

proach of two nuclei. By including the Debye relation,  $\tau_{\text{rot}} \propto \eta/T$ , and the Stokes Einstein relation,  $D \propto T/\eta$  where  $T$  is the temperature

$$1/T_1 \propto \eta/T \propto D. \quad (1b)$$

Benedek's studies show that: (1)  $T_1(P)/T_1(1)$  is higher than that predicted. (2)  $D(P)/D(1)$  and  $\eta(1)/\eta(P)$  do not have the same pressure dependence.

Bull and Jonas<sup>15</sup> have recently shown that the reason for the discrepancy (besides the paramagnetic impurity effects in Benedek's samples) arises because the simple Debye theory for  $\tau_{\text{rot}}$  is incorrect. It has been pointed out that  $T_1$  must first be separated into its inter and intra parts before a comparison with  $D(P)$  or  $\eta(P)$  can be made. Consequently Bull and Jonas have reported a deuterated-protonated separation study as a function of pressure in several mobile liquids to study the inter and intra parts as a function of pressure. They have found that  $1/T_{1 \text{ inter}}(P)$  roughly follows the predictions of the BPP theory for  $D(P)$  and  $\eta^{-1}(P)$  and  $1/T_{1 \text{ intra}}$  digresses from the predictions of Eq. (1b).

The above considerations have motivated and guided this study. The chief concerns of this work are: (1) to critically evaluate the translational relaxation theory with all available data; (2) to study the effect of pressure and temperature on the nuclear magnetic spin-lattice and spin-spin relaxation times  $T_1$  and  $T_2$  in three highly viscous associated liquids: glycerol; 1,3-butanediol; and 2-methyl-2,4-pentanediol (BUT, MPD for short), also to infer from these macroscopic times the pressure and temperature dependence of the microscopic nuclear correlation time,  $\tau_c$ , and its association with the translational diffusion constant; and (3) as a secondary objective to compare the nuclear correlation time as a function of temperature and pressure ( $T, P$ ) with microscopic relaxation times obtained from other types of studies.

## II. THEORY

The correct formulation of the Torrey translational relaxation theory taking into account the Kubo-Tomita<sup>16</sup> correction has been given elsewhere<sup>12,17</sup> and will only be briefly reviewed here for the sake of clarity.

Under the conditions of isotropic motion the auto-correlation function for the  $m$ th term of dipole-dipole interaction Hamiltonian, which provides the major contribution to the proton spin-lattice and spin-spin relaxation in the liquids under consideration, is given by

$$K^{(m)}(\tau) = C^{(m)} N \iiint \rho \exp\{- (2\tau/\tau_j)[1 - A(\rho)]\} \\ \times J_{5/2}(\rho r) J_{5/2}(\rho r_0) r^{-3/2} r_0^{-3/2} p(r_0) d\rho dr dr_0 \quad (2)$$

with  $m=0, 1, 2$  and

$$C^{(0)} = 48\pi/15, \quad C^{(1)} = 8\pi/15, \quad C^{(2)} = 32\pi/15. \quad (2')$$

$N$  is the total number of spins,  $J_{5/2}(\rho r)$  is the Bessel

function of order 5/2,  $p(r_0)$  describes the initial physical distribution of the spins,  $A(\rho)$  depends on the model for diffusive motion, and  $\tau_j$  is the average time between flights defined in terms of the average squared flight distance and the translational self-diffusion constant  $\tau_j \equiv \langle r^2 \rangle / 6D$ .

With a model for  $p(r_0)$ ,  $K^{(m)}(\tau)$  can be further reduced without giving an explicit form for  $A(\rho)$ . Torrey has assumed an initial probability distribution of the form

$$p(r_0) = n/N, \quad r_0 \geq d, \\ = 0 \quad r_0 < d, \quad (3)$$

that is, a uniform probability of finding  $n$  spins/cc in the volume element  $dr_0$  beyond a distance of closest approach,  $d$ . It has also been assumed in this formulation that the spins under consideration are at the center of the diffusing molecules upon which the spins ride. Hubbard's formulation<sup>18</sup> considers these off center spin effects in the extreme narrowing limit. Harmon and Muller<sup>17</sup> have recently included the effects of a non-uniform spin density and off center spins by using the radial distribution function and the Hubbard correction in the low frequency limit of the Torrey theory. Since incorporation of these effects is presently intractable in the general frequency theory presentations here, these effects will be considered separately below. For now a uniform probability density will be assumed. Then, from Eq. 2,

$$K^{(m)}(\tau) = C^{(m)} (n/d^3) \int d\rho [J_{3/2}(\rho d)/\rho] \\ \times \exp(- (2\tau/\tau_j)[1 - A(\rho)]), \quad (4)$$

$$J^{(m)}(\omega) = C^{(m)} \tau_j (n/d^3) \int d\rho [J_{3/2}(\rho d)/\rho] \\ \times \{1 - A(\rho)/[1 - A(\rho)]^2 - \frac{1}{4}(\omega\tau_j)^2\}. \quad (5)$$

