







# Atomic quantum dynamics in water: neutron experiments to benchmark state-of-the-art modeling

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Erice School "NEUTRON SCIENCE AND INSTRUMENTATION": WATER AND WATER SYSTEMS

## TITI LVCRETI CARI DE RERVM NATVRA LIBER SECVNDVS

....Quod quoniam constat, ni mirum nulla quies est reddita corporibus primis...

....As it is well assessed, no rest is given to prime bodies (*atoms*) ...

Restless motion which persists to absolute zero..

#### Costituents of matter are quantum objects

- Thermal energy—often expressed as temperature—makes all objects vibrate; the warmer the object, the more pronounced the vibrations, though they are on the order of much less than an Angstrom
  - More subtle vibrations that all objects possess is due to a quantummechanical property called zero-point motion
    - Primary thermometry: combine thermal vibration to the quantum motion-connect temperature to the quantum mechanical fluctuations of a particle

#### NIST Creates Fundamentally Accurate Quantum Thermometer March 15, 2016

# Where does this come from? Binding of atoms in materials is described by atoms in potential wells



# Depending on the atomic mass, quantum effects on the zero temperature motion will be different



a) and b) are atoms of different masses in the same binding potential

# Depending on the stiffness of the potential, quantum effects on the zero temperature motion will be different





M'=M

#### Why published in Nature Comm.?



**Figure 1 | Rocksalt crystal structure of uranium nitride.** Each N atom (small red spheres) is centred in a regular octahedron of U atoms (large blue spheres).

#### Because in perfectly harmonic binding potentials are uncommon!





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**Figure 7.7** The potential energy of interaction between atoms in a solid. (a) The *harmonic approximation*: How the energy would vary if the atoms were connected by 'perfect springs'. (b) The typical deviation from the harmonic approximation of a real interatomic potential. The sloping line indicates the increasing average separation as the average energy of oscillation (i.e. the temperature) is increased. (a)

Mechanical properties of solids and details of atomic binding

(b)



Distance between atoms

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**Figure 7.9** Schematic illustration of the potential energy of an Fe–Ni bond in an invar alloy (Table 7.8). The asymmetry of the potential (over a certain range) is opposite to that which occurs in normal bonds (Figure 7.7).



#### Mechanical properties of solids and details of atomic binding

The zero-point motion depends on the atomic displacements around equilibrium positions

$$\Delta p_x \Delta x \simeq \hbar/2$$

$$\langle u^2 \rangle = 3 \langle \Delta x^2 \rangle \qquad \langle p^2 \rangle = 3 \langle \Delta p_x^2 \rangle$$

#### Zero-point kinetic energy

$$\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M} = \frac{3 \langle \Delta p_x^2 \rangle}{2M} = \frac{\hbar^2}{8M} \frac{3}{\langle \Delta x^2 \rangle}$$

$$\langle E_K \rangle = \frac{9}{8} \frac{\hbar^2}{M \langle u^2 \rangle}$$
Lindemann ratio  $\gamma = \frac{\langle u^2 \rangle^{1/2}}{R}$ 

$$\langle E_K \rangle = \frac{9}{8} \frac{\hbar^2}{M \gamma^2} \frac{\rho^{2/3}}{\bullet}$$
Density
$$\langle E_K \rangle >> 1.5k_BT !!$$

Is zero point kinetic energy responsible for helium being persistently liquid down to T= 0 K?



Only at P= 25 bar !!

## Solidification of helium at T= 0 K requires to overcome zero point kinetic energy

Consider the Gibbs free energy, G, at absolute zero, as a function of applied pressure (acting as an external energy). If G shows a minumum a stable phase is obtained

$$G = \langle E_K \rangle + V + E_{ext}$$

## Solidification of helium at T= 0 K requires to overcome zero point kinetic energy

-CONJECTURE: He atom pairs are at equilibrium distance R, but they can oscillate in a region  $R - \sigma$ , where  $\sigma$  is a hard-core repulsion potential due to near neighbour interaction.

$$\left\langle E_{K}\right\rangle = \frac{\hbar^{2}}{M_{He}(R-\sigma)^{2}}$$

-Potential energy will be half of the pair interactions times the number of nearest neighbours, z:

$$V = \frac{1}{2}zv(R)$$

-External energy due to pressure is:

Solidification of helium at T= 0 K requires to overcome zero point kinetic

$$G(P,R) = \frac{\hbar^2}{2M_{He}(R-\sigma)^2} + \frac{1}{2}zv(R) + PR^3$$

-Gibbs energy, as a function of R, P has a minimum for

 $P \simeq 25 \ bar$   $R \simeq 3.7 \text{\AA}$ 

In agreement with experiments!



