Nuclear Magnetic Relaxation by Intermolecular Dipole-Dipole Interactions*

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The contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of identical spin-$\frac{1}{2}$ nuclei at equivalent positions in spherical molecules in a liquid is calculated. The assumptions made are that: (1), the effect of cross correlations of different dipole-dipole interactions is negligible, so that the relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays with relaxation times T_1 and T_2, respectively; (2), the motions of the molecules can be considered to be translational and rotational diffusion; and (3), the correlation time $\tau_0 \equiv (2a^2/D)$, where a is the radius of a molecule and D is the translational diffusion coefficient, is sufficiently short that $(\omega_0\tau_0)^2 \ll 1$, where ω_0 is the Larmor frequency of the nuclei. As a result of the short correlation time assumption (3), the contributions of the intermolecular interactions to $(1/T_1)$ and $(1/T_2)$ are found to be the same and are given by an infinite series, the first three terms of which are

$$\left(\frac{1}{T_1}\right)'' = \left(\frac{1}{T_2}\right)'' = \frac{n\pi\gamma^4\hbar^2}{5aD}\left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 + \cdots\right],$$

where n is the number of spins per unit volume, γ is the gyromagnetic ratio of each nucleus, and b is the distance of each nucleus from the center of the molecule in which it is contained. The first term in the series is the result obtained in previous calculations in which the effect of the rotations of the molecules was neglected. In a typical case in which $(b/a) \approx \frac{1}{2}$, the second and third terms are 6.8% of the first term.

1. INTRODUCTION

THE dipole-dipole interactions between the magnetic moments of spin-$\frac{1}{2}$ nuclei in molecules in a liquid contribute significantly to the nuclear magnetic relaxation of the liquid. The dipole-dipole interaction between a pair of spins depends upon the position vector of one spin with respect to the other. The relative position of nuclei in liquid molecules changes with time as a result of the translational and rotational motions of the molecules. The dipole-dipole interactions thus act as time-dependent perturbations on the Zeeman energy levels of the nuclei and produce transitions between these energy levels, which results in the relaxation of the nuclear magnetization.

Since the distance between nuclei in the same molecule is effectively constant, the time dependence of intramolecular dipole-dipole interactions in liquid molecules is due just to the rotational motion of the molecules. The time dependence of the relative position of two nuclei in different molecules depends on the translational motion of the molecules and also on the rotational motion of the molecules, unless both nuclei are at the centers of their respective molecules. Hence, the contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of polyatomic molecules in a liquid depends on both the translational and rotational motions of the molecules.

Previous treatments of the contribution of intermolecular dipole-dipole interactions to nuclear magnetic relaxation in liquids have taken into account only the translational motion of the molecules, on the assumption that the nuclei can be considered to be at the centers of spherical molecules which approach each other no more closely than a molecular diameter.[1-4] This assumption is valid only for liquids containing monatomic molecules. In the case of liquids containing polyatomic molecules, the distance of closest approach of nuclei in different molecules is less than the diameter of a molecule, which means that a correct treatment might give a greater contribution to the relaxation rate, since the magnitude of the dipole-dipole interaction varies inversely as the cube of the distance between the spins. On

[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).
[2] H. C. Torrey, Phys. Rev. 92, 962 (1953).
[3] I. Oppenheim and M. Bloom, Can. J. Phys. 39, 845 (1961).
[4] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), p. 300.

the other hand, if the nuclei are not at the centers of molecules, and the rotational motion is taken into account in addition to the translational motion, the time dependence of the relative position of nuclei in different molecules is different from the case in which the nuclei are at the centers of molecules. This additional motion can be expected to reduce the relaxation effect, since the previous calculations indicate that the rate of relaxation decreases as the rate of molecular motion increases for the conditions that exist in most liquids.[1] It is not obvious *a priori* which of the two effects mentioned above is more important. The following calculation shows that the first effect dominates, and that the contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of polyatomic molecules in a liquid is greater than that predicted by the previous approximate treatments.

2. RELAXATION BY DIPOLE-DIPOLE INTERACTIONS

Consider a system of N identical nuclei, each having a spin of $\frac{1}{2}$ and gyromagnetic ratio γ. Suppose that the nuclei are at equivalent positions in spherical molecules in a liquid. The calculation of the nuclear magnetic relaxation of the system resulting from the time-dependent dipole-dipole interactions between the nuclei can be formulated by use of the density operator theory of relaxation.[5] The equations so obtained are found to involve certain correlation functions of each dipole-dipole interaction with itself and with other dipole-dipole interactions. The calculation predicts a simple exponential decay of the longitudinal and transverse nuclear magnetization if one retains in the equations only those terms that involve the correlation of each dipole-dipole interaction with itself. The validity of the omission of the other terms is not obvious *a priori*, since the magnitudes of some of the omitted terms are as large as the magnitudes of the terms that are retained. However, in the few calculations in which the cross correlation terms have been included, it has been found that they produce a negligible effect.[6-8] These calculations do not prove that the cross correlation terms always have negligible effect. Nonetheless, in order to obtain a tractable expression for the relaxation effect of the intermolecular dipole-dipole interactions, in this paper we shall employ the approximate expressions obtained by omitting the cross correlation terms. Thus, the longitudinal relaxation time T_1 and the transverse relaxation time T_2 are given, respectively, by[9]

$$(1/T_1)=2\sum_{l=-2}^{2}(-1)^l l^2 J_{l,-l}(-l\omega_0) \qquad (2.1)$$

[5] P. S. Hubbard, Rev. Mod. Phys. **33**, 249 (1961).
[6] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958); **111**, 1746 (E) (1958).
[7] G. W. Kattawar and M. Eisner, Phys. Rev. **126**, 1054 (1962).
[8] P. S. Hubbard, Phys. Rev. **128**, 650 (1962).
[9] Reference 5, Eqs. (165a) and (165b).

