Over the Horizon: Future Roles of Electron Volt Neutron Spectroscopy

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The final session of the VI Workshop on Electron Volt Neutron Spectroscopy was devoted to an open discussion of the future roles of the technique, taking as starting point the results and perspectives presented and discussed over this two-day event. In this context, it is recognised that VESUVIO at ISIS has already been successful at providing unique insights into Nuclear Quantum Dynamics (NQD) of light nuclides in condensed matter, so far with an emphasis on model systems that provide precise and much-needed benchmarks for state-of-the-art theoretical predictions. More recent infrastructure and scientific developments have also shown the yet-to-be-tapped potential of MAss-selective Neutron SpEctroscopy (MANSE) to study functional materials, a convenient gateway to expand the core capabilities of the Deep Inelastic Neutron Scattering (DINS) technique beyond its current remit.

To conclude these proceedings, we provide a summary of ideas and perspectives brought up during this final discussion session, emphasizing the importance of joint experimental and theoretical efforts to understand and describe NQD in condensed matter, growing synergies across a number of scientific disciplines, and ongoing and further developments in novel instrumentation across the globe.

The Evolving State of DINS

What became immediately clear from this meeting is that DINS has been in a state of evolution from its very inception, representing a technique that is unique to spallation neutron sources that produce a suitable flux of epithermal neutrons. The VESUVIO spectrometer has been in operation at ISIS in one form or another since 1989 as its initial incarnation, EVS \cite{1}. The user programme on EVS soon produced experiments examining NDQ of protons in condensed matter, culminating in the first single-crystal measurements of momentum distributions in potassium dihydrogen phosphate \cite{2}. This represented a stark departure from previous applications of DINS, which centred around helium and the associated macroscopic phenomena of superfluidity and...
Bose-Einstein condensation [3]. DINS was then at the level whereby, in favourable circumstances regarding sample availability, the effective single-particle potential energy surface for protons in condensed matter could be accessed experimentally. Continued efforts were made to upgrade instrumentation, with the VESUVIO (2004) and eVERDI (2008) projects being the major milestones towards the instrument as it stands today. The current user programme on VESUVIO has witnessed another evolution in recent years, towards the investigation of functional materials, and those of increasingly complex nature. Our discussion session allowed us to clarify where we are in terms of research themes, the manner in which data is both collected and analysed, and the increasingly important role of computation and materials modelling in the future of DINS.

NQD and MANSE: Fundamental Systems and Beyond

Nuclear quantum effects underpin much of the current research in the field of DINS. In addition to systems of fundamental interest, such as water (as represented in this meeting by the work of Andreani, Reiter, Romanelli, Drechsel-Grau, and Ceriotti), there is increasing interest in functional materials that demonstrate a distinctly non-harmonic proton environment (Wikfeldt and Krzystyniak). DINS thus has a place within the fields of applied materials research, such as proton conductors, organic piezo- and ferroelectrics and ionic liquids. It is particularly worthy to note that, through the VESUVIO user programme, interest has been shown recently for all of these systems.

This meeting has also brought to the fore the more recent emergence of MANSE. In the preceding sessions on this topic, we were presented with light nuclides that are of interest in both fundamental and applied science (such as Li, C, N, O) and accessible for currently operational DINS spectrometers such as VESUVIO. Furthermore, Krzystyniak presented additional possibilities to extract mean kinetic energies for heavier nuclei via the use of resonant Dopplerimetry.

Both NQD and MANSE are areas in continual development, both in terms of experimental and computational techniques, and the interplay between them. As such, the results of our discussion session are presented below so as to highlight the next steps in examining NQD in condensed matter, as driven by an increasing need to routinely examine complex materials in which they are exhibited, and the complementary MANSE technique.

[1] Emerging experimental requirements. The first question we must ask is just how sensitive is DINS to the physico-chemical environment of the proton, or any given mass, and to intrinsic nuclear quantum effects. To first approximation, by how much should we expect the mass-specific Compton width, $\sigma_M$, to vary in a given system? The long measurement time on VESUVIO has limited the number of truly parametric studies that have been conducted to date, and this limitation was immediately highlighted in this discussion session. An expedient ‘next step’ for this field would be to increase the number of studies conducted over varying temperatures, pressures, or chemical trends. Such parametric studies would not only be informative in terms of experimental sensitivity, giving a bounded region for the environmental sensitivity for the proton and heavier masses, but also act as a benchmark for computational studies that are capable of simulating experimental conditions.