Atomic binding potentials change depending on the -Phase of the material -External stimuli -Geometric confinement, -Fluctuations...

## Thermal motion in proteins: Large effects on the time-averaged interaction energies

Martin Goethe,<sup>1,a</sup> Ignacio Fita,<sup>2</sup> and J. Miguel Rubi<sup>1</sup>



As a consequence the Zeropoint kinetic energy shows rich and sometimes suprising behaviour Is it possible to measure it?

$$\left|\Psi(p)\right|^{2} = n(p)$$

$$\left\langle E_{K}\right\rangle = \frac{\left\langle p^{2}\right\rangle}{2M} = \int d^{3}p \ p^{2} \ n(p)$$

Such measurements are «simple» (not complicated), but are difficult -just like preparing a dish requiring a small number of ingredients: Tortilla, Pasta, Fish&Chips...

$$\left|\Psi(p)\right|^{2} = n(p)$$
$$E_{K} = \frac{\left\langle p^{2} \right\rangle}{2M} = \int d^{3}p \ p^{2} \ n(p)$$

These measurements are precise -Provide absolute numbers

$$\langle E_K \rangle$$
 or  $\Delta \langle E_K \rangle = (\langle E_K \rangle - 1.5 k_B T)$ 

-Or distributions

Amenable to be quantitatively modeled at any level of sophistication!!

> Heuristic-Semiclassical PIMC PIMD AIMD PICPMD DMC DFT Classical-MD

# Quantitative tests with theories, for monatomic fluids and solids:Helium

These measurements are precise -Provide absolute numbers

$$\langle E_K \rangle$$
 or  $\Delta \langle E_K \rangle = (\langle E_K \rangle - 1.5 k_B T)$   
-Or distributions  $n(p)$ 





FIG. 5. The excess kinetic energy as a function of temperature at two densities: triangles (26 nm<sup>-3</sup>) and squares (10 nm<sup>-3</sup>). The solid and dashed lines are the excesses computed using the first-order cluster expansion, Eq. (1), at the same densities. The density matrix was calculated using the matrix squaring method [2].

From Ceperley et al, PRL 1996

#### Experiments meet Quantum Monte Carlo modeling





Diffusion Monte Carlo by Boronat et al.

[R. S. et al. PRL 86, 4584 (2001)] <sup>19</sup>

#### Experiments meet Quantum Monte Carlo modeling «Not-so-Simple» monoatomic systems: liquid <sup>3</sup>He at 2 K, SVP



Which type of nuclear quantum effects are expected for water? Few examples:

• Macroscopic: Triple point; Temperature of Density maximum; Thermal expansion...

- Microscopic: Temperature dependence of excess kinetic energy, momentum distribution in anharmonic potentials; Isotope effects;..
- Microscopic: Nanoscale confinement effects; Nuclear quantum effects on the oxygens;...

# Which type of nuclear quantum effects are expected for water? Few examples:

#### **Chemical Reviews**

#### Table 1. Experimentally Observed Isotope Effects in $Water^a$

property	H <sub>2</sub> O	$D_2O$	T <sub>2</sub> O	$H_2^{18}O$
malting point $T_{-}(V)$ (at 1 atm)	272.15	276 07 (1.40%)	277 64 (1 648)	272 46 (0.11%)
temperature of maximum density (TMD) (K)	277.13	2/0.97 (1.40%) 284.34 (2.60%)	286.55 (3.40%)	277.36 (0.11%)
critical temperature (K)	647.10	643.85 (-0.50%)	641.66 (-0.84%)	277.50 (0.0007)
molar density (mol/L)	55.35	55.14 (-0.38%)	55.08 (-0.49%)	55.42 (0.13%)
molar density at the TMD (mol/L)	55.52	55.22 (-0.53%)	55.17 (-0.63%)	55.59 (0.13%)
liquid/vapor surface tension (N/m)	0.07198	0.07187 (-0.15%)		
specific heat capacity, C <sub>v</sub> [J/(K mol)]	74.54	84.42 (13.2%)		

From Ceriotti et al., Chem Rev. 2016

#### PHYSICAL REVIEW B 83, 220302(R) (2011)

#### Momentum distribution, vibrational dynamics, and the potential of mean force in ice



#### Which type of nuclear quantum effects are expected for water?



FIG. 1 (color online). The OO (top) and OH (bottom) RDFs in liquid water from an open PI CPMD simulation at 300 K (solid line) and standard CPMD simulations at 300 K (dashed line) and 330 K (dotted line) are reported with neutron [4] (circles) and recent joint neutron/x-ray data [5] (triangles) that utilize different x-ray input for A [6] and B [7].

