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NMR study of spectral densities over a large frequency range for intermolecular relaxation in liquids: Pair correlation effects

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In order to study the dynamic effects of pair correlation functions on intermolecular translational relaxation in liquids, we have measured the relaxation times T_1 of the protons in neopentane in the presence of di-*t*-butylnitroxide free radicals with concentrations varying up to 6.5×10^{20} paramagnetic centers $\times \text{cm}^{-3}$. Under these conditions, the dominant relaxation mechanism for the resonating protons arises from their interactions with the electronic spins of the free radicals. NMR experiments were performed between 2.2 and 250 MHz and these allowed us to obtain information about the behavior of the relevant spectral densities over a very wide range of frequencies $0 < \omega_s \tau \lesssim 50$, where ω_s is the electronic resonance frequency of the radical and where τ is the translational correlation time. It is shown that a model in which the effects of eccentricity of the spins are included and where the translational motion of the molecules is described by a Smoluchowski diffusion equation, (i.e., taking into account their impenetrability and the nonuniform relative distribution of the molecules calculated in the approximation of Lee and Levesque) gives good agreement with experiment. It is also emphasized that introducing pair correlation effects provides a model without any adjustable parameters which is an advantage compared to a theory of random jumps.

I. INTRODUCTION

Recently, nuclear spin relaxation due to intermolecular magnetic dipole coupling between spins undergoing relative translational diffusion has been extensively studied both from theoretical and experimental points of view. Sholl¹ has reviewed this subject in detail. We are concerned here with the case of nonviscous liquid solutions at room temperature containing paramagnetic molecules used to probe the dynamics of the system. This technique has already been used by several authors.²⁻⁵ In such systems, intermolecular dipolar interaction with the electronic spins of the paramagnetic centers is the only efficient relaxation mechanism for the resonating nuclei. The relevant spectral densities are taken at the $\omega_s \tau \gg \omega_I \tau$ instead of at $\omega_I \tau$ (ω_s and ω_I are the electronic and nuclear angular frequencies and τ is the translational correlation time). Thus, experimental information about the behavior of the spectral densities may be obtained in the range $0 < \omega \tau \lesssim 10^2$.

From the theoretical point of view, three models have essentially been used for calculating the spectral densities in such systems.

(i) Description of the molecular translational diffusion by random flights or "jump diffusion" following the pioneering work of Torrey.⁶ This is in particular the case for the work of Hexem *et al.*⁵ concerning liquid CCl_4 in dilute solutions of tris-(acetylacetonato)

chromium(III). Their study was performed at various temperatures, but only at two given resonance frequencies.

(ii) Description of the molecular diffusion by a continuous Brownian motion. In the simplest approach⁷ the relative translational motion of both kinds of spins is given by a simple truncated Gaussian law which is a solution of the usual diffusion equation. Unfortunately, this Gaussian law is not normalized to unity. To overcome this simple, but erroneous hypothesis, the usual diffusion equation must be solved by correctly taking into account the impenetrability of the molecules.^{2,8} It is then necessary to consider the effects of the eccentricity of the spins which generally are not located at the center of the molecules. In this case, the spectral densities resulting from the intermolecular dipolar coupling between the spins I and S depend on both translational and rotational motions of the molecules.^{9,10} To further improve this description of the dynamics of these molecules, one must consider their averaged radial relative distribution given by the pair correlation function $g_{IS}(R)$. The relative translational motions are then described by probability laws which are solutions of a Smoluchowski equation which takes into account the existence of effective intermolecular forces directly determined by the pair correlation function $g_{IS}(S)$.^{8,11-13}

(iii) The time correlation function characteristic of

the intermolecular dipolar spin relaxation in a liquid solution may also be calculated by a Monte-Carlo diffusive simulation. In this model, we consider a cubic box containing a mixture of a finite number of molecules of the liquid mixture. Only hard-sphere potentials are considered. The time correlation function is evaluated by averaging all the dipolar interactions of the system at successive times, i.e., including many body dynamic effects.¹⁴

In this paper, we are concerned with solutions of nearly spherical molecules of neopentane $C(CH_3)_4$ with paramagnetic free radicals DTBN: di-tertiarybutyl-nitroxide $[(CH_3)_3C]_2NO$. Extensive studies of the ^{13}C relaxation of neopentane have been reported elsewhere.^{3,15} Here we discuss the relaxation times of the 12 equivalent protons of neopentane over a rather large range of resonance frequencies: $2.2 \text{ MHz} < \nu_I < 250.1 \text{ MHz}$. This system has already been studied⁴ at very low proton resonance frequencies $1.4 \text{ kHz} < \nu_I < 2 \text{ MHz}$ in order to determine the relative diffusion constant of both kinds of molecules in this solution.

