RELAXATION AND SHAPE OF PARAMAGNETIC RESONANCE LINES IN HIGHLY VISCOUS MEDIA

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Submitted to JETP editor May 8, 1963

J. Exptl. Theoret. Phys. (U.S.S.R.) **45**, 1523-1534 (November, 1963)

Relaxation and the paramagnetic resonance line shape are considered for media to which the Bloch-Redfield theory [1,2] is inapplicable, that is, when the condition $\sigma\tau_c \ll 1$ is not satisfied (σ is the line width and τ_c the molecular-motion correlation time). The general approach consists in considering only nonsecular interaction terms as perturbations on the condition that $\sigma \ll \omega_0$ (ω_0 is the resonance frequency) that is, in strong fields. Expressions for the longitudinal relaxation time and line shape are derived in the local field model. With a spin $^3/_2$ coupled to the medium by electric quadrupole interaction taken as an example, it is shown that contrary to the usual opinion, it is not always possible to neglect nonsecular interaction terms even when $\sigma\tau_c \gtrsim 1$ and $\sigma \ll \omega_0$. An expression for the line shape valid for all values of $\sigma\tau_c$ is deduced for a magnetically dilute liquid in which only spin $^1/_2$ pairs interact. It is shown that the Bloch-Redfield formula for the longitudinal relaxation time is valid in strong fields for all $\sigma\tau_c \lesssim \omega_0/\sigma$. It is predicted that longitudinal relaxation in a liquid in a medium field will not follow a simple exponential law.

1. INTRODUCTION

THE theory of paramagnetic resonance is most fully developed for two limiting cases: for liquids with intense molecular motion, and for solids. The intermediate region—the region of transition from the solid to the liquid state, is characterized by the condition $\sigma\tau_c \sim 1$, where σ is the width of the resonance line and τ_c is the correlation time of the molecular motion. In spite of the large number of experimental investigations of the relaxation and the line shape of paramagnetic resonance in the transition region, this region has not been sufficiently well studied theoretically.

The difficulty in describing paramagnetic resonance in the region where $\sigma\tau_c \sim 1$ is due to the fact that the kinetic theory of Bloch and Redfield [1,2] (see also [3]), which is based on perturbation theory, is valid only if $\sigma\tau_c \ll 1$.

From general considerations (see, for example [3]), it follows that for $\sigma\tau_c \gtrsim 1$ only the secular part of the interaction Hamiltonian is of importance in the determination of the line shape. In addition, the problem of determining the shape of the resonance line is a particular case of the problem of random frequency modulation of the signal, and we can write

$$g(\omega) = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} \overline{\exp\left\{i\int\limits_0^t \omega(t')\,dt'\right\}} e^{-i\omega t}\,dt, \tag{1.1}$$

where the superior bar denotes averaging over the distribution for the random process $\omega(t')$.

The present paper is aimed at obtaining an expression for the line shape and the longitudinal-relaxation time in the region $\sigma\tau_c \gtrsim 1$ for some simple spin systems, in which the local-field model is applicable [3,5], that is, for systems whose Hamiltonian is of the form

$$\mathcal{H} = \hbar[E + G(t)], \quad E = -\omega_0 I_z,$$
$$G(t) = \sum_{l,m}(-1)^m I_l^m F_l^{-m}(t), \tag{1.2}$$

where ω_0 is the precession frequency in a constant magnetic field, directed along the z axis; I_l^m is an irreducible tensor operator, made up of the spin components I_x, I_y, I_z (for a definition see, for example, the book by Fano and Racah [6] and the paper of Karyagin and Korst [7]). $F_l^m(t)$ are random functions of the time, with the aid of which the local fields produced by the environment at the spin location point are described.

Let us consider isotropic media, for which the correlation functions of the stochastic fields have the form

$$\overline{(-1)^m F_l^m(t) F_{l'}^{-m'}(t+\tau)} = \delta_{mm'}\delta_{ll'}\sigma_l^2 \exp(-|\tau|/\tau_c), \tag{1.3}$$

where $\delta_{mm'}$ and $\delta_{ll'}$ are the Kronecker symbols and τ_c is the correlation time.

