

Calculation of NMR T₂ Relaxation time from Molecular Dynamics Simulations

The theory of nuclear magnetic relaxation (NMR) in liquids is well established^{1,2}, based on a semiclassical theory where the motion of the molecules is treated classically, whereas the nuclear spin is described quantum-mechanically. For hydrogen proton bearing liquids, the nuclear spin relaxation is dominated by the ¹H-¹H dipole-dipole interaction. (N.B at high temperatures (e.g > 373 K for water) the spin-rotation contribution should be taken into account).

Central to the development of NMR relaxation theory in liquids is the autocorrelation function $G_{R,T}^{(m)}(t)$ of fluctuating magnetic dipole-dipole interactions³,

$$G_{R,T}^{(m)}(t) = \frac{12\pi}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \hbar^2 \gamma^4 I \left(I + \frac{1}{2} \right) \frac{1}{N} \sum_{i \neq j}^N \left\langle \frac{Y_{2,m}(\Omega_{ij}(t+\tau))}{r_{ij}^3(t+\tau)} \frac{Y_{2,m}^*(\Omega_{ij}(\tau))}{r_{ij}^3(\tau)} \right\rangle_\tau \quad (1)$$

where μ_0 is the permeability of free space, \hbar is the reduced Planck's constant, γ is the gyromagnetic ratio, I is the spin, t is the lag time in the autocorrelation and N is the number of interacting spins. $Y_{2,m}(\Omega_{ij}(t+\tau))$ and $Y_{2,m}^*(\Omega_{ij}(\tau))$ are spherical harmonics and r_{ij} is the distance between spins i and j . The subscripts R and T denote the intramolecular and intermolecular spin interactions respectively. $\Omega \equiv (\theta, \phi)$ where θ is the polar angle (see Figure 1) and ϕ the azimuthal angle. For $m=0$, $Y_{2,0} = \sqrt{5/16\pi} (3\cos^2\theta - 1)$. Thus;

$$G_{R,T}(t) = \frac{3}{16} \left(\frac{\mu_0}{4\pi} \right)^2 \hbar^2 \gamma^4 \frac{1}{N} \sum_{i \neq j}^N \left\langle \frac{3(\cos^2\theta_{ij}(t+\tau) - 1)}{r_{ij}^3(t+\tau)} \frac{3(\cos^2\theta_{ij}(\tau) - 1)}{r_{ij}^3(\tau)} \right\rangle_\tau \quad (2)$$

for spin $I = 1/2$.

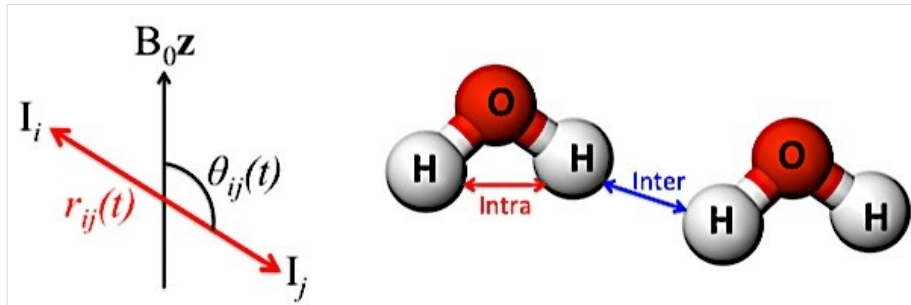


Figure 1: Illustration of water molecules, with hydrogen (white) and oxygen (red) atoms. A ¹H nuclear spin is shown interacting with a neighboring ¹H nuclear spin on the same water molecule, known as the intramolecular dipole-dipole interaction (red) which is characterized by the rotation correlation time τ_R of a single molecule. The same ¹H nuclear spin is also shown interacting with a ¹H nuclear spin from a different water molecule, known as the intermolecular dipole-dipole interaction (blue) which is characterized by the translational correlation time τ_T between molecules. Axes illustrate the distance $r_{ij}(t)$ between nuclear spins I_i and I_j with respect to the applied static magnetic-field direction $B_0 = B_0\mathbf{z}$, and corresponding polar angle $\theta_{ij}(t)$.

