Correlated Brownian interface and translational dynamics simulation for nuclear spin relaxation in fluid membrane phases

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Lyotropic phases display complex dynamics involving thermally excited interface modes, with collective molecular motion of lipids and solvents, in addition to the dynamics at the individual molecule level (molecular rotation, vibrations etc.). Understanding these processes provides insight in how fundamental interactions (electrostatic and van der Waals) lead to colloidal interactions such as repulsive entropic forces.[1] In experimental study of membrane phases, the NMRD profile provides an outstanding capability of detecting the relevant, slow timescales,[2] complemented by NMR lineshape studies.

Theoretical explanation of NMR relaxation rates may be based on phenomenological assumptions, for instance $T_1^{-1}=\omega^{-1}$ dispersion[3] (where ω is the resonance frequency), continuum description of solvent-lipid interface (leading to analytical models[4]), Brownian translational dynamics (BTD) on a curved interface[5] and atomistic molecular dynamics (MD).[6] The MD simulation is attractive in its detail and has been shown to be promising in describing the structural properties of solvent D_2O.[6] However, MD does not explain the T_2^{-1} rate, has a too narrow linewidth and is able to straightforwardly *only* provide field-independent relaxation rates (not observed in experiments). The analytical models[4] may have assumptions of uncorrelated processes, not necessarily always valid.

In this work we present a mesoscopic Brownian dynamics simulation procedure level that mimics a lamellar, on average flat, bilayer with thermally induced interface undulations, combined with a spin system undergoing correlated reorientation due to BTD on the 2D interface. This enables a simulating system of 200 nm size (50 times larger than in a typical MD simulation) with sufficiently long (μs-ms) trajectories. We show that this procedure, combined with the D_2O structure and fast dynamics from the MD simulation[6] gives encouraging agreement with experimental relaxation rates and provides a framework that may be further generalized to interacting membranes, as well as furnished with time dependent quantum chemical spin tensors computed for the MD simulation.[7]

References:

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