As already mentioned, in the region under consideration the ordinary perturbation theory is not applicable, but at the same time the main contribution to the interaction is made by $G_0(t)$, which is the secular part (commuting with E) of the interaction operator $G(t)$. The perturbation will be regarded to be only the nonsecular part $G_1(t)$. The transition to the interaction representation will be realized by an operator $S(t)$, satisfying the equation

$$dS(t)/dt = -i[E + G_0(t)]S(t) \qquad (1.4)$$

with initial condition $S(t_0) = 1$. The operator A in the interaction representation will be of the form

$$A^*(t) = S^{-1}(t)AS(t). \qquad (1.5)$$

For the spin-system density matrix we have in second-order perturbation theory

$$\rho^*(t) - \rho(t_0) = -i\int_{t_0}^{t}[G_1^*(t_1), \rho(t_0)]\,dt_1 - \int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2[G_1^*(t_1), [G_1^*(t_2), \rho(t_0)]]. \qquad (1.6)$$

For $\rho(t)$ we get from (1.5) and (1.6) the relation

$$\rho(t) - S(t)\rho(t_0)S^{-1}(t) = -S(t)\left\{i\int_{t_0}^{t}[G_1^*(t_1), \rho(t_0)]\,dt_1 + \int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2[G_1^*(t_1), [G_1^*(t_2), \rho(t_0)]]\right\}S^{-1}(t). \qquad (1.7)$$

Multiplying both halves of (1.7) by an arbitrary spin operator Q and taking the mean value, we obtain

$$\langle Q\rangle_t - \langle Q^*(t)\rangle_{t_0} = -i\int_{t_0}^{t}\langle[Q^*(t), G_1^*(t_1)]\rangle_{t_0}dt_1 - \int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\langle[G_1^*(t_2), [G_1^*(t_1), Q^*(t)]]\rangle_{t_0}, \qquad (1.8)$$

where $\langle A\rangle_t = \mathrm{Sp}[A\rho(t)]$. This equation will be considered in the succeeding sections for several specific cases.

2. MAGNETIC DIPOLE INTERACTION BETWEEN THE SPIN AND A LOCAL FIELD

When the spin I is in a local magnetic field $H(t)$, the operator $G(t)$ is of the form

$$G(t) = \sum_{m=-1}^{1}(-1)^m I^m F_1^{-m}(t), \qquad (2.1)$$

where

$$I^0 = I_z,$$

$$I^{\pm 1} = \mp I_\pm = \mp(I_x \pm iI_y)/\sqrt{2}, \quad F_1^0(t) = -\gamma H_z(t) = -\omega_z(t)$$

$$F_1^{\pm 1}(t) = \pm\gamma[H_x(t) \pm iH_y(t)]/\sqrt{2} = \pm\omega^\pm(t).$$

The solution of (1.4) is then written in the form

$$S(t) = \exp[i\varphi(t)I_z],$$

where

$$\varphi(t) = \omega_0(t - t_0) + \int_{t_0}^{t}\omega_z(t')\,dt'. \qquad (2.2)$$

Hence

$$G_1^*(t) = -[\omega^+(t)e^{i\varphi(t)}I_- + \omega^-(t)e^{-i\varphi(t)}I_+]. \qquad (2.3)$$

On the basis of (1.8) and (2.3) we obtain the following relation for the arbitrary spin component

$$\langle I_z\rangle_t - \langle I_z\rangle_{t_0} = i\,\mathrm{Im}\left\{\int_{t_0}^{t}\omega^-(t_1)e^{-i\varphi(t_1)}dt_1\langle I_+\rangle_{t_0}\right\} - \mathrm{Re}\left\{\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\omega^-(t_1)\omega^+(t_2)e^{-i[\varphi(t_1)-\varphi(t_2)]}\langle I_z\rangle_{t_0}\right\}. \qquad (2.4)$$

This equation must now be averaged over the distribution for $\omega_z(t)$, $\omega^\pm(t)$. Let us assume that the time interval $\Delta t = t - t_0$ can be chosen, on the one hand, sufficiently small to be able to employ perturbation theory, and on the other hand sufficiently large to satisfy the inequality

$$\Delta t \gg \tau_c. \qquad (2.5)$$

Under this condition the integrands in the right halves of (2.4) do not correlate with $\langle I_\pm\rangle_{t_0}$ and $\langle I_z\rangle_{t_0}$ in the entire integration region, with the exception of a negligibly small part of this region (accurate to $\tau_c/\Delta t$). Consequently, these quantities can be averaged independently.

It follows from (1.3) that

$$\overline{\omega_z(t_1)\omega^\pm(t_2)} = \overline{\omega^+(t_1)\omega^+(t_2)} = \overline{\omega^-(t_1)\omega^-(t_2)} = 0, \qquad (2.6)$$

$$\overline{\omega_z(t_1)\omega_z(t_2)} = \overline{\omega^-(t_1)\omega^+(t_2)} = \overline{\omega^+(t_1)\omega^-(t_2)} = \sigma_1^2\exp(-|t_1 - t_2|/\tau_c). \qquad (2.7)$$

