

Integrating by parts between the limits 0 and π yields

$$c_1(s) = \frac{(-)^{s+1}}{2\pi(s+\frac{1}{2})} \left\{ \frac{1}{\tau} \int_0^\pi \frac{\cos(s+\frac{1}{2})\beta \sin\frac{1}{2}\beta \cos\frac{1}{2}\beta d\beta}{2(\tau^2 + \sin^2\frac{1}{2}\beta)^{3/2}} \right\}. \quad (C3)$$

On integrating the factor $\cos(s+\frac{1}{2})\beta$ by parts again, a

contribution of order $1/(s+\frac{1}{2})^2$ is obtained, but the integrated term clearly vanishes at both limits. A further integration by parts yields a nonvanishing term of order $1/(s+\frac{1}{2})^3$, thereby confirming the result (6.15) quoted in the text. In a similar way, one may derive all the other asymptotic expressions of the Green's function elements which are quoted.

Nuclear Spin-Lattice Relaxation in Liquids

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(Received 9 July 1963)

The spin-lattice relaxation in liquids has been investigated on the basis of quasicrystalline models for them. Explicit expressions for spin-lattice relaxation time T_1 are derived for the jump-diffusion model and the stochastic model. The theory has been applied to the case of water and the constants used in the calculation are derived from the experimental data on the cold-neutron scattering. The spin-lattice relaxation is found to be quite insensitive to the details of the models.

I. INTRODUCTION

NUCLEAR spin-lattice relaxation involves the exchange of energy between the nuclear-spin system and the "lattice" of the material in which the spins are located. The rate at which the thermal equilibrium is established among the nuclear spin-energy levels is expressed in terms of a parameter T_1 , called the spin-lattice relaxation time. Bloembergen, Purcell, and Pound have discussed a general theory of relaxation in liquids and have shown that T_1 can be expressed in terms of the Fourier transforms of the correlation function of the interactions coupling the nuclear spins to the lattice of the liquid.^{1,2} In ordinary liquids, the important relaxation mechanisms are the couplings of the nuclear spins to the random translational and rotational motions of the molecules via the magnetic dipolar interaction of the nuclear moments. Recently, cold-neutron spectroscopy has given detailed information about the atomic motions in liquids,³⁻⁵ and has led many workers to propose quasicrystalline models⁶⁻⁹ for them. The present work is concerned with the in-

terpretation of T_1 measurement for water on the basis of these models, on the lines of approach of Bloembergen, Purcell, and Pound. Sections II and III are devoted to the discussion of the spin-lattice relaxation in liquids on the basis of the jump-diffusion model and the stochastic model, respectively. In Sec. IV, the theory is applied to the case of water and the results are compared with the experiment.

II. JUMP-DIFFUSION MODEL

We shall start with the general expression^{1,10} for T_1

$$T_1^{-1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) [J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)]. \quad (1)$$

Here, γ is the nuclear gyromagnetic ratio, ω_0 the Larmor frequency of nuclei, I the nuclear-spin number and

$$J^{(m)}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} k_m(t) dt; \quad m=1, 2. \quad (2)$$

The correlation function $k_m(t)$ is related to the random functions $F_m(t)$ by the relation

$$k_m(t) = N \langle F_m(t') F_m^*(t'+t) \rangle_{av(t')}, \quad (3)$$

where N is the number of molecules per cm^3 . For dipole-dipole interactions

$$F_1(t) = \left(\frac{8\pi}{15} \right)^{1/2} \frac{Y_2^1(\theta, \phi)}{r^3}, \quad F_2(t) = \left(\frac{32\pi}{15} \right)^{1/2} \frac{Y_2^2(\theta, \phi)}{r^3}, \quad (4)$$

where $Y_2^m(\theta, \phi)$ is a spherical harmonic and (r, θ, ϕ) denote the spherical polar coordinates of a spin relative

¹ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

² N. Bloembergen, thesis, Leiden, 1948 (Martinus, Nijhoff, The Hague).