and

$$(1/T_2)=\sum_{l=-2}^{2}(-1)^l(6-l^2)J_{l,-l}(-l\omega_0), \qquad (2.2)$$

where ω_0 is the Larmor frequency, which in terms of the applied magnetic field H_0, is given by $\omega_0=\gamma H_0$. The function $J_{lk}(\omega)$ is defined by

$$J_{lk}(\omega)=\sum_i(1-\delta_{ij})J_{(ij)(ij)}{}^{lk}(\omega), \qquad (2.3)$$

where

$$J_{(ij)(ij)}{}^{lk}(\omega)=\frac{1}{2}\int_{-\infty}^{\infty}C_{(ij)(ij)}{}^{lk}(\tau)e^{i\omega\tau}d\tau. \qquad (2.4)$$

The correlation function in Eq. (2.4) is defined by

$$C_{(ij)(ij)}{}^{lk}(\tau)=\langle U_{ij}{}^l(t+\tau)U_{ij}{}^k(t)\rangle, \qquad (2.5)$$

where

$$U_{ij}{}^k=(3\pi/10)^{1/2}\gamma^2\hbar(r_{ij}')^{-3}(-1)^k Y_2{}^{-k}(\theta_{ij}',\phi_{ij}'). \qquad (2.6)$$

The $Y_2{}^k$ are normalized spherical harmonics. The magnitude of the position vector $\mathbf{r}_{ij}'$ of the ith nucleus with respect to the jth is denoted by r_{ij}', and its polar angles by $(\theta_{ij}',\phi_{ij}')$. The time dependence of the functions $U_{ij}{}^k$ is due to the change with time of $\mathbf{r}_{ij}'$ as a result of the molecular motion in the liquid. In the present paper, the molecular motion will be considered to be classical, and a stationary random process. Hence, the correlation functions (2.5) are independent of t. By replacing t by $t-\tau$ in (2.5), one obtains

$$C_{(ij)(ij)}{}^{lk}(\tau)=C_{(ij)(ij)}{}^{kl}(-\tau). \qquad (2.7)$$

The quantity $(1/T_1)$ given by Eq. (2.1) can be written as the sum of two terms which contain, respectively, the effects of intramolecular and intermolecular dipole-dipole interactions:

$$(1/T_1)=(1/T_1)'+(1/T_1)'', \qquad (2.8)$$

where

$$(1/T_1)'=2\sum_{l=-2}^{2}(-1)^l l^2\sum_i' J_{(ij)(ij)}{}^{l,-l}(-l\omega_0), \qquad (2.9)$$

the sum $\sum_i'$ being over the other nuclei in the same molecule as the jth nucleus, and

$$(1/T_1)''=2\sum_{l=-2}^{2}(-1)^l l^2\sum_i'' J_{(ij)(ij)}{}^{l,-l}(-l\omega_0), \qquad (2.10)$$

the sum $\sum_i''$ being over all the nuclei not in the same molecule as the jth nucleus. Similarly, it follows from (2.2) and (2.3) that

$$(1/T_2)=(1/T_2)'+(1/T_2)'', \qquad (2.11)$$

where

$$(1/T_2)'=\sum_{l=-2}^{2}(-1)^l(6-l^2)\sum_i' J_{(ij)(ij)}{}^{l,-l}(-l\omega_0), \qquad (2.12)$$

and

$$(1/T_2)''=\sum_{l=-2}^{2}(-1)^l(6-l^2)\sum_i'' J_{(ij)(ij)}{}^{l,-l}(-l\omega_0). \qquad (2.13)$$

3. INTERMOLECULAR CONTRIBUTION

Let N'' be the total number of spins in the sample less the number of spins in a single molecule. Since the spins are all in equivalent positions, it follows that

$$\sum_i{}'' C_{(ij)(ij)}{}^{lk}(\tau) = N'' C_{(ij)(ij)}{}^{lk}(\tau), \qquad (3.1)$$

where the i and j subscripts in the right-hand member of the equation refer to any two nuclei in different molecules. By use of Eqs. (2.5) and (2.6), one can obtain from (3.1) the relation

$$\sum_i{}'' C_{(ij)(ij)}{}^{lk}(\tau) = N''(3\pi/10)(\gamma^2\hbar)^2(-1)^{k+l}$$
$$\times \langle [f_2{}^{-l}(\mathbf{r}_{ij}')]_{t+\tau}[f_2{}^{-k}(\mathbf{r}_{ij}')]_t \rangle, \quad (3.2)$$

where

$$f_L{}^M(\mathbf{r}_{ij}') \equiv (r_{ij}')^{-L-1} Y_L{}^M(\theta_{ij}',\phi_{ij}'). \qquad (3.3)$$

The position vectors of the ith and the jth nuclei with respect to the laboratory coordinate system are denoted, respectively, by $\mathbf{r}_i'$ and $\mathbf{r}_j'$, so that $\mathbf{r}_{ij}' = \mathbf{r}_i' - \mathbf{r}_j'$. The position vector of the ith nucleus with respect to the center of the spherical molecule in which it is contained is denoted by $\mathbf{r}_i$, and the position vector of the center of the molecule with respect to the laboratory coordinate system by $\mathbf{R}_i$. Hence, $\mathbf{r}_i' = \mathbf{R}_i + \mathbf{r}_i$ and $\mathbf{r}_j' = \mathbf{R}_j + \mathbf{r}_j$. Therefore, $\mathbf{r}_{ij}' = (\mathbf{R}_i - \mathbf{R}_j) + (\mathbf{r}_i - \mathbf{r}_j)$. It is convenient to introduce the quantities $\mathbf{R} \equiv \mathbf{R}_i - \mathbf{R}_j$ and $\mathbf{r} \equiv \mathbf{r}_i - \mathbf{r}_j$, in terms of which $\mathbf{r}_{ij}' = \mathbf{R} + \mathbf{r}$. No confusion arises from the omission of subscripts i and j on $\mathbf{R}$ and $\mathbf{r}$ because we henceforth are concerned only with a single pair of spins in different molecules, as in Eq. (3.1).