Quantum effects destabilizing H-Bond network

From Morrone, Car, PRL 2008

#### Which type of nuclear quantum effects are expected for water?



FIG. 3. Radial distribution functions for heavy (solid line) and light (dashed line) water. Also shown are the RDFs found in a previous study [21] in which both heavy and light water data were refined against the same box of molecules. The results are shown in the order HH (a), OH (b), and OO (c) and are shifted for clarity. The inset shows the second OO peak in more detail.

It is found that heavy water is a more structured liquid than light water. We find the OH bond length in  $H_2O$  is ~3% longer than the OD bond length in  $D_2O$ . This is a much larger change than current predictions. Corresponding to this, the hydrogen bond in light water is ~ 4% shorter than in heavy water, while the intermolecular HH distance is ~ 2% longer. From Soper, Benmore, PRL 2008

#### Which type of nuclear quantum effects are expected for water? Radial Momentum distributions of protons and deuterons in $H_2O$ and $D_2O$



From R. Car et al.

From Romanelli et al. JPCL 2013

#### Which type of nuclear quantum effects are expected for water? Want to build a new Nuclear Reactor?



(a) Total neutron cross section for H<sub>2</sub>O.



Figure 5. Total neutron cross section for light water (left) and heavy water (right) at room temperature.

From Marquez et al. Phys Procedia 2014

Which type of nuclear quantum effects are expected for water? Is it possible to tune nuclear quantum effects in the O-H binding in water?



Tuning the strength of a single hydrogen bond formed at a water-salt interface, using tip-enhanced inelastic electron tunneling spectroscopy. Anharmonic quantum fluctuations of hydrogen nuclei weaken the weak hydrogen bonds and strengthen the relatively strong ones Which type of nuclear quantum effects are expected for water? Is it possible to model the phase diagram of water?



**Fig. 3** Phase diagram of water from path integral simulations of the TIP4PQ/2005 model. Experimental results (blue points) are also shown.<sup>1,56</sup>

From McBride et al. PCCP 2012

#### Which type of nuclear quantum effects are expected for water? Quantum effects in competition



Figure 1. Competing quantum effects in the hydrogen bonding between two water molecules. There are two qualitatively different contributions to the vibrational ZPE. One is associated with the O-H stretch, shown on the left. The second contribution comes from the two bending vibrational modes: one in the plane of the water molecule, shown on the right, and the other perpendicular to the plane. As the distance, *R*, between the oxygen atoms decreases, the contribution of the stretch decreases, and that of the bend increases. Consequently, the two contributions strengthen and weaken the hydrogen bond, respectively.

#### Which type of nuclear quantum effects are expected for water? Enhance quantum effects: promote protons to the excited state!



Which type of nuclear quantum effects are expected for water? Nanometric confinement can induce changes in the hydrogen binding potential





Water's response to confinement is to develop a shallow hydrogen potential

From Kolesnikov et al. PRL 2004

Which type of nuclear quantum effects are expected for water? Nanometric confinement can induce changes in the hydrogen binding potential



FIG. 2. Projection of water proton momentum distribution  $n(\mathbf{p})$  in beryl onto the xy and yz planes (a) and (b), respectively, obtained from the DINS data. The second maximum in the radial direction [along yellow line in (a)] indicates that the proton is coherently delocalized in the channel, as a consequence of its ground state being coherently distributed (tunneling) between the six minima of the beryl potential.

From Kolesnikov et al. PRL 2016

Generic conclusions not straightforward, as water-confining matrix interactions are matrix-specific (See for example Cerveny, Mallamace, Swenson, Vogel, Xu, Chem Rev 2016)



SCHOOL OF NEUTRON SCATTERING

FRANCESCO PAOLO RICCI

2004-Palau: Small Angle (SANS) and Ultra Small Angle (USANS) Scattering R. Triolo, F. Aliotta

SoNS

2006-Pula: Structure and Dynamics of Magnetic Systems P. G. Radaelli, D. Gatteschi

2008-Pula: Near and Intermediate Range Order in Liquids and Soft Matter M. A. Ricci, M. Zoppi

2010- Frascati: Electron-volt neutron spectroscopy of materials R. Senesi, C. Vasi 2012- Taormina: Neutron Investigation of Biosystems C. Andreani, S. Magazù

2014- Erice: Introduction to the theory and techniques of neutron scattering and applications to Cultural Heritage I. A. Anderson, G. Salvato, A. Scherillo

2015- Erice: ERICE School "NEUTRON SCIENCE AND INSTRUMENTATION": Instruments and devices for neutron scattering experiments K. H. Andersen, R. Caciuffo

