

ON THE THEORY OF NUCLEAR PARAMAGNETIC RESONANCE IN LIQUIDS

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The quantum theory of magnetic resonance absorption due to Kubo and Tomita<sup>1</sup> is used to describe the phenomenon of nuclear paramagnetic resonance in liquids. The thermal motion of the molecules, which leads to a narrowing of the absorption line, is taken into account on the basis of diffusion theory. The transverse and the longitudinal relaxation times and the correction to the gyromagnetic ratio are computed.

1. The general method developed by Kubo and Tomita<sup>1</sup> for the determination of the line shape of magnetic resonance absorption in radio frequency fields has been employed to discuss nuclear magnetic resonance absorption in liquids and exchange narrowing in paramagnetic crystals.

With the aid of this method it has turned out to be possible to take into account the effect of the anisotropy of the *g*-factor on the line shape<sup>2</sup> and to determine the effect of the exchange interaction on the hyperfine structure in electron paramagnetic resonance.<sup>3</sup> On the basis of this method, Chirkov and Kokin<sup>4</sup> calculated the line shape of electron resonance absorption in powdered free radicals. Skrotskiĭ and Kokin<sup>5</sup> obtained the equations of motion for the magnetization vector and expressions for the coefficients appearing in these equations.

To take thermal motion into account, both Kubo and Tomita<sup>1</sup> and Bloembergen, Purcell, and Pound<sup>6</sup> chose the simplest correlation function

$$f(t) = \exp(-|t|/\tau_c). \tag{1}$$

It is assumed that this form of the function describes both the rotational and the translational Brownian motion. The correlation time  $\tau_c$  for the rotational Brownian motion is expressed in terms of the temperature, the mobility, and the dimensions of the molecule, while in the case of the translational motion it is expressed in terms of the relative position of the paramagnetic molecules or ions.

Such a choice of  $f(t)$  is not general and, strictly speaking, is applicable only to the description of rotational Brownian motion.

The results obtained by Skrotskiĭ and Kokin<sup>5</sup> are employed in this paper for the determination of the transverse and longitudinal relaxation times in liquids. In carrying this out the form of the function is determined on the basis of diffusion theory.

2. In what follows we shall assume that the sample is situated in a constant magnetic field  $H_0 = H_z$  and a weak radio frequency field  $\mathbf{h}(t)$ .

The part of the Hamiltonian  $\hat{\mathcal{H}}$  which does not depend on the time may be written in the form of three terms

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2 + \hat{\mathcal{H}}', \tag{2}$$

where

$$\hat{\mathcal{H}}_1 = -\hbar\omega_0 \sum_i \hat{I}_{iz}; \quad \hbar\omega_0 = g\mu_0 H_0 \tag{3}$$

is the operator for the interaction of the system of magnetic moments with the external constant field  $H_0$ . The operator  $\hat{\mathcal{H}}_2$  contains the kinetic energy and the interactions which do not depend on the spins  $I_j$ . The magnetic dipole-dipole interactions are described by the operator  $\hat{\mathcal{H}}'$  which is regarded as a perturbation.

When the condition  $\hbar\omega_0 \ll kT$  is satisfied the equilibrium density matrix  $\hat{\rho}_0$  does not depend on the spins, and in the case of a homogeneous and isotropic liquid in the first approximation does not depend on the coordinates.

In this case we shall obtain for the relaxation times  $T_\perp$  and  $T_\parallel$  and for the shift in the resonance frequency  $\Delta\omega_0$  in accordance with reference:<sup>5</sup>

$$\frac{1}{T_\alpha} = \sum_\lambda \Omega_{\alpha\lambda}^2 \tau'_\lambda, \quad T_{\pm 1} = T_\perp, \quad T_0 = T_\parallel; \tag{4}$$

$$\Delta\omega_0 = \sum_\lambda \Omega_{1\lambda}^2 \tau''_\lambda, \tag{5}$$

where

$$\tau'_\lambda + i\tau''_\lambda = \int_0^\infty \exp(i\lambda\omega_0\vartheta) f_{\alpha\lambda}(\vartheta) d\vartheta, \tag{6}$$

$$\Omega_{\alpha\lambda}^2 f_{\alpha\lambda}(\vartheta) = \langle \{ [\hat{M}_\alpha \hat{\mathcal{H}}'_{-\lambda}(\vartheta)] [\hat{\mathcal{H}}'_{-\lambda}(0) \hat{M}_\alpha] \} \rangle / \hbar^2 \langle |\hat{M}_\alpha|^2 \rangle. \tag{7}$$