Let us consider the case when $\omega^\pm(t)$ and $\omega_z(t)$ describe a Gaussian random process and $\overline{\omega_z(t)} = \overline{\omega^\pm(t)} = 0$. Then, using the known properties of Gaussian random functions (see, for example, [8]) and relations (2.6) and (2.7), we can readily average (2.4), getting

$$\langle\overline{I_z}\rangle_t - \langle\overline{I_z}\rangle_{t_0} = -2\sigma_1^2\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2 f(t_1 - t_2)\cos\omega_0(t_1 - t_2)\langle\overline{I_z}\rangle_{t_0}, \qquad (2.8)$$

$$f(\tau) = \exp\{-|\tau|/\tau_c - \sigma_1^2\tau_c|\tau| + \sigma_1^2\tau_c^2[1 - \exp(-|\tau|/\tau_c)]\}. \qquad (2.9)$$

The change of variable $\tau = t_1 - t_2$ and integration with respect to t_1 yield

$$\langle \overline{I_z} \rangle_t - \langle \overline{I_z} \rangle_{t_0} = -2\sigma_1^2 \int_0^{\Delta t} (\Delta t - \tau) f(\tau) \cos \omega_0 \tau \, d\tau \, \langle \overline{I_z} \rangle_{t_0}. \quad (2.10)$$

Since the function $f(\tau)$ decreases not any more slowly than $\exp(-|\tau|/\tau_c)$, we have at the assumed accuracy, neglecting terms of order $\tau_c/\Delta t$, in place of (2.10)

$$\langle \overline{I_z} \rangle_t - \langle \overline{I_z} \rangle_{t_0} = -\Delta t \int_0^{\infty} f(\tau) \cos \omega_0 \tau \, d\tau \, \langle \overline{I_z} \rangle_{t_0}. \quad (2.11)$$

In other words, the motion $\langle \overline{I_z} \rangle_t$ is described approximately by the equation

$$d \langle \overline{I_z} \rangle_t / dt = -(\langle \overline{I_z} \rangle_t - \langle I_z \rangle_0) / T_1, \quad (2.12)$$

where

$$1/T_1 = 2\sigma_1^2 \int_0^{\infty} f(\tau) \cos \omega_0 \tau \, d\tau \quad (2.13)$$

and $\langle I_z \rangle_0$ is the equilibrium value of $\langle \overline{I_z} \rangle_t$, which is included in (2.12) from physical considerations. As is clear from the derivation, Eq. (2.12) is valid if condition (2.5) and the condition $\Delta t \ll T_1$ are satisfied; combining the two, we have

$$T_1 \gg \tau_c. \quad (2.14)$$

Let us estimate T_1 for strong fields, that is, fields in which the resonant frequency is much larger than the line width. This condition is satisfied in the majority of paramagnetic-resonance installations. To calculate the integral in (2.13) we can employ the known asymptotic expansion

$$\int_0^{\infty} f(\tau) \cos \omega_0 \tau \, d\tau = -\omega_0^{-2} f'(0) + \omega_0^{-4} f'''(0) - \ldots, \quad (2.15)$$

which yields

$$1/T_1 = (2\sigma_1^2/\omega_0^2 \tau_c)(1 + (4\sigma_1^2 \tau_c^2 - 1)/\omega_0^2 \tau_c^2 + \ldots). \quad (2.16)$$

It must be noted that the integral in (2.13) is expressed in terms of the incomplete γ-function, and the expansion (2.16) can be obtained from asymptotic expansions for the incomplete γ-functions, which are valid for $\sigma_1 \tau_c \lesssim \omega_0/\sigma_1$. When $\sigma_1 \ll \omega_0$, that is, in strong fields, condition (2.14) is satisfied, and (2.16) can be written in the form

$$1/T_1 = 2\sigma_1^2 \tau_c / (1 + \omega_0^2 \tau_c^2), \quad (2.17)$$

which coincides with the formula derived from the Bloch-Redfield theory. Thus, in strong fields, formula (2.17) for the time of longitudinal relaxation is valid in the entire range of values $\sigma_1 \tau_c \lesssim \omega_0 \sigma_1$. In Sec. 4 we shall obtain the same conclusion from an analysis of a two-spin system with non-Gaussian random process.

As is well known, it follows from qualitative considerations that if $\sigma_1 \tau_c \gtrsim 1$ and $\omega_0 \gg \sigma_1$, then we can neglect the influence of the non-secular terms of the interaction on the motion of the transverse components of the magnetic moment. For the case under consideration we have obtained an estimate of the influence of the nonsecular terms on the motion $\langle I_\pm \rangle_t$, when $t \gg \tau_c$. To this end it would be necessary to substitute in (1.8) in place of Q the operator $I_\pm$ and follow a reasoning analogous to that used above for I_z. As a result we obtain the equation

$$\langle I_\pm \rangle_t = \langle I_\pm \rangle_{t=0} \exp[\mp i\omega_0 t - (\sigma_1^2 \tau_c + 1/T_2') t], \quad (2.18)$$

where the term t/T_2' is due to the nonsecular terms and $\sigma_1^2 \tau_c t$ is due to the secular terms. If $\sigma_1 \tau_c \sim 1$, then

$$1/T_2' \approx \sigma_1^2 / \omega_0^2 \tau_c. \quad (2.19)$$

Thus, for the system under consideration with $t \gg \tau_c$, the error due to neglecting the nonsecular terms has the same order of magnitude as $1/\omega_0^2 \tau_c^2$. We shall show below, however, that the general premise that the nonsecular terms can be neglected in the region $\sigma_1 \tau_c \gtrsim 1$ is not always true.

