$^1$H NMR dipole-dipole relaxation of fluids cannot be explained by mono-exponential autocorrelation of individual $^1$H-$^1$H pairs

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The intra-molecular $^1$H-NMR dipole-dipole relaxation of molecular fluids has traditionally been interpreted within the Bloembergen-Purcell-Pound (BPP) theory of NMR intra-molecular relaxation. The BPP theory draws upon Debye’s theory of polar molecules in describing the rotational diffusion of the $^1$H-$^1$H pair and thus predicts a mono-exponential decay of the $^1$H-$^1$H dipole-dipole autocorrelation function between distinct spin pairs. Using molecular dynamics (MD) simulations, we show that for both $n$-heptane and water this is not the case. In particular, the autocorrelation function of individual $^1$H-$^1$H intra-molecular pairs itself evinces a rich stretched-exponential behavior, implying a distribution in rotational correlation times. However for the high-symmetry molecule neopentane, the individual $^1$H-$^1$H intra-molecular pairs do conform to the BPP description, suggesting an important role of molecular symmetry in aiding agreement with the BPP model. The inter-molecular autocorrelation functions for $n$-heptane, water, and neopentane do not admit a mono-exponential behavior of individual $^1$H-$^1$H inter-molecular pairs at distinct initial separations. Our study emphasizes the need for care in adapting ideas from the traditional BPP theory to predict NMR relaxation dispersion (i.e. frequency dependence) in fluids.

I. INTRODUCTION

In nuclear magnetic resonance (NMR) relaxation experiments, the nuclear magnetic moments (i.e. the nuclear spins) in the sample are aligned using a static magnetic field and then suitably perturbed using an oscillating magnetic field perpendicular to the static field. The relaxation time back to equilibrium following the perturbation is interpreted to gain insights into fluctuations of the local magnetic fields.

In fluids, the fluctuations in local magnetic fields happen primarily due to two effects: (1) the tumbling of the nuclear spins on the same molecule, which is responsible for intra-molecular relaxation, and (2) the relative motion between nuclear spins on different molecules, which is responsible for inter-molecular relaxation. Intra-molecular relaxation is ascribed to rotational diffusion, while inter-molecular relaxation is ascribed to translational diffusion. In the case of liquid $n$-alkanes and water, molecular dynamics (MD) simulations previously showed that intra-molecular relaxation dominates, especially with increasing carbon number [1,2]. On the other hand, for benzene and cyclohexane, inter-molecular relaxation dominates [3]. In other words, the molecular geometry and internal motions play a crucial role in the origins of the NMR relaxation mechanism in fluids.

Bloembergen, Purcell, and Pound (BPP) pioneered the use of NMR and specifically considered intra-molecular relaxation for a pair of nuclear spins [4]. Treating each spin pair as a rotationally diffusing unit, BPP assumed an exponential decay with time (similar to the Debye model) of the intra-molecular autocorrelation between the spin pair. Using MD simulations of a series of $n$-alkanes and water, we previously showed that the decay of the intra-molecular autocorrelation for $^1$H spin pairs on the same molecule does not conform to a mono-exponential behavior [1,3]. It is important to emphasize that in that study, even for water, which has only a pair of spins, the autocorrelation did not conform to a mono-exponential behavior. But water is also unique because of the strong inter-molecular hydrogen bonding and it is possible that this invalidates the freely rotating picture [5].

More recently, researchers sought to understand NMR relaxation in a molecular dynamics simulation of an ionic liquid [6]. These researchers suggested that the decay of the intra-molecular autocorrelation of $^1$H spins on the same molecule can be fit to a mono-exponential decay for distinct spin pairs. The researchers also described the inter-molecular autocorrelation of $^1$H spins on different molecules can be fit to a mono-exponential decay for distinct spin pairs and distinct initial spin-pair separations. These results stand in sharp contrast to our earlier study, and raise the natural question whether the behavior that we found for the intra-molecular relaxation in $n$-alkanes can be described by treating distinct spin pairs as distinct rotationally diffusing units.