2016- Erice: ERICE School "NEUTRON SCIENCE AND INSTRUMENTATION": Designing and building a neutron instrument

K. H. Andersen, K. W. Herwig

2016- Erice: ERICE School "NEUTRON SCIENCE AND INSTRUMENTATION": Water and water systems R. Car, F. Mallamace

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•From 2014: at the Ettore Majorana Foundation and Centre for Scientific Culture I. A. Anderson C. Andreani R. Caciuffo







# Atomic quantum dynamics in water: neutron experiments to benchmark state-of-the-art modeling

## Lecture 2

#### Roberto Senesi

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# How to measure nuclear quantum effects in an experiment? Measurements of momentum distributions using inelastic neutron scattering

The Fourier Transform of  
•Can we measure 
$$\Psi(x), \Psi(p)$$
 ? No  
•Deep Inelastic Neutron Scattering allows to measure  $|\Psi(p)|^2$  is  
•Not exactly- DINS can probe  $n(p)$   
•That is, the distribution (probability density) of atomic  
(nuclei) momentum being equal to p  
The Variance of  $n(p)$  is  
 $\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M}$  Kinetic energy



 $\langle E_K \rangle >> 1.5 k_B T !!$ 

Experiments can be designed in a similar way to X-Ray Compoton scattering. Difference: X-ray Compton is for electrons, DINS is for nuclei! Momentum resolution- similar to X-Ray Compton scattering



Compton profile of Na; p- resolution≈13% S. Huotari et al, PRL 105, 086403 (2010)

Neutron Compton profile of water; p-resolution≈14% A. Pietropaolo et al, PRL 100, 127802 (2008)

$$q = \vec{p} \cdot \hat{q}$$

$$y = \frac{\vec{p}}{\hbar} \cdot \hat{q}$$

Typical neutron spectrum from modern neutron sources is rich of neutrons of energies above 0.4 eV!

Energy [eV]	Wave length [Å]
0.4	0.45
1	0.29
10	0.09
20	0.06
50	0.04
100	0.03

Which energy and length scales can be probed?

Which energy and length scales can be probed? Collective and single-particle excitations

Energy [eV]	Wave length [Å]
0.4	0.45
1	0.29
10	0.09
20	0.06
50	0.04
100	0.03



From: "Elementary Scattering Theory For X-ray and Neutron Users" D.S. Sivia OUP (2011)

## Does this wave length range match with atomic binding scales ?



Neutron Energy [eV]	Wave length [Å]
0.4	0.45
1	0.29
10	0.09
20	0.06
50	0.04
100	0.03
H-H binding (Morse pot	ential) in

H-H binding (Morse potential) in the H<sub>2</sub> molecule

#### Temptation: use inelastic neutron scattering



# Temptation: use inelastic neutron scattering-needs assumptions and more complicated



#### **Deep inelastic Neutron Scattering does the job**

Rule of thumb: Small width= small quantum effects Large width= large quantum effects



Please recall the lecture by Carla Andreani!

#### Deep Inelastic Neutron Scattering (DINS)- a recoil excitation spectroscopy **VESUVIO** spectrometer at ISIS



Neutron Energy [eV]	Wave length [Å]
10	0.09
20	0.06
50	0.04

Pulsed source: Time of flight technique

Cu



Measurement of the stoichiometry 2) Width of recoil peaks is  $\propto \langle E_K \rangle^{\frac{1}{2}}$ 

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Nuclear quantum effects on kinetic energy and momentum distribution across the water's phase diagram

- Polycrystalline hexagonal ice
- Disorder: amorphous ices
- Competing quantum effects across melting
- Supercooled (and room temperature) bulk liquid water
- Nano confined water: Silica nanopores; Graphene oxides; surface of proteins and DNA, cements
- Supercritical water

#### Polycrystalline hexagonal ice-Experiments meet Quantum Monte Carlo modeling: H-bonded systems

#### Will use this system at T=271K as a benchmark

If quantum effects were absent, then kinetic energy would be 35 meV. Experiments and theory show that for protons kinetic energy is above 150 meV!

l ice





FIG. 3. Example of normalized  $F_l(y, q)$  (markers with error bars), for three scattering angles. Two of the spectra are shifted upwards for clarity. For

#### Polycrystalline hexagonal ice-Experiments meet Quantum Monte Carlo modeling: H-bonded systems



Momentum distribution, vibrational dynamics, and the potential of mean force in ice

Lin Lin,<sup>1</sup> Joseph A. Morrone,<sup>2,\*</sup> Roberto Car,<sup>1,2,3,†</sup> and Michele Parrinello<sup>4</sup>

## Nuclear quantum effects on disordered systems: amorphous ices

For disordered systems, interpretation of vibrational spectra is not straightforward. Measurements of momentum distribution can probe the difference between polycrystalline and disordered phase of materials at the same temperature



Fig. 3. Kinetic energy for the glass and crystal phase obtained from our experiment and those calculated from Eq. (6). Inset: densities of states used in the calculation (see text for details).