3. QUADRUPOLE INTERACTION

The local field model is used successfully for an analysis of interaction of a spin $I \geq 1$ with the gradients of electric fields of the crystal lattice or with the gradients produced by defects in the crystal lattice, at sufficiently low concentration of the magnetic nuclei. In a liquid, inasmuch as the interaction of the spin particle belonging to different molecules averages out as a result of the molecular motion, the line shape and the spin relaxation are determined almost always by the quadrupole interaction.

When the interaction of the spin with the local field is in the form of an electric quadrupole interaction, then the operator $G(t)$ is of the form

$$G(t) = \sum_{m=-2}^{2} (-1)^m I_2^m F_2^{-m}(t), \quad (3.1)$$

where

$$I_2^0 = [3I_z^2 - \mathbf{I}^2]/\sqrt{6}, \qquad I_2^{\pm 1} = (I^{\pm 1} I_z + I_z I^{\pm 1})/\sqrt{2},$$
$$I_2^{\pm 2} = I^{\pm 1} I^{\pm 1}$$

are the components of an irreducible tensor operator of second rank, and $F_2^m(t)$ describes the fluctuations of the electric field gradients.

As is well known[3,9], the line shape is determined by the relation

$$g(\omega)=\frac{3}{4\pi I(I+1)}\int_{-\infty}^{\infty}[\overline{X_1^+(t)}+\overline{X_1^-(t)}]\,e^{i\omega t}dt,$$

$$X_l^{\mp}(t)=-\frac{1}{2I+1}\operatorname{Sp}[I_l^{\pm 1}(t)I^{-1}],\qquad l=1,2,\ldots \quad (3.2)$$

The superior bar, as before, denotes averaging over the distribution for the random functions.

Assuming that $\omega_0 \gg \sigma_2$ and $\sigma_2\tau_c \gtrsim 1$, we neglect on the basis of the foregoing the nonsecular terms in G(t). The initial equation will then be

$$\frac{dI_l^{\pm 1}}{dt}=i\Big[-\omega_0 I_z+\frac{1}{\sqrt{6}}(3I_z^2-I(I+1))F_2^0(t),\quad I_l^{\pm 1}\Big]. \quad (3.3)$$

The commutators in the right half of (3.3) can be expanded in the irreducible tensor operators with the aid of the formula

$$[I_2^m, I_l^n]=\sqrt{2}\Big\{\sqrt{l(l+2)}\,C(l,2,l+1;n,m)\,I_{l+1}^{n+m}-\sqrt{l^2-1}\,\frac{l[(2I+1)^2-l^2]}{4\sqrt{4l^2-1}}\,C(l,2,l-1;n,m)\,I_{l-1}^{n+m}\Big\}, \quad (3.4)$$

which was obtained in [7]. If we multiply the system (3.3) from the left or from the right by the operators I^+ and I^- and carry out diagonal summation, then we obtain a system of 2I equations directly for the quantities $X_l^{\mp}$

$$\frac{dX_l^{\mp}}{dt}=\mp i\omega_0 X_l^{\mp}\mp i\omega(t)\Big\{2\sqrt{\frac{l(l+2)}{(2l+1)(l+1)}}\,X_{l+1}^{\mp}+\frac{(2I+1)^2-l^2}{2(2l+1)}\sqrt{\frac{l(l^2-1)}{2l-1}}\,X_{l-1}^{\mp}\Big\},\qquad l=1,2,\ldots,2I. \quad (3.5)$$

Here

$$\omega(t)=-\sqrt{3/2}\,F_2^0(t). \quad (3.6)$$

From the definition of the quantities $X_l^{\mp}(t)$ follow the initial conditions

$$X_l^{\mp}(0)=0 \text{ for } l\neq 1;\quad X_1^{\mp}(0)=\tfrac{1}{3}I(I+1). \quad (3.7)$$

For the spin I = 1 the system (3.5) reduces to a system of two equations for X_1^+ and X_1^-. Substitution of the solution of this system with initial conditions (3.7) in (3.2) yields

$$g(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\overline{\cos\Big[\int_0^t\omega(t')\,dt'\Big]}\cos\omega_0 t\,e^{i\omega t}\,dt. \quad (3.8)$$

We note that (3.8) differs somewhat from (1.1).

