

Water as a Lévy Rotor

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A probability density function describing the angular evolution of a fixed-length atom-atom vector as a Lévy rotor is derived containing just two dynamical parameters: the Lévy parameter α and a rotational time constant τ . A Lévy parameter $\alpha < 2$ signals anomalous (non-Brownian) motion. Molecular dynamics simulation of water at 298 K validates the probability density function for the intramolecular ^1H – ^1H dynamics. The rotational dynamics of water is found to be approximately Brownian at subpicosecond time intervals, becomes increasingly anomalous at longer time intervals due to hydrogen-bond breaking and reforming, before becoming indistinguishable from Brownian dynamics beyond about 25 ps. The Lévy rotor model is used to estimate the intramolecular contribution to the longitudinal nuclear-magnetic-resonance (NMR) relaxation rate $R_{1,\text{intra}}$. It is found that $R_{1,\text{intra}}$ contributes $65\% \pm 7\%$ to the overall relaxation rate of water at room temperature.

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Water is a complex liquid and the most important substance in nature. The water dynamics is critical to the understanding of protein folding, biomolecular water interface dynamics, water dynamics at the surfaces of porous materials, and the behavior of solvated ions, to list but a few examples. Each of these processes is fundamental to life itself.

The dynamics of water may be probed by ^1H nuclear magnetic resonance (NMR) techniques. For instance, the longitudinal relaxation rate R_1 is exquisitely sensitive to changes in the magnetic dipole-dipole interaction due to the relative motion of pairs of ^1H spins arising from the collective effects of vibration, bond stretching, libration, tumbling, collisions, and the breaking and reforming of H bonds [1]. Time constants associated with specific motions may be measured or inferred using infrared spectroscopies or isotope-enhanced NMR methods (see [2–5] and sources therein).

The complex combination of translational and rotational motions can be subcategorized into inter and intramolecular contributions. The intermolecular dynamics describes the evolution in space and time of a vector connecting a ^1H spin on one molecule to a second ^1H spin on a different molecule. The intramolecular contribution accounts for pairs of spins on the same molecule. The time evolution of both the angular rotation and the vector length contribute to the observed relaxation rate.

This Letter focuses on intramolecular ^1H – ^1H spin dynamics. A description of the rotational dynamics of an intramolecular ^1H – ^1H spin vector is presented which encapsulates the complex dynamics with just two parameters. The dynamics is described as a Lévy random walk [6]. Lévy statistics have been used to characterize an

enormous range of physical phenomena from foraging albatrosses to entropy, from stock price fluctuations to heart beats [7]. Lévy statistics applies to phenomena in which the more extreme events occur more frequently than predicted by a Brownian process leading to tails of the probability density that follow a power law rather than an exponential decay. This is often referred to as “anomalous” diffusion.

The Lévy model may be used to describe anomalous rotational diffusion in liquids in the bulk or confined in a porous medium, in large-molecular systems, and even in aqueous solutions containing ionic complexes. Here, the Lévy rotor model is applied to liquid water. Water is a relatively simple system that can be used to validate the Lévy model through molecular dynamics (MD) simulations using well-characterized force fields. Hydrogen-bond breaking and reforming is the known source of sudden angular changes leading to anomalous rotational dynamics. The Lévy model is then used to estimate the intramolecular contribution to the spin-lattice relaxation rate $R_{1,\text{intra}}/R_1$. In pure water, R_1 is independent of the Larmor frequency over the frequency range 0.01–40 MHz and equal to 0.280 s^{-1} [8]. In ionic complexes, chemically bound or physisorbed environments, R_1 is a function of Larmor frequency.