Further to the above, discussion centred on modern measurements of systems such as $\text{H}_2/\text{D}_2/\text{HD}$ where NQD phenomena such as particle exchange can be effectively ‘switched on/off.’ A systematic overview of these systems would enable quantification of our current experimental sensitivity to specific NQD effects. In this context, important too is the selection of samples for investigation in terms of availability, stability, and form. Access to single-crystal samples, large enough for DINS measurements, is the only route towards direct measurement of truly multidimensional (in a non-spherically-averaged sense) proton Compton profiles, kinetic energies, and eventually potential energy surfaces.
Emerging conceptual, theoretical and computational needs. The most significant factor in the modelling and interpretation of NQD has been the move beyond the harmonic approximation and periodic media. This landed approximation still represents the cheapest way to calculate zero-point energies, and is still the workhorse for the interpretation of neutron spectroscopy probing atomic vibrations at lower energy transfers. The aim of computation as applied to spectroscopic interpretation or modelling is to establish well-defined protocols to explore NQD at various levels of controlled and hierarchical approximation. This task can be achieved via recourse to classical molecular dynamics (exhibiting no NQD), harmonic calculations (as a starting point to include or identify dominant quantum effects such as zero-point-energy motions), quasiharmonic and anharmonic corrections including increasingly popular self-consistent approaches, and through to fully quantum-mechanical methodologies which necessarily need to include particle delocalisation, interference, and exchange in condensed-matter media. In this manner, these computational tools would be available for any given system measured by DINS, from the more classical end and the overlap with MANSE, through to the fully quantum nature of proton dynamics in a plethora of situations of both fundamental and practical interest.

Experimental design could be greatly aided through a combination of (the more widespread) phonon calculations (primarily using first-principles electronic structure codes, generally DFT), as well as PIMD methods (as highlighted in this meeting by the i-Py programme of Ceriotti et al [4]). The more widespread use of these tools would allow for the identification of systems possibly exhibiting pronounced NQD, or wherein nuclear dynamics show a strong variance with temperature, as well as for the subsequent interpretation of experimental data. At this point, it is important to address a recurring theme arising from this discussion session, namely, the link between DINS experiments and PIMD calculations. Of particular importance is the study of protons and the manner in which the momentum distribution \( n(p) \) is interpreted. On the one hand, the experimental DINS community have traditionally used a Gram-Charlier expansion to fit measured neutron Compton profiles and yield the isotropic \( n(p) \). On the other hand, a multivariate Gaussian model is more conducive to physical interpretation and comparison with PIMD. It is therefore important to reach a future synergy between computation and experimental interpretation for the investigation of NQD, particularly in isotropic systems. This must also include deviations from the ‘ideal response’ under the celebrated impulse approximation, also known as final-state effects.

Systems and frontiers for DINS. Our discussion on NDQ and MANSE ended with the suggestion of systems that could (and should) be highlighted for further experimental and theoretical scrutiny. Included too are their associated challenges. Chief amongst these were complex hydrogen-bonding systems, both natural and man-made, for the study of NQD via DINS. An example field mentioned was mineralogy, where the proton response in a series of chemically related, hydrogen-bonded frameworks could be determined. This would enable a direct link between the observables of DINS (such as \( \sigma_M \)) and chemical binding parameters such as bond strength, acidity/basicity, or toughness. This area is also of interest for the future development of MANSE, where it was recognised that this ‘parametric link’ is a crucial step to open up the field of DINS and NQD to the wider chemistry and materials communities.

Selective deuteration was also commented upon as crucial for future investigations of proton-containing systems. This is particularly true for increasingly complex organic materials that comprise distinctly different proton environments, with discernibly different NQD at each site (accessible through computation). The ability of DINS to isolate the proton from its heavier isotopic analogue the deuteron (and to measure both simultaneously) renders it a
unique tool for NQD studies in organic materials. This mass-specific isolation of the proton is also not affected by temperature in the same way as the Debye-Waller factor in diffraction or inelastic neutron scattering. These factors are particularly important were the field of DINS to evolve in the direction of biological processes, whereby NQD plays a central role in catalytic processes in biology (as discussed in the presentation of Major), provided that selective deuteration is available to isolate relevant protons.