If $\omega(t)$ describes a Gaussian process, then we obtain from (3.8) after averaging a formula for $g(\omega)$, which coincides with the formula which Kubo and Tomita obtained by expansion in semi-invariants (formula (6.26) of [9]). However, as will be shown below, their formula is incorrect for non-Gaussian processes.

For the spin I = $^3/_2$, the system (3.5) comprises three equations for each of the functions X_1^+ and X_1^-. The solution of these systems, with initial conditions (3.7), yields

$$X_1^{\pm}(t)=\frac{3}{4}e^{\mp i\omega_0 t}\Big\{\cos\Big[2\int_0^t\omega(t')\,dt'\Big]+\frac{2}{3}\Big\}. \quad (3.9)$$

Substitution of (3.9) in (3.2) leads to

$$g(\omega)=\frac{3}{10\pi}\int_{-\infty}^{\infty}\overline{\cos\Big[2\int_0^t\omega(t')\,dt'\Big]}\cos\omega_0 t\,e^{i\omega t}+\frac{1}{5}\delta(\omega-\omega_0). \quad (3.10)$$

Here the δ function is due to the undamped terms in (3.9). Obviously, an account of the non-secular terms, which could be carried out starting from the general equation (1.8), would lead to a vanishing of the singularity in the expression for the line shape. It is precisely the presence of undamped terms in (3.9) which makes inapplicable the arguments which we used at the end of Sec. 2 to base the possibility of neglecting the nonsecular terms. This example demonstrates the caution with which such neglect must be approached.

4. TWO INTERACTING $^1/_2$-SPINS

We consider now a strongly viscous liquid, in which only isolated pairs of spins, each equal to $^1/_2$, interact. We must consider here only the rotational motions of the molecules.

The Hamiltonian of the dipole-dipole interaction of two $^1/_2$-spins can be expressed in terms of the components of their total spin and written in a form which coincides formally with (3.1), where I_2^m are operators made up of the components of the summary spin and

$$F_2^0=\frac{k}{2}\sqrt{\frac{3}{2}}(1-3\cos^2\theta),\qquad F_2^{\pm 1}=\pm\frac{3k}{2}\sin\theta\cos\theta e^{\pm i\varphi},\qquad F_2^{\pm 2}=-\frac{3k}{4}\sin^2\theta e^{\pm 2i\varphi} \quad (4.1)$$

($k=\hbar\gamma^2/b$, γ — gyromagnetic ratio, θ, φ — polar coordinates of the vector **b** joining the spins). Thus, the problem of the interacting pair of $^1/_2$-spins reduces the problem of a 1-spin in a quadrupole local spin, which was considered in the preceding section.

As follows from (3.8), the problem of determining the line shape reduces to a calculation of the function

$$E(t_1,t_2)=\overline{\exp\Big[i\int_{t_2}^{t_1}\omega(t)\,dt\Big]}, \quad (4.2)$$

where $\omega(t)$ is, in accordance with (3.6) and (4.1), a function of the random orientation $\theta(t)$.

The most widely used model of rotational molecule motion in a liquid is the rotational Brownian motion of a sphere. In this model $\theta(t)$ describes a continuous Markov process. For such processes, an expression of type (4.2) can be calculated with the aid of the auxiliary quantity [1)]

$$A(t_1, t_2, \theta) = \left\langle \exp\left\{i\int_{t_2}^{t_1} \omega[\theta(t)]\,dt\right\}\right\rangle_{\theta(t_2)=\theta}, \quad (4.3)$$

where the averaging is carried out under the condition $\theta(t_2) = \theta$. For a continuous Markov process, $A(t_1, t_2, \theta)$ satisfies an equation proposed by Dynkin[10]

$$\partial A/\partial t_2 + a(\theta, t_2)\,\partial A/\partial\theta + \tfrac{1}{2}b(\theta, t_2)\,\partial^2 A/\partial\theta^2 + i\omega(\theta)A = 0;$$

$$a(\theta, t_2) = \lim_{\Delta t\to 0}\frac{1}{\Delta t}\langle\theta(t_2+\Delta t) - \theta(t_2)\rangle_{\theta(t_2)=\theta},$$

$$b(\theta, t_2) = \lim_{\Delta t\to 0}\frac{1}{\Delta t}\langle[\theta(t_2+\Delta t) - \theta(t_2)]^2\rangle_{\theta(t_2)=\theta} \quad (4.4)$$

with initial condition

$$A|_{t_2=t_1} = 1. \quad (4.5)$$

For rotational Brownian motion of a sphere

$$a = D\cot\theta, \qquad b = 2D \quad (4.6)$$

(see, for example, [11]), where D — coefficient of rotational diffusion.