A three-dimensional Taylor series expansion of the function $f_2{}^k(\mathbf{r}_{ij}')$ about the point $\mathbf{R}$ gives the expression

$$f_2{}^k(\mathbf{r}_{ij}') = \sum_{\kappa=0}^{\infty} \frac{1}{\kappa!} (\mathbf{r}\cdot\nabla_R)^\kappa f_2{}^k(\mathbf{R}). \qquad (3.4)$$

But $(\mathbf{r}\cdot\nabla_R)$ can be expressed as

$$(\mathbf{r}\cdot\nabla_R) = x_0\partial_0 - x_{-1}\partial_1 - x_1\partial_{-1}, \qquad (3.5)$$

where

$$x_0 \equiv z, \quad x_{\pm 1} \equiv \mp 2^{-1/2}(x\pm iy), \qquad (3.6)$$

and

$$\partial_0 \equiv \frac{\partial}{\partial Z}, \quad \partial_{\pm 1} \equiv \mp 2^{-1/2}\left(\frac{\partial}{\partial X} \pm i\frac{\partial}{\partial Y}\right). \qquad (3.7)$$

Furthermore,

$$(x_0\partial_0 - x_{-1}\partial_1 - x_1\partial_{-1})^\kappa$$
$$= \sum_{\mu\nu\eta} \frac{\kappa!}{\mu!\nu!\eta!}(x_0\partial_0)^\mu(-x_{-1}\partial_1)^\nu(-x_1\partial_{-1})^\eta, \quad (3.8)$$

where the summation extends over all non-negative integers μ, ν, η, such that $\mu+\nu+\eta=\kappa$. Use of (3.5) and (3.8) in (3.4) gives

$$f_2{}^k(\mathbf{r}_{ij}') = \sum_{\kappa=0}^{\infty} \sum_{\mu\nu\eta} \frac{1}{\mu!\nu!\eta!}(x_0)^\mu(-x_{-1})^\nu(-x_1)^\eta$$
$$\times \partial_0{}^\mu\partial_1{}^\nu\partial_{-1}{}^\eta f_2{}^k(\mathbf{R}). \quad (3.9)$$

It is assumed that the rotational motions of the molecules and their translational motions are independent, so that $\mathbf{r}$ and $\mathbf{R}$ are independent. Thus, if (3.9) is used in Eq. (3.2), the result can be written

$$\sum_i{}'' C_{(ij)(ij)}{}^{lk}(\tau) = \left(\frac{3\pi}{10}\right)(\gamma^2\hbar)^2(-1)^{k+l} \sum_{\kappa=0}^{\infty} \sum_{\mu\nu\eta} \frac{1}{\mu!\nu!\eta!} \sum_{\kappa'=0}^{\infty} \sum_{\mu'\nu'\eta'} \frac{1}{\mu'!\nu'!\eta'!}$$

$$\times \langle [(x_0)^\mu(-x_{-1})^\nu(-x_1)^\eta]_{t+\tau}[(x_0)^{\mu'}(-x_{-1})^{\nu'}(-x_1)^{\eta'}]_t \rangle N''\langle [\partial_0{}^\mu\partial_1{}^\nu\partial_{-1}{}^\eta f_2{}^{-l}(\mathbf{R})]_{t+\tau}[\partial_0{}^{\mu'}\partial_1{}^{\nu'}\partial_{-1}{}^{\eta'}f_2{}^{-k}(\mathbf{R})]_t \rangle. \quad (3.10)$$

The first correlation function in Eq. (3.10) depends on the rotational motion of the molecules, and the second correlation function depends on their translational motion. If a model of the rotational and translational motions of the molecules is adopted which permits the calculation of these correlation functions, the contribution of the intermolecular dipole-dipole interactions to the nuclear magnetic relaxation can then be obtained by use of (3.10) in (2.10) and (2.13).

The correlation function in (3.10) that depends upon the translational motion can be written in a different form which facilitates its evaluation. It is a consequence of Eq. (A11) of Appendix A that

$$\partial_0{}^\mu\partial_1{}^\nu\partial_{-1}{}^\eta f_2{}^k(\mathbf{R}) = (-1)^\kappa \left[\frac{5(2-k+\kappa-\nu+\eta)!(2+k+\kappa+\nu-\eta)!}{2^{\kappa-\mu}(2\kappa+5)(2-k)!(2+k)!} \right]^{1/2} f_{2+\kappa}{}^{k+\nu-\eta}(\mathbf{R}). \qquad (3.11)$$

Hence,

$$N''\langle [\partial_0{}^\mu\partial_1{}^\nu\partial_{-1}{}^\eta f_2{}^{-l}(\mathbf{R})]_{t+\tau}[\partial_0{}^{\mu'}\partial_1{}^{\nu'}\partial_{-1}{}^{\eta'}f_2{}^{-k}(\mathbf{R})]_t \rangle$$

$$= \left[\frac{(2+l+\kappa-\nu+\eta)!(2-l+\kappa+\nu-\eta)!(2+k+\kappa'-\nu'+\eta')!(2-k+\kappa'+\nu'-\eta')!}{2^{\kappa+\kappa'-\mu-\mu'}(2\kappa+5)(2\kappa'+5)(2+l)!(2-l)!(2+k)!(2-k)!} \right]^{1/2}$$

$$\times (-1)^{\kappa+\kappa'} 5 N''\langle [f_{2+\kappa}{}^{-l+\nu-\eta}(\mathbf{R})]_{t+\tau}[f_{2+\kappa'}{}^{-k+\nu'-\eta'}(\mathbf{R})]_t \rangle. \quad (3.12)$$

In order to evaluate the correlation function on the right-hand side of Eq. (3.12), we assume that the translational motion of the spherical molecules is a classical diffusion with diffusion coefficient D, and that the distance

of closest approach of two molecules is $2a$, where a is the radius of the molecules. By use of this model, it is shown in Appendix B that

$$G_{LL'}{}^{MM'}(\tau) \equiv N''\langle [f_L{}^M(\mathbf{R})]_{t+\tau}[f_{L'}{}^{M'}(\mathbf{R})]_t\rangle$$
$$= n\delta_{L'L}\delta_{-M'M}(-1)^M G_L(\tau), \tag{3.13}$$

where

$$G_L(\tau) = (2a)^{-2L+1}\int_0^\infty \exp\left(\frac{-D|\tau|u^2}{2a^2}\right)[J_{L-1/2}(u)]^2 u^{-1}du, \tag{3.14}$$

and n is the number of spins per unit volume. Use of Eq. (3.13) leads to the following expression for the right-hand side of Eq. (3.12):

$$n\delta_{\kappa\kappa'}\delta_{-l+\nu-\eta,k-\nu'+\eta'}\frac{5(2+l+\kappa-\nu+\eta)!(2-l+\kappa+\nu-\eta)!(-1)^{-l+\nu-\eta}}{(2\kappa+5)[2^{2\kappa-\mu-\mu'}(2+l)!(2-l)!(2+k)!(2-k)!]^{1/2}}G_{2+\kappa}(\tau). \tag{3.15}$$

