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NEW TECHNIQUES IN NEUTRON SCATTERING

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ABSTRACT

New neutron sources being planned, such as the Advanced Neutron Source (ANS) or the European Spallation Source (ESS), will provide an order of magnitude flux increase over what is available today, but neutron scattering will still remain a signal-limited technique. At the same time, the development of new materials, such as polymer and ceramic composites or a variety of complex fluids, will increasingly require neutron-based research. This paper will discuss some of the new techniques which will allow us to make better use of the available neutrons, either through improved instrumentation or through sample manipulation. Discussion will center primarily on unpolarized neutron techniques since polarized neutrons will be the subject of the next paper.

INTRODUCTION

The fluxes of today's best reactors and spallation sources are within about an order of magnitude of what is achievable with current technology and that limit is going to be approached closely by next generation sources such as the ANS and ESS. Although such a flux increase will offer some new opportunities in itself, neutron scattering experiments will remain signal-limited in most cases, and it will be important to continue the trend started in Europe two decades ago to make the best possible use of the available neutrons. There are four main areas of opportunity. First, to place as many instruments as possible on a given source and to transport the beams to them in an optimal fashion. This has led to extensive use of focussing crystal optics and of neutron guides, but further improvements in beam transport are still possible, especially with supermirrors. Second, the instruments can be improved, either through new methods based on physical ideas such as phase-space transformations or through improvements in hardware such as multidetectors. Third, better theoretical understanding of many complex systems has allowed far more information to be extracted from certain experiments than was thought possible only a decade ago, and this will continue to improve. Finally, clever tricks can be

played with the samples themselves to increase the information content of a given experiment.

In the fields of beam delivery and instrumentation, neutron optics has become a rich field for new development. Techniques being explored today include microbending and microfocussing through capillary guides[1], divergent beam reflectometry in which the surface is treated analogously to an imaging slit, optical filters for straight neutron guides, and reflectometry studies of interfaces under non-equilibrium conditions such as shear. On pulsed sources, imaging (radiographic) techniques have been extended to thermal imaging by resonant radiography. Tomographic methods developed for medical magnetic resonance imaging (MRI) applications are now being applied to radiography, and interferometer-based phase-contrast microtomography is becoming a possibility as multidetector resolution approaches the few micron level. Phase-space transformations are being considered for a variety of applications. These may simply use focussing or defocussing, or they may trade wavelength bandpass against divergence to obtain a better match between different parts of a spectrometer, for example in backscattering.

The past decade has seen an amazing variety of new fields in neutron science, ranging from experiments related to the astrophysics of the early universe to studies of human biology. Studies of surface and interfacial structure have developed around reflectometry, with liquid surfaces providing an especially rich field, while tunelling spectroscopy has provided a sensitive probe of the dynamics of molecules on surfaces. New techniques based on theoretical as well as experimental progress have opened up the rich field of complex new materials, which offer a wide variety of practical applications as well as a wealth of basic research topics. Other practical uses are being developed in several engineering fields. Residual strain measurements, for example, are now coming into widespread use at both reactors and pulsed sources.

Sample modification by contrast variation has been limited by chemical difficulties in some important areas such as biochemistry. That situation is now beginning to change as new laboratory techniques are developed. In structural studies, both at small and wide angles, resonance modulation techniques which vary the scattering amplitude of atoms at a given symmetry site in the structure are also starting to be explored again as appropriate instrumentation becomes more readily available. Another sample modification technique coming into widespread use is orientational alignment of structures in complex fluids, which overcomes theoretical difficulties related to correlation of orientation with position; that problem disappears if all structures have the same orientation. In this paper I shall address some of the new techniques which are either just being implemented or are the subject of active research and development. Rather than providing a lengthy catalog of methods, many of which have been discussed in other papers at this conference, I shall concentrate on just a few representative areas which are currently being explored and which may be routine by the time new sources come on line.

