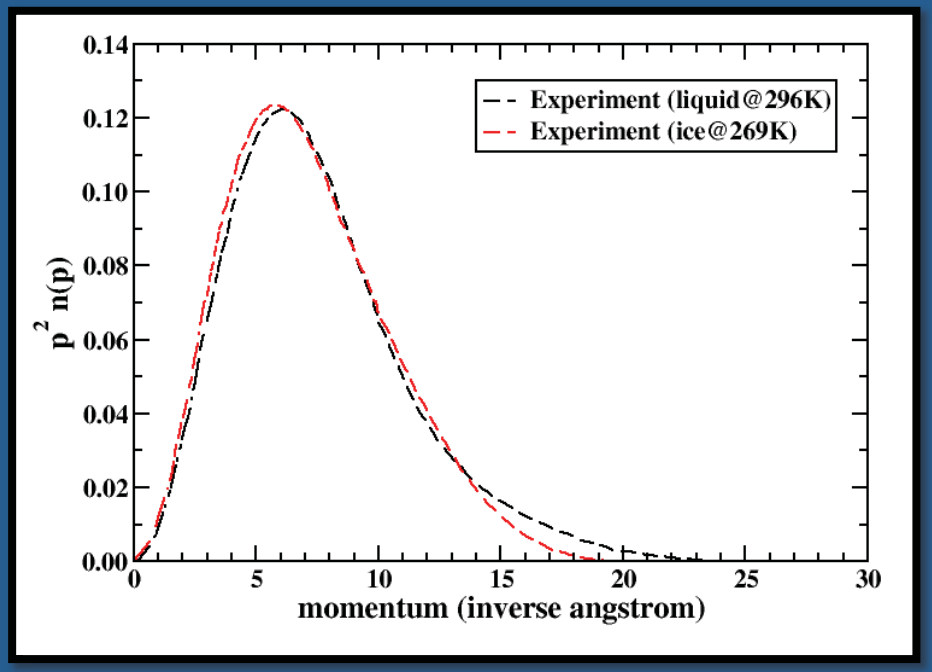
$$\begin{aligned} e^{-(T(p)+V(x))/kT} &\neq e^{-T(p)/kT}\, e^{-V(x)/kT} \\ \text{if} : [x,p] &\neq 0 \end{aligned}$$

- The momentum distribution contains information about the potential energy surface the particle experiences.

Example: Red-shift of the OH stretch

- Water spectra[1]:

	Stretching frequency (cm^{-1})
Gas	3657, 3756
Liquid	3490
Ice I_h	3220



- Hydrogen bonding ➔ weakens covalent bond.
- Shift is reflected in experimental p-distributions of liquid water and ice.[2]

[1] D. Eisenberg et al. The structure and properties of water, Clarendon, Oxford (1969).
[2] Reiter, et al. Brazilian J. Phys. 34 142 (2004)

Path integral formulation of quantum statistical mechanics

- Position representation of density matrix:

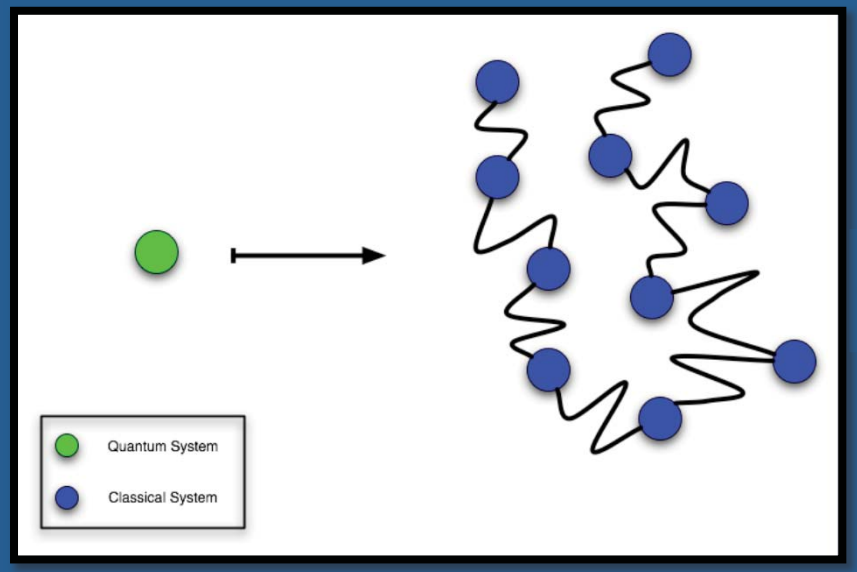
$$\rho(x,x') = \left\langle x \left| e^{-\beta H(p,x)} \right| x' \right\rangle$$

- Split ρ into "P" segments and recover discretized path integral formulation:

$$\rho(x,x') = \lim_{P\to\infty} \int_{\substack{x = x_1 \\ x' = x_{P+1}}} \mathrm{d}x_2 \ldots \mathrm{d}x_P \; e^{-\beta \sum_{i=1}^{P} \left[\frac{m}{2} \frac{P}{(\hbar\beta)^2} (x_i - x_{i+1})^2 + \frac{1}{2P} (V(x_i) + V(x_{i+1})) \right]}$$

Classical Isomorphism

- Path integral Molecular Dynamics:
  - Map quantum problem onto system that obeys classical mechanics



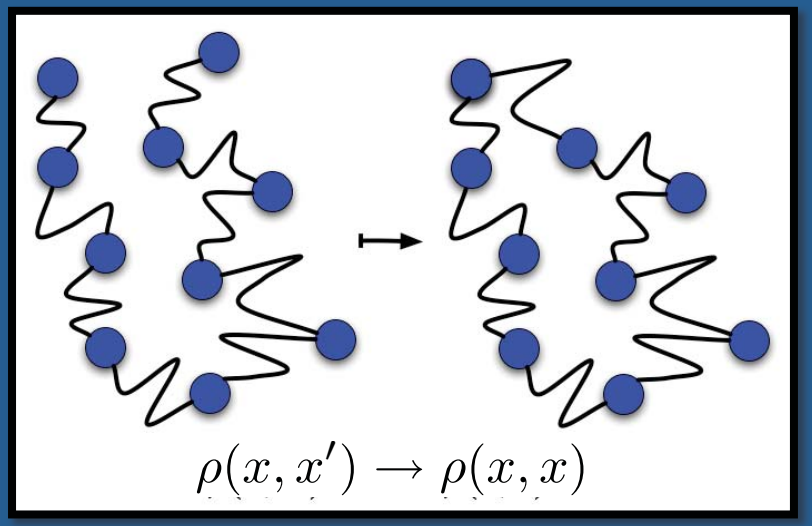
Now we can employ MD!

$$\rho(x,x') = \lim_{P\to\infty} \int_{\substack{x = x_1 \\ x' = x_{P+1}}} \mathrm{d}x_2 \ldots \mathrm{d}x_P \; e^{-\beta \sum_{i=1}^{P} \left[\frac{m}{2} \frac{P}{(\hbar\beta)^2} (x_i - x_{i+1})^2 + \frac{1}{2P} (V(x_i) + V(x_{i+1})) \right]}$$

Open path integral sampling[1]

- Closed path integral compute averages of the form:

$$\langle A \rangle = \int \mathrm{d}x \; \rho(x,x) A(x)$$



- To compute momentum distribution, one needs the off-diagonal components of density matrix (open paths)

$$n(p) = \int \mathrm{d}x \, \mathrm{d}x' \, e^{-\imath(x-x')\cdot p} \rho(x,x')$$

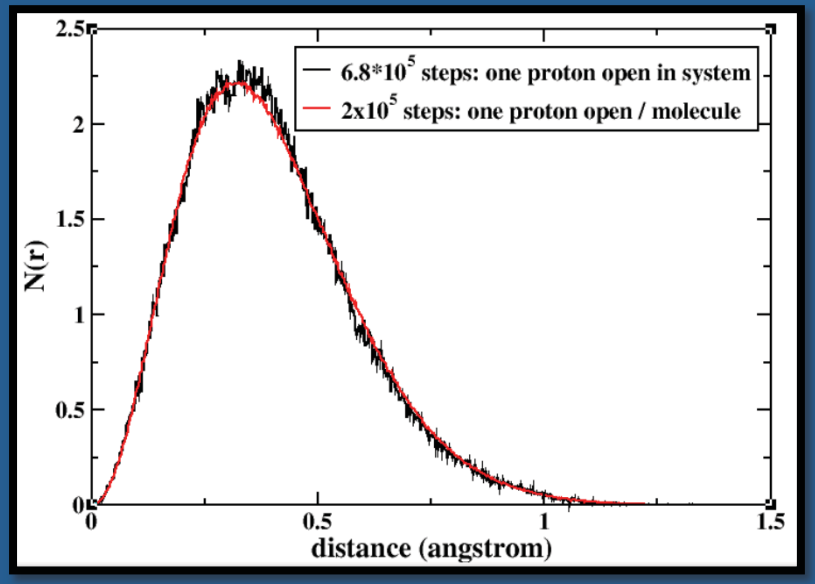
[1] J.A. Morrone et al. JCP 126 234504 (2007). See also C.J. Burnham et al. PCCP 8 3966 (2006), D. Ceperley et al. Can. J. Phys. 65 1416 (1987), J.A. Morrone et al. JCP 130 204511 (2009).

