NMR spin-rotation relaxation and diffusion of methane

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The translational diffusion-coefficient and the spin-rotation contribution to the ^1H NMR relaxation rate for methane (CH_4) are investigated using MD (molecular dynamics) simulations, over a wide range of densities and temperatures, spanning the liquid, supercritical, and gas phases. The simulated diffusion-coefficients agree well with measurements, without any adjustable parameters in the interpretation of the simulations. A minimization technique is developed to compute the angular velocity for non-rigid spherical molecules, which is used to simulate the autocorrelation function for spin-rotation interactions. With increasing diffusivity, the autocorrelation function shows increasing deviations from the single-exponential decay predicted by the Langevin theory for rigid spheres, and the deviations are quantified using inverse Laplace transforms. The ^1H spin-rotation relaxation rate derived from the autocorrelation function using the “kinetic model” agrees well with measurements in the supercritical/gas phase, while the relaxation rate derived using the “diffusion model” agrees well with measurements in the liquid phase. ^1H spin-rotation relaxation is shown to dominate over the MD-simulated ^1H - ^1H dipole-dipole relaxation at high diffusivity, while the opposite is found at low diffusivity. At high diffusivity, the simulated spin-rotation correlation time agrees with the kinetic collision time for gases, which is used to derive a new expression for ^1H spin-rotation relaxation, without any adjustable parameters. Published by AIP Publishing. <https://doi.org/10.1063/1.5027097>

I. INTRODUCTION

Theoretical and experimental investigations into ^1H NMR (nuclear magnetic resonance) spin-rotation relaxation rate R_{1J} and translational diffusion D_T of methane (CH_4), deuterio derivatives ($\text{CH}_{4-n}\text{D}_n$), and halide derivatives ($\text{CH}_{4-n-m}\text{F}_n\text{Cl}_m$) date back over 50 years.^{1–16} Likewise, the theoretical and experimental investigations into molecular beam magnetic resonance of methane and its derivatives date back over 50 years,^{17–22} from which came (among many other things) the coupling constants used to interpret R_{1J} .

More recently, the influence of dissolved methane on R_1 , R_2 , and D_T of complex crude oils and hydrocarbon mixtures has been investigated,^{23–27} which reveals the important influence of the spin-rotation contribution from methane. Of particular significance is the well-established ^1H spin-rotation relaxation rate for methane in the fast-motion regime,^{13,24}

$$R_{1J}^A = \frac{1}{T_{1J}^A} = A \frac{T^{3/2}}{\rho}, \quad (1)$$

where A is an empirically derived constant, ρ is the density, T is the temperature, and T_{1J} is the spin-rotation relaxation time. Equation (1) states that R_{1J} increases with T . This is in stark contrast to the ^1H - ^1H dipole-dipole relaxation rate R_{1RT} that decreases with T , for all liquid-state hydrocarbons including methane. Also of interest recently is the influence of pore confinement on the NMR response of methane,^{28–37} which has practical applications for characterizing the light hydrocarbons in the organic nanopores of kerogen and bitumen in organic-rich shale. One of the current mysteries is why the T_{1S}/T_{2S} ratio for surface relaxation of methane in organic shale

is typically $T_{1S}/T_{2S} \lesssim 2$, while for higher order alkanes it is typically higher, $T_{1S}/T_{2S} \gtrsim 4$. This has practical applications for separating the NMR response of light hydrocarbon from water in organic shale and for determining the hydrocarbon saturation in the organic-shale reservoir.

In order to properly characterize NMR relaxation of methane in the bulk and under nanopore confinement, one must first separate the ^1H spin-rotation relaxation R_{1J} from ^1H - ^1H dipole-dipole relaxation R_{1RT} . Traditionally this has been done by partially deuterating CH_4 to, for instance, CHD_3 , which dramatically reduces the dipole-dipole contribution. However, this has the drawback of turning a spherical top (CH_4) with one principle moment of inertia into a symmetric top (CHD_3) with two principle moments of inertia. The theory of spin-rotation relaxation for symmetric tops is more complex than for spherical tops, thereby making comparisons with measurements more challenging.

MD (molecular dynamics) simulations provide an ideal tool for separating ^1H NMR relaxation mechanisms. As already shown for liquid-state n -alkanes in Refs. 38 and 39, MD simulations can naturally separate intramolecular R_{1R} from intermolecular R_{1T} ^1H - ^1H dipole-dipole relaxation, without deuteration and without any adjustable parameters in the interpretation of the simulations. Such simulations yield unique insights into (a) the relative strengths of intramolecular versus intermolecular relaxation, (b) the influence of internal motions on the molecular dynamics of non-rigid molecules, and (c) the validity of traditional models^{40–42} for different molecular geometries.

Of related interest is the study of the conversion between nuclear spin isomers of methane in the gas phase and

cryomatrices,^{43–48} where (for instance) nuclear spin conversion is known to impact the interpretation of molecular spectra in the interstellar medium. The ($I = \frac{1}{2}$) ^1H nuclei of CH_4 result in three spin isomers: *meta*- CH_4 ($I = 2$), *ortho*- CH_4 ($I = 1$), and the NMR-silent *para*- CH_4 ($I = 0$), with relative populations (i.e., spin statistical weights) of 5:9:2 in the high temperature limit ($T \gg 50$ K), respectively. Both the ^1H spin-rotation and the ^1H - ^1H dipole-dipole interactions cause conversion between nuclear spin isomers, which are dictated by selection rules based on the tetrahedral symmetry group T_d and transitions in angular momentum J of the molecule. It is plausible that integrating an appropriate quantum relaxation model with MD simulations has the potential to enrich this area of research, although this is beyond the scope of this work.