#### Dawidowski, Bermejo, Ni-B metallic glass probed by DINS, PLA 1996



FIG. 2. Contour plot of the PIMC kinetic energy of <sup>4</sup>He as a function of temperature and density. The experimental phase transitions (to fluid, superfluid, hcp, and fcc crystals) are shown as dark lines. The kinetic energy contours are shown every 5 K. Their values can be ascertained by their intercepts on the

Fluid and solid 4HE in the same temperature-density range

Ceperley et al PRL 1996

## Nuclear quantum effects on disordered systems: amorphous ices Evolution of Hydrogen Dynamics in Amorphous Ice with Density JPCL 2015

A. Parmentier,<sup>†</sup> J. J. Shephard,<sup>‡,§</sup> G. Romanelli,<sup>†</sup> R. Senesi,<sup>†,||</sup> C. G. Salzmann,<sup>\*,‡</sup> and C. Andreani<sup>\*,†,||</sup>



bulk densities at 77 K and ambient pressure • LDA: 0.94 g/cm<sup>3</sup> • uHDA: 1.15 g/cm<sup>3</sup> • vHDA: 1.26 g/cm<sup>3</sup>  $n_M(p) = \mathcal{N} \int_{\Omega} \frac{d\Omega}{4\pi} \exp\left(-\frac{p^2}{2} \left[\frac{\sin^2\theta\cos^2\phi}{\sigma_x^2} + \frac{\sin^2\theta\sin^2\phi}{\sigma_y^2} + \frac{\cos^2\theta}{\sigma_z^2}\right]$ 

Measured mean kinetic energies of the hydrogen nuclei are found to increase with increasing density, indicating the weakening of hydrogen bonds as well as a trend toward steeper and more harmonic hydrogen vibrational potential energy surfaces.

$$\begin{array}{c} \mathbf{A} \\ \mathbf{$$

## Nuclear quantum effects on disordered systems: amorphous ices Evolution of Hydrogen Dynamics in Amorphous Ice with Density JPCL 2015

A. Parmentier,<sup>†</sup> J. J. Shephard,<sup>‡,§</sup> G. Romanelli,<sup>†</sup> R. Senesi,<sup>†,||</sup> C. G. Salzmann,<sup>\*,‡</sup> and C. Andreani<sup>\*,†,||</sup>



Sensitivity to anisotropic momentum distribution

### Nuclear quantum effects on disordered systems: amorphous ices



The combination of the two measurement allows to define an anharmonic constant ...

$$\hbar\omega_{str}^{INS} + \frac{\hbar\omega_{str}^{NCS}}{2} = \frac{3}{2}\hbar\omega_{str}^{INS}\left(1 - \frac{3}{2}\boldsymbol{\chi_e}\right) = \left(1 + \frac{1}{2}\right)\hbar\tilde{\omega}_{str}$$



Experiments meet Quantum Monte Carlo modeling: Competing quantum effects across melting



# Calculations using flexible potentials by Habershon et al JCP 2009 showed that

« ..Intramolecular zero point fluctuations increase the average O–H bond length and the average molecular dipole moment, leading to stronger intermolecular interactions and slower diffusion, while intermolecular quantum fluctuations disrupt the hydrogen-bonding network leading to more rapid diffusion. In our q-TIP4P/F model, these two effects nearly cancel one another, leading to a comparatively small net quantum effect on the diffusion coefficient..»



What happens to atomic kinetic energies across melting?

Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting Giovanni Romanelli, Michele Ceriotti, David E. Manolopoulos, Claudia Pantalei, RS and Carla Andreani, J Phys Chem Lett (2013)





«Imaging» of directional Components of <Ek> which are in competition when water transforms from liquid to polycrystal

PIMD+ generalised Langevin By M. Ceriotti and D. Manolopoulos

#### The Journal of Physical Chemistry Letters

Table 1. Comparison between Theoretical and Experimental Components of the Quantum Kinetic Energy for D and O in Heavy Water, At Different Temperatures<sup>a</sup>