Thus, Eq. (3.10) can be written

$$\sum_i{}'' C_{(ij)(ij)}{}^{lk}(\tau) = n\pi(\gamma^2\hbar)^2(-1)^k\sum_{\kappa=0}^\infty C_{lk}{}^{(\kappa)}(\tau), \tag{3.16}$$

where

$$C_{lk}{}^{(\kappa)}(\tau) = \sum_{\mu\nu\eta}^{\kappa}\frac{1}{\mu!\nu!\eta!}\sum_{\mu'\nu'\eta'}^{\kappa}\frac{1}{\mu'!\nu'!\eta'!}\delta_{-l+\nu-\eta,k-\nu'+\eta'}\frac{3(2+l+\kappa-\nu+\eta)!(2-l+\kappa+\nu-\eta)!}{2(2\kappa+5)[2^{2\kappa-\mu-\mu'}(2+l)!(2-l)!(2+k)!(2-k)!]^{1/2}}$$
$$\times G_{2+\kappa}(\tau)\langle[(x_0)^\mu(x_{-1})^\nu(x_1)^\eta]_{t+\tau}[(x_0)^{\mu'}(-x_{-1})^{\nu'}(-x_1)^{\eta'}]_t\rangle. \tag{3.17}$$

The first term in the sum in Eq. (3.16) does not depend upon the rotational motions of the molecules. It is

$$C_{lk}{}^{(0)}(\tau) = \delta_{-l,k}(\tfrac{3}{10})G_2(\tau). \tag{3.18}$$

Previous treatments of relaxation by intermolecular dipole-dipole interactions have included only this term.

If $\kappa=1$ in Eq. (3.17), there are nine terms in the sums, in each of which one of the indices μ, ν, η is unity and the other two are zero, and one of the indices μ', ν', η' is unity and the other two are zero. Hence, there occur correlation functions of the form $\langle[x_p]_{t+\tau}[x_q]_t\rangle$. It is shown in Appendix C that, if the rotational motion of the molecules is isotropic rotational diffusion,

$$\langle[x_p]_{t+\tau}[x_q]_t\rangle = (2/3)b^2\delta_{-q,p}(-1)^p e^{-2D'|\tau|}, \tag{3.19}$$

where b is the distance of each spin from the center of the molecule in which it is contained, and D' is the rotational diffusion coefficient introduced by Furry in his theory of isotropic rotational Brownian motion.[10] Thus, the only nonzero terms in the sums in (3.17) are the three terms for which $\mu'=\mu=1$, $\nu=\nu'=\eta=\eta'=0$; $\nu=\eta'=1$, $\mu=\mu'=\nu'=\eta=0$; and $\eta=\nu'=1$, $\mu=\mu'=\nu=\eta'=0$. Hence, one finds that

$$C_{lk}{}^{(1)}(\tau) = \delta_{-l,k}3b^2e^{-2D'|\tau|}G_3(\tau). \tag{3.20}$$

The calculation of $C_{lk}{}^{(2)}(\tau)$ from (3.17) is more complicated. When $\kappa=2$, it is apparent that the correlation functions that occur in (3.17) are of the form $\langle[x_px_{p'}]_{t+\tau}[x_qx_{q'}]_t\rangle$. These correlation functions can be evaluated by the same procedure used in Appendix C to calculate (3.19). It is found that they are zero unless

$p+p'+q+q'=0$, and that in particular the only nonzero values are

$$\langle[x_{\pm1}x_{\pm1}]_{t+\tau}[x_{\mp1}x_{\mp1}]_t\rangle$$
$$= (4/45)b^4(5e^{-4D'|\tau|}+3e^{-6D'|\tau|}), \tag{3.21a}$$

$$\langle[x_{\pm1}x_{\mp0}]_{t+\tau}[x_{\mp1}x_0]_t\rangle$$
$$= -(2/45)b^4(5e^{-4D'|\tau|}+3e^{-6D'|\tau|}), \tag{3.21b}$$

$$\langle[x_{\pm1}x_{\mp1}]_{t+\tau}[x_{\pm1}x_{\mp1}]_t\rangle$$
$$= (2/45)b^4(10+5e^{-4D'|\tau|}+e^{-6D'|\tau|}), \tag{3.21c}$$

$$\langle[x_{\pm1}x_{\mp1}]_{t+\tau}[x_0x_0]_t\rangle = \langle[x_0x_0]_{t+\tau}[x_{\pm1}x_{\mp1}]_t\rangle$$
$$= -(4/45)b^4(5-e^{-6D'|\tau|}), \tag{3.21d}$$

$$\langle[x_0x_0]_{t+\tau}[x_0x_0]_t\rangle$$
$$= (4/45)b^4(5+5e^{-4D'|\tau|}+2e^{-6D'|\tau|}). \tag{3.21e}$$

If the above quantities are used in Eq. (3.17) to evaluate $C_{lk}{}^{(2)}(\tau)$, one obtains the surprisingly simple result

$$C_{lk}{}^{(2)}(\tau)$$
$$= \delta_{-l,k}(14/5)b^4(5e^{-4D'|\tau|}+3e^{-6D'|\tau|})G_4(\tau). \tag{3.22}$$

It is of interest to note that the three terms in the expansion (3.16) which have been calculated above are each zero unless $k=-l$. In the derivation of the expressions (2.1) and (2.2) for the relaxation times, terms containing the functions $J_{lk}(\omega)$ with $k\neq-l$ can be omitted because their rapid oscillation makes their effect on the relaxation negligible. However, the above calculation indicates that the contribution of the intermolecular dipole-dipole interactions to $J_{lk}(\omega)$ is zero unless $k=-l$. At least, such is the case for the three terms in (3.16) which have been calculated.

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[10] W. H. Furry, Phys. Rev. 107, 7 (1957).

