

Why are T_1 and T_2 of water what they are?

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Relaxation is one of the most basic and obvious effects in nuclear magnetic resonance (NMR) experiments. Relaxation describes how the nuclear magnetization returns to its equilibrium state after an excitation by a pulsed radio-frequency field. The transverse magnetization (precessing in the plane perpendicular to the external magnetic field \mathbf{B}_0 and yielding the measurable NMR signal) decays exponentially with a time constant called T_2 ; the longitudinal magnetization (parallel to \mathbf{B}_0) recovers exponentially with a time constant called T_1 .

For pure (distilled) water, these relaxation times are in the order of 1 to 5 seconds as established by numerous experiments. However, the calculation of these relaxation time constants is known to be notoriously complicated and difficult (requiring detailed quantum mechanical analysis of the spin ensembles and the spin interactions); a typical result of such an analysis is shown in the figure below.

So I wondered if the NMR relaxation time constants T_1 or T_2 of pure water can be roughly estimated using only some simple assumptions and considerations such that the resulting quantities are at least in the correct order of magnitude.

The main reason for transverse and longitudinal relaxation is the magnetic dipole-dipole interaction between spins (other effects such as interaction with the thermal radiation field or electric interactions with the electrons can be neglected for the water protons). The dipole field of a magnetic moment \mathbf{m} is

$$\mathbf{B}_{\text{dipole}}(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{3\mathbf{r}(\mathbf{m} \cdot \mathbf{r}) - \mathbf{m}r^2}{r^5} \quad (1)$$

or, which is enough for our order-of-magnitude estimations,

$$B_{\text{dipole}}(r) \sim \frac{\mu_0}{4\pi} \frac{|\mathbf{m}|}{r^3}, \quad (2)$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ T}^2\text{m}^3/\text{J}$ is the vacuum permeability.

The magnetic moment \mathbf{m} of the proton can be easily expressed by the gyromagnetic ratio $\gamma \approx 267.5 \times 10^6 \text{ rad}/(\text{sT})$, which is defined as the ratio between magnetic moment

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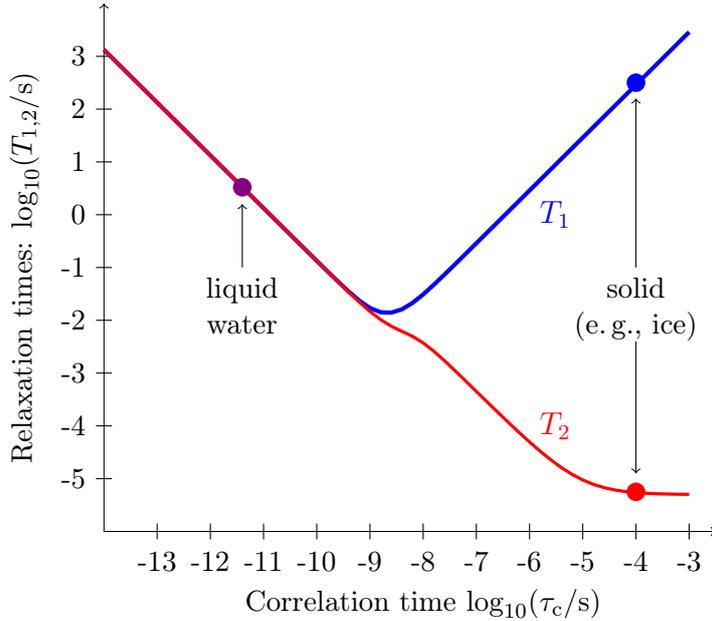


Figure 1: Relaxation times as function of the viscosity expressed by the correlation time τ_c . Short correlation times (on the left) correspond to low viscosity; long correlation times (on the right) to high viscosity.

and angular momentum \mathbf{I} , $\mathbf{m} = \gamma\mathbf{I}$. Approximating the angular momentum I of the proton by $I \sim \hbar \approx 1.055 \times 10^{-34}$ Js leads to $|\mathbf{m}| \sim \gamma\hbar \approx 3 \times 10^{-26}$ J/T and

$$B_{\text{dipole}}(r) \sim \frac{\mu_0 \gamma \hbar}{4\pi r^3} \approx 3 \times 10^{-33} \frac{\text{T m}^3}{r^3}. \quad (3)$$

