FIZIKA, 1 (1968) 57–58

LETTERS TO THE EDITOR

ON THE INTRODUCTION OF DISTRIBUTION CORRELATION TIMES IN PARAMAGNETIC RELAXATION

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Received 18 March 1968

In our study of molecular motion in starch[1], we studied the applicability of BPP theory [2–4] to the proton spin-lattice relaxation in a solid polymer such as starch. The simple theory presupposes the uniform relaxation mechanism via the isotropic motion of spin pairs and gives for the spin-lattice relaxation time, T_1:

$$\frac{1}{T_1} = \frac{1}{10\pi^2}\gamma^4 h^2 I(I+1)\sum_k r_{jk}^{-6}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c^2}{1+4\omega_0^2\tau_c^2}\right), \tag{1}$$

where γ, h, I, τ_c, ω_0 and r_{jk} are the gyromagnetic ratio, Planck constant, spin, correlation time, resonant frequency and the distance between spin »*j*« and »*k*«, respectively. Assuming the spin motion is a thermally activated process with an activation energy E_a,

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{kT}\right), \tag{2}$$

where τ_0, k and T are the constant characteristic of the system (the value of τ_c for infinite temperature), Boltzman constant and absolute temperature, respectively, measurements of relaxation time T_1 as a function of temperature can be used in a study of molecular motion. Contrary to the findings on solid polymers by other authors[5–10] we have found the BPP theory inconsistent with experiment in the case of starch. In the field of dielectric relaxation good agreement has been obtained between theory and experiments by the presumption of distribution of relaxation times[11]. The correlation between dielectric and magnetic relaxations[10, 12–16] stimulated many authors[5–9, 17–21] to replace the single BPP correlation time, τ_c, with the continuous distribution of correlation times, $G(\tau)$,

$$\frac{1}{T_1} = \text{const.}\left[\int_0^\infty \frac{G(\tau)\,d\tau}{1+\omega_0^2\tau^2} + 4\int_0^\infty \frac{G(\tau)\,d\tau}{1+4\omega_0^2\tau^2)}\right], \tag{3}$$

$$\int_0^\infty G(\tau)\,d\tau = 1, \tag{4}$$

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and to use a more general relation instead of eq. (2),

$$\tau = \tau_0 \exp\left[\frac{E_a}{k(T - T_0)}\right], \tag{5}$$

where T_0 is a constant, $T_0 < T$.

In the choice of $G(\tau)$ the mentioned authors searched for the simplest form from the calculational point of view, because the connection between the distribution and the real character of molecular motion leads to significant mathematical difficulties[17, 18]. Although such distribution can help to fit the theory to experimental results, in our opinion it is a mathematical speculation rather than a physical approach. The distribution generally introduces two degrees of freedom (a shape of the distribution and a width of the distribution), so its formal success is not surprising. However, physically it has no value unless it is related to the dynamical parameters of the lattice. From eq. (2) it generally follows $G = G(\tau_0, E_a)$ and in an artificially introduced distribution the source of distribution is not unambiguous. Furthermore, eq. (1) can be modified in a manner different from an introduction of the distribution but with the same efficiency[22].

We believe that the right way is to deduce an adequate relation instead of eq. (1) rather than to modify this equation.

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