Discussion: Nuclear Quantum Dynamics - Protons and Beyond

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1. Quantal Nuclear Motions in Condensed H-bonded Systems (Carla Andreani, Rome, Italy)

Dr Refson opened the discussion of the lecture by Prof Andreani: Which are the next experimental prospects to include other phases of water ice?

Prof Andreani replied: Next 3-5 years will be critical. The temperature trend of ice is not well understood, yet so full of meaning. The convergence of theory, INS and DINS is needed to characterize anharmonicity. Three major investigation areas: ice, liquid water, supercooled water.

Prof Greaves communicated: Have you considered levitation techniques to reach supercooled water.
state for water? Below the melting point there are anomalous changes in compressibility and 
\( C_p \) which might be mirrored in proton energy changes. An interesting issue is the trends. These 
reveal the direction of a possible second critical point for water.

**Prof Andreani** communicated in response: I’m very interested in the possibility of using levitation methods. As to the second critical point, my group is experimentally trying to probe that region starting from amorphous phases of solid water.

**Dr Krzystyniak** queried: Are there any hints about anomalous mean kinetic energy from \(^{17}\)O NMR?

**Prof Andreani** replied: Not to my knowledge

**Dr Krzystyniak** remarked: Could one measure O-projected VDOS on TOSCA?

**Prof Andreani** replied: There is no reliable way to do that due to no variation in Q on such a machine.

**Mr Wiles** queried: Is there a chance to make simultaneous measurements on VESUVIO?

**Prof Andreani** remarked: There is a chance to derive some vibrational information, but with low resolution. MARI has a better resolution, as well as SEQUOIA.

**Prof Fernandez-Alonso** communicated: Is there a minimum in the mean kinetic energy of liquid water at about 300 K? What is its origin?

**Prof Andreani** communicated in response: The origin is not clear yet. Data should be remeasured. The region which actually needs to be investigated best is the supercooled one, as well as the one around 280 K.

**Mr Wiles** queried: Do you use any other spectroscopic techniques on the ice sample in situ (e.g., diffraction)? This is important as the sample changes rapidly with time and is inhomogeneous in my understanding.

**Prof Andreani** replied: The sample is homogenous for the time scale of the measurements, and we do not use other spectroscopic techniques in situ.

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2. The Quantum Mechanics of Nano-Confined Water: New Cooperative Effects Revealed with Neutron and X-Ray Compton Scattering (George Reiter, Houston, TX, USA)

**Prof Gidopoulos** opened the discussion of the lecture by Prof Reiter: How do you distinguish external from internal water in nanotubes?

**Prof Reiter** replied: The nanotubes come in bundles with a hexagonal lattice. A Bragg peak of this lattice is nearly extinguished by the form factor of the nanotubes. The form factor of the nanotubes depends on the neutron dielectric constant of the water. The resultant small peak from the cancellation of the Bragg peak by the form factor would shift in the opposite direction from that observed upon filling if the water was on the outside of the nanotube.

**Prof Greaves** communicated: Confinement reduces the melting point. Is there a link between confinement in pores of different dimensionality (such as nanotubes vs Nafion)?

**Prof Reiter** communicated in response: We have considered this issue. It appears like it is a scale-matter, in the sense that the 20Å correlation length dominates.
Prof Greaves commented: Is shape not relevant above 20 Å?
Prof Reiter replied: Exactly.

3. MANSE and Beyond (M. Krzystyniak, STFC, UK))

Dr Ceriotti opened the discussion of the lecture by Dr Krzystyniak: Are there indications of deviations from the Maxwell-Boltzmann distribution for Cs?
Dr Krzystyniak replied: At room temperature, Cs behaves pretty much as an ideal classical gas from the n(p) point of view. However all and by itself the measurement of the kinetic energy of a heavy nucleus directly from a resonance opens up a new way for electron-volt spectroscopy with neutrons. For the first time, widths of momentum distributions of some heavy nuclei, measured directly from time of flight spectra recorded on VESUVIO, can be compared with ab initio calculation.