Some Technical Details…

- Coordinate transformation to decouple harmonic interactions between beads which can hinder sampling.
  - "Open" staging transformation[1] – extension of staging PIMD[2]
- Exact open PIMD: only one path open lead to poor sampling efficiency as N increases.
  - Bulk Approximation[1] – One open path per molecule

$$U_{\text{harm}} = \sum_{i=1}^{P} \frac{m\omega_P^2}{2} |x_i - x_{i+1}|^2$$

$$U_{\text{harm}} = \frac{m(kT)^2}{2} u^2 + \sum_{i=2}^{P} \frac{m_i \omega_P^2}{2} u_i^2$$



[1] J.A. Morrone et al. JCP 126 234504 (2007).
[2] M.E. Tuckerman et al. JCP 99 2796 (1993).

Describing the potential

- First principles Car-Parrinello method[1]:
  - Electronic structure computed “on-the-fly” as the simulation progresses.
  - Fictitious electron dynamics:

$$
\begin{aligned}
M_I \ddot{\boldsymbol{R}}_I &= -\frac{\partial E_{KS}}{\partial \boldsymbol{R}_I} \\
\mu \ddot{\phi}_i &= \frac{\delta}{\delta \phi_i^*}\left[-E_{KS} + \sum_{i,j}^{M} \Lambda_{ij}\left[\int \mathrm{d}\boldsymbol{r}\phi_i^*(\boldsymbol{r})\phi_j(\boldsymbol{r}) - \delta_{ij}\right]\right] \\
&= -f_i \hat{H}_{KS}\,\phi_i + \sum_j \Lambda_{i,j}\phi_j
\end{aligned}
$$

  - Success depends upon adiabatic separation of the electronic and ionic dynamics.

[1] R. Car, M. Parrinello PRL 55 2471 (1985).

Simulation Details

- Car-Parrinello path integral MD[1,2]
  - 32 replicas
  - Bulk approximation: one open hydrogen path per molecule.
  - Staging transformation[2]
  - μ=340 AU, Δt=3.0 AU
  - Massive Nose-Hoover chain thermostats[3]
  - Electron thermostat
- Electronic structure:
  - DFT, BLYP functional[4,5]
  - Norm-conserving pseudopotentials[6]
  - Plane wave basis set, 75 Ry cutoff
- Liquid (T=300K):
  - 64 molecules, cubic cell
  - 12.6 ps after 6 ps equilibration
- Hexagonal Ice (T=269K):
  - 96 molecules, orthorhombic cell
  - 3.8 ps after 1 ps equilibration
- High Pressure Ice (T=100K)
  - 16 molecules, cubic cell
  - Three different phases at three volumes
- Supercritical water (T=673K)
  - Empirical SPC/F2 force field[7]
  - ρ=0.64 g/cm^3

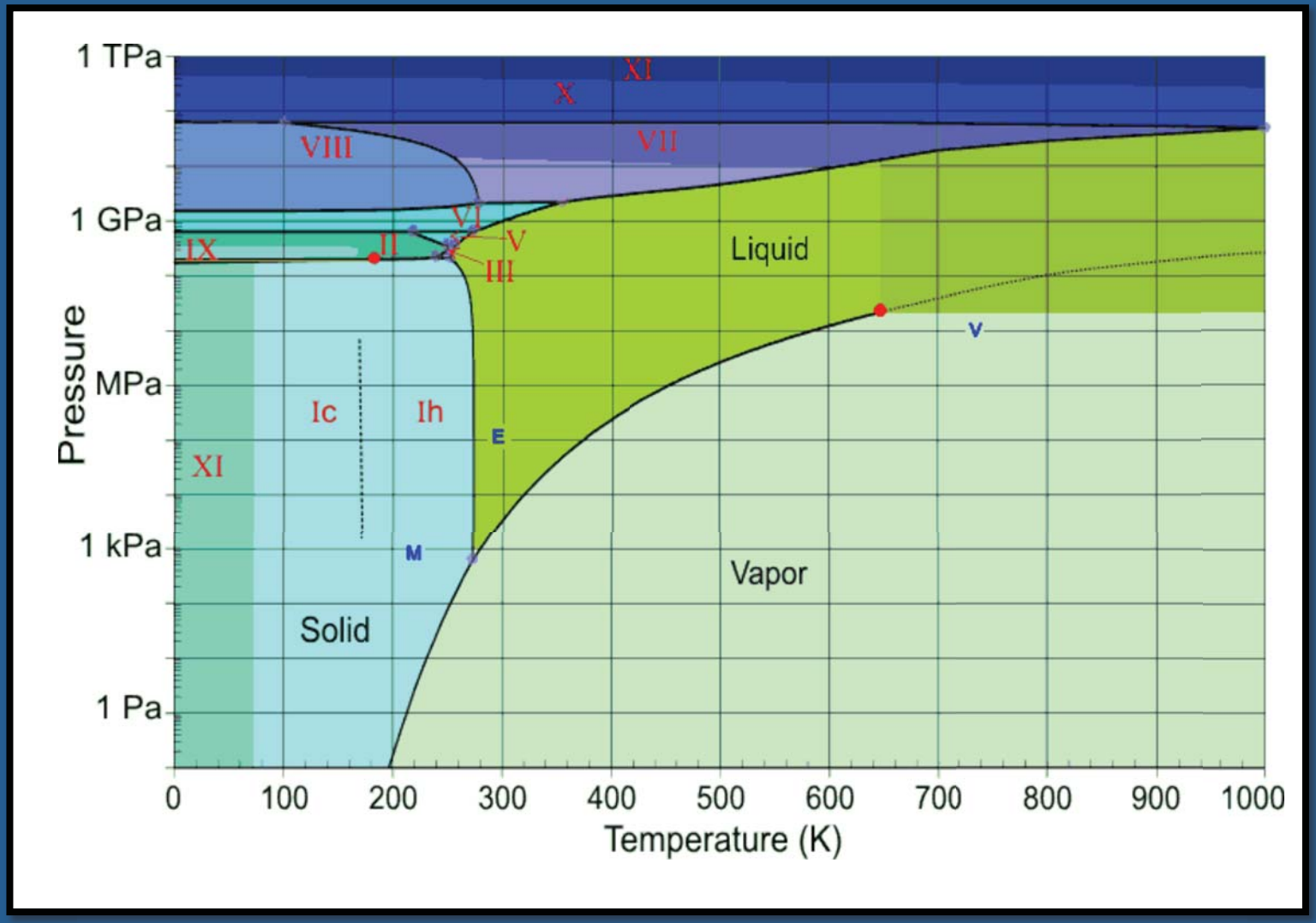
[1] R. Car M. Parrinello PRL 55 2471 (1985)
[2] M.E. Tuckerman et al. JCP 104 5579 (1996), MET et al. JCP 99 2796 (1993).
[3] G.J. Martyna et al. JCP 97 2635 (1992) [4] A. Becke Phys. Rev. A 38 3098 (1988)
[5] Lee et al. Phys. Rev. B 37 785 (1988) [6] N. Troullier et al. Phys. Rev. B 43 1993 (1991)
[7] J. Lobaugh et al JCP 106 2400 (1997).

Computing Resources

- These are LARGE ab initio systems:
  - (64×3×32=6144) atoms
  - (64×4×32=8192) electronic states
- **CPMD**[1] on IBM Blue Gene/L[2]
- Very well parallelized: ≈linear scaling up to 32K processors.
- 512 Nodes - 19 sec/step
- Orangena (Princeton, NJ)
- IBM BG Watson (Yorktown, NY)

[1] CPMD V3.11 Copyright IBM Corp 1990-2006, Copyright MPI fuerFestkoerperforschung Stuttgart 1997-2001
[2] J. Hutter et al. ChemPhysChem 6 1788 (2005)