Here we study the aforementioned question for $n$-heptane, neopentane, and water. We reason that if a mono-exponential decay of the autocorrelation function for distinct $^1$H spin pairs holds for an ionic liquid, it must also hold for $n$-heptane and neopentane, fluids that admit a van der Waals description. However, we find that the intra-molecular relaxation in water does not conform to a mono-exponential behavior, and importantly, the relaxation of distinct intra-molecular autocorrelation function for spin pairs of $n$-heptane also does not evince a mono-exponential behavior. Likewise, for all the fluids, the inter-molecular autocorrelation function of distinct spins pairs and distinct initial separation do not admit...
a mono-exponential behavior. Overall, our results show that much care is needed in adapting ideas from the traditional BPP theory to predict the NMR relaxation dispersion (i.e. frequency dependence) from MD simulations.

In light of these findings, we propose a general solution to interpreting the autocorrelation function for spin pairs involving inverse Laplace transforms (ILT) \[9\]. The ILT analysis does not depend on a model for the autocorrelation function of spin-pairs such as the mono-exponential decay by BPP or stretched exponents \[10\]. Instead, the ILT of the autocorrelation function yields a distribution of correlation times, which can then be used to predict the NMR relaxation dispersion, without assuming a model of the molecular motion. The resulting NMR relaxation dispersion from ILT analysis was previously shown to agree with measurements in the case of viscous polymers \[11\] and \textit{n}-heptane under nanoc confinement in a polymer matrix \[8\], which validates the approach.

II. METHODS

A. Autocorrelation of spin magnetic moments

Following our earlier studies, for an \textit{isotropic} system, the autocorrelation function \( G(t) \) for fluctuating magnetic \( 1\text{H}-1\text{H} \) dipole-dipole interactions is given as \[12\] \[13\]:

\[
G_{R,T}(t) = \frac{3}{16} \left( \frac{\mu_0}{4\pi} \right)^2 h^2 \gamma^4 \left( \frac{1}{N_{R,T}} \sum_{i \neq j} \left( \frac{3 \cos^2 \theta_{ij}(t + \tau) - 1}{r_{ij}^3(t + \tau)} - \frac{3 \cos^2 \theta_{ij}(\tau) - 1}{r_{ij}^3(\tau)} \right) \right)
\]

where \( t \) is the lag time of the autocorrelation, \( \tau \) is the trajectory time in the simulation, \( \mu_0 \) is the vacuum permeability, \( h \) is the reduced Planck constant, \( \gamma \) is the natural gyro-magnetic ratio for \( 1\text{H} \) (spin \( I = 1/2 \)), \( r_{ij} \) is the magnitude of the vector connecting the \((i,j) \) \( 1\text{H}-1\text{H} \) dipole-pairs, and \( \theta_{ij} \) is the polar angle between \( \vec{r}_{ij} \) and the external magnetic field. The subscript \( R \) refers to intra-molecular interactions from rotational diffusion, while the subscript \( T \) refers to inter-molecular interactions from translational diffusion.

An equivalent form of Eq. \[1\] for an \textit{isotropic} system is \[13\]:

\[
G_{R,T}(t) = \frac{3}{16} \left( \frac{\mu_0}{4\pi} \right)^2 h^2 \gamma^4 \times \left( \frac{1}{N_{R,T}} \sum_{i \neq j} \left( \frac{3 \cos^2 \psi_{ij}(t + \tau) - 1}{r_{ij}^3(t + \tau)} - \frac{3 \cos^2 \psi_{ij}(\tau) - 1}{r_{ij}^3(\tau)} \right) \right)
\]

where \( \psi_{ij}(t+\tau) \) is the angle between \( \vec{r}_{ij}(t+\tau) \) and \( \vec{r}_{ij}(\tau) \). Eqs. \[1\] and \[2\] predict a quantitative value for \( G_{R,T}(t) \), and therefore a quantitative value for the NMR relaxation times, \textit{without any adjustable parameters} \[11\]. This is an important step for validating the MD simulations against NMR measurements, which does not rely on adjustable parameters. (Please note that such a validation procedure was not carried out in \[6\].)

