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

Lecture 2

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Associazione School of Neutron Scattering "Francesco Paolo Ricci "

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

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

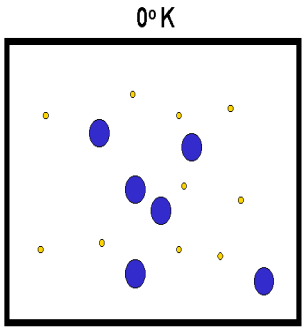
- **Can we measure** $\Psi(x), \Psi(p)$ **? No**
- **Deep Inelastic Neutron Scattering allows to measure** $|\Psi(p)|^2$
- **Not exactly- DINS can probe** $n(p)$
- **That is, the distribution (probability density) of atomic (nuclei) momentum being equal to *p***

The Fourier Transform of $|\Psi|^2$ is $n(p)$ Momentum distribution

The variance of $n(p)$ is

$$\langle E_K \rangle = \frac{\langle p^2 \rangle}{2M}$$ Kinetic energy

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

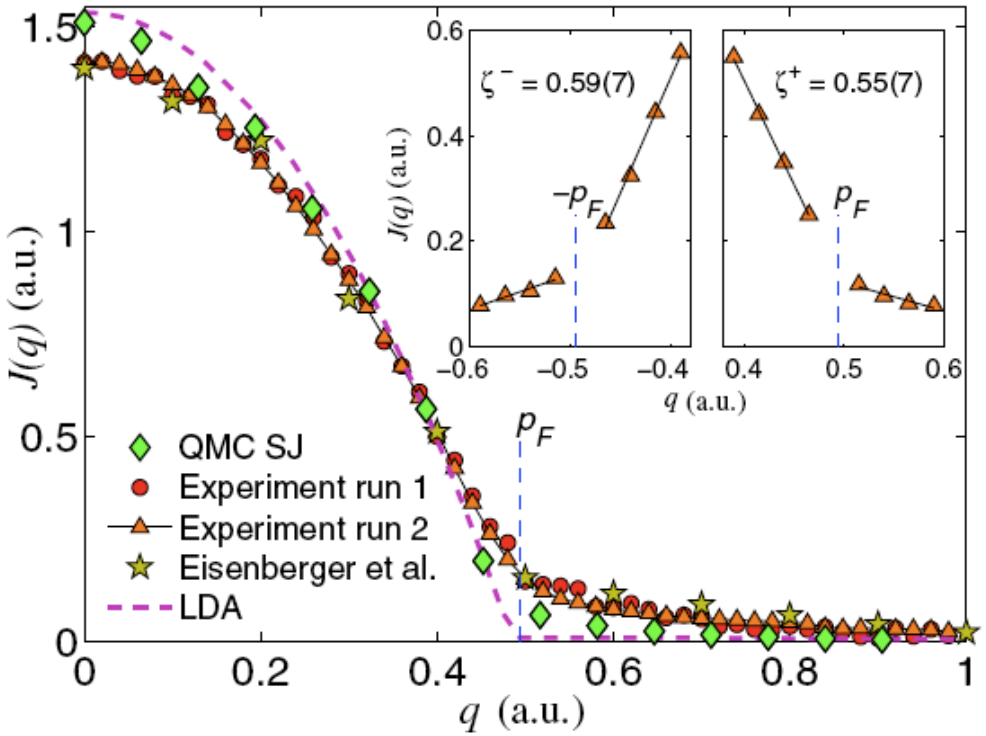


Experiments can be designed in a similar way to X-Ray Compoton scattering.

Difference: X-ray Compton is for electrons, DINS is for nuclei!

Momentum resolution- similar to X-Ray Compton scattering

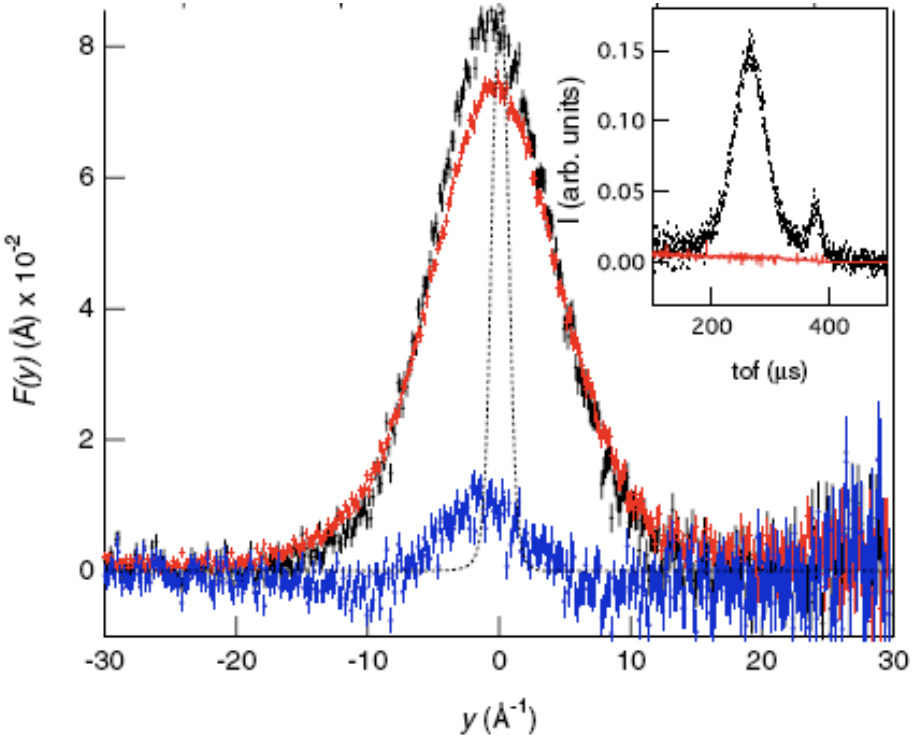
Electrons, using ID16 at ESRF



Compton profile of Na; p- resolution≈13%

S. Huotari et al, PRL 105, 086403 (2010)

Protons, using VESUVIO at ISIS



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
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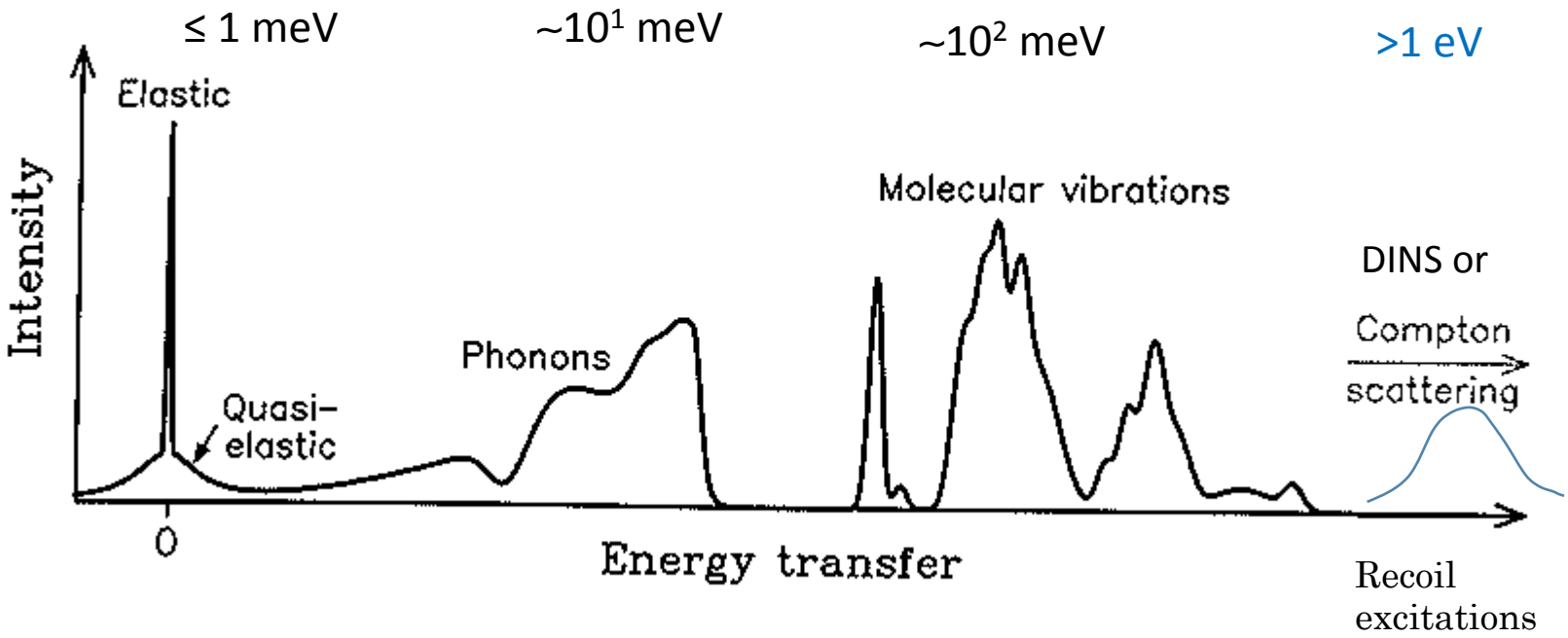
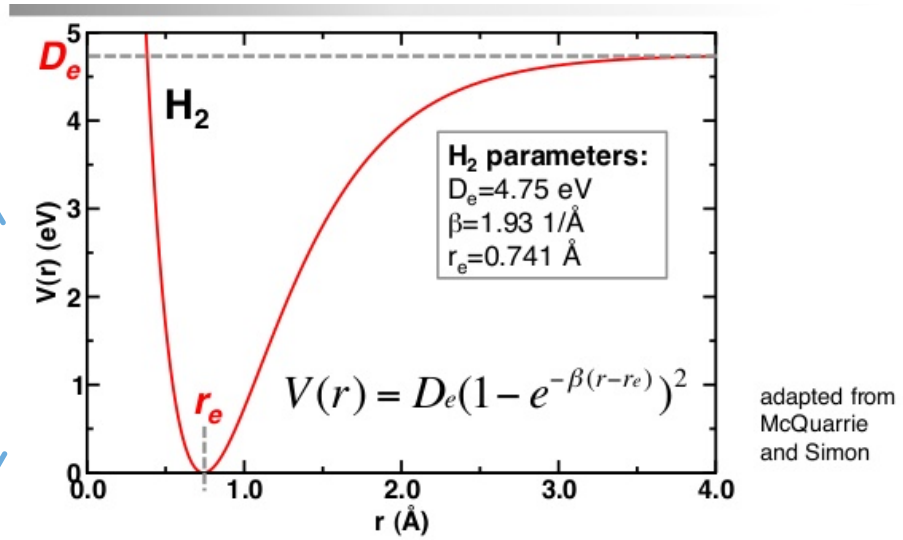
100	0.03



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 ?

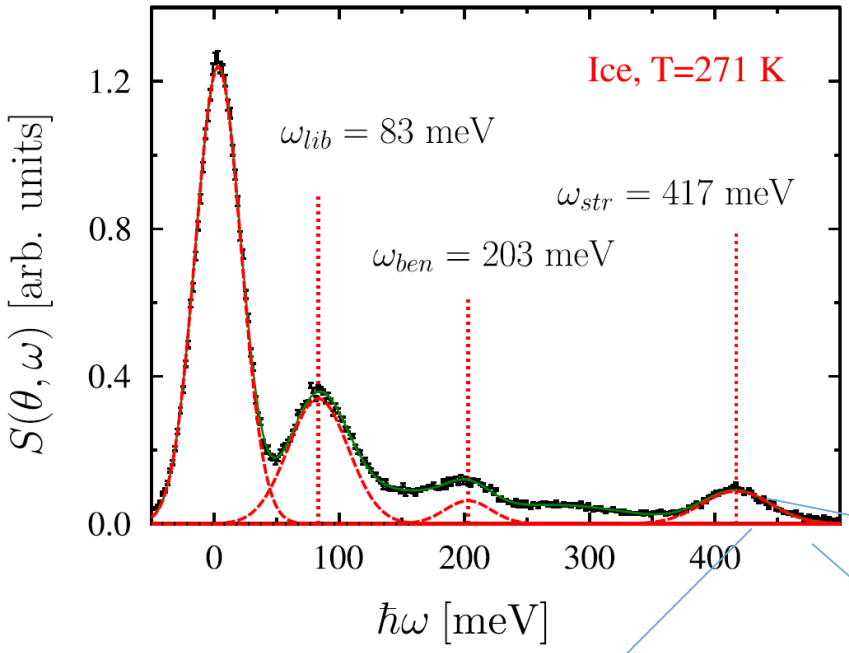


adapted from McQuarrie and Simon

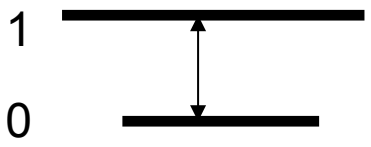
Neutron Energy [eV]	Wave length [Å]
0.4	0.45
1	0.29
10	0.09
20	0.06
50	0.04
100	0.03

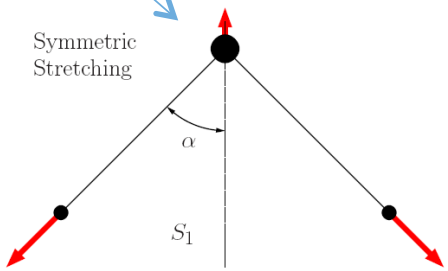
H-H binding (Morse potential) in the H_2 molecule

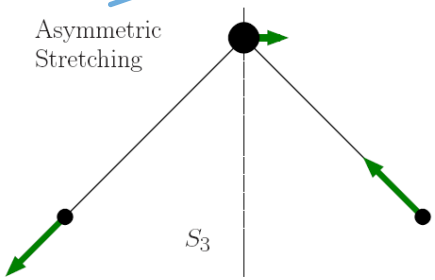
Temptation: use inelastic neutron scattering



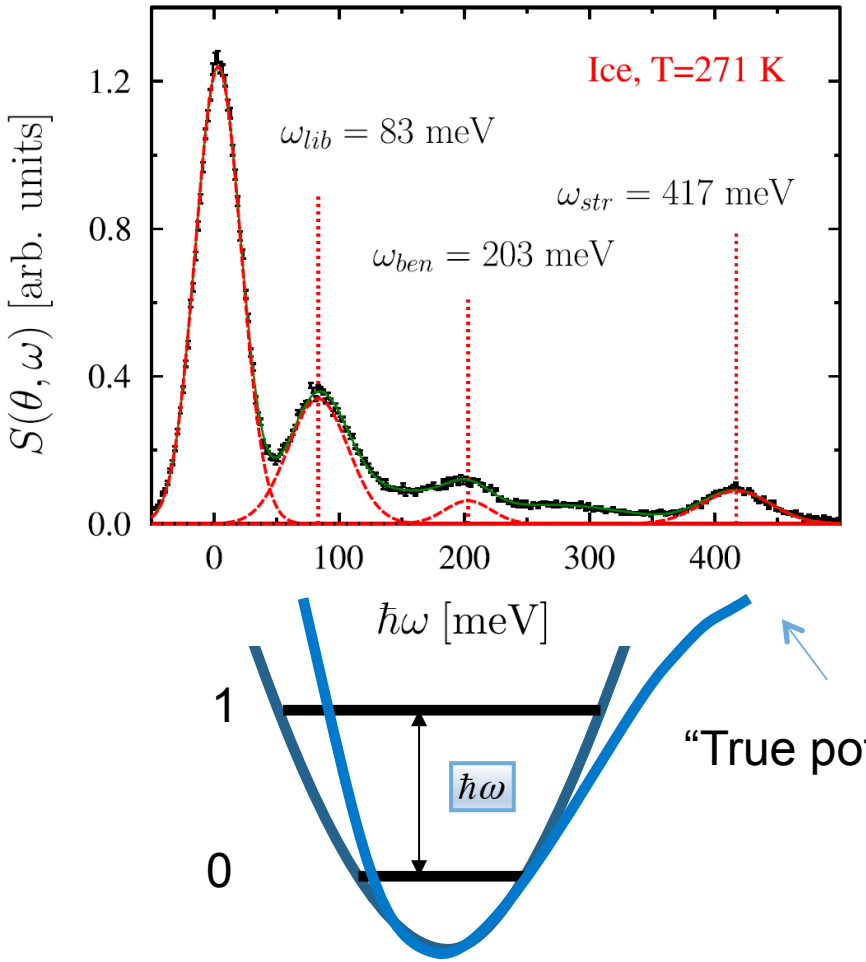
Measure single-particle Excitation, es. Stretching : 0 to 1







