

Report on the First Niels Bohr International Academy Workshop-School on ESS Science

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The Niels Bohr International Academy (NBIA) Meeting on ESS Science was the first of a series of annual workshops which are designed to bring together widely recognized experts to promote advanced training for young post-graduates, postdocs and researchers with the aim of developing a practical approach to neutron scattering methods and complementary techniques.

This first meeting was devoted to the combined application of neutron scattering, NMR, and molecular dynamics simulations for studies of the dynamics of molecules in condensed matter. Presentations on the ESS and ongoing planning and instrumentation design activities were also included in the program. A total of 50 registered participants, among them 22 students, attended the meeting.

This workshop was sponsored by the Niels Bohr International Academy, the ESS Science Symposia, the PhD School of the University of Copenhagen, the Helmholtz-Zentrum Berlin and the Øresund Materials Innovation Community Program.

Key Findings:

- Effective participation by scientists in the planning and design of the instrumentation suite should be encouraged to ensure that ESS will be a truly multidisciplinary facility.
- The ESS is urged to give high priority to investments in infrastructure which provide user-oriented services, including facilities such as a deuteration laboratory as well as *simple* in-situ analytical facilities such as lab X-rays, thermal analysis, bulk magnetic measurements, etc...
- A clear need for better co-ordination between experimentalists and molecular dynamics experts in the field of neutron scattering.
- Urgent need for joint strategies to develop a theoretical group to work together with the ESS users.

- (i) **Accessibility of discussions of decisions on scientific research facilities.** Information on the development and design of the ESS facilities should be shared so that common points of interest among the scientific community can be easily targeted. The user community should be able to participate on a cooperative basis and be made aware of all stages of development, from the choice of the target design, and instrument specifications and layout to sample preparation, data collection, processing and interpretation. In the final analysis it is, of course, the outcome from of the data collection that the scientific (as well as industrial community) is interested in, such as information leading to new discoveries or to the possible design of new materials.
- (ii) **User-oriented services and partnerships.** Access to large scientific research facilities, which provide a wide range of user oriented services, is of critical importance to the development of state of the art research. It is therefore essential that a number of such services, or partnerships be discussed, planned and developed in parallel with the instrument suite. Examples include chemical and deuteration laboratories, extensive computing support, and the establishment of a theoretical group whose collaboration will needed for detailed interpretation of many of the experiments carried out at the ESS.
- (iii) **Creation of a strong “Science Link”.** Knowledge, experience, competence and creativity in a group of researchers are the foundation for taking up new initiatives. A key element of the development of the ESS facility must therefore be to establish venues for bringing together researchers from the neutron scattering community at large and the ESS AB. The establishment of the ESS Science Symposia is an extremely valuable element in this effort, but several other activities should be envisaged to create a stronger network between the new large research infrastructures and academia, research institutes and industry. For instance small group workshops should be held to discuss specifics of instrument design, software development, needs for theoretical support, ancillary experimental equipment, etc...
- (iv) **Improved coordination strategies.** Common challenges but diverse strengths should be unified: while individual approaches to promote innovation are fundamental, these must be extremely well coordinated in order to achieve

efficiency. Along these lines the user community should be able to readily contact a given instrument design team, be able to provide input on the great variety of scientific questions to be addressed with the aid of the ESS instrumentation. Moreover, ESS researchers, technical and support teams should be present in events organized (sponsored) by ESS AB, and available for discussions with, and to receive feedback from participants and prospective users.

Instrumentation for Studies of the Dynamics of Molecules

Observations of the various dynamic processes discussed in this workshop requires a range of instruments to cover the wide dynamic range of molecular motions from internal molecular vibrations to slow diffusion.