From Eqs. (2.4) and (3.16) it follows that

$$\sum i'' J_{(ij)(ij)}{}^{l,-l}(-l\omega_0)$$

$$=n\pi(\gamma^2\hbar)^2(-1)^{-l}\sum_{\kappa=0}^{\infty}\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(\kappa)}(\tau)e^{-il\omega_0\tau}d\tau. \quad (3.23)$$

The first term in the sum over κ in (3.23) can be re-written by use of Eqs. (3.18) and (3.14). After performing the integration over τ, one obtains the following expression for the first term:

$$\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(0)}(\tau)e^{-il\omega_0\tau}d\tau$$

$$=\left(\frac{3}{40Da}\right)\int_{0}^{\infty}[J_{3/2}(u)]^2[u^4+(l\omega_0\tau_0)^2]^{-1}udu, \quad (3.24)$$

where the correlation time τ_0 is defined by

$$\tau_0\equiv 2a^2/D. \quad (3.25)$$

In most liquids the correlation time τ_0 is sufficiently short that $(\omega_0\tau_0)^2\ll1$. If the correlation time is short, little error is introduced in the evaluation of (3.24) by neglecting $(l\omega_0\tau_0)^2$ in comparison to u^4, in which case one obtains the result[11]

$$\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(0)}(\tau)e^{-il\omega_0\tau}d\tau$$

$$=\left(\frac{3}{40Da}\right)\int_{0}^{\infty}[J_{3/2}(u)]^2u^{-3}du=(100Da)^{-1}. \quad (3.26)$$

The second term in the sum in (3.23) can be rewritten by use of Eqs. (3.20) and (3.14). After performing the integration over τ, one obtains the expression

$$\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(1)}(\tau)e^{-il\omega_0\tau}d\tau=\left(\frac{3b^2}{16a^3D}\right)\int_{0}^{\infty}[J_{5/2}(u)]^2$$

$$\times[(A^2+u^2)^2+(l\omega_0\tau_0)^2]^{-1}(A^2+u^2)u^{-1}du, \quad (3.27)$$

where $A^2\equiv(4a^2D'/D)$. Here again if $(\omega_0\tau_0)^2\ll1$, or if $(\omega_0\tau_0)^2\ll A^4$, which is also usually satisfied in practice, the term $(l\omega_0\tau_0)^2$ can be neglected with little error, in which case

$$\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(1)}(\tau)e^{-il\omega_0\tau}d\tau$$

$$=\left(\frac{3b^2}{16a^3D}\right)\int_{0}^{\infty}[J_{5/2}(u)]^2(A^2+u^2)^{-1}u^{-1}du. \quad (3.28)$$

In a similar manner, it follows from Eqs. (3.22) and (3.13) that the third term in Eq. (3.23) can be expressed as

$$\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(2)}(\tau)e^{-il\omega_0\tau}d\tau=\left(\frac{7b^4}{160a^5D}\right)\int_{0}^{\infty}[J_{7/2}(u)]^2$$

$$\times\{5(B^2+u^2)^{-1}+3(C^2+u^2)^{-1}\}u^{-1}du, \quad (3.29)$$

where $B^2\equiv(8a^2D'/D)$ and $C^2\equiv(12a^2D'/D)$. In obtaining Eq. (3.29) it has again been assumed that $(\omega_0\tau_0)^2\ll1$, or that $(\omega_0\tau_0)^2\ll B^4$, C^4.

According to the theory of the translational Brownian motion of spherical particles, the translational diffusion coefficient can be expressed as $D=kT/f$, where k is the Boltzmann constant, T is the temperature, and f is the viscous retarding force per unit velocity. If the viscous force is given by the Stokes expression, $-6\pi a\eta\mathbf{v}$, it follows that $f=6\pi a\eta$, where a is the molecular radius, and η is the coefficient of viscosity of the fluid. Hence, $D=kT/6\pi a\eta$.[12] Similarly, the rotational diffusion coefficient can be expressed as $D'=kT/f'$, where f' is the viscous retarding torque per unit angular velocity.[6] The viscous torque is given by the expression $-8\pi\eta a^3\omega$,[13] so that $f'=8\pi\eta a^3$, and $D'=kT/8\pi\eta a^3$. Therefore, the translational and rotational diffusion coefficients for spherical particles are related by

$$D=\tfrac{4}{3}a^2D'. \quad (3.30)$$

Hence the quantities A, B, and C introduced previously have the values

$$A^2=3, \quad B^2=6, \quad C^2=9. \quad (3.31)$$

After substitution of the values (3.31), the integrals occurring in Eqs. (3.28) and (3.29) have been evaluated numerically.[14] The results are

$$\int_{0}^{\infty}[J_{5/2}(u)]^2(3+u^2)^{-1}u^{-1}du=0.0124, \quad (3.32a)$$

$$\int_{0}^{\infty}[J_{7/2}(u)]^2\{5(6+u^2)^{-1}$$

$$+3(9+u^2)^{-1}\}u^{-1}du=0.034. \quad (3.32b)$$

The contribution of the intermolecular dipole-dipole interactions to the longitudinal relaxation can be expressed in the following form by use of Eq. (3.23) in Eq. (2.10):

$$\left(\frac{1}{T_1}\right)''=2n\pi\gamma^4\hbar^2\sum_{l=-2}^{2}l^2\sum_{\kappa=0}^{\infty}\frac{1}{2}\int_{-\infty}^{\infty}C_{l,-l}{}^{(\kappa)}(\tau)e^{-il\omega_0\tau}d\tau. \quad (3.33)$$

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[11] The value of the integral is obtained by putting $\mu=\nu=\frac{3}{2}$, $a=1$, and $\lambda=3$ in Eq. (S_2), p. 35, of *Special Functions of Mathematical Physics*, by W. Magnus and F. Oberhettinger (Chelsea Publishing Company, New York, 1949).

[12] S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943), Chap. II, Sec. 2.

[13] H. Lamb, *Hydrodynamics* (Cambridge University Press, Cambridge, 1930), 5th ed., p. 558.

[14] The numerical values of the Bessel functions were taken from *Tables of Spherical Bessel Functions*, Mathematical Tables Project, N. B. S. (Columbia University Press, New York, 1947).