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



"True potential"

Measure single-particle Excitation, es. 0 to 1

Assume an underlying parabolic potential

Derive the density of vibrational state $g(\omega)$

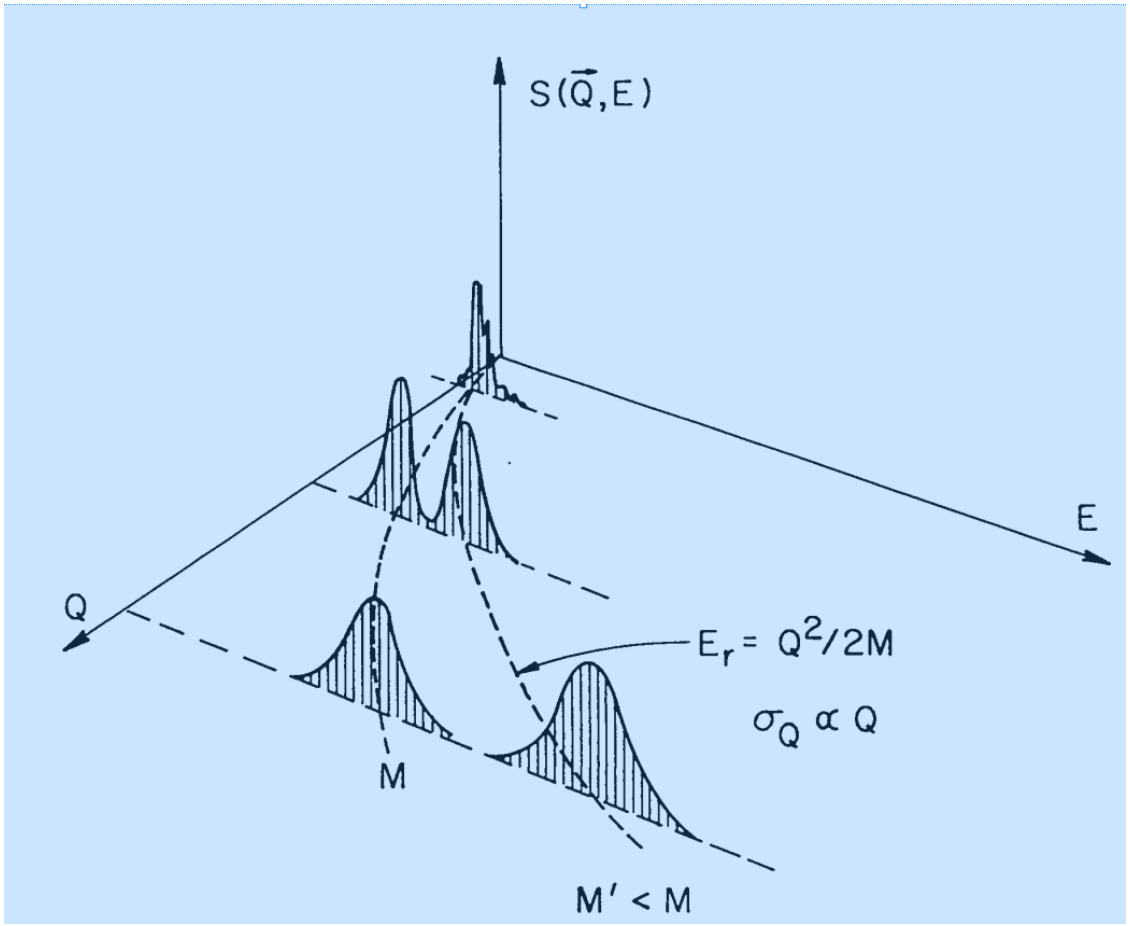
Integrate the density of states

$$\langle E_K \rangle = \frac{3}{4}\int d\hbar\omega\, \hbar\omega\, g(\hbar\omega) \coth\left(\frac{\hbar\omega}{k_B T}\right)$$

Deep inelastic Neutron Scattering does the job

thumb:
vidth= small quantum

vidth= large quantum

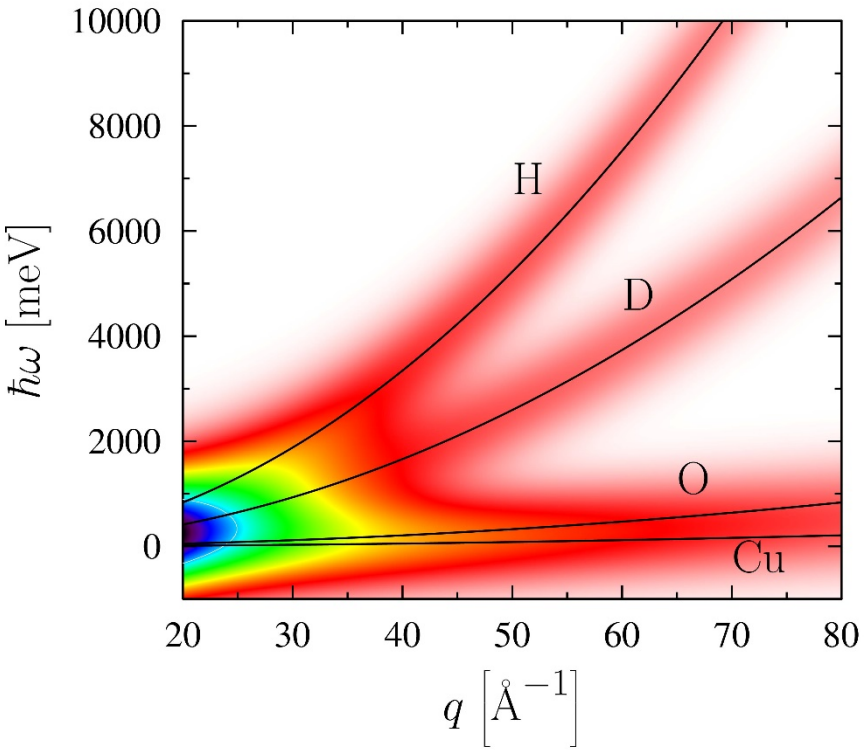


From R.O. Simmons
LA-10227-C (1984)

Please recall the lecture by Carla Andreani!

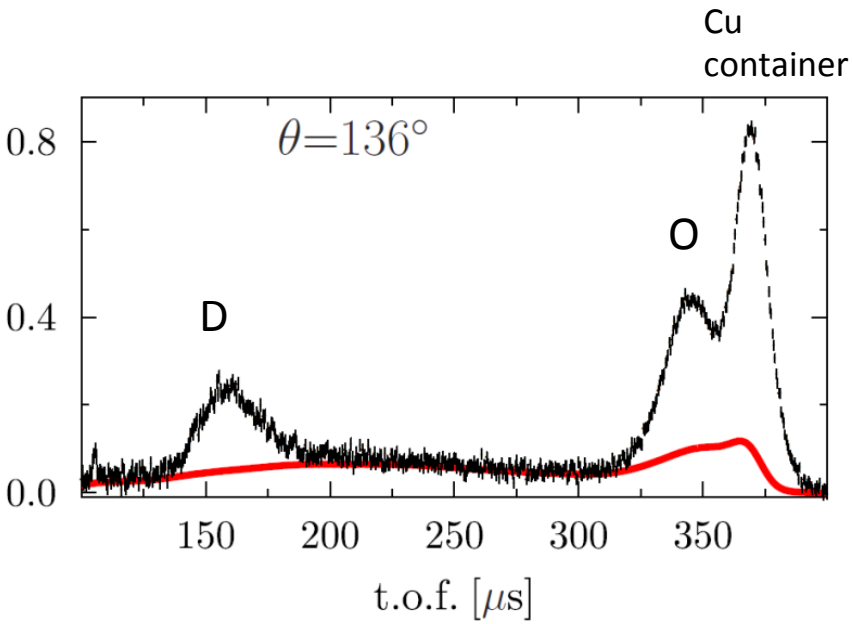
Deep Inelastic Neutron Scattering (DINS)- a recoil excitation spectroscopy
VESUVIO spectrometer at ISIS

$$\frac{M}{\hbar^2 q}\left(\hbar\omega - \hbar\omega_r\right) = \frac{1}{2}\vec{p}\cdot\hat{q}$$



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

Pulsed source: Time of flight technique



1) Measurement of the stoichiometry

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

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

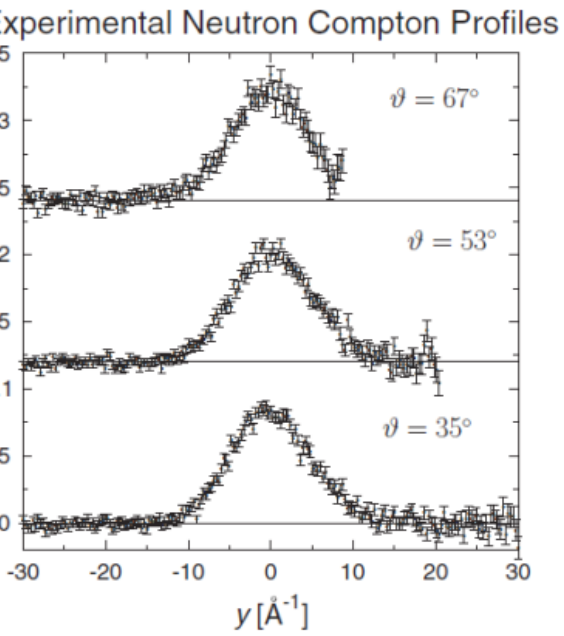
- Polycrystalline hexagonal ice
- Disorder: amorphous ices
- Competing quantum effects across melting
- Supercooled (and room temperature) bulk liquid water
- Nano confined water: Silica nanopores; Graphene oxides; surface of proteins and DNA, cements
- Supercritical water

crystalline hexagonal ice-Experiments meet Quantum Monte Carlo modeling: H-bonded syst

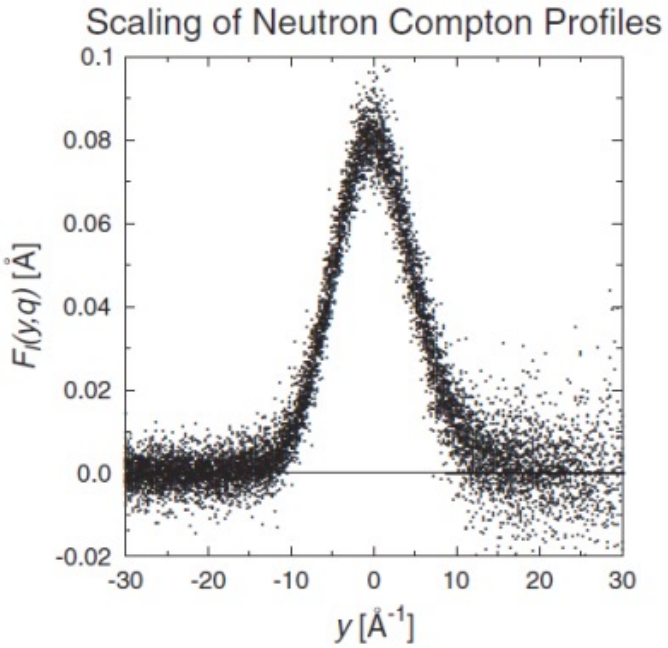
Will use this system at T=271K as a benchmark

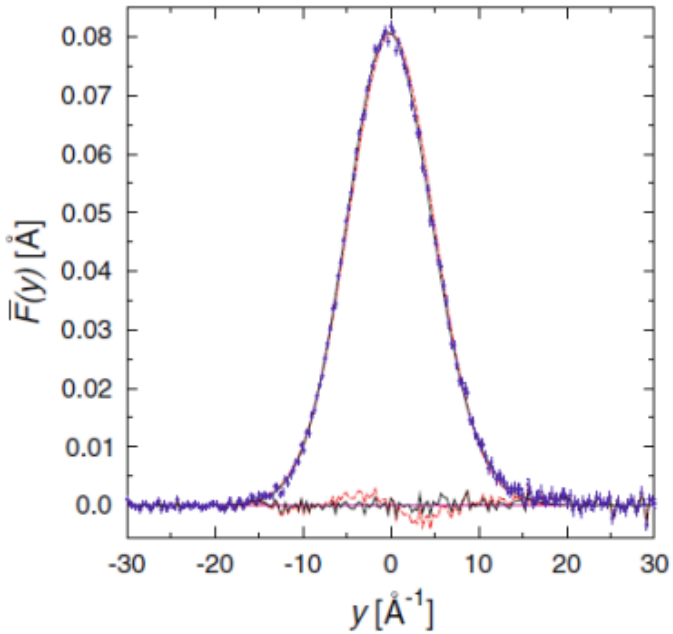
If quantum effects were absent, then kinetic energy would be 35 meV. Experiments and theory show that for protons kinetic energy is above 150 meV!

J. Chem. Phys. **136**, 024504 (2012)



ample of normalized $F_I(y, q)$ (markers with error bars), for three ngles. Two of the spectra are shifted upwards for clarity. For





crystalline hexagonal ice-Experiments meet Quantum Monte Carlo modeling: H-bonded syst

Spherical momentum distribution of the protons in hexagonal ice from modeling of inelastic neutron scattering data, D. Flammini , A. Pietropaolo, RS, C. Andreani, F. McBride, A. Hodgson, M. A. Adams, L. Lin, and R. Car, JCP 2012

HOW?