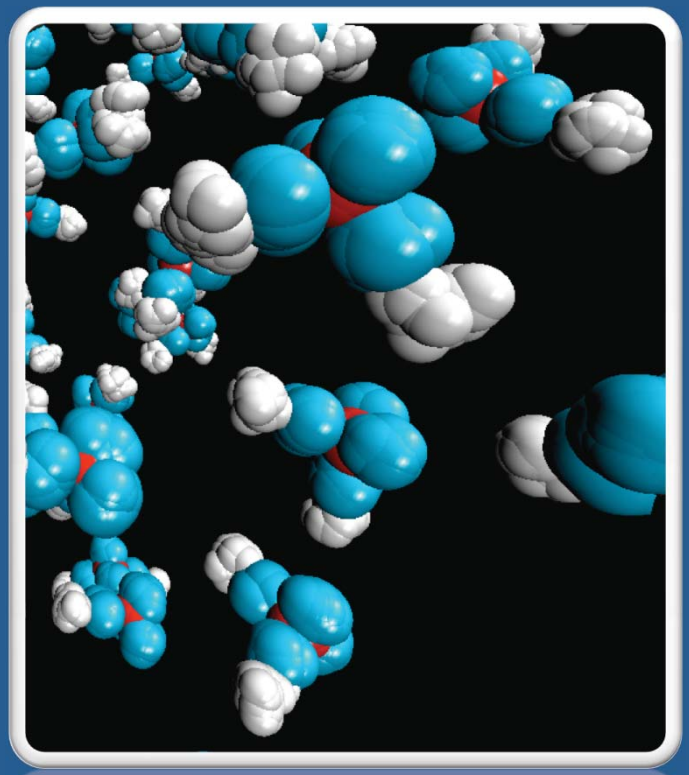
Open PIMD simulations of water



Martin Chaplin, http://www.lsbu.ac.uk/water/phase.html

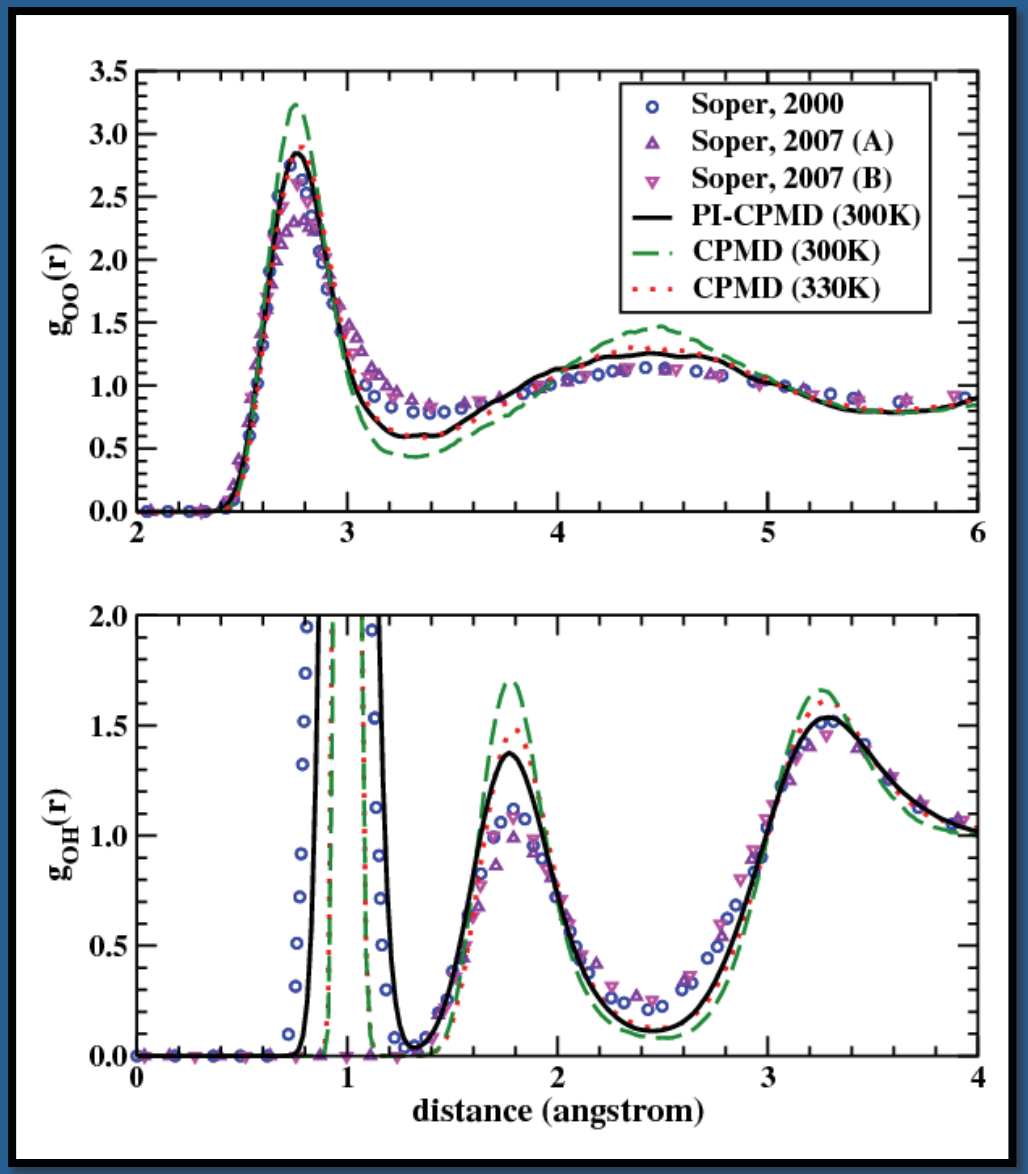
Liquid Water and Hexagonal Ice

- Impact of nuclear quantum effects on liquid structure.
- Differences between proton momentum distribution in liquid and ice; comparisons with experiment.



Liquid Structure: Radial Distribution Function

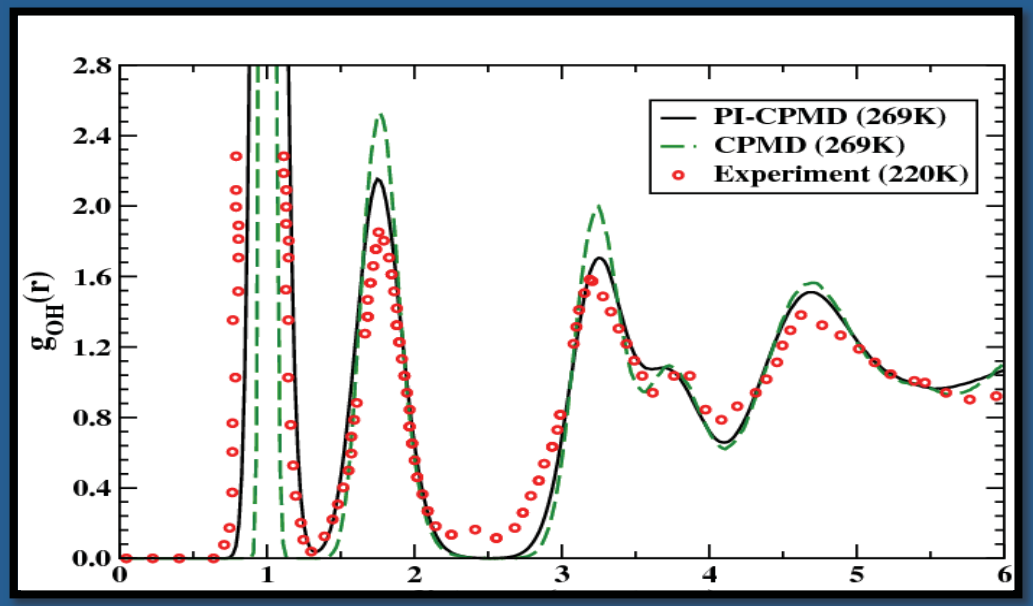
- PI-CPMD closer to experiment[1] than standard simulation.[2]
- Quantum effects broaden distribution (≈30K).
- Features remain sharper than experiment.



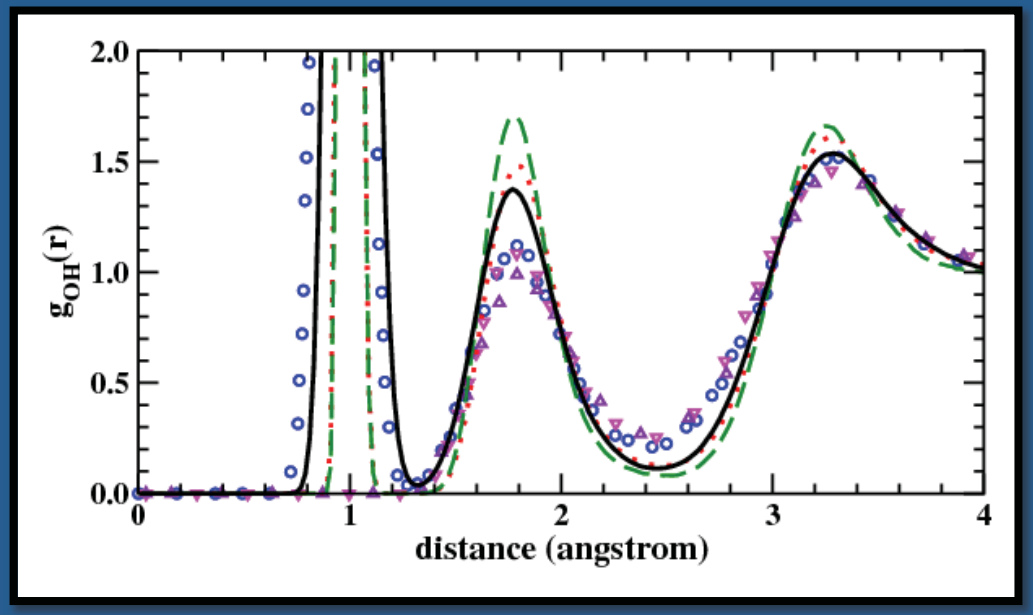
[1] A.K. Soper Chem. Phys. 258 121 (2000), J. Phys. Cond. Matt. 19, 335206 (2007). [2] J. Grossman et al. JCP 120 300 (2004) Y. Mantz JPC B 110 3540 (2006).