	D [exp]	D [TAG/MSD]	O [exp]	O [TAG/MSD]
D <sub>2</sub> O, 7	Г = 300 К, liquid			$\langle E_{\rm COM} \rangle = 42.1$
$\langle E_x \rangle$	$20.1 \pm 1.1$	19.5/18.9	$15.8 \pm 1.7$	13.6/13.7
$\langle E_y \rangle$	$36.1 \pm 2.3$	26.1/25.6	19.5 ± 1.3	19.4/20.4
$\langle E_z \rangle$	$55.1 \pm 2.3$	64.6/65.7	$26.3 \pm 1.5$	23.4/22.3
$\langle E_{\rm K} \rangle$	$111.3 \pm 3$	110.2	61.6 ± 3.1	56.4
$D_2O_{, 1}$	Г = 280 K, liquid			$\langle E_{\rm COM} \rangle = 39.5$
$\langle E_x \rangle$	$18.8 \pm 1.1$	19.4/18.9	$16.0 \pm 2.3$	13.6/13.7
$\langle E_y \rangle$	$38.6 \pm 2.5$	25.7/25.2	$21.0 \pm 0.6$	19.2/20.2
$\langle E_z \rangle$	$54.2 \pm 2.4$	63.6/64.6	$24.1 \pm 2.1$	23.2/22.2
$\langle E_{\rm K} \rangle$	$111.6 \pm 2$	108.7	61.1 ± 3.1	56.1
$D_2O_1$ , 1	17 = 274 K, liquid			$\langle E_{\rm COM} \rangle = 38.9$
$\langle E_x \rangle$		19.3/19.0		13.4/13.5
$\langle E_y \rangle$		25.8/25.3		19.1/20.1
$\langle E_z \rangle$		63.2/64.1		23.1/22.0
$\langle E_{\rm K} \rangle$		108.3		55.6
$D_2O_1$	Г = 274 K, solid			$\langle E_{\rm COM} \rangle = 39.2$
$\langle E_x \rangle$	$22.5 \pm 1.8$	20.1/19.8	$16.1 \pm 2.3$	13.7/13.8
$\langle E_y \rangle$	$37.4 \pm 2.5$	26.3/25.9	$20.1 \pm 1.6$	19.0/19.9
$\langle E_z \rangle$	$48.1 \pm 3.4$	61.9/62.4	$24.2 \pm 1.4$	23.0/21.9
$\langle E_{\rm K} \rangle$	$108.0 \pm 2$	108.3	60.4 ± 4	55.7

<sup>*a*</sup>All values are in meV, and the theoretical results have a statistical error bar smaller than 0.1 meV. We also report the computed centerof-mass mean kinetic energy  $\langle E_{\rm COM} \rangle$  of the D<sub>2</sub>O molecules.

#### Experiments meet Quantum Monte Carlo modeling: H-bonded systems

#### Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting

Giovanni Romanelli, Michele Ceriotti, David E. Manolopoulos, Claudia Pantalei, RS and Carla Andreani, J Phys Chem Lett (2013)



#### HOW?

«Imaging» of directional Components of <Ek> which are in competition when water transforms from liquid to polycrystal PIMD+ generalised Langevin By M. Ceriotti and D. Manolopoulos



Sensitivity to probe Oxygen binding environment (quantum) Maybe suitable for water dissociation?

		Light water		Heavy water	
Oxygen kinetic ener	gy	$\langle E_K \rangle$ [meV]	T [K]	$\langle E_K \rangle$ [meV]	T [K]
	Liquid	51 ± 3	276	61 ± 3	280
	Solid	56 ± 3	270	$60 \pm 4$	274

#### Supercooled (and room temperature) bulk liquid water: What is the expected temperature dependence of the proton kinetic energy?



**Fig. 2.** Calculated Ke(H) values (solid curve) together with the error margins (dashed curves). Solid asterisks are recent (red) and old (black) DINS results. Solid circles (blue) are new INS results. Open squares are Ke(H) values deduced by Colognesi [4,34] using thermodynamic data. The numerical values together with

## Calculations by Finkelstein and Moreh, Chem Phys 2014 point for an almost «continuous» dependence using

$$Ke(H) = 3S_T \int_{\nu_{TD}}^{\nu_T} g_T(\nu) \alpha(\nu) d\nu + 3S_L \int_{\nu_{LD}}^{\nu_L} g_L(\nu) \alpha(\nu) d\nu + \sum_{j=1}^3 S_j \alpha(\nu_j)$$
(2)

With  $\alpha(v) = \frac{hv}{2} \left( \frac{1}{e^{hv/k^2} - 1} + \frac{1}{2} \right)$  with  $\alpha(v) = v_j$ , v the kinetic energy of



Fig. 1. Heat capacity of water measured as a function of temperature. Full and open diamonds: data obtained in this study with two different samples; full line: curve fitting the experimental points  $[C_p = 0.44 * (T/222 - 1)^{-2.5} + 74.3].$ 