The rest of this report is briefed into sections as follows. In Sec. II A, we develop a technique to determine the autocorrelation function for angular velocity $G_J(t)$ of non-rigid spherical molecules. In Sec. II B, we interpret $G_J(t)$ to yield the ^1H spin-rotation relaxation rate R_{1J} using the kinetic model and the diffusion model. In Sec. III A, we compare simulation versus measurement for both spin-rotation relaxation and translational diffusion. In Sec. III B, we compare and analyze the correlation times for the different relaxation mechanisms. In Sec. III C, we propose a new kinetic model to account for Eq. (1).

II. METHODOLOGY

A. Molecular simulation

The MD simulations were performed using NAMD⁴⁹ version 2.11. Methane was modeled using the CHARMM General Force field (CGenFF).⁵⁰ The protocol for setting up the initial simulation configuration was exactly as before,^{38,39} where we created the initial simulation system by packing N copies of the molecule into a cube of volume L^3 using the Packmol program.⁵¹ The volume was chosen such that the number density N/V corresponds to the experimentally determined number density at the specified temperatures listed in Table I. The simulation approach for these systems using NAMD was as before.^{38,39}

The translational diffusion-coefficient D_T was derived using the following relation:

$$D_T = \frac{1}{6} \frac{\delta \langle \Delta r^2 \rangle_L}{\delta t} + \frac{kT}{6\pi\eta} \frac{\xi}{L}. \quad (2)$$

The first term on the right is the derivative of the mean square displacement $\langle \Delta r^2 \rangle_L$ of the center-of-mass of a methane molecule as a function of the diffusion evolution time t for box size L , where the early ballistic regime ($t < 5$ ps) is excluded from the derivative calculation. The second term on the right (amounting to a $\lesssim 10\%$ boost) is the periodic-boundary correction term^{52,53} derived using viscosity η and box size L listed in Table I, where $\xi = 2.837\,297$ is the same quantity that arises in the calculation of the Madelung constant in electrostatics. The resulting diffusion-coefficient D_T in Eq. (2) is independent of L within uncertainties.

TABLE I. List of MD-simulated state points, chosen to coincide with measured (meas.) methane data taken from Refs. 9–12, including phase (liquid, supercritical, or gas), temperature (T), pressure (P), density (ρ), translational diffusion (D_T), ^1H NMR relaxation rate (R_1), viscosity (η), and MD cube size L , in order of increasing D_T . Predicted quantities (pred.) are taken from the NIST database. Critical points for methane are $T_{cr} = 190.6$ K and $P_{cr} = 46$ bars.

Phase	T (K)	P (bar)	ρ (g/cm ³)	D_T (10 ⁻⁹ m ² /s)	R_1 (s ⁻¹)	η (cP)	L (Å)
Pred.	Meas.	Pred.	Meas.	Meas.	Meas.	Pred.	Simul.
L	90.9	0.120	0.451	2.52	0.103	0.192	31.15
L	105.3	0.578	0.432	4.35	0.069	0.134	31.62
L	125.0	2.69	0.402	7.76	0.053	0.089	32.37
L	142.9	7.41	0.372	11.8	0.050	0.064	33.23
S	194.8	389.8	0.359	18.0	0.061	0.056	33.63
S	194.8	141.0	0.303	25.5	0.067	0.037	35.56
S	194.8	71.24	0.255	34.0	0.078	0.027	37.69
S	194.8	59.76	0.230	39.4	0.086	0.024	38.96
S	194.8	52.53	0.173	56.2	0.110	0.017	43.35
S	298.2	349.1	0.232	56.5	0.141	0.027	38.89
S	298.2	250.0	0.188	74.5	0.168	0.022	41.69
S	194.8	46.53	0.089	116.1	0.210	0.010	40.20
S	298.2	151.1	0.120	120.4	0.277	0.016	48.50
S	273.2	99.46	0.089	160.0	0.329	0.014	40.14
S	273.2	82.56	0.072	200.0	0.410	0.013	43.07
S	273.2	64.68	0.054	264.0	0.575	0.012	47.41
G	273.2	45.29	0.036	404.0	0.826	0.011	54.51
S	307.7	51.73	0.035	439.0	1.042	0.012	54.76

The angular velocity computation went as follows. From simulations, for each atom in a molecule, we have a site velocity $\mathbf{v}_i$. Without loss of generality, we assume that $\mathbf{v}_i$ is relative to the velocity of the center of mass. By the definition of angular velocity, we have

$$\boldsymbol{\omega} \times \mathbf{r}_i = \mathbf{v}_i. \quad (3)$$

But a direct application of the above equation cannot be used to calculate $\boldsymbol{\omega}$ because the matrix equation is singular. We therefore define

$$\mathcal{L} = \sum_i |\mathbf{v}_i - \boldsymbol{\omega} \times \mathbf{r}_i|^2. \quad (4)$$

We minimize $\mathcal{L}$ with respect to the x , y , z components of $\boldsymbol{\omega}$, giving the following matrix equation:

$$\begin{pmatrix} \sum_i z_i^2 + y_i^2 & -\sum_i x_i y_i & -\sum_i x_i z_i \\ -\sum_i x_i y_i & \sum_i x_i^2 + z_i^2 & -\sum_i y_i z_i \\ -\sum_i x_i z_i & -\sum_i y_i z_i & \sum_i x_i^2 + y_i^2 \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix} = \begin{pmatrix} \sum_i (\mathbf{r}_i \times \mathbf{v}_i)_x \\ \sum_i (\mathbf{r}_i \times \mathbf{v}_i)_y \\ \sum_i (\mathbf{r}_i \times \mathbf{v}_i)_z \end{pmatrix}. \quad (5)$$

In tensor notation, we can write this more compactly as

$$r_j \omega_p r_q \epsilon^{ijk} \epsilon_{pqk} = r_j v_k \epsilon_{jkl}, \quad (6)$$

summed over all sites.

