We remember that the full validity of the present treatment fails if the radiative energy losses are appreciable. Nevertheless, even at an initial energy of a few MeV, a substantial decrease in asymmetry can be avoided by the use of sufficiently thin target foils, as can be deduced from the calculations by Blunck and Westphal,[9] and by Schultz.[10]

APPENDIX

The presented calculations of energy straggling with allowance for spin can be easily extended to particles other than electrons. The case of helical muons has been considered. As can be derived from the cross section given by Backenstoss *et al.*,[11] in this case the coefficient a_{-2} is still expressed by Eq. (15), while

$$\mu=(1/\rho)[-(\gamma^2-1)/\gamma^2\pm f(\epsilon_m/m_\mu c^2)(1/\gamma)],$$

$$\nu=\frac{1}{\rho}\left[\frac{1}{2\gamma^2}\left(\frac{\epsilon_m}{m_\mu c^2}\right)^2\pm f\left(-\frac{1}{\gamma}\frac{\epsilon_m}{m_\mu c^2}+\frac{1}{2\gamma^2}\frac{\epsilon_m{}^2}{m_\mu{}^2c^4}\right)\right],$$

$$\xi=0,$$

where the maximum energy transfer $\epsilon_{\max}$ is given by

$$\epsilon_{\max}=m_\mu c^2\frac{m_0}{m_\mu}\frac{2(\gamma^2-1)}{1+(m_0/m_\mu)(2\gamma+m_0/m_\mu)}.$$

In the above formulas m_0 and m_μ are the electron and muon rest masses. In order to take into account the density effect, the definition (9) of the reduced variable γ must be modified by the addition of a corrective term.[12] Numerical calculations for $f=0$ gave very good agreement with the results obtained by Vavilov.[13] In the case of a magnetized target ($f=0.06$), a very low parallel-antiparallel difference was found in every realistic condition. This fact is due to the very great number of single scatterings which occur in a foil which is thick enough to give a mean energy loss comparable with the resolving power of an actual experimental apparatus.

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Nuclear Spin Relaxation by Translational Diffusion in Liquid Ethane*

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Torrey's theory for nuclear spin relaxation by translational diffusion has been extended to take into account the effect of the radial distribution function. By suitable expansions, the frequency dependence of the intermolecular relaxation rate has been made explicit and shown to be more significant than previously suspected. Measurements of self-diffusion and of the intermolecular relaxation of protons in liquid ethane have been made over a wide range of temperatures and at three frequencies in order to test the theory. Good agreement is obtained with the assumption of an rms flight distance which varies monotonically from about 0.8 to 1.3 times the molecular diameter over the liquid range.

I. INTRODUCTION

In his classic paper on nuclear spin relaxation by translational diffusion in 1953, Torrey pointed out that the essentially microscopic character of nuclear spin relaxation would reflect details of the process of random flights of which diffusion is only the limiting macroscopic approximation.[1] He predicted that studies of relaxation would allow the independent measurement of $\langle r^2\rangle$, the mean-squared flight distance, and τ, the mean time between flights. He well understood that measurement of the self-diffusion constant D would provide the familiar combination

$$D=\langle r^2\rangle/6\tau \tag{1}$$

and he foresaw that the spin-lattice relaxation time T_1 would be a function of these parameters also.

To our knowledge, no one has yet experimentally investigated in detail these suggestions as they relate to motion in liquids. The 16-yr delay between Torrey's

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theory and the kind of study we wish to report is principally due to the difficulties of (1) preparing a sample sufficiently free of paramagnetic impurities to allow the measurement of intrinsic relaxation times, and (2) separating reliably the intermolecular contribution to relaxation, to which Torrey's theory applies, from the intramolecular contribution, to which it does not.

Extensive measurements of the proton relaxation time and the self-diffusion constant in liquid ethane have been made from 91 to 273°K. This covers most of the liquid range, which extends from the melting point, 89.82°K (Ref. 2) to the critical point, 305.48°K (Ref. 3). In this paper we report the noteworthy agreement of our data for the intermolecular contribution to relaxation, R_B, with Torrey's theory for relaxation and the consequent measurement of $\langle r^2\rangle$ and τ as functions of temperature. To match our data, it is necessary to generalize Torrey's theory to take into account the liquid radial distribution function, to expand the results to include the first-order frequency term, and to use the Hubbard correction[4,5] for multispin molecules.

Some of the results of the modified Torrey theory may be anticipated by physical arguments using the Bloembergen-Purcell-Pound (BPP) model for intermolecular relaxation.[6] BPP assumed an exponential form for the correlation function of the position coordinates of two spins. The correlation time for the relative translational motion was taken to be the time it took the two spins to drift a relative distance R if they were intially separated by a distance R. This time is $\tau_0=R^2/12D$. The correlation time is seen to increase rapidly as the distance separating the spins gets greater as does the number of spins with a given correlation time. However, the interaction strength decreases as $1/R^6$. This leads to a relaxation rate R_B proportional to

$$\int_\sigma^\infty \frac{4\pi R^2 dR}{R^6}\left(\frac{\tau_0}{1+\omega^2\tau_0^2}+\frac{4\tau_0}{1+4\omega^2\tau_0^2}\right),$$

in which ω is the angular Larmor frequency and σ is the molecular diameter. BPP assumed that since $\omega\tau_0\ll 1$ for the nearest neighbors and since the most important contribution to the integral comes from these neighbors, one could neglect $(\omega\tau_0)^2$ compared to 1 for all R. This does simplify the integral, but it also throws away the frequency dependence. It turns out, however, that for some cases, for example, low-temperature liquid ethane, there is a range of R for enough sufficiently close neighbors such that their longer correlation times are effective in producing an appreciable frequency dependence in R_B. Indeed, the BPP integral can be done exactly and can be shown in the low-frequency limit to be proportional to $(1-kn\omega^{1/2}/D^{3/2})$, in which k is a constant and n is the number density of resonant nuclei.

Some insight into the dependence of R_B on $\langle r^2\rangle$ can also be obtained with the help of the BPP model. This model assumed that the diffusive process takes place by very small steps. Thus, a very large number of steps are required to change the dipolar interaction between neighboring spins appreciably and $\tau_0=R^2/12D$ is the expression for the correlation time for a pair of spins whatever their distance of separation. However, if the spin-bearing molecules perform jumps of the order of a molecular diameter, one jump will be sufficient to change appreciably the dipolar interaction between the nuclei of neighboring molecules. Thus, for these molecules the waiting time between jumps, $\frac{1}{2}\tau=\langle r^2\rangle/12D$, becomes significant because this time is a lower limit for the correlation time. As a consequence, the correlation time is larger than τ_0 and it is a function of the mean-squared flight distance. Since the nearest neighbors are the most important contributors, the net effect on R_B is appreciable. It will be shown later that for jump distances equal to the molecular diameter, R_B is increased by about 40% if a uniform density is assumed and by about 70% if a realistic radial distribution is taken into account. This argument is independent of the Larmor precession frequency ω. Thus, contrary to Abragam's physical argument,[7] the details of the random-walk motion can be significant whatever the magnitude of $\omega\tau$.