The angle brackets denote averaging over spins and coordinates using  $\hat{\rho}_0 = \text{const}$ , the curly brack-

ets denote the symmetrized product of the operators, and  $f_{\alpha\lambda}(\varphi) = 1$ .

By utilizing the expressions given in reference 5 for  $\hat{\mathcal{C}}_{\lambda}^{\alpha}(\varphi)$  and  $\hat{\mathcal{C}}_{\lambda}^{\alpha}(0)$ , and by averaging over spins, we obtain for an isotropic liquid:

$$\Omega_{12}^2 = \Omega_{1-1}^2 = 2/3\Omega_{11}^2 = 2/3\Omega_{10}^2 = 1/2\Omega_{0\pm 2}^2 = 2\Omega_{0\pm 1}^2 = 2/3\Omega^2, \\ \Omega_{1-2}^2 = \Omega_{00}^2 = 0, \quad (8)$$

where

$$\Omega^2 = (12\pi/5) I(I+1) g^4 \mu_0^4 \hbar^{-2} \sum_k \langle r_{jk}^{-6} | Y_{20}(\vartheta_{jk}\varphi_{jk})|^2 \rangle. \quad (9)$$

The summation over  $k$  is carried out for fixed arbitrary  $j$ .

The function

$$f_{\alpha\lambda}(\tau) = f_{\lambda}(\tau) \\ = \frac{\sum_k \langle r_{jk}^{-3}(\tau) r_{jk}^{-3}(0) Y_{2\lambda}(\vartheta_{jk}(\tau)\varphi_{jk}(\tau)) Y_{2\lambda}^*(\vartheta_{jk}\varphi_{jk}) \rangle}{\sum_k \langle r_{jk}^{-6} | Y_{2\lambda}(\vartheta_{jk}\varphi_{jk})|^2 \rangle} \quad (10)$$

will henceforth be called the correlation function.

3. To calculate the relaxation times  $T_{\perp}$  and  $T_{\parallel}$  and the correction to the gyromagnetic ratio it is necessary to obtain the explicit form of the correlation function  $f_{\lambda}(\tau)$ .

The direct calculation of  $f_{\lambda}(\tau)$  from (10) does not appear to be possible, since for this it would be necessary to have expressions specifying the motion of each molecule. However, we can get around this difficulty.

We base our discussion on the concept that the molecules in the liquid undergo translational and rotational Brownian motion.

To describe the translational Brownian motion we make use of the equation of free diffusion:

$$\frac{\partial U}{\partial t} - D\Delta U = 0, \quad D = kT/6\pi\eta a, \quad (11)$$

where  $a$  is the radius of the molecule.

The probability that at a time  $t$  one molecule is contained within a volume element  $d\mathbf{r}_1$  at a distance  $r_{12}$  from a second molecule contained within  $d\mathbf{r}_2$  is given by the following expression:

$$U(\mathbf{r}_1, \mathbf{r}_{10}, \mathbf{r}_2, \mathbf{r}_{20}, t) d\mathbf{r}_1 d\mathbf{r}_2 \\ = (4\pi Dt)^{-3} \exp\left(-\frac{(\mathbf{r}_1 - \mathbf{r}_{10})^2 + (\mathbf{r}_2 - \mathbf{r}_{20})^2}{4Dt}\right) d\mathbf{r}_1 d\mathbf{r}_2, \quad (12)$$

where  $\mathbf{r}_{10}$  and  $\mathbf{r}_{20}$  define the positions of the molecules at time  $t = 0$ .