In the next section, we present our experimental results concerning the proton relaxation times of neopentane vs the DTBN concentration for nine different resonance frequencies. In Sec. III, we derive the "experimental" variation of the relevant spectral densities at the electronic frequency and their behavior is discussed from the theoretical point of view in Sec. IV.

II. EXPERIMENTAL

A. Apparatus

Proton spin-lattice relaxation times T_1 at $\nu_I = 250.1 \text{ MHz}$ and $\nu_I = 100 \text{ MHz}$ were measured with the standard $180-t-90$ pulse sequence using a Bruker WM 250 and a Varian XL 100-15 spectrometer, respectively, as previously described.³ Measurements between 75 and 2.2 MHz were made on a Bruker CXP spectrometer using the Freeman-Hill¹⁶ modification of the inversion-recovery method. The values reported are averages of at least four separate determinations. All measurements were made at $T = 303 \pm 0.5 \text{ K}$. The method of preparation of the samples has been described previously.³ The number density N_S of paramagnetic centers DTBN was varied in the range $0 < N_S < 6.5 \times 10^{20} \text{ cm}^{-3}$.

B. Results

In Fig. 1, we give the variation of the measured relaxation times of the protons of neopentane vs the number density N_S of DTBN free radicals for nine different proton resonance frequencies: $\nu_I = 2.217, 4, 10.15, 25.15, 37.5, 60, 75, 100.06$, and 250.13 MHz . As expected³ we obtain linear variations of the relaxation rates:

$$\frac{1}{T_1} = \alpha + \beta N_S, \quad (1)$$

where α is the proton relaxation rate of neopentane in the absence of free radicals ($\alpha = 0.06 \text{ s}^{-1}$). Here βN_S represents the dipolar intermolecular relaxation rate between the protons of neopentane and the electronic spins $S = \frac{1}{2}$ of the DTBN molecules. In Fig. 1 the full lines represent the linear laws expressed by Eq. (1) obtained by a least-squares fit. The slopes β which characterize

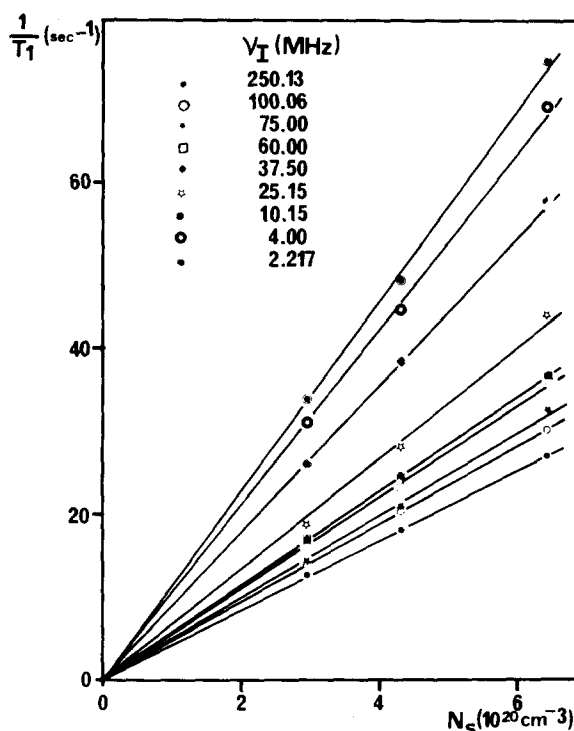


FIG. 1. Experimental values of the observed relaxation rates $1/T_1$ of the 12 equivalent protons of neopentane vs the number density N_S of DTBN molecules at $T = 303 \text{ K}$, for nine different resonance frequencies. Different symbols are used for each frequency ν_I . Straight lines represent the linear laws expressed by Eq. (1).

the magnitude of the intermolecular relaxation process are given in the second column of Table I for the nine proton frequencies ν_I .

