

# A Cold Neutron Chopper Spectrometer for the Spallation Neutron Source

1	Introduction.....	2
2	Scientific Case.....	2
2.1	Quantum Liquids.....	3
2.2	Rotational Tunneling Spectroscopy.....	4
2.3	Magnetism.....	6
2.4	Septroscopy: Adsorbates at Interfaces and Nanoporous Materials .....	7
2.5	Dynamics of Water .....	8
2.5.1	Confined and Interfacial Water.....	8
2.5.2	Environmental Chemistry: Water and Reactions at the Water-Solid Interface .....	9
2.5.3	Solvent Structure and Dynamics in Restricted Environments .....	10
2.6	Complex Fluids .....	11
2.6.1	Lubrication, Selective Adsorption and Diffusion at Interfaces .....	11
2.6.2	Polymer Dynamics .....	13
2.6.3	Diffusion in Biological Gels .....	14
3	Development Plan.....	<b>Error! Bookmark not defined.</b>
4	Instrument Description.....	<b>Error! Bookmark not defined.</b>
5	Instrument Performance .....	<b>Error! Bookmark not defined.</b>
6	Instrument Development Team.....	<b>Error! Bookmark not defined.</b>
7	Budget and Schedule.....	<b>Error! Bookmark not defined.</b>
8	Appendix 1 .....	<b>Error! Bookmark not defined.</b>
9	Appendix II.....	<b>Error! Bookmark not defined.</b>
10	Appendix III.....	<b>Error! Bookmark not defined.</b>
11	Referencers.....	16

# 1 Introduction

We propose the formation of an Instrument Development Team to pursue the construction and operation of a high resolution multi-chopper spectrometer. This instrument would have variable resolution and would simultaneously cover a broad range of both energy and momentum transfer. The resolution of the instrument, and the energy-momentum range covered, allow it to address a broad variety of scientific problems in areas as diverse as biomaterials, polymers, cements, magnetic system, geological systems, and quantum liquids. Furthermore, it will have 2 orders of magnitude more flux on sample than existing disc chopper spectrometers allowing it to address problems not possible at present.

The proposed instrument with energy resolution that is variable between 10 and 100  $\mu\text{eV}$ , over an incident energy ( $E_i$ ) range of 2–20 meV, is a high priority of the Instrument Oversight Committee<sup>i</sup> (IOC) and the user community<sup>ii</sup> of the Spallation Neutron Source (SNS) since it address a broad range of science. In addition, the spectrometer provides energy resolution and momentum transfer ( $Q$ ) ranges complimentary to the Backscattering and Fermi chopper instruments planned for the SNS.

The design of the proposed instrument is similar to IN5 at ILL and DCS at NIST. However, the instrument we propose will have much greater intensity, greater angular coverage at low angles above and below the scattering plane, and will utilize position sensitive detectors throughout. Thus, we expect that this instrument will support a broad range of science ranging from the motion of water in cements to single crystal studies of magnetic systems.

In this proposal we first describe some of the scientific areas on which the proposed instrument will have a major impact. We then describe the proposed instrument and our plan of action for constructing this instrument. We then describe the conceptual design of the instrument and its performance characteristics. Finally, we describe the structure of the IDT, the estimated cost of the instrument and the expected funding for construction of the instrument.

An important aspect of this proposal is that we are planning a two phase construction project. The first phase would see a limited capability instrument at IPNS in three years. The second phase would see the instrument fully operational at SNS on day one. We believe that this two phase approach, while increasing costs slightly, offer many overwhelming benefits. Among these are an extended commissioning period, an invaluable opportunity for the SNS to debug and evaluate systems such as detector electronics, data acquisition systems, and chopper controls, a chance to develop data analysis and visualization software, the opportunity to commission sample environment equipment, the ability to train students and develop a user community, and, if all goes well, the opportunity to carry out some science. We believe that the advantages of this plan to the SNS, the IDT, and the neutron scattering community far outweigh the additional costs it imposes.

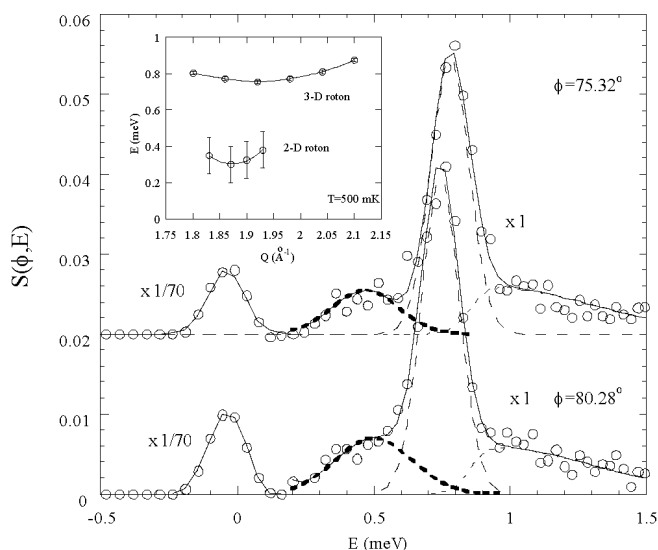
## 2 Scientific Case

The proposed instrument will addresses a broad range of scientific topics ranging from quantum liquids to magnetism to the dynamics of water in a wide range of environments from biological systems to cements. These topics are at the forefront in many different areas such as condensed

matter physics, materials science, chemistry, biology and environmental science. The proposed spectrometer, with its high intensity and adjustable resolution, will provide a powerful and flexible tool for addressing these problems. In the remainder of this section we describe just a few of the possible areas where this instrument will have a major impact.