Hexagonal ice structure

Hexagonal ice



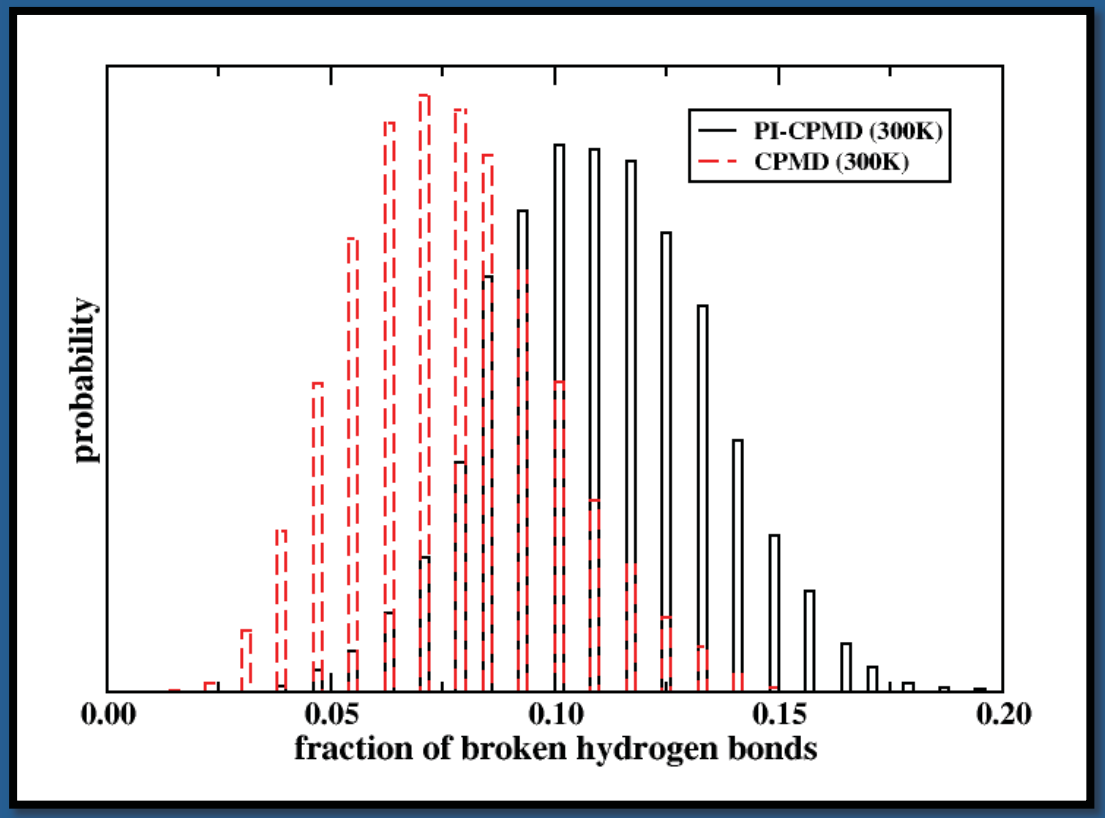
Liquid water



Experiment: A.K. Soper Chem. Phys. 258 121 (2000).

Hydrogen Bonding distribution

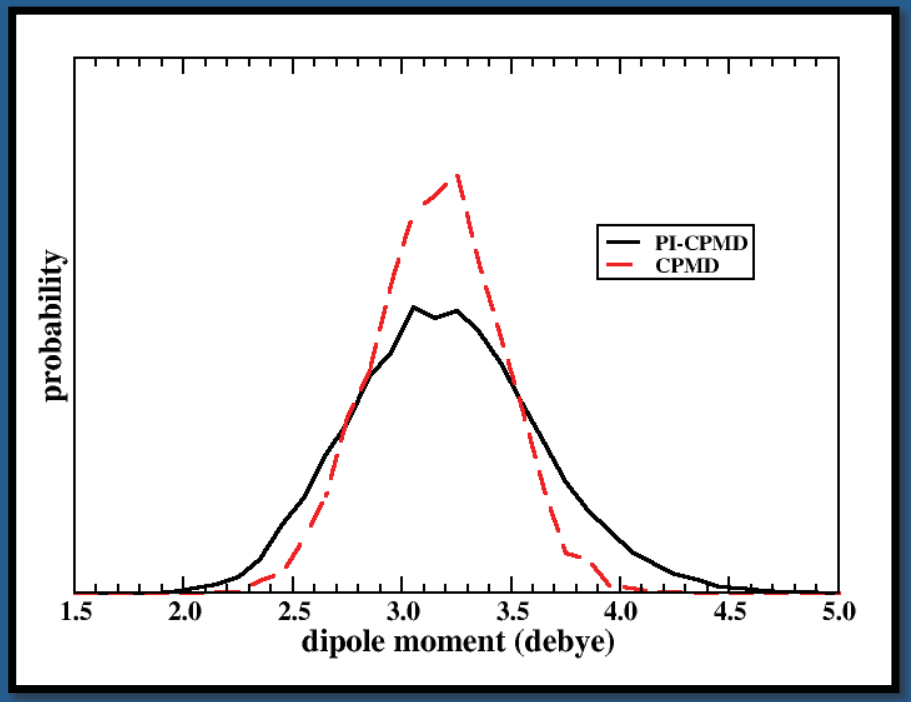
- Simple geometric criteria.
- More broken hydrogen bonds in PI-CPMD simulation than standard CPMD.
- Average % broken hydrogen bond:
  - PI-CPMD: 11%
  - CPMD: 7%



	Melting point[1]	Boiling point[1]	Enthalpy of fusion[2]
H_2O	0.0°C	100.0°C	6.01 kJ/mol
D_2O	3.8°C	101.4°C	6.28 kJ/mol

Estimate of dipole moment distribution

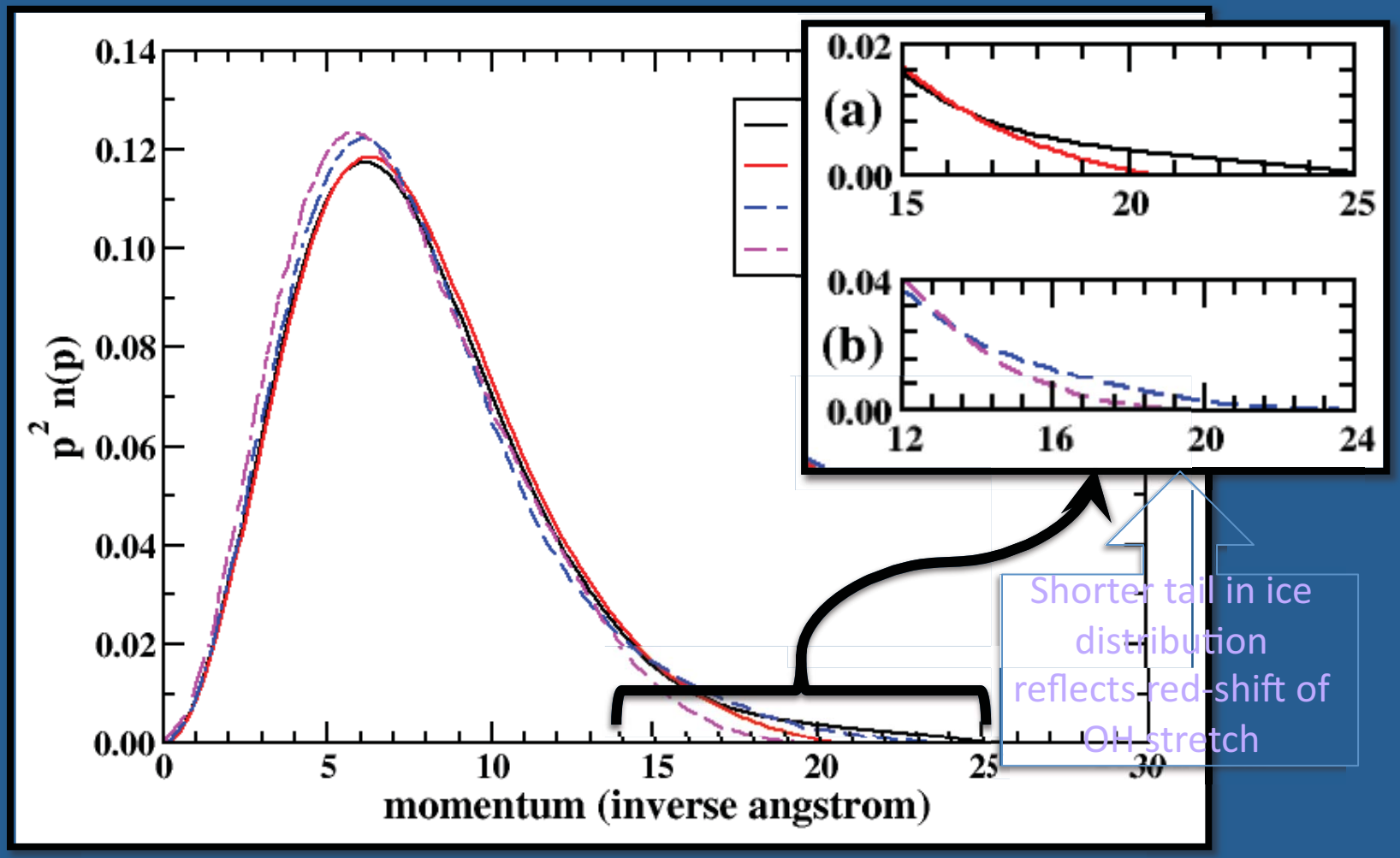
- Computed from selected configurations
- Nuclear quantum effects broaden dipole moment distribution.
- Broader dipole indicates larger root mean square dipole moment.