III. FREQUENCY DEPENDENCE OF THE SPECTRAL DENSITIES

A. Physical data

We give here the various geometrical parameters (see Fig. 2) and the physical constants relevant to this study. Denoting by I and S the spins of the protons of neopentane and of the free electron of DTBN, we have

$$\gamma_I = 2.675 \times 10^4 \text{ rad s}^{-1} \text{ G}^{-1},$$

$$\gamma_S = 1.76 \times 10^7 \text{ rad s}^{-1} \text{ G}^{-1}.$$

The radius a_I of the neopentane molecule approximated to a hard sphere was estimated from its van der Waals volume^{3,17}

$$a_I = 2.8 \times 10^{-8} \text{ cm}.$$

The distance between the protons and the central carbon of the neopentane molecule is 2.16 \AA . However, due to the very fast rotation of the methyl group, the effective distance which must be used in order to take into account the effects of eccentricity of the protons in the intermolecular relaxation^{9,10} is the projection of the true distance on the closest C-C bond. We thus obtain

$$\rho_I = 1.89 \times 10^{-8} \text{ cm}.$$

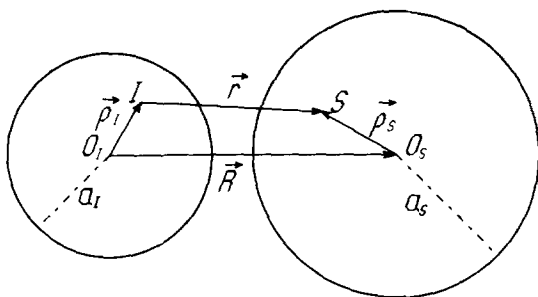


FIG. 2. Characteristic parameters of the intermolecular dipolar interaction between the spins I and S .

The DTBN molecule looks like a roughly spherical ellipsoid^{18,19} of which the hard sphere mean radius is³

$$a_s = 3.4 \times 10^{-8} \text{ cm}.$$

Thus, the minimum distance of approach of the centers of a neopentane molecule and of a DTBN molecule (both considered as hard spheres) is

$$b = 6.2 \times 10^{-8} \text{ cm}. \quad (2)$$

A simple study of the geometry of a DTBN molecule, using a compact model, shows the presence of a slight concavity near the N-O bond. So the true minimum distance of approach of the centers of neopentane and DTBN molecules can be as small as $b_e = 5.0 \times 10^{-8} \text{ cm}$. As the effects of eccentricity of the spins play an important role only when the molecules are in close contact, it is clear that the minimum distance of approach which must be considered for these effects is b_e instead of b .

The average position of the free electron in DTBN is not known accurately. However recent experiments using polarized neutrons have shown that it is localized on the N-O bond.²⁰ This means that the distance ρ_s between the spin S and the center of the DTBN molecule is

$$\rho_s = (1.6 \pm 0.3) \times 10^{-8} \text{ cm}.$$

The following values of the parameters of eccentricity of the spins I and S have been taken in our calculations:

$$\left(\frac{\rho_I}{b_e}\right)^2 = 0.144; \quad \left(\frac{\rho_S}{b_e}\right)^2 = 0.102. \quad (3)$$

The relative translational diffusion constant D of neopentane and DTBN molecules may be determined from the low frequency values of the intermolecular relaxation rate ($1/T_1^S$) of the protons in neopentane, due to the DTBN electronic spins S . We have⁴

$$\frac{1}{T_1^S}(\nu_I) = \frac{1}{T_1^S}(0) - B \sqrt{2\pi\nu_I}, \quad (4)$$

where the constant B is model independent,^{1,4,10} which is a property of the three-dimensional character of the molecular diffusion in the sample. It is related to the relative diffusion constant D of our solution by the relation⁴

$$B = \frac{4.45 \times 10^{-30}}{D^{3/2}} N_s. \quad (5)$$

From the values of $1/T_1$ measured at $\nu_I = 2.217 \text{ MHz}$

and $\nu_I = 4 \text{ MHz}$, where the law expressed by Eq. (4) is valid, it is easy to deduce the following value of D :

$$D = 7.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}. \quad (6)$$

This value is in agreement with a previous determination⁴ of D based on the same principle but with measurements of the proton relaxation rates at very low frequencies ($1.4 \text{ kHz} < \nu_I < 2 \text{ MHz}$) and for only one DTBN number density $N_s = 0.51 \times 10^{20} \text{ cm}^{-3}$: $D = 7.3 \pm 0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. However, our present determination of D expressed by Eq. (6) is more accurate because the main source of error arises from the uncertainty in N_s . Here, we use the slopes of the curves shown on Fig. 1 which are obtained by a least-squares fit for five different concentrations.

