CREATION AND OBSERVATION OF POLARISATION DOMAINS: A NEW TOOL IN SANS

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Due to the strong spin dependence of thermal neutron scattering on protons, the scattering length density can be changed appreciably by polarising the protons in materials which contain hydrogen at sufficient concentration . By the method of dynamic nuclear polarisation (DNP) large positive and negative proton polarisations can be established in organic solvents like glycerol-H_2O mixtures, ideally suited as solvents for biomolecules, or in toluene, a standard solvent for polymers. In the past uniform proton (and deuteron) polarisations were used to change the scattering contrast between parts of a sample with different hydrogen density [1,2].

In the DNP method the thermal equilibrium polarisation of dilute paramagnetic centres is transferred to nearby nuclei by microwave irradiation close to the electron paramagnetic resonance (EPR) frequency, taking advantage of the electron-nucleus dipolar interaction. This interaction falls off with the third power of the distance between electron and nuclear moments, so nuclei close to a paramagnetic centre are polarised first while far away (bulk) nuclei rely on spin diffusion to reach equilibrium in a reasonable time. A very useful property of DNP is the fact that either positive or negative polarisations can be selected by an appropriate choice of the irradiating microwave frequency.

The large polarisations of the paramagnetic centres are generally obtained in fields of a few teslas at liquid helium temperatures. This implies the use of frozen samples.

For times that are short compared to spin diffusion the DNP process can create polarisation gradients. They are too short-lived, of the order of seconds, to collect SANS spectra with sufficient precision in one polarisation cycle.

We devised a time resolved acquisition scheme which allows the addition of the corresponding time frames of many identical cycles in a stroboscopic way [3]. The principle of the method is to switch the microwave frequency periodically from positive to negative polarisation.

As an example fig. 1 shows the SANS spectra at different times during the whole cycle of positive and negative polarisation obtained from a sample of 98% deuterated solution containing 5×10^{19} protiated Cr^V complexes/cm^3 [4].

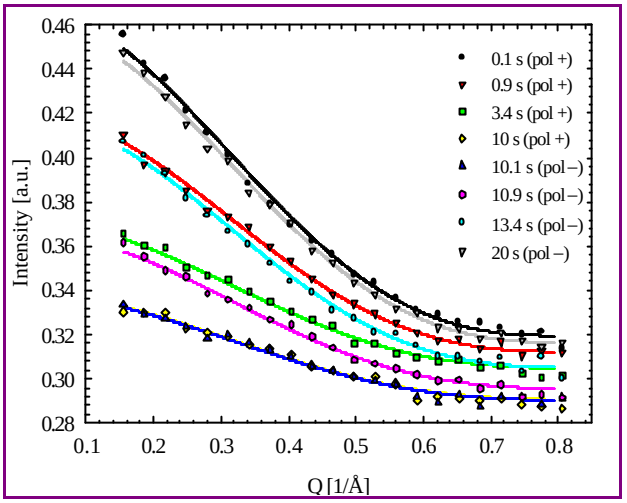

Figure 1. Time-dependent SANS

In this particular sample the scattering length density of the solvent is very weakly dependent on polarisation, so that the coherently scattered neutron intensity depends only on the polarisation of the 20 protons of the Cr^V complexes. Their polarisation could thus be inferred by fitting the SANS spectra of each time frame with a model function for the paramagnetic complex. NMR measurements, insensitive to these close protons, recorded simultaneously the evolution of the bulk proton polarisation.

The difference in the time-evolution of the polarisation between close and bulk protons shown in fig. 2 reflects the mechanism of DNP: a strong initial gradient develops due to a fast polarisation of the protons close to the paramagnetic centre which then spreads out to the bulk with a slower rate.

Polarised proton domains have been observed around several different paramagnetic centers (EHBA-Cr^V, "waxy"DPPH) and in different solvents (glycerol-water with up to 12% ^1H and polystyrene). Different cycling schemes, creating different initial conditions have also been used.

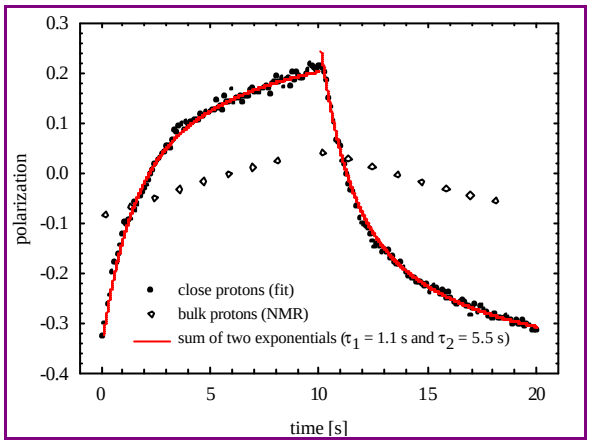

Figure 2. Close proton polarisation deduced from the SANS fit and bulk proton polarisation recorded by NMR

They all confirm the existence of transient polarization domains around paramagnetic centres. These observations open the possibility to increase strongly and selectively the contrast for neutron scattering from paramagnetic centres. For example, the scattering contrast of the 20 protons of the Cr^V complex polarised to 50% in a non-polarised protiated solvent would be two orders of magnitude larger than the magnetic scattering of the complex alone.

It could be possible to locate paramagnetic centres in macromolecules, like *e.g.* relatively stable radicals appearing in biologically active intermediates of enzymes (provided they can be frozen-in at low temperatures). By appropriate spin labelling it could also be possible to investigate selectively details of the structure of macromolecules. Preliminary results have been obtained from catalase samples containing tyrolsyl radicals.

Site selectivity in still another way could be obtained in samples containing several species of paramagnetic centres. Owing to their different EPR frequencies, polarised proton domains will only be established around those centres tuned to DNP.

All experiments have been performed on the PAPOL polarised neutron SANS instrument using our polarising set-up and at PSI and ILL (D22) with a similar PSI equipment in collaboration with scientists from PSI, ILL, IBS and TU Munich.

References

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