

Macroscopic nuclear spin diffusion constants of rotating polycrystalline solids from first-principles simulation



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ARTICLE INFO

Article history:

Received 20 November 2014

Revised 12 February 2015

Available online 7 March 2015

Keywords:

Solid-state NMR

Low-order correlations in Liouville space (LCL)

Polarization transport

Numerical simulation

ABSTRACT

A method for quantitatively calculating nuclear spin diffusion constants directly from crystal structures is introduced. This approach uses the first-principles low-order correlations in Liouville space (LCL) method to simulate spin diffusion in a box, starting from atomic geometry and including both magic-angle spinning (MAS) and powder averaging. The LCL simulations are fit to the 3D diffusion equation to extract quantitative nuclear spin diffusion constants. We demonstrate this method for the case of ¹H spin diffusion in ice and L-histidine, obtaining diffusion constants that are consistent with literature values for ¹H spin diffusion in polymers and that follow the expected trends with respect to magic-angle spinning rate and the density of nuclear spins. In addition, we show that this method can be used to model ¹³C spin diffusion in diamond and therefore has the potential to provide insight into applications such as the transport of polarization in non-protonated systems.

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1. Introduction

Nuclear spin diffusion, the spontaneous exchange of polarization via dipolar coupling, plays a fundamental role in modern magnetic resonance. In hyperpolarization techniques such as dynamic nuclear polarization (DNP) [1–5] and optical pumping [6–8], it is spin diffusion that transports the hyperpolarization away from the source and into the bulk of the spin system. In NMR crystallography, the dependence of observed polarization transfer rates on the underlying crystal structure is exploited to obtain information about nuclear proximities [9–14]. In quantum computing applications, spin diffusion is responsible for the low fidelity and short coherence lifetimes of solid state NMR quantum gates [15]. The concept of macroscopic nuclear spin diffusion, first introduced by Bloembergen in 1949 to account for anomalous relaxation rates in single crystals of CaF₂ [16] is simultaneously one of the oldest concepts nuclear magnetic resonance and one of the least well understood. On a microscopic level, the exchange of polarization via dipolar coupling is well defined and can be readily simulated for small spin systems ($N \leq 13$) using standard density-matrix-type approaches [17–19]. However, the calculation

of macroscopic spin diffusion rates directly from atomic coordinates is complicated by the very large number of spins involved [20] as well as by effects such as powder averaging and, in the case of high-resolution NMR spectroscopy, magic-angle spinning (MAS). Typically, spin diffusion is described on the macroscopic scale using the diffusion equation or a kinetic model where the polarization transfer rates are determined either empirically or from approximations based on simulations of small spin systems [21–24]. While some analytical results have been obtained for model compounds such as CaF₂ [25–28], no general method currently exists for the calculation of macroscopic spin diffusion rates for large spin systems, directly from the atomic coordinates.

We have recently introduced a new simulation method, called LCL for low-order correlations in Liouville space, which uses a reduced Liouville space that includes only low spin orders to efficiently simulate spin diffusion in very large spin systems, directly from atomic coordinates and including the effects of magic-angle spinning and powder averaging [29]. LCL simulations of proton spin diffusion (PSD) and proton-driven spin diffusion (PDS) were shown to be in excellent agreement with experimental measurements of spin diffusion in powdered organic compounds, such as β-L-aspartyl-L-alanine and thymol [30], and L-histidine [31]. The LCL approach has been found to be effective for the numerical simulation of spin diffusion in systems of more than 100 spins undergoing MAS ($2\pi \times 2.5 \text{ kHz} < \omega_r < 2\pi \times 50 \text{ kHz}$) [30,32]. Related state-space restriction methods have been shown to accurately simulate the dynamics of very large spin systems in liquid-state NMR [33].

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In this work, we combine large- N simulations of spin diffusion, made possible by the LCL methodology, with an analytical solution of the 3D diffusion equation to extract macroscopic spin diffusion constants directly from crystal structures and including experimentally relevant effects such as MAS and powder averaging. We first describe the basic principles of the LCL approach and show how it can be used to simulate spin diffusion in a box. We then describe how a straight forward solution of the 3D diffusion equation can be adapted to model the LCL simulation results such that quantitative diffusion constants are obtained. This method is demonstrated for ^1H spin diffusion in two example spin systems derived from the crystal structures of hexagonal ice and L-histidine. The effect of MAS rate and ^1H spin density are discussed. In our final example we show that this method is also applicable to ^{13}C spin diffusion and explore how our approach could be used to examine the dependence of ^{13}C spin diffusion constants on the level of ^{13}C enrichment in diamond.

2. Theoretical methods

2.1. Low-order correlations in Liouville space (LCL)

The first step in our method for calculating macroscopic spin diffusion constants from atomic coordinates is to use LCL to simulate spin diffusion within a bulk crystal. The basic principles of the LCL approach are described below. A more complete description of this methodology can be found in Ref. [32].