A first idea about T_2 or transverse relaxation (introduced already 1946 in the [seminal NMR paper by F. Bloch](#)) is to consider spins (protons) in a rigid lattice, where the magnetic field of the nearest neighboring proton induces a phase shift at the spin of interest leading to signal dephasing. Using the shortest distance that is relevant for the nuclei in water molecules, namely the intramolecular proton-proton distance $d_{\text{pp}} \approx 0.15 \times 10^{-9}$ m, the additional, dephasing dipole field of a single neighboring proton is $\delta B = B_{\text{dipole}}(d_{\text{pp}})$. This yields a dephasing angular frequency $\delta\omega = \gamma\delta B = \gamma B_{\text{dipole}}(d_{\text{pp}})$ (in addition to the Larmor frequency due to the external \mathbf{B}_0 field). Assuming that transverse relaxation requires an additional phase angle of the order of 1, the time constant T_2 can be estimated to be of the order

$$\frac{1}{T_2} \sim \delta\omega = \gamma B_{\text{dipole}}(d_{\text{pp}}) \approx \frac{\mu_0 \gamma^2 \hbar}{4\pi d_{\text{pp}}^3} \approx \frac{1}{5 \mu\text{s}}. \quad (4)$$

Well, this value for $T_2 \sim 5 \mu\text{s}$ is obviously way too small for water – by about 6 orders of magnitude! So we are not even close ... but there is still something to learn from this: The very short T_2 is in fact quite exactly what we find in solids (as e.g. in water ice with $T_2 \approx 4 \mu\text{s}$ as measured by [T. G. Nunes et al.](#)), which shouldn't be too surprising

since we have assumed a rigid spin configuration above. Consequently, we've learned now that the constant random motion of water molecules in liquid water must play a very important role for the quantitative understanding of relaxation.

To obtain at least an order-of-magnitude estimation of the actual T_2 relaxation time (and in fact also of T_1) of *liquid* water, we have to include some additional information about the random motion of water molecules. A handy physical parameter to describe the effects of this random motion is the *correlation time* τ_c , which can be used to describe, e. g., a fluctuating magnetic field component $\langle B(t)B(t + \tau) \rangle = \langle B(t)^2 \rangle \exp(-|\tau|/\tau_c)$, where $\langle \cdot \rangle$ denotes the ensemble average over all spins and the result is assumed to be independent of the time t . So basically, after the correlation time τ_c the fluctuating field strength becomes statistically independent of its former values.

For the protons of water, this correlation time is extremely short, in the order of picoseconds: $\tau_c \approx 5 \times 10^{-12}$ s. This value is in fact about the diffusion time of a water molecule over a region with diameter d_{pp} , which is $d_{pp}^2/(6D) \approx 2 \times 10^{-12}$ s for $D \approx 2 \times 10^{-9}$ m²/s. It is important to note that there is almost no dephasing over the correlation time, i. e., $\tau_c \delta\omega \approx 10^{-6} \ll 1$. This means that the static dephasing as assumed above cannot take place since the protons move too quickly and the static effects are averaged out. After about τ_c , the motion has completely changed the orientation of the vector distance \mathbf{r} between the protons and, hence, also the magnetic dipole field direction and the magnitude of each field component.

To obtain an estimation of T_2 using this correlation time, we now consider the phase angles $\phi(t)$ within our ensemble of spins after a time t – more exactly, the *additional* phase angles (as seen in a rotating frame of reference) due to the fluctuating random magnetic fields $\delta B(t)$. These phase angles exhibit a random distribution with mean value $\langle \phi(t) \rangle = 0$, but the width of this distribution $\langle \phi(t)^2 \rangle$ increases proportional to the time $\langle \phi(t)^2 \rangle = \alpha t$. Similarly as above, we estimate our relaxation time T_2 to be the time required for this standard deviation to become of order 1; i. e., $T_2 \sim \frac{1}{\alpha} = \frac{t}{\langle \phi(t)^2 \rangle}$.

What can we say about the value of α ? The factor α must have the dimension of 1/time; it should increase with the local magnetic field strength $\delta B = \delta\omega/\gamma$ and also with the correlation time τ_c (the longer the correlation time, the less effective becomes the averaging). So, the simplest approach to express α by the given quantities with the correct physical dimension is to set $\alpha = \delta\omega^2 \tau_c$. With this guess, we find

$$\frac{1}{T_2} \sim \delta\omega^2 \tau_c \approx \left[\frac{\mu_0 \gamma^2 \hbar}{4\pi d_{pp}^3} \right]^2 \tau_c \approx 0.25 \text{ s}^{-1} \approx \frac{1}{4 \text{ s}} \quad (5)$$

in surprisingly good agreement with the experimental data.