## 2.1 Quantum Liquids

The atomic-scale dynamical responses of liquid and solid  $^3\text{He}$  and  $^4\text{He}$  are of special interest because they are strongly interacting quantum systems. Both liquid  $^3\text{He}$  and  $^4\text{He}$  exhibit superfluid properties at low temperatures and serve as model systems for studies of strongly interacting fluids<sup>1-3</sup>, critical phenomena<sup>4,5</sup>, superconductivity<sup>6</sup> and even - in the case of He - for exploring big bang dynamics relating to the birth of the universe. The spectrometer proposed here would be without equal as a device for measuring the dynamical structure factor,  $S(Q, \omega)$ , of quantum liquids in the wave vector range  $0.1 < Q < 3.0 \text{ \AA}^{-1}$  where collective excitations, such as phonons, rotons and zero-sound excitations, are observed in quantum liquids.



**Figure 2-1**  $S(\phi, E)$ , with background subtracted, for two scattering angles,  $75.32^\circ$  and  $80.28^\circ$ , located near the (bulk) roton momentum ( $1.92 \text{ \AA}^{-1}$ ). Shaded areas indicate additional scattering intensity lower than the bulk roton. Dashed lines denote fits to each individual scattering component (long dash: 3-D roton, short dash: multiphonon, bold dash: 2-D roton) and the solid line is the sum of these components. Inset: the dispersion of the 3-D and 2-D roton (shaded region) extracted from the scattering data.

Quantum liquids will undoubtedly continue to be of widespread interest for many years to come. Currently, for instance, there is much effort devoted to exploring the effects of disorder on the superfluid phase transition<sup>7-9</sup>. Disorder can have a profound impact on phase changes, even to the extent of altering the universality class of the transition. Spatial disorder can be introduced by confining liquid helium in porous media, such as aerogels and xerogels. A multi-chopper spectrometer is ideal for observing the small changes in the microscopic excitations that appear to be associated with the modified transport properties of such systems. For example, recent studies of these systems have reported the appearance of a new excitation — the two-dimensional roton. This excitation has a lower energy than the roton associated with the bulk

liquid. The observation of this new excitation allows the modified properties of confined helium, such as its heat capacity and superfluid fraction, to be understood in terms of the microscopic excitations of the system.

A different kind of disorder can be introduced into superfluid  $^4\text{He}$  by the addition of  $^3\text{He}$ . This “statistical” type of disorder is very different from spatial disorder because  $^3\text{He}$  atoms are fermions and therefore are not participants in the Bose-Einstein condensation, which is responsible for the superfluid properties of  $^4\text{He}$ . There is very little understanding of the microscopic effects of spatial and statistical disorder at the present time. High quality measurements are expected to be essential as further guides to the theory. Also multiphonon effects are important in distinguishing between the various theories.

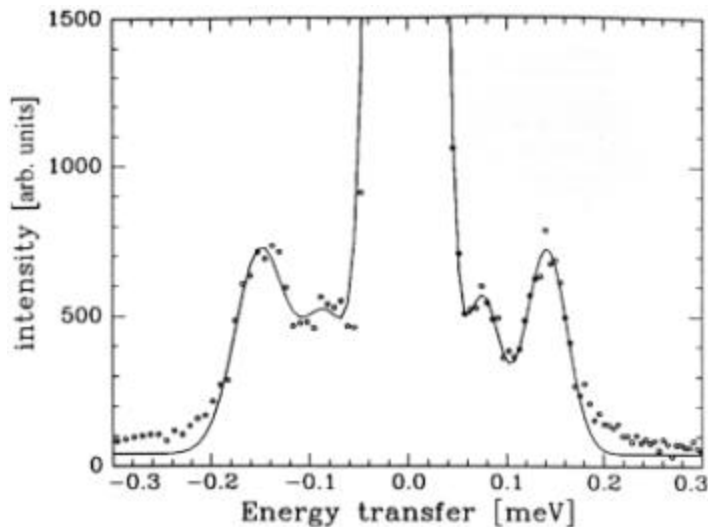
**Add discussion of measurements at negative pressures (ref Maris)**

## ***2.2 Rotational Tunneling Spectroscopy***

Hindered rotation and quantum rotational tunneling measured via inelastic neutron scattering can provide extremely detailed information on the shape and magnitude of intermolecular potentials<sup>10</sup>. Methods such as electron energy loss spectroscopy, helium atom scattering, and optical techniques can provide information on the higher energy molecular motions but do not provide the same sensitivity to the details of intermolecular potentials as high resolution neutron spectroscopy. Therefore neutron scattering is an ideal measurement technique for developing a fundamental understanding of intermolecular forces.