Measure the quasi-harmonicity of the directional motions of hydrogen in ice

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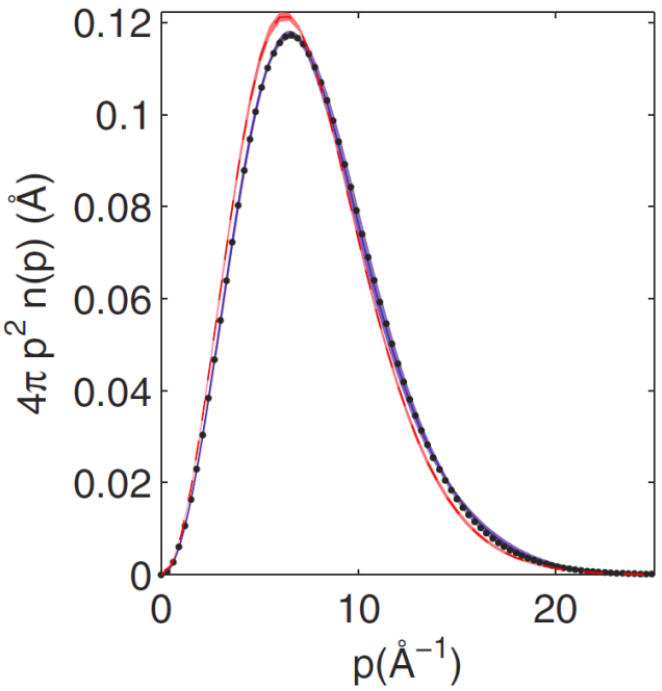
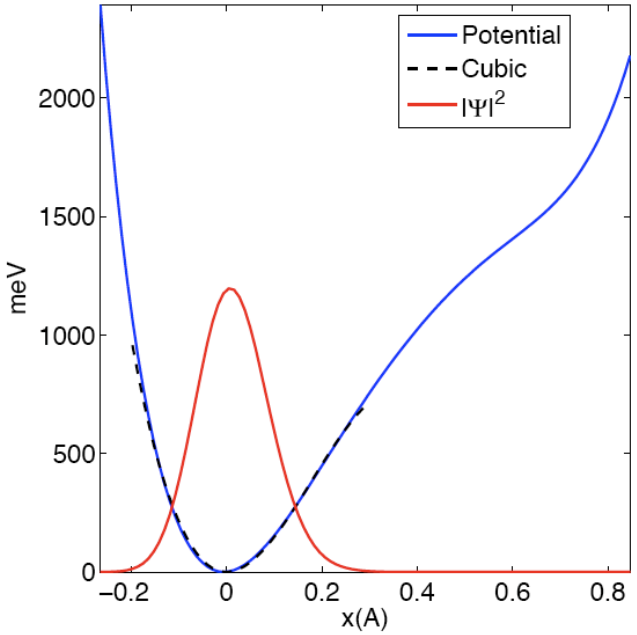
PICPMD by Roberto Car and Lin Lin





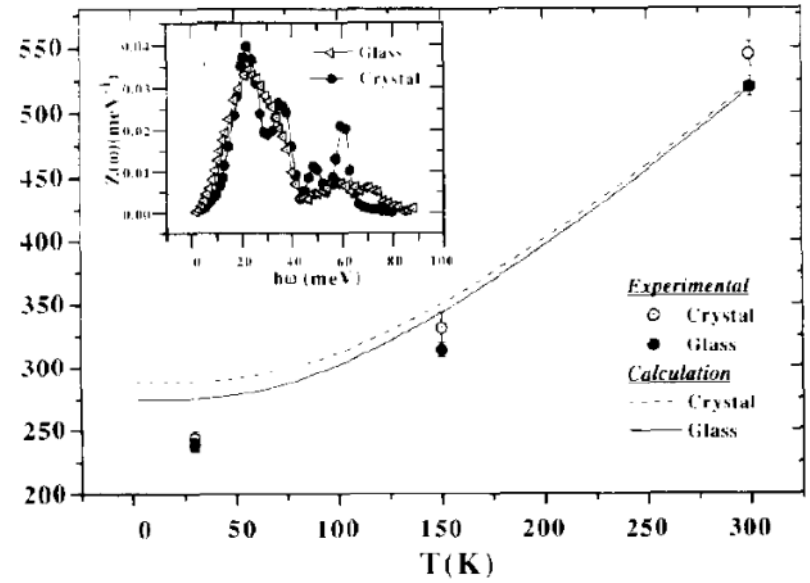
PHYSICAL REVIEW B 83, 220302(R) (2011)

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

Lin Lin,[1] Joseph A. Morrone,[2,*] Roberto Car,[1,2,3,†] and Michele Parrinello[4]

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



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

widowski, Bermejo, Ni-B metallic glass
obed by DINS, PLA 1996

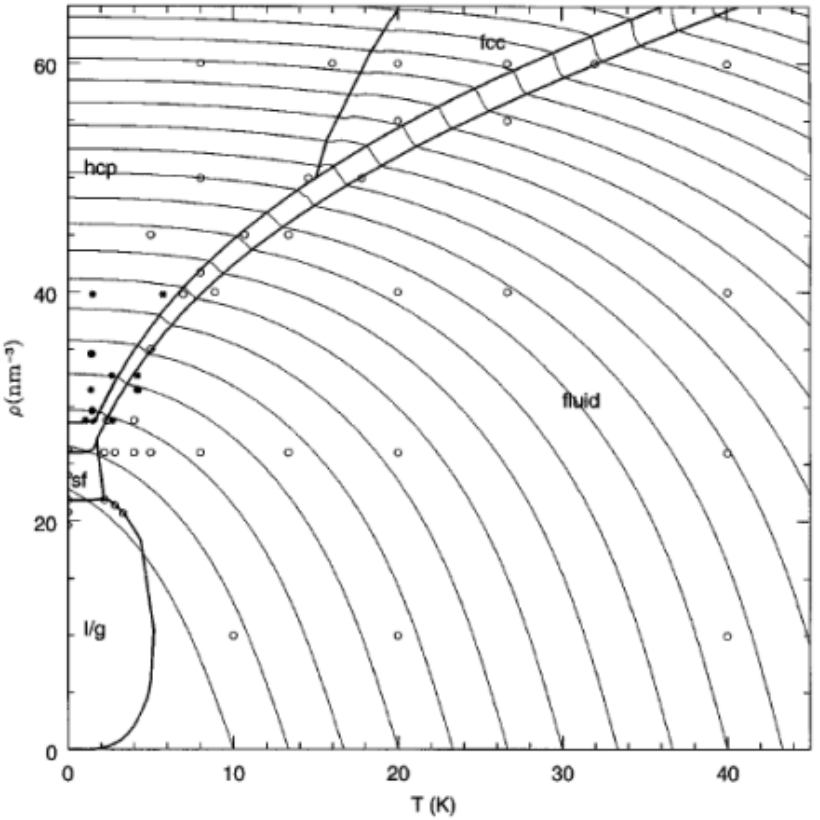


FIG. 2. Contour plot of the PIMC kinetic energy of ^{4}He as a function of temperature and density. The experimental phase transitions (to fluid, superfluid, hcp, and fcc crystals) are shown as dark lines. The kinetic energy contours are shown every 5 K. Their values can be ascertained by their intercepts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

Fluid and solid 4
in the same
temperature-de
range

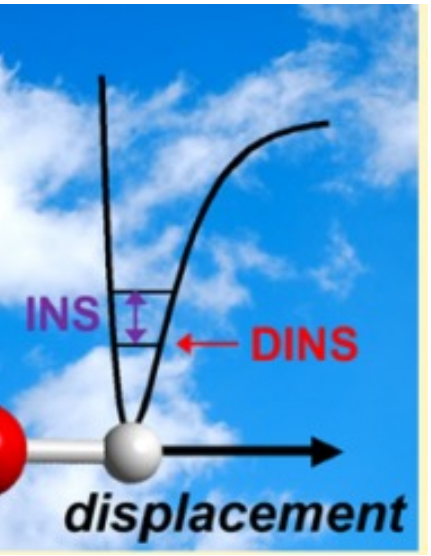
Ceperley et al PR

Nuclear quantum effects on disordered systems: amorphous ices

Evolution of Hydrogen Dynamics in Amorphous Ice with Density

JPCL 2015

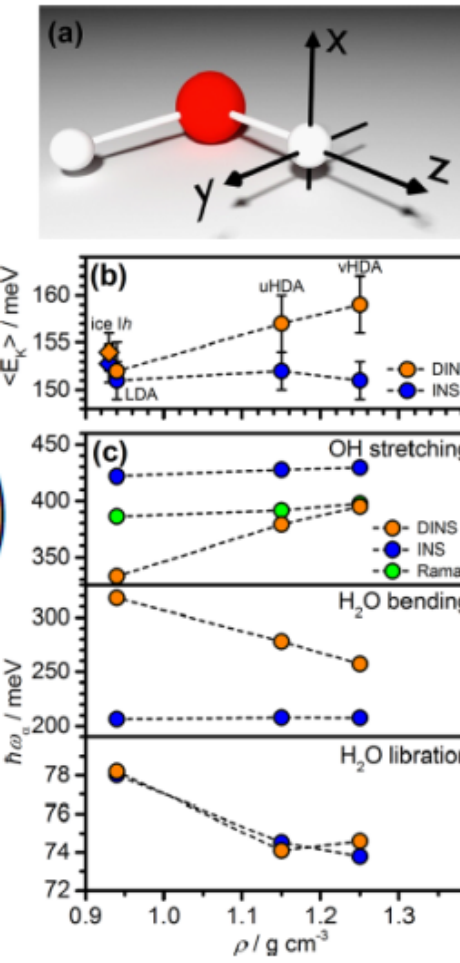
A. Parmentier,[†] J. J. Shephard,[‡,§] G. Romanelli,[†] R. Senesi,[†,∥] C. G. Salzmann,[*,‡] and C. Andreani[*,†,∥]



bulk densities at 77 K and ambient pressure

- LDA: 0.94 g/cm^3
- uHDA: 1.15 g/cm^3
- vHDA: 1.26 g/cm^3

$$n_M(p) = \mathcal{N} \int_\Omega \frac{d\Omega}{4\pi} \exp\left(-\frac{p^2}{2}\left[\frac{\sin^2\theta\cos^2\phi}{\sigma_x^2} + \frac{\sin^2\theta\sin^2\phi}{\sigma_y^2} + \frac{\cos^2\theta}{\sigma_z^2}\right]\right)$$

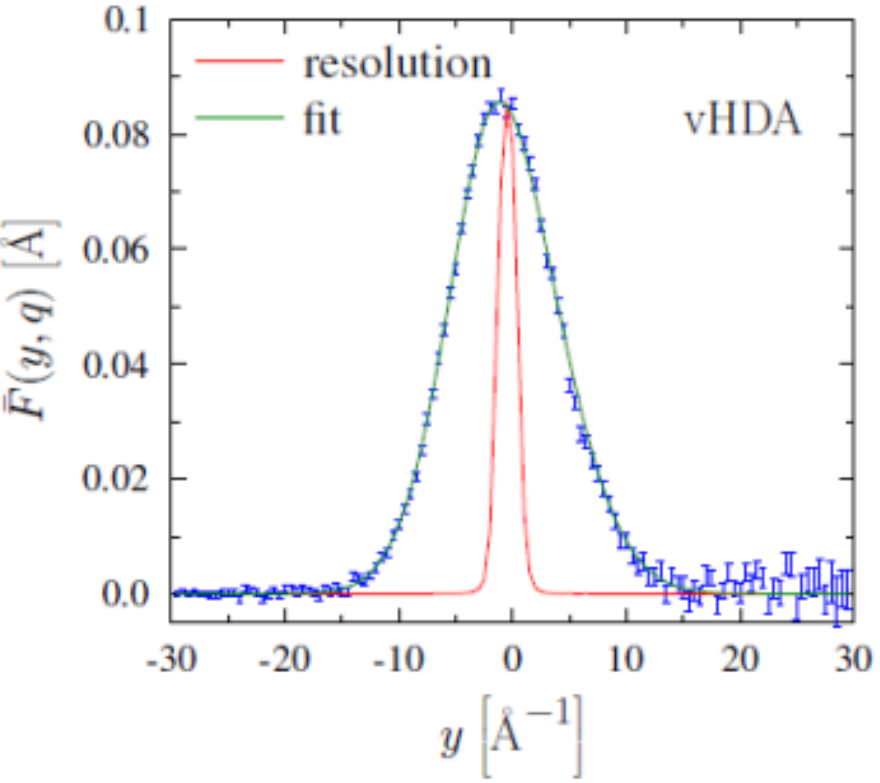


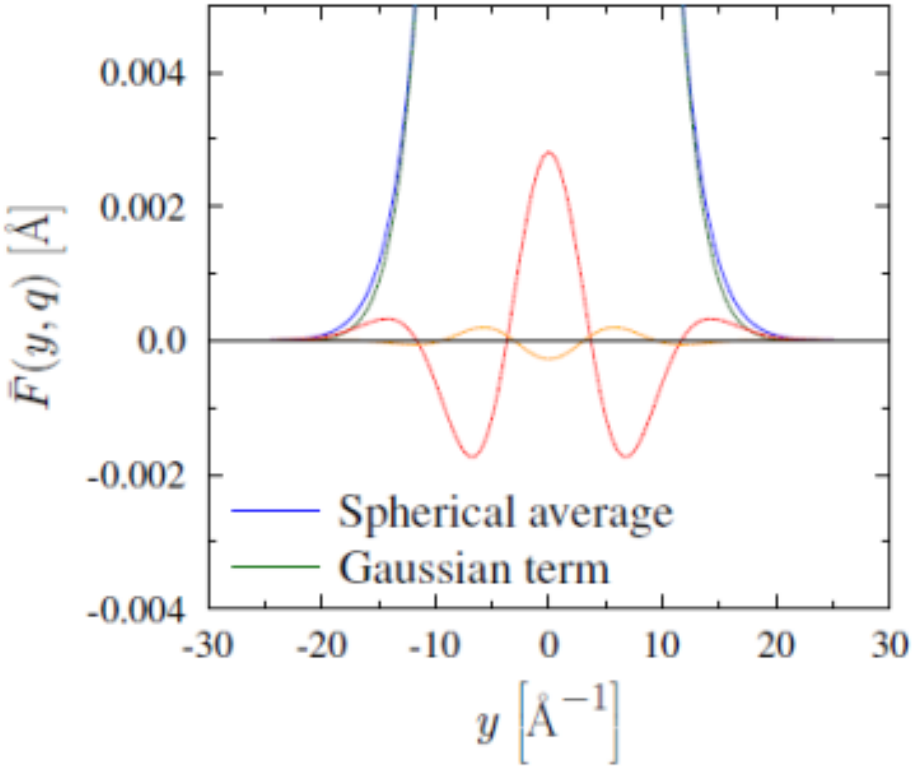
Measured mean kinetic energies of the hydrogen nuclei are found to increase with increasing density, indicating the weakening of hydrogen bonds as well as a trend toward steeper and more harmonic hydrogen vibrational potential energy surfaces.