It was pointed out by Seiden[8] that the effect of the radial distribution function should be included in any correct theory of intermolecular spin-lattice relaxation. The radial distribution function for a liquid is characterized by a maximum at the nearest-neighbor location. This implies that there are more nearest neighbors than would be expected if the liquid state were purely random in character. The increased effectiveness to relaxation due to this excess number of nearest neighbors is taken into account in the Oppenheim-Bloom[9] theory in a natural way, but in their papers the diffusive motion is assumed to obey the Langevin equation in the diffusion-equation limit. We find this assumption to be incorrect, at least for liquid ethane and liquid He^3. While the dynamic formalism of the Oppenheim-Bloom theory is more appealing than Torrey's stochastic approach, and in principle, jump diffusion could be incorporated in their theory,[10] we have found Torrey's theory more tractable.

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II. MODIFICATION OF TORREY'S GENERAL THEORY

The spin-lattice relaxation rate can be expressed in terms of the correlation functions $k_n(t)$ of those interactions which enable energy to be exchanged between the spins and their surroundings. For dipolar coupling among identical nuclei of spin I and gyromagnetic ratio γ, the relaxation rate is given by

$$1/T_1 = R_B = \tfrac{3}{2}\gamma^4\hbar^2 I(I+1)[J_1(\omega)+J_2(2\omega)], \qquad (2)$$

where

$$J_n(\omega) = \int_{-\infty}^{\infty} k_n(t)e^{i\omega t}dt, \quad n=1,\,2.$$

Equation (2) includes the proper weighting of the 2ω term, as pointed out by Kubo and Tomita.[11] Later, in fact, we will present experimental evidence that the 2ω term enters with the weight described by this equation. This term is in error in Torrey's classic paper and therefore, many of Torrey's calculations will be repeated using Eq. (2). Now the correlation functions are the ensemble averages

$$k_n(t) = \langle (m|\mathcal{H}_n(t')|p)(p|\mathcal{H}_n(t'+t)|m)\rangle_{\text{av}}, \qquad (3)$$

where $\mathcal{H}_1(t')$ and $\mathcal{H}_2(t')$ are the parts of the Hamiltonian which couple the spins and their surroundings and which cause transitions from the state m to the state p. The ensemble averages are performed by Torrey by introducing suitably defined probability functions yielding

$$k_1(t) = n\int\int P(\mathbf{r},\mathbf{R},t)F_{ij}^{(1)}(\mathbf{R})F_{ij}^{(1)*}(\mathbf{r})g(\mathbf{R})d\mathbf{R}d\mathbf{r}, \qquad (4)$$

with a similar expression for $k_2(t)$. Here, $g(\mathbf{R})$ represents the radial distribution of the fluid and n is the average number density of the resonant nuclei. For dipolar coupling the $F_{ij}^{(n)}$ are related to the spherical harmonics as

$$F_{ij}^{(1)} = (8\pi/15)^{1/2}Y_2^1(\theta_{ij},\phi_{ij})/r_{ij}^3 \qquad (5\text{a})$$

and

$$F_{ij}^{(2)} = (32\pi/15)^{1/2}Y_2^2(\theta_{ij},\phi_{ij})/r_{ij}^3, \qquad (5\text{b})$$

where $(r_{ij},\theta_{ij},\phi_{ij})$ are the spherical coordinates, with respect to H_0 in the z direction, of the vector joining a pair of spins and are assumed to be random functions of time.

An integral expression for the relevant $P(\mathbf{r},\mathbf{R},t)$ can be obtained from the theory of random flights[12] as done by Torrey, who finds

$$P(\mathbf{r},\mathbf{R},t) = \frac{1}{8\pi^3}\int \exp\left\{-i\boldsymbol{\rho}\cdot(\mathbf{r}-\mathbf{R}) - \frac{2t}{\tau}[1-A(\boldsymbol{\rho})]\right\}d\boldsymbol{\rho}. \qquad (6)$$

The form of $A(\boldsymbol{\rho})$ in Eq. (6) depends upon the model chosen to describe the diffusive motion in the fluid. Substitution of Eqs. (5) and (6) into (4) gives

$$k_1(t) = \frac{8\pi n}{15}\int\int\int \rho H(\rho)J_{5/2}(\rho R)J_{5/2}(\rho r) \times R^{-3/2}r^{-3/2}g(R)d\rho dr dR \qquad (7)$$

and $k_2(t) = 4k_1(t)$, with

$$H(\rho) = e^{-(2t/\tau)[1-A(\rho)]},$$

where it has been assumed that the diffusive process is isotropic. To proceed further we note the following properties of $g(R)$:

(a) $g(R)=0,\ 0<R<\sigma$;
(b) $g(R)$ is a function that exhibits damped oscillations about unity for $\sigma<R<b$;
(c) $g(R)\sim 1,\ R\geq b$.

Thus, the integral over R in Eq. (7) can be split into two regions of integration, the first from σ to b, the second from b to infinity. This division gives for Eq. (7)

$$k_1(t) = \frac{8\pi n}{15}\int_0^{\infty}\rho H(\rho)d\rho\int_{\sigma}^{\infty}J_{5/2}(\rho r)r^{-3/2}dr \times\left[\int_{\sigma}^{b}J_{5/2}(\rho R)R^{-3/2}g(R)dR + \int_{b}^{\infty}J_{5/2}(\rho R)R^{-3/2}dR\right].$$

The integral from b to infinity is well known.[13] Hence, we find

$$k_1(t) = \frac{8\pi n}{15\sigma^{3/2}b^{3/2}}\int_0^{\infty}H(\rho)J_{3/2}(\sigma\rho)J_{3/2}(b\rho)\rho^{-1}d\rho + \frac{8\pi n}{15\sigma^{3/2}}\int_0^{\infty}H(\rho)J_{3/2}(\rho\sigma)d\rho \times\int_{\sigma}^{b}J_{5/2}(\rho R)R^{-3/2}g(R)dR. \qquad (8)$$

The Fourier transform of Eq. (8) can be taken to give

$$J_1(\omega) = \frac{8\pi n\tau}{15\sigma^{3/2}b^{3/2}}\int_0^{\infty}\left\{\frac{1-A(\rho)}{[1-A(\rho)]^2+(\frac{1}{2}\omega\tau)^2}\right\} \times J_{3/2}(\sigma\rho)J_{3/2}(b\rho)\frac{d\rho}{\rho} + \frac{8\pi n\tau}{15\sigma^{3/2}} \times\int_0^{\infty}\left\{\frac{1-A(\rho)}{[1-A(\rho)]^2+(\frac{1}{2}\omega\tau)^2}\right\}J_{3/2}(\rho\sigma)d\rho \times\int_{\sigma}^{b}J_{5/2}(R\rho)g(R)R^{-3/2}dR, \qquad (9\text{a})$$

$$J_2(\omega) = 4J_1(\omega). \qquad (9\text{b})$$

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Equation (9) is similar to Torrey's Eq. (28); however, we have retained the radial distribution function.