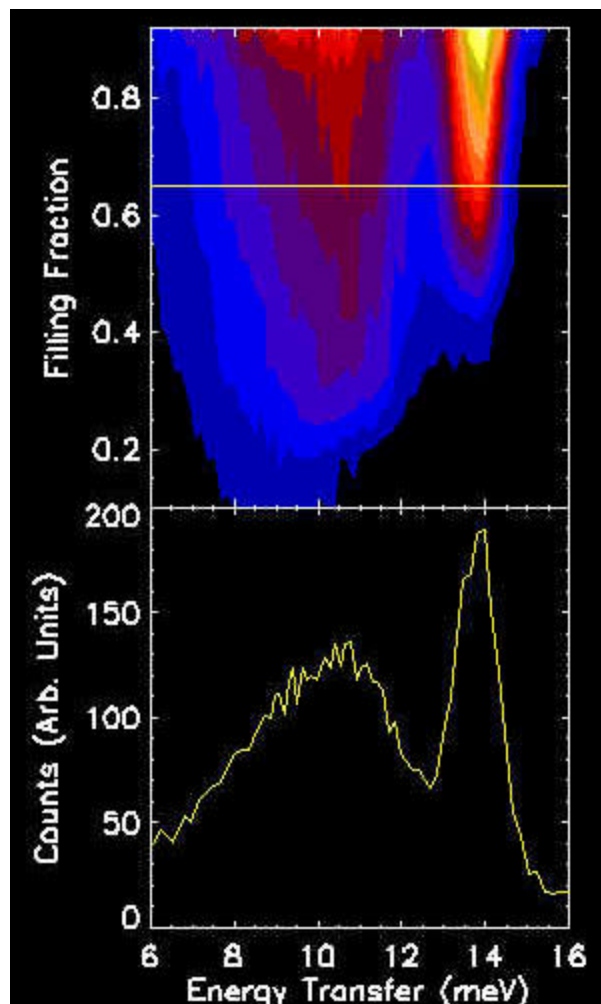
One of the recent developments in rotational tunneling spectroscopy (RTS) is its application to the study of adsorbed molecules<sup>11-14</sup>. These porous materials are playing an increasingly important role in the exploration of fundamental scientific issues related to diverse technological applications including adhesion, lubrication, tribology and engineering of materials. The surface interactions and finite size effects both play a key role in the qualitative modification of the properties of materials contained within the porous host. The rotational dynamics of the adsorbed species can be affected directly by the interactions with the surface so the resulting neutron spectra reflect the changes in the intermolecular potential.

Methane adsorbed on various surfaces and into porous hosts (Figure 2-2) is an excellent example in which a detailed understanding of changes to the intermolecular orientational potential due to the presence of a surface has been obtained<sup>12,13</sup>. RTS has also been used to illustrate that the effects of disorder on the tunnel spectrum in a simple molecular solid confined to a porous host<sup>14</sup> are similar to those observed in a glassy polymer system<sup>15</sup> where the structural disorder yields a distribution of local orientational potentials. These applications of RTS are useful in obtaining a fundamental understanding of the role of nanoscale disorder in the quantum dynamics and static structure of the adsorbed molecular system.



**Figure 2-2** INS spectrum of methane in a controlled pore glass taken with the high resolution chopper spectrometer MIBEMOL<sup>12</sup>. The excellent energy resolution was necessary to resolve the peaks at  $\pm 77 \mu\text{eV}$  and  $\pm 145 \mu\text{eV}$ .

**Figure 2-3** The top panel shows a contour plot of the inelastic scattering from H<sub>2</sub> in Vycor at various pore fillings at 6 K. The bottom panel is a cut through the contour plot at  $f=0.65$  (indicated by the line).



Another example, which exploits the broad energy range available with a multi-chopper spectrometer, is hydrogen adsorbed on surfaces. Free H<sub>2</sub> is well described as a quantum rigid rotor with discrete energy levels labeled by the rotational quantum number,  $J$ , and energies given by  $E_J = BJ(J + 1)$  where  $B$  is the rotational constant which is equal to  $7.35 \text{ meV}$  for H<sub>2</sub>. These energy levels are relatively insensitive to interactions that bind the molecule to a surface. However, they are very sensitive to orientational interactions which cause a shift in the rotational energies from their free molecule value. Figure 2-3 shows the scattering from H<sub>2</sub> adsorbed on porous glass as a function of hydrogen filling. The evolution of the system as the filling is increased clearly illustrates the crossover from surface dominated behavior to bulk like behavior.

Studying the rotational dynamics of adsorbed species requires both high intensity neutron beams because of the relatively dilute samples, and good energy resolution ( $\delta E < 100 \mu\text{eV}$ ) in order to resolve the low-energy tunneling modes. The multi-chopper spectrometer at the Spallation Neutron Source will be capable of providing the high intensity and excellent energy resolution necessary to study these interesting systems.

## 2.3 Magnetism

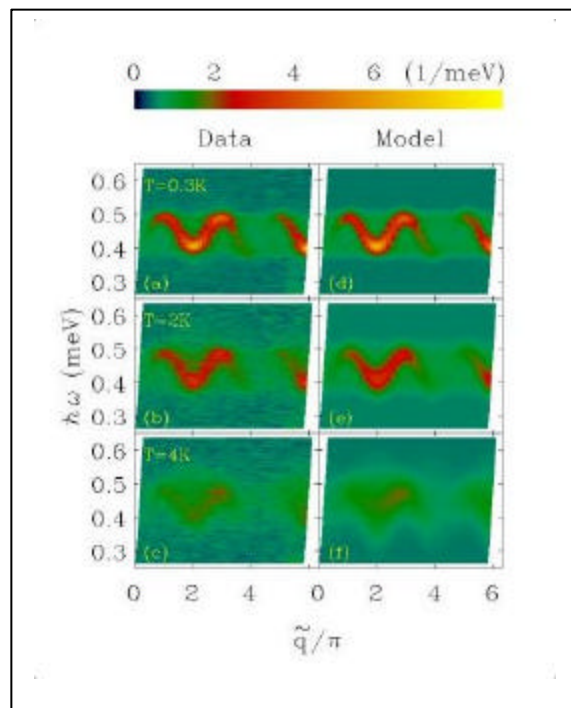
Despite many years of study, the fields of superconductivity and magnetism continue to provide new surprises as exemplified, for example, by the recent discoveries of high temperature superconductivity, giant magnetoresistance and colossal magnetoresistance. Apart from their basic scientific interest, magnetic materials in which electron correlations produce macroscopic effects are central to new developments in technologically important areas such as power transmission and information storage.

