

ON NUCLEAR SPIN RELAXATION IN LIQUIDS IN THE PRESENCE OF CONTINUOUS DISTRIBUTION OF THE CORRELATION TIMES

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The influence of Log-Gauss distribution of the correlation times on the frequency dependence of nuclear spin relaxation times T_1 and T_2 is considered.

Distributions of the correlation times and their effect on the nuclear spin relaxation times T_1 and T_2 were considered in the series of papers [1–15]. In these papers several types of distributions were used. The most realistic of them seems to be Log-Gauss distribution, which reflects a Gaussian distribution of the activation free energy, provided that the temperature variations of the correlation time is given by the Arrhenius form of the activation law. It was shown [14–15] that the observed temperature dependence and frequency dependence of the proton spin-lattice relaxation time T_1 for water adsorbed by charcoal and for protein solutions may be explained assuming Log-Gauss distribution of the correlation times.

The purpose of this note is to show the theoretical calculations of the frequency dependence of the spin-spin relaxation time T_2 and the ratio T_1/T_2 in the presence of Log-Gauss distribution of the correlation times. According to the theory of nuclear spin relaxation [16–18] the relaxation times T_1 and T_2 are functions of the correlation time τ and Larmor precession angular frequency $\omega = \gamma H_0$ (γ — the gyromagnetic ratio H_0 — the external magnetic field). In the system of identical nuclear spins (like spins) and in the presence of dipolar interaction the theory gives

$$\frac{1}{T_1(\omega, \tau)} = A \left[\frac{\tau}{1 + \omega^2 \tau^2} + \frac{4\tau}{1 + 4\omega^2 \tau^2} \right] \quad (1)$$

$$\frac{1}{T_2(\omega, \tau)} = \frac{A}{2} \left[3\tau + \frac{5\tau}{1 + \omega^2 \tau^2} + \frac{2\tau}{1 + 4\omega^2 \tau^2} \right] \quad (2)$$

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where the constant A is proportional to the second moment M_2 for a rigid lattice [18]

$$A = \frac{2}{3} M_2. \quad (3)$$

In the presence of the continuous distribution of correlation times described by density function $G(\tau)$ the average values of the relaxation times may be expressed in the form

$$\frac{1}{T_n(\omega)} = \int_0^{\infty} \frac{1}{T_n(\omega, \tau)} G(\tau) d\tau, \quad (n = 1, 2) \quad (4)$$

where

$$\int_0^{\infty} G(\tau) d\tau = 1. \quad (5)$$

The density function $G(\tau)$ may be expressed in terms of a logarithmic correlation time scale. Namely, introducing a new variable [7] $s = \ln \frac{\tau}{\tau_0}$ where τ_0 is a centre of the distribution on a logarithmic scale one can replace $G(\tau)$ by a function $F(s)$, provided that

$$F(s) ds = G(\tau) d\tau \quad (6)$$

$$\int_{-\infty}^{\infty} F(s) ds = 1. \quad (7)$$

Assuming a Gaussian distribution in the logarithmic scale and taking into account the last condition, one gets

$$F(s) = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 s^2} \quad (8)$$

where α is a parameter determining the width of the distribution. The relaxation times T_1 and T_2 in the presence of the Log-Gauss (logarithmic-Gaussian) distribution $F(s)$ may be calculated from the following expression

$$\frac{1}{T_n(\omega)} = \int_{-\infty}^{+\infty} \frac{1}{T_n(\omega, s)} F(s) ds \quad (9)$$

where

$$\frac{1}{T_n(\omega, s)} = \left(\frac{1}{T_n(\omega, \tau)} \right)_{\tau = \tau_0 e^s} \quad (n = 1, 2). \quad (10)$$

From the above equations one can easily obtain the explicit form of $T_1(\omega)$, $T_2(\omega)$ and $T_1(\omega)/T_2(\omega)$ in very low and high frequency limits. At low frequencies for $\omega^2 \tau^2 \ll 1$

one gets

$$\frac{1}{T_1(\omega)} = \frac{1}{T_2(\omega)} = 5A\tau_0 e^{\frac{1}{4\alpha^2}} \quad (11)$$

whereas at high frequencies for $\omega^2\tau^2 \gg 1$ one finds

$$\frac{1}{T_1(\omega)} = \frac{2A}{\omega^2\tau_0} e^{\frac{1}{4\alpha^2}} \quad (12)$$

$$\frac{1}{T_2(\omega)} = \frac{3}{2} A\tau_0 e^{\frac{1}{4\alpha^2}} \quad (13)$$

$$\frac{T_1(\omega)}{T_2(\omega)} = \frac{3}{4} (\omega\tau_0)^{-2}. \quad (14)$$

Generally, the above-considered values may be found by numerical integration.