The solution of (4.4) can be sought by separating the variables: $A = P(t)S(\cos\theta)$. On the basis of (3.6), (4.1), (4.4), and (4.6) we get

$$dT/dt_2 = D\mu T,$$

$$dS^2/d\theta^2 + \cot\theta\, dS/d\theta + (\lambda + h\cos^2\theta)S = 0, \quad (4.7)$$

where $D\mu$ is the separation constant, $h = {}^9\!/_4\, ik/D$, and $\lambda = \mu - h/3$.

As is well known (see, for example, [12]), $D = {}^1\!/_6\,\tau_c$, and consequently $h = 9i\sqrt{5}\,\sigma_2\tau_c$, where σ_2 — second moment of the line, which can be shown to be independent of τ_c. Equation (4.7) is the equation of spheroidal wave functions of zero order in the complex parameter h. From the theory of these functions it follows that the solution of (4.4) has in our case the form

$$A(\tau,\theta) = \sum_{n=0}^{\infty} T_n(\tau)S_n(\cos\theta),$$

where $\tau = t_1 - t_2$ and S_n is the eigenfunction of (4.7) corresponding to the eigenvalue λ_n. Averaging of A over the initial distribution yields

$$E(\tau) = \tfrac{1}{2}\sum_n d_0^{2n}T_{2n}(\tau), \qquad d_0^{2n} = \int_{-1}^{1} S_{2n}(x)\,dx. \quad (4.8)$$

Using the expansion S_{2n} in Legendre polynomials, we obtain from the initial condition (4.6)

$$T_{2n}(0) = d_0^{2n} \Big/ \sum_{r=0}^{\infty}(d_{2r}^{2n})^2\frac{2}{4r+1},$$

where d_{2r}^{2n} — coefficient of expansion of S_{2n} and the Legendre polynomial of order 2r. As a result we have

$$E(t) = \sum_{n=0}^{\infty} c_n \exp\left\{-\left(\lambda_{2n} + \frac{h}{3}\right)Dt\right\};$$

$$c_n = (d_0^{2n})^2 \Big/ \sum_{r=0}^{\infty}\frac{1}{4r+1}(d_{2r}^{2n})^2. \quad (4.9)$$

Let us introduce the notation

$$c_n = \alpha_n + i\beta_n, \qquad \frac{1}{6}\left(\lambda_{2n} + \frac{h}{3}\right) = p_n + iq_n, \quad (4.10)$$

where α_n, β_n, p_n, and q_n are real functions of $\sigma_2\tau_c$. On the basis of (3.8) and (4.9) we obtain a final expression for the line shape

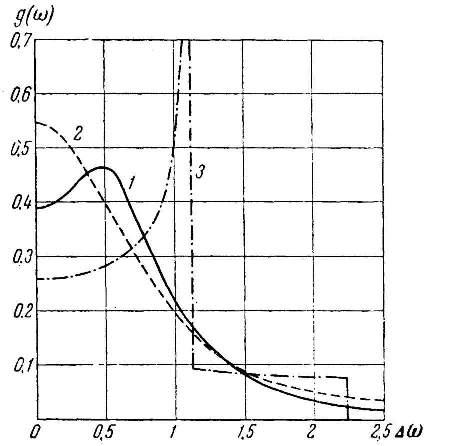
$$g(\omega) = \frac{\tau_c}{\pi}\sum_{n=0}^{\infty}\frac{(p_n^2 - q_n^2 + \tau_c^2\Delta\omega^2)(\alpha_n p_n - \beta_n q_n) + 2p_n q_n(\alpha_n q_n + \beta_n p_n)}{(p_n^2 - q_n^2 + \tau_c^2\Delta\omega^2)^2 + 4p_n^2 q_n^2} \quad (4.11)$$

($\Delta\omega = \omega - \omega_0$), which differs essentially from formula (6.26) of Kubo and Tomita[9]. The series (4.11) converges well in the region $\sigma_2\tau_c \sim 1$, that is, in the region of greatest interest to us. (When $\sigma_2\tau_c \gg 1$ the expression for the line shape can be obtained by expanding the solution of (4.4) in the small parameter 1/D. In particular, for 1/D = 0 we obtain for the line shape the known expression for the rigid lattice[13].)

We were unable to find in the literature tables of spheroidal wave functions of complex parameter, so that we present a short table of the values of p_n, q_n, α_n, and β_n (see the table), calculated by the variational method of Blanche and Bouwcamp[14]. In the indicated region of variation of the parameter h, the first two terms of the series (4.11) are sufficient for practical calculations.

The figure shows the line shapes calculated by (4.11) and by the formula of Kubo and Tomita[9] with $\sigma_2\tau_c = 1$, and also the line shape for the rigid lattice. Comparison of the line shapes indicates that from the point of view of the theory of paramagnetic resonance the molecular motion in a liquid is essentially a non-Gaussian process.

1)The authors are grateful to A. N. Shiryaev who pointed out the method of calculating expressions of the type (4.2) for continuous Markov processes.