A. Zero-Frequency Limit

We must now choose a model describing the diffusive motion. The usual treatment of intermolecular relaxation assumes that the motion of the molecules is described by the diffusion equation. This assumption leads to an $A(\rho)$ of the form

$$A(\rho)=1-D\tau\rho^2+O(\rho^4). \qquad (10)$$

The above expression for $A(\rho)$ allows all integrations over ρ in Eq. (9) to be performed in the limit $(\omega\tau)\ll 1$, giving

$$J_1(0)=\frac{4\pi n}{45D}\left[\frac{1}{b}\left(1-\frac{\sigma^2}{5b^2}\right)+\int_\sigma^b\frac{g(R)dR}{R^2}-\frac{3\sigma^2}{5}\int_\sigma^b\frac{g(R)dR}{R^4}\right] \qquad (11)$$

and $J_2(0)=4J_1(0)$. Using Eq. (1), we find the relaxation rate to be

$$R_B(0)=\frac{2\pi n\gamma^4\hbar^2I(I+1)}{3D}\left[\frac{1}{b}\left(1-\frac{\sigma^2}{5b^2}\right)+I_1-\frac{3\sigma^2}{5}I_2\right], \qquad (12)$$

where

$$I_k=\int_\sigma^b R^{-2k}g(R)dR, \quad k=1,2. \qquad (13)$$

Now if $b\rightarrow\sigma$, $I_k=0$. This is just the usual assumption of a hard-sphere radial distribution function in the zero-density limit; that is,

$$\begin{aligned} g(R)&=0, \quad R<\sigma\\ g(R)&=1, \quad R>\sigma. \end{aligned} \qquad (14)$$

Equation (12) reduces to the usual expression in this case,[14] namely,

$$R_B(0)=(8\pi n/15\sigma D)\gamma^4\hbar^2I(I+1). \qquad (15)$$

The validity of using the diffusion equation to describe motion in the liquid has been questioned elsewhere.[1,10] We will show later than neither Eq. (12) nor (15) will describe the data for ethane or He^3.

Quite early, Frenkel[15] suggested a model for liquid motion that includes an oscillatory motion about an equilibrium position followed by a diffusive jump. A model of this nature has been used to interpret cold neutron scattering experiments by, among others, Larsson and Dahlborg.[16] Torrey is led to an $A(\rho)$ of the form

$$A(\rho)=(1+D\tau\rho^2)^{-1} \qquad (16)$$

by considering the following model: A molecule is bound in a "well" for a time $\tau-\tau'$, then it may jump out of the trapping site and move about in a random manner for a time τ' before falling into another well. It is assumed that the motion in the excited state is described by the diffusion equation and that this motion does not contribute to the relaxation. It is to be noted that Torrey's $A(\rho)$ reduces to Eq. (10) in the limit $D\tau\rho^2\ll 1$ and thus Torrey's theory includes continuous diffusion as a special case.

In the limit $\omega\tau\ll 1$, Eqs. (9), (13), and (16) yield

$$J_1(0)=\frac{8\pi n\tau}{45\sigma^3}\left[\frac{\sigma^3}{b^3}+\frac{3\sigma^3}{b\langle r^2\rangle}\left(1-\frac{\sigma^2}{5b^2}\right)+3\sigma^3I_2+\frac{3\sigma^3}{\langle r^2\rangle}\left(I_1-\frac{3\sigma^2}{5}I_2\right)\right]. \qquad (17)$$

Using Eq. (2), we obtain

$$R_B(0)=\frac{8\pi n\gamma^4\hbar^2I(I+1)}{15\sigma D}\left[\frac{5\langle r^2\rangle\sigma}{12b^3}+\frac{5\sigma}{4b}\left(1-\frac{\sigma^2}{5b^2}\right)+\frac{5}{4}\langle r^2\rangle\sigma I_2+\frac{5\sigma}{4}\left(I_1-\frac{3\sigma^2}{5}I_2\right)\right]. \qquad (18)$$

For the hard-sphere radial distribution function in the zero-density limit the use of Eq. (14) gives

$$R_B(0)=\frac{8\pi n\gamma^4\hbar^2I(I+1)}{15\sigma D}\left(1+\frac{5\langle r^2\rangle}{12\sigma^2}\right), \qquad (19)$$

as may be found from Torrey's paper with the use of the Kubo-Tomita correction. The importance of the jump term $\langle r^2\rangle/\sigma^2$ in Eq. (19) has been discussed by Muller[17] and Muller, Harmon, and Finch.[18] We will show later that Eq. (18), which includes both the jump term and the radial distribution function, gives excellent agreement to experimental data for ethane with reasonable values for σ and $\langle r^2\rangle/\sigma^2$ over a good part of its liquid range.

In order to write Eqs. (12) and (18) in forms that can be compared with experiment it is necessary to perform the integrals I_k, using the appropriate $g(R)$. Unfortunately, experimental radial distribution functions are not known for a number of liquids including ethane. If this experimental information is available for a particular liquid, one need only to integrate the I_k numerically. Another approach when experimental distribution functions are not available is to calculate $g(R)$, assuming Kirkwood's superposition principle. Extensive tables exist[19] which allow one to determine $g(R)$ in this approximation for a variety of temperatures

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and pressures. For the noble liquids this procedure gives a reasonably good approximation for $g(R)$. It is clear, however, that for a liquid as complicated as ethane, this approximation is very crude. The integrals I_k for heptane have been evaluated using both the experimental $g(R)$ and the results of Kirkwood *et al.*[19] The results differ by less than 10%, indicating that the details of $g(R)$ are not important in the integrals I_k. That this should be so is not surprising when one considers the rapid convergence of the integrand due to the factor $1/R^{2k}$, which smooths out quickly the structure in $g(R)$. All that is important is the first maximum in $g(R)$ at the nearest-neighbor location. Since the experiment, at least in the limit $\omega\tau \ll 1$, is not sensitive to the details of $g(R)$, an approximate analytical form for $g(R)$ is now derived. The procedure is as follows: It is well known[20] that the radial distribution function can be expanded in powers of the molecular number density n'; thus,

$$g(R_{12}) = e^{-\phi(R_{12})/kT}\left[1+n'\int(e^{-\phi(R_{13})/kT}-1)\right.$$
$$\left.\times(e^{-\phi(R_{23})/kT}-1)d\mathbf{R}_3+O(n'^2)\right], \qquad (20)$$

where $\phi(R)$ is the intermolecular potential. A hard-sphere intermolecular potential is assumed for $\phi(R)$:

$$\begin{aligned}\phi(R)&=\infty, \quad R<\sigma\\ \phi(R)&=0, \quad R>\sigma.\end{aligned} \qquad (21)$$

With this assumption, the first term in Eq. (20) will generate Eq. (14), the usual approximation made in calculating R_B. Carrying Eq. (20) with $\phi(R)$ as given by Eq. (21) to first order in n', one obtains[21]

$$\begin{aligned}g(R)&=0, && R<\sigma\\ g(R)&=1+\Omega(1-\tfrac{3}{4}R/\sigma+\tfrac{1}{16}R^3/\sigma^3), && \sigma<R<2\sigma \quad (22)\\ g(R)&=1, && R>2\sigma\end{aligned}$$

where

$$\Omega=\tfrac{4}{3}\pi n'\sigma^3.$$

This form of $g(R)$ gives the required maximum at the nearest-neighbor location, can easily be integrated in the I_k, and introduces no new parameters. Furthermore, the temperature dependence predicted by Eq. (22) in the I_k is in good agreement with that of the more complicated Kirkwood theory.