³ B. N. Brockhouse, Suppl. Nuovo Cimento **9**, 45 (1958).

⁴ B. N. Brockhouse, Phys. Rev. Letters **2**, 287 (1959).

⁵ D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. Letters **3**, 91 (1959).

⁶ K. S. Singwi and A. Sjölander, Phys. Rev. **119**, 863 (1960).

⁷ C. T. Chudley and R. J. Elliott, Proc. Phys. Soc. (London) **77**, 353 (1961).

⁸ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **122**, 9 (1961).

⁹ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 997 (1962).

¹⁰ R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

to the other. The time average in Eq. (3) can be replaced by ensemble average^{11,12} by introducing a probability function $P(\mathbf{r}, \mathbf{r}_0, t)$. This gives

$$k_m(t) = N \int \int [g(\mathbf{r}_0)g(\mathbf{r})]^{1/2} \times F_m(\mathbf{r}_0)F_m^*(\mathbf{r})P(\mathbf{r}, \mathbf{r}_0, t) d\mathbf{r}d\mathbf{r}_0. \quad (5)$$

Here, $g(r)$ is the radial distribution function. $P(\mathbf{r}, \mathbf{r}_0, t)$ represents the probability per unit time that the two spins separated by \mathbf{r}_0 at $t=0$, are separated by \mathbf{r} at time t .

The calculation of T_1 , therefore, involves the construction of the probability function $P(\mathbf{r}, \mathbf{r}_0, t)$. It will depend upon the details of the atomic motions. We shall now use a simple model in which a molecule in a liquid performs an oscillatory motion for a mean time τ_0 and then diffuses in a continuous manner for a mean time τ_1 and again repeats this sort of motion. On the basis of this model, Singwi and Sjölander⁶ have calculated the Fourier transform of Van Hove's self-diffusion function $G_s(\mathbf{r}, t)$, which gives the probability of finding a molecule within unit volume at \mathbf{r} at time t , if it was at origin at $t=0$. If \mathbf{r} denotes, not a vector from a fixed point, but the relative distance $\mathbf{r}-\mathbf{r}_0$ between two identical diffusing molecules, the theory of random flight gives¹³

$$P(\mathbf{r}, \mathbf{r}_0, t) = G_s(\mathbf{r}-\mathbf{r}_0, 2t). \quad (6)$$

Hence, according to Singwi and Sjölander⁶

$$P(\mathbf{r}, \mathbf{r}_0, t) = (2\pi)^{-4} \frac{2\tau_0}{1+\tau_1/\tau_0} \int \int \frac{(c+d\omega^2\tau_0^2)b}{b^2+\omega^2\tau_0^2(f+\omega^2\tau_0^2g)} \times \exp\{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)+2i\omega t-\frac{1}{2}k^2\gamma(\infty)\} d\mathbf{k}d\omega, \quad (7)$$

where

$$\begin{aligned} b &= 1+k^2D_1\tau_1-e^{-\frac{1}{2}k^2\gamma(\infty)}, \\ c &= 1+k^2D_1\tau_1+2\tau_1/\tau_0+(\tau_1/\tau_0)^2e^{\frac{1}{2}k^2\gamma(\infty)}, \\ d &= (\tau_1/\tau_0)^2e^{\frac{1}{2}k^2\gamma(\infty)}, \\ f &= (1+k^2D_1\tau_1)^2+(\tau_1/\tau_0)^2+2(\tau_1/\tau_0)e^{-\frac{1}{2}k^2\gamma(\infty)}, \\ g &= \tau_1^2/\tau_0^2. \end{aligned} \quad (8a)$$

D_1 is the diffusion coefficient of continuous motion and is related to the actual diffusion coefficient D through the relation

$$D_1\tau_1 \simeq D\tau_0(1+\tau_1/\tau_0) \quad (8b)$$

and

$$\gamma(\infty) = \frac{\hbar^2}{M} \int_0^\infty \frac{f(z)}{z} \coth(z/2k_B T) dz. \quad (8c)$$

Here, M is the mass of the molecule, T is the absolute temperature of the system, k_B is the Boltzmann con-

stant, and $f(z)$ is the normalized frequency-distribution function. In the Debye approximation

$$\gamma(\infty) = \frac{\hbar^2}{M} \frac{6T}{k_B \Theta^2} \quad \text{for } T \gg \Theta, \quad (9)$$

Θ being the Debye temperature of the quasicrystalline liquid.