At this point it is convenient to introduce the concept of correlation time for the translational model. Kubo<sup>19</sup> defined this time for the case of nonexponential relaxation functions<sup>20</sup> as

$$\tau_c \equiv \int_0^\infty \frac{K(\tau)}{K(0)} d\tau. \quad (6)$$

This  $\tau_c$  is identified as the fundamental microscopic time associated with the diffusion of spins giving rise to the relaxation of these spins, i.e.,

$$\tau_c \equiv \tau_{\text{NMR}} \equiv \tau_c = \frac{3}{2} \tau_j \int_0^\infty \frac{d\rho}{\rho} \frac{J_{3/2}(\rho d)}{[1 - A(\rho)]}. \quad (7)$$

The final solution of the theory under the above assumption then reduces to giving a physical model for  $A(\rho)$  or equivalently its Fourier transform  $P_1(r)$ . Kruger<sup>12</sup> has shown that an  $A(\rho) = (1 + D\tau_j\rho^2)^{-1}$  arising from Torrey's thermally activated diffusion model

gives rise to a  $J^{(m)}(\omega)$  of the form

$$J^{(m)}(\omega) = C^{(m)}(n/d^3)^{2/3} f_i(\alpha, \omega\tau_i)\tau_i, \quad (8)$$

where  $f_i(\alpha, \omega\tau_i)$  is defined by Kruger as

$$f_i(\alpha, y) \equiv 3(1/5 + \alpha)(v[1 - (u^2 + v^2)^{-1}] \\ + \exp(-2v) \cos 2u \{v[1 + (u^2 + v^2)^{-1}] + 2\} \\ + \exp(-2v) \sin 2u \{u[1 - (u^2 + v^2)^{-1}]\})(1/y^2), \quad (9)$$

where

$$y \equiv \omega\tau_i, \quad (9')$$

$$\left(\frac{u}{v}\right) = (2\alpha^{1/2})^{-1} [q(1 \mp q)]^{1/2}, \quad (9'')$$

and

$$q = \{1 + [1 + (5\alpha)^{-1}]^2(1/y^2)\}^{-1/2}. \quad (9''')$$

Here  $\alpha = \langle r^2 \rangle / 12d^2$  and from Eq. (7)

$$\tau_i = (d^2/5D)(1 + 5\alpha) = (d^2/5D) + \frac{1}{2}\tau_j. \quad (10)$$

Using the Kubo-Tomita<sup>16</sup> correction for Bloembergen's  $1/T_1$ ,  $1/T_2$  expressions and Eqs. (8) and (2'), the following expressions can be obtained

$$1/T_{1i} = (C_i/\omega) [f_i(\alpha, y) + 4f_i(\alpha, 2y)]y, \quad (11)$$

$$1/T_{2i} = (C_i/\omega) [\frac{3}{2} + \frac{5}{2}f_i(\alpha, y) + f_i(\alpha, 2y)]y, \quad (12)$$

where

$$C_i = \frac{2}{5}\pi\gamma^4\hbar^2(n/d^3),$$

and the  $\lim_{y \rightarrow 0} f(\alpha, y) = 1$  has been used to specify  $J^{(0)}(0)$  in the  $1/T_2$  equation.

It is of considerable interest to consider the limiting forms of  $1/T_{1i}$ ,  $1/T_{2i}$  for large and small values of  $\alpha$  and  $\omega\tau_j$ .

### III. LIMITING CASES OF THE KRUGER FORMULAS FOR $1/T_{1i}$

#### A. Diffusive Limit ( $\alpha \rightarrow 0$ )

In this limit the mean jump length squared is very small compared to the distance of closest approach. This implies that  $\frac{1}{2}\tau_j \ll d^2/5D$  so that  $\tau_i \rightarrow d^2/5D$ . In this case it is easy to show that in this limit, Eq. (9) reduces to

$$f_i(\alpha=0, y) = \frac{3}{5}([u - (2u)^{-1}] + \{[u + (2u)^{-1}] + 2\} \\ \times \cos 2u + [u - (2u)^{-1}] \sin 2u \exp(-2u))(1/y^2), \quad (13)$$

where  $u = v = x/2 \equiv \frac{1}{2}(\omega d^2/D)^{1/2}$ .