What has been done here, essentially, is to carry the usual theory for R_B to the next order in the molecular number density. Using Eq. (22) in the I_k integrals, we obtain

$$I_1=\int_\sigma^{2\sigma} R^{-2}g(R)dR=\frac{1}{\sigma}(0.500+0.0739\Omega) \qquad (23a)$$

and

$$I_2=\int_\sigma^{2\sigma} R^{-4}g(R)dR=\frac{1}{\sigma^3}(0.292+0.0537\Omega), \qquad (23b)$$

from which Eq. (18) becomes

$$R_B(0)=\frac{8\pi n\gamma^4\hbar^2 I(I+1)}{15\sigma D}\left[1+\frac{\langle r^2\rangle}{\sigma^2}\left(\frac{5}{12}+0.0672\Omega\right)\right.$$
$$\left.+0.0521\Omega\right]. \qquad (24)$$

This expression, which takes into account diffusive jumps and the radial distribution function, should describe the relaxation in ideal liquids in the zero-frequency limit. Note that for liquid ethane, the coefficient of the jump term, $\langle r^2\rangle/\sigma^2$, is about 0.70.

For polyatomic liquids, such as ethane, a further effect must be considered. Hubbard[4] has pointed out that if the spins are not at the center of the molecule, the distance of closest approach of two spins will no longer be σ, the molecular diameter, but something less. Also one must consider the effect of rotation of the spin-bearing molecules on the purely translational relaxation. It turns out that these effects compete, the former tending to increase the relaxation rate, the latter decreasing it. This last effect is similar to the phenomenon of motional narrowing since the rotational motion averages out part of the intermolecular interaction. Muller[5] has extended Hubbard's treatment in order that the actual rotational correlation time may be used instead of a value calculated from the simple Debye tumbling model, which is not applicable to ethane. These corrections are included by modifying the R_B equations as

$$R_B{}^c=R_B(1+\delta), \qquad (25)$$

where $1+\delta$ is a power series which converges rapidly,

$$1+\delta=1+\alpha(2d/\sigma)^2+\beta(2d/\sigma)^4+\cdots. \qquad (26)$$

The quantity d is the distance of the proton from the center of its molecule and α and β are factors taken from Ref. 5 and a knowledge of the intramolecular correlation time obtained from the experimental results. While it should be noted that the inclusion of the off-center spin effect as given in Eq. (25) is purely an *ad hoc* correction, δ is at most 0.09 for ethane. It should be possible to include the Hubbard effect into the Torrey theory rigorously, as has been done for $g(R)$, but this has not yet been done.

B. Low-Frequency Limit

Experimentally, R_B is found to be frequency-dependent in the low-temperature liquid. It is clear, of course, that Eq. (24) will not describe this effect since it has been assumed that $\omega\tau\ll1$, the "white" spectrum limit for the motion. The frequency depen-

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dence of the theory is included in the general form of the spectral density, which may be obtained by combining Eqs. (9) and (16) in a manner very similar to that by which Torrey proceeds from his Eqs. (28) and (39) to Eq. (48). We find

$$J_1(\omega)=\frac{16\pi^2 n}{15\sigma^{3/2}\omega}\mathrm{Re}\left[\frac{J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(b\beta)}{b^{3/2}(2-i\omega\tau)}+\frac{\beta J_{3/2}(\sigma\beta)}{(2-i\omega\tau)}\int_\sigma^b R^{-3/2}g(R)H_{5/2}^{(1)}(R\beta)dR\right], \quad (27)$$

where

$$\beta^2=i\omega/D(2-i\omega\tau).$$

The Bessel and Hankel functions in Eq. (27) have complex arguments as a result of the integration of Eq. (9). This makes it difficult to find the real part in brackets for the general case. However, the observed frequency effect was small. Thus the Bessel and Hankel functions can be expanded in a power series of the arguments and only leading terms in the frequency retained. The real parts of the resulting expansion can then readily be found. This procedure has the added advantage of exhibiting the analytic form of the leading frequency-dependent term, allowing better insight into the sensitivity of the relaxation rate to the resonance frequency. The quantities in the brackets in Eq. (27) can be simplified considerably by working with the derivative of $g(R)$, which is written

$$g'(R)=(d/dR)g(R).$$

To simplify Eq. (27), a well-known property of the Hankel function[13] is used:

$$\frac{1}{z}\frac{d}{dz}\left[\frac{H_\nu^{(1)}(z)}{z^\nu}\right]=-\frac{H_{\nu+1}^{(1)}(z)}{z^{\nu+1}}.$$

With the aid of this property, an integration by parts can be performed:

$$\beta\int_\sigma^b R^{-3/2}g(R)H_{5/2}^{(1)}(R\beta)dR=-R^{-3/2}g(R)H_{3/2}^{(1)}(R\beta)\Big|_\sigma^b+\int_\sigma^b R^{-3/2}H_{3/2}^{(1)}(R\beta)g'(R)dR.$$

Substituting this result into Eq. (27), one obtains for the term in brackets

$$\mathrm{Re}\left[\frac{J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(b\beta)}{b^{3/2}(2-i\omega\tau)}-\frac{g(b)J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(b\beta)}{b^{3/2}(2-i\omega\tau)}+\frac{g(\sigma)J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(\sigma\beta)}{\sigma^{3/2}(2-i\omega\tau)}+\frac{J_{3/2}(\sigma\beta)}{(2-i\omega\tau)}\times\int_\sigma^b\frac{H_{3/2}^{(1)}(R\beta)g'(R)dR}{R^{3/2}}\right].$$

By definition $g(b)=1$, therefore, the first two terms cancel, giving for the spectral density

$$J_1(\omega)=\frac{16\pi^2 n}{15\sigma^{3/2}\omega}\mathrm{Re}\left[\frac{g(\sigma)J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(\sigma\beta)}{\sigma^{3/2}(2-i\omega\tau)}+\int_\sigma^b\frac{J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(R\beta)g'(R)dR}{R^{3/2}(2-i\omega\tau)}\right]. \quad (28)$$