The NMR spectral density function \( J_{R,T}(\omega) \) is determined from the Fourier transform of \( G_{R,T}(t) \) as such

\[
J_{R,T}(\omega) = 2 \int_{0}^{\infty} G_{R,T}(t) \cos(\omega t) \, dt,
\]

where \( G_{R,T}(t) \) is real and an even function of \( t \). \( J_{R,T}(\omega) \) is then used to compute \( T_1 \) and \( T_2 \) as a function Larmor frequency \( \omega_0 = 2\pi f_0 \) \[1\], i.e. the \( T_1 \) and \( T_2 \) dispersion.

One limitation with the MD simulations is that the typical maximum autocorrelation time computed for \( G_{R,T}(t) \) is \( t_{\text{max}} \approx 1 \text{ ns} \), which is limited by computational cost. Assuming \( t_{\text{max}} = 1 \text{ ns} \), the bin width (i.e. resolution) of \( J_{R,T}(\omega) \) from Eq. \[3\] is \( \Delta f = 1/2t_{\text{max}} = 500 \text{ MHz} \). In other words, using Eq. \[3\] on the \( G_{R,T}(t) \) data directly cannot determine dispersion below \( f_0 < 500 \text{ MHz} \), which is much larger than typical dispersion results require.

A work around for predicting \( J_{R,T}(\omega) \) below \( f_0 \lesssim 500 \text{ MHz} \) is to assume a model for \( G_{R,T}(t) \) above \( t > t_{\text{max}} \). One such model is the BPP picture used in the recent study of ionic liquids \[6\], where the autocorrelation function of a rotating spin-pair \( k = ij \) obeys:

\[
G_{R,k}(t) \propto \frac{1}{r_k^6} \exp \left( -\frac{t}{\tau_{R,k}} \right).
\]

The summation over all spin pairs \( k \) is then given by:

\[
G_R(t) \propto \sum_k \frac{1}{r_k^6} \exp \left( -\frac{t}{\tau_{R,k}} \right),
\]

which assumes that each distinct pair of intra-molecular spins can be fit to a mono-exponential, and where the proportionality constant is a free parameter. As shown below, we show that using Eq. \[5\] for spin-pairs is not accurate in the relatively simple cases of \textit{n}-heptane and water. Consequently, it is logical that using Eq. \[5\] for more complex fluids such as ionic liquids is not accurate, implying that the resulting \( T_1 \) and \( T_2 \) dispersion will also not be accurate.

B. Simulation Details

We follow our earlier study \[11\] in modeling the system. The molecular simulations were performed using NAMD
The bulk alkanes were modeled using the CHARMM General Force field, CGenFF. Water was described using the TIP4P/2005 model. For \( n \)-heptane, we used the data from our earlier study. In that study, the system was rigorously equilibrated at 20 °C by reassigning velocities (obtained from a Maxwell-Boltzmann distribution) every 250 fs. Subsequently, the production run lasted 2 ns under \( NVE \) conditions. The time step for integration was 1 fs, and during the production phase configurations were archived every 100 fs for analysis. We used the last 16384 (= \( 2^{14} \)) frames out of the total 20,000 frames for autocorrelation analysis.

For TIP4P/2005 water simulation, because we did not have the final velocities from our earlier study, the final configuration from our earlier \( NVE \) simulations was once again equilibrated under \( NVT \) conditions for over 0.5 ns. Subsequently, the production phase lasted 2 ns with frames archived every 100 fs. The average temperature in the \( NVE \) phase was 296 K. (We use SHAKE to constrain the structure of water.) The production phase lasted 2 ns with frames archived every 100 fs.

For neopentane, as for TIP4P/2005, we took the final configuration from our earlier study and after equilibrating under \( NVT \) for 1 ns, we ran the production under \( NVE \) conditions. The production phase lasted 2 ns with frames archived every 100 fs. The average temperature in the \( NVE \) phase was 294 K.