Line shape for two-spin system: 1—line shape calculated by the formula (4.11) with $\sigma_2\tau_c = 1$; 2—calculated by formula (6.26) of [9] with $\sigma_2\tau_c = 1$; 3—line shape for rigid lattice. Scale chosen to make $\sigma_2 = 1$.

When $\sigma_2\tau_c \ll 1$, both formulas give the same Lorentz line shape. (Calculation shows that agreement is observed even when $\sigma_2\tau_c = 0.1$.)

We now proceed to investigate longitudinal relaxation in the system under consideration. The time development of $\langle I_z\rangle_t$ is determined in accordance with the same scheme as in Sec. 2. In our case the solution of (1.4) is of the form

$$S(t) = \exp\left[i\omega_0 I_z - i\int_0^t F_2^0(t')\,dt' I_2^0\right]. \qquad (4.12)$$

In the calculation of $G_1^*(t)$ it is convenient to use (3.4). Substituting the thus obtained values of $G_1^*(t)$ in (1.8) and calculating the commutators with the aid of (3.4), we obtain

$$\langle I_z\rangle_t - \langle I_z\rangle_{t_0}$$

$$= -\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \Big(\Big\{-\frac{1}{2}\cos\varphi(t_1,t_2)\,[F_2^1(t_2)F_2^{-1}(t_1)e^{-i\omega_0(t_1-t_2)}$$

$$+ F_2^{-1}(t_2)F_2^1(t_1)e^{i\omega_0(t_1-t_2)}\,] + 2\,[F_2^2(t_2)F_2^{-2}(t_1)\,e^{-2i\omega_0(t_1-t_2)}$$

$$+ F_2^{-2}(t_2)F_2^2(t_1)\,e^{2i\omega_0(t_1-t_2)}\,]\Big\}\langle I_z\rangle_{t_0}$$

$$- i\sqrt{\frac{3}{2}}\sin\varphi(t_1,t_2)\,[F_2^1(t_2)F_2^{-1}(t_1)e^{-i\omega_0(t_1-t_2)}$$

$$- F_2^{-1}(t_2)F_2^1(t_1)e^{i\omega_0(t_1-t_2)}]\,\langle I_2^0\rangle_{t_0}\Big), \qquad (4.13)$$

where

$$\varphi(t_1, t_2) = \int_{t_2}^{t_1}\omega(t')\,dt'.$$

We have omitted here the term linear in G_1^*, since it vanishes in the subsequent averaging. Carrying out an averaging of (4.13) with the aid of arguments analogous to those which have led to (2.12), we obtain an equation for $\langle \overline{I_z}\rangle_t$:

$$d\langle \overline{I}_z\rangle_t/dt = -(\langle \overline{I}_z\rangle_t - \langle I_z\rangle_0)/T_1 - \langle I_2^0\rangle_t/T_{12}; \quad (4.14)$$

$$\frac{1}{T_1} = \frac{1}{T_1'} + \frac{1}{T_1''}, \qquad \frac{1}{T'} = \int_0^\infty \Phi^+(t)\cos\omega_0 t\,dt, \qquad \frac{1}{T_1''} = \frac{4\sigma_2^2\tau_c}{1+4\omega_0^2\tau_c^2},$$

$$\frac{1}{T_{12}} = \int_0^\infty \Phi^-(t)\sin\omega_0 t\,dt; \qquad (4.15)$$

$$-\Phi^+(t_1 - t_2) = \overline{F_2^1(t_2)F_2^{-1}(t_1)\cos\varphi(t_1,t_2)}$$

$$= \overline{F_2^{-1}(t_2)F_2^1(t_1)\cos\varphi(t_1,t_2)},$$

$$-\Phi^-(t_1 - t_2) = \overline{F_2^1(t_2)F_2^{-1}(t_1)\sin\varphi(t_1,t_2)}$$

$$= \overline{F_2^{-1}(t_2)F_2^1(t_1)\sin\varphi(t_1,t_2)}. \qquad (4.16)$$

In the same manner as used to derive (2.16), we estimate T_1 and T_{12} with the aid of asymptotic series of the type (2.15). We introduce the auxiliary quantity

$$\mathscr{E}(t', t'') = \overline{Y_2^{-m}(t'')Y_2^m(t')\exp\left[is\int_{t'}^{t''}Y_2^0(t)\,dt\right]}$$

(Y_l^m is the spherical function and $s = 2\sqrt{\pi}\,\sigma_2$), in terms of which we express in obvious fashion the functions $\Phi^{\pm}(t'', t')$. We write $\mathscr{E}(t', t'')$ in the form of a series

$$\mathscr{E}(t', t'') = \sum_{n=0}^{\infty}(is)^n\int_{t'}^{t''}dt_n\int_{t'}^{t_n}dt_{n-1}\ldots\int_{t'}^{t_2}dt_1 F_n^m(t', t_1, \ldots, t_n, t''), \qquad (4.17)$$