This expression is considerably simpler to handle than Eq. (27) since only the real part of the expansion of $J_{3/2}H_{3/2}^{(1)}$ need be found. After the expansion to leading terms in the frequency, the integrals containing $g(R)$, I_1, and I_2 can be recovered by partial integration. This procedure is shown in the Appendix. From the Appendix the frequency-dependent spectral density, to leading terms in the frequency, is

$$J_1(\omega)=\frac{8\pi n\tau}{45\sigma^3}\left[\frac{\sigma^3}{b^3}+\frac{3\sigma^3}{\langle r^2\rangle b}\left(1-\frac{\sigma^2}{5b^2}\right)+3\sigma^3 I_2+\frac{3\sigma^3}{\langle r^2\rangle}\left(I_1-\frac{3\sigma^2}{5}I_2\right)-\frac{\sigma^2}{\langle r^2\rangle}\left(\frac{\omega\sigma^2}{D}\right)^{1/2}\right] \quad (29)$$

which, as is shown in the Appendix, is accurate to better than 1% for $(\omega\sigma^2/D)^{1/2}<0.44$, its largest value in our study of liquid ethane. Note that the frequency term is independent of $g(R)$. Using Eq. (23) for the I_k, one obtains

$$J_1(\omega)=\frac{8\pi n\tau}{45\sigma^3}\left[1+\frac{12}{5}\frac{\sigma^2}{\langle r^2\rangle}+\frac{\Omega\sigma^2}{8\langle r^2\rangle}+(0.1612\Omega)-\frac{\sigma^2}{\langle r^2\rangle}\left(\frac{\omega\sigma^2}{D}\right)^{1/2}\right]. \quad (30)$$

Combination of Eqs. (2) and (30) now provides the frequency-dependent relaxation rate:

$$R_B(\omega)=\frac{8\pi n\gamma^4\hbar^2 I(I+1)}{15\sigma D}\left[1+\frac{\langle r^2\rangle}{\sigma^2}\left(\frac{5}{12}+0.0672\Omega\right)+0.0521\Omega-0.555\left(\frac{\omega\sigma^2}{D}\right)^{1/2}\right]. \quad (31)$$

The sensitivity of the experiment to the resonance frequency can be better understood if the frequency term is rewritten as

$$(\omega\sigma^2/D)^{1/2}=(12\pi\sigma^2/\langle r^2\rangle)^{1/2}(\tau/T_L)^{1/2},$$

where T_L is the Larmor period. If $\tau\ll T_L$, which is usually the case, it can be seen that there are many diffusive jumps per Larmor period and the experiment is insensitive to the magnitude of ω. When the ratio $(\tau/T_L)^{1/2}\geq 10^{-2}$, the frequency term is no longer negligible and a frequency-dependent R_B results.

III. EXPERIMENTAL RESULTS

The extensive temperature range for which ethane is in the liquid state makes it a good candidate for a relaxation study even though it is not an ideal liquid in the sense described by the theory. The intermolecular relaxation rate R_B^c can be measured reliably by the dilution method[22] once the paramagnetic oxygen is reduced to small enough proportions.

The starting material for the undeuterated samples was Phillips Petroleum Co. research grade ethane described in their catalog as having a minimum purity of 99.96 mole %. Melting-point studies[2] of the samples showed that they contained a liquid-soluble solid-insoluble impurity concentration of 0.03 mole%.

Completely deuterated ethane, CD_3CD_3, was obtained from Merck, Sharp, and Dohme of Canada, Ltd., who reported that this lot number contained 98.27% CD_3CD_3 and 1.73% CHD_2CD_3 and very little air if any. The mixture samples were prepared by progressively diluting CD_3CD_3 with CH_3CH_3. The concentration of CD_3CD_3 was measured by observing pressures, with a Hg manometer, before and after addition of CH_3CH_3 in the same volume. This procedure provided dilution ratios with an uncertainty of about 1% of the ratio. Then oxygen was removed from the ethane gas by the misch metal gettering technique[23] before it was condensed into small glass sample vials loaded to approximately critical density, which were then sealed. All measurements were therefore taken along the vapor-pressure curve. Detailed comparison[24] of the experimental results reported here and the results of a study by Gaven, Stockmayer, and Waugh[25] on ethane with oxygen impurity allows an estimate to be made of the upper limit of oxygen in our samples. Our oxygen content was less than four parts in ten million and negligible for the purposes of this paper.

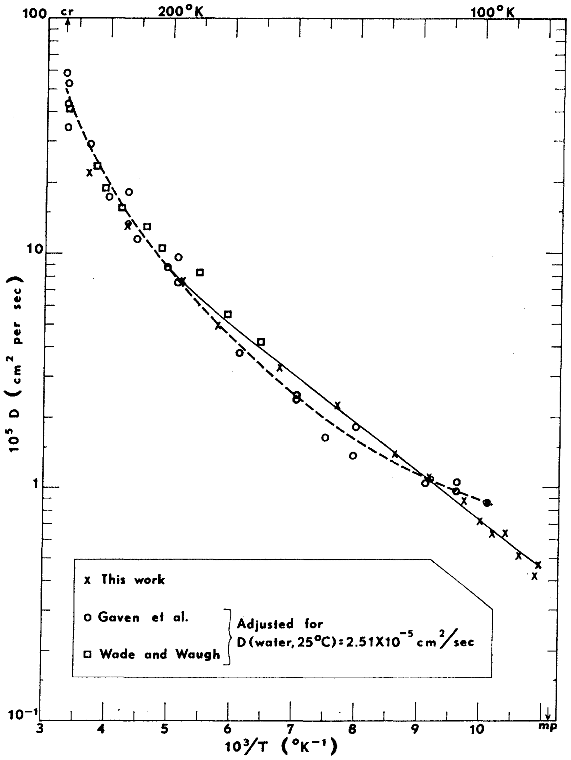

FIG. 1. Temperature dependence of the self-diffusion constant of liquid ethane. The solid curve in the range $5.5<10^3/T<11.0/°K$ is a least-squares fit of our data in the linear region. The dashed curve is that published by Gaven, Stockmayer, and Waugh (Ref. 25).

Since accurate knowledge of the self-diffusion constant D is clearly essential for an understanding of relaxation in liquids and since our experimental measurements of the intermolecular contribution to relaxation in liquid ethane did not appear to be compatible with the values of D in the literature,[25] we undertook to measure this quantity. The self-diffusion data were obtained with the aid of the spin-echo technique.[26] The fixed external gradient was calibrated using the known self-diffusion constant of water as measured in a careful experiment performed by Trappeniers *et al.*[27] The temperature is known to at least 1°K for all these points. The data are presented in Fig. 1, along with the data of Gaven *et al.*[25] and Wade and Waugh.[28] In order to include the data of the other authors for comparison, we renormalized their data for the Trappeniers value of the diffusion constant of water. The agreement apart from a few of their points, particularly in the inverse temperature region $6<10^3/T<9/°K$, is good. The differences in this region led Gaven *et al.* to infer a significantly different temperature dependence for D from ours. We cannot reconcile our relaxation measurements with their curve, the dashed curve in Fig. 1. Our value of D at $10^3/T=10.94/°K$ was done with special care and is clearly incompatible with their curve. We argue that our data are more self-consistent. Instead of a changing activation energy in the low-temperature region, we find that the activation energy of self-diffusion in ethane is constant within experimental error and is 0.94 kcal/mole in the inverse temperature range $5.5<10^3/T<11.0/°K$. Using our curve in the region $10^3/T\geq 5.0/°K$ and theirs in the region $10^3/T\leq 5.0/°K$ (where our data are sparse), we believe that we know D with a 6% uncertainty over the entire temperature range of interest. It may be noted that all of these measurements are in good agreement with Noble and Bloom's careful measurements in the vicinity of the critical point.[29]

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[27] J. Trappeniers, C. J. Gerritsma, and P. H. Oosting, Physica 31, 202 (1965).

