

Peculiar effects in NMR relaxometry

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Nuclear Magnetic Resonance (NMR) relaxometry is an unique experimental method probing mechanisms and characteristic time constants of dynamical processes in condensed matter on the molecular (atomistic) level. The remarkably broad range of magnetic fields covered by NMR relaxometry: from about 10kHz to 40MHz (referring to the ^1H resonance frequency) implies that one can investigate, by a single experiment, motional processes across a huge range of time scales (from ms to ns). NMR relaxometry is widely applied to inquire into dynamical and structural properties of liquid and solid systems of various complexity: from simple liquids, via electrolytes and macromolecules to complex solids; the studies encompass diamagnetic, paramagnetic and superparamagnetic systems. The variety of dynamical features of the systems is reflected by their, often unusual relaxation properties. Interplay between spin interactions modulated by various motional processes leads to relaxation effects from which unique information about the dynamics can be revealed, provided appropriate theoretical models are available. I will discuss some of the relaxation phenomena, illustrating them by experimental examples; for instance:

- Relaxation in molecular liquids is a sum of intra-molecular and inter-molecular contributions. Intramolecular dipolar interactions fluctuate in time due rotation of the molecule, while inter-molecular couplings are modulated by translation diffusion of the interacting molecules. This implies that NMR relaxometry allows for probing rotational and translational dynamics by a single experiment, which is exceptional. Moreover, translation diffusion coefficients can be straightforwardly determined from the low frequency slope of the relaxation rate versus square root of the resonance frequency.
- Discussing relaxation processes for electrolytes (ionic liquids) one has to take into account that the system, in most cases, contains different types of NMR active nuclei (for instance ^1H containing cations and ^{19}F containing anions). In consequence, the shape of the relaxation dispersion data stems from several intra-es and inter-ionic relaxation pathways including interferences between ^1H - ^1H , ^1H - ^{19}F and ^{19}F - ^{19}F relaxation pathways. Moreover, for liquids in confinement, the motion in restricted geometry is reflected by the shape of the relaxation profiles that show then unusual properties.
- For solids containing nuclei possessing quadrupole moments one can observe frequency specific enhancement of the spin 1/2 (^1H , ^{19}F) relaxation, referred to Quadrupole Relaxation Enhancement. The relaxation maxima (“quadrupole peaks”) can be seen for systems undergoing slow dynamics when the magnetic field is set to a value for which the Zeeman splitting of the spin 1/2 nucleus matches the energy splitting of the quadrupolar nucleus (determined by its residual quadrupolar coupling and Zeeman interaction).
- In paramagnetic solutions the nuclear relaxation originates from strong magnetic dipole-dipole interactions between the electron spin of the paramagnetic molecule and the nuclear spin of the solvent molecules. Moreover, the electron spin relaxation acts as an additional factor modulating the electron spin – nuclear spin interactions, considerably influencing the nuclear relaxation and leading to Paramagnetic Relaxation Enhancement. For superparamagnetic nanocrystals the dipolar interactions with the large electronic magnetic moments lead to specific relaxation effects.