Nuclear quantum effects on disordered systems: amorphous ices

Evolution of Hydrogen Dynamics in Amorphous Ice with Density **JPCL 2015**

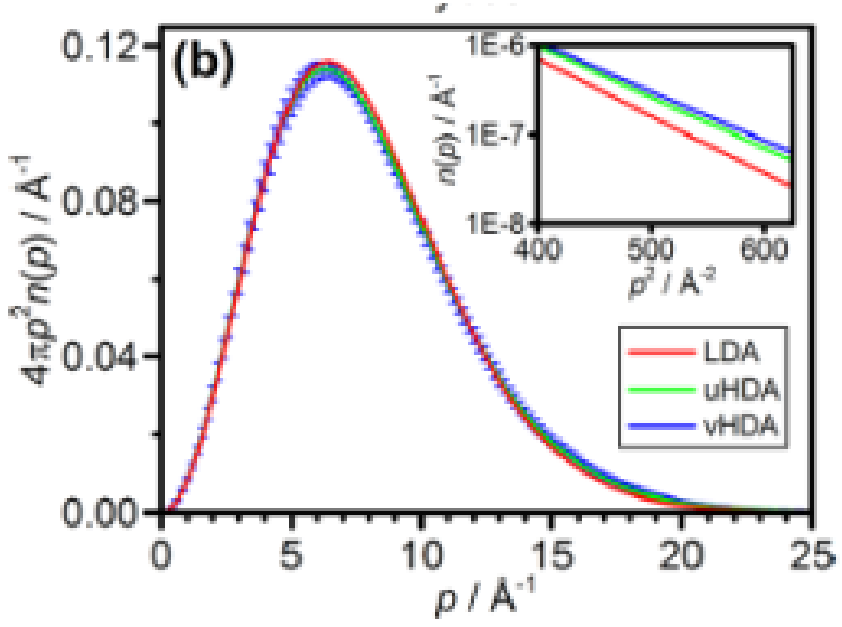
A. Parmentier,[†] J. J. Shephard,[‡,§] G. Romanelli,[†] R. Senesi,[†,∥] C. G. Salzmann,[*,‡] and C. Andreani[*,†,∥]

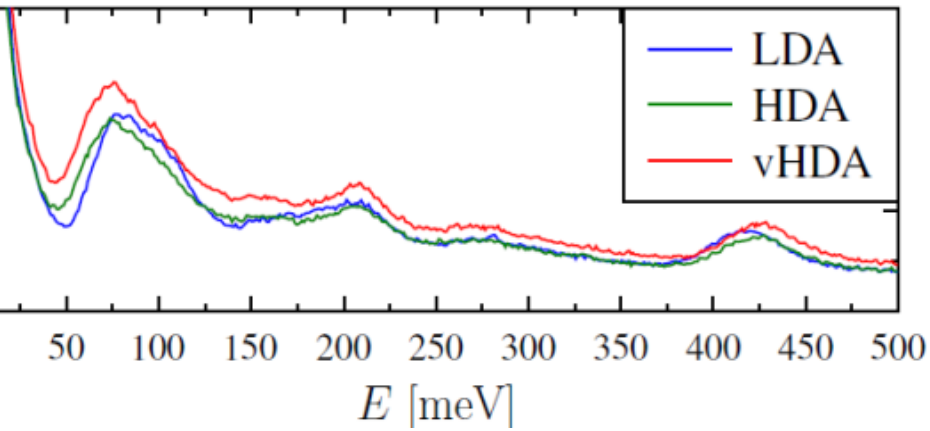




Sensitivity to anisotropic momentum distribution

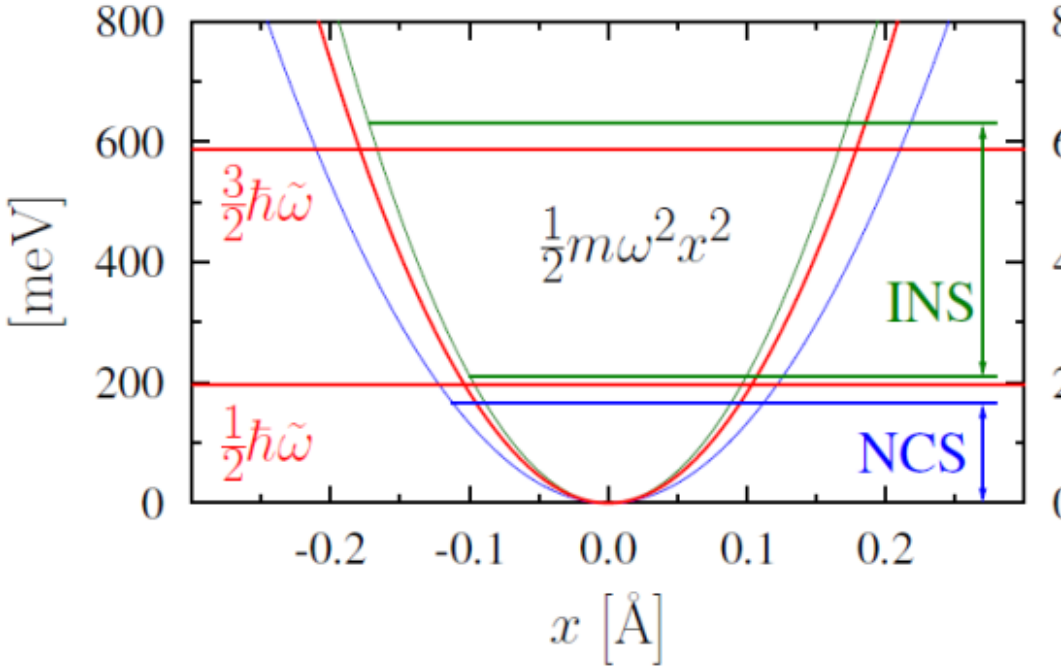
Nuclear quantum effects on disordered systems: amorphous ices



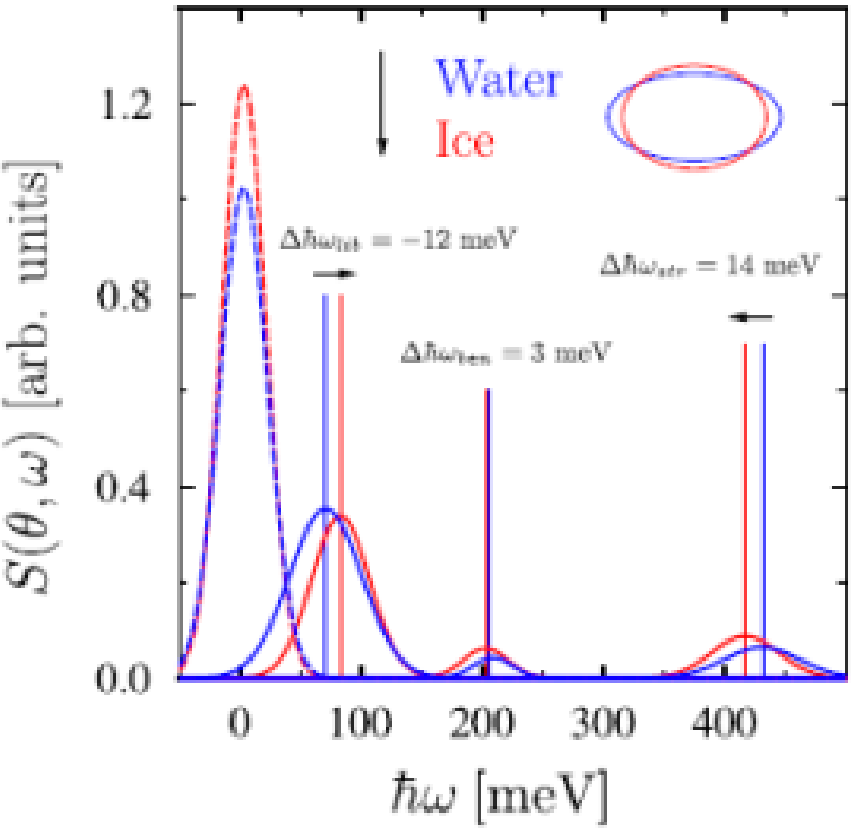


The combination of the two measurement allows to define a anharmonic constant ...

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

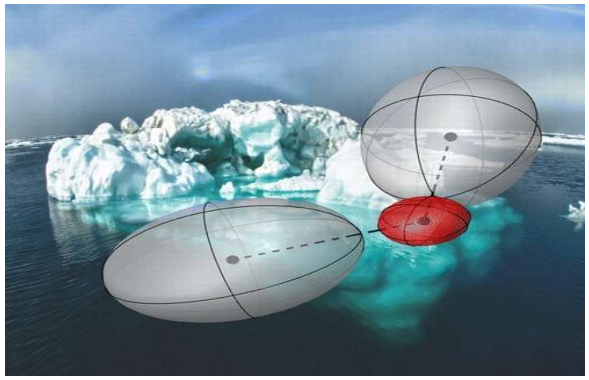


Experiments meet Quantum Monte Carlo modeling: Competing quantum effects across melting



Calculations using flexible potentials by Habershon et al JCP 200 showed that

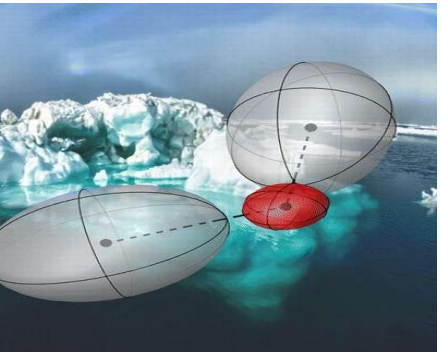
« ..Intramolecular zero point fluctuations increase the average O–H bond length and the average molecular dipole moment, leading to stronger intermolecular interactions and slower diffusion, while intermolecular quantum fluctuations disrupt the hydrogen-bonding network leading to more rapid diffusion. 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..»

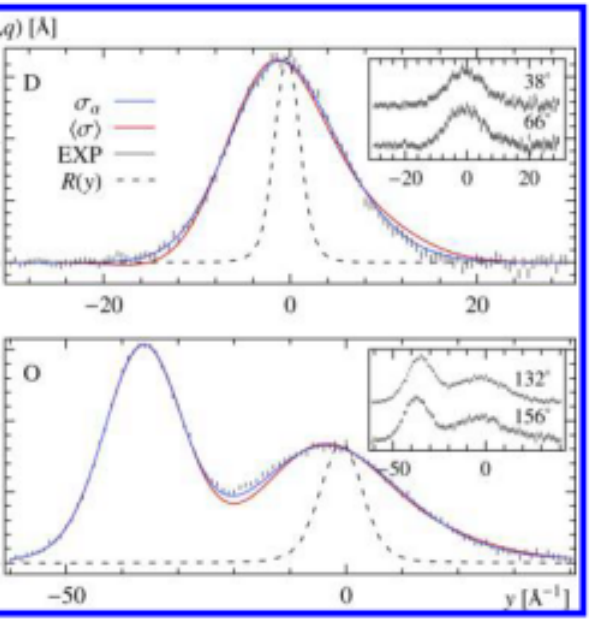


What happens to atomic kine energies across melting?

Measurement of Competing Quantum Effects on netic Energy of Heavy Water upon Melting

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





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

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

The Journal of Physical Chemistry Letters

Table 1. Comparison between Theoretical and Exper Components of the Quantum Kinetic Energy for D a Heavy Water, At Different Temperatures[a]

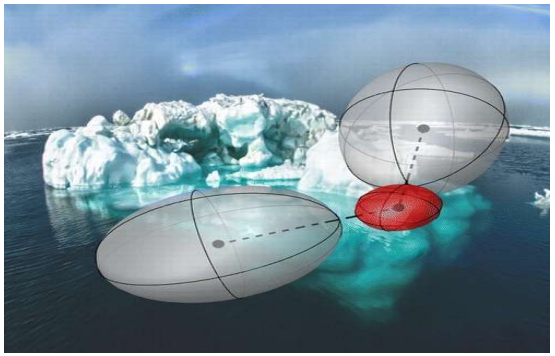
	D [exp]	D [TAG/MSD]	O [exp]	O [TA
D_2O, T = 300 K, liquid				$\langle E_{COM}$
$\langle E_x\rangle$	20.1 ± 1.1	19.5/18.9	15.8 ± 1.7	13.6/
$\langle E_y\rangle$	36.1 ± 2.3	26.1/25.6	19.5 ± 1.3	19.4/
$\langle E_z\rangle$	55.1 ± 2.3	64.6/65.7	26.3 ± 1.5	23.4/
$\langle E_K\rangle$	111.3 ± 3	110.2	61.6 ± 3.1	56.4
D_2O, T = 280 K, liquid				$\langle E_{COM}$
$\langle E_x\rangle$	18.8 ± 1.1	19.4/18.9	16.0 ± 2.3	13.6/
$\langle E_y\rangle$	38.6 ± 2.5	25.7/25.2	21.0 ± 0.6	19.2/
$\langle E_z\rangle$	54.2 ± 2.4	63.6/64.6	24.1 ± 2.1	23.2/
$\langle E_K\rangle$	111.6 ± 2	108.7	61.1 ± 3.1	56.1
D_2O, T = 274 K, liquid				$\langle E_{COM}$
$\langle E_x\rangle$		19.3/19.0		13.4/
$\langle E_y\rangle$		25.8/25.3		19.1/
$\langle E_z\rangle$		63.2/64.1		23.1/
$\langle E_K\rangle$		108.3		55.6
D_2O, T = 274 K, solid				$\langle E_{COM}$
$\langle E_x\rangle$	22.5 ± 1.8	20.1/19.8	16.1 ± 2.3	13.7/
$\langle E_y\rangle$	37.4 ± 2.5	26.3/25.9	20.1 ± 1.6	19.0/
$\langle E_z\rangle$	48.1 ± 3.4	61.9/62.4	24.2 ± 1.4	23.0/
$\langle E_K\rangle$	108.0 ± 2	108.3	60.4 ± 4	55.7

[a] All values are in meV, and the theoretical results have a error bar smaller than 0.1 meV. We also report the compute of-mass mean kinetic energy $\langle E_{COM}\rangle$ of the D_2O 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

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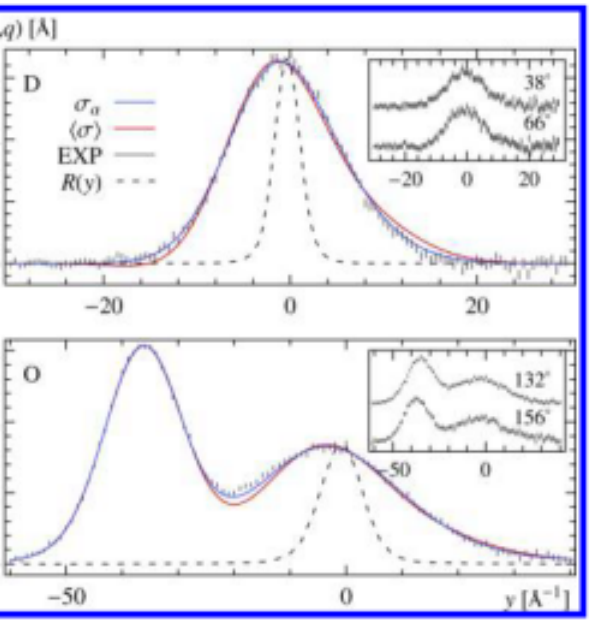
PIMD+ generalised Langevin By M. Ceriotti and D. Manolopoulos



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

Oxygen kinetic energy

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

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

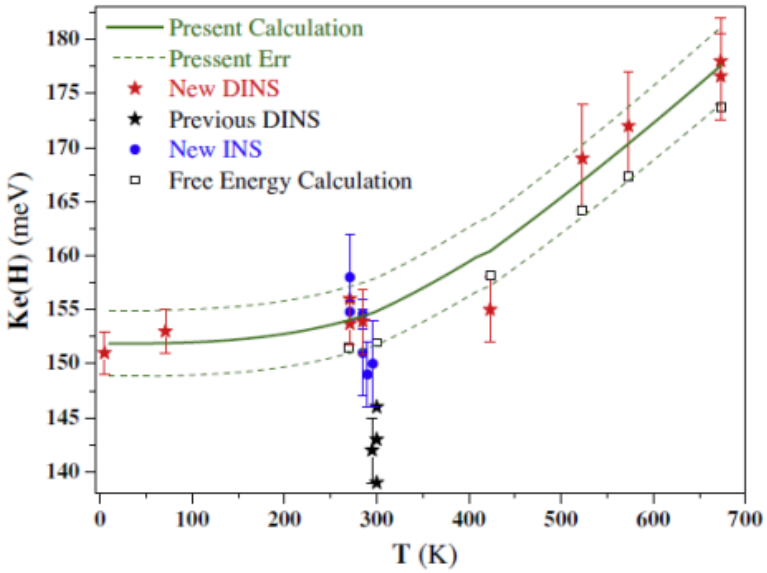
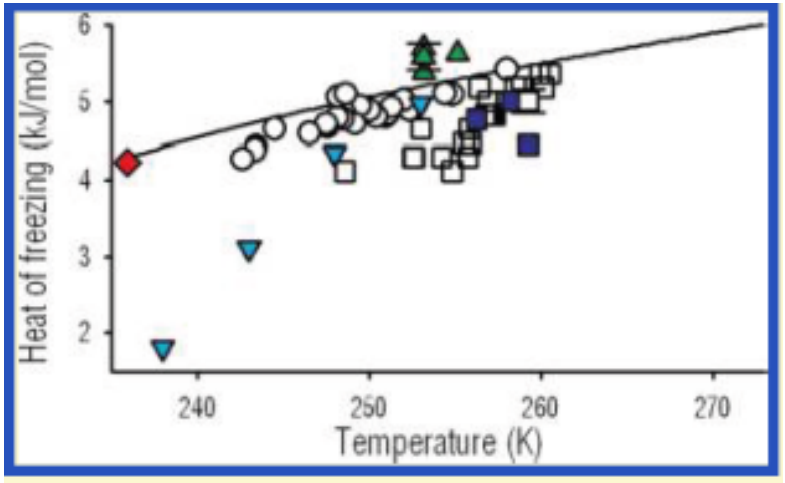