NEUTRON OPTICAL FILTERS

Most neutron guide installations have used curved guides, which have the advantage of providing a filtering action against fast neutron and γ background from the source. However, this filtering action also has a disadvantage. To ensure no line-of-sight, the curvature must be such that the guide bends through at least its own width in the length

available. For practical geometries, this leads to characteristic cutoff wavelengths typically around 0.2 - 0.4 nm, so that instruments on cold neutron guides are deprived of shorter wavelengths, and this often restricts the dynamic range of the data which can be taken on the instrument. Further, the neutron optical coating properties determine the guide width once the length and characteristic wavelength have been specified.

Straight guides offer the advantage that the length is decoupled from the width, so that the guide cross-section for a given instrument may be optimized without other restraints. They also transport all available wavelengths (with the usual wavelength dependent solid angle), but whether or not this is an advantage depends on the level of noise transmitted at the same time. Experience at the National Institute of Standards and Technology, which has installed straight guides, confirms theoretical expectations that the $1/r^2$ dilution of noise with distance usually provides adequate signal-to-noise at the distances from the source typical of guide hall instruments (of order 50 m). However, it will almost certainly be desirable to provide even lower noise for certain experiments and some form of filter will be needed. Crystalline filters, such as cooled single crystal silicon or bismuth, may be used as insertion devices to remove fast neutron or γ background, but these also cost a non-trivial loss of intensity in the desired wavelength range. We are currently studying the possibility of using a neutron optical deflector as a filter[2]. This deflector should have the characteristics of a high-pass filter which only transports neutrons above a specified wavelength, but which preserves the beam divergence. Curved neutron guides do not have the latter property; their exit divergence is a function of the guide properties, independent of the incident beam divergence.

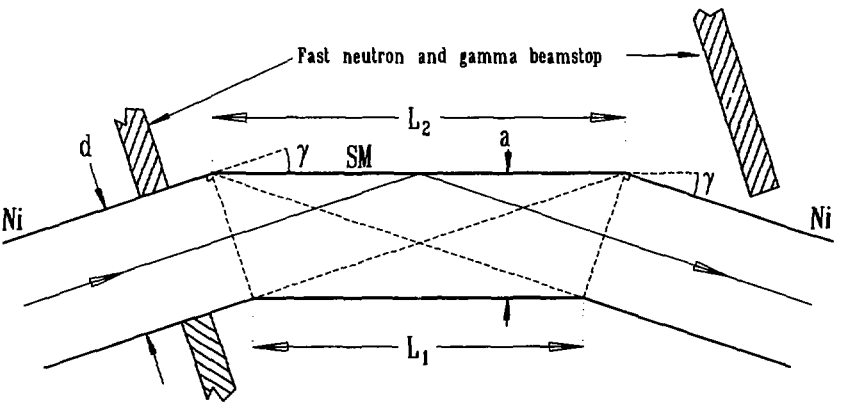

Fig 1. Plan view of an optical filter geometry

Figure 1 shows a plan view of one possible layout for this type of filter. Conceptually, it is equivalent to one section of a polygonal approximation to a curved guide. The initial Ni guide of width d is followed at an angle γ by a length of supermirror guide (SM), after which the Ni guide continues at a further angle γ. This geometry has the property that a parallel beam is transported with unchanged divergence, unlike the case of a curved guide. (Note that only the horizontal component of momentum is affected, so that the

top and bottom guide coatings may be chosen independently and may, for example, be supermirror throughout.) If γ is taken to be the critical angle for Ni at the shortest wavelength of interest, the supermirror critical angle must be twice that of Ni.