#### Heat of freezing Cantrell et al JPCB 2011

Specific heat Tombari et al CPL 1999 Supercooled (and room temperature) bulk liquid water:

First set of experiments pointed out a large excess of  $\langle E_K \rangle$  as compared to ice at same temperature T=271 K. Most recent exp reported here, from Andreani et al, JPCL 2016





#### Supercooled (and room temperature) bulk liquid water:

- Supercooled water and ice polycrystal at same T=271 K show competing quantum effects and have similar kinetic energies
- This is in agreement with new simulations appearing on the same journal issue («blind»joint exp-theory work) for Water vapor, liquid, ice at the triple point

Table 1. The  $\langle E_{\rm K} \rangle$  and individual  $\langle E_{\rm K} \rangle_{\alpha}$  values, from present DINS measurements in bulk SW and ice at  $T = 271 \text{ K}^{\alpha}$ 

		SW	Ice	$Ice^{25}$
Т	[K]	271	271	271
M1				
$\sigma$	$[Å^{-1}]$	$5.01 \pm 0.02$	$5.03 \pm 0.03$	$5.01 {\pm} 0.03$
$c_4$		$0.11 \pm 0.01$	$0.11 \pm 0.02$	$0.10 {\pm} 0.01$
$\langle E_K \rangle$	[meV]	$156.0 {\pm} 2.0$	$157.0{\pm}2.0$	$156.0{\pm}2.0$
M2				
$\sigma_x$	$[Å^{-1}]$	$2.9 \pm 0.5$	$3.7 \pm 0.1$	$3.7 \pm 0.3$
$\sigma_y$	$[Å^{-1}]$	$5.0 \pm 0.5$	$4.3 \pm 0.3$	$4.3 \pm 0.4$
$\sigma_z$	$[Å^{-1}]$	6	0.0.10.2	$6.5 \pm 0.4$
$\langle E_K \rangle_x$	[meV]	$17\pm5$	$28 \pm 2$	$29 \pm 4$
$\langle E_K \rangle_y$	[meV]	$52 \pm 10$	$38\pm5$	$38 \pm 9$
$\langle E_K \rangle_z$	[meV	$86 \pm 5$	$91\pm 5$	87±9
$\langle E_K \rangle$	[meV]	$156.0 \pm 2.0$	$157.0{\pm}2.0$	$154.0 {\pm} 2.0$
	-			



Quantitative agreement on total kinetic energies; quantitative agreement on directional kinetic energies in ice Andreani et al, JPCL 2016; Cheng et al, JPCL 2016 23

#### Supercooled (and room temperature) bulk liquid water: problems solved?

Investigation needed on electron kinetic energies in supercooled water measured by X-Ray Compton scattering



**Fig. 3**  $\Delta \langle E_{kin} \rangle = \langle E_{kin}(7) \rangle - \langle E_{kin}(277 \text{ K}) \rangle$ . The solid line is a linear fit with slope  $c = -3.3 \pm 0.7 \text{ kJ} \pmod{\text{K}}^{-1}$ .

Lehmkuhler et al PCCP 2016: increased tethrahedral ordering by XRS but increased electron kinetic energy and structural modifications by X-Ray Compton What happens near 300 K?



#### Mallamace's and co-workers hypothesis near 315 K- MAGIC Temperature

T= 315 K is a special locus of thermodynamic properties in water

Is there a counterpart on the hydrogen's kinetic energy? Preliminary DINS experiment analysis- Delta is the increase (decrease) of momentum width with respect to 300 K

upper bound

320

310

T

K



-0.02

300

#### F. Mallamace et al, JCP 2014

330

# Water protons in shallow potentials: high pressure phases in ice and hydration shells of globular proteins

0.0006

*Tunneling and delocalization effects in hydrogen bonded systems: A study in position and momentum space*. J. Morrone, L. Lin, R. Car, JCP 2009 Proton momentum distribution in protein hydration shell. RS, A. Pietropaolo, A. Bocedi, S. Pagnotta, F. Bruni, PRL



#### Water in nanopore confinement



Modeling of quantum kinetic energy?