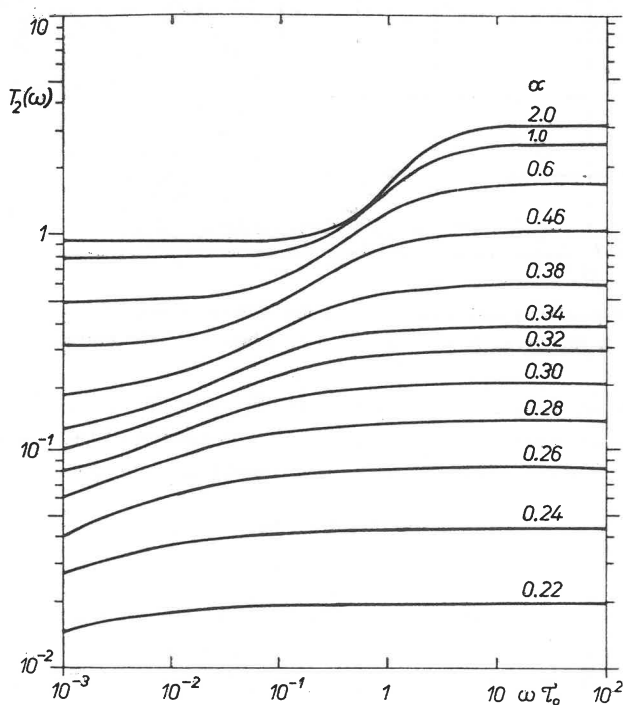


Fig. 1. Frequency dependence of the spin-spin relaxation time (in arbitrary units $5A\tau_0 = 1$) in the presence of Log-Gauss distribution of the correlation times

In Figs 1 and 2 are presented frequency dependences of $T_2(\omega)$ and $T_1(\omega)/T_2(\omega)$ respectively, calculated for different values of the parameter α . The numerical calculations were carried out using the "Odra 1204" digital computer at the Computing Centre of the Institute of Nuclear Physics in Cracow.

The theoretical results for $T_1(\omega)/T_2(\omega)$ in Fig. 2 can be compared with experimental data for protein solutions. At low concentration of proteins the observed values of the relaxation times T_1 and T_2 may be expressed in the following form [15]:

$$\frac{1}{T_n} = \frac{1}{T_{nw}} + k_n c \quad (n = 1, 2) \quad (15)$$

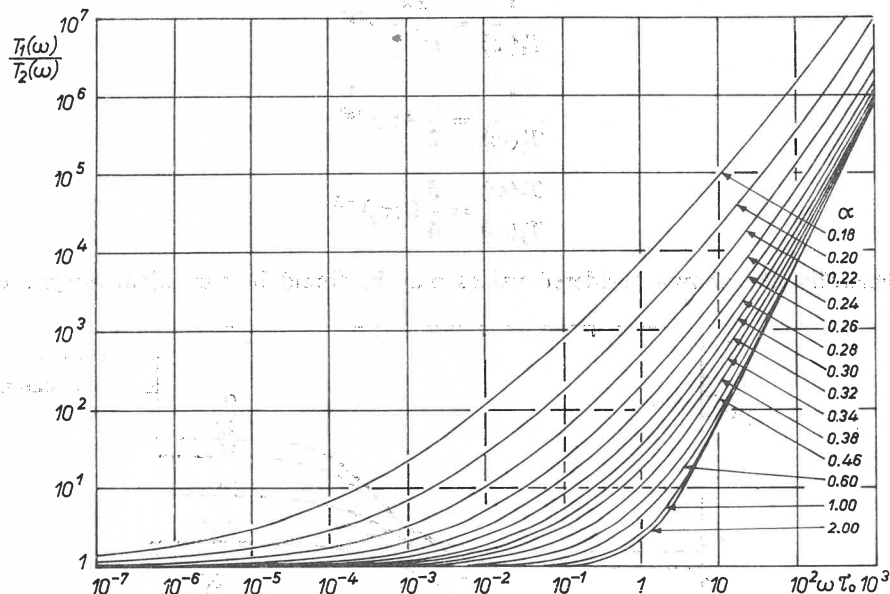


Fig. 2. Frequency dependence of the ratio of the spin-lattice relaxation time to spin-spin relaxation time in the presence of Log-Gauss distribution of the correlation times

where c is the relative concentration of protein, T_{nw} are the relaxation times for protons in free water (solvent), and the coefficients k_n are proportional to the relaxation rate $T_n^{-1}(\omega)$ for protons bound to the protein molecules. Therefore one gets

$$\frac{T_1(\omega)}{T_2(\omega)} = \frac{k_2}{k_1} \quad (16)$$

Taking the theoretical dependence $T_1(\omega)$ for $\tau_0 = 1.5$ ns and $\alpha = 0.34$ and 0.46 , it was possible to explain the observed frequency dependence of T_1 in aqueous solutions of protein at the concentration 9.3% and 4.5% respectively [15]. Using the above-mentioned values τ_0 and α for the concentrations 9.3% and 4.5% one can find from Fig. 2, the ratio $\frac{T_1(\omega)}{T_2(\omega)}$ at the resonant frequency 14 MHz should be equal to 3.3 and 1.7 respectively. The observed experimental value $k_2/k_1 = (2.5 \pm 0.8)$ within limits of the experimental error is in agreement with the theoretical prediction.

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