Vibrational spectroscopy is most efficiently carried out with an inverse geometry spectrometer using graphite analyzer crystals such as TOSCA – ISIS, VISION - SNS or LAGRANGE - ILL, although in some cases the Q-dependence of the vibrational spectra may need to be explored with the aid of a high incident energy chopper spectrometer such as MARI - ISIS or SEQUOIA - SNS. On the other hand, low frequency molecular excitations as well as fairly rapid rotational and translational diffusive processes can be observed with a wide variety of instruments, mostly in direct geometry (IN5 - ILL, CNCS – SNS, LET - ISIS) but also in inverse geometry (IRIS, QENS at the defunct IPNS). The latter instruments have a distinct advantage in terms of having high-energy resolution over a wide range of energy transfers in energy loss away from the elastic peak. At the ESS the concept of a cold-high resolution chopper spectrometer allowing for high resolution down to 4 μeV , reaching incoming energies beyond 80 meV is being carefully considered. Moreover, efforts are being placed to extend the spectral range of cold neutron spectrometers into the thermal range by using the so-called multi-spectral extraction system.

Measurements of motions at highest Q-range and longest time scales are made possible by using backscattering (IN16B - ILL, BASIS – SNS, SPHERES – FRM2) and Neutron Spin Echo (In10 and In15 – ILL, NSE – SNS) spectrometers.

Backscattering spectrometer with high *and* variable resolution

The scientific community represented at this meeting has expressed a strong interest in putting forward a scientific case for a backscattering instrument at the ESS with variable energy resolution in the μeV range in order to facilitate investigations, which can extend over a much greater dynamic range (range of accessible energy transfers) than is currently possible at other sources. Much of the molecular dynamics discussed at this meeting involves longer length scales, which in turn requires an increase of the corresponding time scale, i.e. higher energy resolution, for their observation. This strong scientific demand for higher resolution neutron spectroscopy instrumentation must be balanced by the need for a broad dynamic range including shorter timescales, which can be achieved by varying the energy resolution. A broadly conceived and

designed neutron backscattering spectrometer can cover a wide range of time- and length scales (Fig. 1) in between those probed with time-of-flight chopper spectrometers (ToF) and spin-echo experiments (NSE).

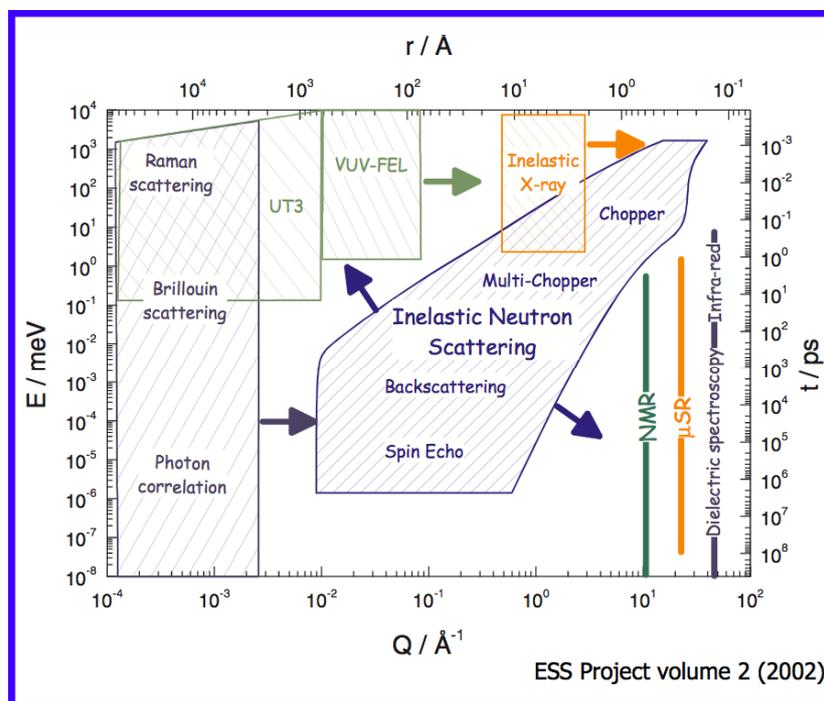


Figure 1 – Why do we need high-energy resolution?