This result yields a normalized intensity function which is equivalent to that obtained by Noack and Preissing<sup>7</sup> and Abragam<sup>21</sup> for a  $P(r, r_0, \tau)$  given by Fick's law. This same result can be derived using the Torrey formalism by choosing  $A(\rho) = 1 - \langle r^2 \rangle \rho^2/6$ , the first two terms of an expansion of  $A(\rho)$  in powers of  $\rho^2$ .

This result then is interpreted as the limit of the

random flight theory when  $\langle r^2 \rangle$  and  $\tau_j$  are small. The resulting  $1/T_1$  expression for the  $\alpha=0$  case has the following limiting forms:

$$1/T_{1i} = [6(5)^{1/2}/25]\pi\gamma^4\hbar^2(n/d^3)(\omega^{3/2}\tau_i^{1/2})^{-1}, \\ \alpha=0, \omega\tau_j \gg 1, \quad (14a)$$

$$= 2\pi\gamma^4\hbar^2(n/d^3)\tau_i, \quad \alpha=0, \omega\tau_j \ll 1. \quad (14b)$$

#### B. Jump Limit ( $\alpha \rightarrow \infty$ )

In this case  $A(\rho) \rightarrow 0$  so that Eq. (5) directly gives a single correlation time spectrum which yields the following:

$$1/T_{1i} = (2\pi/5)\gamma^4\hbar^2(n/d^3) \{[\tau_i/(1 + \omega^2\tau_i^2)] \\ + [4\tau_i/(1 + 4\omega^2\tau_i^2)]\}, \quad (15)$$

where

$$\tau_i = \tau_j/2, \quad (d^2 \ll \langle r^2 \rangle).$$

This result is formally identical to BPP rotational formula with a different strength factor.

It is noted from these limiting case discussions on  $\alpha$  that the important differences of the processes, i.e.,  $1/T_1(\alpha=0) \propto \omega^{-3/2}$  and  $1/T_1(\alpha \rightarrow \infty) \propto \omega^{-2}$ , only become evident at values of  $\omega\tau \geq 1$ . This indicates the necessity of high frequency measurements. It is further noted that  $1/T_1$  for  $\omega\tau_j \ll 1$  is independent of the value of  $\alpha$  since from Eqs. (4), and (6),  $J_{\omega\tau_j \ll 1}(\omega) = 16\pi n\tau_i/45d^3$  so that  $1/T_1(\omega\tau_j \ll 1) = 2\pi n\gamma^4\hbar^2\tau_i/d^3$  for all  $\alpha$ . In the  $\omega\tau_j \ll 1$  limit a distinction between rotational and translational contributions is extremely difficult if the temperature dependences of  $\tau_{\text{rot}}$  and  $\tau_i$  are similar since  $1/T_{1 \text{ rot}}(\omega\tau_{\text{rot}} \ll 1) = 2\gamma^4\hbar^2\tau_{\text{rot}}/5d_{\text{intra}}^6$ .

### IV. EXPERIMENTAL PROCEDURE

A hydrostatic oil generating system capable of attaining 3500 kg/cm<sup>2</sup> with control to  $\pm 10$  kg/cm<sup>2</sup> was constructed with standard high pressure equipment. The oil was separated from the sample vessel by a piston type separator cell. CS<sub>2</sub> was used as the intermediate transmitting fluid. Measurement of the pressure was accomplished by direct reading of a Heise type "c" (0-3500 kg/cm<sup>2</sup>) Bourdon gauge whose guaranteed accuracy is 1% of full scale. The pressure vessel used was constructed of 304 stainless steel (2 in. o.d.,  $\frac{1}{2}$  in. i.d.) and fitted with high pressure thermocouple and electrical feedthroughs. Details of this system will be presented in a future work.

The sample cell used to transmit the pressure to the liquid under investigation is identical to that described by Stejskal, Brooks, and Weiss<sup>22,23</sup> and was found useable through the range of the measurements (-30 to +70°C, 0-3000 kg/cm<sup>2</sup>). It was found useful to only fill the sample cell to 85% of its total capacity to allow for expansion of the liquid at elevated temperatures.

The temperature of the high pressure bomb and sample holder were maintained by a liquid bath set