We write (12) in the form:

$$U(\mathbf{r}_1, \mathbf{r}_{10}, \mathbf{r}_2, \mathbf{r}_{20}, t) d\mathbf{r}_1 d\mathbf{r}_2 \\ = \frac{1}{(2\pi)^3} \int \exp(-k^2 D|t| - k'^2 D|t| \\ + ik(\mathbf{r}_1 - \mathbf{r}_{10}) + ik'(\mathbf{r}_2 - \mathbf{r}_{20})) dk dk' d\mathbf{r}_1 d\mathbf{r}_2 \quad (13)$$

and introduce new variables  $\mathbf{r}_1 = \mathbf{r} + \mathbf{r}_2$ ,  $d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{r} d\mathbf{r}_2$ .

Then after integrating over  $\mathbf{r}_2$  we obtain:

$$U(\mathbf{r}, \mathbf{r}_0, t) = \left\{ \int U(\mathbf{r}_1, \mathbf{r}_{10}, \mathbf{r}_2, \mathbf{r}_{20}, t) d\mathbf{r}_2 \right\} d\mathbf{r} \\ = \frac{1}{(2\pi)^3} \int \exp(-2k^2 D|t| - ik(\mathbf{r} - \mathbf{r}_0)) dk d\mathbf{r}. \quad (14)$$

The last expression gives the probability that during a time  $t > 0$  the distance between the molecules will have changed by an amount  $|\mathbf{r} - \mathbf{r}_0|$ .

By making use of the identity

$$\exp(ikr) = \sum_{lm} g_l(kr) Y_{lm}^*\left(\frac{k}{k}\right) Y_{lm}\left(\frac{r}{r}\right), \quad (15)$$

where

$$g_l(\rho) = (2\pi)^{1/2} i^l J_{l+1/2}(\rho) / \sqrt{\rho}, \quad (16)$$

and after carrying out the integration over the angles of  $dk$ , we obtain:

$$U(\mathbf{r}, \mathbf{r}_0, t) = \frac{1}{(2\pi)^3} \int_0^{\infty} \exp(-2k^2 D|t|) \\ \times \sum_{lm} g_l(kr) g_l^*(kr_0) Y_{lm}(\vartheta\varphi) Y_{lm}^*(\vartheta_0\varphi_0) k^2 dk. \quad (17)$$

We obtain the average in expression (10) with the aid of the function  $U(\mathbf{r}, \mathbf{r}_0, t)$ :

$$f_{\lambda}(\tau) = 3(2a)^3 \int r^{-3} r_0^{-3} Y_{2\lambda}(\vartheta, \varphi) \\ \times Y_{2\lambda}^*(\vartheta_0\varphi_0) U(\mathbf{r}, \mathbf{r}_0, t) d\mathbf{r} d\mathbf{r}_0, \quad (18)$$

where we have taken into account the fact that

$$\sum_k \langle r_{jk}^{-6} | Y_{2\lambda}(\vartheta_{jk}\varphi_{jk})|^2 \rangle = \frac{1}{3(2a)^3} \frac{N}{V}. \quad (19)$$

Now, by utilizing the properties of spherical harmonics and expression (17) for  $U(\mathbf{r}, \mathbf{r}_0, t)$ , we obtain

$$f_{\lambda}(\tau) = f(\tau) \\ = 3\left(\frac{a}{\pi}\right)^3 \int_0^{\infty} k^3 dk \exp(-2k^2 D|t|) \left| \int_{2a}^{\infty} g(kr) \frac{dr}{r} \right|^2. \quad (20)$$

The integrals over  $r$  and  $r_0$  may be evaluated with the aid of the recurrence relation:<sup>7</sup>

$$-\rho^{-l} g_{l+1}(\rho) = \frac{d}{d\rho} [\rho^{-l} g_l(\rho)]. \quad (21)$$

Then

$$f(\tau) = \frac{3}{(2\pi)^3} \int_0^{\infty} \exp\left(-\frac{\rho^2 |\tau|}{9\tau_c}\right) |g_l(\rho)|^2 d\rho, \quad (22)$$

where we have used the notation  $\tau_c = (4\pi/3) a^3 \eta / kT$ .