- Larger dielectric constant

	Dielectric Constant
H_2O	87.9 (T=0°C) 78.4 (T=25°C)
D_2O	85.8 (T=5°C) 78.06 (T=25°C)

Radial momentum distribution

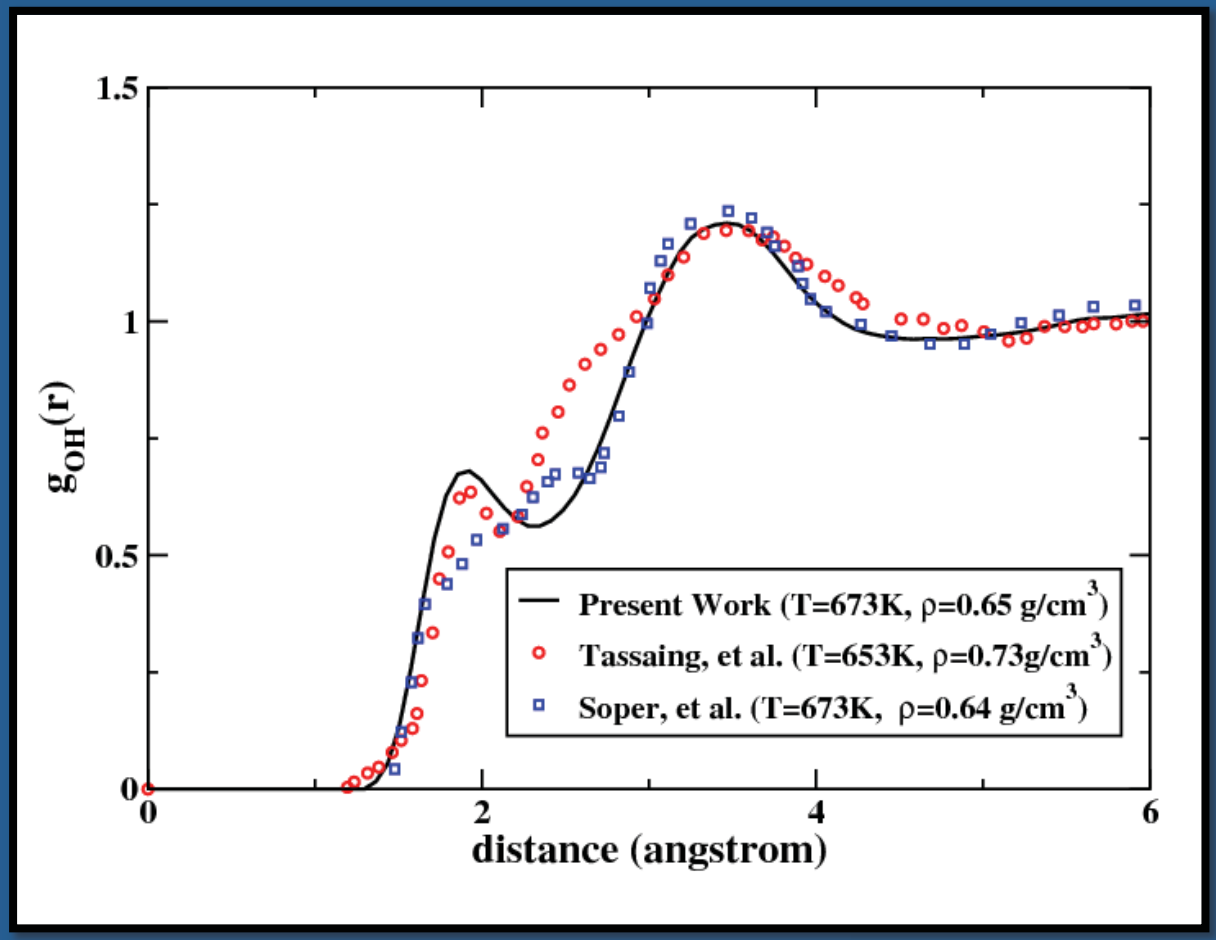


- Simulation broader in momentum space, narrower in position than experimental measures[1]
- Simulation qualitatively reproduces experimental differences between phases of water.

[1] Reiter, et al. Brazilian J. Phys. 34 142 (2004)

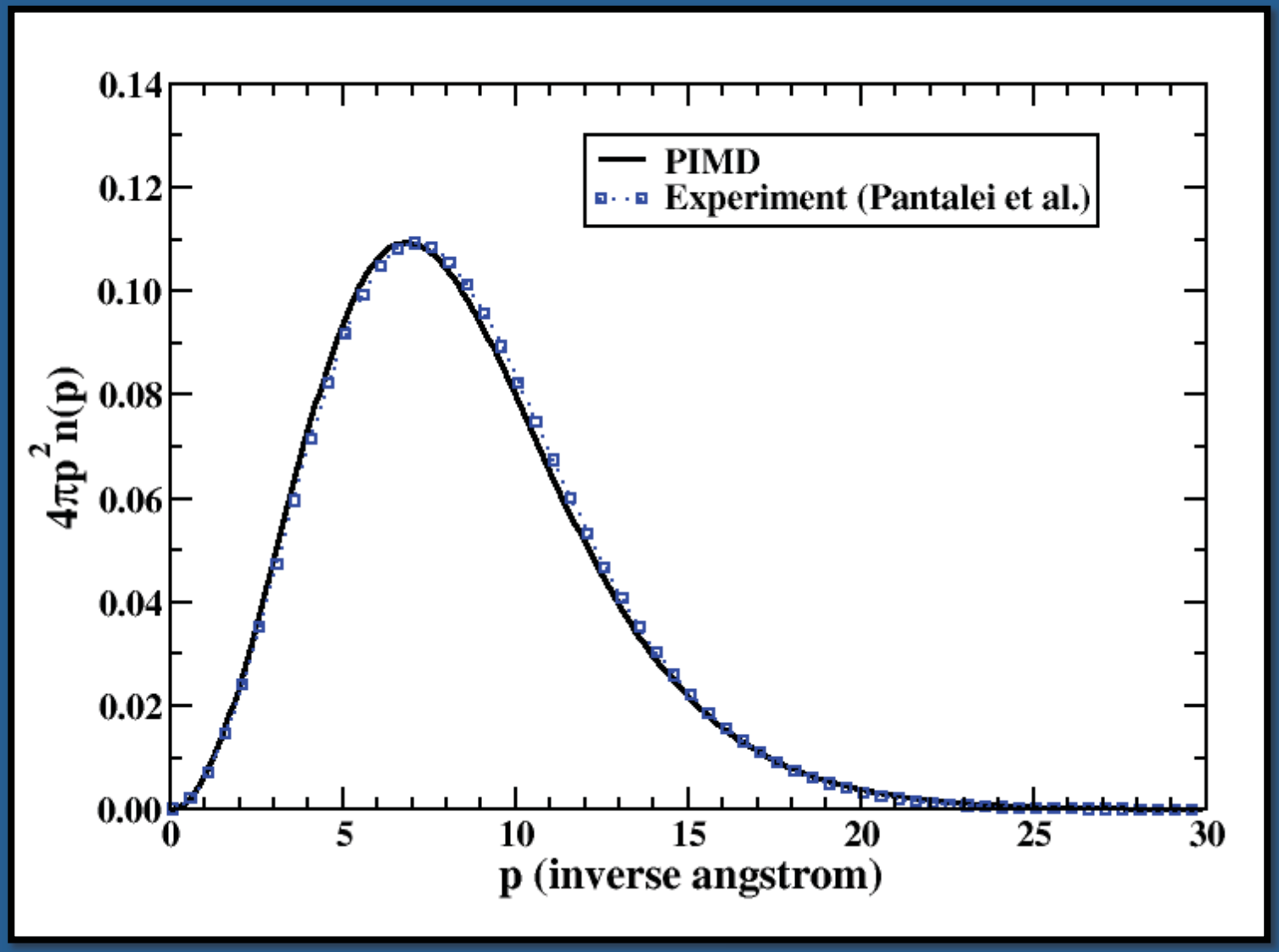
Supercritical Water

- Water under high pressure, temperature.
- Less hydrogen bonding present than solid, liquid phases.
- Simulation performed with SPC/F2 force field[1].



[1] J. Lobaugh et al JCP 106 2400 (1997).
Experiment: T. Tassaing, et al. Europhys. Lett. 42, 265 (1998). A. Soper Chem. Phys. 258, 121 (2000).