We constructed the above matrix for each molecule and solved for ω_x , ω_y , ω_z . This calculation is repeated for all the frames in the trajectory. Then we calculated the autocorrelation of each component. Since the system is isotropic, all the component relaxations are the same. The above calculation is repeated for other molecules and the results are averaged.

B. Spin-rotation relaxation

The Hamiltonian for the spin-rotation interaction is given by the following:^{17–21}

$$\mathcal{H}_J = \hbar \sum_{i=1}^4 \mathbf{I}_i \cdot \mathbf{C}_i \cdot \mathbf{J}. \quad (7)$$

$\mathbf{I}_i$ are the four ^1H nuclear spins on the methane molecule. $\mathbf{J}$ is the angular momentum of the molecule, which is related to the angular velocity $\boldsymbol{\omega}$ by the following $\hbar \mathbf{J} = I \boldsymbol{\omega}$, where $I = 5.33 \times 10^{-47} \text{ kg m}^2$ ⁵⁴ is the moment of inertia for methane. The coupling tensor $\mathbf{C}$ has two principle components $C_\perp$ and $C_\parallel$, which are proportional to the magnetic field (per unit J) generated at a ^1H by rotations about an axis $\perp$ ($\parallel$) to the C–H bond axis, respectively. The most practical formulation separates $\mathcal{H}_J$ into a scalar component proportional to the average coupling constant $C_a = (2C_\perp + C_\parallel)/3$ and a tensor component proportional to the diagonal coupling constant $C_d = (C_\perp - C_\parallel)$. The most accurate values of the coupling constants, and the ones used here, are²² $C_a/2\pi = 10.372(83) \text{ kHz}$, $C_d/2\pi = 18.370(23) \text{ kHz}$ (which are the experimentally determined quantities), from which the following can be inferred: $C_\perp/2\pi = 16.495 \text{ kHz}$, $C_\parallel/2\pi = -1.875 \text{ kHz}$.

The expression for the autocorrelation function $G_J^{lk}(t)$ used to determine R_{IJ} for liquids² and gases^{3,4,6} can be summarized as follows (in units of s^{-2}):

$$G_J^{lk}(t) = \frac{I^2}{2\hbar^2} \left(C_a^2 \langle \omega_l(t+\tau) \omega_k(\tau) \rangle_\tau + \frac{2}{9} C_d^2 \sum_{m,n,o,p} \alpha_{l,m,n}^{k,o,p} Y_2^n(t+\tau) \omega_m(t+\tau) Y_2^p(\tau) \omega_o(\tau) \right)_\tau. \quad (8)$$

The first term in Eq. (8) is the scalar term, while the second term is the tensor term. The more general expression also includes a cross-term proportional to $C_a C_d$; however, it reduces to zero for spherical tops such as methane. The term $\omega_k(t)$ is the angular velocity around the k -axis at time t , and $Y_2^m(t)$ is the spherical harmonic of rank 2 and order m at time t . $\alpha_{l,m,n}^{k,o,p}$ is composed of two sets of 3- j symbols defined in Ref. 2.

The tensor term greatly simplifies, provided the rotational motion $Y_2^m(t)$ is independent of the angular velocity $\omega_k(t)$. In such cases, the bracketed term separates as $\langle Y_2^{l*}(t+\tau) Y_2^k(\tau) \rangle_\tau \langle \omega_l(t+\tau) \omega_k(\tau) \rangle_\tau$. Traditional theories then state the following expressions for rigid spheres:

$$\langle \omega_l(t+\tau) \omega_k(\tau) \rangle_\tau = \delta_{l,k} \frac{kT}{I} \exp(-t/\tau_J), \quad (9)$$

$$\langle Y_2^{l*}(t+\tau) Y_2^k(\tau) \rangle_\tau = \delta_{l,k} \exp(-t/\tau_R). \quad (10)$$

The angular velocity autocorrelation function in Eq. (9) is derived from the Langevin model with correlation time τ_J .^{2,55,56} The orientation autocorrelation function in Eq. (10) defines the rotational correlation time τ_R .⁴⁰ The orientation and angular velocity autocorrelations can be separated, provided either $\tau_J \gg \tau_R$ (gases) or $\tau_J \ll \tau_R$ (liquids).² In the case of liquids ($\tau_J \ll \tau_R$), this has the effect of making $\langle Y_2^{l*}(t+\tau) Y_2^k(\tau) \rangle_\tau = \delta_{l,k}$ in Eq. (8). Based on comparison with measurements, the relation $\langle Y_2^{l*}(t+\tau) Y_2^k(\tau) \rangle_\tau = \delta_{l,k}$ is also

used in the case of gases.^{6,13,16} In such cases, Eq. (8) simplifies to the following expression, which is used in the MD simulations:

$$G_J(t) = \frac{I^2}{2\hbar^2} \left(C_a^2 + \alpha \frac{2}{9} C_d^2 \right) \langle \omega_k(t+\tau) \omega_k(\tau) \rangle_\tau. \quad (11)$$

The resulting expression $G_J(t)$ is independent of the direction k in $G_J^{kk}(t)$; therefore, the superscript is removed for clarity. The MD simulations compute all three k directions independently, and the average is then taken to improve the signal-to-noise ratio. The simulation results for $G_J(t)$ are shown in Fig. 1(a), where both x - and y -axes have been normalized for better comparison of the functional form of the decay between different states points, and this allows for comparison with the Langevin model in Eq. (9). Also, the limits on the x - and y -axes are chosen such that Fig. 1(a) shows the region below $G_J(t)/G_J(0) \lesssim 3 \times 10^{-3}$, where uncertainties become significant (see Ref. 39 for more details).