We obtain from (9) and (19):

$$\Omega^2 = \frac{4\pi}{5} I(I+1) g^4 \mu_0^4 \hbar^{-2} \frac{N}{V} (2a)^{-3}. \quad (23)$$

4. The correlation function in the case of rotational Brownian motion can be found in a manner similar to the one utilized above for translational

motion. We consider the molecule as a whole to be a sphere of radius  $a$ , and the distance between the magnetic moments  $b_{jk}$  within the molecule is assumed constant. Moreover, we assume that the molecule contains two identical nuclei with magnetic moments different from zero.

The solution of the diffusion equation for rotational motion similar to (17) is of the form:

$$v(\vartheta, \varphi, \vartheta_0, \varphi_0, t) = \sum_{lm} Y_{lm}(\vartheta, \varphi) Y_{lm}^*(\vartheta_0, \varphi_0) \exp\left(-\frac{l(l+1)D'}{a^2}|t|\right), \quad (24)$$

where  $D' = kT/8\pi\eta a$  is the diffusion coefficient for rotational motion. The expression  $v(\vartheta, \varphi, \vartheta_0, \varphi_0, t) d\Omega$  determines the probability that the molecule is oriented within the solid angle  $d\Omega = \sin\vartheta d\vartheta d\varphi$ , if at time  $t = 0$  its orientation is determined by the angles  $\vartheta_0, \varphi_0$ .

The evaluation of the correlation function leads in this case to the expression

$$f(\tau) = \exp\left(-\frac{6D'|\tau|}{a^2}\right) = \exp\left(-\frac{|\tau|}{\tau_c}\right), \quad (25)$$

which agrees in form with (1).

Averaging over the angles in (9), we obtain:

$$\Omega^2 = \frac{3}{5} I(I+1) g^4 \mu_0^4 \hbar^{-2} b_{12}^4. \quad (26)$$

5. We now proceed to evaluate the quantities  $\tau'_\lambda$  and  $\tau''_\lambda$  which appear in the expressions for  $T_\perp, T_\parallel$ , and  $\Delta\omega_0$ .

In the case of translational Brownian motion we obtain after substituting (22) into (6) and after carrying out the integration over  $\tau$ :

$$\tau'_\lambda + i\tau''_\lambda = 27\tau_c \int_0^\infty J_{3/2}^2(\rho) d\rho / \rho(\rho^2 - 9i\lambda\tau_c\omega_0). \quad (27)$$

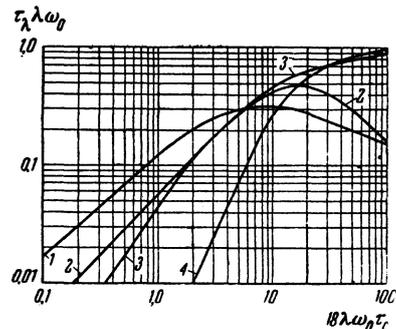
This integral can be evaluated if we recall that  $J_{3/2}(\rho)$  may be expressed in terms of trigonometric functions.

We denote

$$\begin{aligned} I(x) &= \int_0^\infty J_{3/2}^2(\rho) d\rho / \rho(\rho^2 - \frac{i}{2}x^2) \\ &= (x^{-3} - 2x^{-5}) + \exp(-x) [\cos x(x^{-3} + 4x^{-4} + 2x^{-5}) \\ &\quad + \sin x(x^{-3} - 2x^{-5})] \\ &\pm i \left\{ \left( -\frac{2}{3}x^{-2} + x^{-3} + 2x^{-5} \right) + \exp(-x) [\cos x(x^{-3} - 2x^{-5}) \right. \\ &\quad \left. - \sin x(x^{-3} + 4x^{-4} + 2x^{-5})] \right\}, \\ x &= \sqrt{18|\lambda|\tau_c\omega_0}, \end{aligned} \quad (28)$$

where both in the above and in the following expressions we choose the upper sign for  $\lambda < 0$  and the lower sign for  $\lambda > 0$ .

FIG. 1. Curves showing the dependence of  $\tau'_\lambda\lambda\omega_0$  and  $\tau''_\lambda\lambda\omega_0$  on  $18\lambda\omega_0\tau_c$  labelled respectively 1 and 3 for translational Brownian motion, and 2 and 4 for rotational Brownian motion.