In all the simulations, the Lennard-Jones interactions were terminated at 14.00 Å (11 Å for water) by smoothly switching to zero starting at 13.00 Å (10 Å for water). Electrostatic interactions were treated with the particle mesh Ewald method with a grid spacing of 0.5 Å; the real-space contributions to the electrostatic interaction were cutoff at 14.00 Å. As before, the autocorrelation function \( G_{R,T}(t) \) was constructed using fast Fourier transforms, for lag time ranging from 0 ps to \( \approx 75 \) ps in steps of 0.1 ps.

### III. RESULTS AND DISCUSSION

#### A. Intra-molecular relaxation

Figure shows the autocorrelation of intra-molecular spin interactions as the molecule undergoes rotational diffusion. We normalize the \( x \) and \( y \)-axes to present the results for different fluids on the same graph. The correlation time \( \tau_R \) used to normalize the \( x \)-axis is given by:

\[
\tau_R = \frac{1}{G_R(0)} \int_0^\infty G_R(t) \, dt.
\]

Figure makes it clear that \( G_R(t) \) cannot be described by a mono-exponential decay. In fact for water, which has only a single pair of spins, \( G_R(t) \) is clearly not mono-exponential, in contrast to what BPP assumed. Among the molecules considered, tetrahedrally symmetric neopentane comes closest to being spherical, and therefore closest to obeying BPP.
We next consider whether the observed decay (Figure 1) for \( n \)-heptane or neopentane can be modeled by a sum over the decay of pairs of intra-molecular spins, with each pair assumed to relax in an exponential fashion (Eq. 5). To this end, using linear regression we fit the first 1 ps of \( G_R(t) \) of each spin pair to the function

\[
G_R(t) = G_R(0) \exp \left( -\frac{t}{\tau^*} \right) \tag{7}
\]

where \( G_R(0) \) and \( \tau^* \) are free parameters. Subsequently, for the fit function we shift the intercept to 0. If the decay does conform to a mono-exponential behavior, then the slope \((-1/\tau^*)\) should agree with the slope of the normalized autocorrelation \((G_R(t)/G_R(0))\) obtained from simulations. Please note that we use \( \tau^* \) to differentiate the fit time-constant from the bona fide autocorrelation time obtained using Eq. 4. Also, as would be clear below, our physical conclusions are insensitive to the choice of 1 ps length of data used in the fitting procedure.

\( n \)-Heptane has 16 protons and thus there are 120 distinct pairs of protons and for neopentane we need to consider 66 distinct spin pairs. But to test whether each pair conforms to the mono-exponential behavior, it proves helpful to focus on only a select subset of this rather large set of pairs. To this end, we select particular molecules from the simulation trajectory and for the particular molecule, extract a defined spin pair and compute the autocorrelation. (Please note this procedure conforms to that suggested in Ref. 6) Figure 2 shows the autocorrelation functions for distinct pairs of intra-molecular spins.

It is obvious that for \( n \)-heptane and water, the autocorrelation for distinct spin-pairs does not admit a mono-exponential behavior. However, for neopentane, the autocorrelation does closely conform to the BPP model. This makes good physical sense since neopentane is a high-symmetry molecule, and also expected to be fairly rigid since the carbon-hydrogen bond length and bond angle fluctuations are not expected to be large. Thus the tumbling of intra-molecular spin-pairs in neopentane is expected to better conform to the assumptions underlying the BPP theory.

The above result brings us to an important conclusion. In general, the relaxation of pairs of intra-molecular \( ^1H \) spins will not conform to the BPP description, except in cases involving fairly rigid molecules with a high degree of symmetry. We can thus safely conclude that if Eq. 3 cannot form an adequate basis to model the pair-wise intra-molecular auto-correlation for simple cases such as \( n \)-heptane and water (Fig 2), it will fail for more complex cases such as ionic liquids. As such, Eq. 3 cannot reliably predict the dispersion of intra-molecular NMR relaxation times for simple fluids, let alone ionic liquids.