Fields of research involving backscattering spectroscopy

Scientific applications of high resolution spectroscopy with a backscattering spectrometer can roughly be divided into two main areas of the $S(Q, \omega)$ space covered by this technique (Fig. 2), namely *low frequency inelastic spectroscopy* and *quasi-elastic neutron scattering*.

1. low frequency inelastic spectroscopy

- rotational tunneling spectroscopy (H_2 , CH_4 , $-CH_3$, NH_4 , ...)
- hyperfine interactions
- low frequency excitations in glasses, (e.g. aerogels & fractons);
and liquids (e.g. rotons in liquid helium)
- magnetic excitations, as in molecular magnets

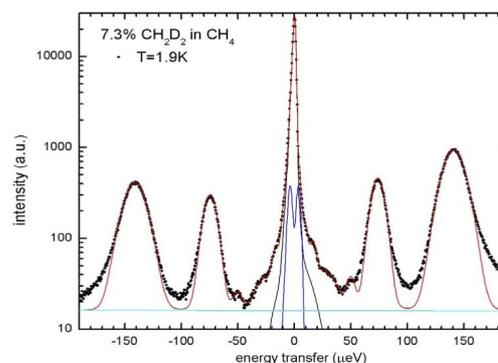


Fig.3 Data with fit on $CH_4:CH_2D_2(7.3\%)$ II measured at BASIS, SNS (ORNL) with a resolution of $3.0\mu eV$ (black line) at $T = 1.90K$. Fit results of all tunneling peaks are represented by the red line, the double peak in the centre is shown in blue and the background in light blue. The intensity is given in a logarithmic presentation in order to amplify the contributions of lower intensity - like that from CH_2D_2 II at energies between 10 and $55\mu eV$.

Q- ω map for high resolution spectrometers - TOF / - backscattering / NSE

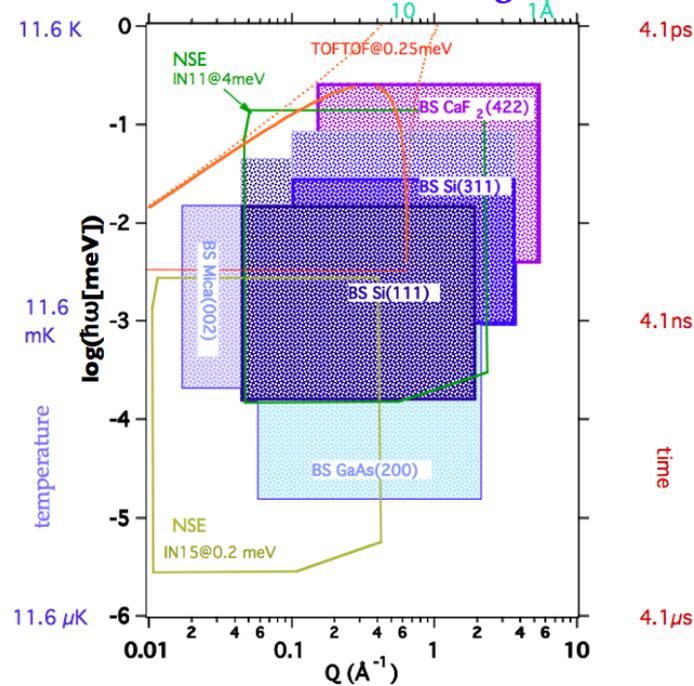


Figure 2 – The $S(Q, \omega)$ landscape, adapted from Bernhard Frick, 12th Oxford School on Neutron Scattering.