A high-resolution inelastic scattering spectrometer provides a powerful tool for the study of magnetic systems. In such forefront areas such as the study of quantum magnetism an instrument capable of measuring with energy resolutions of tens of  $\mu\text{eV}$  and momentum transfers of 0.1 to several  $\text{\AA}^{-1}$  is ideally suited to the study of low energy magnetic excitations, and subtle changes induced by small shifts of temperature or field. Many of the most interesting problems now under investigation, including quantum criticality, spin gaps, and non-Fermi-liquid materials, demand an instrument with these capabilities.

The potential impact of the instrument we propose on studies of magnetic systems is hinted at by results obtained to date using the IRIS spectrometer at the ISIS pulsed neutron source. Figure 2-4 shows measurements of magnetic excitations in the alternating chain system  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{D}_2\text{O}$ <sup>16</sup>. With a gap of 0.4 meV and a bandwidth of 100  $\mu\text{eV}$ , excellent resolution is an absolute requirement for obtaining the dispersion.

In addition to the one-magnon mode shown here, there is a much weaker two-magnon mode near energy transfers of 1 meV. This has been observed<sup>17</sup> using a cold triple axis spectrometer. Our proposed instrument would have the resolution and intensity to characterize both excitations simultaneously. The quasi two-dimensional antiferromagnet  $\text{K}_2\text{V}_3\text{O}_8$  has a small energy gap of order 100  $\mu\text{eV}$ , with dispersion ranging up to a few meV. The dispersion measured at IRIS<sup>18</sup> is shown in Figure 2-5. Neutron diffraction<sup>19</sup> has revealed that a small magnetic field closes the gap and leads to an exotic spin-reorientation transition. The proposed instrument at SNS would allow for simultaneous measurements of the gap and full dispersion as a function of applied field and temperature, offering the possibility of a much better understanding of quantum critical phenomena associated with the closing of spin gaps by applied magnetic fields.

As a final example of a physical system where the new instrument would have an impact, we consider the non-Fermi-Liquid material  $\text{UCu}_{5-x}\text{Pd}_x$ , for which measurements on different machines<sup>20</sup> had to be combined to obtain evidence for unconventional scaling of the magnetic fluctuations. Better resolution combined with a large bandwidth would enable similar studies to be carried out on a single machine. Accounting for the additional intensity available at SNS, one may also



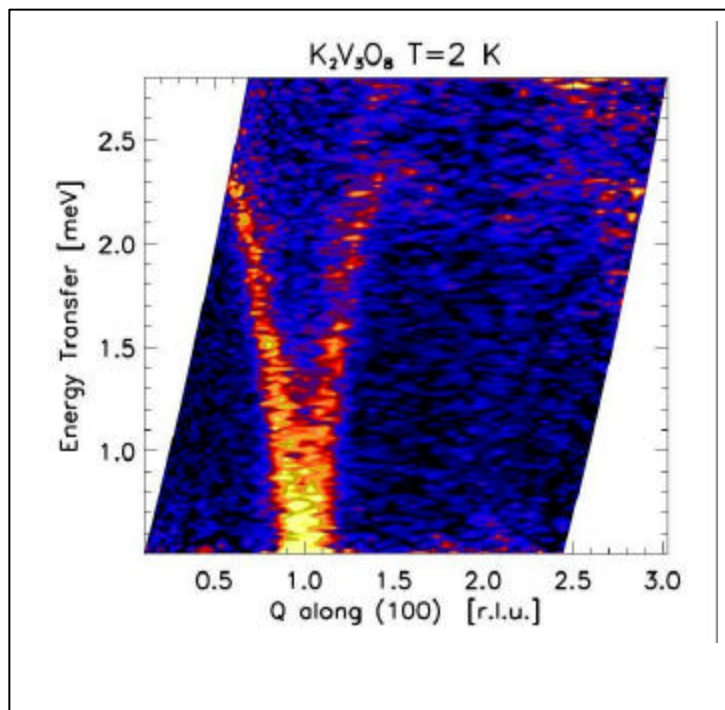
## CNCS Proposal

consider studies with smaller samples. All of these factors point to some

remarkable opportunities for forefront research on magnetic materials using the proposed instrument.

**Figure 2-4** One-magnon mode in the alternating chain material  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{D}_2\text{O}$  measured using IRIS.

**Figure 2-5** Dispersion of magnetic excitations in the quasi-two dimensional antiferromagnet  $\text{K}_2\text{V}_3\text{O}_8$  as seen with the IRIS spectrometer.



## 2.4 Spectroscopy: Adsorbates at Interfaces and Nanoporous Materials

The chemical changes that occur at interfaces during heterogeneous catalysis using zeolites (for example) represents a challenge to experimental and theoretical techniques. The shape selectivity of these materials derives from the shape and size of the voids and pores in these inorganic crystals. The interaction of adsorbates with the active sites and the diffusion of reactants and products in the internal voids enhance the production of specific products. These are commonly used to provide basic feed stocks for the chemical industry. Neutron scattering is well suited as a probe of these properties. Vibrational spectroscopy studies of adsorbates located at preferred sites in the catalyst allow for the in-situ characterization of reaction intermediates. The weak interaction of the neutron with most isotopes allows for bulk measurements, focusing on the intra-crystalline species.