G. Romanelli et al, Carbon 2016; G. Romanelli et al, PCCP 2016; C. Pantalei et al PCCP 2011; V. Garbuio et al JCP 2007

# Dental materials: setting of Glass Ionomer Cements role of water's NQE to be investigated.

*"Atomic and vibrational origins of mechanical toughness in bioactive cement during setting", K. V. Tian et al., Nature Comm. (2015)* 



#### To be explored by experiment and modeling

PRL 110, 065701 (2013)	PHYSICAL	REVIEW	LETTERS	week ending 8 FEBRUARY 2013
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#### **Role of Quantum Effects in the Glass Transition**

V. N. Novikov<sup>1,2</sup> and A. P. Sokolov<sup>1,2,3</sup>

It is shown that quantum effects lead to a significant decrease of the glass transition temperature  $T_g$  with respect to the melting temperature  $T_m$ , so that the ratio  $T_g/T_m$  can be much smaller than the typical value

# To be explored by modeling: quantum effects in the water adsorption energetics in DNA grooves

PRL 105, 148101 (2010) PHYSICAL REVIEW LETTERS 1 OCTOBER	PRL 105, 148101 (2010)	PHYSICAL	REVIEW	LETTERS	1 OCTOBER 20
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#### Changes in the Zero-Point Energy of the Protons as the Source of the Binding Energy of Water to A-Phase DNA

G. F. Reiter,<sup>1</sup> R. Senesi,<sup>2</sup> and J. Mayers<sup>3</sup>

The measured changes in the zero-point kinetic energy of the protons are entirely responsible for the binding energy of water molecules to *A* phase DNA at the concentration of 6 water molecules/base pair.

#### Supercritical water:nuclear quantum effects across the pseudocritical line(s)



DINS measurements along the 25 Mpa isobar to cross the liquid-like to vapour like boundaries Technological relevance for next generation reactors

CK Loong, C. Andreani, A. Kolesnikov, A. Parmentier, G. Romanelli, RS, R. Car

#### Supercritical water:nuclear quantum effects across the pseudocritical line(s)



Data analysis under Consolidation (see presentations by A. Parmentier)

Figure 4: Density of states g(E) (blue) and stretching contribution  $g_{str}(E)$  (red) for T=280 C, 350 C, 460 C, 550 C. The main difference between the lower temperatures (top) and the higher temperatures (bottom) is the shift, in opposite directions, of stretching and libration contributions, while the bending is not effected.

Table 7.4: Directional energies and  $\langle E_k \rangle$  as deduced from the harmonic decoupled model described in Eqs. 7.1-7.3 for the liquid case.

	SUB	SUB	SUPER	SUPER	SUPER
Temperature [K]	553	623	673	663	733
Pressure [MPa]	25	25	80	25	25
Density $\left[\frac{g}{cm^3}\right]$	0.777	0.625	0.660	0.215	0.104
$\langle E_k \rangle_x $ [meV]	25.20	27.92	30.06	29.23	32.17
$\langle E_k \rangle_y  [\text{meV}]$	37.12	39.00	40.54	40.00	42.15
$\langle E_k \rangle_z  [\text{meV}]$	104.62	105.74	106.70	108.59	110.19
$\langle E_k \rangle [\text{meV}]$	166.94	172.66	177.30	177.82	184.44

$$\langle E_k \rangle_x = 2S_{lib} \frac{\hbar\omega_{lib}}{4} \coth\left(\frac{\hbar\omega_{lib}}{2K_BT}\right) + S_{tra} \frac{1}{2} K_B T$$

$$< E_k >_y = S_{lib} \frac{\hbar \omega_{lib}}{4} \coth\left(\frac{\hbar \omega_{lib}}{2K_B T}\right) + S_{ben} \frac{\hbar \omega_{ben}}{4} \coth\left(\frac{\hbar \omega_{ben}}{2K_B T}\right) + S_{tra} \frac{1}{2} K_B T$$
$$< E_k >_z = 2S_{str} \frac{\hbar \omega_{str}}{4} \coth\left(\frac{\hbar \omega_{str}}{2K_B T}\right) + S_{tra} \frac{1}{2} K_B T$$



Sensitivity and consistency checks between modeling of DINS line shapes and vibrational INS data, relevant for low density measurements <0.15 g/cm3 Supercritical water:nuclear quantum effects across the pseudocritical line(s)



Models of hydrogen kinetic energy as temperature increases towards the water liquid-vapour critical point (Finkelstein, Moreh, Chem Phys 2014)



# THANK YOU

#### OUTLOOK

Combination of phonon (DFT) calculations and Path Integral

To model experiments on atomic quantum dynamics of more complex water systems in the context of

- Ionic conductors
- Disordered materials
- Molten salts containing Li

ROTAX

SANDALS

MAPS

Glasses

**TS-1** 

Macromolecules

VESUVIO is now aiming at exploiting elementspecific and mass resolved spectroscopy for complex and disordered materials



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POLARIS

PEARL

GEM

CRISP

MERLIN MARI

For a recent overview and discussion please download (FOR FREE): JOURNAL OF PHYSICS: CONFERENCE SERIES VOLUME 571 (2014). doi:10.1088/1742-6596/571/1/011001