![Figure 2](image-url)

**FIG. 2. Normalized autocorrelation function of distinct pairs of intra-molecular spins.** "Pair m-n" refers to the pair formed by protons \( m \) and \( n \). For \( C_7 \), the \(^1H \) nuclei are labeled according to the following scheme: \( C_{11}, H_{12}, H_3 - C_{14}, H_5 - C_{16}, H_7 - C_{18}, H_9 - C_{10}, H_{11} - C_{12}, H_{13} - C_{14}, H_{15}, H_{16} \). For neopentane, we follow a similar scheme. Pair '1-2' refers to hydrogens within the same methyl group, whereas Pair '1-4' refers to hydrogen on a methyl group with a hydrogen on an adjoining methyl group. For water, there is of course only one intra-molecular pair. The mono-exponential behavior is shown by the black dashed line. The correlation time (Eq. 4) is noted in each figure.
B. Inter-molecular relaxation

For a hard-sphere fluid, by building on a previous theory by Torrey [18] by explicitly incorporating finite size effects (i.e. a distance of minimum approach) into relaxation theory, Hwang and Freed [19] have shown that the autocorrelation due to translational diffusion should obey:

\[ G_T(t) \propto \frac{54}{\pi} \int_0^\infty \frac{x^2}{81 + 9x^2 - 2x^4 + x^6} \exp \left( -x^2 \frac{t}{\tau_T} \right) dx \]

(8)

where the factor 9/4 is explained in [3]. Figure 3 shows the inter-molecular autocorrelation by translational diffusion for the molecules considered in this work. The numerical agreement with the hard-sphere model is necessarily deficient, but qualitatively one can observe a similar decay between the model and the actual data. Importantly, it is evident that the decay does not conform to a mono-exponential decay.

Following the claims by the recent study [6], we asked if the autocorrelation function of spin-pairs on different molecules can be adequately described by a mono-exponential decay. Figure 4 compares the autocorrelation of select spin-pairs, whose initial separations are noted in the figure. As done in Fig. 2, we fit Eq. 7 to the first 1 ps of the data and then shift the intercept to 0. Clearly, the inter-molecular autocorrelation for select spin pairs does not conform to a mono-exponential behavior, contrary to what has been suggested recently [6].

Note that in contrast to intra-molecular spin pairs (Fig. 2), for inter-molecular spin pairs we see an increase in the noise as the lag time increases. Note that the noise takes the form of oscillations rather than Gaussian noise, although a 2σ uncertainty can still be computed (see Supplementary Material in Ref. [3]).

To better understand the origin of noise, we constructed synthetic data-sets for the diffusive evolution of the distance, r, between a pair of spins (data not shown). The angle θ (Eq. 1) is also held fixed. From such synthetic data sets, we find that the oscillations occur when the reaction coordinate, r, makes periodic returns to smaller r values and dwells around that value before escaping to a different value. The effect of such behavior is expected to be washed out when we average over many different pairs and also allow for rotation of the vector connecting the spins, as we do in computing the overall autocorrelation (Fig. 3). Nevertheless, Figure 4 makes it clear that the decay of autocorrelation function for select spin-pairs does not conform to a mono-exponential behavior, emphasizing that it is incorrect to model the overall decay curve using Eq. 5. As such, Eq. 5 cannot accurately predict the dispersion (i.e. the frequency dependence) of inter-molecular NMR relaxation times.

C. Proposed solution

In order to surmount the computational limitations of maximum autocorrelation times in \( G_{R,T}(t) \), and thereby surmount the limitations in determining \( T_1 \) and \( T_2 \) dis-
We have shown that using Eq. 5 to model \( G \) one has to make predictions of 
\[ \sigma^2(0) \]

correlation (especially at frequencies below \( f_0 \ll 500 \text{ MHz} \)), one has to make predictions of \( G_{R,T}(t) \) above \( t > t_{max} \). We have shown that using Eq. 5 to model \( G_{R,T}(t) \) is not accurate for spin-pairs on relatively simple molecules such as \( n \)-heptane, and water. It therefore follows that using Eq. 5 will be even more inaccurate for more complex fluids such as ionic liquids [6], thereby leading to inaccuracies in predicting the \( T_1 \) and \( T_2 \) dispersion.