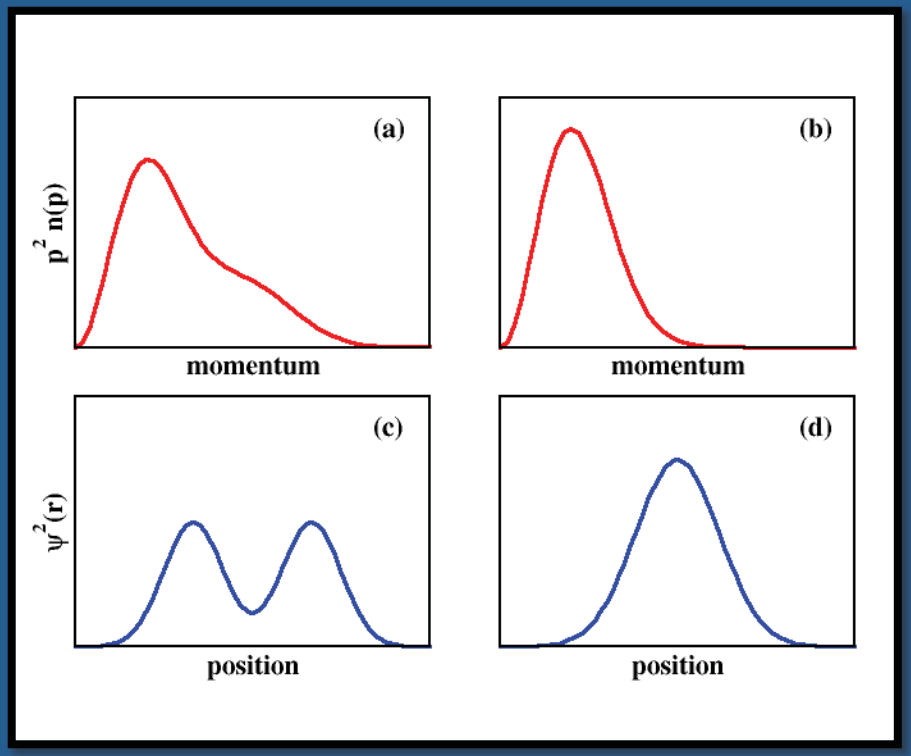
Radial Momentum distribution



Experiment: C. Pantalei et al., PRL 100, 177801 (2008).

Experimental evidence of tunneling

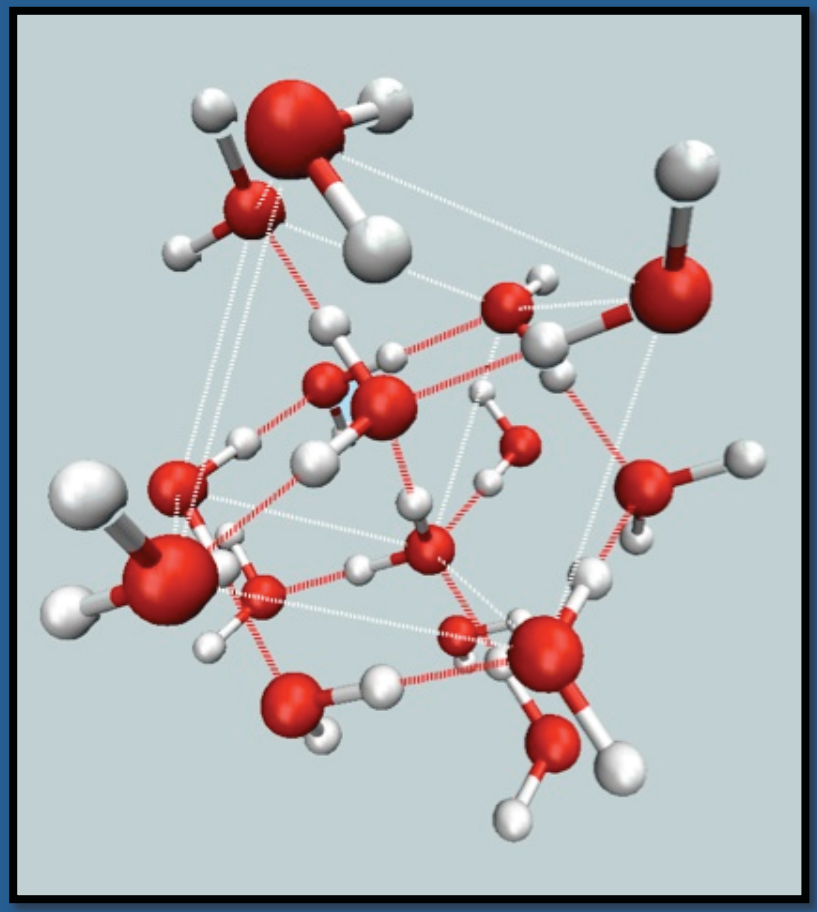
- Quantum tunneling has been used to explain bimodal features in experimentally observed momentum distribution.
- Observed in confined water in a variety of systems[1]
- Can this phenomena be studied via simulation?



[1] G.F. Reiter, et al. PRL 89 135505 (2002).
V. Garbuio et al. JCP 127 154501 (2007).
R. Senesi et al. Phys. Rev. Lett. 98 138102 (2007).

High Pressure ice

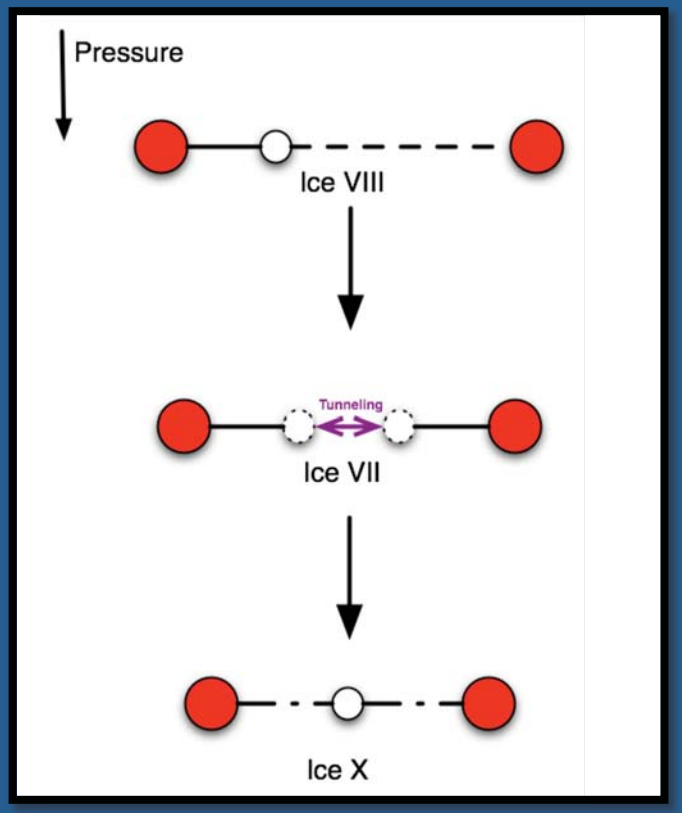
- BCC ice: Two interpenetrating cubic H-bond lattices.
- Three phases (increasing pressure):
  - ICE VIII: Proton ordered
  - ICE VII: Proton disordered
  - ICE X: “Symmetric”
- Previous PI CPMD simulations have shown evidence of quantum tunneling.[1]



[1] Benoit et al. Nature 392 258 (1998).

Possible phases

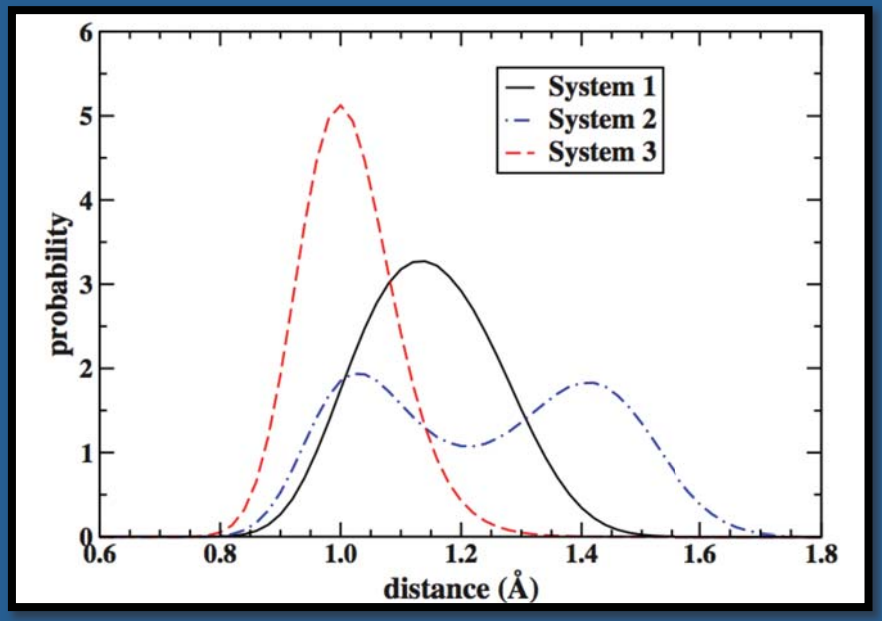
- System 1: Ice X
  - Proton is shared equally between oxygen
- System 2: Ice VII
  - Proton disordered, tunneling events along hydrogen bond
- System 3: Ice VIII
  - Proton ordered, anti-ferroelectric
- **Phases may be tuned via decreasing the volume of the system.**