[28] C. G. Wade and J. S. Waugh, J. Chem. Phys. 43, 3555 (1965).

[29] J. D. Noble and M. Bloom, Phys. Rev. Letters 14, 250 (1965).

The spin-lattice relaxation times were measured by a variety of pulse techniques. The spectrometers used were incoherent and therefore careful steps were taken to account for the nonlinearity of the receiving systems. The major source of nonlinearity was due to the diode detector. Two approaches were used to correct for this effect:

1. The signal amplitude at the diode was kept relatively constant by means of precision attenuators.
2. The amplitude response of the receiver was carefully calibrated and a linear portion of the response curve was selected as the operating range.

Both methods gave consistent T_1 values. The first method is probably the best, but is inconvenient for long relaxation times.

To illustrate the mixture data, the measured relaxation rate, $R=1/T_1$, is plotted in Fig. 2 as a function of the concentration of CD_3CD_3 at a temperature of 90.71°K and frequency of 3 MHz. The plots for each of the fixed temperature points studied were straight lines within experimental error. The 100% CD_3CD_3 intercept,

$$R_{100\%}=R_{\text{intra}}+(0.0419)R_B{}^c,$$

where the factor (0.0419) takes into account the intermolecular relaxation by deuterons, and the 0% intercept,

$$R_{0\%}=R_{\text{intra}}+R_B{}^c,$$

where R_{intra} is the intramolecular contribution to relaxation, allow one to calculate an experimental $R_B{}^c$. The uncertainty in the intercepts generated by the scatter of the experimental data from the least-squares line was taken to be the uncertainty in $R_B{}^c$. This separation procedure assumes that the motion of a molecule of CH_3CH_3 is not appreciably affected by the substitution of molecules of CD_3CD_3 for its normal molecular neighbors. To check this point, the ratio of the diffusion constant of CH_3CH_3 in 50% CD_3CD_3 to the self-diffusion constant of CH_3CH_3 was measured and found to be unity within experimental error (4%).

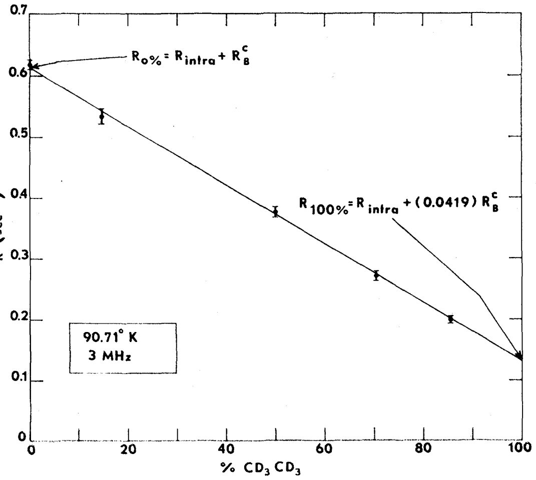

FIG. 2. Spin-lattice relaxation rate of protons in mixtures of CH_3CH_3 with CD_3CD_3 as a function of the concentration of CD_3CD_3.

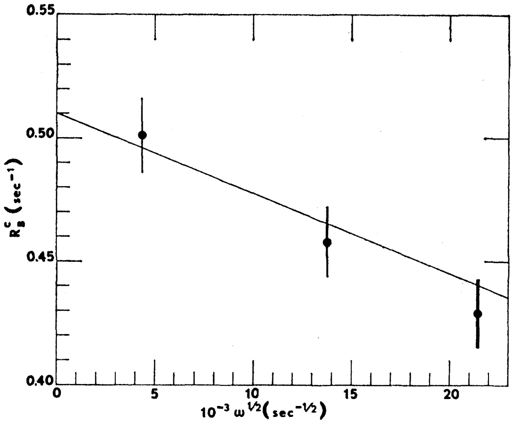

FIG. 3. Frequency dependence of the intermolecular relaxation rate of protons in liquid ethane at 90.71°K. The slope of the solid line is given by the theory and its zero-frequency intercept is a measure of the mean-squared flight distance at this temperature.

To test the frequency dependence of the relaxation rate, the mixture experiment was performed at 90.71°K in three different magnetic fields at Larmor frequencies of 3, 30, and 73 MHz known to better than 0.5%. The measured values of the intermolecular contribution to relaxation, $R_B{}^c(\omega)$, at these frequencies are plotted in Fig. 3 as a function of $\omega^{1/2}$. The standard deviation in the measurement of each of these values was about 1%. The uncertainty shown in Fig. 3 is 3%. Equations (31) and (25) predict a straight line through these points with a slope given by

$$-(4.77\times10^{-14})\rho(1+\delta)/D^{3/2}=-3.4\pm0.2\times10^{-6}\,\text{sec}^{-1/2}.$$

Note that this slope has no adjustable constants and that its chief uncertainty originates from the experimental uncertainty in the measured value of D. This range of slopes and the three measured values of $R_B{}^c(\omega)$ define a range of zero frequency $R_B{}^c$, that is, $R_B{}^c(0)=0.510\pm0.010$ sec^{-1}. The line on the figure through this zero-frequency value with the theoretical slope just calculated thus illustrates the fit of our data to the theory. This measurement of $R_B{}^c(0)$ also implies from Eqs. (31) and (25) a value for the jump distance in terms of the molecular diameter, $\langle r^2\rangle/\sigma^2=0.67\pm0.05$. To calculate this ratio, $\delta=0.03$ is obtained from the interpretation of the intramolecular contribution to relaxation[24] and the molecular diameter was chosen here and in the rest of our calculations to be the Lennard-Jones parameter, $\sigma=4.38$ Å (Ref. 20, p. 1213).

This frequency dependence corroborates the Kubo-Tomita correction, for neglecting it reduces the theoretical slope to a value incompatible with our data. As a further argument for our diffusion data, it can be observed that the use of the curve of Gaven *et al.*[25] for

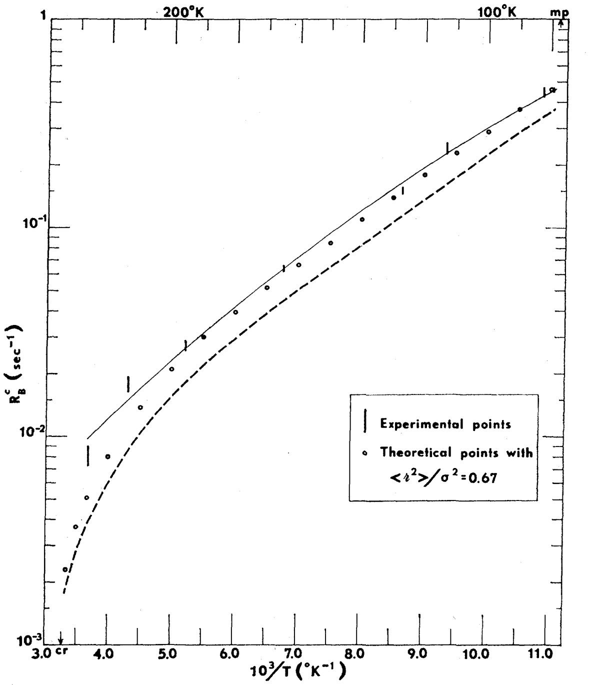

FIG. 4. Intermolecular relaxation rate of protons in liquid ethane measured at 30 MHz as a function of inverse temperature and compared to the theory of relaxation by translational diffusion. The lines are the experimental points with their uncertainty and the solid curve is a computer fit to these data. The dashed curves represents relaxation due to very small diffusive steps. The open circles are calculated from the amended theory of relaxation due to diffusive jumps whose mean-square flight distance is 0.67 times the square of the molecular diameter.