For this geometry, $L_2 = d/\sin\gamma$, $L_1 = L_2 - 2d\sin\gamma$, and $a = d\cos\gamma$. If d = 50 mm and γ corresponds to the Ni critical angle at a characteristic wavelength of 0.2 nm, a = 50 mm, L_1 = 14.323 m and L_2 = 14.324 m. The response of this arrangement has been estimated by a simple Monte Carlo simulation in which the divergence of the Ni guide was taken as uniform within the angular range corresponding to each wavelength, with an illumination angular cutoff corresponding to 1 nm. Figure 2 shows the results. The rectangles are simulation results for the device of fig. 1. The solid line is the response of a curved Ni guide of the same length as the filter and the dashed line is for an equivalent curved guide with a supermirror coating having twice the critical angle of Ni. The results show that the optical filter response is very satisfactory and permits all of the advantages of straight guides to be retained.

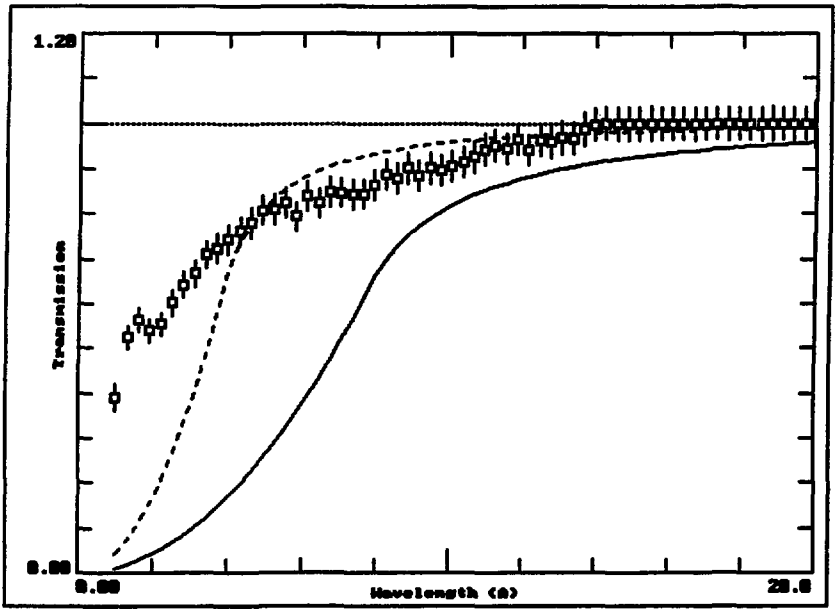

Fig. 2. Transmission as a function of wavelength for straight and curved optical filters (see text).

SAMPLE ALIGNMENT AS AN EXPERIMENTAL TOOL

Many of the fascinating properties of new materials are due to anisotropy of one kind or another, often in a structure which has no long range translational symmetry. Composites prepared *via* sol-gel methods provide a typical class of examples. The

correlation lengths of interest in these materials are typically in the range nanometers to micrometers, so that small angle neutron scattering (SANS) is often a method of choice. However, if the particles in the structure are correlated (as is usually the case in interesting systems), the scattering theory for such systems has proved highly intractable. The reason for this is that we have no statistical mechanical approach which allows us to compute the probability of a given orientation of one particle with respect to another as a function of distance and the thermal averages cannot be evaluated. However, if all particles have the same orientation, this problem no longer arises.

In many cases of interest, the sample is a colloidal dispersion of anisotropic particles, for example long cylindrical micellar structures in a surfactant or biosurfactant based complex fluid[3),4),5)]. In such systems, application of a hydrodynamic shear is often sufficient to align all of the micelles parallel, allowing fully anisotropic data to be collected and interpreted. There is an interesting variation on this technique when the system is dilute (*i.e.* the particles do not interact). In this case, a hydrodynamic approximation is available which allows the particle length tc be determined from the rate at which the scattering develops anisotropy as a function of the applied shear[3)]. This means that a SANS measurement on a sheared sample can assess lengths which are too large to measure directly by scattering alone.