One solution we have developed is to use an inverse Laplace transform (ILT) of the autocorrelation function as such [20][21]:

\[
G_{R,T}(t) = \int_0^\infty P_{R,T}(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau, \tag{9}
\]

where \( P_{R,T}(\tau) \) is the distribution in molecular correlation times. Details of the ILT procedure can be found in [7][9] and the supplementary material in [3][10]. The advantage of using the ILT to predict \( P_{R,T}(\tau) \) is that the ILT does not depend on a specific model for \( G_{R,T}(t) \) such as the mono-exponential BPP model (Eq. 5) or the use of stretched exponents [10]. The justification for the multi-exponential (i.e. stretched) nature of \( G_R(t) \) in Eq. 9 comes from Woessner’s theoretical treatment of NMR relaxation of \(^1\text{H}-^1\text{H} \) spin-pairs [22][23]. Woessner’s theories show that anisotropic rotation [22] and internal motions [23] of a spin-pair gives rise to a multi-exponential decay in \( G_R(t) \). Furthermore, the larger the anisotropy and internal motion of the spin-pair, the more exponential decays are required to describe \( G_R(t) \), implying a broader distribution in correlation times \( P_R(\tau) \).

Once \( P_{R,T}(\tau) \) is determined from Eq. 9, the spectral density \( J_{R,T}(\omega) \) is straightforwardly determined from the Fourier transform (Eq. 3) of \( G_{R,T}(t) \) (Eq. 9) as such:

\[
J_{R,T}(\omega) = \int_0^\infty \frac{2\tau}{1 + (\omega\tau)^2} P_{R,T}(\tau) d\tau, \tag{10}
\]

from which \( T_1 \) and \( T_2 \) dispersion can be determined [1]. In the case of viscous fluids [9] and fluids under confinement [8], we have shown that this approach yields good agreement with \( T_1 \) and \( T_2 \) measurements, even at low frequencies \( f_0 = 2.3 \text{ MHz} \). Furthermore, as discussed in [1][8], \( P_{R,T}(\tau) \) yields insights into the contribution of collective molecular modes in the observed autocorrelation, which can prove useful for interpreting \( T_1 \) and \( T_2 \) dispersion.

\[ \text{FIG. 4. Normalized autocorrelation of inter-molecular spin-pair interactions for select spin-pairs in } n \text{-heptane, neopentane, and water. The initial separation of the spin-pair is noted in the legend. The dashed line is a mono-exponential fit to the first 1 ps of the data. The fit function is then translated to have an intercept of 0 (on the log-scale). The correlation time (Eq. 7) is noted in each figure.} \]
symmetry such as n-heptane and water, the autocorrelation function between distinct spin pairs within the same molecule evince a stretched-exponential decay, implying a distribution in rotational correlation times. Likewise, modeling the inter-molecular autocorrelation function between spin pairs for a given initial separation using a mono-exponential is not accurate. Such assumptions will cause inaccurate predictions of the NMR relaxation dispersion (i.e. frequency dependence) in fluids.

Our work to date [1–3, 7–9] shows that provided we have reasonable forcefields, MD simulation techniques can predict NMR relaxation in good agreement with measurements, without any adjustable parameters in the interpretation of the simulation data. Further, the inverse Laplace transform (ILT) approach can account for the stretched exponential decay of the autocorrelation function, and determine the underlying distribution in correlation times which can be used to determine the NMR relaxation dispersion, without having to assume a model of molecular motion. Besides their utility in enhancing the interpretation of experiments, these developments can also aid in efforts to devise improved forcefields for use in molecular modeling and in the quest to better model NMR relaxation.

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