Dynamically polarized sample at the Spallation Neutron Source

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Abstract. We report on the progress of the Dynamically Polarized Sample at the Spallation Neutron Source. The SNS DPS is a collaborative project with the Univ. of Virginia constructed for the purpose of polarized neutron scattering and diffraction. The project aims at significantly enhancing the signal-to-noise ratio by utilizing the strong spin dependent scattering cross section of hydrogen. One of the areas that are expected to benefit from this project is neutron protein crystallography, where a 10 fold gain in diffraction intensity and 10 fold reduction in incoherent background are within reach. The first step of the SNS DPS project uses a simple one Kelvin refrigerator and a 5 Tesla magnet. Our final goal is to design and build optimized setups for instruments such as the neutron protein diffractometer at the SNS (MaNDi). A brief overview of the DPS project will be given.

1. Introduction
The spin polarization of the nuclei in samples has the potential to greatly improve current experimental techniques. This is due to polarization dependence of neutron scattering. This polarization dependence is expressed by the spin dependent scattering amplitude, shown in Equation 1, where $\mathbf{I}$ is the spin vector for the nucleus, and $\mathbf{s}$ is the spin vector for the neutron.

$$b = b_0 + b_1(\mathbf{I} \cdot \mathbf{s})$$ (1)

The coherent (Equation 2) and incoherent (Equation 3) scattering cross sections vary as a function of sample polarization $P_I$, neutron polarization $P_n$ and nuclear spin $I$, as well as the quantities $b_0$ and $b_1$ shown in Equation 1. The effect is especially strong for the case of the hydrogen nucleus, which can be highly polarized in a variety of materials, including biological ones [1].

$$\sigma_{coh} = 4\pi(b_0^2 + P_nP_I \cdot b_0b_1 + \frac{1}{4}P_n^2I^2b_1^2)$$ (2)

$$\sigma_{inc} = \pi(I(I+1)b_1^2 - P_nP_I \cdot b_1^2 - P_n^2I^2b_1^2)$$ (3)

For the case of polarized neutrons, as the polarization of the hydrogen in the sample increases (where positive polarization is defined as polarization parallel to that of the neutron), the coherent scattering increases dramatically, while the incoherent scattering cross section drops
quickly, until the case of 100% sample hydrogen polarization, for which the incoherent scattering from hydrogen vanishes. For material which contains large quantities of hydrogen, notably biological materials such as proteins, the incoherent scattering from hydrogen is often the dominant source of background. This means that a possible ten fold increase in signal associated with the increase in the coherent scattering can be coupled with a ten fold decrease in the incoherent scattering, resulting in an overall factor of 100 gained in the signal to noise ratio. The cross section for a polarized neutron scattering off a proton as a function of proton polarization are shown in Figure 1.

![Cross section of polarized neutrons scattering off of a proton as a function of proton polarization](image.png)

**Figure 1.** Cross section of polarized neutrons scattering off of a proton, as a function of proton polarization, where positive proton polarization is defined as the proton be polarized along the direction of the neutron polarization \([2]\). Hydrogen (proton) polarizations of 97% have been achieved in optimized materials, with polarizations in the 75% to 85% range being achievable in a variety of materials, including biological ones \([1]\).

2. Dynamically Polarized Sample
The Dynamically Polarized Sample (DPS) program at the SNS hopes to develop a process and apparatus for polarizing sample materials in support of the beamlines at the Spallation Neutron Source (SNS). The polarization of samples will be done through a process known as Dynamic Nuclear Polarization (DNP) \([3]\). A full description of DNP is beyond the scope of this report, but briefly, it uses high magnetic fields (in this case, 5 Tesla), low temperatures (1 Kelvin or lower) and microwave radiation to induce high nuclear polarizations in specially prepared sample materials.

Materials to be polarized (with some exceptions) must be constantly in the high magnetic field and low temperature region, as well as being constantly subjected to microwave radiation in order to create or maintain polarization. This requires the design and construction of a magnet and cryostat that meet the necessary conditions, but still can accommodate the requirements of a neutron scattering instrument, such as overall size, construction materials, stray magnetic fields, and acceptance for scattered neutrons.