The vibrational spectroscopy of adsorbates is mainly concerned with the lower frequency intramolecular and external modes of the adsorbate. When a molecule attaches to a characteristic site in the adsorbate, the strength of that interaction can be probed using vibrational spectroscopy. It is also in principle possible to probe the dynamics of adsorbents such as zeolites, where the frequency and amplitude of the framework motion is related to inter-void diffusion. The straightforward amplitude weighting of the neutron intensities is of considerable benefit in such studies. At higher frequencies, the vibrational spectroscopy of adsorbates that form intermediates (e.g. proton transfer from H-ZSM-5 to bases) can provide considerable insight into the nature of the chemical forces which shape the catalytic activity of such materials.

For the case of diffusion, neutron scattering can provide dynamical information on the characteristic length scales of zeolite structures, and the time-scale for site-site movement. A characterization of such microscopic details regarding the adsorbate-zeolite interaction provides

a quantitative basis for the understanding of the performance of these catalysts, in addition to the important question of the verification of computational modeling approaches.

Although some characterization of adsorbates is currently possible, the experiments are typically limited to adsorbates containing hydrogen. Even in such favorable cases (hydrogen incoherent neutron scattering cross-section is 16x greater than most other atoms) it is often not possible to obtain sufficient signal from such dilute systems. It is often also the case that the resolution of the instrument limits the interpretation of the data. A significant increase in intensity is required, some of which could be sacrificed in those cases where resolution is of importance. For the dynamics of non-hydrogenous adsorbents and adsorbates, extra intensity is a fundamental requirement for further development in this field.

The planned multi-chopper instrument is well suited to studies of adsorbates in nanoporous compounds as the length scales probed by such an instrument spans the range of characteristic lengths in, for instance, zeolites. The time scale of the diffusive motion in nanopores is typically suited to the good energy resolution envisaged for CNCS, and the energy transfer range will be very useful to explore unusual non-Lorentzian broadening effects. The low frequency vibrational motion characteristic of the interaction of the adsorbate with the nanopores typically occurs in the range 5-20 meV, and this energy range will be accessible on CNCS. Furthermore, the higher momentum transfers up to about  $4 \text{ \AA}^{-1}$ , and the better Q resolution obtainable using the proposed spectrometer will make coherent quasiclastic scattering studies a realistic option. This will also be aided by the expected improvements in signal-to-noise.

## **2.5 Dynamics of Water**

### **2.5.1 Confined and Interfacial Water**

Questions regarding the nature of diffusive motions of water in confined geometry and on surfaces of macromolecules have not been answered definitively in spite of the fact that it has been studied by every generation of neutron physicists. The reason is that these pioneers had access to only quasi-elastic spectrometers with resolutions of about 100 meV. They were forced to analyze their data with a model consisting of an elastic peak plus quasielastic contributions (all Lorentzians). It was not until Bellissent and Chen carried out studies with a resolution of 10  $\mu\text{eV}$  (IN5 at ILL) that we discovered that the quasi-elastic peak was not Lorentzian<sup>21</sup>. In fact, at lower temperatures, it was very well approximated by the Fourier transform of a stretched exponential relaxation function. Furthermore, there was no need of postulating the existence of an elastic peak, because the Fourier transform of the stretched exponential has a cusp at the elastic position, and it has a broad wing which can also be fitted with Lorentzians<sup>21,22</sup>. This is significant because the mode coupling theory shows that the lineshape is not necessarily Lorentzian. Spectrometers capable of studying the line shape are essential if the motion of water is to be understood. For this to be possible, the resolution has to be below 15  $\mu\text{eV}$ . One cannot forget that water molecules also undergo simultaneous rotational motion but those contributions are much broader. That means an ideal QENS instrument should have a variable energy resolution ranging from say 5 to 30  $\mu\text{eV}$  and the energy range covered (the dynamic range) should be as broad as possible because one is dealing with a broad shoulder.

The wave vector transfer range of  $0.1\text{-}4.0\text{ \AA}^{-1}$  is well suited to the study of diffusive motions of water. For a non-Lorentzian line shape the signal-to-noise ratio is very important as Fourier transform of a stretched exponential has a long tail which is difficult to resolve from a flat background. This will allow a broad range of problems to be addressed. These include:

- Coherent dynamics of heavy water in porous glass where a semi-localized, mixed, longitudinal-transverse branch of short-wave length sound dispersion relation may exist. Experimentally, the existence of a branch of propagating high frequency sound has been observed<sup>23</sup>. Also, supercooled D<sub>2</sub>O in Vycor has exhibited clear evidence of an alpha relaxation as predicted by MD<sup>24,25</sup>.
- Short-time confined diffusional motions of lipid molecules as well as the hydration water on lipid bilayers without and with peptide channels imbedded in them (experiments carried out using back scattering and Fermi chopper spectrometers at NIST recently).
- Single-particle, relaxational dynamics of hydration water in Portland cement as functions of temperature, additives, and aging of the cement paste (experiments carried out using MIBEMOL multi-chopper spectrometer at Saclay, France and a Disk-chopper Spectrometer at NIST recently).

### **2.5.2 Environmental Chemistry: Water and Reactions at the Water-Solid Interface**

Environmental chemistry has emerged recently as an important discipline within chemistry and, in its broadest definition, includes the study of chemical processes in atmospheric, aquatic, marine, soil, geological, biological and related engineered systems. A common component in all these systems is water, where it has been estimated that there is  $3.2 \times 10^{20}$  g of water in the biosphere. Furthermore, water is a major component of living organisms, e.g., comprising upwards of 70% by weight of the human body. As a result, most environmental chemical and biochemical reactions proceed in aqueous systems.