From Eqs. (5) and (7), the correlation function can, therefore, be written as

$$\begin{aligned} k_m(t) &= (2\pi)^{-4} N c_m \frac{2\tau_0}{1+\tau_1/\tau_0} \int \int \int [g(\mathbf{r}_0)g(\mathbf{r})]^{1/2} \\ &\times \frac{Y_2^m(\theta_0, \phi_0) Y_2^{m*}(\theta, \phi)}{r_0^3 r^3} \frac{(c+d\omega^2\tau_0^2)b}{b^2+\omega^2\tau_0^2(f+\omega^2\tau_0^2g)} \\ &\times \exp\{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)+2i\omega t-\frac{1}{2}k^2\gamma(\infty)\} \\ &\times d\mathbf{k}d\omega d\mathbf{r}d\mathbf{r}_0, \end{aligned} \quad (10)$$

where $c_1=8\pi/15$ and $c_2=32\pi/15$.

The integrals appearing in (10) are similar to those considered by Torrey.¹³ Following his procedure, we get

$$\begin{aligned} k_m(t) &= \frac{N c_m}{\pi} \frac{\tau_0}{1+\tau_1/\tau_0} \int \int \left[\int_0^\infty [g(r)]^{1/2} \frac{J_{5/2}(kr)}{r^{3/2}} dr \right]^2 \\ &\times \frac{k(c+d\omega^2\tau_0^2)b}{b^2+\omega^2\tau_0^2(f+\omega^2\tau_0^2g)} \exp\{-\frac{1}{2}k^2\gamma(\infty)+2i\omega t\} \\ &\times dk d\omega, \end{aligned} \quad (11)$$

where J_l is a Bessel function of order l . The Fourier transform of $k_m(t)$ appearing in expression (1) for T_1 can now be immediately calculated. If the molecules are regarded as spheres of diameter a , then $g(r)=0$ for $r < a$ and $g(r)=1$ for $r > a$. In this hard-sphere approximation, the r integration becomes trivial, giving

$$\begin{aligned} J^{(m)}(\omega_0) &= \frac{N c_m}{a^3} \frac{\tau_0}{1+\tau_1/\tau_0} \int_0^\infty \frac{J_{3/2}^2(ka)}{k} \\ &\times \frac{(c+d\omega_0^2\tau_0^2/4)b}{b^2+(\omega_0^2\tau_0^2/4)[f+(\omega_0^2\tau_0^2g/4)]} e^{-\frac{1}{2}k^2\gamma(\infty)} dk. \end{aligned} \quad (12)$$

In two limiting cases (i) $\tau_1 \gg \tau_0$ and (ii) $\tau_1 \ll \tau_0$, expression (12) is further simplified. For $\tau_1 \gg \tau_0$, using (8b) and (12) we get

$$J^{(m)}(\omega_0) = \frac{N c_m}{a^3} \int_0^\infty \frac{J_{3/2}^2(ka)}{k} \frac{k^2 D}{(k^2 D)^2 + \omega_0^2/4} dk. \quad (13)$$

This is the same expression as obtained by Bloembergen, Purcell, and Pound¹ using for $P(\mathbf{r}, \mathbf{r}_0, t)$, the

¹¹ I. Oppenheim and M. Bloom, Can. J. Phys. 37, 1324 (1959).

¹² I. Oppenheim and M. Bloom, Can. J. Phys. 39, 845 (1961).