FIG. 1. (a) MD simulations of the autocorrelation function $G_J(t)$ for spin-rotation interactions using Eq. (11), colored in order of increasing D_T . The y -axis has been normalized by zero time value $G_J(0)$ in Eq. (12), and the x -axis has been normalized by correlation time τ_J in Eq. (15). The dotted line is the Langevin prediction in Eq. (9). (b) Probability distribution function $P_J(\tau)$ of spin-rotation correlation time τ derived from the inverse Laplace transform [Eq. (21)] of the $G_J(t)$ simulations in (a). Also shown is the Langevin prediction $G_J(t)$ from Eq. (9), generated with an arbitrarily chosen value of $\tau_J = 2 \text{ ps}$. The y -axis has been divided by $G_J(0)$, which normalizes the area of the distributions to unity (except for the Langevin model).

A significant parameter in the analysis is the autocorrelation at $t = 0$, which is given by the following expression:

$$G_J(0) = \frac{I^2}{2\hbar^2} \left(C_a^2 + \alpha \frac{2}{9} C_d^2 \right) \langle \omega_k^2(\tau) \rangle_\tau = \frac{IkT}{2\hbar^2} \left(C_a^2 + \alpha \frac{2}{9} C_d^2 \right) = \frac{1}{2} \Delta\omega_\alpha^2, \quad (12)$$

where the first equality is directly from Eq. (11). The second equality uses the time zero expression $\langle \omega_k^2(\tau) \rangle_\tau = kT/I$ from Eq. (9), which was verified from MD simulations to be within $\pm 2\%$ over the entire temperature range of interest.

The third equality defines the second moment $\Delta\omega_\alpha^2$ (i.e., strength) of the spin-rotation interaction,^{56,57} given by

$$\Delta\omega_{km}^2 = \frac{IkT}{\hbar^2} \left(C_a^2 + \frac{4}{45} C_d^2 \right) [\text{k.m.}, \alpha = \frac{2}{5}], \quad (13)$$

$$\Delta\omega_{dm}^2 = \frac{IkT}{\hbar^2} \left(C_a^2 + \frac{2}{9} C_d^2 \right) [\text{d.m.}, \alpha = 1]. \quad (14)$$

The only free parameter is α , which is given by $\alpha = 1$ in the diffusion model “dm” for liquids² or by $\alpha = 2/5$ in the kinetic model “km” for gases.^{6,13} In describing the kinetic model, we have adopted the exact relation for the scalar term $\hbar^2 \langle J(J+1) \rangle / 3 = IkT$, and for the tensor term, we assume (without loss in accuracy) that $\langle (2J-1)(2J+3) \rangle / 4 \langle J(J+1) \rangle \simeq 1$ in the classical limit $J \gg 1$.⁴ The kinetic model for gases predicts that $\alpha = 2/5$ since the oscillatory terms $\Delta J \neq 0$ do not contribute (giving rise to $\times 1/5$) and from the statistical independence of $\omega_k(t)$ and $Y_2^m(t)$ (giving rise to $\times 2$).⁴

The next quantity of interest is the spin-rotation correlation time τ_J determined from the MD simulations, which is determined from the integral of the normalized $G_J(t)$ as such⁵⁷

$$\tau_J = \frac{1}{G_J(0)} \int_0^\infty G_J(t) dt. \quad (15)$$

The ^1H spin-rotation relaxation rates are then derived from the spectral density $J_f^\alpha(\omega)$:²

$$\begin{aligned} J_f^\alpha(\omega) &= 2 \int_0^\infty G_J(t) \cos(\omega t) dt, \\ R_{1J}^\alpha &= 2J_f^\alpha(\omega_0), \\ R_{2J}^\alpha &= J_f^\alpha(0) + J_f^\alpha(\omega_0), \end{aligned} \quad (16)$$

where $\omega_0 = \gamma B_0$ is the Larmor frequency for ^1H . Given the short correlation times $\tau_J \simeq 1$ ps and given the typical Larmor frequencies $\omega_0/2\pi < 500$ MHz, it is clearly the case that $\omega_0\tau_J \ll 1$, i.e., the fast-motion regime applies. In such cases, $J_f^\alpha(0) = J_f^\alpha(\omega_0) = \Delta\omega_\alpha^2\tau_J$, and therefore, $R_{1J}^\alpha = R_{2J}^\alpha$. Using the relation $R_{1J}^\alpha = 2J_f^\alpha(0) = 2\Delta\omega_\alpha^2\tau_J$ results in the following final expressions (in units of s^{-1}):

$$R_{1J}^{km} = \frac{2IkT}{\hbar^2} \left(C_a^2 + \frac{4}{45} C_d^2 \right) \tau_J, \quad (17)$$

$$R_{1J}^{dm} = \frac{2IkT}{\hbar^2} \left(C_a^2 + \frac{2}{9} C_d^2 \right) \tau_J. \quad (18)$$

Note that R_{1J}^{dm} is often expressed in terms of $C_\perp$ and $C_\parallel$ instead,² where $(C_a^2 + \frac{2}{9} C_d^2) = \frac{1}{3}(2C_\perp^2 + C_\parallel^2)$.