Because of its ubiquity in the environment, its importance to biological functioning, and its host of unique properties, water is the most extensively studied of all compounds.

Much of what is known about the structural and dynamical properties of water has been determined using neutron scattering techniques. In fact, the first diffraction study of liquids was conducted in 1946 using water. Since that time, the radial distribution function for liquid water, as determined using neutron scattering, has been a standard against which all molecular models of liquid water have been compared. The ability or inability of a given potential function to reproduce the experimentally-derived radial distribution function is a convenient and powerful test of that model potential's ability to reproduce the density and structural features of liquid water. A second test of a molecular dynamics-type computational model is its ability to properly reproduce the self-diffusion coefficient of water; here again, neutron scattering studies have played a significant role, where quasielastic neutron scattering studies have quantified the temperature and pressure dependence of the translational and rotational mobility of water. Similar studies have been conducted using the solid form(s) of water, and related neutron scattering studies have quantified ion solvation and the structure and properties of water at

surfaces. Of particular importance to environmental chemistry are reactions at surfaces. It has been estimated that there exists  $\sim 10^{18}$  m<sup>2</sup> of inorganic, organic and biological surfaces in soils and waters. Soils can have specific surface areas of <1 to >100 m<sup>2</sup>/g, and the role of surfaces in atmospheric reactions is well-known. A consequence of the abundance of both surfaces and water in the environment is that many important chemical processes in the environment occur at the solid-water interface. Examples of such processes include the dissolution and precipitation of minerals and the sorption and release of contaminants. Some argue that life itself began at the mineral-water interface.

Such reactions are ultimately important to a wide range of environmental quality and related health issues, and are important to waste containment, water treatment, contaminant transport, and a host of other natural and engineered processes.

Application of neutron scattering techniques will provide new insights into the environmental chemistry of water and reactions at the water-solid and other interfaces. Quasielastic neutron scattering has been used to quantify the translational and rotational mobility of water in layer silicate clay minerals, zeolites and other solid phases. Nevertheless, this approach has not been used extensively by environmental chemists, and there is considerable scope for further work, particularly in the area of organic contaminants. Finally, as described above, the capability for vibrational spectroscopy of adsorbed species should offer needed details about the state of adsorbed molecules, particularly for systems not amenable to traditional photon-based techniques.

CNCS is well suited for such studies because of its momentum transfer range, which probes on length scales of a fraction of an angstrom, to length scales which are characteristic of the cross-over from three to two-dimensional behavior in layered compounds such as clays. Furthermore, it is likely that the use of coherent quasielastic scattering will provide further insight into the transport properties of adsorbates, and the excellent Q-resolution will be an important asset.

### **2.5.3 Solvent Structure and Dynamics in Restricted Environments**

The nature of solvent structure and mobility can change drastically when the solvent is in a restricted environment. The aim of my research is learn how solvent structure and dynamics vary for molecules at surfaces, especially molecules at the liquid-liquid interface of reverse micelles. There are several different goals for our studies. We aim to learn how the specific interactions that molecules experience at interfaces influence the solvent structure and dynamics. We can then use this information to predict the role of restriction in chemical reactivity in these environments. We have designed further experiments to create and investigate novel reverse micelles that solubilize nonaqueous polar solvents and water/polar solvent mixtures in a nonpolar continuous phase. Such studies, that vary each component of the reverse micellar solution, will reveal the role of polar and nonpolar solvent and the role of the surfactant in reverse micelle formation and create new restricted media for chemical reactions.

Our initial experiments have focused on water in Aerosol-OT reverse micelles in isooctane. The water/Aerosol-OT/isooctane water-in-oil reverse micellar solutions have been exceptionally well characterized by various methods. Our studies have shown that the water in smaller sized micelles is largely bound to the Aerosol-OT polar head group while in larger micelles a water pool approaching bulk characteristics is observed; the dynamics of the water molecules vary with

micellar size. The efficacy of quasielastic neutron scattering (QNS) for determining water motion in Aerosol O1 (AOI) reverse micelles has recently been demonstrated. Our experiments at Colorado State University probe the dynamics of polar solvation indirectly via a probe molecule located inside the reverse micelles. To learn more about these systems, we have initiated a collaboration to probe the translational and rotational motion of water in various AOI reverse micelles.

Systems that we plan to explore include a range of polar solvents, polar solvent/water mixtures, surfactants and nonpolar solvents. The first investigations will focus on Aerosol O1 microemulsions sequestering nonaqueous polar solvents. However, many other systems are planned. Polar solvent properties such as dielectric constant, surface tension and hydrogen bonding will be varied to discover their role in reverse micelle formation. Potential polar solvents include methanol, acetonitrile, nitromethane, dimethylsulfoxide, formamide, N-methylformamide, N-methylacetamide, dimethylformamide, propylene carbonate, ethylene glycol, propylene glycol, and glycerol. Surfactants will be varied to explore the role of the surfactant head group interactions. In particular, anionic, cationic, nonionic and zwitterionic surfactants will be used to form microemulsions. Furthermore, the influence of nonpolar shape will be explored. Some nonpolar solvents to be studied include straight chain alkanes such as decane, branched alkanes such as isooctane, cyclic alkanes such as cyclohexane, and haloalkanes such as carbon tetrachloride.