The simplest description of the intramolecular rotational dynamics dates from 1929 and the work of Debye [9] in which an atom-to-atom vector is described as a Brownian rotational diffuser executing a random sequence of small rotational steps. The simple model provides a prediction for the NMR relaxation rate R_1 [1,10]. Ivanov [11] provided a general mathematical treatment of rotational diffusion and identified that the rotational time constants should be experimentally measurable. A recent examination of water dynamics undertaken by Laage and co-workers in a series

of articles [12–16] provides insight into the dynamics not only of water but also of hydrated ions and complexes. The reorientation dynamics of water due to hydrogen bonding is discussed [14]. After a H bond is broken, the H bond may reform with the same or a different oxygen acceptor. Each process is characterized by a different time constant resulting in a highly complex dynamical picture only partially clarified by experiment and MD simulations. Popov and co-workers [17] provide a detailed review of H-bond network dynamics and its influence on particle dynamics, describing the role of processes (macroscopic motion, vibrational modes, libration) on multiple time-scales up to 10 THz.

The Lévy model for a water molecule is illustrated in Fig. 1. The vector \mathbf{r}_0 connects the two H atoms in a single water molecule at time $t = 0$ and is of fixed length a . The water molecule is in motion and the vector \mathbf{r} changes direction (but not length) as a function of time. The angle ψ is the smallest angle between the two vectors \mathbf{r}_0 and \mathbf{r} at time t . Small fluctuations of angle ψ may be described by Brownian dynamics. Occasionally the rotor undergoes a large change of angle which might be due to H-bond breaking and reforming with a different water molecule. The process repeats with the angular evolution of \mathbf{r}

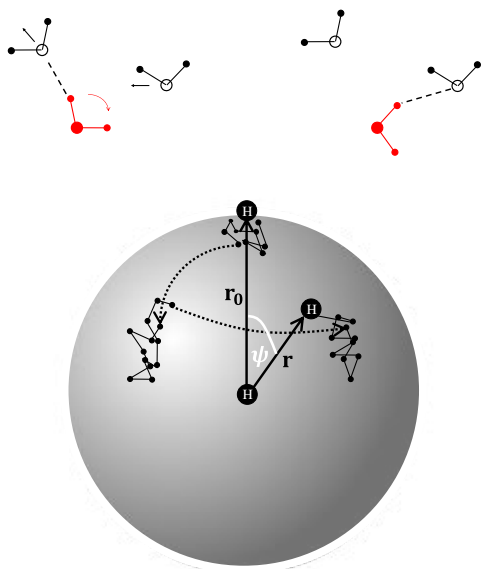


FIG. 1. The Lévy model accommodates non-Brownian rotation dynamics such as H-bond breaking and reforming, illustrated top left by three water molecules with a H bond (dashed line) which breaks and reforms with a different water molecule (top right). Below, a coordinate system places one H-atom of a water molecule at the origin. The second H atom is a fixed distance a from the first and shown on the surface of a sphere of radius a . The ^1H – ^1H vector at $t = 0$ is labeled \mathbf{r}_0 . Rapid small angular movements of the ^1H – ^1H vector (solid lines) are punctuated by sudden large angular changes (dotted arrows). An example ^1H – ^1H vector at time t is labeled \mathbf{r} . The smallest angle between \mathbf{r}_0 and \mathbf{r} is ψ .

described as a Lévy rotor as seen in MD simulations [3] and NMR experimentation [18,19].

The key result of this Letter is a time-dependent angular probability density function $P(\psi, t)$ of a fixed-length rotor that captures the anomalous diffusion as a Lévy random walk and which fully accounts for the angular boundary conditions; ψ cannot take values less than zero or greater than π . The expression for $P(\psi, t)$ is justified in Supplemental Material [20–22] as

$$P(\psi, t) = N(t) \left[1 + 2 \sum_{p=1}^{\infty} e^{-p^\alpha t/\tau} \cos p\psi \right], \quad (1)$$

where τ is a characteristic rotational time constant and $N(t)$ is a normalization constant (found in Supplemental Material [20–22]). The Lévy parameter α is a measure of the departure from Brownian motion. If $\alpha = 2$, Brownian rotational dynamics is recovered. Anomalous diffusion is associated with $\alpha < 2$ with $\alpha = 1$ a special case of Cauchy-Lorentz dynamics. The rotational time constant τ in Eq. (1) is defined differently to time constants bearing the same name in previous work. Here, $\tau/2$ is the average time taken for a rotor to move through an angle of one radian.