Substitution of expressions (3.26), (3.28), and (3.29) for the first three terms in the sum over κ in Eq. (3.33) and use of the values given by Eqs. (3.32) gives

$$(1/T_1)'' = (n\pi\gamma^4\hbar^2/5aD)$$
$$\times\{1+0.233(b/a)^2+0.15(b/a)^4+\cdots\}. \quad (3.34)$$

The same expression is obtained for $(1/T_2)''$ by use of Eqs. (3.23), (3.26), (3.28), (3.29), and (3.32), which was to be expected since the correlation time τ_0 has been assumed to be short. The first term in Eq. (3.34) is the expression that has previously been calculated.[3,4]

The above calculations have been based on the assumption that the Taylor series expansion (3.4) converges if $|r| < |R|$, which is plausible but difficult to prove rigorously. Since, in the calculations following the expansion (3.4), one has $|r| \leq 2b$ and $|R| \geq 2a$, the condition $|r| < |R|$ is satisfied if $b < a$. The series in the result, Eq. (3.34), appears to converge if $b < a$. In a typical case, (b/a) might have the value $\frac{1}{2}$, so that Eq. (3.34) would give

$$(1/T_1)'' = (n\pi\gamma^4\hbar^2/5aD)$$
$$\times\{1+0.0583+0.0094+\cdots\}. \quad (3.35)$$

If the ratio of the successive terms in the remainder of the series were not greater than $(b/a)^2 = \frac{1}{4}$, the remaining terms would not contribute more than 0.31% to the value of $(1/T_1)''$.

4. INTRAMOLECULAR CONTRIBUTION

The contributions of intramolecular dipole-dipole interactions between identical spin-$\frac{1}{2}$ nuclei in equivalent positions to the longitudinal and transverse relaxation rates are given, respectively, by Eqs. (2.9) and (2.12), if the effect of cross correlations of different dipole-dipole interactions is neglected. The vectors r_{ij}' between nuclei in the same molecule vary with time only in direction and not in magnitude. If the liquid molecules undergo isotropic rotational Brownian motion, the correlation functions (2.5) involving two nuclei in the same molecule can be calculated by use of Furry's theory in the same manner described in Appendix C. Thus, one can obtain the result

$$C_{(ij)(ij)}{}^{lk}(\tau) = \delta_{-l,k}(3/40)(\gamma^2\hbar)^2(r_{ij}')^{-6}(-1)^l$$
$$\times\exp(-|\tau|/\tau_2), \quad (4.1)$$

where

$$\tau_2 = (6D')^{-1}, \quad (4.2)$$

and D' is the rotational diffusion coefficient. Hence one obtains from Eqs. (2.4), (2.9), and (2.12) the familiar results

$$(1/T_1)' = (3/10)\gamma^4\hbar^2\tau_2 \sum_i{}'(r_{ij}')^{-6}$$
$$\times\{[1+(\omega_0\tau_2)^2]^{-1}+4[1+(2\omega_0\tau_2)^2]^{-1}\}, \quad (4.3)$$

$$(1/T_2)' = (3/20)\gamma^4\hbar^2\tau_2 \sum_i{}'(r_{ij}')^{-6}$$
$$\times\{3+5[1+(\omega_0\tau_2)^2]^{-1}+2[1+(2\omega_0\tau_2)^2]^{-1}\}. \quad (4.4)$$

5. CONCLUSIONS

The contribution of intermolecular dipole-dipole interactions to the nuclear magnetic relaxation of identical spin-$\frac{1}{2}$ nuclei at equivalent positions in spherical molecules in a liquid has been calculated. The assumptions made were that: (1), the effect of cross correlations of different dipole-dipole interactions is negligible, so that the relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays with relaxation times T_1 and T_2 given, respectively, by Eqs. (2.1) and (2.2); (2), the motions of the molecules can be considered to be translational and rotational diffusion; and (3), the correlation time τ_0, Eq. (3.25), is sufficiently short that $(\omega_0\tau_0)^2 \ll 1$, where ω_0 is the Larmor frequency. As a result of the short correlation time assumption, the contributions to the longitudinal and transverse relaxation rates were found to be the same, and are both given by Eq. (3.34) in the form of an infinite series, the first three terms of which have been evaluated. The first term in the series is the result obtained in previous calculations, in which the effect of the rotations of the molecules was neglected. In a typical physical situation, in which $(b/a) = \frac{1}{2}$, the sum of the infinite series appears to differ from the sum of the first three terms by less than 0.31%, and the sum of the first three terms is greater than the previously obtained first term by 6.8%.

APPENDIX A

Hobson has shown that, if $n \geq m \geq 0$,

$$\frac{\partial^{n-m}}{\partial z^{n-m}}\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}\right)^m \frac{1}{r}$$
$$= \frac{(-1)^{n-m}(n-m)!}{r^{n+1}}e^{\pm im\phi}P_n{}^m(\mu), \quad (A1)$$

where θ and ϕ are the polar angles of r, and $\mu = \cos\theta$.[15] Hobson's definition of the associated Legendre function is[15]

$$P_n{}^m(\mu) = \frac{(-1)^m}{2^n n!}\sin^m\theta\frac{d^{n+m}}{d\mu^{n+m}}(\mu^2-1)^n. \quad (A2)$$

The spherical harmonics $Y_n{}^m(\theta,\phi)$ used in the present paper[16] are given in terms of (A2) by

$$Y_n{}^m(\theta,\phi) = \left[\frac{(2n+1)(n-m)!}{4\pi(n+m)!}\right]^{1/2}e^{im\phi}P_n{}^m(\mu). \quad (A3)$$

[15] E. W. Hobson, *The Theory of Spherical and Ellipsoidal Harmonics* (Cambridge University Press, Cambridge, 1931), p. 134.

[16] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press), 2nd ed., Eqs. (2.5.29) and (2.5.17).