Incidentally we may note that as the absolute translational diffusion constant D_I^t of neopentane at 303 K is known²¹ to be $D_I^t = 4.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, we may deduce the absolute diffusion constant of the DTBN radicals in our solution at the same temperature: $D_S^t = D - D_I^t = 3.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Using the value of b given by Eq. (2), we may introduce a translational correlation time τ defined by

$$\tau = \frac{b^2}{D} = 5.0 \times 10^{-11} \text{ s}. \quad (7)$$

Finally, the following values of the rotational diffusion constants of neopentane and DTBN molecules have been estimated³

$$D_I^r = 3.0 \times 10^{11} \text{ s}^{-1}; \quad D_S^r = 1.75 \times 10^{11} \text{ s}^{-1}.$$

B. Experimental relaxation times and spectral densities

In our liquid solution of neopentane with DTBN free radicals, the dominant dipolar intermolecular relaxation rate $1/T_1^S$ of the protons I due to the presence of the electronic spins S is given by^{7,2,12}

$$\frac{1}{T_1^S} = \beta N_s = \frac{2}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \times [j_2(\omega_I - \omega_S) + 3j_2(\omega_I) + 6j_2(\omega_I + \omega_S)]. \quad (8)$$

We recall that the function $j_2(\omega)$ is the Fourier transform

$$j_2(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} g_2(t) \exp(-i\omega t) dt \quad (9a)$$

of the correlation function

$$g_2(t) = \langle f_2^{(q)}[r(0)] \times f_2^{(q)*}[r(t)] \rangle, \quad (9b)$$

which is independent of the index q for an isotropic medium. The

$$f_2^{(q)}(r) = r^{-3} Y_{2q}(\theta, \varphi) \quad (-2 < q < +2) \quad (9c)$$

are random functions of the relative position $r = (r, \theta, \varphi)$ of two interacting spins I and S (see Fig. 2).

Now it is convenient to introduce¹² a dimensionless spectral density $\bar{j}_2(\omega\tau)$ defined by

$$j_2(\omega) = \frac{N_s \tau}{\pi b^3} \bar{j}_2(\omega\tau), \quad (10)$$

where b and τ are given by Eqs. (2) and (7). Using the physical data of the previous section and taking into account the fact that $\omega_I \ll \omega_S$, Eq. (8) reduces, for $N_S = 10^{20} \text{ cm}^{-3}$, to

$$10^{20}\beta = 6.49[3\bar{j}_2(\omega_I\tau) + 7\bar{j}_2(\omega_S\tau)]. \quad (11)$$

We know^{1,10} that for $\omega\tau \ll 1$,

$$\bar{j}_2(\omega\tau) = \bar{j}_2(0) - \frac{\sqrt{2}\omega\tau}{18}. \quad (12)$$

For $0 < \nu_I < 250 \text{ MHz}$, we have $0 < \omega_I\tau < 0.16$, so that $\bar{j}_2(\omega_I\tau)$ in Eq. (11) may always be replaced by expression (12).

The value of $j_2(0)$ has been determined in the same way as D in the previous subsection: Using the relation in Eq. (4) and the experimental values of $(1/T_1^S)$ measured at $\nu_I = 2.17$ and 4 MHz , we obtain $(1/T_1^S)(0) = 13.6$ for $N_S = 10^{20} \text{ cm}^{-3}$. Then using Eq. (11) for $\omega_I = \omega_S = 0$, we obtain

$$\bar{j}_2(0) = 0.210. \quad (13)$$

In the above determination, the validity of relations (4) or (12) at $\nu_I = 4 \text{ MHz}$ for which $\omega_S\tau = 0.83$ could be questionable. But we checked with our theoretical models that these relations were still valid within an accuracy of the order of 1%.