Dr Refson communicated: If I understand correctly, you are using discrepancy between harmonic phonon calculation and experimental n(p) as a measure of the size of non-adiabatic effects. But anharmonicity also contributes to this. How large is the anharmonic contribution?
Dr Krzystyniak communicated in response: Actually both LiH and LiD are very harmonic. In a recent paper [Phys. Rev. B, 87, 144302 (2013)], a formalism was described for studying temperature dependent anharmonic vibrational properties in periodic systems using first-principles calculations. Within this formalism, the BO energy surface is mapped using a principal axes approximation, and the resulting equations are solved using a Hartree mean-field approach and second-order perturbation theory. Following this, the vibrational anharmonic wave function is used to calculate expectation values of phonon-dependent quantities. The authors have tested the formalism on diamond, lithium hydride, and lithium deuteride, which exhibit quite small anharmonicities. However, while diamond is nearly harmonic, the small anharmonicity in lithium hydride arises from a cancellation of the contributions from single-phonon and two-phonon terms.

Dr Walewski queried: Is the momentum distribution corresponding to the total VDOS? Is it possible to measure the anisotropy of the momentum distribution in the DINS experiments?
Dr Krzystyniak replied: Yes, the momentum distribution corresponds to the VDOS, and the anisotropy can be measured.

Dr Seel remarked: Are there factors other than the thermal broadening that affect the width of the recoil, excluding resolution effects? Is there only a single decay process?
Dr Krzystyniak replied: The instrumental resolution contribution to a resonance peak measured on VESUVIO can be calculated analytically in the limit of the vanishing final flight path L1 and the thick sample limit. Comparison of the synthetic VESUVIO response including the resolution function calculated in this limit for the case of Cs resonances in CsHSO4 with experimental data on shows that any possible contributions from VESUVIO analyser foils (primary and secondary) is negligible. The Doppler broadening of resonances of caesium in CsHSO4 as observed on VESUVIO does not seem to be dependent on decay processes. Different resonances observed for different incident neutron energies show the same extent of Doppler broadening.
4. Origins of Mechanical Toughness in Bio-Cement During Setting (Gregory Chass and Neville Greaves, QMUL, Aberystwyth University, UK)

Prof Fernandez-Alonso opened the discussion of the lecture by Prof Chass and Prof Greaves: It is quite remarkable that the mechanical (macroscopic) properties can be linked to (atomic-scale) NCS data. Can you further comment on this?

Dr Chass replied: Mechanical toughness in composites derives from interfaces, and it is dominated by coordination.

Prof Fernandez-Alonso communicated: Is then the interface predominant in these materials, to be so clearly seen in the Compton data?

Dr Chass replied affirmatively.

Prof Andreani commented: What do you need for future experiments? Will D₂O help?

Prof Chass replied: D₂O would be useful. Also we need to explore different temperatures and different additives that affect setting point times. Also time slicing reduces statistics, so repeated measurements are needed.

Dr Walewski remarked: What is the accuracy of DFT in this case?

Dr Chass replied: The DFT accuracy is acceptable but model sizes are poor.

Dr Drechsel-Grau communicated: How reliable is the model you use?

Dr Chass replied: The model is representative. It’s based on similar trends for analogous materials.

5. Direct Measurement of Competing Quantum Effects on the Kinetic Energy of Heavy Water upon Melting (Giovanni Romanelli, Rome, Italy)

Prof Greaves opened the discussion of the lecture by Mr Romanelli: How do your calculations based on stretching modes compare with Lindemann’s melting law where periodicity is lost when root-MSD approaches the size of interatomic distances?

Mr Romanelli replied: The interpretation of these experimental results is based on a harmonic potential and no dependence on the MSD is considered.

Prof Andreani remarked: Exploring MSD should be unimportant.

Dr Walewski commented: Why don’t you present the bending mode contribution to the kinetic energy of a water molecule? Is it not available from the experiment?

Mr Romanelli commented in reply: The mean kinetic energy we measure is the sum of the contributions of all the rotations, translations and vibrations. The interpretation of the multivariate Gaussian fit is straightforward only for the component along the stretching modes, since in this direction the principal contribution comes from the most energetic modes. The motion along the other two directions is principally due to combination of rotations and bending, and then a model is needed in order to extract the information of the bending contribution from the directional kinetic energies.