By use of (A3), Eq. (A1), written with the upper sign, can be expressed as

$$\frac{\partial^{n-m}}{\partial z^{n-m}}\left(\frac{\partial}{\partial x}+i\frac{\partial}{\partial y}\right)^m\frac{1}{r}$$

$$=\frac{(-1)^{n-m}}{r^{n+1}}\left[\frac{4\pi(n-m)!(n+m)!}{(2n+1)}\right]^{1/2}Y_n{}^m(\theta,\phi). \quad (A4)$$

A similar equation, but with $-i$ in the left-hand member, can be obtained by taking the complex conjugate of (A4) and using the relation $Y_n{}^{-m}(\theta,\phi)=(-1)^mY_n{}^{m*}(\theta,\phi)$. If one introduces the operators

$$D_0\equiv\frac{\partial}{\partial z}, \quad D_{\pm1}\equiv\mp2^{-1/2}\left(\frac{\partial}{\partial x}\pm i\frac{\partial}{\partial y}\right), \quad (A5)$$

Eq. (A4) and its complex conjugate lead to the equation

$$D_0{}^{n-m}D_{\pm1}{}^m(1/r)$$

$$=\frac{(-1)^n}{r^{n+1}}\left[\frac{4\pi(n-m)!(n+m)!}{2^m(2n+1)}\right]^{1/2}Y_n{}^{\pm m}(\theta,\phi). \quad (A6)$$

Since $\nabla^2(1/r)=0$ if $r>0$, it follows that

$$D_1{}^kD_{-1}{}^k(1/r)=(\tfrac{1}{2})^k(D_0{}^2-\nabla^2)^k(1/r)$$
$$=(\tfrac{1}{2})^kD_0{}^{2k}(1/r). \quad (A7)$$

Hence, if a, b, and c are non-negative integers whose sum is n, and if $b\geq c$,

$$D_0{}^aD_1{}^bD_{-1}{}^c(1/r)=(\tfrac{1}{2})^cD_0{}^{n-(b-c)}D_1{}^{(b-c)}(1/r). \quad (A8)$$

Similarly, if $b\leq c$,

$$D_0{}^aD_1{}^bD_{-1}{}^c(1/r)=(\tfrac{1}{2})^bD_0{}^{n-(c-b)}D_{-1}{}^{(c-b)}(1/r). \quad (A9)$$

It follows from (A6), (A7), and (A8) that, for any non-negative integers a, b, and c whose sum is n,

$$D_0{}^aD_1{}^bD_{-1}{}^c(1/r)=\frac{(-1)^n}{r^{n+1}}\left[\frac{4\pi(n-b+c)!(n+b-c)!}{2^{n-a}(2n+1)}\right]^{1/2}Y_n{}^{b-c}(\theta,\phi). \quad (A10)$$

Finally, it follows from Eqs. (A10) and (A6) that, if μ, ν, and η are non-negative integers with sum κ, and $|m|\leq k$,

$$D_0{}^\mu D_1{}^\nu D_{-1}{}^\eta(Y_k{}^m/r^{k+1})=(-1)^\kappa\left[\frac{(2k+1)(k-m+\kappa-\nu+\eta)!(k+m+\kappa+\nu-\eta)!}{2^{\kappa-\mu}(2k+2\kappa+1)(k-m)!(k+m)!}\right]^{1/2}(Y_{k+\kappa}{}^{m+\nu-\eta}/r^{k+\kappa+1}). \quad (A11)$$

APPENDIX B

Substitution of the expression (3.3) for $f_L{}^M$ into the definition (3.13) gives

$$G_{LL'}{}^{MM'}(\tau)$$
$$=N''\langle[Y_L{}^M(\Omega)/R^{L+1}]_{t+\tau}[Y_{L'}{}^{M'}(\Omega)/R^{L'+1}]_t\rangle, \quad (B1)$$

where R is the magnitude of $\mathbf{R}$, and Ω represents the polar angles specifying the direction of $\mathbf{R}$. If $P(\mathbf{R},\mathbf{R}_0,\tau)$ is the conditional probability density that the relative displacement of the centers of the molecules is $\mathbf{R}$ at time $t+\tau$ if it is $\mathbf{R}_0$ at the earlier time t, and if $P(\mathbf{R}_0)$ is the probability density that the relative displacement is $\mathbf{R}_0$ at time t, then

$$G_{LL'}{}^{MM'}(\tau)=N''\int\int\left[\frac{Y_L{}^M(\Omega)}{R^{L+1}}\right]P(\mathbf{R},\mathbf{R}_0,\tau)$$

$$\times\left[\frac{Y_{L'}{}^{M'}(\Omega_0)}{R_0{}^{L'+1}}\right]P(\mathbf{R}_0)d^3Rd^3R_0. \quad (B2)$$

The above expression can be evaluated in the same manner used by Abragam.[4] If the translational diffusion coefficient of the molecules in the liquid is D,

$$P(\mathbf{R},\mathbf{R}_0,\tau)=(8\pi D\tau)^{-3/2}\exp\{-(\mathbf{R}-\mathbf{R}_0)^2/8D\tau\}. \quad (B3)$$

The probability density $P(\mathbf{R}_0)$ is simply unity divided by the volume of the sample. Hence, since N'' is large and differs negligibly from the total number of spins in the sample, $N''P(\mathbf{R}_0)$ is equal to n, the number of spins per unit volume in the sample. The integrals in (B3) are over all space for which $\mathbf{R}$ and $\mathbf{R}_0$ are greater than $2a$, the distance of closest approach of the centers of two molecules.

The expression (B3) can be expanded in terms of spherical harmonics by first using the Fourier integral expansion

$$\exp\left\{\frac{-(\mathbf{R}-\mathbf{R}_0)^2}{8D\tau}\right\}$$

$$=\left(\frac{2D\tau}{\pi}\right)^{3/2}\int\exp(-2D\tau\rho^2)e^{i\boldsymbol{\rho}\cdot(\mathbf{R}-\mathbf{R}_0)}d^3\varrho, \quad (B4)$$

and then replacing $\exp(i\boldsymbol{\varrho}\cdot\mathbf{R})$ and $\exp(-i\boldsymbol{\varrho}\cdot\mathbf{R}_0)$ by their expansion of the form

$$e^{i\boldsymbol{\rho}\cdot\mathbf{R}}=4\pi(\pi/2\rho R)^{1/2}\sum_{m,l}i^lY_l{}^{m*}(\Omega)Y_l{}^m(\Omega')J_{l+1/2}(\rho R), \quad (B5)$$

where Ω' specifies the orientation of ϱ, and the $J_{l+1/2}$ are Bessel functions of the first kind. After these expressions are substituted in (B2), and use is made of the orthogonality of the spherical harmonics, one obtains

$$G_{LL'}{}^{MM'}(\tau)=n\delta_{L'L}\delta_{-M'M}(-1)^M\int_0^\infty\rho\exp(-2D\tau\rho^2)$$

$$\times\left[\int_{2a}^\infty J_{L+1/2}(\rho R)R^{-L+1/2}dR\right]^2d\rho. \quad (B6)$$