The time-dependent probability density function of Eq. (1) fully accounts for angular boundary conditions and has broad applicability. For example, $P(\psi, t)$ may be used to describe both Brownian or anomalous rotational motion of any vector connecting atom pairs in single molecules such as those containing paramagnetic markers for image enhancement in medical and biological research, or for rotors connecting aqueous ions and atoms in its first hydration shell.

The validity of the expression for $P(\psi, t)$ was checked using MD simulation for water. All MD simulations rely on force fields that describe the intramolecular and intermolecular interactions between atom types. The flexible extended single-point charge (SPC/E) force field [39] was chosen because it has been widely used in previous MD studies supporting NMR experimentation [2,3,34]. The MD model using the SPC/E force field incorporates fully flexible bonds including angular vibration and bond stretching. The LAMMPS package was used for all simulations [40]. A system of 13 500 water molecules in a cubic box was pre-equilibrated to a temperature of 298 K and zero applied pressure under isothermal and isobaric conditions. The simulation temperature was controlled using the Hoover thermostat [41] and periodic boundary conditions were applied. The data gathering used the NVT (constant number of particle, volume, and temperature) ensemble for a time period of 100 ps with atomic positions recorded at 1 ps intervals.

The probability density function $P(\psi, t) \sin \psi$ is computed for times $t = 0.01$ –25 ps using Eq. (1) and fit to the distribution obtained from MD simulation. The optimum fit as judged by minimizing the least-squared deviation to

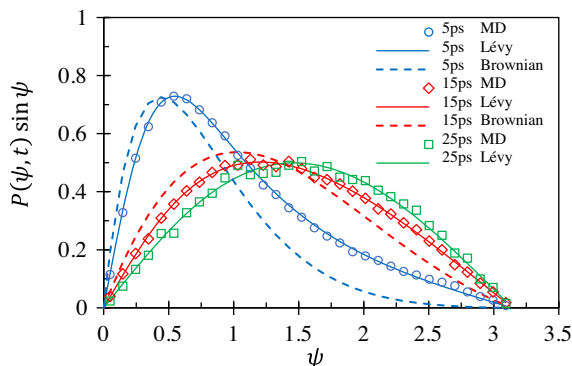


FIG. 2. The figure presents the probability density function $P(\psi, t) \sin \psi$ obtained from MD simulations (symbols). The Lévy model (solid lines) and Brownian models (dashed lines: 5 and 15 ps only for clarity) are obtained using Eq. (1).

provide α and τ . Figure 2 compares the evolutions at $t = 5$, 15, and 25 ps. The distributions for a Brownian rotor provide a poor match to the MD results. By contrast, the Lévy model of Eq. (1) provides excellent fits confirming that the rotational dynamics of water is anomalous. For times $t \geq 25$ ps (not shown), the distinction between Lévy and Brownian dynamics disappears (see Supplemental Material [20,25]).

The results for α and τ are presented in Fig. 3. As anticipated, $\alpha \rightarrow 2$ at very short time intervals indicating Brownian rotational dynamics with small angular changes characterized by a picosecond time constant. The rotational motion becomes increasingly anomalous for longer time intervals due to large changes in angle associated with H-bond breaking and reforming causing α to decrease. α attains a constant value of approximately 0.8 for time intervals in excess of 15 ps. The uncertainties in τ and α based on a 5% deviation from the minimum of the least squares quality-of-fit parameter are ± 0.2 ps and ± 0.04 , respectively. At longer times, however, $P(\psi, t)$ becomes less sensitive to α , the uncertainties increase (as shown for $t = 23$ –25 ps), and the distinction between the Lévy and Brownian models diminishes (see Supplemental Material [20,25] for further details).