Therefore, calculation of T₂ relaxation time from molecular dynamics (MD) simulations involves the computation of $G_{R,T}(t)^{3-5}$. Specifically, from MD position

trajectories, we analyze the evolution of the relative distances r_{ij} and angles θ_{ij} between hydrogen atoms of the molecules involved. Once the autocorrelation function $G_{R,T}(t)$ is determined from MD simulations, $T_{2,R,T}$ is calculated from the following equation:

$$\frac{1}{T_{2,R,T}} = \frac{3}{2} J_{R,T}(0) + \frac{5}{2} J_{R,T}(\omega_0) + J_{R,T}(2\omega_0) \quad (3)$$

where $\omega_0 = \gamma B_0$ is the Larmor frequency and $J_{R,T}(\omega)$ is the spectral density of the local magnetic-field fluctuations determined by the Fourier transform of $G_{R,T}(t)$:

$$J_{R,T}(\omega) = 2 \int_0^{\infty} G_{R,T}(t) \cos(\omega t) dt \quad (4)$$

The total T_2 relaxation time is the obtained from $T_{2,R}$ and $T_{2,T}$ as:

$$\frac{1}{T_2} = \frac{1}{T_{2,R}} + \frac{1}{T_{2,T}} \quad (5)$$

From $G_{R,T}(t)$, the correlation times $\tau_{R,T}$ are obtained as follows:

$$\tau_{R,T} = \frac{1}{G_{R,T}(0)} \int_0^{\infty} G_{R,T}(t) dt = \frac{1}{2} \frac{J_{R,T}(0)}{G_{R,T}(0)} \quad (6)$$

NMR relaxation theory also states a simple relation between $G_{R,T}(0)$ and the second-moment $\Delta \omega_{R,T}^2$ of the dipole- dipole interaction as:

$$G_{R,T}(0) = \frac{1}{3} \Delta \omega_{R,T}^2 \quad (7)$$

In the fast regime, $\omega_0 \tau_{R,T} \ll 1$, thus $J(0) = J(\omega_0) = J(2\omega_0)$. Equation (3) then becomes:

$$\frac{1}{T_{2,R,T}} = 5 J_{R,T}(0) = \frac{10}{3} \Delta \omega_{R,T}^2 \tau_{R,T} \quad (8)$$

In the fast regime, T_2 relaxation time is therefore given by:

$$\frac{1}{T_2} = \frac{10}{3} \Delta \omega_R^2 \tau_R + \frac{10}{3} \Delta \omega_T^2 \tau_T \quad (9)$$

In summary, the following are the steps to calculate T_2 relaxation time from MD simulations for bulk liquids:

- i. Save the position trajectories (x,y,z) of the hydrogen atoms from a molecular dynamics simulation e.g lammprj file from a MD simulation using LAMMPS.
- ii. Compute the HH autocorrelation function $G_{R,T}(t)$ to monitor the evolution of $r_{ij}(t)$ and $\theta_{ij}(t)$ for both intermolecular and intramolecular interactions.
- iii. Apply equations (3) or (8) to obtain the respective $T_{2,R,T}$ relaxation rates.
- iv. T_2 relaxation time is finally obtained from equations (5) or (9).

[Description of input parameters for the calculation of $G_{R,T}(t)$ (step ii above)]

You have three files: input, main.f90 and routines.f90

The input file includes the parameters described below. The main.f90 is the main program, while the routines.f90 contains the subroutines.

The input file:

tsim 25000	! Total number of snapshots
dt 10	! number of windows
twin 2500	! size of window
dumpfile dump-water.lammpstrj	! the lammps trajectory file
outfile water-out.dat	! the output file

In the main.f90 file, modify the following depending on the system

MOL1	! number of atoms per molecule
HNO	! number of hydrogen atoms per molecule
NATOMS	! Total number of atoms
NMOL	! Total number of molecules

The output file contains the following:

Line 1: $G_R(0)$, $G_T(0)$

Column 1: time (t)

Column 2: $G_R(t)/G_R(0)$

Column 3: $G_T(t)/G_T(0)$

Column 4: $G_R(t)$

Column 5 : $G_T(t)$

To run the code : ./compile

: ./corr.x < input

References

1. Abragam, A. *The principles of nuclear magnetism*. (Oxford university press, 1961).
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3. Singer, P. M., Asthagiri, D., Chapman, W. G. & Hirasaki, G. J. Molecular Dynamics Simulations of NMR Relaxation and Diffusion of Bulk Hydrocarbons and Water. (2016). doi:10.1016/j.jmr.2017.02.001
4. Calero, C., Martí, J. & Guàrdia, E. H Nuclear Spin Relaxation of Liquid Water from Molecular Dynamics Simulations. *J. Phys. Chem. B* **119**, 1966–1973 (2015).
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