To obtain a very similar result by an actual calculation, we can quantitatively determine the width of the distribution $\langle \phi(t)^2 \rangle$. The relation between the fluctuating magnetic field component $\delta B(t)$ seen by an individual spin and the phase evolution of this spin is

$$\phi(t) = \int_0^t \omega(t') dt' = \gamma \int_0^t \delta B(t') dt' \quad (6)$$

yielding

$$\langle \phi(t)^2 \rangle = \gamma^2 \langle (\int_0^t \delta B(t') dt')^2 \rangle = \gamma^2 \int_0^t dt' \int_0^t dt'' \langle \delta B(t') \delta B(t'') \rangle \quad (7)$$

or, by substituting $\tau = t'' - t'$,

$$\langle \phi(t)^2 \rangle = \gamma^2 \int_0^t dt' \int_{-t'}^{t-t'} d\tau \langle \delta B(t') \delta B(t' + \tau) \rangle. \quad (8)$$

We can now use the correlation time relation from above for the fluctuating random magnetic field component $\delta B(t)$, namely $\langle \delta B(t) \delta B(t + \tau) \rangle = \langle \delta B(t)^2 \rangle \exp(-|\tau|/\tau_c)$ with the average squared field strength $\langle \delta B(t)^2 \rangle \sim B_{\text{dipole}}(d_{\text{pp}})^2 \sim \delta\omega^2/\gamma^2$ to obtain

$$\langle \phi(t)^2 \rangle \sim \delta\omega^2 \int_0^t dt' \int_{-t'}^{t-t'} d\tau \exp(-|\tau|/\tau_c). \quad (9)$$

To solve this double integral without long calculations (which are nevertheless straightforward), we need the fact that $\tau_c \ll t$ and therefore almost always $\tau_c \ll \tau$ (the second integration variable), so the exponential function in the integral is almost always 0.

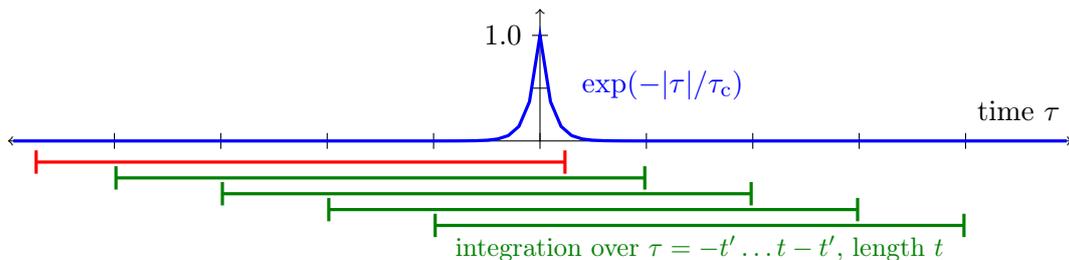


Figure 2: The integrals over $\tau = -t' \dots t - t'$ (integration ranges shown as colored lines at the bottom) can be approximated by the integral over $\tau = -\infty \dots \infty$ for almost all values of t' (green examples); errors occur only for few values of $t' \approx 0$ or $t' \approx t$ (red example).

Hence, the second (inner) integral can be approximated for almost all values of t' as $\int_{-\infty}^{\infty} \exp(-|\tau|/\tau_c) d\tau = 2 \int_0^{\infty} \exp(-\tau/\tau_c) d\tau = 2\tau_c$. With this approximation, we find

$$\langle \phi(t)^2 \rangle \approx \delta\omega^2 \int_0^t dt' 2\tau_c = 2\delta\omega^2 \tau_c t \quad (10)$$

and, consequently,

$$\frac{1}{T_2} \sim 2\delta\omega^2 \tau_c \approx 0.5 \text{ s}^{-1} \approx \frac{1}{2 \text{ s}}, \quad (11)$$

which is again an estimation that agrees well with the observed values.

A final short comment on T_1 : In non-viscous liquids such as water, T_1 and T_2 are approximately the same. While loss of phase coherence is required for T_2 relaxation, energy

transfer from individual spins to the liquid is causing T_1 relaxation. This energy transfer occurs due to transverse fluctuating magnetic fields $\delta B_{x,y}(t)$ with spectral components agreeing with the Larmor frequency $\omega = \gamma B_0$. Since these frequencies are much lower than the inverse correlation time, i. e., $\gamma B_0 \ll 1/\tau_c$, they basically occur with the same probability as the dephasing T_2 effects considered above. A more detailed analysis of T_1 and T_2 requires quantitative estimations of the spectral density functions $J(\omega)$ of the dynamic processes involved.

Update (2019-02-29)

A concise introductory summary about some approaches and results of quantitative relaxation theory can be found in the text book [“Principles of Nuclear Magnetic Resonance Microscopy”](#) by Paul T. Callaghan, section 2.5.

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