Infrared (IR) spectroscopy may be used to measure rotational time constants in water. An O—H bond switching time of approximately 2.5 ps is suggested from both experiment and MD [4]. Ultrafast 2D IR vibrational-echo chemical-exchange spectroscopy has been used to measure an anion-oxygen H-bond switching time constant of 6.5 ps [42]. The rotational time constant $\bar{\tau}/2 \approx 4$ ps found here corresponds to the characteristic time for an angular change of 1 radian, approximately the H-bond switching angle, and is consistent with the experimental values.

Experimental ^1H NMR relaxometry of water measures R_1 but cannot resolve the individual dynamic components that contribute to the relaxation rate. In a model, however, the contributions of the intramolecular and intermolecular

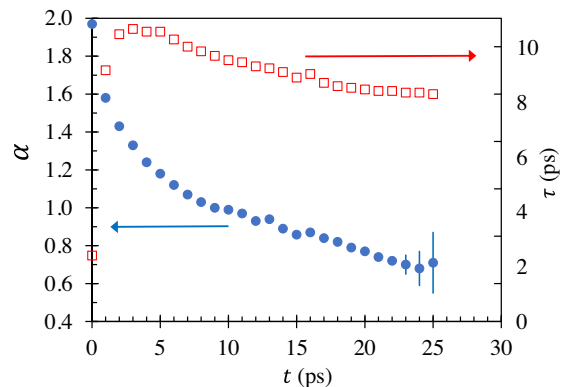


FIG. 3. The figure presents the Lévy parameter α and rotational time constant τ obtained from fits to MD results using Eq. (1) for time intervals $t = 0.01$ ps and 1–25 ps. The uncertainty in τ based on a 5% range of best-fit quality-of-fit parameter is ± 0.2 ps (see Supplemental Material [20,25]). The uncertainty in α is ± 0.04 except for $t \geq 23$ ps shown as error bars.

components may be separately estimated. The intramolecular contribution is associated with the rotation of the fixed-length ^1H — ^1H vector in the applied magnetic field and the intermolecular contribution is due to the relative translational motion of pairs of ^1H spins on different molecules and includes changes in both vector length and angle. The rotational time constant τ presented in Fig. 3 as a function of time interval characterizes the average intramolecular ^1H — ^1H bond rotation due to all dynamical processes.

Equation (1) supplies an excellent description of the rotational dynamics of any vector \mathbf{r} of fixed length a connecting two hydrogen nuclei in water as a Lévy rotor in terms of just two parameters, α and τ . Equation (1) is used to estimate the intramolecular contribution to the longitudinal relaxation rate R_1 of pure water. The room temperature relaxation rate for pure water was studied extensively by ^1H NMR relaxometry from the 1950s to the 1970s. Consistent values of R_1 were achieved once the contribution of dissolved oxygen had been identified and removed. Krynicky [8] summarized the collective data for air-free pure water at room temperature. The room-temperature relaxation rate interpolated from Fig. 1 is $R_1 = 0.280 \pm 0.010 \text{ s}^{-1}$.

The Lévy model for intramolecular rotation assumes that the distance between the two ^1H spins on the same water molecule is fixed and that the rotational evolution is described by the probability density function $P(\psi, t)$ given by Eq. (1). The time-dependent dipolar correlation function $G(t)$ describes how spin pairs move relative to each other and is derived in Supplemental Material, Note 2 [20,23,24] as

$$G(t) = \frac{1}{a^6} \int_0^\pi P_2(\cos \psi) P(\psi, t) \sin \psi d\psi, \quad (2)$$

where $P_2(x)$ is the second-rank Legendre polynomial, and a is the intramolecular ^1H – ^1H distance. Critical to an accurate determination of R_1 is the choice of a . Sawyer [28] has proposed that, for NMR applications, $a = \langle r_{\text{HH}}^{-3} \rangle^{-1/3}$ recognizing the r^{-3} distance dependence of the dipolar interaction. A summary discussion in Supplemental Material [20,26,27,29–33] justifies $a = 0.1545 \pm 0.0007$ nm.