Other areas that were highlighted include interfacial phenomena, reduced-dimensionality materials (exemplified by graphitic and Li-conducting materials) and industrially important observables such as H/D/T levels in materials for fusion technology (in the included contribution from Dawidowski et al). For reduced dimensionality samples, whilst single-crystals may not be available, we can often find partially orientated (or stratigraphically disordered) samples that can be aligned relative to the incident neutron beam. Two-dimensional momentum distributions can thus be accessed experimentally. For protons at interfaces and defects, it was pointed out that the main limitation for these systems lies in the potentially low concentration of protons at these sites, and that the absolute sensitivity for current instrumentation is yet to be ascertained in depth. Nevertheless, a lower bound for proton concentration has already been estimated experimentally, as discussed below.

**Instrumentation and Data Analysis Protocols**

Whereas our discussion was intended to highlight areas of research or specific systems that we could approach with DINS, there occurred throughout (from both experimentalists and theorists) comment and clarification for the future developments in instrumentation and data analysis. As such, we have collected here the most significant ways in which both instrumentation and data analysis could be developed in line with the user community and science cases highlighted above.

[1] **Useful flux and epithermal neutrons.** The primary limitation of current instrumentation, particularly in inverted-geometry as in the case of VESUVIO, is flux (commented upon by Seel and Senesi). This is both a problem of available and detected flux, the former being how many epithermal neutrons irradiate the sample, the latter reflecting how many are counted. Any increase in available flux is reliant upon the target station to which the spectrometer is attached (in the case of VESUVIO this would be ISIS Target Station I), and so is in a sense instrument independent. Nevertheless, an increase of a factor of 5 in incident flux would revolutionise the manner in which DINS measurements are conducted, particularly in relation to parametric studies as highlighted above. In terms of detected flux, there are a number of ways the effective count-rate for VESUVIO in particular can be increased, not least of which is an increase in the number of detectors, particularly in backscattering. Included in discussion towards this goal was a decrease in detector size or synchronous measurement with several analyser foils. Further to this was a discussion on the manner in which we analyse data, be it on a detector-by-detector basis, groupings of detectors to effectively reduce signal-to-noise and increase count-rate (Seel), or using cumulative strategies aimed at a determination of specific experimental observables such as mean kinetic energies within some level of confidence (Krzystyniak).

[2] **Improving instrument resolution.** Resolution is an important factor when studying NDQ in detail or in terms of mass-isolation in MANSE. As commented on by Seel and Senesi, this can be done in a number of ways through the alteration and redesign of detector-bank geometry. The angular component to proton resolution on VESUVIO could be vastly improved by redesigning the forward-scattering detector banks, with an energy resolution dependent upon analyser foils and foil cycling (Gorini). The manner in which the isolation and separation of light-mass components could be improved was commented upon (see contributions to these proceedings by Krzystyniak and Seel), always dependent upon an increase in incident neutron flux. The resolution of the instrument
for resonant Dopplerimetry (applicable to heavy masses) was also discussed, in terms of possible extensions to existing detector technologies for finer resolution and improved count rates.

[3] Establishing element-specific parameters. As discussion on the typical duration of experiments progressed, particularly in light of MANSE, it became apparent that the absolute sensitivity of current instrumentation is not well defined. For a given sample (including proton-containing systems), a guide to sample size and measurement duration regarding spectral statistics should be benchmarked. For the proton (and carbon), an experiment has recently been conducted on various thicknesses of polyethylene, but for systems containing any mass accessible in the DINS regime, particularly lithium, a lower-bound to mass-specific concentration needs to be determined. For complex systems containing many masses (as presented by Greaves and Chass) it would be of great help for users to have access to a spectral simulator, whereby a sample stoichiometry is defined and an idealised MANSE spectra in time of flight simulated. This has recently been implemented within the MANTID framework, but does not as yet take into account instrumental noise levels.