In order to compare with measurements, we also include contributions from the ^1H - ^1H dipole-dipole interactions,

which separate into intramolecular R_{1R} and intermolecular R_{1T} relaxation. Details of the methodology behind the MD simulations of R_{1R} and R_{1T} can be found in Refs. 38 and 39. The final expression for the total ^1H relaxation rate is given by

$$\begin{aligned} R_1^\alpha &= R_{1R} + R_{1T} + R_{1J}^\alpha \\ &= \frac{10}{3} \Delta\omega_R^2 \tau_R + \frac{10}{3} \Delta\omega_T^2 \tau_T + 2\Delta\omega_\alpha^2 \tau_J, \end{aligned} \quad (19)$$

which takes on two different values R_{1J}^{km} and R_{1J}^{dm} , depending on the model R_{1J}^{km} and R_{1J}^{dm} used. $\Delta\omega_{R,T}^2$ and $\tau_{R,T}$ are the second moments and correlation times for intramolecular (R) and intermolecular (T), respectively. For comparison purposes, the square root of the second moments at 298 K and 349.1 bars (for instance) are $\Delta\omega_R/2\pi \simeq 23.7$ kHz, $\Delta\omega_T/2\pi \simeq 7.5$ kHz, and $\Delta\omega_J^{km}/2\pi \simeq 52.1$ kHz (see the [supplementary material](#) for a complete list). We also define the total relaxation from ^1H - ^1H dipole-dipole interactions R_{1RT} as such:

$$R_{1RT} = R_{1R} + R_{1T}. \quad (20)$$

Given that the fast-motion regime applies, all of the above results for longitudinal relaxation R_1 apply equally to transverse relaxation R_2 . As such, the subscript 2 has been dropped everywhere for clarity.

1. Distribution in correlation times

As shown in Fig. 1(a), $G_J(t)$ deviates from single exponential decay predicted by the Langevin model in Eq. (9). More specifically, $G_J(t)$ has a more “stretched” (i.e., multi-exponential-like) decay, which we quantify by inverting the following Laplace transform,^{58,59}

$$G_J(t) = \int P_J(\tau) \exp(-t/\tau) d\tau. \quad (21)$$

$P_J(\tau)$ (in units of s^{-3}) is the probability distribution function derived from the inversion. In the case of the Langevin sphere model, $P_J(\tau)$ is a delta function at τ_J ; i.e., $P_J(\tau) = G_J(0) \delta(\tau - \tau_J)$. However, as shown in Fig. 1(a), $G_J(t)$ is always stretched (i.e., multi-exponential) to some degree; therefore, $P_J(\tau)$ has a finite distribution. The decomposition of $G_J(t)$ into a sum of exponential decays is a common practice,⁶⁰ where the more complex the molecule dynamics, the more the terms are required. This justifies our general approach of decomposing $G_J(t)$ into a sum of exponential decays in Eq. (21), solely for the purposes of quantifying the departure from the Langevin rigid-sphere model.

The resulting $P_J(\tau)$ distributions, shown in Fig. 1(b), were determined by using the discrete form of Eq. (21), using 100 logarithmically spaced τ bins ranging from $0.03 \text{ ps} \leq \tau \leq 30 \text{ ps}$. The inverse Laplace transform is ill-conditioned and non-unique; therefore, a (fixed) regularization parameter^{58,59} of 10^{-2} is used to smooth the inverted $P_J(\tau)$ distributions. Despite this limitation, using a *fixed* value of the regularization parameter (and given that the signal-to-noise ratio is comparable between state points) gives reasonable certainty that the widths of the $P_J(\tau)$ distributions can be compared between state points. Figure 1(b) shows that the mean correlation times τ_J get longer with increasing D_T and that the width of the distributions gets somewhat larger with increasing D_T . In all cases,

the widths are much larger than the delta function prediction from the Langevin model in Eq. (9).

The widths of the $P_J(\tau)$ distributions are quantified using the following:

$$\begin{aligned}\mu_J &= \frac{1}{G_J(0)} \int P_J(\tau) \ln(\tau) d\tau, \\ \sigma_J^2 &= \frac{1}{G_J(0)} \int P_J(\tau) (\ln(\tau) - \mu_J)^2 d\tau,\end{aligned}\quad (22)$$

where σ_J is the standard deviation and μ_J is the mean of the variable $\ln(\tau)$. A natural logarithm in τ is used as the variable since the underlying $P_J(\tau)$ distributions are discrete and evenly spaced in $\ln(\tau)$. Also shown in Fig. 1(b) is the Langevin model that predicts $\sigma_J = 0$ (i.e., a delta function) or $\sigma_J \approx 0.038$ due to regularization. Equivalent quantities were also derived from the autocorrelation functions for intramolecular σ_R and intermolecular σ_T ^1H - ^1H dipole-dipole interactions.³⁹

III. RESULTS

A. Simulation versus measurement

The cross-plot of measured versus simulated translational diffusion-coefficient D_T in Fig. 2(a) indicates a strong correlation coefficient $R^2 = 0.996$ and an average absolute deviation of $\delta_{abs} = 9.2\%$, where δ_{abs} is defined as

$$\delta_{abs} = \frac{1}{N} \sum_{i=1}^N \left| \frac{Y_i - X_i}{X_i} \right| \times 100, \quad (23)$$

where Y_i are the simulated values, X_i are the measured quantities, and N is the number of points. The deviation is noticeable at the lowest temperature in the liquid phase ($T < T_{cr}$), which may be due to the proximity of the liquid-vapor phase transition. Another explanation is that temperatures are low enough that nuclear quantum effects may play a role, given that the thermal de Broglie wavelength approaches the intermolecular distance in the liquid phase (further investigations are beyond the scope of this work).