Thus, in the case of translational Brownian motion

$$\tau'_\lambda = \frac{1}{|\lambda|\omega_0} \frac{3}{2} x^2 \operatorname{Re} I(x), \quad \tau''_\lambda = \frac{1}{|\lambda|\omega_0} \frac{3}{2} x^2 \operatorname{Im} I(x). \quad (29)$$

In weak fields when  $\tau_c\omega_0 \ll 1$ :

$$\begin{aligned} \tau'_\lambda &= \frac{18}{5} \tau_c - \frac{9}{\sqrt{2}} \tau_c \sqrt{|\lambda|\tau_c\omega_0}, \\ \tau''_\lambda &= \mp \frac{9}{\sqrt{2}} \tau_c \sqrt{|\lambda|\tau_c\omega_0}, \end{aligned} \quad (29')$$

while in the case of strong fields when  $\tau_c\omega_0 \gg 1$ :

$$\begin{aligned} \tau'_\lambda &= \frac{18}{5} \tau_c \delta_{\lambda 0} + \frac{1}{2\sqrt{2}} \tau_c (|\lambda|\tau_c\omega_0)^{-3/2} (1 - \delta_{\lambda 0}), \\ \tau''_\lambda &= \mp \left( \frac{1}{|\lambda|\omega_0} - \frac{1}{2\sqrt{2}} \tau_c (|\lambda|\tau_c\omega_0)^{-3/2} \right) (1 - \delta_{\lambda 0}). \end{aligned} \quad (29'')$$

In the case of rotational Brownian motion, on substituting (25) into (6) and on carrying out the integration with respect to  $\tau$ , we obtain in a similar fashion

$$\tau'_\lambda = \frac{1}{|\lambda|\omega_0} \frac{18x^2}{x^4 + 324}, \quad \tau''_\lambda = \frac{1}{\lambda\omega_0} \frac{x^4}{x^4 + 324}, \quad (30)$$

which have simple asymptotic expressions.

In the case of weak fields:

$$\tau'_\lambda = \tau_c - \lambda^2 \omega_0^2 \tau_c^3, \quad \tau''_\lambda = \lambda \omega_0 \tau_c^2. \quad (30')$$

In the case of strong fields:

$$\begin{aligned} \tau'_\lambda &= \tau_c \delta_{\lambda 0} + \frac{1}{\lambda^2 \omega_0^2 \tau_c} (1 - \delta_{\lambda 0}), \\ \tau''_\lambda &= \left( \frac{1}{\lambda \omega_0} - \frac{1}{\lambda^3 \omega_0^3 \tau_c^2} \right) (1 - \delta_{\lambda 0}). \end{aligned} \quad (30'')$$

The dependence of  $\tau'_\lambda |\lambda|\omega_0$  and  $\tau''_\lambda |\lambda|\omega_0$  on  $\tau_c\omega_0$ , both for translational and rotational motion, is shown in Fig. 1.

Using (8), we obtain

$$T_\perp \Omega^2 = (2/3 \tau'_2 + 5/3 \tau'_1 + \tau'_0)^{-1}; \quad (31)$$

$$T_\parallel \Omega^2 = (2/3 \tau'_1 + 5/3 \tau'_2)^{-1}; \quad (32)$$

$$\Omega^2 / \Delta\omega_0 = (2/3 \tau''_2 + 1/3 \tau''_1)^{-1}. \quad (33)$$

Thus, to obtain the dependence of  $T_\perp, T_\parallel$ , and  $\Delta\omega_0$  on  $\tau_c\omega_0$  both for translational and for rotational Brownian motion it is sufficient to know the value of  $\Omega^2$ , which depends on the structure of the molecules and on the structure of the liquid. Curves

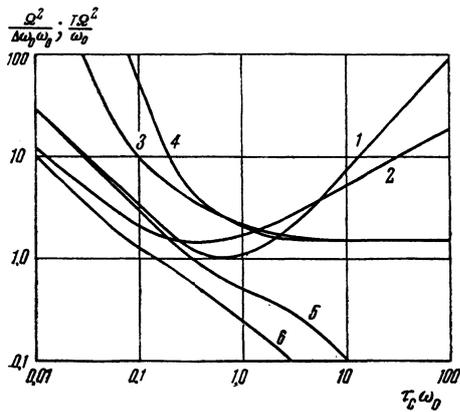


FIG. 2. Curves showing the dependence of  $T_{\parallel}\Omega^2/\omega_0$ ,  $T_{\perp}\Omega^2/\omega_0$  and  $\Omega^2/\Delta\omega_0\omega_0$  on  $\tau_c\omega_0$ , labelled respectively 2, 6, and 3 for translational Brownian motion and by 1, 5, 4 for the case of rotational Brownian motion.