2. Quasi-elastic scattering.

Neutrons are said to be scattered quasi-elastically by a wide range of atomic and molecular motions not subject to essentially static, well-defined potential energy wells, the likes of which give rise to discrete excitations. Some examples of processes observable by quasi-elastic neutron scattering, and their relevance are as follows:

- Atomic diffusion and self-diffusion in metals and alloys
- Diffusion of hydrogen (H_2 , atomic H, H ions), or Li^+ , in metals, alloys, or porous materials (e.g. for H-storage materials), fuel cells (understanding of basic transport in membranes), materials for fuel cell electrodes, battery materials.
- Diffusion of atoms and molecules on surfaces in porous materials (gas storage) or in catalytic materials
- Dynamics of polymers, including thin polymer films, polymer blends, and nanocomposites,

- local motions of main chain and side chains,
- polyelectrolytes, dendrimers,
- changes of dynamics under stretching (orientation dependent studies),
effect of fillers on polymers dynamics (carbon black, silica, C60,..)
- microemulsion freezing phenomena
- Dynamics of biological or bio-related molecules
 - dynamical transition (e.g. glass like transition),
 - relationship between local mobility and function / stability,
 - role of water in bio-materials:
 - hydration water / confined water,
 - biological membranes,
 - natural materials (spider silk,)
 - Pharmaceutical systems: potential drug delivery systems,
 - functional molecules, relationship of local mobility to storage and stability
- Dynamics near the glass transition and in under-cooled liquids, P, T dependence of local dynamics near T_g , supercooled water, strong-to-fragile transition
- Dynamics of positional and of orientational glasses, liquid crystals
- Dynamics of molecules in confinement (nano-confinement in porous materials, nanotubes,...):
 - small molecules (e.g. clathrates), water, aqueous ionic solutions
 - mixtures in confinement,
 - water in geological materials, concrete, clays, surface water,
 - glass forming liquids, liquid crystals in confinement
- Dynamics of liquids: highly viscous liquids (oils,..), ionic liquids, ionomers, liquids under shear
- Proton transfer in hydrogen bonds
- Rotational diffusion (stochastic reorientation) of large molecules
- Dynamics of phase transitions, critical scattering
- Magnetism: spin glasses and frustrated magnets, spin ice

Both the time and spatial domains for the above dynamic processes are accessible to quasielastic neutron scattering, but it is the backscattering spectrometers which have the advantage of giving information over a wider range of Q when compared with direct geometry instruments of comparable resolution, whereby more detailed of the the geometry of the motion under study is obtained. Direct geometry instruments such as IN5 (ILL), DCS (NIST), and CNCS (SNS) can only reach relatively small values of Q at their highest resolution, while a backscattering spectrometer with several crystal analyzer banks can have an available Q -range from 0.02 \AA^{-1} to 6 \AA^{-1} .

Matching of time scales

QENS can therefore be considered to be an excellent technique for the observation of diffusive dynamics:

- Length scales/geometry accessible through Q -dependence
- Many phenomenological models form a framework for comparison
- Large range of time scales (sub-picosecond < t < nanosecond
- Sensitivity to molecules with H atoms
- Direct connection to theory (Molecular Dynamics Simulations).

However selection of the most appropriate instrument is a critical to the success of such an experiment since the resolution must match the time scale of the expected motion (Figure 3).

| | | ← (slow) ——— $S(Q, \omega)$ ——— (fast) → | | | | |
|---------------------------|-----------|--|----------------|-------------------------|---------------|-------------------------|
| Resolution ↑ ↓ | | delta- function peak | Narrow peak | Medium width peak | Broad peak | Flat back- ground |
| | | Low resn. (broad) | (Elastic) | Elastic | Elastic | Match |
| Med. resn. (medium) | (Elastic) | Elastic | Match | Flat | (Flat) | |
| High resn. (narrow) | (Elastic) | Match | Flat | Flat | (Flat) | |

Figure 3. Using variable resolution to match time scales. Adapted from John Copley (NIST School on Neutron Scattering).