The cross-plot of measured R_1 versus simulated R_1^α [defined in Eq. (19)] total relaxation rate in Fig. 2(b) indicates strong correlation coefficients of $R^2 = 0.995$ for R_1^{km} and $R^2 = 0.994$ for R_1^{dm} , while δ_{abs} varies as a function of measured R_1 . At high D_T (i.e., low ρ) where the measured $R_1 > 0.2 \text{ s}^{-1}$ (i.e., where spin-rotation relaxation dominates), the deviation is lower for the kinetic model R_1^{km} ($\delta_{abs} = 10.3\%$) than for the diffusion model R_1^{dm} ($\delta_{abs} = 18.0\%$). This is expected, given that the kinetic model is more appropriate for fluids at high D_T and low ρ .

At low D_T (i.e., high ρ) where the measured $R_1 < 0.2 \text{ s}^{-1}$ and $T > T_{cr}$ (i.e., still in the supercritical phase), the deviation is lower for the diffusion model R_1^{dm} ($\delta_{abs} = 9.1\%$) than for the kinetic model R_1^{km} ($\delta_{abs} = 16.6\%$). This is expected, given that the diffusion model is more appropriate for fluids at low D_T and high ρ .

In the liquid phase where $T < T_{cr}$, ^1H - ^1H dipole-dipole relaxation dominates over the ^1H spin-rotation interaction, and the two interpretations R_1^{km} and R_1^{dm} become comparable. Nevertheless, the deviation is still lower for the diffusion model R_1^{dm} ($\delta_{abs} = 14.2\%$) than for the kinetic model

FIG. 2. (a) Cross-plot of simulated translational diffusion-coefficient D_T on the y-axis versus measured D_T on the x-axis taken from Refs. 9–12 for both the liquid state ($T < T_{cr}$) and the supercritical or gas state ($T > T_{cr}$), as listed in Table I. (b) Cross-plot of simulated total relaxation rate R_1^α on the y-axis defined in Eq. (19) versus measured R_1 on the x-axis taken from Refs. 9–12, as listed in Table I. The simulated R_1^α includes the kinetic model R_1^{km} and the diffusion model R_1^{dm} .

R_1^{km} ($\delta_{abs} = 21.8\%$). The observed deviation for $T < T_{cr}$ is from the dipole-dipole contribution R_{1RT} , more specifically from the dominating intermolecular contribution R_{1T} . This systematic deviation is potentially due to the proximity of the liquid-vapor phase transition. Another explanation may be that temperatures are low enough that the relative populations of nuclear spin isomers start to deviate from the high temperature limit ($T \gg 50 \text{ K}$),^{43–48} which could affect both spin-rotation and dipole-dipole relaxations (further investigations are beyond the scope of this work).

B. Correlation times

A summary of the simulated correlation times is shown in Fig. 3(a). The spin-rotation correlation time τ_J shows a monotonic increase with increasing D_T/T (translational

FIG. 3. (a) MD-simulated correlation times for intermolecular τ_T and intramolecular τ_R ^1H - ^1H dipole-dipole interactions, spin-rotation interaction τ_J [Eq. (15)], and mean collision time τ_K [Eq. (24)], plotted against measured D_T/T . (b) Simulation results for the standard deviation σ_J [Eq. (22)] in correlation times, determined from the $P_J(\tau)$ distributions [Eq. (21)] in Fig. 1(b), plotted against measured D_T/T . Also shown is the Langevin model that predicts a delta function $\sigma_J = 0$ or $\sigma_J \approx 0.038$ due to regularization. Equivalent quantities σ_R and σ_T for ^1H - ^1H dipole-dipole interactions are also shown, where $\sigma_T/4$ is plotted for clarity.

diffusion divided by absolute temperature). At high D_T/T , i.e., in the supercritical/gas phase ($T > T_{cr}$), τ_J is consistent with the kinetic collision time τ_K defined as

$$D_T = \frac{1}{3} \lambda \bar{v}, \quad \bar{v} = \sqrt{\frac{8kT}{\pi M}}, \quad (24)$$

$$\tau_K = \frac{\lambda}{\bar{v}} = \frac{3D_T}{\bar{v}^2} = \frac{3\pi M D_T}{8kT},$$

where $M = 2.664 \times 10^{-26}$ kg is the mass of the methane molecule, λ is the mean free path, and $\bar{v}$ is the mean thermal velocity. More specifically, the correlation between τ_J and τ_K is strong $R^2 = 0.997$ and the absolute deviation is $\delta_{abs} = 7.7\%$ in this region ($T > T_{cr}$). Given the compelling observation $\tau_J \approx \tau_K$ and the relation $\tau_K \propto D_T/T$ in Eq. (24) motivates using D_T/T for the x -axis in Fig. 3. The relation $\tau_J \approx \tau_K$ is indicative of the “strong collision” regime^{4,11} and is used below to infer a new relation for R_{IJ}^{km} . As expected, the relation $\tau_J \approx \tau_K$ breaks down in the liquid phase ($T < T_{cr}$) where the diffusion model is more appropriate.

