

Theory and Modeling of Molecular Modes in the NMR Relaxation of Fluids

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Nuclear magnetic resonance (NMR) relaxation is a powerful technique for probing matter non-destructively, with applications spanning medicine to material science to petrophysics. At high NMR frequencies, quantum effects are usually negligible, and a semi-classical statistical mechanical description is sufficient to model relaxation. Traditional theories of the NMR autocorrelation function for intramolecular dipole pairs assume single-exponential decay, yet the calculated autocorrelation of realistic systems display a rich, multi-exponential behavior resulting in anomalous NMR relaxation dispersion (i.e., frequency dependence). We develop an approach to model and interpret the multi-exponential autocorrelation using simple, physical models within a rigorous statistical mechanical development. We recast the problem of evaluating the autocorrelation in terms of averaging over a diffusion propagator whose evolution is described by a Fokker-Planck equation. Drawing inspiration from the idea of inherent structures in liquids, we interpret each of the spatial contributions as a specific molecular mode. These modes can be used to model and predict NMR dipole-dipole relaxation dispersion of fluids on the molecular level. We validate our statistical mechanical description of the molecular modes with molecular dynamics simulations interpreted without any relaxation models or adjustable parameters.