D at this temperature reduces the theoretical slope to a value outside our experimental uncertainty.

The temperature dependence of R_B^c was studied by measuring R_B^c with the mixture experiment at eight temperatures from 90.71 to 273°K at a Larmor precession frequency of 30 MHz. The solid curve of Fig. 4 is a computer fit of R_B^c as a function of inverse temperature to these eight points, which are shown on the graph as bars whose length indicates their uncertainty. To examine how well the model of self-diffusion by small steps fits these data, R_B^c from Eqs. (12) and (25), with D taken from our measurements given in Fig. 1, and the radial distribution integrals I_k evaluated using Eqs. (22) and (23), is also plotted in Fig. 4 as the dashed curve. It is clear from the figure that even with the effect of $g(R)$ included, the simple diffusion model can only be rescued with an unrealistic molecular diameter. Next, the jump diffusion model is examined in Fig. 4 by plotting as open circles R_B^c from Eqs. (31), (25), (22), and (23) with $\langle r^2\rangle/\sigma^2$ taken to be temperature-independent and equal to 0.67, the value obtained in the frequency experiment at 90.71°K. Comparison of these theoretical points with the experimental points shows unusual agreement for this type of measurement. In the inverse temperature range $5.2<10^3/T<11.0/°\text{K}$, this theoretical curve fitted with only one parameter at the low-temperature anchor point fits the experimental points almost as well as the computer fit. At the higher temperatures, the open circles fall below the experimental values. We interpret this to mean that the mean-square flight distance is increasing in this region in the manner shown in Fig. 5. In this figure, the temperature dependence of the value of $\langle r^2\rangle/\sigma^2$ required to fit the theory to our data is plotted. Also shown in Fig. 5 is the temperature dependence of the mean time between diffusive jumps τ, evaluated using Eq. (1), Fig. 1, and the mean-square flight distance just obtained. It is of interest to note that measurements of cold neutron scattering on hydrogeneous liquids[16] have been interpreted as implying diffusive jump times which approach a limiting value of 1×10^{-12} sec at high temperatures.

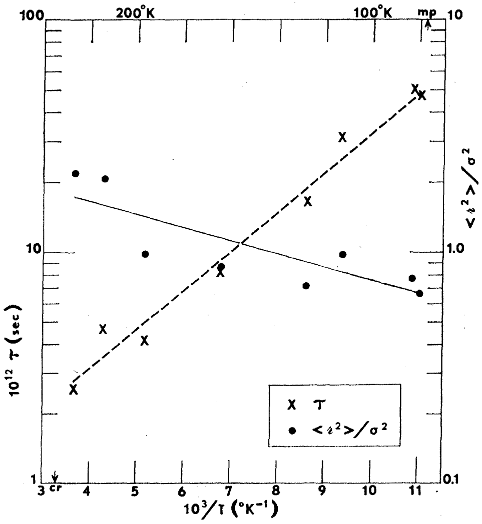

FIG. 5. Temperature dependence of the mean-square flight distance, solid line, and the mean time between diffusive jumps, dashed line, in liquid ethane.

IV. COMPARISON WITH OTHE LIQUID SYSTEMS

It has already been reported[17] that for the other liquids known to us for which reasonably reliable experimental measurements have been made of the intermolecular contribution to relaxation, namely, benzene, methane, and He^3, a jump distance of the order of a molecular diameter will fit the data. With the correction for a realistic $g(R)$ which has been developed since then, the comparison of the theory with the ideal liquid He^3 can be done in a clearer fashion. Beal and Hatton[30] have reported that in liquid He^3 from 0.65 to 4.2°K,

$$R_B=(T_1)^{-1}{}_{\rm bulk}=C_1'\rho/D,$$

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[30] B. T. Beal and J. Hatton, Phys. Rev. 139, A1751 (1965).

where $C_1'=2.6\times10^{-6}$ cm^5/g sec^2 is independent of pressure or temperature, and is known to an uncertainty of 10%. With the aid of Eq. (24), with $\sigma=2.55$ Å (Ref. 31), one can show that these results are compatible with the theory presented in this paper for $\langle r^2\rangle/\sigma^2=0.7\pm0.3$.

V. CONCLUSIONS

A detailed study of intermolecular relaxation in liquid ethane has shown that Torrey's theory of relaxation by translational diffusion with a simple model of jump diffusion and the addition of the effect of the radial distribution function provides an excellent description of this relaxation. The choice of the one adjustable parameter needed to fit the theory to the data, the mean-squared jump distance, then becomes a measurement of this distance. Thus it has been demonstrated that the root-mean-squared flight distance and the mean time between flights of diffusive motion in liquids can be measured from studies of diffusion and nuclear spin relaxation. It has also been shown how the intermolecular contribution to relaxation can be calculated to reasonable accuracy from a knowledge of the density, the self-diffusion constant and the molecular diameter. Therefore, attempts to estimate the intramolecular contribution to relaxation from the total measured relaxation rate[32,33] can now be done more reliably.

ACKNOWLEDGMENTS

The authors are grateful to E. D. Finch for his help with the self-diffusion measurements and to J. Lees for the preparation of our samples.

APPENDIX: FREQUENCY-DEPENDENT SPECTRAL DENSITIES

With the simplification introduced by the partial integration of Eq. (27) yielding Eq. (28), only the expansions of the quantity

$$F=\mathrm{Re}\left[\frac{J_{3/2}(z)H_{3/2}{}^{(1)}(kz)}{(2-i\omega\tau)}\right]=\mathrm{Re}\left[\frac{(2+i\omega\tau)J_{3/2}(z)H_{3/2}{}^{(1)}(kz)}{(4+\omega^2\tau^2)}\right]\qquad\text{(A1)}$$

need be considered, where

$$z=\sigma\beta\quad\text{and}\quad k=1\text{ or }k=R/\sigma,$$

depending upon which term in Eq. (28) we are considering.