of  $T_{\perp}\Omega^2/\omega_0$ ,  $T_{\parallel}\Omega^2/\omega_0$ , and  $\Omega^2/\Delta\omega_0\omega_0$  vs.  $\tau_c\omega_0$  are shown in Fig. 2.

6. As an example we consider the case of nuclear magnetic resonance in a liquid whose molecules contain two identical nuclei with magnetic moments differing from zero (water) with spins  $I = \frac{1}{2}$ .

In this case the operator  $\hat{\mathcal{H}}_2$  can be separated into two parts  $\hat{\mathcal{H}}_{2t}$  and  $\hat{\mathcal{H}}_{2r}$ , which describe the motion of the centers of masses of the molecules and the rotation of the molecule as a whole about the common center of mass. The distance  $b$  between nuclei belonging to the same molecule is constant.

The rotational Brownian motion leads only to a variation in the angle between the straight line joining these nuclei and the direction of the field  $H_0$ .

The translational Brownian motion alters the relative position of nuclei belonging to different molecules.

If we neglect the correlation between the translational and the rotational Brownian motions, each of the expressions for  $T_{\perp}^{-1}$ ,  $T_{\parallel}^{-1}$ , and  $\Delta\omega_0$  defined by (4) and (5) can be separated into two terms corresponding to the translational and the rotational Brownian motion of the molecules.

In calculating  $\Omega^2$  for the translational motion of the molecule we should take into account the fact that a fraction of the molecules ( $\frac{3}{4}$ ) has a total nuclear spin equal to unity while the remaining fraction of the molecules ( $\frac{1}{4}$ ) has a spin equal to zero.

Then for the translational motion we have

$$\Omega_t^2 = \frac{3\pi}{20} g^4 \mu_0^4 \hbar^{-2} \frac{N}{V} a^{-3}, \quad (34)$$

where  $N/V$  is the number of water molecules per unit volume.

In the case of rotational motion we have:

$$\Omega_r^2 = \frac{9}{20} g^4 \mu_0^4 \hbar^{-2} b^{-6}. \quad (35)$$

Now, by utilizing (29) – (32) and (33) – (35) we can obtain expressions for the relaxation times  $T_{\perp}$  and  $T_{\parallel}$  and for  $\Delta\omega_0$ .

In weak fields when  $\tau_c\omega_0 \ll 1$  we have:

$$\frac{1}{T_{\perp}} = \frac{1}{T_{\parallel}} = \frac{1}{T} = \frac{3}{2} g^4 \mu_0^4 \hbar^{-2} \tau_c \left( \frac{6\pi}{5} \frac{N}{V} a^{-3} + b^{-6} \right). \quad (36)$$

The transverse and the longitudinal relaxation times are equal.

The effective gyromagnetic ratio is of the form

$$\gamma^* = \gamma \left( 1 + \frac{\Delta\omega_0}{\omega_0} \right) = \gamma \left( 1 + \frac{6\sqrt{2}+3}{\sqrt{2}} \Omega_t^2 \tau_c \sqrt{\frac{\tau_c}{\omega_0}} \right). \quad (37)$$

In the first approximation the correction is determined by the translational Brownian motion where  $\Omega_t^2$  is given by (34).

In the case of strong fields when  $\tau_c\omega_0 \gg 1$  we have:

$$\frac{1}{T_{\perp}} = \frac{9}{20} g^4 \mu_0^4 \hbar^{-2} \tau_c \left( \frac{6\pi}{5} \frac{N}{V} a^{-3} + b^{-6} \right); \quad (38)$$

$$\frac{1}{T_{\parallel}} = \frac{\sqrt{2}+1}{20\sqrt{2}} \pi g^4 \mu_0^4 \hbar^{-2} \frac{N}{V} a^{-3} \omega_0^{-3/2} \tau_c^{-1/2}; \quad (39)$$

$$\gamma^* \approx \gamma. \quad (40)$$

Here  $T_{\parallel}$  is determined largely by the translational Brownian motion.