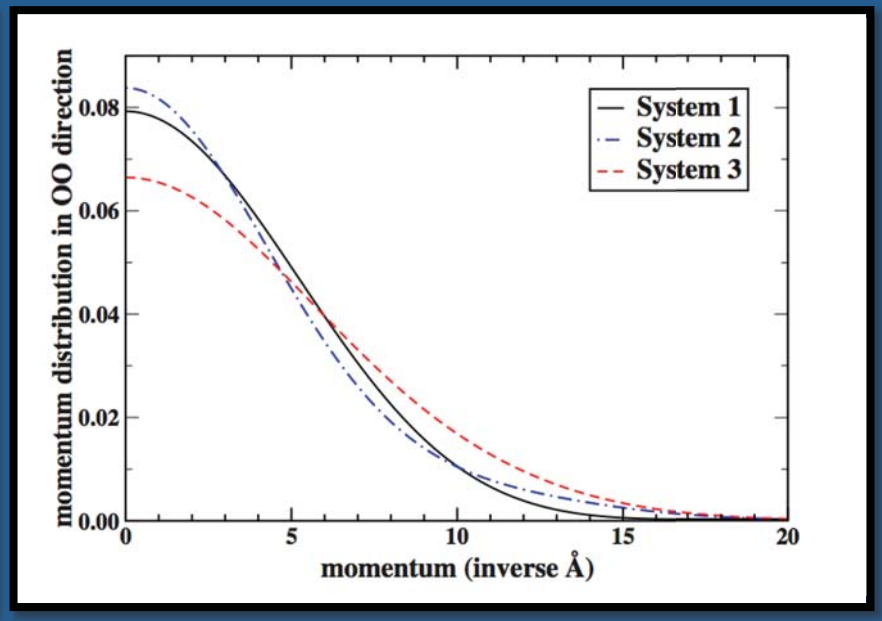
System number	Lattice constant (Å)	Molar volume (cm^3/mol)	Approximate pressure (GPa)	d_{OO}^{mp} (Å)
1	2.67	5.74	90	2.31
2	2.84	6.90	45	2.45
3	2.94	7.62	31	2.53

Looking along the bonding direction…

Position space



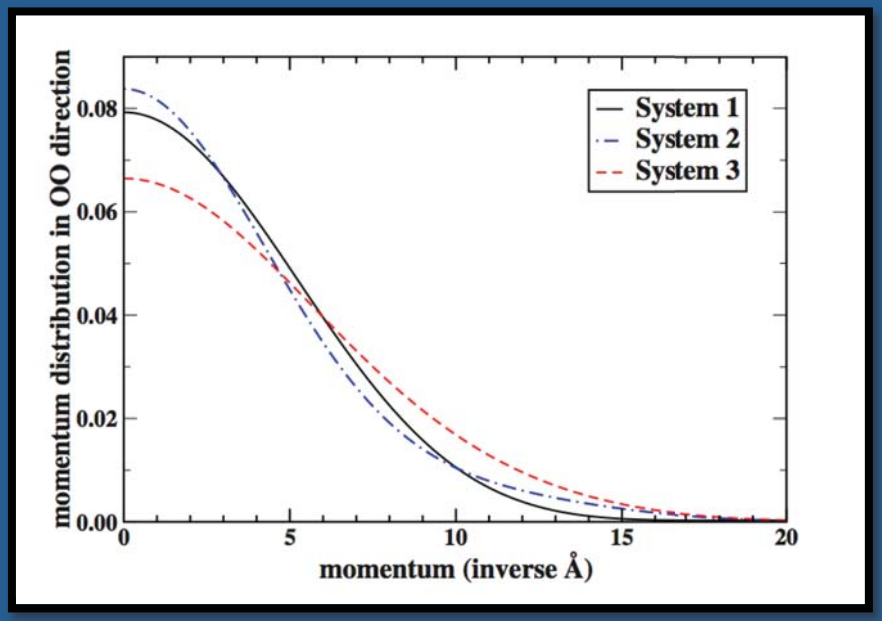
Momentum space



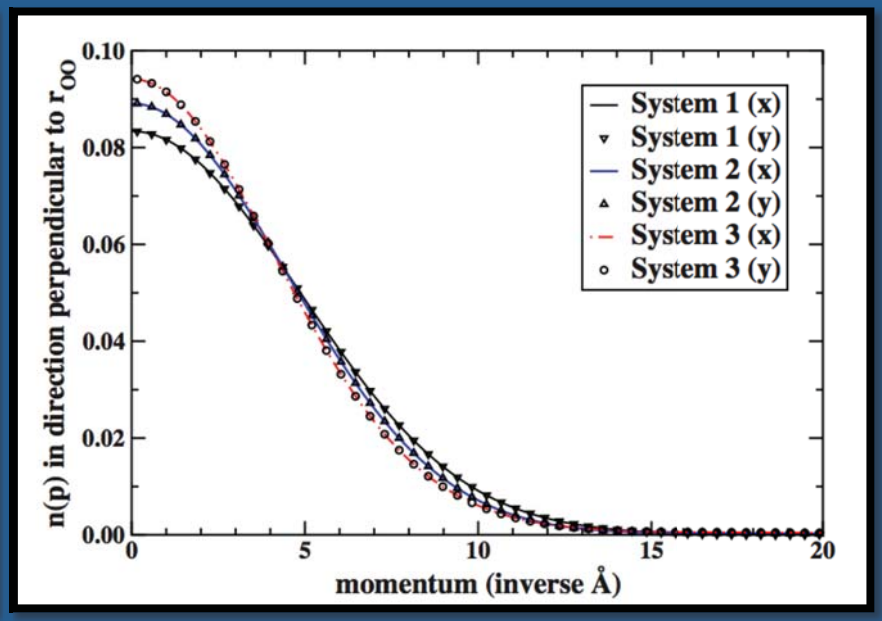
- Narrower in position space → broader in momentum space
- Symmetric bond has much shorter tail owing to absence of OH covalent stretch.
- Tunneling momentum distribution is narrow at low p, with extended tail to match covalently bonded distribution.

Perpendicular to the bond direction

Bonding direction



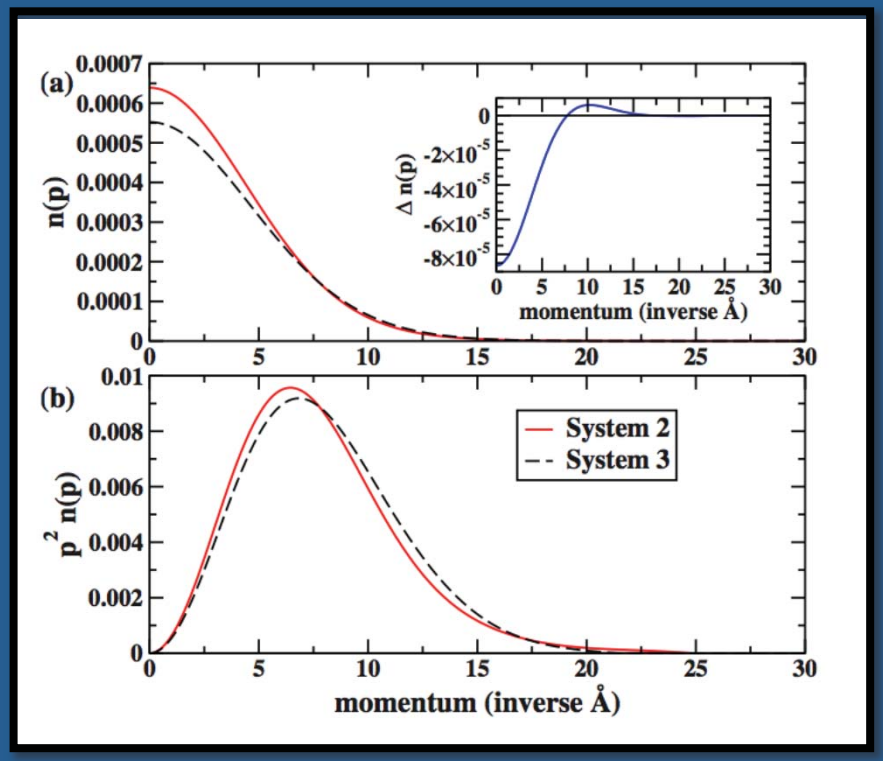
Perpendicular direction



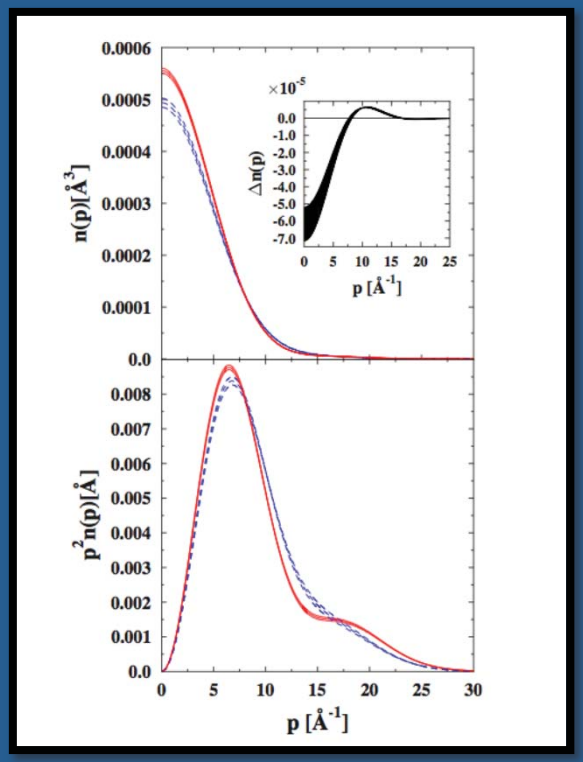
- Perpendicular directions broaden with decreasing volume. Effectively in opposite direction as bonding trend. Consistent with fact that stronger hydrogen bonds:
  - Red-shift OH stretch
  - Blue-shift other modes

Radial momentum distribution

Simulation



Experiment[1]



- Similarities between simulation and experimental results on hydration shell of a globular protein.
- No secondary feature present in simulation.

[1] R. Senesi et al. Phys. Rev. Lett. 98 138102 (2007).