QNS measurements on these systems can reveal basic information about the relative contribution of rotational and translational motion to ultrafast polar solvation dynamics, an issue of intense discussion among researchers studying solvation dynamics. In solvation dynamics experiments, the experimental results cannot distinguish contributions from solvent rotations and translations. In contrast, the QNS technique provides information about both solvent rotational and translational motions. Therefore, it may be possible to use the QNS results to determine the relative contribution of rotation and translation to solvation dynamics. Solvation dynamics measurements show that water is essentially immobilized in the smallest AOI reverse micelles but that for slightly larger reverse micelles, an ultrafast, bulk-like component appears, increasing with micellar size. QNS measurements will reveal whether both rotational and translational motion increase commensurately as the micelles grow.

The proposed research has the potential for tremendous impact on nanomaterial synthesis. New restricted environments will be discovered in which nonaqueous chemistry can be scaled down to nanoscopic proportions. This proposed research will not only push forward the limits of nanoscale chemistry, it will also provide in depth understanding of the forces driving reverse micellization. By solubilizing liquids in addition to water, specific molecular interactions can be correlated with micelle formation.

## **2.6 Complex Fluids**

### **2.6.1 Lubrication, Selective Adsorption and Diffusion at Interfaces**

Selective adsorption of a single chemical species onto a solid surface from a multicomponent fluid mixture is a phenomenon of wide interest in materials science and has far-reaching technological applications. An example of particular interest occurs in soft materials and

involves the adsorption of long flexible-chain molecules. Such polymers at solid interfaces are often used as coatings, lubricants, and adhesives. A microscopic understanding of their selective adsorption could potentially lead to significant advances in these technologies.

As discussed in a number of reviews considerable progress has been made in understanding the structure and thermodynamics of polymer mixtures near interfaces. This work has led to very interesting studies of polymer kinetics near interfaces at the macroscopic level. However, understanding of the microscopic dynamics of these systems is only at a very early stage of development. Some of the fundamental questions to be addressed are: how do long, flexible molecules anchor, diffuse, and desorb from a surface. At what rate do these motions occur and on what do these rates depend? In particular, how does the presence of solvent molecules in the interfacial region affect these motions?

The dynamical complexity of selective adsorption derives from the size and flexibility of the polymer molecules which introduces several time and length scales into the problem as well as the number of competing interactions involving the polymer, solvent, and interface. In the last five years, probably the most significant advances in studying polymer dynamics near interfaces have been made with computer simulations. The simulations that have treated the dynamics of the selective adsorption process in the most detail have necessarily used solutions of relatively short molecular chains with the molecules of choice being alkanes having the structure  $[C_nH_{2n+2}]_j$ . At present, intermediate-sized alkanes ( $20 < n < 40$ ) are at the limit of available computer power for simulations of fluid structure and dynamics near interfaces.

One of the most detailed studies of the dynamics of selective adsorption at the atomic level was performed by Xia and Landman. In their investigation of the segregation of a binary alkane mixture on a gold substrate, they found evidence of a dynamical adsorption mechanism involving a sequential, segmental, reptation-like penetration and adsorption process of the long-alkane chain. Such a mechanism had been proposed and discussed on the basis of macroscopic experimental studies of the adsorption-desorption kinetics of longer polymer chains. Thus, there is reason to believe that a quantitative understanding of the microscopic structure and dynamics of these model systems will aid in interpreting selective adsorption of more complex polymers.

Despite the effort which has been invested in simulations of the dynamics of flexible chains near interfaces, there have been strikingly few experimental studies with which to compare them. We describe here a comprehensive research program which responds to these recent developments in selective adsorption and builds on our own experimental investigations of the structure and dynamics of alkane films. It is comprised of quasielastic neutron scattering (QNS) experiments and computer simulations to probe, at the atomic level, the dynamics of binary alkane solutions near a solid interface. QNS is well matched to measure the diffusion rates which are calculated for the adsorbed intermediate-sized alkanes. In addition, structural studies will include new experiments utilizing techniques of synchrotron x-ray scattering and ellipsometry as well as an extension of our neutron diffraction experiments. Knowledge of the equilibrium structure of these alkane solutions provides a critical benchmark for validating the computer simulations and is a prerequisite for studies of molecular diffusive motion in these mixtures by quasielastic neutron scattering.

An extremely important stimulus for the computer simulations of flexible chain molecules near interfaces has been experiments utilizing the surface force apparatus (SFA) which have measured

the solvation forces between parallel surfaces enclosing a variety of complex fluids. These studies have demonstrated the remarkable effects of confinement on the structure and dynamics of fluids near a solid interface. However, the SFA experiments can only probe atomic length scales in a direction normal to the solid interface and are sensitive to the dynamic response of a confined liquid to shear on macroscopic time scales. Our neutron and x-ray diffraction experiments will probe molecular ordering in adsorbed films in directions both parallel and perpendicular to a solid interface, while our quasielastic neutron scattering experiments will probe molecular diffusive motion in these films.

