Neutron Scattering from Dynamically Polarized Protons Close to Paramagnetic Centers

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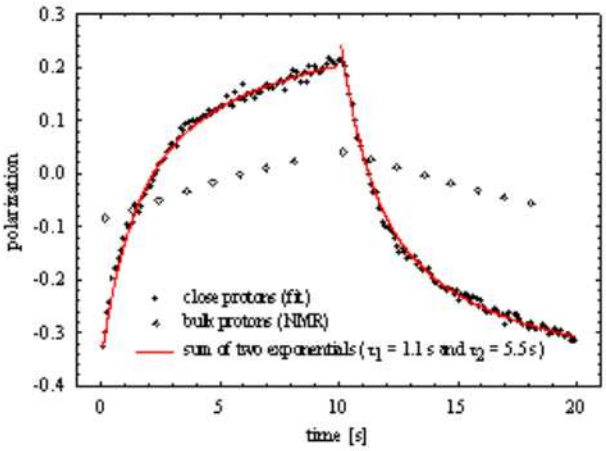
Dynamic nuclear polarization (DNP) is an efficient and widely employed method to create a high polarization of protons in hydrogeneous samples. The gist of the method consists in transferring a high thermal equilibrium polarization of the free electrons in paramagnetic centers to nearby nuclei by an off-center microwave irradiation of the electron spin resonance line. This creates a local nuclear polarization which then spreads out into the bulk of the sample via spin diffusion. We are developing new methods to obtain detailed information on this process in space and time. The first goal is a better understanding of DNP. Secondly, the technique described here and in more detail in [1], may open the way to novel structural studies, where domains of nuclear polarization may be exploited e.g. to earmark radicals in macromolecules for neutron scattering. The nuclear bulk polarization in very dilute electron paramagnetic materials (some 1000 protons on one paramagnetic center) is commonly measured via the integral of the nuclear magnetic resonance absorption line. Due to strongly shifted NMR frequencies, the polarization of protons in the range of the local magnetic fields of the paramagnetic impurities cannot be measured that simply. Scattering of polarized neutrons provides us a complementary method. As a consequence of the strong spin dependence of neutron-proton scattering, any local proton polarization creates contrast, which can be employed to monitor the dynamics of polarization domains. In recent and ongoing experiments at the ILL, LLB and PSI we have observed time dependent small angle neutron scattering (SANS) in samples of glassy glycerol-water mixtures at different deuteration, doped with a small concentration of the paramagnetic EHBA-Cr(V) complex, which contains 20 protons per molecule. The polarization direction was reversed periodically every 10 seconds by switching between two microwave frequencies, and we measured stroboscopically the corresponding change in the scattering intensity in time bins of 0.1 s length. Using a simple but realistic approximation of the scattering length density of the EHBA complex, the dependence of the intensity on momentum transfer could thus be fitted at all times with the polarization of the 20 protons of the Cr(V) centers as a fit parameter. The figure shows neutron and NMR data obtained with the solvent at 98% deuteration. The time dependence of the polarization of the 20 EHBA protons can be described with two exponentials, providing two different time constants of 1.1 s and 5.5 s.



Ongoing experiments will extend the method towards larger paramagnetic molecules and apply different NMR and microwave pulsing techniques. Issues are to study the diffusion barrier of the flow of nuclear polarization away from the paramagnetic centers and, from the viewpoint of possible applications, the stabilization of polarization gradients by suitable hf-fields.

References

[1] B. van den Brandt *et al.*,Europhys. Lett. **59** (2002) 62