In the case of spherical molecules, the following simple theoretical predictions exist for relations between the intramolecular correlation time τ_R and spin-rotation correlation time τ_J :

$$\tau_R = \frac{\tau_J}{2l+1} = \frac{\tau_J}{5} \quad [\text{k.m.}], \quad (25)$$

$$\tau_R \tau_J = \frac{I}{l(l+1)kT} = \frac{I}{6kT} \quad [\text{d.m.}]. \quad (26)$$

In the kinetic model ($T > T_{cr}$) for the supercritical/gas phase, Eq. (25) states that $\tau_R = \tau_J/5$,^{4,5} where $l = 2$ is the rank of rotational-diffusion tensor for rigid spheres. As shown in Fig. 3(a), for $T > T_{cr}$, the relation $\tau_R \propto \tau_J$ is indeed found; however, Eq. (25) overestimates τ_R by a factor ≈ 2.5 . In the diffusion model ($T < T_{cr}$) for liquids, Eq. (26)² makes use of the Stokes-Einstein relation for rigid spheres, which predicts that rotational-diffusion $D_R = 1/l(l+1)\tau_R = 1/6\tau_R$ and translational diffusion D_T are related by $D_T = 4a^2 D_R/3$,² where a is the methane radius. At the lowest D_T value, the relation $\tau_R \propto 1/\tau_J$ is indeed found; however, Eq. (26) underestimates τ_R by a factor ≈ 2.5 .

In the liquid phase ($T < T_{cr}$), the intermolecular correlation time τ_T decreases with increasing D_T , in general accordance with the Stokes-Einstein relation for rigid spheres $\tau_D = \frac{9}{4}\tau_T = 2a^2/D_T$.³⁹ The transport radius tends toward $a \approx 1.0 \text{ \AA}$ at the lowest D_T value, which is consistent with the C–H internuclear distance of $a \approx 1.093 \text{ \AA}$ deduced from the relation $I = \frac{8}{3}ma^2$,⁵⁴ where m is the ^1H mass. At high D_T , i.e., in the supercritical/gas phase ($T > T_{cr}$), the Stokes-Einstein relation breaks down and τ_T becomes independent of D_T .

A summary of the simulated standard deviations σ in correlation times is shown in Fig. 3(b). For spin rotation, σ_J increases by a factor of ≈ 2 from the lowest D_T to the highest D_T , indicating a larger distribution in correlation times for the gas phase. In the case of intramolecular dipole-dipole, σ_R shows a low value in the liquid phase and a possible increase with increasing D_T . In the supercritical/gas phase, $G_R(t)$ shows signs of oscillations at early times $t \lesssim 0.3$ ps and then decays monotonically for $t \gtrsim 0.3$ ps. As such, σ_R is not computed for $T > T_{cr}$. Note that oscillations in $G_R(t)$ for $T > T_{cr}$ were previously predicted using the extended diffusion model.^{8,15}

Meanwhile, σ_T decreases with increasing D_T , which is the opposite trend to σ_J and σ_R . At high D_T , σ_T plateaus to the $\sigma_T \approx 1.0$ [note that Fig. 3(b) displays $\sigma_T/4$ for clarity], which is consistent with the inherent multi-exponential value of the Hwang-Freed model ($\sigma_T \approx 1.04$)³⁹ for rigid spheres.⁴²

As stated in Eqs. (17) and (18), the longer the spin-rotation correlation time τ_J , the larger the ^1H relaxation rate R_{IJ} , i.e., the more significant the relaxation mechanism. The same is true for the ^1H - ^1H dipole-dipole mechanism.^{38,39} It is therefore informative to compare the ratio of relaxation rates between different mechanisms in order to determine which mechanism is dominant. Figure 4(a) shows the ratio R_{IJ}^{km}/R_{1RT} , where R_{1RT} is the total dipole-dipole relaxation defined in Eq. (20). A large value $R_{IJ}^{km}/R_{1RT} \gg 1$ indicates that spin rotation dominates over dipole-dipole, as found at high D_T in the supercritical/gas phase ($T > T_{cr}$). Meanwhile, a small value $R_{IJ}^{km}/R_{1RT} \ll 1$ indicates that dipole-dipole dominates over spin rotation, as found at low D_T in the liquid phase ($T < T_{cr}$).

FIG. 4. (a) Ratio of simulated ^1H relaxation rates R_1 to display relative strengths of the interactions, including the ratio of spin-rotation R_{1IJ}^{km} [Eq. (17)] to total dipole-dipole R_{1RT} [Eq. (20)] and ratio of intramolecular dipole-dipole R_{1R} to intermolecular dipole-dipole R_{1T} , plotted against measured D_T . (b) Simulated ^1H spin-rotation relaxation rate R_{1IJ}^{km} [Eq. (17)], empirical expression R_{1IJ}^A [Eq. (1)], new prediction R_{1IJ}^K [Eq. (27)], and total relaxation rate R_1^{km} [Eq. (19)], plotted against measured D_T .

A similar analysis can be made between the intramolecular and the intermolecular dipole-dipole interactions. A large value $R_{1R}/R_{1T} \gg 1$ indicates that intramolecular dominates over intermolecular, as found at high D_T in the supercritical/gas phase ($T > T_{cr}$). Meanwhile, a small value $R_{1R}/R_{1T} \ll 1$ indicates that intermolecular dominates over intramolecular, as found at low D_T in the liquid phase ($T < T_{cr}$), where $\tau_T \gg \tau_R$. Meanwhile, in the supercritical/gas phase ($T > T_{cr}$), even though $\tau_T \approx \tau_R$, the intermolecular second-moment $\Delta\omega_T^2 \propto \rho^{38,39}$ and therefore $\Delta\omega_T^2$ decreases with increasing D_T (i.e., decreasing ρ).