The spectral density function $J(\omega)$ is the Fourier transform of the dipolar correlation function,

$$J(\omega) = 2 \int_0^\infty G(t) \cos \omega t dt, \quad (3)$$

and the longitudinal relaxation rate is expressed as [1]

$$R_1 = \frac{1}{5} \beta_{\text{II}} [J(\omega) + 4J(2\omega)], \quad (4)$$

where ω is the Larmor frequency of a ^1H spin in the applied static field, $\beta_{\text{II}} = (\mu_0/4\pi)^2 \gamma_1^4 \hbar^2 I(I+1)$, γ_1 is the proton gyromagnetic ratio, and $I = \frac{1}{2}$. For water $\beta_{\text{II}} = 4.275 \times 10^{11} \text{ m}^6 \text{ s}^{-2}$.

The spin-lattice relaxation rate R_1 is computed directly from the values of α and τ . Contributions beyond 20 ps are found to be negligible indicating that only dynamics with time constants less than 20 ps contribute to the relaxation rate in water. Therefore, the numerical values of α and τ presented in Fig. 3 for times 1–20 ps are used directly with $G(t)$ at intermediate times obtained by quadratic interpolation. $R_{1,\text{intra}}$ is computed using Eqs. (2)–(4).

We find $R_{1,\text{intra}} = 0.183 \text{ s}^{-1}$ and is independent of frequency over the range 1 kHz–40 MHz. The experimental value of R_1 is 0.280 s^{-1} at 28 MHz and at room temperature [8] so that $R_{1,\text{intra}}/R_1 = 0.65$. The uncertainties in the dynamical time constants and their impact on $R_{1,\text{intra}}$ are assessed in Supplemental Material [20,36–38]. Time constants for specific motions may differ from experiment by up to 20% but the single τ used here encompasses all dynamics that contribute over a time interval. It is argued that a reasonable estimate of the overall uncertainty of the flexible SPC/E force field to reproduce τ is $\pm 10\%$. The value of τ in Fig. 3 is changed by $\pm 10\%$ to obtain $R_{1,\text{intra}}/R_1 = 0.65 \pm 0.07$.

The first estimation of the intramolecular contribution to R_1 in the 1960s treated a molecule as a rotating sphere in a viscous fluid concluding that the intramolecular contribution was approximately 50% of the total rate [1,43]. The most recent comparable work is by Calero and co-workers [34] who determined R_1 from MD simulations of water using four different intra- and interatomic force fields. Force field TIP4P/2005 yielded the best estimate of R_1 at room temperature for which $R_{1,\text{intra}}/R_1 = 0.67$. Calero *et al.* determine both $R_{1,\text{inter}}$ and the diffusion coefficient from MD simulation. Their diffusion coefficient is 13% lower than the experimental value [35]. It is calculated in

Supplemental Material that, if their MD simulations had yielded the experimental diffusion coefficient, this would yield $R_{1,\text{intra}}/R_1 = 0.65$. Calero’s overall value for R_1 is 6% lower than the experimental value. The relaxation rate scales as a^{-6} and this remaining error is probably associated with the quality of the TIP4P/2005 force field to reproduce the ^1H – ^1H distance.

In summary, the key result is Eq. (1) which provides the first description of an anomalous (Lévy) rotor. Equation (1) may be used to model rotational dynamics of pairs of atoms in molecular liquids, molecules with restriction motion such as biomolecules or proteins, and aqueous ionic complexes. Equation (1) is shown to provide an excellent description of the rotational dynamics of the intramolecular ^1H – ^1H vector in water. Water is found to be a highly anomalous diffuser over timescales $t \leq 25$ ps due to H-bond breaking and reforming with the distinction between the Lévy and Brownian models diminishing for timescales longer than 25 ps. The headline values for $R_{1,\text{intra}}/R_1$ obtained here and from Calero *et al.* (corrected) are identical, despite different methods of calculation, and found to be $65\% \pm 7\%$.

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