¹³ H. C. Torrey, Phys. Rev. 92, 962 (1953).

solution of the diffusion equation given by¹⁴

$$P(\mathbf{r}, \mathbf{r}_0, t) = (8\pi Dt)^{-3/2} \exp\{-(|\mathbf{r} - \mathbf{r}_0|)^2/8Dt\}. \quad (14)$$

In the second case of $\tau_1 \ll \tau_0$, neglecting τ_1/τ_0 as compared to unity, Eq. (12) gives

$$J^{(m)}(\omega_0) = \frac{Nc_m}{a^3} \tau_0 \int_0^\infty \frac{J_{3/2}^2(ka)}{k} e^{-\frac{1}{2}k^2\gamma(\infty)} \times \frac{1 - e^{-\frac{1}{2}k^2\gamma(\infty)}/1 + k^2 D \tau_0}{\omega_0^2 \tau_0^2/4 + [1 - e^{-\frac{1}{2}k^2\gamma(\infty)}/(1 + k^2 D \tau_0)]^2} dk. \quad (15)$$

III. STOCHASTIC MODEL

Recently, Rahman *et al.*⁹ have developed a stochastic model of liquid which is based on the concept that the heat motions in a liquid are very similar to that in a solid. They regard the frequency spectrum to be of the Debye type with upper limit ω_D . Assuming the modes from zero to ω' to be diffusive and the rest vibratory, the solution of the stochastic equation for atomic motions in liquids gives

$$P(\mathbf{r}, \mathbf{r}_0, t) = [4\pi\rho(2t)]^{-3/2} \exp[-(|\mathbf{r} - \mathbf{r}_0|^2/4\rho(2t))], \quad (16)$$

where

$$\rho(t) = \frac{k_B T}{M} \left[\left(\frac{\omega'}{\omega_D} \right)^3 \frac{e^{-\beta t} - 1 + \beta t}{\beta^2} + \frac{3}{\omega_D^3} (\Phi(\omega_D, t) - \Phi(\omega', t)) \right], \quad (16a)$$

with

$$\Phi(\omega, t) = \omega \frac{1}{t(1+\Gamma^2)^{1/2}} \exp\left(-\frac{\Gamma\omega t}{(1+\Gamma^2)^{1/2}}\right) \times \left[(1-\Gamma^2) \sin\left(\frac{\omega t}{(1+\Gamma^2)^{1/2}}\right) - 2\Gamma \cos\left(\frac{\omega t}{(1+\Gamma^2)^{1/2}}\right) \right], \quad (16b)$$

and

$$1 + \Gamma^2 = (1 - \alpha^2)^{-1}. \quad (16c)$$

Here β and α are the damping parameters of the diffusive modes and the vibratory modes, respectively, and are introduced to account for the damped motions in a liquid.

If we made use of the Fourier expansion

$$\exp(-|\mathbf{r} - \mathbf{r}_0|^2/4\rho(2t)) = (2\pi)^{-3/2} [2\rho(2t)]^{3/2} \int \exp(-\rho(2t)k^2) \times e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)} d\mathbf{k}, \quad (17)$$

¹⁴ S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

the correlation function can be written from Eqs. (5) and (16)

$$k_m(t) = \frac{Nc_m}{a^3} \int_0^\infty \frac{J_{3/2}^2(ka)}{k} e^{-\rho(2t)k^2} dk. \quad (18)$$

The Fourier transform of (18) is

$$J^{(m)}(\omega_0) = \frac{Nc_m}{a^3} \int_0^\infty \frac{J_{3/2}^2(ka)}{k} \times \left(\int_{-\infty}^\infty e^{i\omega_0 t} \exp(-\rho(2t)k^2) dt \right) dk. \quad (19)$$

IV. DISCUSSION

The theory developed in previous sections will now be applied to water in the calculation of proton-relaxation time. As mentioned earlier, the intermolecular and intramolecular interactions responsible for spin-lattice relaxation in a liquid are, respectively, the coupling of the nuclear spins to the translational motion and to the rotational motion of the molecules. Equations (12) and (19) yield only the intermolecular contribution to T_1 . For the intramolecular contribution we take the expression¹⁵

$$\left(\frac{1}{T_1} \right)_{\text{intra}} = \frac{3}{10} \frac{\gamma^4 \hbar^2}{b^6} \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]. \quad (20)$$

