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CONTRIBUTION TO THE MICROSCOPIC THEORY OF NUCLEAR MAGNETIC RELAXATION IN A LIQUID

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Results of a microscopic theory of nuclear magnetic relaxation in a liquid are presented for electric quadrupole intermolecular interactions of the nuclear spins. The formulas do not contain phenomenological parameters of the self-diffusion or viscosity type, but are completely defined by the molecular properties of the medium (integrals of the radial distribution function, reduced mass and thermal energy of the interacting particles). A new feature of the traditional relaxation-time temperature dependences that are ordinarily associated with diffusion motions of the particles is revealed.

ALLOWANCE for the thermal motion of particles in the theory of nuclear magnetic relaxation of spins in a liquid[1-7] has so far been made only phenomenologically. The principal parameter for the analysis of the intermolecular mechanisms of relaxation is usually the self-diffusion coefficient D 1). Yet the use of this parameter is meaningful only for particle displacements $r \gg a \sim 10^{-8}$ cm during a time interval $t \gg \tau_c = a^2/2D \sim 10^{-12}$ sec (a and τ_c are parameters characteristic of relaxation in liquids).

The theory can be constructed entirely on a microscopic basis, by using a simple statistical method to calculate the time correlation functions (TCF) of the "lattice" part of the spin perturbations in the method of Kubo and Tomita.[8] The gist of this method is as follows. The TCF needed to determine the spectral densities can be represented, for small time intervals, in the form

$$\langle P_\beta{}^*(0)P_\beta(t)\rangle = \left\langle \sum_{n=0}^{\infty} P_\beta{}^*(0)\,\frac{t^n}{n!}\,L^n P_\beta(0)\right\rangle$$

$$= \langle |P_\beta(0)|^2\rangle \exp(-t^2/\tau^2),$$

$$\tau^{-2} \doteq {}^1\!/_2 |\langle P_\beta{}^*(0)\hat{L}^2 P_\beta(0)\rangle / \langle |P_\beta(0)|^2\rangle. \tag{1}$$

The calculations in (1) can be carried through to conclusion for an arbitrary intermolecular relaxation mechanism with the aid of the Liouville operator $\hat{L}$ and an equilibrium distribution function in the cannonical ensemble. The numerical estimates give for τ values $\sim 10^{-12}$ sec. Owing to the strong decrease of the spin perturbations with distance ($\sim r^{-n}$, $n = 3, 4$), their time correlation turns out to be quite weak, so that the form (1) is perfectly suitable.

Concrete calculations were made for quadrupole interactions of nuclear spins with the liquid particles. For electric interactions between the spin and the charged ions of one kind, the expressions for the longitudinal and transverse relaxation times were found to be:

$$T_1^{-1} = \pi^{1/2}\tau\sigma^2\{\exp(-\omega^2\tau^2/4) + 4\exp(-\omega^2\tau^2)\},$$

$$T_2^{-1} = \pi^{1/2}\tau\sigma^2\{{}^3\!/_2 + {}^5\!/_2\exp(-\omega^2\tau^2/4) + \exp(-\omega^2\tau^2)\};$$

$$\tau^{-2} = \frac{15k_BT}{m^*}\int_0^\infty g_{iA}(r)r^{-6}\,dr \Big/ \int_0^\infty g_{iA}(r)r^{-4}\,dr,$$

$$\sigma^2 = \frac{3}{4\pi}\left[I(I+1) - \frac{3}{4}\right]\frac{N_A}{V}\left\{\frac{4\pi e e_A Q\beta}{5\hbar I(2I-1)}\right\}^2 \int_0^\infty g_{iA}(r)r^{-4}\,dr,$$

$$\beta = (1+\gamma_\infty)\frac{2\varepsilon+3}{5\varepsilon}, \qquad m^* = \frac{2m_i m_A}{m_i + m_A}.$$

For quadrupole interactions between the nuclear spin and electric dipole molecules of a solvent[6,9], we have in the limit of fast motion ($\omega\tau \ll 1$)

$$T_1^{-1} = T_2^{-1} = 48\pi^{5/2}\left[I(I+1) - \frac{3}{4}\right]\left\{\frac{eQ\beta d_A}{\hbar I(2I-1)}\right\}^2 \tag{2}$$

$$\frac{N_A}{V}\int_0^\infty g_{iA}(r)r^{-6}\,dr \cdot \left\{\frac{m^*}{28k_BT}\int_0^\infty g_{iA}(r)r^{-6}\,dr\right.$$

$$\left. \Big/ \int_0^\infty g_{iA}(r)r^{-8}\,dr\right\}^{1/2}. \tag{3}$$

We put here: ω—resonant frequency, Q—quadrupole moment of the nucleus, γ_∞—antiscreening coeffi-

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1)The simultaneous use of this parameter together with the radial distribution function in [5,6] is not perfectly correct, especially when the particle displacements are small.

cient, ϵ—dielectric polarizability of the medium, N_A/V—number of electric charges e_A or dipoles d_A per unit volume, k_BT—thermal energy, m_i and m_A—masses of diamagnetic ion with nuclear spin I and of solvent particle ($m^*/2$—their reduced mass), and $g_{iA}(r)$—radial distribution function of the liquid particles near the investigated ion.

The foregoing formulas do not contain parameters connected with translational self-diffusion or with viscosity. The relaxation times are determined completely by integrals of radial distribution functions, the reduced masses of the solution particles, and their kinetic energy. The results show an interesting unexpected dependence of T_1 and T_2 on m^*—a parameter which is perfectly natural for gases and which is connected with collisions between two particles. A careful analysis shows also how the traditional temperature dependence of T_1 and T_2, usually related to D, follows readily from (2) and (3). When $\omega\tau \ll 1$ (rapid motion) we have

$$T_1^{-1},\ T_2^{-1} \sim \exp\,(U_0\,/\,k_BT)$$

(U_0—energy parameter), and this dependence, unlike in the diffusion model, is connected not with the correlation time τ, which depends little on the temperature ($\sim T^{-1/2}$), but only with the rms spin perturbations in the equilibrium state. When $\omega\tau \gg 1$ (slow motion) we obtain

$$T_1^{-1} \sim \exp\,[\,(U_0 - \omega^2 a)\,/\,k_BT],$$

where the second term in the exponential is connected with τ and prevails over the first. In this case the sign of the temperature dependence under the exponential sign is reversed, just as in glycerin[1].

Numerical estimates based on (2) and (3) for I^-_{127} and Br^-_{79} ions show better agreement with experiment[10] than earlier in[4,6,9]. In addition, the microscopic theory developed here yields detailed information on the intermolecular close-range interactions of particles in a liquid. In those cases when the radial distribution functions are well known (for example, from x-ray scattering experiments), the formulas obtained for the nuclear relaxation rates admit of a precise comparison between theory and experiment on a purely molecular basis.

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