It is possible to write $J_{3/2}(z)H_{3/2}{}^{(1)}(kz)$ in an infinite series[34]

$$\tfrac{1}{2}\pi k^{1/2}(2+i\omega\tau)J_{3/2}(z)H_{3/2}{}^{(1)}(kz)=\sum_{p=0}^{\infty}d_pz^p,\qquad\text{(A2)}$$

in which

$$d_p=2(1+iy)C_p+2[(i-y)/k]C_{p+1},\qquad\text{(A3)}$$

with y *defined as*

$$y\equiv\tfrac{1}{2}\omega\tau.$$

The first seven C_p are

$$\begin{aligned}&C_0=0,\\&C_1=-\tfrac{1}{3},\\&C_2=-\tfrac{1}{3}ik,\\&C_3=1/30+\tfrac{1}{6}k^2,\\&C_4=ik(1/30+k^2/18),\\&C_5=-(1/840+k^2/60+k^4/72),\\&C_6=-ik(1/840+k^2/180+k^4/360).\end{aligned}\qquad\text{(A4)}$$

In general, we find

$$\begin{aligned}&\text{odd }p,\quad C_p=\sum_{l=0}^{\infty}a_{2l}b_{(p+1-2l)/2},\qquad\text{real}\\&\text{even }p,\quad C_p=\sum_{l=0}^{\infty}a_{2l+1}b_{[p+1-(2l+1)]/2},\quad\text{imag.}\end{aligned}\qquad\text{(A5)}$$

where

$$\begin{aligned}&a_m=(ik)^m/m!,\\&b_n=[1/(2n)!-1/(2n+1)!](-1)^n.\end{aligned}$$

If now the complex quantities z^p are evaluated[34] and substituted into Eq. (A1) along with Eqs. (A2)–(A4) we find, upon taking the real part,

$$\begin{aligned}F=(y/3\pi k^{3/2})[&1+\tfrac{3}{5}C(5k^2-1)-2\sqrt{3}k^3C^{3/2}y^{3/2}\\&\times(y^{-1}+\tfrac{5}{2}-(15/8)y\cdots)+(6/5)\sqrt{3}C^{5/2}k^5\\&\times(1+k^{-2})y^{5/2}(y^{-1}-\tfrac{5}{2}\cdots)+\cdots],\end{aligned}\qquad\text{(A6)}$$

in which $C=\sigma^2/\langle r^2\rangle$ and terms of higher order than $y^{3/2}$ have been neglected. We wish to write $J_1(\omega)$ only to the leading term in the frequency which is contained in the term $y^{1/2}$; thus, we will henceforth ignore the higher-order terms in y. The equation for the spectral density, Eq. (28), requires the quantities

$$\begin{aligned}A&=\mathrm{Re}\left[\frac{g(\sigma)J_{3/2}(\sigma\beta)H_{3/2}{}^{(1)}(\sigma\beta)}{\sigma^{3/2}(2-i\omega\tau)}\right]\\&\approx\frac{y}{3\pi\sigma^{3/2}}\left[g(\sigma)+\frac{12C}{5}g(\sigma)-2\sqrt{3}C^{3/2}g(\sigma)y^{1/2}\right]\end{aligned}$$

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[31] K. A. Brueckner, *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 70.

[32] W. B. Moniz, W. A. Steele, and J. A. Dixon, J. Chem. Phys. **38**, 2418 (1963).

[33] M. Bloom, *Magnetic Resonance and Relaxation* (North-Holland Publishing Co., Amsterdam, 1967), p. 65.

[34] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Government Printing Office, National Bureau of Standards—National Research Council, Washington, D. C., 1965).

and

$$B=\mathrm{Re}\left[(2-i\omega\tau)^{-1}\int_{\sigma}^{b}R^{-3/2}J_{3/2}(\sigma\beta)H_{3/2}^{(1)}(R\beta)g'(R)dR\right]$$

$$\approx(y\sigma^{3/2}/3\pi)[(1-\tfrac{3}{5}C)S_1+(3C/\sigma^2)S_2-2\sqrt{3}C^{3/2}\sigma^{-3}y^{1/2}S_3],\quad\text{(A7)}$$

where

$$S_1=\int_{\sigma}^{b}R^{-3}g'(R)dR=b^{-3}-\sigma^{-3}g(\sigma)+3I_2,$$

$$S_2=\int_{\sigma}^{b}R^{-1}g'(R)dR=b^{-1}-\sigma^{-1}g(\sigma)+I_1,$$

$$S_3=\int_{\sigma}^{b}g'(R)dR=1-g(\sigma),$$

and the notation of Eq. (13) has been used. Equation (28), written in terms of A and B just defined, gives

$$J_1(\omega)=(16\pi^2n/15\sigma^{3/2}\omega)\{A+B\}.$$

Therefore,

$$J_1(\omega)\approx\frac{8\pi n\tau}{45\sigma^3}\left[\frac{\sigma^3}{b^3}+\frac{3\sigma^3}{b\langle r^2\rangle}\left(1-\frac{\sigma^2}{5b^2}\right)+3\sigma^3I_2+\frac{3\sigma^3}{\langle r^2\rangle}(I_1-\tfrac{3}{5}\sigma^2I_2)-\frac{\sigma^2}{\langle r^2\rangle}\left(\frac{\omega\sigma^2}{D}\right)^{1/2}\right].\quad\text{(A8)}$$

Note that in the limit $\omega/D\propto\omega\tau\rightarrow0$ this gives Eq. (17), the zero-frequency limit of the theory.

A measure of the accuracy of our expansion can be obtained by comparison with Torrey's numerical calculations of $J_1(\omega)$ using the exact form for the limit obtained by setting $b=\sigma$. In this limit, I_1 and I_2 vanish and Eq. (A8) becomes

$$J_1(\omega)\approx\frac{8\pi n\tau}{45\sigma^3}\left[1+\frac{12}{5}\frac{\sigma^2}{\langle r^2\rangle}-\frac{\sigma^2}{\langle r^2\rangle}\left(\frac{\omega\sigma^2}{D}\right)^{1/2}\right].$$

This can be written in the form

$$J_1(\omega)\approx\frac{8\pi n}{15\sigma^3\omega}[f(\alpha,x)]_A,$$

in which the function in brackets is

$$[f(\alpha,x)]_A=\tfrac{2}{3}\alpha x^2(1+1/5\alpha-x/12\alpha),$$

with

$$x=(\omega\sigma^2/D)^{1/2},\quad\alpha=\langle r^2\rangle/12\sigma^2.$$

For our case, $\langle r^2\rangle/\sigma^2\approx1$, it follows that $\alpha=\frac{1}{12}$. Thus,

$$[f(\tfrac{1}{12},x)]_A=(x^2/18)(3.4-x).$$

This expression is the approximation to Torrey's numerical calculations of the exact function $f(\alpha,x)$ given in Table I, p. 966, of his paper. Comparison of $[f(\frac{1}{12},x)]_A$ with $f(\frac{1}{12},x)$ is given in Table I below.

Our largest experimental effect in ethane is when $\omega=2\pi\times73\times10^6$ sec^{-1} and $T=90.71$°K, where $D=0.45\times10^{-5}$ cm^2 sec^{-1}. Taking $\sigma=4.38$ Å, we find $x\approx0.44$, which means that an error of $<1\%$ is made using the expansion.

TABLE I. Numerical comparison of $[f(\alpha,x)]_A$ with Torrey's $f(\alpha,x)$.

x	$f(\frac{1}{12},x)$	$[f(\frac{1}{12},x)]_A$	% Difference
0.4	0.0266	0.0267	0.4
0.6	0.0552	0.0560	1
0.8	0.0890	0.0924	4
1.0	0.1265	0.1333	5