Fig. 2. Calculated Ke(H) values (solid curve) together with the error margins (dashed curves). Solid asterisks are recent (red) and old (black) DINS results. Solid circles (blue) are new INS results. Open squares are Ke(H) values deduced by Colognesi [4,34] using thermodynamic data. The numerical values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

lculations by Finkelstein and Moreh, Chem Phys 2014
int for an almost «continuous» dependence using

$$\text{H}) = 3S_T \int_{\nu_{T0}}^{\nu_T} g_T(\nu)\alpha(\nu)d\nu + 3S_L \int_{\nu_{L0}}^{\nu_L} g_L(\nu)\alpha(\nu)d\nu + \sum_{j=1}^{3} S_j\alpha(\nu_j) \qquad (2)$$

With $\alpha(\nu) = \frac{h\nu}{2}\left(\frac{1}{e^{h\nu/kT}-1}+\frac{1}{2}\right)$ with $\alpha(\nu) = \nu_j$, ν the kinetic energy of



Heat of f
Cantrell
JPCB 201

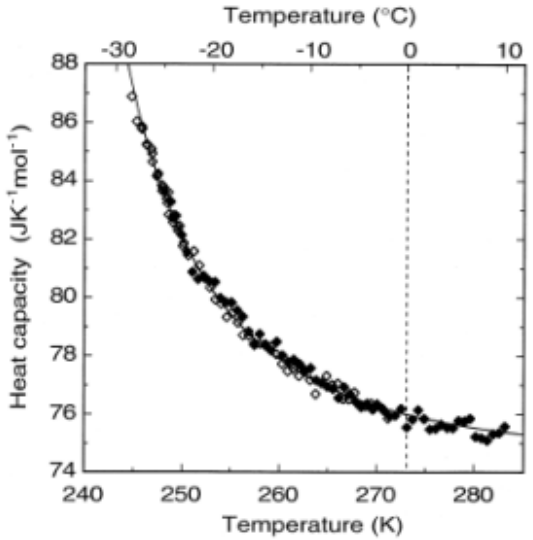


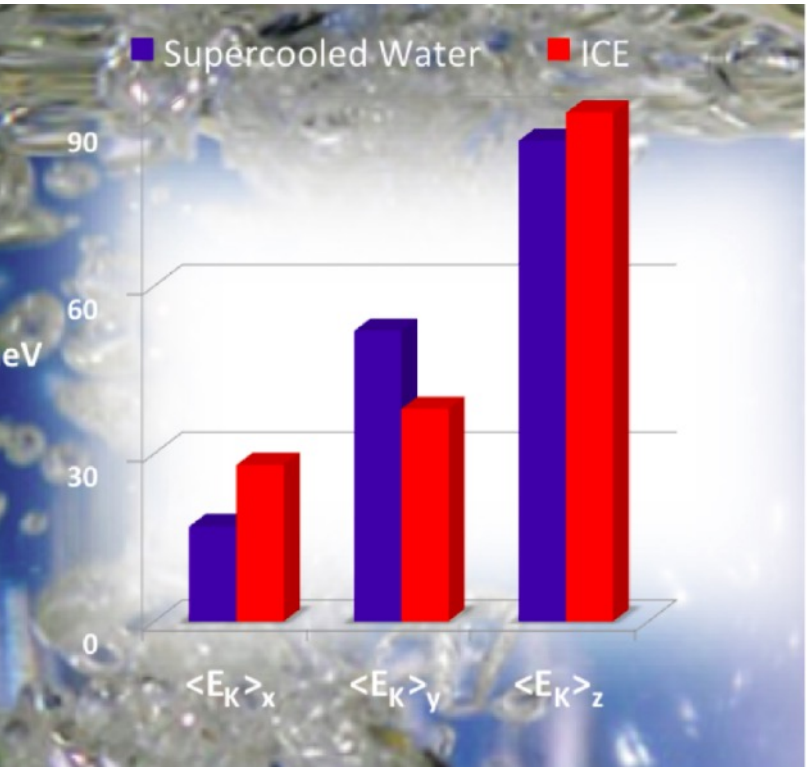
Fig. 1. Heat capacity of water measured as a function of temperature. Full and open diamonds: data obtained in this study with two different samples; full line: curve fitting the experimental points [$C_p = 0.44*(T/222-1)^{-2.5}+74.3$].

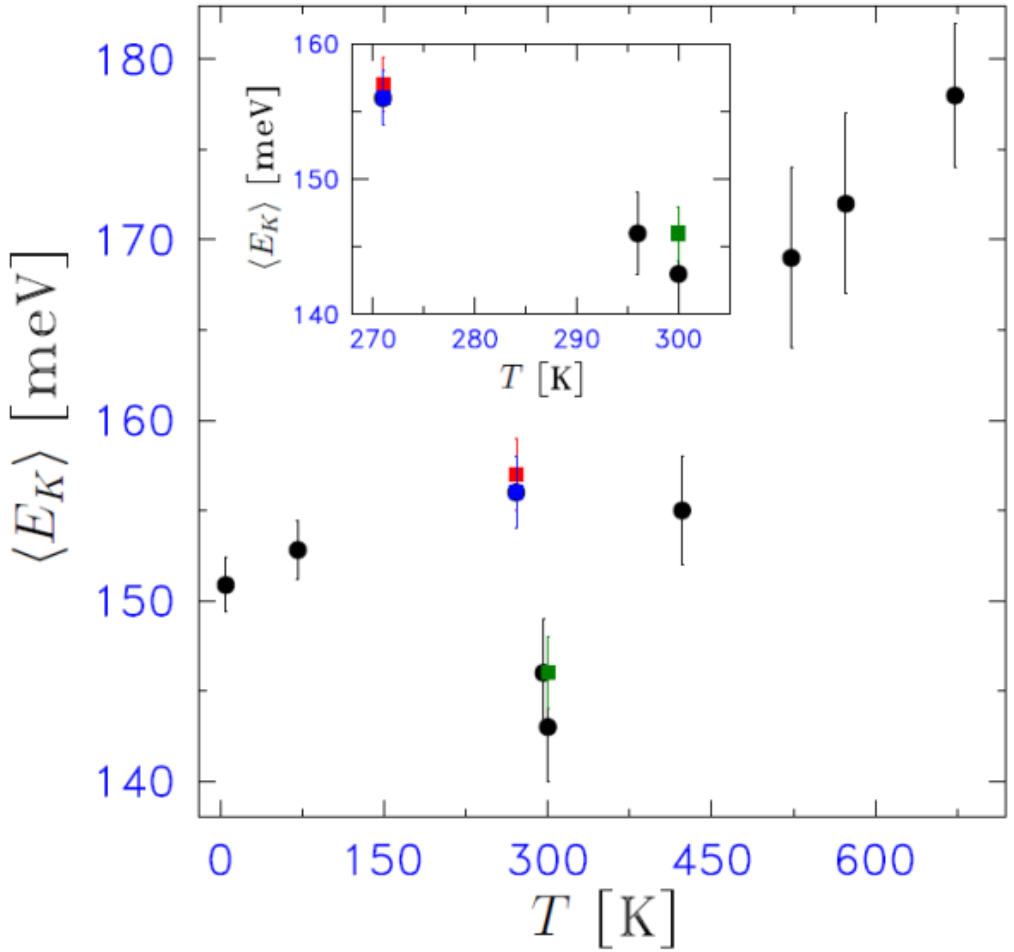
Specific
Tombar
CPL 199

Supercooled (and room temperature) bulk liquid water:

First set of experiments pointed out a large excess of $<E_K>$ as compared to ice at sar

temperature T=271 K. Most recent exp reported here, from Andreani et al, JPCL 201



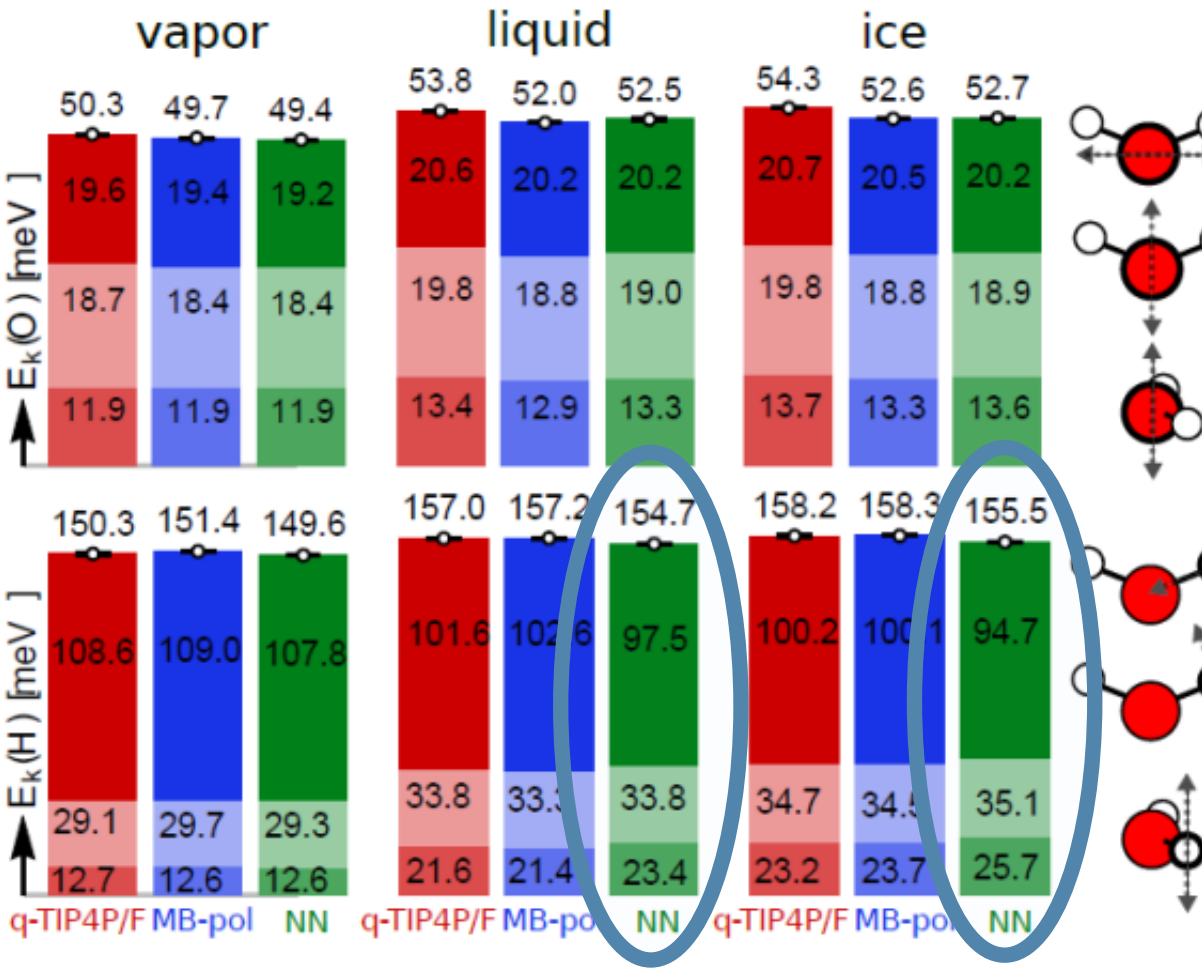


Supercooled (and room temperature) bulk liquid water:

ooled water and ice polycrystal at same T=271 K
ompeting quantum effects and have similar kinetic
es
n agreement with new simulations appearing on the
ournal issue («blind»joint exp-theory work) for
vapor, liquid, ice at the triple point

le 1. The $\langle E_K \rangle$ and individual $\langle E_K \rangle_\alpha$ values, from present S measurements in bulk SW and ice at $T = 271$ K[a]

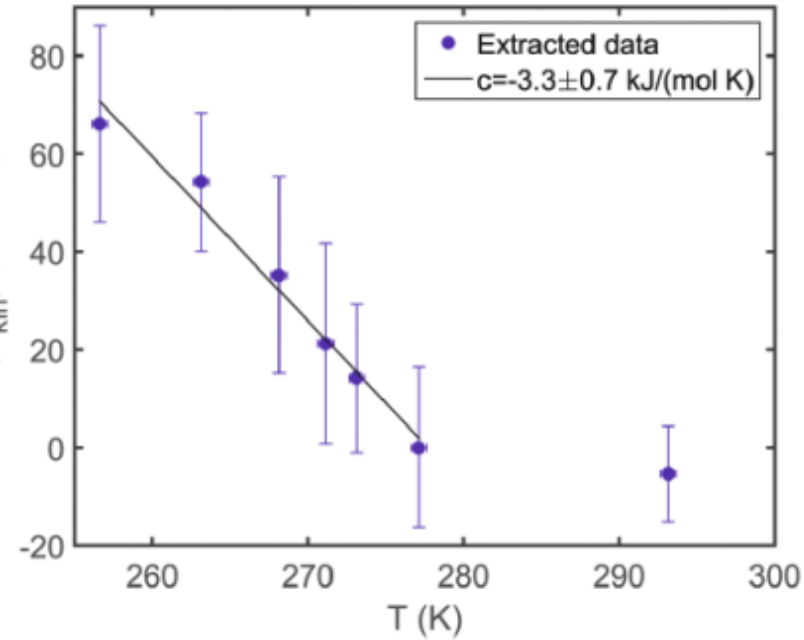
		SW	Ice	Ice[25]
T	[K]	271	271	271
M1				
σ	[Å^{-1}]	5.01±0.02	5.03±0.03	5.01±0.03
c_4		0.11±0.01	0.11±0.02	0.10±0.01
$\langle E_K \rangle$	[meV]	156.0±2.0	157.0±2.0	156.0±2.0
M2				
σ_x	[Å^{-1}]	2.9±0.5	3.7±0.1	3.7±0.3
σ_y	[Å^{-1}]	5.0±0.5	4.3±0.3	4.3±0.4
σ_z	[Å^{-1}]	6.5±0.2	6.5±0.2	6.5±0.4
$\langle E_K \rangle_x$	[meV]	17±5	28±2	29±4
$\langle E_K \rangle_y$	[meV]	52±10	38±5	38±9
$\langle E_K \rangle_z$	[meV]	86±5	91±5	87±9
$\langle E_K \rangle$	[meV]	156.0±2.0	157.0±2.0	154.0±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