There is an additional requirement that the sample material be specially prepared before it can be polarized. This preparation amounts to the addition of a small number of paramagnetic centers (unpaired electrons that are free to align in the magnetic field). These centers will be
added primarily by introducing commercial chemical dopants to the material. Polarization is
generated in the immediate vicinity of the paramagnetic centers. The polarization then diffuses
throughout the bulk of the sample. The optimal concentration of these centers will vary from
material to material. It is therefore desirable to have a test setup, not on a beamline, which would
allow for the polarization of samples in parallel with any running polarized sample experiment,
in order to carry out tests of dopant levels. The test setup also has the advantage of being
much easier to build and operate, since it does not share any of the design requirements of the
in-beam apparatus. A test setup has been assembled at the SNS, which consists of a 1 Kelvin
helium-4 cryostat, a 5 Tesla magnet, a 140 GHz microwave EIO tube, and a 213 MHz NMR
system, which is used to measure the polarization.

3. Science Projects

3.1. Polarized Protein Crystals

Neutron scattering with protein crystals has been used widely to explore protein structure.
Typical techniques involve growing crystals as large as possible, and possibly deuterating the
sample in order to increase the signal size and lower the backgrounds. However, some proteins
do not lend themselves well to these techniques. They may not form very large crystals, or
the crystal structure may be altered or destroyed by deuteration. These protein systems could
benefit from the DPS program. The improvement in signal to noise ratio associated with nuclear
polarization is very evident in proteins, which generally have a very high hydrogen content. By
polarizing the protein crystals, it would be possible to get more data, with lower backgrounds
in the same amount of time, even with a smaller crystal and without the need to deuterate the
sample.

Polarization tests have recently been carried out at the University of Virginia, where we
polarized samples composed of lysozyme crystals dialyzed in a solution with TEMPO (a
commercially available paramagnetic dopant). Tests with lysozyme are done as a proof of
principle, since lysozyme is inexpensive, and crystalizes relatively easily. Initial tests were
done with just one concentration of TEMPO. While enhanced polarization was observed, the
polarization reached (approximately 20%) shows that it is necessary to produce samples with a
wide variety of TEMPO concentrations to determine what the optimum dopant level is. This
will be carried out both at the University of Virginia, and at the Spallation Neutron Source,
using the test setup, which is currently being commissioned. The process of finding the optimum
concentration for the paramagnetic centers may have to be performed for many different samples,
requiring that the test setup be run frequently.

3.2. Site Specific Polarization

It may be advantageous to polarize only the nuclei in a specific part of the sample. For instance,
one may want to polarize only the nuclei near a specific part of a protein, thereby highlighting
that site. The paramagnetic centers in the material cause the nuclei nearby them to experience
different local magnetic field. This means that there will be a shift in thier NMR frequency.
The bulk of the sample can be depolarized with continuous, high power RF radiation at the
NMR frequency associated with the DNP magnetic field. While this is done, the polarization
near the paramagnetic centers will remain high, so long as the DPS system remains operating.

A test of this technique was carried out at the University of Virginia, using samples prepared
at Oak Ridge National Laboratory. The samples were a solution containing the GAPDH protein,
along with a spin label derived from TEMPO. This spin label has an affinity for the active site of
the GAPDH, which will cause it to bind there. The sample was polarized to a reasonable level to
verify the usefulness of the spin label (for this technique high bulk polarization is not necessary).
Figure 2 shows the NMR signal when the sample was polarized to $-40\%$ (DNP is capable of
producing negative polarization as easily as positive, in this test negative was used), and Figure 3
shows the polarization of the sample as a function of time. After the sample was polarized, it was subjected to a de-polarizing NMR pulse, which succeeded in destroying the bulk polarization, leaving the polarization near the spin-label undisturbed. This was verified by watching the polarization near the spin label diffuse through the bulk. In a neutron scattering experiment, the depolarizing NMR pulse and DNP would be used continuously, resulting in a steady and high polarization near the spin-label, and zero polarization in the bulk of the sample.

Figure 2. Hydrogen NMR signal for polarized, spin labeled GAPDH. The NMR signal for enhanced polarization is a large and distinct peak, with a broad, parabolic background which is easily subtracted.

Figure 3. Hydrogen polarization of spin labeled GAPDH as a function of time.

4. Development
Work is underway to design and build a Dynamically Polarized Sample, which can be used in a variety of the neutron scattering instruments at Oak Ridge. The goal is to design a system which could be used on instruments such as MaNDi, the SNS neutron protein crystallography diffractometer. Such a system would have to be very compact, yet have large enough scattering angles available to acquire useful diffraction data. This may lead to the design of a 2.5 Tesla, dilution based system, or a frozen spin system [3]. This system would be used along side the test system that has already been assembled.

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