A simple model for tunneling

- Further investigate tunneling with one-dimensional potential:

$$V(z) = \tfrac{1}{2}m\omega^2 z^2 + Ae^{-m\xi z^2},$$

with $m=1836$, $\omega=0.005$, $A=0.012$, and $\xi=0.0087$

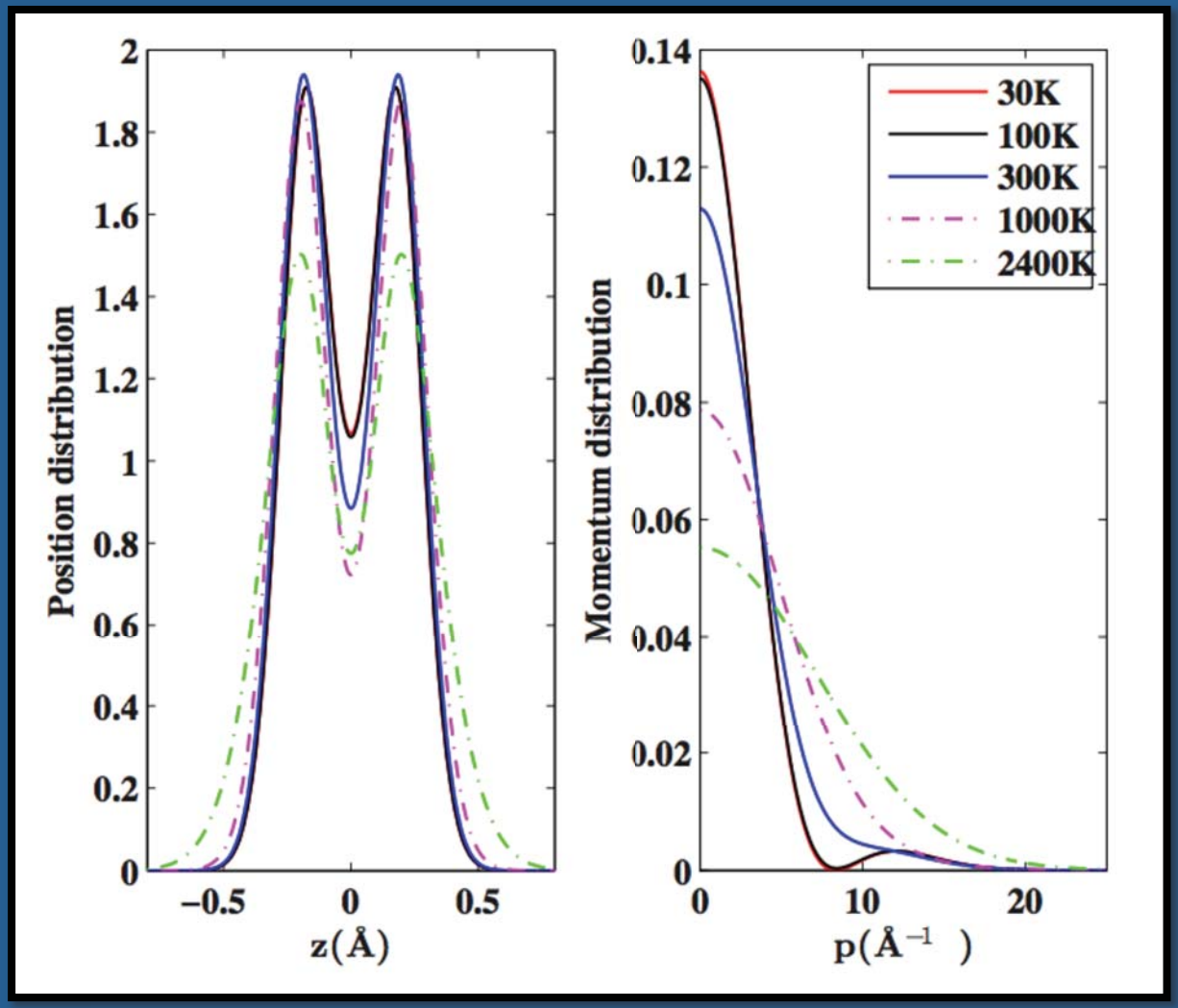
- Solve problem exactly at several temperatures
  - Population of energy eigenstates:

T	30 K (%)	100 K (%)	300 K (%)	1000 K (%)	2400 K (%)
P_0	100	99.1	82.8	57.1	37.5
P_1	0.00	0.881	17.2	35.6	30.8
P_{2+}	0.00	0.00	0.00	7.29	31.7

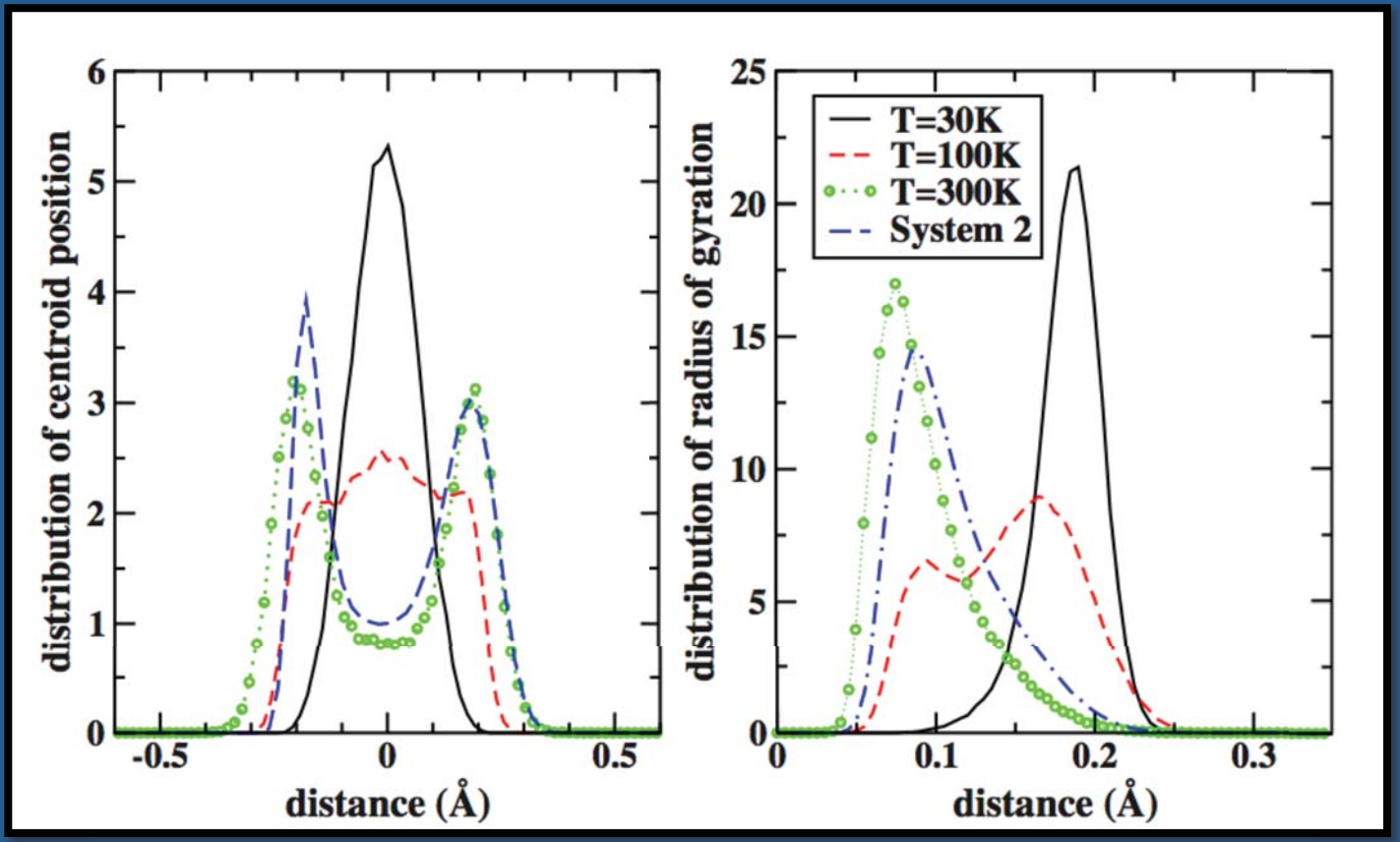
States above barrier

Position and momentum space distributions

- Larger differences in momentum than position space.
- Momentum shapes range from those with prominent nodes to Gaussian.
- Reflects the different means of crossing the barrier.



Temperature dependence of localization



- Path integral calculation at three “tunneling” temperatures.
- As temperature increases, paths become smaller, more localized around the wells: Transition from ground state to mixed state tunneling.
- Ice VII resembles T=300K: Both have no distinguishable secondary features in momentum distribution.

Conclusions

- Nuclear quantum effects play an important role in aqueous systems.
- The proton momentum distribution may be computed via open PIMD.
- Uncertainty principle in action:
  - Sharper position distribution → Broader momentum distributions.
- Nuclear quantum effects decrease the structuring of liquid water.
- Difference in hydrogen-bonding environment reflected in momentum distribution.

Conclusions (cont…)

- Symmetric hydrogen bond:
  - Narrower momentum distribution in bonding direction with shortened tail.
- Proton tunneling
  - Narrow at low momentum, with extended tail
  - Secondary features more prominent at low temperatures, gradually washed out as T increases.
- References:

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