$\lvert h\rvert$	p_0	q_0	p_1	q_1	α_0	β_0	α_1	β_1
6	0.0910	0.0205	0,937	—0,212	1,09	0,05	—0,09	—0,05
8	0,1606	0,0565	0,889	—0,311	1,15	0.15	—0.15	—0,15
10	0,235	0,136	0,842	—0.442	1,11	0,30	—0,11	—0,30
12	0,291	0.215	0,818	—0,598	0,98	0,38	0,02	—0,38
14	0,331	0,310	0,818	—0,758	0,88	0,37	0,12	—0.37
16	0,361	0,402	0,834	—0,917	0.82	0,35	0,18	—0.35
18	0,386	0,492	0,856	—1,074	0.78	0,33	0,22	—0.33
20	0,409	0,581	0,887	—1,230	0,75	0,31	0,24	—0,31
22	0,431	0,668	0,921	—1,388	0,73	0,29	0,25	—0,29
24	0,453	0,756	0,960	—1,548	0.72	0,28	0,26	—0,29

$$F_n^m = \overline{Y_2^m(t')\,Y_2^0(t_1)\ldots Y_2^0(t_n)\,Y_2^{-m}(t'')}. \qquad (4.18)$$

We denote by **k** the unit vector in the direction of the line joining the spins. From the theory of the rotational Brownian motion (see, for example,[11]) we know the probability distribution for $\mathbf{k}_2$ at the instant of time t_2, under the condition that in the preceding instant t_1 the orientation was determined by the vector $\mathbf{k}_1$:

$$W(\mathbf{k}_2, t_2;\ \mathbf{k}_1, t_1) = \sum_{l=0}^{\infty} \varphi_l \sum_{m=-l}^{l} Y_l^{-m}(\mathbf{k}_1)\,Y_l^m(\mathbf{k}_2),$$

$$\varphi_l = \exp\left[-\frac{l(l+1)}{6\tau_c}(t_2 - t_1)\right].$$

Recognizing that Brownian motion is a Markov process, we have for the distribution of the values of **k** in succeeding instants of time $t_0, t_1, \ldots, t_{n+1}$,

$$W(\mathbf{k}_0, t_0;\ \ldots;\ \mathbf{k}_{n+1} t_{n+1}) = \frac{1}{4\pi}\prod_{i=0}^{n} W(\mathbf{k}_{i+1}, t_{i+1};\ \mathbf{k}_i, t_i). \qquad (4.19)$$

Averaging of (4.18) with the aid of the distribution (4.19) yields

$$F_n^m = \frac{5^{n/2}}{(4\pi)^{1+n/2}} \sum_{l_0, l_1, \ldots, l_n} \delta_{l_0,2}\,\delta_{l_n,2}\,\varphi_{l_0}(t_1 - t_0) \prod_{i=1}^{n} \varphi_{l_i}(t_{i+1} - t_i)$$
$$\times\, C(2,\ l_i,\ l_{i-1};\ 0,\ m)\, C(2,\ l_i,\ l_{i-1};\ 0,\ 0). \qquad (4.20)$$

From the properties of the Clebsch-Gordan coefficients it follows that $F_n^m = F_n^{-m}$. Since only the terms of the series (4.17) with $n \le k$ contributes to the derivative $d^{(k)}\mathscr{E}/dt''^{(k)}|_{t''=t'}$ it is convenient to use this series for the calculation of the first coefficients in the asymptotic expansions. As a result we have

$$\frac{1}{T_1'} = \frac{2\sigma_2^2}{3\omega_0^2\tau_c}\left(1 + \frac{25\sigma_2^2\tau_c^2 - 7}{7\omega_0^2\tau_c^2} - \ldots\right),$$

$$\frac{1}{T_{12}} = \frac{2\sqrt{30}}{21}\,\frac{\sigma_2^3}{\omega_0^3\tau_c}. \qquad (4.21)$$

In strong fields ($\omega_0 \gg \sigma_2$) we can neglect $1/T_{12}$, and (4.15) assumes the simple form (2.13), while the expression for the time of longitudinal relaxation again coincides with the expression that follows from the theory of Bloch and Redfield. However, in "average" fields, when only quantities of order $(\sigma_2/\omega_0)^2$ can be neglected, the condition (2.14) is still satisfied, but $1/T_{12}$ can no longer be neglected, and this leads to deviations from the simple exponential relaxation law. For a Gaussian random process this phenomenon is not observed.

The authors are grateful to Professor N. D. Sokolov and I. V. Aleksandrov for a discussion of the work and to A. A. Ivanova for help with the calculations.

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Translated by J. G. Adashko
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