C. New kinetic model

Building on the observations that $\tau_J \approx \tau_K$ in the supercritical/gas phase ($T > T_{cr}$) [see Fig. 3(a)] and that spin rotation dominates over dipole-dipole $R_{1IJ}^{km}/R_{1RT} \gg 1$ in this region [Fig. 4(b)], it is informative to infer a new relation for $R_{1IJ}^{km} \approx R_1^{km}$ in the supercritical/gas phase. Assuming $\tau_J = \tau_K$ in Eq. (17) and using the definition for τ_K in Eq. (24) result in the following prediction:

$$R_{1IJ}^K = \frac{3\pi IM}{4\hbar^2} \left(C_a^2 + \frac{4}{45} C_d^2 \right) D_T \quad [\text{k.m.}]. \quad (27)$$

The new prediction in the kinetic regime R_{1IJ}^K is plotted in Fig. 4(b) against the simulated R_{1IJ}^{km} and the measured D_T . In the supercritical/gas phase ($T > T_{cr}$), the correlation coefficient between R_{1IJ}^{km} and R_{1IJ}^K is found to be $R^2 = 0.998$, and the absolute deviation is found to be $\delta_{abs} = 7.7\%$, without any adjustable parameters in the derivation of R_{1IJ}^K in Eq. (27). Moreover, there are no assumptions about an effective molecular radius. In the liquid phase ($T < T_{cr}$), R_{1IJ}^{km} starts to deviate from the kinetic model R_{1IJ}^K , as expected, and the total relaxation R_1^{km} deviates from R_{1IJ}^K due to the R_{1RT} contribution, also as expected.

Also shown in Fig. 4(b) is the empirical relation R_{1IJ}^A from Eq. (1), where $A = 6.37 \times 10^{-6}$ ²⁴ in units of temperature T (K), density ρ (g/cm³), and R_{1IJ}^A (s⁻¹). In the supercritical/gas phase ($T > T_{cr}$), the correlation between R_{1IJ}^A and R_{1IJ}^K is strong $R^2 = 0.991$, and the absolute deviation is $\delta_{abs} \approx 21.7\%$. Equations (1) and (27) imply that the T and ρ dependences in R_{1IJ} come entirely from $D_T \propto T^{3/2}/\rho$. The relation $D_T \propto T^{3/2}/\rho$ is confirmed in the supercritical/gas phase ($T > T_{cr}$), where the correlation between measured D_T and measured $T^{3/2}/\rho$ in Table I is strong $R^2 = 0.991$.

IV. CONCLUSIONS

We developed a minimization technique to compute the angular velocity for non-rigid spherical molecules, which is used to simulate the autocorrelation function $G_J(t)$ for the ^1H spin-rotation interaction of methane over a wide range of densities ρ and temperatures T , spanning the liquid ($T < T_{cr}$), and supercritical/gas ($T > T_{cr}$) phases. The Langevin model predicts that $G_J(t)$ should decay with a single exponential function with correlation time τ_J . However, inverse Laplace transforms of $G_J(t)$ indicate a distribution in correlation times τ , with a standard deviation σ_J (i.e., width) that increases with increasing D_T (i.e., decreasing ρ).

The ^1H spin-rotation relaxation rate R_{1IJ}^α is derived from $G_J(t)$ using the kinetic model “km” for gases (R_{1IJ}^{km})⁴ and the diffusion model “dm” for liquids (R_{1IJ}^{dm}).² The total ^1H relaxation rate R_1^{km} shows good agreement with measurements for $R_1 > 0.2 \text{ s}^{-1}$ (i.e., at high D_T), with an absolute deviation of $\delta_{abs} = 10.3\%$ in this region. At lower D_T , R_1^{dm} shows good agreement with measurements for $R_1 < 0.2 \text{ s}^{-1}$ and $T > T_{cr}$ (i.e., still in the supercritical/gas phase), with $\delta_{abs} = 9.1\%$ in this region. In the liquid phase ($T < T_{cr}$), $\delta_{abs} = 14.2\%$ is found between R_1^{dm} and measured R_1 . Meanwhile, the simulated D_T agree well with measurements $\delta_{abs} = 9.2\%$, without any adjustable parameters in the interpretation of the simulations.

MD simulations of the intramolecular and intermolecular ^1H - ^1H dipole-dipole relaxation are computed at the same state points. R_{1IJ}^{km} is shown to dominate over the total dipole-dipole relaxation R_{1RT} in the supercritical/gas phase ($T > T_{cr}$), while the opposite trend is found in the liquid phase ($T < T_{cr}$). Furthermore, in the liquid phase, the intermolecular relaxation R_{1T} is shown to dominate over the intramolecular relaxation R_{1R} .

The predicted relations between the intramolecular correlation time τ_R and the spin-rotation correlation time τ_J is tested, both in the liquid ($T < T_{cr}$) and the supercritical/gas phases ($T > T_{cr}$). At the highest D_T in the supercritical/gas phase, the relation $\tau_R = \tau_J/5^{4,5}$ is found to hold within a factor ≈ 2.5 . At the lowest D_T in the liquid phase, the relation $\tau_R \tau_J = 1/6kT^2$ is found to hold within a factor ≈ 2.5 .

In the supercritical/gas phase ($T > T_{cr}$), τ_J is found to agree with the kinetic collision time τ_K , with $\delta_{abs} = 7.7\%$ in this region. Given this compelling finding, a new expression for the ^1H spin-rotation relaxation $R_{1J}^K \propto D_T$ is inferred without any adjustable parameters and shows a strong correlation $R^2 = 0.991$ with the previously reported empirical finding $R_{1J}^A \propto T^{3/2}/\rho$.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a table for all data plotted in Figs. 2–4 and the square root of the second moments $(\Delta\omega_{J,R,T}^\alpha/2\pi)$.

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