[4] Sample environment and ancillary measurements. For DINS measurements beyond the lightest masses, contributions to spectra from sample environment often complicates analysis. This is particularly true due to long measurement times rendering equal time on background measurement unfeasible in many cases. To this end, discussion on manners to improve upon existing sample environment turned to the use of aluminium as a sample container and instrument material. By verity of its mass (27 amu), aluminium signals always overlap with any mass greater than lithium. As pointed out by Seel, a move towards thinner sample containers of a heavy metal, such as tin, would render spectral isolation of sample environment far simpler. A prototype CCR that includes tin rather than aluminium windows is currently being produced in order to further enlarge upon this concept. Often overlooked is the existing ability of DINS spectrometers to act as diffractometers, particularly those operating in inverted geometry as with VESUVIO, where resolution in the thermal region in backscattering is particularly good. This ability to simultaneously measure diffraction and DINS has already been utilised in the study of layered materials [5]. Furthermore, by including analyser foils in the incident flight path, it was pointed out during this discussion session that the capability of the instrument to measure vibrational data (albeit with relatively poor resolution) could be enhanced. Beyond DINS spectrometers, this could be tested on instruments with similar incident energy profiles, such as SXD at ISIS [6]. As pointed out by Dawidowski in these proceedings, these also exists great potential for the measurement of total neutron scattering cross sections via the operation of instruments such as VESUVIO in transmission mode. DINS spectrometers operate in an energy region that is poorly quantified in comparison to those both higher and lower in incident neutron energy, and should be of interest in the field of nuclear engineering. This capability would act as a natural partner to the resonance analysis discussion of Krzystyniak.

[5] Data analysis and mining. The manner in which users view, access and can analyse DINS data from VESUVIO is currently being standardised under the umbrella of the MANTID framework, as illustrated within these proceedings by Jackson et al. Existing capabilities including the handling of raw data, data reduction and correction (for both $\gamma$-background and multiple scattering effects) and data fitting will soon be routinely available. This was met with a favourable response from experimentalists within this discussion session, with a further call to enhance existing capabilities to include more robust statistical methods, such as Bayesian inference or principal-component analysis. The sparse nature of DINS spectra was highlighted as the driving force for these initiatives, and these statistical techniques are currently being examined for implementation within MANTID. Of equal interest from the
computational members of this session was the possibility of moving beyond an experimental probe of atomic momentum distributions and kinetic energies, into a standardised mean-force determination and future emphasis on the exploitation of final-state effects (those ‘non-ideal’ parameters mentioned above) including their overlap with theory.

It was clear from these discussions that the manner in which we treat and analyse DINS data has evolved over the years (see contributions from Romanelli, Senesi and Reiter) and that there exists much measured data that could be reanalysed in light of this and the capabilities of modern computational methods. Such ‘data mining’ has the possibility to quickly extend the interplay between experiment and computation without reliance on future measurements alone. It would also be possible to produce a current database of measured and computed kinetic energy values available to the community which would underpin the position of DINS within a wider scientific context. Furthermore, as more instruments capable of DINS measurements become available there will be an increased need to standardise the manner in which data is presented. This was mentioned in light of future MANSE developments, where data is often presented in time-of-flight and is thus instrument dependent. Were this scale to be transformed to a standardised ‘shift,’ future data representation could be rendered instrument-independent in the same manner as techniques such as NMR (chemical shift) or diffraction (d-spacing).

**Quo Vadis DINS**

It became clear from this intense and productive two-and-a-half-hour discussion session, and when compiling these proceedings, that there already exists a strong and growing user community for DINS, both in terms of experimentalists and computational researchers. Representatives from the fields of physics, chemistry, applied materials and biological research each had some input in the current and future role of DINS as a spectroscopic technique utilising electron-volt neutrons. In particular, we must remind ourselves what renders DINS unique, special and exciting; something that we believe can be divided into two complementary manners of viewing DINS measurements. On the one hand we have a ‘quantum diffractometer’ - a technique that can access nuclear probability distributions through detailed analysis of DINS line shapes. On the other hand we have an ‘atomic quantum thermometer’ - a mass-specific technique able to determine atomic kinetic energies as a direct measure of chemical environment. Admittedly, these are somewhat simplified views of the power of DINS, the full potential of which is yet to be reached. The *VI Workshop on Electron Volt Spectroscopy* has shown that this field is continuing to develop along new pathways, and in a likewise fashion we hope to see the potential of DINS grow as we progress towards the next meeting in this series.

**Acknowledgments**

This work was supported within the CNR-STFC Agreement No. 06/20018 concerning collaboration in scientific research at the ISIS Pulsed Neutron & Muon Source. A.G.S., M.K. and F.F.A. gratefully acknowledge the UK Science and Technology Facilities Council for financial support.

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