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

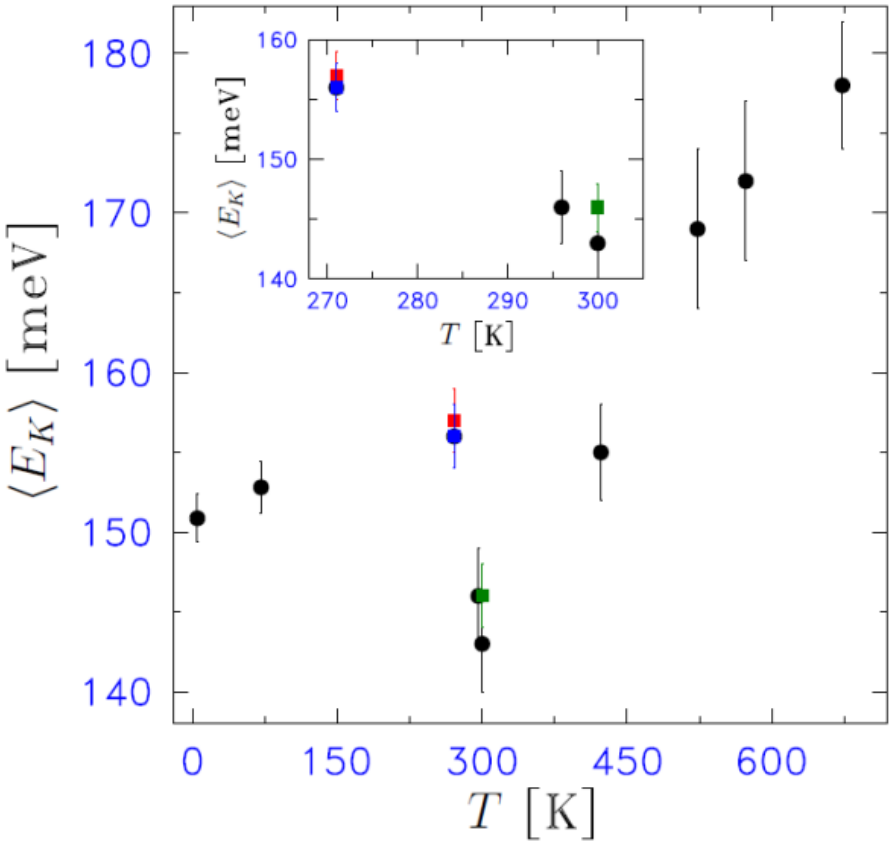
estigation needed on electron kinetic
ergies in supercooled water measured by
ay Compton scattering



$\Delta\langle E_{kin}\rangle = \langle E_{kin}(T)\rangle - \langle E_{kin}(277\ K)\rangle$. The solid line is a linear fit with $c = -3.3 \pm 0.7$ kJ (mol K)$^{-1}$.

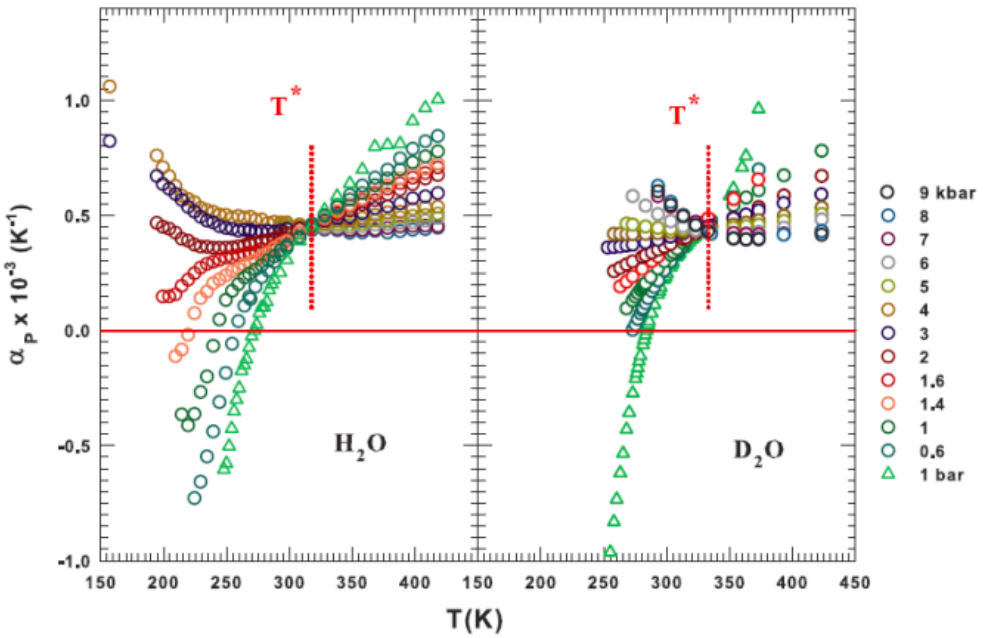
ehmkuhler et al PCCP 2016: increased
ethrahedral ordering by XRS but increased
lectron kinetic energy and structural
nodifications by X-Ray Compton

What happens near 300 K?



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

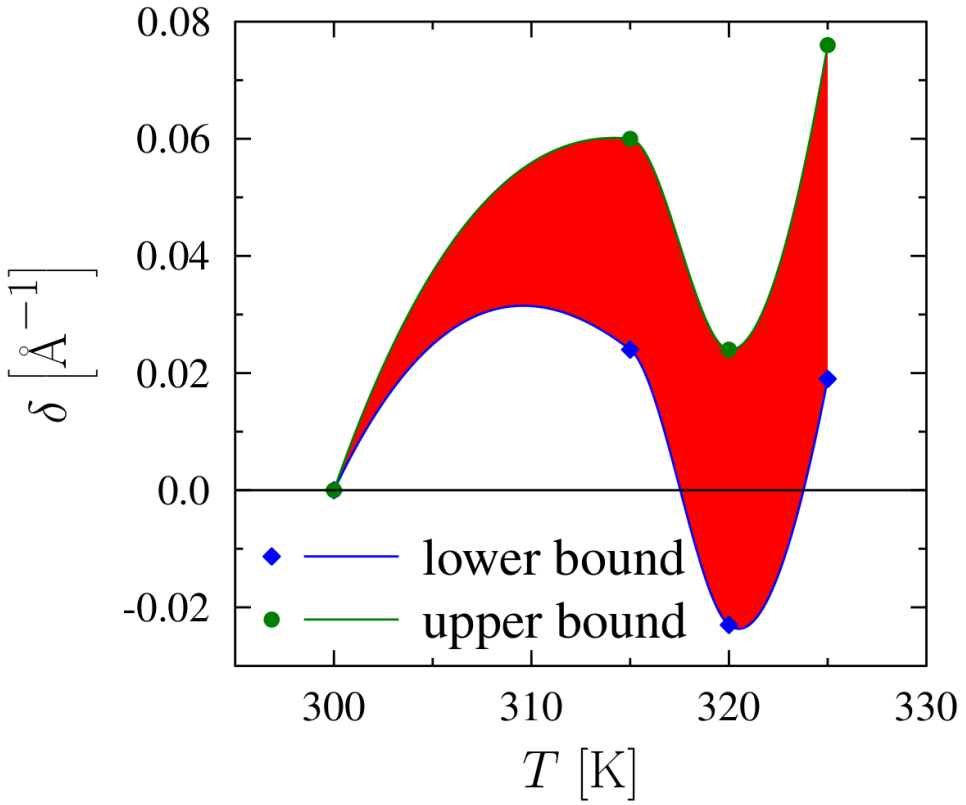
T= 315 K is a special locus of thermodynamic properties in water



oefficient of thermal expansion for bulk (left panel) and heavy (right panel) water as a function of the temperature at different pressures.

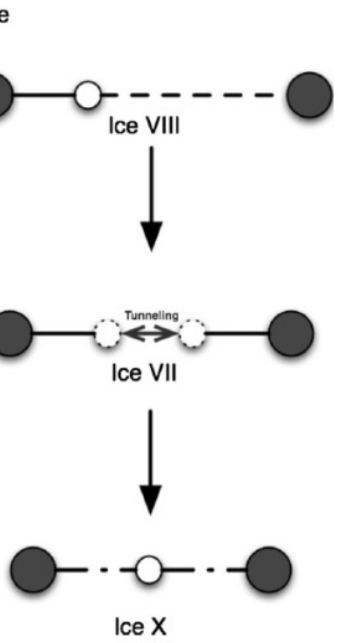
F. Mallamace et al, JCP 2014

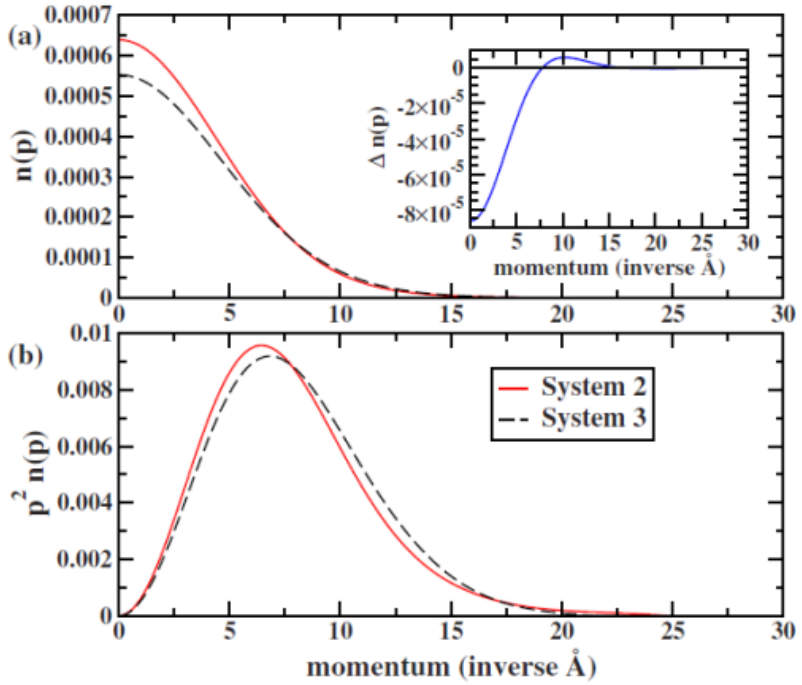
Is there a counterpart on the hydrogen's kinetic energy? Preliminary DINS experiment analysis- Delta is the increase (decrease) of momentum width with respect to 300 K



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

eling and delocalization effects in hydrogen bonded ms: A study in position and momentum space. J. Morrone, R. Car, JCP 2009

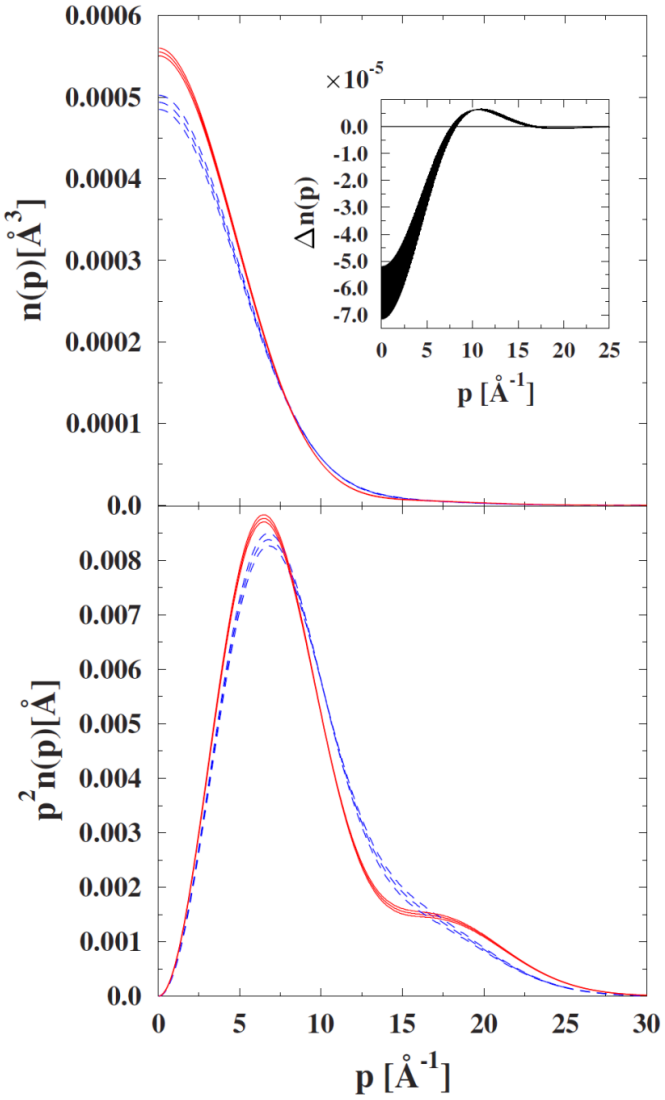


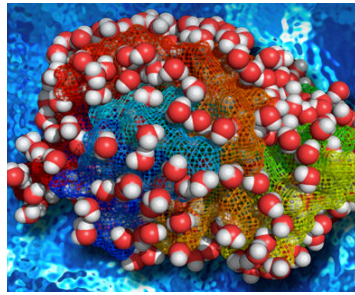


Open Path Car Parrinello Molecular Dynamics

Proton momentum distribution in protein hydration s

RS, A. Pietropaolo, A. Bocedi, S. Pagnotta, F. Bruni, PF





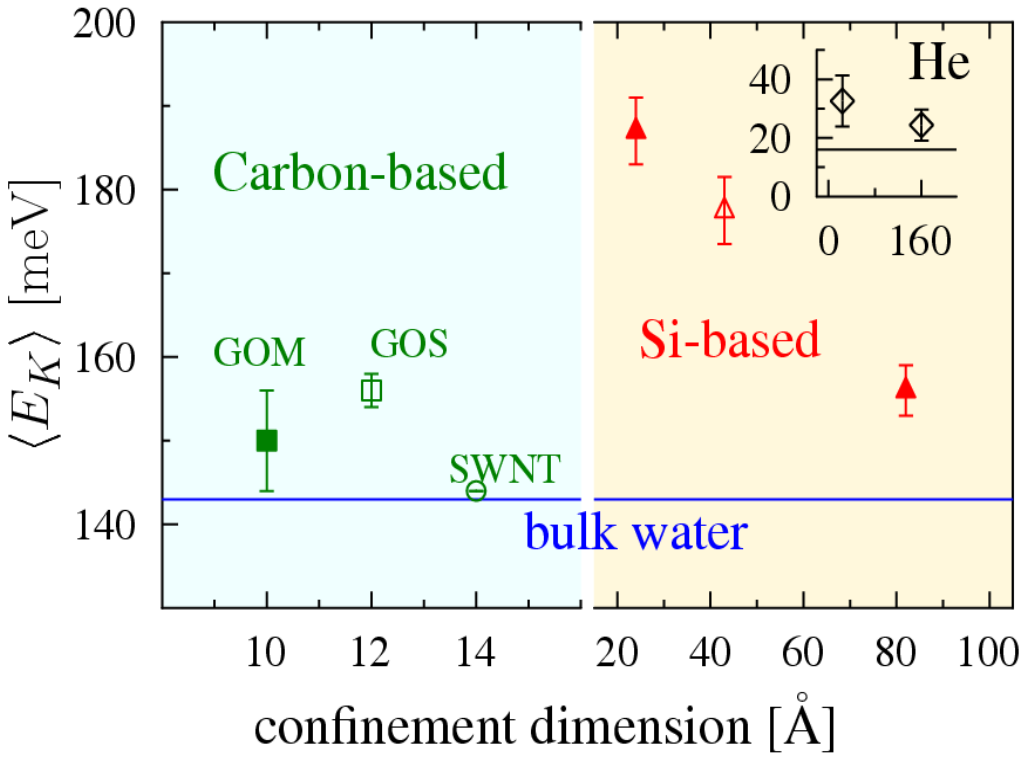
290 K Reduced

180 K O-O distanc

At 290 K

Water in nanopore confinement

DINS experiments



Modeling of quantum kinetic energy?