It is imperative to remember that the reason for the spread in the values of available instrumental resolution, and as a consequence, the importance of having various types of instruments at a neutron facility, rests on two factors:

- i) improvement of each term in the resolution function has a cost that is linear in neutron flux (ideally)
- ii) **a gain of a factor of 2 in energy resolution has a cost a factor of 4 in flux at a minimum.**

Current backscattering instrumentation

Available neutron backscattering spectrometers may be classified as reactor and spallation-source based instruments. Third generation reactor-based instruments such as HFBS (NIST), SPHERES (FRM II) and, very soon, IN16b (ILL) use phase space transformation (PST) in the primary spectrometer to increase the incoming flux on the sample. Further gains in intensity can be realized from an optimized guide design, a faster Doppler drive and an expansion of the available analyzer surface. The new IN16b instrument at the ILL is expected to be the '*best in its class*' on account of its projected high signal to noise ratio resulting from the fact that entire spectrometer will be placed under vacuum. It has also been estimated that IN16b with an energy window of $\pm 30 \mu\text{eV}$ will have superior resolution than that of spallation source backscattering spectrometers, such as BASIS (SNS), DNA (J-Parc), IRIS and OSIRIS (ISIS), and should also be competitive in terms of neutron flux.

Backscattering spectrometers at spallation sources, however, can offer a significantly wider energy window in the range of several hundreds of μeV . The reason for this is the fact that the dynamic range of such a spectrometer is only limited by frame overlap, and consequently determined by the source repetition rate, the length of the neutron flight path and the bandwidth-limiting choppers. This idea is shown schematically in Figure 4, where $\Delta\tau/\tau$, θ and t are the spread of the analyzer lattice constant, the Bragg angle of the analyzer and the overall time-of-flight between the neutron source and the detectors, respectively.

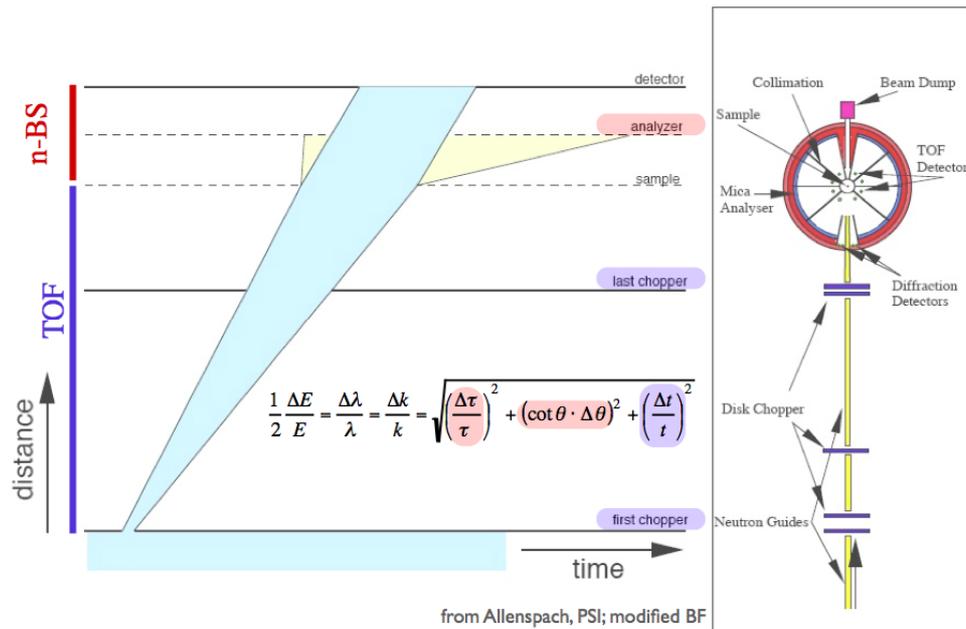


Figure 4. Backscattering spectrometers at spallation sources, examples: IRIS at ISIS, MARS at PSI, BASIS at SNS and DNA at JPARC.

The critical parameters, which determine the energy resolution are, however, in direct conflict with one another. For example, high-energy resolution comes at the expense of signal intensity, longer neutron flight paths improve the resolution, but decrease the dynamic range, and the available Q-range is reduced when analyzer crystals with large d-spacing are used to improve the energy resolution.