Here, τ_c is the correlation time for the reorientation process and b the interproton distance within the molecule. τ_c is related to the diffusion coefficient D through the relation¹

$$\tau_c = a^2/18D. \quad (21)$$

T_1 is given in terms of these two contributions by

$$1/T_1 = (1/T_1)_{\text{inter}} + (1/T)_{\text{intra}}. \quad (22)$$

It is convenient to discuss the evaluation of T_1 separately for the jump-diffusion and the stochastic models.

A. Jump-Diffusion Model

Expression (12) in all its generality is somewhat involved for being used in our calculation. We have here investigated some special cases. When $\tau_1 \ll \tau_0$, we can evaluate T_1 from Eqs. (15), (20), and (22). From the experimental measurements on the broadening of the quasielastic peak of the scattered, the value of τ_0 is found to be 6×10^{-12} sec. The values of the other molecular parameters for water used by us throughout

¹⁵ A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961), p. 298.

this calculation are

$$\begin{aligned} M &= 18 \text{ atomic units,} \\ N &= 6.75 \times 10^{22} \text{ cm}^{-3}, \\ a &= 3.48 \times 10^{-8} \text{ cm,} \\ b &= 1.58 \times 10^{-8} \text{ cm,} \\ D &= 1.85 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}, \end{aligned}$$

and

$$\Theta = 135^\circ\text{K.}$$

Making use of these data and the fact that at all practical radio frequencies, the Larmor frequencies of the nuclei are much smaller than the characteristic frequencies of molecular motions, we find $T_1 = 3.69$ sec. In the second case of simple diffusion, i.e., $\tau_1 \gg \tau_0$, using Eq. (13) we get $T_1 = 3.64$ sec. For an intermediate case, taking $\tau_1 = \tau_0 = 3.6 \times 10^{-12}$ sec, we obtain from Eq. (12) and (20), $T_1 = 3.73$ sec. Integrations involved in Eqs. (12) and (15) were performed numerically.

B. Stochastic Model

The best values of the parameters occurring in this model to fit the neutron scattering data are⁹ $\Theta_D = 135^\circ\text{K}$, $\Theta' = 15^\circ\text{K}$, and $\Gamma = 2.0$. Here, ω_D and ω' have been changed into temperatures through the relation $\hbar\omega = k_B\Theta$. The fourth parameter β is obtained from the relation $\beta = (\omega'/\omega_D)^3 k_B T / MD$. The use of Eqs. (20), (21), (22), and the numerical integration of (19) gives $T_1 = 3.67$ sec.

The experimental value¹⁶ of T_1 is 3.6 sec at 20°C for water completely free from dissolved oxygen. A comparison of this value with the calculated ones shows that the use of both the models yields results in good agreement with the experiment. Due to some uncertainty in the estimation of the molecular diameter a , the calculated values of T_1 may not be very reliable.

From the above study, we conclude that T_1 is not very sensitive to the details of molecular motions in a liquid. The present treatment, however, has some special features. Our treatment of nuclear spin relaxation in liquids is based on more realistic and quantitative models for atomic motions in liquids. These theoretical models had fair amount of success in explaining cold-neutron scattering data where simple diffusion theory proved to be a failure. The theory of Bloembergen, Purcell, and Pound provides no basis for a closer study of diffusion mechanism and describes the complicated behavior of liquids in terms of a single macroscopic parameter D .

ACKNOWLEDGMENTS

The authors are deeply indebted to Dr. K. S. Singwi for suggesting the problem and for his help and to Professor T. P. Das for discussions. Financial help from Council of Scientific and Industrial Research is gratefully acknowledged.

¹⁶ G. Chiarotti and L. Giulotto, Phys. Rev. **93**, 1241 (1954).