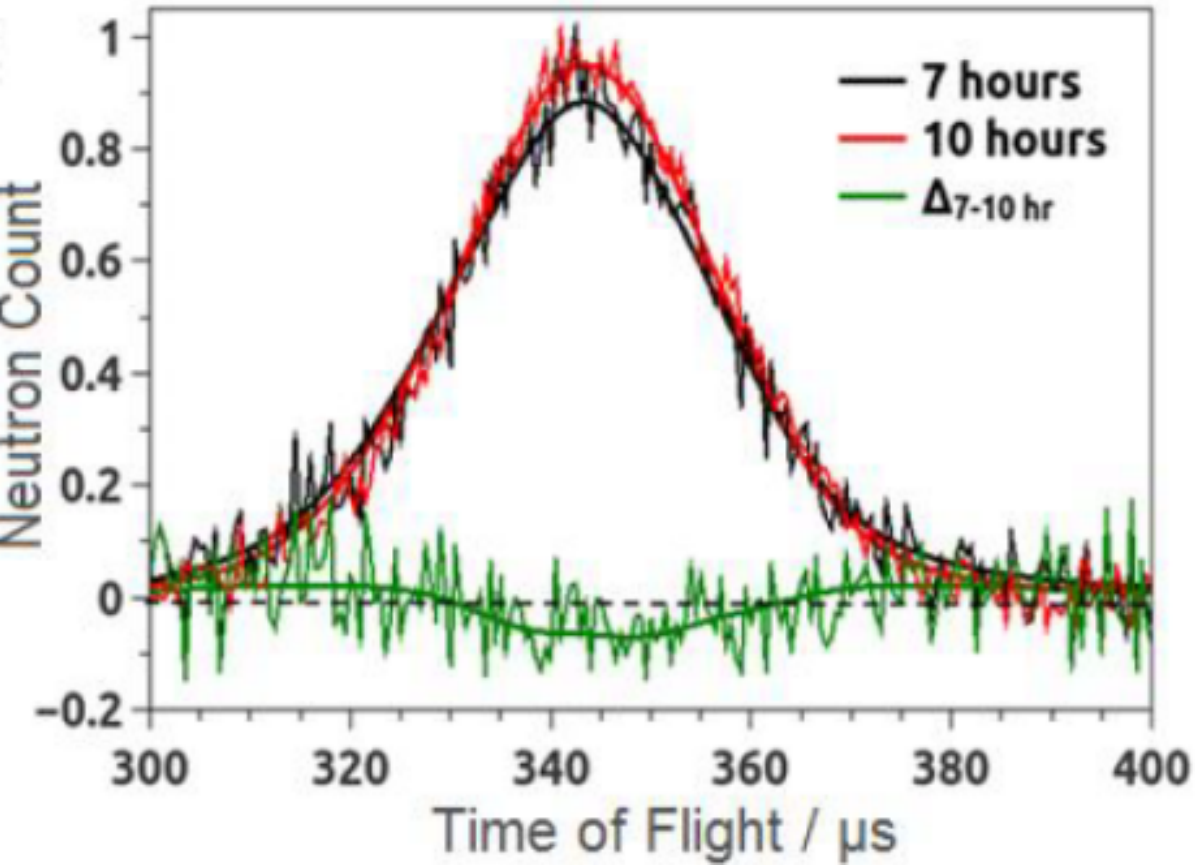
Reactive potentials +quantum nuclei

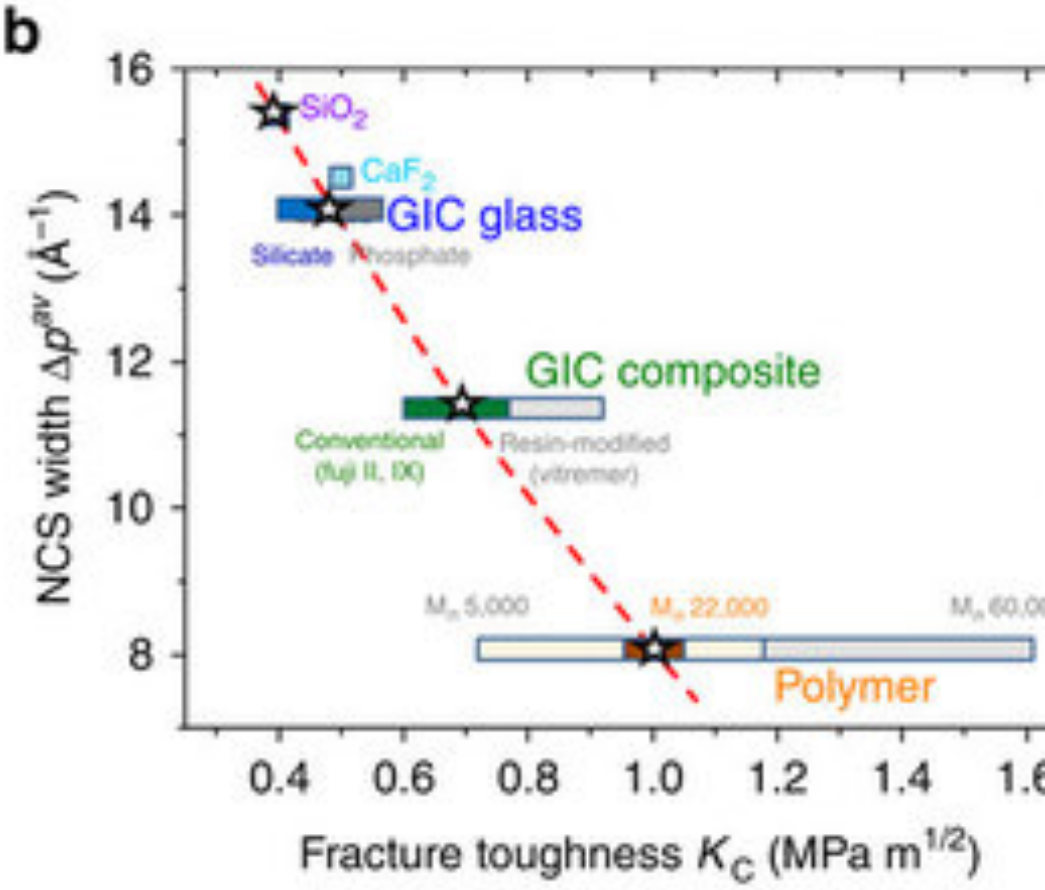
To model the interaction with acidic sites

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

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

c and vibrational origins of mechanical toughness in bioactive cement during setting", K. V. Tian et al., Nature Comm.





To be explored by experiment and modeling

PRL 110, 065701 (2013) PHYSICAL REVIEW LETTERS week ending 8 FEBRUARY 2013

Role of Quantum Effects in the Glass Transition

V. N. Novikov[1,2] and A. P. Sokolov[1,2,3]

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

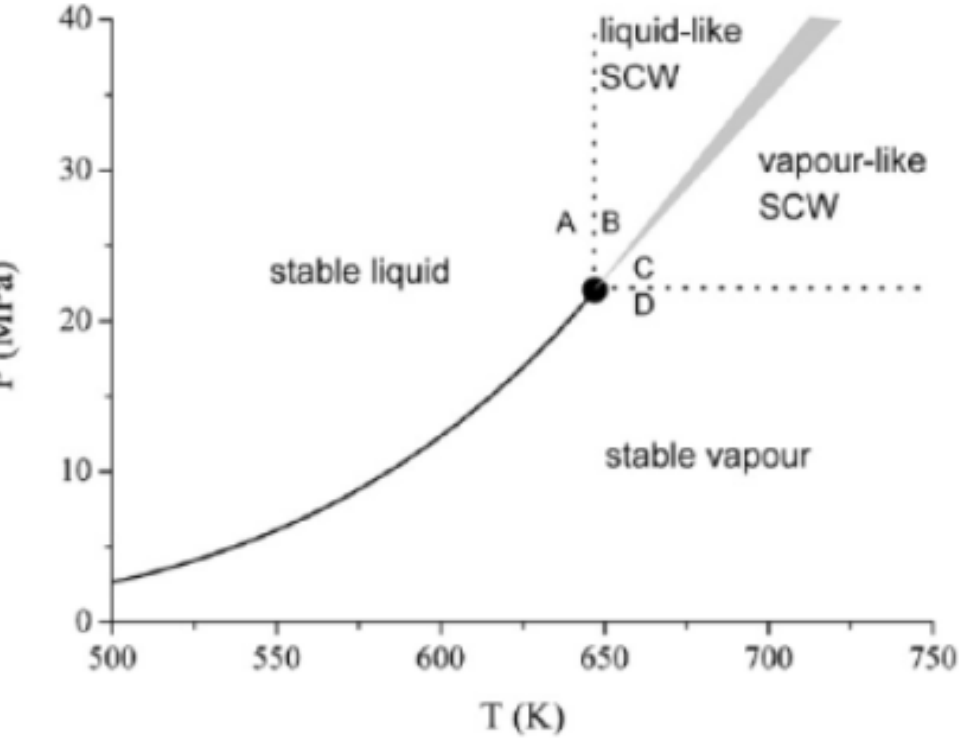
PRL 105, 148101 (2010) PHYSICAL REVIEW LETTERS week ending 1 OCTOBER 2010

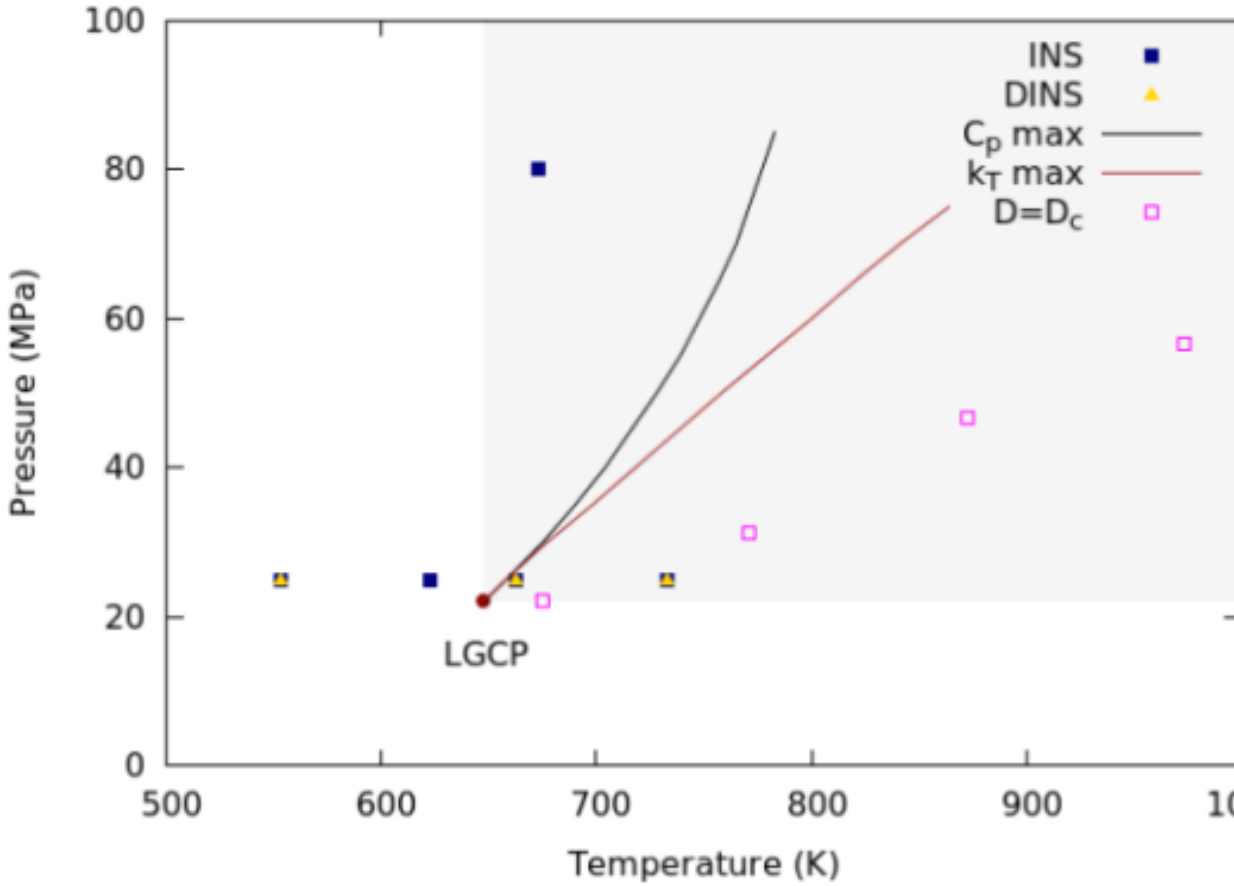
Changes in the Zero-Point Energy of the Protons as the Source of the Binding Energy of Water to *A*-Phase DNA

G. F. Reiter,[1] R. Senesi,[2] and J. Mayers[3]

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)