7. The expressions for  $T_{\perp}$  and  $T_{\parallel}$  in the example discussed above have been obtained by Bloembergen, Purcell, and Pound.<sup>6</sup> In reference 1 it was pointed out that these calculations are not accurate.

The expressions for  $T_{\perp}$  and  $T_{\parallel}$  obtained in reference 6 in the case of weak fields

$$0.88 \frac{1}{T_{\perp}} = \frac{1}{T_{\parallel}} = \frac{9}{10} g^4 \mu_0^4 \hbar^{-2} \tau_c \left( \frac{3}{2} \pi \frac{N}{V} a^{-3} + b^{-6} \right) \quad (41)$$

differ from (36) by numerical coefficients. Taking for water<sup>8</sup> at 20°C  $a = 1.45 \times 10^{-8}$  cm,  $b = 1.54 \times 10^{-8}$  cm,  $\tau_c = 0.32 \times 10^{-11}$  sec,  $V/N = 30 \times 10^{-24}$  cm<sup>3</sup>, we obtain from (36)  $T = T_{\parallel} = T_{\perp} = 3$  sec, which agrees with experimental data ( $T_{\parallel} = T_{\perp} = 3.6 \pm 0.4$  sec).<sup>9</sup> For  $\Delta\omega_0$  we obtain in this case

$$\Delta\omega_0 = 1.4 \sqrt{\omega_0} \cdot 10^{-7} \text{ sec}^{-1} \quad (42)$$

As can be seen from (39) and Fig. 2, in strong fields  $T_{\parallel}$  is proportional to  $\tau_c^{1/2}$ . Such a dependence is determined by the translational Brownian motion, which makes the principal contribution in the case of strong fields.

For strong fields the dependence of  $T_{\parallel}$  on  $\tau_c$ , determined by (39), is given on a logarithmic scale in the region  $\omega_0\tau_c \gg 1$  by a straight line with a slope of 26.5°, and not of 45°, as called for by the

theory of Bloembergen, Purcell, and Pound.<sup>6</sup>

The experimental values given in the paper of Bloembergen, Purcell, and Pound<sup>6</sup> for the relaxation times for glycerine at different values of  $\eta/T$  fall in the case of  $\eta/T \gg 1$  on a less steep straight line with a slope of approximately 30°, which is in good agreement with the conclusions reached above. Moreover, it follows from (41) that in strong fields  $T_{\parallel}$  is proportional to  $\omega_0^{3/2}$ , and not to  $\omega_0^2$ , as in reference 6, which also agrees much better with experimental data.

Thus, for the description of the phenomenon of nuclear resonance in liquids it is necessary to take into account the translational as well as the rotational Brownian motion of the molecules. Moreover the form of the correlation function for the two types of motion turns out to be different. Only in the case of weak fields when  $\omega_0\tau_c \ll 1$  do the relaxation times turn out to be not very sensitive to the specific form of the relaxation function.

<sup>1</sup>R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

<sup>2</sup>M. Yokota and S. Koide, J. Phys. Soc. Japan **9**, 953 (1954).

<sup>3</sup>D. Kivelson, J. Chem. Phys. **27**, 1087 (1957).

<sup>4</sup>A. K. Chirkov and A. A. Kokin, J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 50 (1958), Soviet Phys. JETP **8**, 36 (1958).

<sup>5</sup>G. V. Skrotskiĭ and A. A. Kokin, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 169 (1959), Soviet Phys. JETP **9**, 116 (1959).

<sup>6</sup>Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

<sup>7</sup>L. Schiff, Quantum Mechanics, McGraw-Hill, N. Y., 1955.

<sup>8</sup>R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 1955.

<sup>9</sup>Chiarotti, Cristianini, and Ginlotto, Nuovo cimento **1**, 863 (1955).

Translated by G. Volkoff