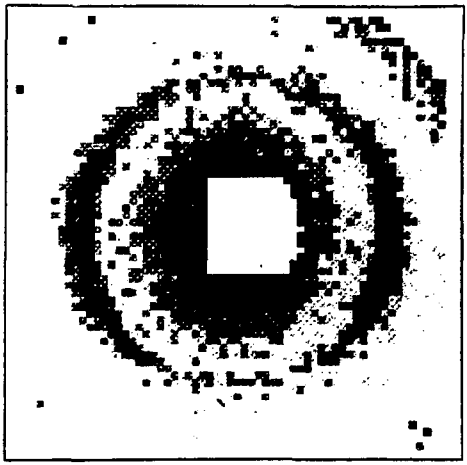

Fig. 3. SANS intensity pattern (Q_{max} = 3.55 nm^{-1}) for ferrodispersed tobacco rattle virus in 0.5 T applied field

Often there is a need to measure the internal structure of a large molecular structure in solution. Biological structures which may change conformation on crystallization or which cannot be crystallized are a case in point. In thses cases the scattering information is very difficult to interpret unless some degree of orientation can be imposed on the system. For systems which are not susceptible to alignment by hydrodynamic shear (because of a small aspect ratio) or by "brute force" magnetic fields (because of insufficient diamagnetic anisotropy) a new method is being tested[6)]. The macromolecules

of interest are dispersed in a magnetic solvent, such as a water-based ferrofluid. and then a modest magnetic field is applied. Application of a modest magnetic field then aligns the macromolecules due to cross-correlations which develop between the magnetic and non-magnetic particles. Figure 3 shows scattering from the internal helical structure of tobacco rattle virus (TRV), which is difficult to align by any other method.

RESONANCE MODULATED DIFFRACTION

Magnetic scattering of neutrons from electron spins has long been one of the most powerful applications of neutron scattering. Scattering from nuclear spins is much less common and generally is only considered insofar as it is a nuisance, causing the strong incoherent scattering background from hydrogenous samples, for example. However, nuclear spin-dependent scattering may be used to great advantage if the nuclear spin polarization in the sample can be manipulated appropriately. Protons, for example, may be turned into "heavy atoms" in diffraction experiments, aiding structure determinations in complicated protonated materials without the need for deuteration and its associated chemical complications. This method, known as resonance modulated diffraction (RMD), required great experimental complexity at the time of its first application[7] and was generally considered too difficult for general use. Advances in high-field, low temperature technology now permit its application fairly easily and there is renewed interest in the method.

Consider a sample in which the atom at position R_ν has nuclear spin I_ν. The coherent (COH) and incoherent (INC) scattering cross-sections for this system at momentum transfer Q are

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{COH} = \left| \sum_\nu \frac{1}{(2I_\nu+1)} [((I_\nu+1)a_\nu^+ + I_\nu a_\nu^-) \pm I_\nu(a_\nu^+ - a_\nu^-)p_\nu] \exp(i\,Q\,.\,R_\nu) \right|^2 \qquad (1)$$

and

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{INC} = \sum_\nu \frac{I_\nu(I_\nu+1)}{(2I_\nu+1)^2} (a_\nu^+ - a_\nu^-)^2 (1 - \tfrac{2}{3}p_\nu - \tfrac{1}{3}p_\nu^2) \qquad (2)$$

where $p_\nu = I_\nu/I_\nu$ is the local nuclear polarization, a_ν^+ and a_ν^- are the singlet and triplet scattering amplitudes, and the sign in eqn (1) is chosen according to the incident neutron polarization. When the nuclear polarization is zero (the usual case) these equations take the usual familiar forms.