The term $\Delta\tau/\tau$ is controlled by the selection of the crystals with a desirably mosaic, (Fig. 5), but it is impractical at spallation sources to choose a Bragg angle θ of 90° to define $\Delta t/t$ and match the analyzer resolution of the primary flight path. This can be understood by noting that it would require an extremely long primary flight path to make the $\Delta t/t$ term sufficiently small to match the $\Delta\tau/\tau$ term.

Typical neutron backscattering monochromators:

| crystal plane | $\Delta\tau/\tau$ (10^{-3}) | ΔE_{ext} (μeV) | $\lambda(\text{\AA})$ for $\Theta=90^\circ$ |
|------------------------|---------------------------------|--|---|
| Si(111) | 1.86 | 0.077 | 6.2708 |
| Si(311) | 0.51 | 0.077 | 3.2748 |
| CaF ₂ (111) | 1.52 | 0.063 | 6.307 |
| CaF ₂ (422) | 0.54 | 0.177 | 2.23 |
| GaAs(400) | 0.75 | 0.153 | 2.8269 |
| GaAs(200) | 0.157 | 0.008 | 5.6537 |
| Graphite(002) | 12 | 0.44 | 6.70 |

<http://www.ill.eu/in16/bs-web-site/>

Figure 5. Primary extinction of some perfect backscattering crystals.

At this time BASIS (SNS) is the first realization of a silicon based time-of-flight backscattering with an energy resolution about one order of magnitude higher, $3.5\mu\text{eV}$ full width at half maximum (FWHM), than that of the ISIS backscattering spectrometers OSIRIS (FWHM= $24\mu\text{eV}$) and IRIS (FWHM= $16.5\mu\text{eV}$).

BASIS, IRIS and OSIRIS have simple ballistic neutron guides: a guide with rectangular geometry and linear tapered converging/diverging sections for increasing the cross-section of the guide with a length of the order of 90 m. Conversely, DNA (J-Parc) is only 40 m long and uses a pulse-shaping chopper (PSC) to shape the pulse and utilize the higher intensity of a coupled moderator. The combination of the PSC with the short pulse length makes it possible to reach μeV resolution. The guide of DNA is elliptical in the vertical plane to achieve maximum transmission at the sample position, and is curved in the horizontal plane to avoid a direct line of sight to the moderator. This type of novel approach is also under consideration for the design of the new FIRES instrument at ISIS (Fig. 6). This planned instrument also demonstrates that the use of a curved geometry, to avoid the direct line of sight, as part of a hybrid design which combines a curved ballistic guide and an elliptic focusing section appears to be the best solution. These spectrometers all work in near backscattering with Bragg angle θ of about 88° .

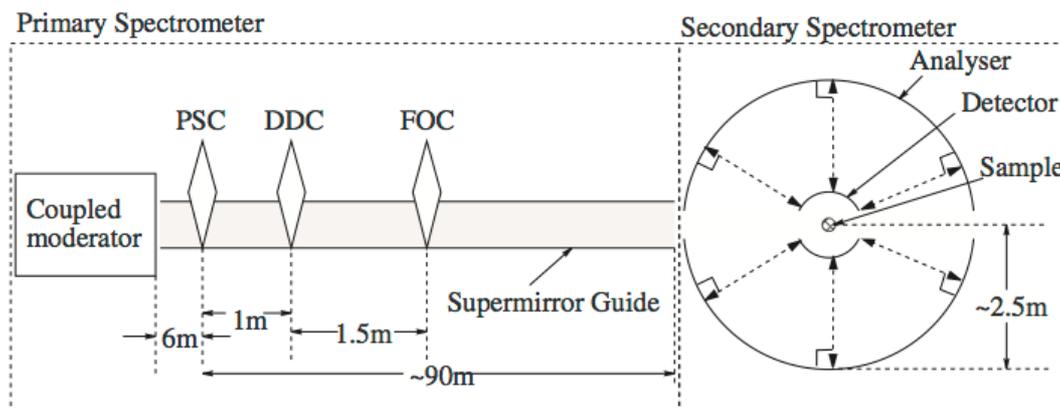


Figure 6. The proposed FIRES set-up, showing the pulse shaping chopper (PSC), double disk chopper (DDC) and frame overlap chopper (FOC).