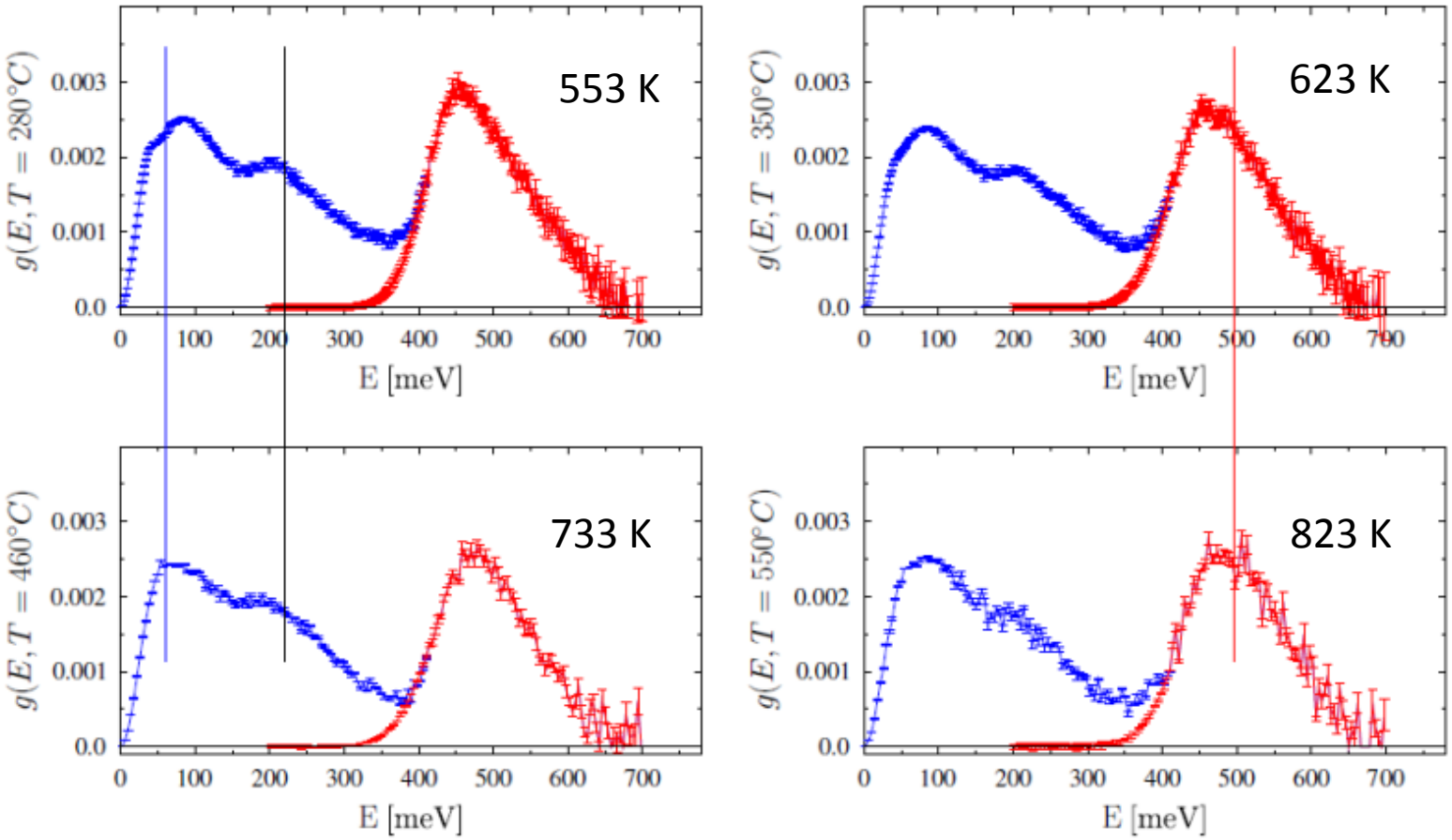


Figure 4: Density of states $g(E)$ (blue) and stretching contribution $g_{str}(E)$ (red) for T=280 C, 350 C, 460 C, 550 C. The main difference between the lower temperatures (top) and the higher temperatures (bottom) is the shift, in opposite directions, of stretching and libration contributions, while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

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

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

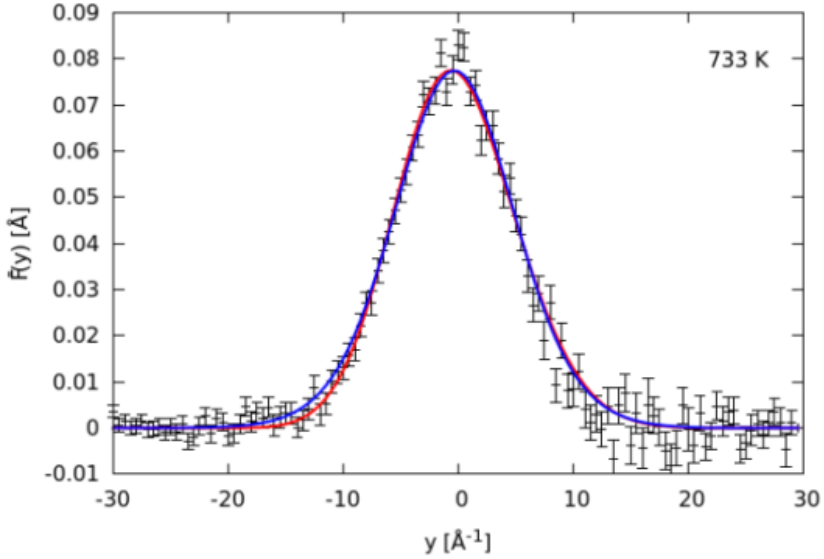
le 7.4: Directional energies and $< E_k >$ as deduced from the harmonic decou-
model described in Eqs. 7.1-7.3 for the liquid case.

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

$$< E_k >_x = 2S_{lib}\frac{\hbar\omega_{lib}}{4}coth\left(\frac{\hbar\omega_{lib}}{2K_BT}\right) + S_{tra}\frac{1}{2}K_BT$$

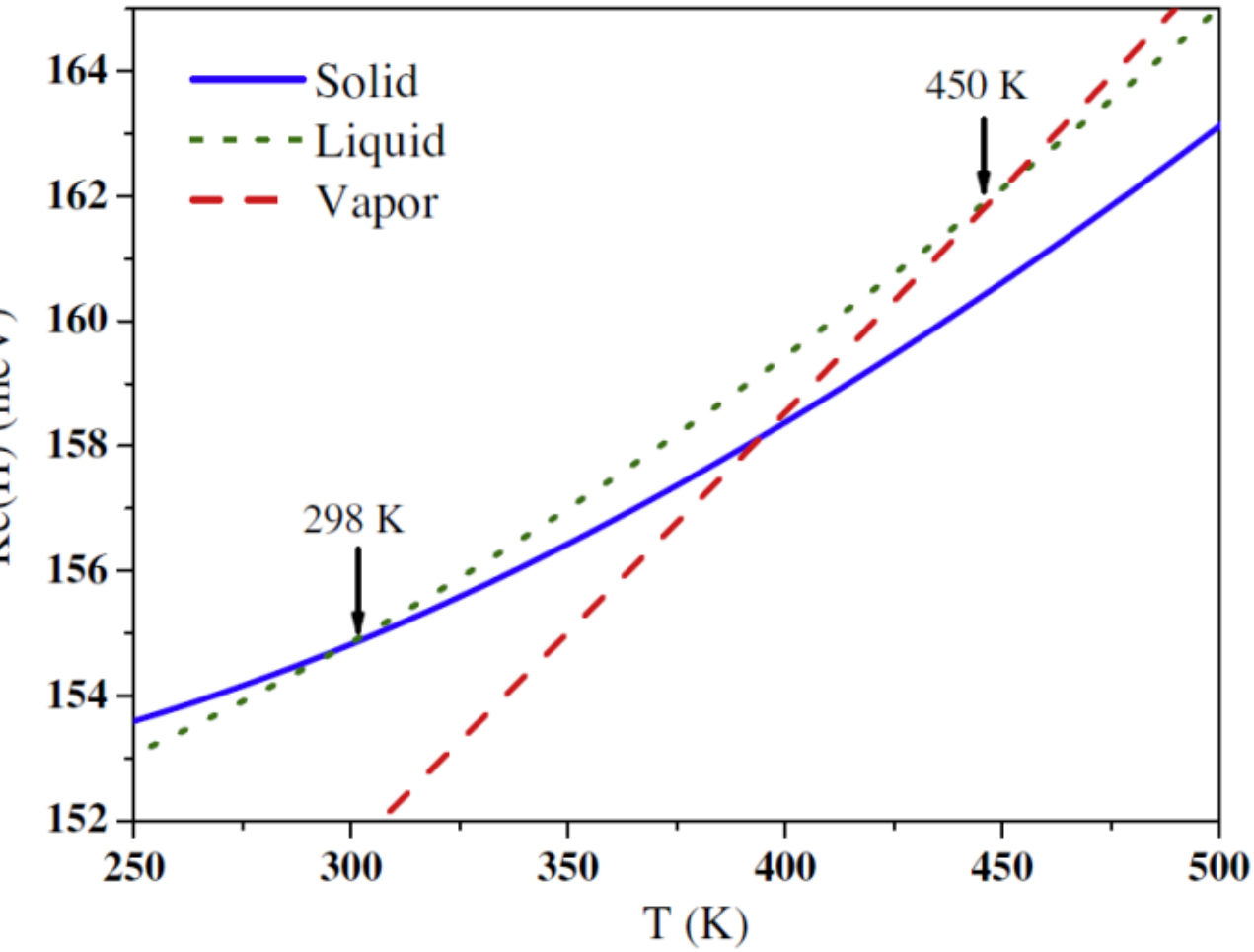
$$< E_k >_y = S_{lib}\frac{\hbar\omega_{lib}}{4}coth\left(\frac{\hbar\omega_{lib}}{2K_BT}\right) + S_{ben}\frac{\hbar\omega_{ben}}{4}coth\left(\frac{\hbar\omega_{ben}}{2K_BT}\right) + S_{tra}\frac{1}{2}K_BT$$

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

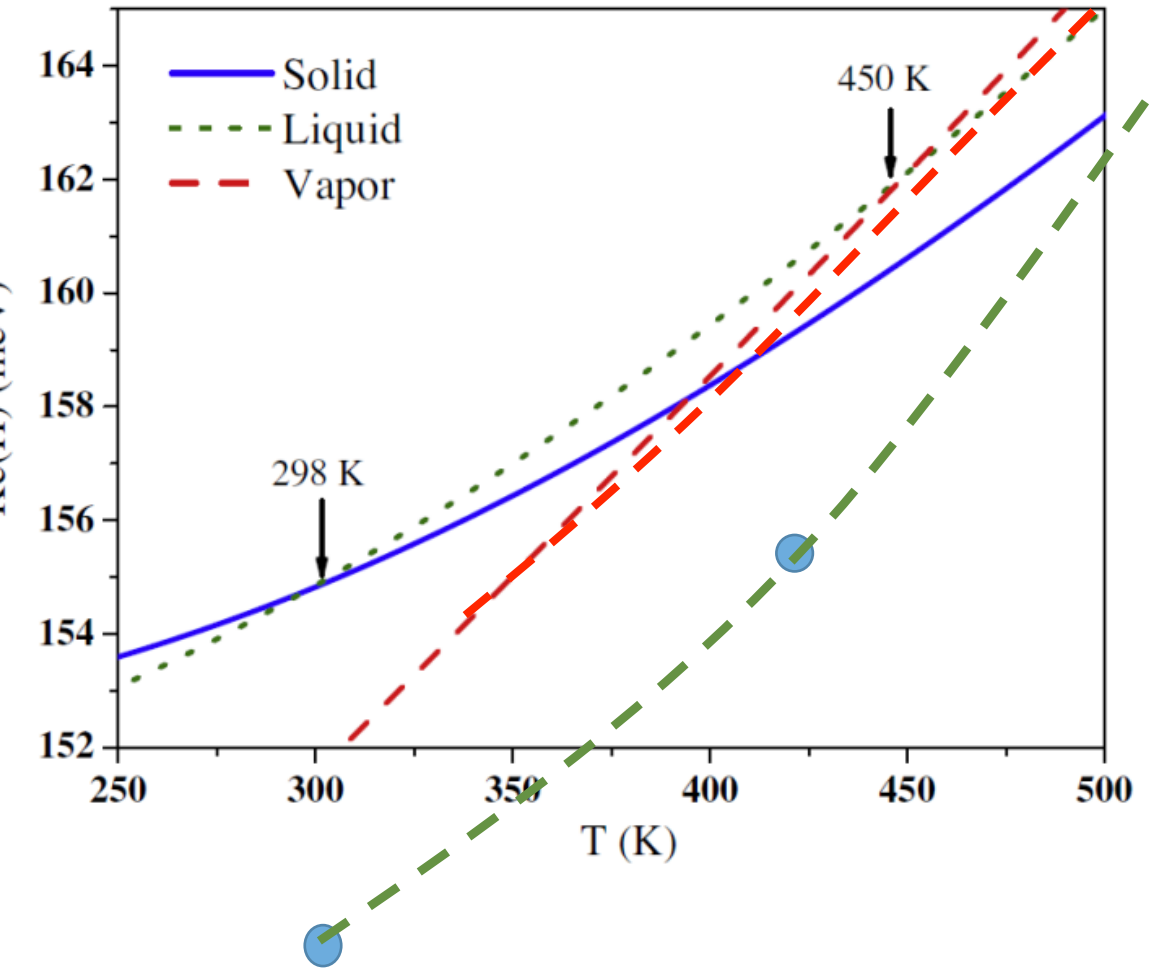


Sensitivity and consistency checks between modeling of DINS line shapes and vibrational INS data, relevant for low density measurements <0.15 g/cm3

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



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



A pseudocritical (Widom) line of kine
energy?

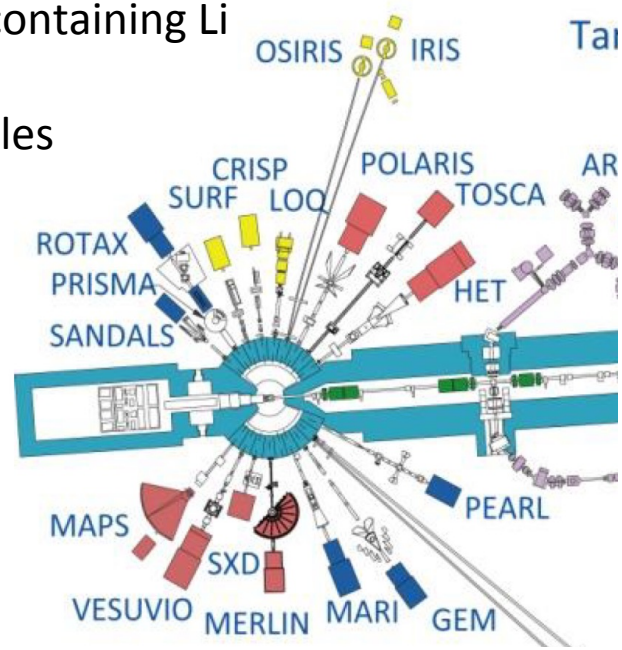
OUTLOOK

Combination of phonon (DFT) calculations and Path Integral

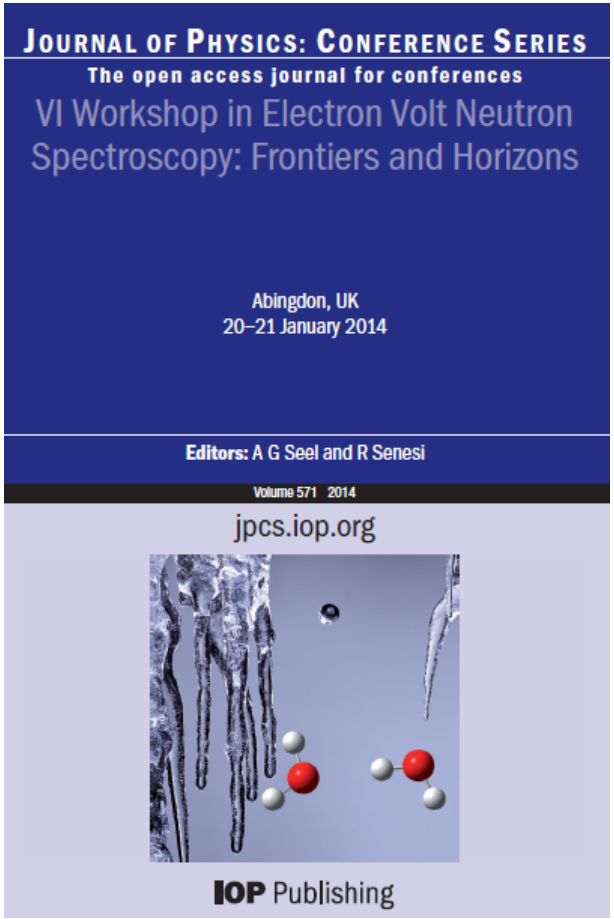
To model experiments on atomic quantum dynamics of more complex water systems in the context of

- Ionic conductors
- Disordered materials
- Molten salts containing Li
- Glasses
- Macromolecules

TS-1



VESUVIO is now aiming at exploiting element-specific and mass resolved spectroscopy for complex and disordered materials



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