The cross-sections (1) and (2) have interesting properties. First, when $p = 1$, the spin-incoherent scattering from the sample disappears completely, greatly improving experimental signal-to-noise. (Any isotopic incoherence will still be present, but for hydrogenous samples the noise is dominated by proton incoherence.) For an unpolarized beam the effects of polarization average to zero in eqn (1), but for a polarized beam the coherent cross-section may be greatly increased or decreased, depending on the relative directions of the neutron and nuclear polarizations. In particular, when the latter are

opposed, the coherent cross-section for a given polarization site becomes zero when

$$|p| = \frac{[(I+1)a^{+}+Ia^{-}]}{I(a^{+}-a^{-})} \tag{3}$$

which for protons ($I = ½$) is 0.27. Thus scattering from atoms at a particular symmetry site may be removed from the cross-section (1) for a polarized neutron beam if the local sample polarization can be appropriately controlled.

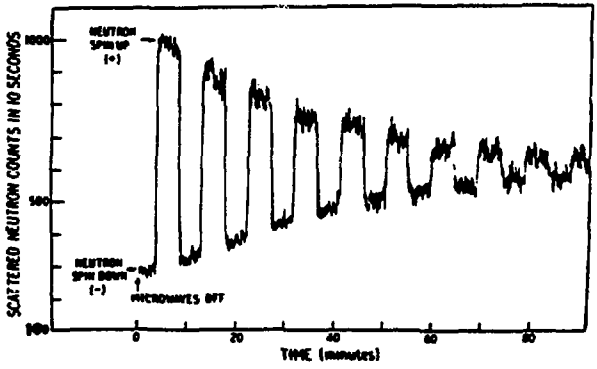

Fig. 4. Spin-dependent Bragg scattering from a hydrogenous sample with polarized nuclear spins

Figure 4 shows the large enhancement in scattering which can be achieved for one neutron spin state, and the suppression of scattering for the other spin-state, for Bragg scattering from a heavily hydrated crystal. In this experiment the nuclei were polarized by double resonance techniques using 69 GHz (4 mm microwave) ESR and 78 MHz NMR at 2.3 T and 1.5 K. When the radiofrequency pumping is removed, the scattering decays to the mean (unpolarized) value with the nuclear spin-lattice relaxation time constant (25 minutes in this case). Double resonance techniques have certain advantages but they are relatively complicated. Fortunately, commercial cryomagnets are now available which allow the use of simple thermal equilibrium in a field to polarize the nuclei.

The major interest of the technique lies not in the ability to enhance the signal and suppress the incoherent scattering, but in the possibilities it offers for the performing the equivalent of selective deuteration, site by site, simply by applying a radiofrequency field. Once the sample is polarized, the scattering from the atoms in a given symmetry class may be selectively "darkened" by applying the appropriate NMR frequency to depolarize that symmetry site. This may be done on a site-by-site basis, so that a series of Bragg intensities may be collected in which the scattering from different sets of atoms has been systematically altered in the unit cell. Figure 5 shows the effect on the system of fig. 4. The radiofrequency pumping is left on while the NMR frequency is scanned, with constsnt "spin up" neutron polarization throughout the scan. The sharp dip in intensity at the resonant frequency is clearly evident.

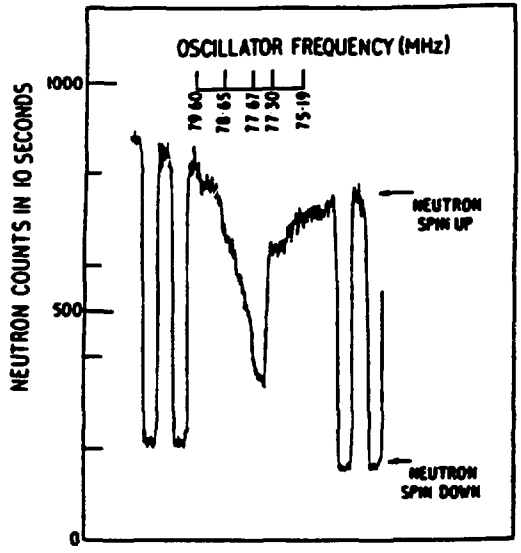

Fig. 5. An NMR scan switches off the enhanced scattering at resonance

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