The density matrix, σ , for a system of N spins $I = 1/2$ in Liouville space can be expanded as a linear combination of 2^{2N} basis operators, B_n .

$$\sigma(t) = \sum_{n=1}^{2^{2N}} b_n(t) B_n \quad (1)$$

Each member of the basis set, B_n , can be described as the product of N single spin operators, where E is the identity.

$$B_n = 2^{p-1} \prod_{i=1}^N I_{i,n} \quad (2a)$$

$$I_{i,n} \in \left\{ E, I_{n,z}, \frac{1}{\sqrt{2}} I_n^+, \frac{1}{\sqrt{2}} I_n^- \right\}. \quad (2b)$$

For each product operator, we define the spin order, p , as the number of constituent single-spin operators that are not the identity (E). For example, the single-spin polarization operator, $I_{1,z}$, has a spin-order of $p = 1$, while the product operator: $2I_{2,z}I_3^+$ has a spin order of $p = 3$. In Fig. 1a, we present a visualization of a density matrix in Liouville space ($N = 7$) where each dot is a single element, and the elements have been organized into rings according to spin order. (Note here we have limited ourselves to the zero-quantum

subspace, i.e. we include only those terms with a coherence order of zero. This can be done in the case of spontaneous polarization transfer with no loss of generality [32].)

A simulation of spin diffusion should calculate the evolution of the single-spin polarizations (the central ring); however, as the number of spins, N , increases the number of elements in the outer rings increases dramatically, driving the overall exponential increase in the size of the density matrix. This can be seen for the example of $N = 20$ spins in Fig. 1b, where we break down the total number of density matrix elements into the different spin orders. It is clear that the number of elements in the density matrix that correspond to low spin orders is insignificant compared to the number of elements that correspond to high spin orders. The central hypothesis of the LCL method states that in order to quantitatively simulate the dynamics of the single-spin polarizations it is not necessary to exactly simulate the full density matrix, but instead only requires the inclusion of spin orders: $p \leq k \ll N$. This corresponds in Fig. 1a, to carrying out the density matrix simulation for only the central k rings (shown here in green for $k = 4$). Using this approximation, systems with $N > 100$ can be simulated because, as shown in Fig. 1c, the growth in the size of the density matrix in the reduced space (green, $k = 4$) is polynomial in N , in contrast to the full-space density matrix (blue, $k = N$), which grows exponentially. It has been shown previously, through comparison with full-space ($k = N$) simulations and experimental measurements, that this approximation is valid when the system is subjected to a time-dependent interaction such as MAS; however, the approximation breaks down and produces non-physical results in the absence of spinning [29,32,34].

In order to use LCL to simulate spin diffusion within a bulk crystal, we define a box of dimension d^3 and fill it with the spins of interest at coordinates according to the structure. The system is initialized with a unit of polarization on the spin at the centre of the box and then it is allowed to evolve with time in the reduced space ($k = 4$) under the influence of the homonuclear dipolar coupling Hamiltonian, where r_{ij} is the distance between spin- i and spin- j and θ_{ij} is the angle between the associated internuclear vector and the bulk magnetic field. Each spin- i is coupled to every other spin- j within the box according to the distance, r_{ij} , between them within the box. Periodic boundary conditions were not applied.

$$H_D = - \sum_{i < k} \frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} \frac{1}{2} (3 \cos^2 \theta_{ij} - 1) (3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j) \quad (3)$$

MAS and powder averaging are included in the simulation as described in Ref. [32]. The LCL simulations do not include the effects of T_1 relaxation. Typical T_1 relaxation times in powdered solids are on the order of seconds or minutes, while the polarization transfer occurs on a millisecond timescale. Dynamic processes, which may be important in non-rigid systems such as polymers,

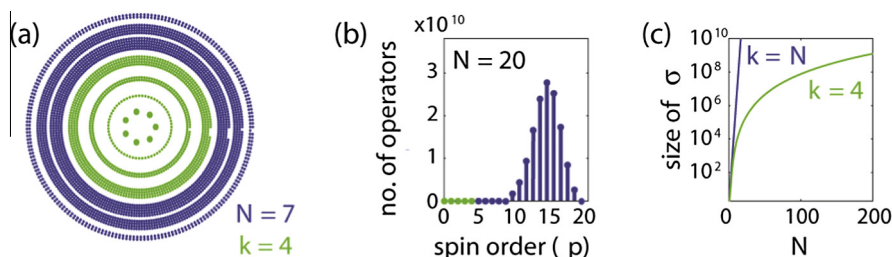


Fig. 1. (a) Liouville-space representation of the density matrix (zero-quantum subspace) for $N = 7$ spins. Each dot represents an element of the density matrix, organized in rings according to spin order, p . (b) Histogram of the number of zero-quantum-basis operators for a system of $N = 20$ spins as a function of spin order. (c) Size of the density matrix as a function of the number of spins, N , for the full-space ($k = N$, blue) and reduced-space ($k = 4$, green) cases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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