Revamp of Inelastic Neutron Scattering Instrumentation at Frank Laboratory of Neutron Physics

case for project justification

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1. Introduction
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Introduction
Atomic motions and NS

- Neutrons can excite atomic vibrations or activate stochastic motions via energy and momentum exchange during inelastic scattering (and of course, too.)
- For inelastic incoherent scattering, the intensity is proportional to the space and time Fourier transforms of the self-correlation function, $G_s(\vec{r}, t)$, the probability of finding a particle at position $\vec{r}$ at time $t$ when the same particle was at $\vec{r} = 0$ at $t = 0$. 

Are neutrons any better a probe to study vibrational properties of condensed matter than photons (e.g. IR or Raman)?

Even if so, do they deliver “value for money”?

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Complementarity i
Complementarity ii

Neutrons:

- “directly” probe atomic (nuclear) vibrations via simple two-body interactions $\rightarrow$ simple theory
- no selection rules
- neutron has a mass $\rightarrow$ 2D or 4D spectroscopy: $S(Q, \omega)$ or $S(Q_x, Q_y, Q_z, \omega)$
- INS spectroscopy allows routine access to the terahertz region ($<$400 cm$^{-1}$)
- large sensitivity to H vibrations ($\rightarrow$ H-bonded structures, etc.) $m_n \approx m_H$
- isotope substitution

IR and Raman:

- probe vibrations “indirectly” through associated variation of electronic properties, such as EDM or polarizability $\rightarrow$ theoretical description difficult.
- operate at $\Gamma$ point only
- high sensitivity
- high spectral resolution
- speed
- $\mu$-spectroscopy gaining popularity
- availability of instrumentation
Complementarity put into practice

Vibrational spectra of $\text{fac-tris[2-phenylpyridinato-C}^2,\text{N]}\text{iridium(III), Ir(ppy)}_3$.

(S.F. Parker, J. Phys. Commun. 3 (2019) 065010)

The resolution of state-of-the-art INS spectrometers is effectively comparable to that of most IR and Raman spectrometers because bandwidths in the solid state are dominated by intermolecular interactions that are typically 10 cm$^{-1}$ or more, and high resolution is unnecessary.

For a complete vibrational characterisation, INS spectra are essential, particularly to understand the low energy metal-to-ligand modes that are important in energy dissipation.
Complementarity put into practice ii

Out-of-phase carbonyl stretch at 1700 cm\(^{-1}\) is very strong in the IR, weak in the Raman and absent in the INS. Conversely, the out-of-plane carbonyl bend at 407 cm\(^{-1}\) is strong in the INS, weak in Raman and absent in the IR.

N-phenylsuccinimide – an important compound in thermosetting resin industry.

Case for special attention to low wavenumber region

- In the previous slide we saw low wavenumber cutoffs:
  for Raman at ca. 200 cm$^{-1}$, and for IR at ca 400 cm$^{-1}$.

- Often IR can be extended towards zero cm$^{-1}$, i.e. into the far IR region, however at a considerable cost.
- "Often" does not mean "always".
- E.g. in studies of supported metal catalysts where the absorption of light by the support results in a spectral cut-off that can be as high as one cm$^{-1}$.
- For INS spectroscopy, this is irrelevant, and most support materials e.g. alumina, silica, carbon, are transparent and the entire spectral range is accessible.
- An INS spectrometer can cover a broad spectral range, routinely reaching down to nearly zero cm$^{-1}$.
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INS instrument geometries
Direct vs. Indirect geometry

Direct geometry

Indirect geometry

Energy transfer (meV)

\[ \phi = 5^\circ \] \[ \phi = 30^\circ \] \[ \phi = 60^\circ \] \[ \phi = 90^\circ \] \[ \phi = 120^\circ \]
Direct vs. Indirect geometry ii

$(Q, \omega)$ plot of iodomethane recorded on MAPS at 20 K with incident energies of 4840 and 2017 cm$^{-1}$. The solid lines are the trajectories of an indirect geometry instrument with a final energy of 40 cm$^{-1}$ for scattering angles of 45$^\circ$ (purple trace) and 135$^\circ$ (olive trace).
In favour of direct geometry:

- Can access a much larger range in $Q$ and, can *always* access smaller $Q$
- Traditionally considered better suited for magnetism
- The existing machines have up to ten-fold larger detector area
- Resolution is a fraction of the incident energy.

In favour of indirect geometry:

- Simple operation
- If $Q$ irrelevant, large acceptance instrument designs also possible
- Generally considered more versatile
- Resolution is a fraction of the energy transfer.
Challenges to INS
Some challenges to Inelastic Spectroscopy

- Study of small samples
  - pharmaceuticals
  - matter under spatial confinement
- In highly correlated systems we need a $4D \ S(Q,\omega)$. Example: topological Hall effect
- Access range of timescales as large as possible
- Study magnetic multilayers
- Study samples under extreme environments
- Study high absorption isotopes (as e.g. the performance of Li-ion batteries)
- Provide flexible resolution
A few hot topics currently under the interest of the INS community at FLNP
• Molecular crystals and glass-formers at low temperatures in connection with complementary studies and \textit{ab initio} quantum chemical calculations.
  - Debye (‘crystal-like’) vs. non-Debye (‘glassy’) $G(\omega)$ at low $\omega$ and l-He temperatures
  - dynamics in glasses of ODIC, CONDIS and like phases

• Pharmaceuticals in bulk (native) state and as “micronized” or amorphized powders

• Matter under spatial confinement
  - “hard” nanomatrices (e.g. membranes)
  - “soft” confinement (e.g. microfibres)

• Materials for energy storage, e.g. plasticizer-SPE systems for Li batteries

• Catalysts

• Photonic materials of industrial applications
- The so-called Boson peak (INS) scales all excess heat capacities

- Excess heat capacity at liq. He temperatures — the domain of adiabatic calorimetry \(\rightarrow\) Japan, soon Inst. Nucl. Phys, Kraków.

- The experimental non-Debye heat capacities are successfully reproduced using the excess vibrational density of states measured INS.

Electrolyte solvents to optimize Li-ion batteries.

Science driver / objective:

- Low ionic conductivity of solvent-free SPEs
- PEO-miscible electrolyte solvent has been used as the plasticizer to promote the segmental motion of PEO chains.
- When the amount of the liquid plasticizer reaches a level where the ionic conduction is dominated by the liquid-in-polymer instead of the segmental motion of polymer chains, the SPE becomes a GPE.
- The GPE combines the advantages of the polymer electrolyte (high viscoelasticity) and liquid electrolyte (high ionic conductivity), and is of great significance in the Li-ion batteries.
Electrolytes to optimize Li-ion batteries. Li coordination

Sulfolane-based concentrated electrolytes

Li ion hopping/exchange mechanism is dominant.

Tetraglyme-based concentrated electrolytes

Vehicular mechanism of Li ion is dominant.

GP membranes for safety of Li-ion batteries.

- (a) 
- (b) 
- (c) 
- (d) 
- (e) 
- (f) 

Scale: 40 μm, 800 nm, 6 μm, 2 μm