Bessel functions satisfy the relation

$$\frac{d}{dR}[R^{-s}J_s(\rho R)] = -\rho R^{-s}J_{s+1}(\rho R). \quad (B7)$$

If s is replaced by $L-\frac{1}{2}$ in (B7), where $L>0$, and the equation is integrated from $2a$ to ∞, one obtains

$$\int_{2a}^{\infty} J_{L+1/2}(\rho R)R^{-L+1/2}dR$$
$$= \rho^{-1}(2a)^{-L+1/2}J_{L-1/2}(2a\rho). \quad (B8)$$

The above equations have been derived on the assumption that $\tau \geq 0$. Since the average in (B1) is independent of t, replacement of t by $t-\tau$ gives $G_{LL'}{}^{MM'}(\tau) = G_{L'L}{}^{M'M}(-\tau)$. Hence, substitution of (B8) into (B6) followed by a change in the variable of integration from ρ to $u=2a\rho$ gives Eq. (3.13).

APPENDIX C

Since $\mathbf{r} \equiv \mathbf{r}_i - \mathbf{r}_j$, where $\mathbf{r}_i$ and $\mathbf{r}_j$ are, respectively, the position vectors of the ith and jth nuclei with respect to the centers of the two different molecules in which they are located, it follows that

$$x_p = x_{ip} - x_{jp}, \quad (C1)$$

where the spherical components are defined by

$$x_{j0} \equiv z_j, \quad x_{j,\pm1} \equiv \mp 2^{-1/2}(x_j \pm iy_j). \quad (C2)$$

Since the motions of $\mathbf{r}_i$ and $\mathbf{r}_j$ are independent,

$$\langle [x_{ip}]_{t+\tau}[x_{jq}]_t \rangle = \langle [x_{ip}]_{t+\tau} \rangle \langle [x_{iq}]_t \rangle.$$

Since the motions of $\mathbf{r}_i$ and $\mathbf{r}_j$ are isotropic, $\langle [x_{ip}]_{t+\tau} \rangle = 0$ and $\langle [x_{jq}]_t \rangle = 0$ for any t. Furthermore, since $\mathbf{r}_i$ and $\mathbf{r}_j$ have the same length b, and undergo the same kind of motion, $\langle [x_{ip}]_{t+\tau}[x_{iq}]_t \rangle = \langle [x_{jp}]_{t+\tau}[x_{jq}]_t \rangle$. Therefore,

$$\langle [x_p]_{t+\tau}[x_q]_t \rangle = 2\langle [x_{jp}]_{t+\tau}[x_{jq}]_t \rangle. \quad (C3)$$

Suppose that $\mathbf{r}_j$ has the value $\mathbf{r}$ at the time t and the value $\mathbf{r}'$ at time $t+\tau$. If the molecule in which $\mathbf{r}_j$ is fixed rotates through an angle α about a direction specified by the unit vector $\hat{c} \equiv (\sin\theta' \cos\phi', \sin\theta' \sin\phi', \cos\theta')$ in the time τ between t and $t+\tau$, then

$$\mathbf{r}' = \mathbf{r} \cos\alpha + (\hat{c} \cdot \mathbf{r})\hat{c}(1 - \cos\alpha) + (\hat{c} \times \mathbf{r}) \sin\alpha \quad (C4)$$
$$\equiv \mathbf{r}'(\mathbf{r},\alpha,\hat{c}).$$

From Furry's theory of rotational Brownian motion[10] it follows that the probability of a rotation of the spherical molecule during time τ through an angle between α and $\alpha+d\alpha$ about an axis $\hat{c}$ pointing into the solid angle $d\Omega' = \sin\theta' d\theta' d\phi'$ is $P(\alpha,\tau)d\alpha d\Omega'$, where

$$P(\alpha,\tau) = (1/4\pi^2)\sum_{n=0}^{\infty}(2n+1)$$

$$\times [\cos n\alpha - \cos(n+1)\alpha]e^{-n(n+1)D'\tau}. \quad (C5)$$

The probability that at time t $\mathbf{r}_j$ points into solid angle $d\Omega$ is simply $d\Omega/4\pi$. Hence,

$$\langle [z_j]_{t+\tau}[z_j]_t \rangle$$

$$= \left(\frac{1}{4\pi}\right)\int d\Omega \int_0^{\pi} d\alpha P(\alpha,\tau) \int d\Omega' z'(\mathbf{r},\alpha,\hat{c})z$$

$$= \left(\frac{1}{4\pi}\right)\int d\Omega \int_0^{2\pi} d\alpha P(\alpha,\tau) \int d\Omega'[z \cos\alpha$$

$$+ (\hat{c} \cdot \mathbf{r})c_z(1 - \cos\alpha) + (c_x y - c_y x) \sin\alpha]z. \quad (C6)$$

The integrations in the above expression can be performed easily, with the result

$$\langle [z_j]_{t+\tau}[z_j]_t \rangle = (1/3)b^2 e^{-2D'\tau}. \quad (C7)$$

The same result is obtained for $\langle [x_j]_{t+\tau}[x_j]_t \rangle$ and $\langle [y_j]_{t+\tau}[y_j]_t \rangle$. The correlation functions that involve two different Cartesian components of $\mathbf{r}_j$, such as $\langle [y_j]_{t+\tau}[z_j]_t \rangle$, are found to be all zero, as is obvious from symmetry considerations. The expressions for the correlation functions of the Cartesian components of $\mathbf{r}_j$ lead to the following expression for the correlation functions of the spherical components:

$$\langle [x_{jp}]_{t+\tau}[x_{jq}]_t \rangle = (1/3)b^2(-1)^p \delta_{p,-q} e^{-2D'\tau}. \quad (C8)$$

The above expressions were derived for $\tau>0$. Since the average in (C8) is independent of t, replacement of t by $t-\tau$ in the correlation function on the left side of (C8) leads to the conclusion that it is an even function of τ. Hence, substitution of (C8) into (C3) gives (3.19).