Although our principal focus in this project is the study of selective adsorption of intermediate-sized linear alkanes as prototypes for a variety of longer chain molecules (polymers), these molecules are themselves of technological interest as lubricants. In fact, many commercial lubricants are mixtures of linear and branched alkanes so that it is of considerable interest to investigate selective adsorption in these systems. Thus far, studies have centered on the degree of layering that occurs in alkane fluids near surfaces, the dependence of this layering behavior on molecular architecture, and the implications of confinement induced ordering on the lubricating properties of films. Several very recent computer simulations of intermediate-sized alkanes have compared the structure and dynamics of linear and branched alkanes near surfaces as well as in the bulk melts. However, there is only a small database of diffusion constants from NMR experiments on bulk samples for testing these simulations. The QNS experiments on intermediate-sized alkanes ( $20 < n < 40$ ) which we are proposing will measure the diffusion rates of pure phases of linear and branched alkanes adsorbed on graphite as functions of temperature and film thickness for comparison with these simulations. Furthermore, our ellipsometry and synchrotron x-ray specular reflectivity experiments will allow us to compare the measured density profiles of linear and branched alkane films adsorbed on a single-crystal metal surface to those calculated in simulations. These experiments will be followed by QNS experiments to investigate the dynamics of linear/branched alkane mixtures.

### **2.6.2 Polymer Dynamics**

A signature of the long-chain nature of polymers is that dynamic processes in polymer melts and solutions occur not only on the picosecond (ps) time scale typically seen in low molecular weight organic liquids (ascribable in polymers to solvent dynamics and repeat-unit scale dynamics), but also on much longer time scales (>nanoseconds) resulting from coordinated motions of the chains. The manner in which local motions in polymers, such as conformational librations and rotations, are related to the coordinated, long time/large length scale motions is an important fundamental question that remains unresolved. The strong coupling of spatial and time scales manifest in polymer dynamics makes neutron scattering techniques the preferred methods in exploring the mechanisms of polymer dynamics. The unique ability of neutrons to variably probe distances on the order of interatomic spacing has led to a greatly increased understanding of local dynamics in polymers. Mechanistic understanding of these motions has been greatly facilitated by quantitatively accurate molecular dynamics simulations of polymer systems identical to those investigated experimentally. For the longer time/large length scale processes, neutrons have also played an important role, again greatly facilitated by quantitative comparison with simulation.

One approach is to focus on elucidating the mechanistic connection between local and chain dynamics in polymer melts, glasses and solutions through combined experimental and simulation studies. The systems of interest include glass forming polymers which exhibits relaxational bifurcation into a high-frequency and a low-frequency process as the temperature is reduced toward the glass transition, the structure and dynamics of aqueous solutions of hydrophilic amphiphilic polymers, and the structure and dynamics of polymer electrolytes. In the latter materials, strong intermolecular interactions strongly influence the conformations and dynamics of the polymer chains on time and length scales accessible to neutron scattering. Molecular dynamics simulations can provide detailed predictions of the motion of the atoms on the length and time scales explored on CNCS.

Fundamental studies of local and chain dynamics in polymers would be greatly facilitated by access an instrument such as CNCS, for the following types of measurements:

- Incoherent scattering of the 10 ps to 1 ns time scale to study conformational and hydration/solvent dynamics.
- Coherent QENS capabilities on the 10 ps to 1 ns time scale in order to study complexation dynamics in polymer electrolytes.
- Low-frequency inelastic scattering to study unusual vibrational features such as the Boson peak (typically below 10 meV)

The proposed momentum transfer range and energy resolution of the CNCS spectrometer is well suited these types of studies, down to approximately 100 ns. It will not be able to probe times down to 1 ns, but that is typically the domain of high-resolution backscattering and neutron spin echo instruments at reactor sources. The energy transfer range of up to 20 meV neutron energy loss, in conjunction with a good energy resolution will make CNCS an excellent choice for studies of the problems such as the relationship between the onset of diffusive motion and vibrational modes such as the Boson peak.

### **2.6.3 Diffusion in Biological Gels**

Hyaluronan (hA) is a naturally occurring polysaccharide and is an important molecule in biological systems. HA is a major component of the connective-tissue polysaccharides (or glycosaminoglycans), and in interstitial matrices. It is abundant in a number of biological fluids such as vitreous humour, synovial fluids, and umbilical cord fluids. The interstitial matrix contains approximately three-quarters of the total extracellular fluid, and the regulation of the water content of the matrix may play an important role in determining blood volume, especially during emergencies such as hemorrhage or dehydration. HA gels exhibit high water retaining and inhibition capacity and HA of high molecular weight ( $MW > 10^6$  Da) forms a gel even at rather low concentrations (~1% HA by weight). The specific roles of HA gels include the influence of the flow of water (hydraulic conductivity) and the inhibition of water in the tissue through relaxation of its concentration gradient (mutual diffusion).

One area of great interest is the physical properties of the gels and solutions formed by HA and HA/protein (such as collagen). In particular, we have concentrated on the mobility and transport of water in these systems. Studies of water mobility in HA gels, the role of HA in the resistance

to water flow, and the interaction of water with the polysaccharide molecules are required to understand the physico-chemical basis of the physiological function of HA. In addition there is evidence in the literature that supports a hypothesis that the release of fluid sequestered in the HA-based interstitial matrix into the blood space is dependent on depolymerization of HA by the action of the enzyme hyaluronidase (HAdase).

Quasielastic neutron scattering (QNS) has been used to probe the dynamics of water molecules in HA gels and gels treated with HAdase. Water that is tightly bound to the biopolymer appears immobile on the time scale of our experiments. A second, majority population of water is also present which exhibits diffusion rates that are reduced relative to water in its bulk liquid state. Time constants for mobile water in the gels range from 0.5 to 1 psec for rotational motion, and 1 to 5 psec for the time between translational jumps. The mean jump distance typically varies from between 2 and 3 Å.

A CNCS represents an ideal instrument to probe the translational dynamics, as it probes the time range from 1 to 30 psec and length scales ranging from 2 to 30 Å.

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