Molecular Dynamics and Neutron Scattering

The interpretation and ultimate utility of quasielastic neutron scattering experiments can be greatly enhanced by parallel molecular dynamics (MD) simulations. From a solution of the equations of motion for all the atoms in the system at each time step in the simulation, the evolution of the positions and velocities of the atoms can be tracked as a function of time. The forces between the atoms can either be taken from empirical force fields, as is necessary for a large number of atoms (biomolecules), or *ab-initio* forces from quantum chemistry for smaller systems. Examination of the atomic positions at various steps leads to the atomic pair-correlation function, which is direct space Fourier Transform of a powder diffraction pattern. The time evolution of the atomic positions, on the other hand, is related to the self diffusion constant, which can be directly compared with the same quantity obtained from analysis of QENS experiment. In somewhat more general terms we see that the dynamic structure factor, which is determined in neutron scattering experiments (both inelastic and quasielastic scattering), is essentially given by the power spectrum obtained from an MD simulation by a Fourier Transform of the velocity autocorrelation function. Time scales of the dynamics that can be studied in this way then depend on the length of the simulation, typically 10fs-100ns, with length scales in the range of 0.1 to 100 nm.

The real power of the QENS technique rests in the fact that both temporal and spatial information on the dynamic processes can be extracted, and both of these are also

accessible by MD simulation. The sort of phenomenological models (e.g. jump diffusion, continuous diffusion, etc.) typically in the analysis of QENS data can thereby be placed on in the context of the specific atomistic model used in the simulation. This in turn greatly enhances the utility and importance of QENS experiments. Some examples of what can be learned from a combined application of QENS and molecular simulation are the self-diffusion of n-alkanes up to C₁₆ in zeolites, that of methane co-adsorbed with n-butane in silicalite-1, and transport diffusion of N₂ and CO₂ in silicalite,

It is therefore imperative that the ability to perform appropriate MD simulations to support virtually any QENS experiment be made available to users of the backscattering spectrometer. This may have to be done in collaboration with a group dedicated to computational support of neutron scattering experiments, as these calculations are not likely to be of routine nature in the foreseeable future.

Concluding Remarks: Why QENS? Why Backscattering?

- **Applicable to wide range of science areas**
 - Biology – dynamic transition in proteins, hydration water
 - Chemistry – complex fluids, ionic liquids, porous media, surface interactions, water at interfaces, clays
 - Materials science – hydrogen storage, fuel cells, polymers
- **Probes true “diffusive” motions**
- **Range of analytic function models**
 - Useful for systematic comparisons
- **Close ties to theory – particularly Molecular Dynamics simulations**
- **Complementary**
 - Light spectroscopy, NMR, dielectric relaxation
- **Unique: Answers Questions you cannot address in other ways.**

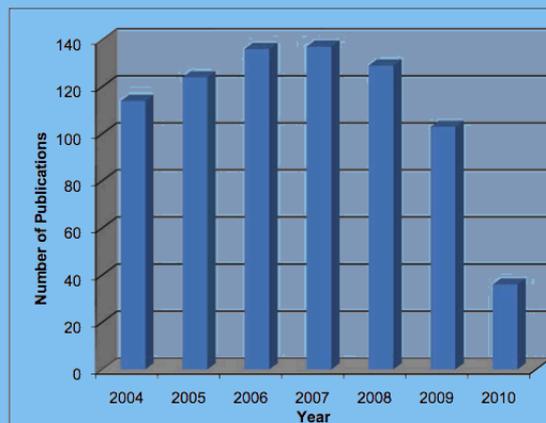


Figure 8. Quasi-elastic Neutron Scattering (Why Should we Care?). Adapted from Ken Herwig - ORNL. Note this talk was given in June 2010, explaining the lower number of publications that year in this graphic.