Finally from Eqs. (11) and (12), we obtain the "experimental" spectral densities $\bar{j}_2(\omega_S\tau)$ given by

$$j_2(\omega_S\tau) = \frac{10^{20}\beta}{45.4} - \frac{3}{7}\bar{j}_2(0) + \frac{\sqrt{2}}{42}\sqrt{\omega_I\tau}. \quad (14)$$

In the right-hand side of Eq. (14), the first term is given by experiment, the second by relation (13), and the third by Eq. (7). The numerical values of $\bar{j}_2(\omega_S\tau)$ are given in the fourth column of Table I for the various proton resonance frequencies and we show in Fig. 3 the variation of $\frac{27}{4}\bar{j}_2(\omega_S\tau)$ vs $\sqrt{\omega_S\tau}$. The factor $\frac{27}{4}$ is introduced because in the simplest theoretical model,^{2,8} $\bar{j}_2(0) = \frac{4}{27}$ (see the next section).

With this procedure, we obtain the experimental variation of $\bar{j}_2(\omega_S\tau)$ for $0 < \omega_S\tau \lesssim 50$. We must now

TABLE I. Experimental values of the intermolecular relaxation rate $(1/T_1^S) = 10^{20}\beta$ for $N_S = 10^{20} \text{ cm}^{-3}$ obtained from the least-squares fit of Fig. 1., $\omega_S\tau$ (obtained by taking $\tau = 5.0 \times 10^{-11} \text{ sec}$), and experimental spectral densities $\bar{j}_2(\omega_S\tau)$ from Eq. (14), for neopentane in a liquid solution with DTBN free radicals at 303 K at nine different proton resonance frequencies ν_I .

$\nu_I \times 10^6 \text{ (Hz)}$	$10^{20}\beta \text{ (s}^{-1}\text{)}$	$\omega_S\tau$	$\bar{j}_2(\omega_S\tau)$
0	13.6	0	0.210
2.217	11.47	0.457	0.164
4	10.61	0.825	0.145
10.15	8.90	2.094	0.108
25.16	6.69	5.19	0.061
37.5	5.98	7.74	0.046
60	5.52	12.4	0.036
75	4.97	15.5	0.025
100	4.70	20.6	0.020
250	4.20	51.6	0.012

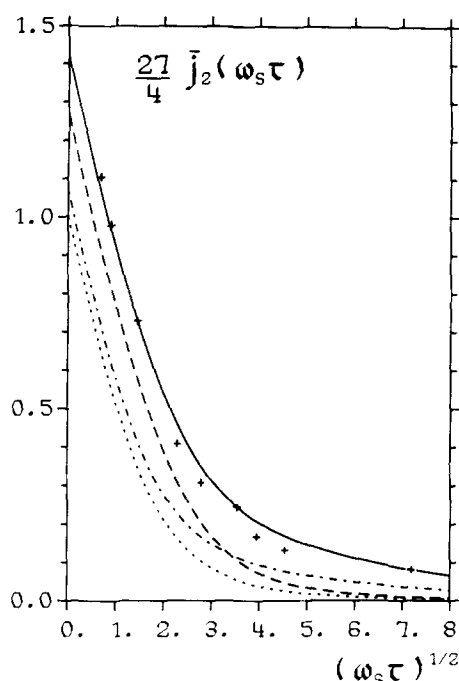


FIG. 3. Variation of the reduced spectral density $(27/4)\bar{j}_2(\omega_S\tau)$ vs $(\omega_S\tau)^{1/2}$ for a liquid mixture of neopentane molecules with DTBN free radicals at $T = 303 \text{ K}$. Experimental values deduced from Eq. (14) and Table I (+) and theoretical models: (A_d) usual diffusion equation (···); (A_e) usual diffusion equation and effects of eccentricity (— · — · —); (F_d) Smoluchowski diffusion equation with pair correlation function (— — —); (F_e) Smoluchowski diffusion equation with pair correlation function and effects of eccentricity (continuous line).

interpret this variation using our theoretical models.

Remark: At the highest concentration, one can ask if spin exchange between free radicals could not cause electron spin relaxation times to be of the same order of magnitude as the correlation times τ for translation. The relevant correlation function would be⁵ $g(t) = \exp(-t/\tau_S)g_2(t)$, where $\exp(-t/\tau_S)$ represents the correlation between two values of the paramagnetic spin taken at two times separated by time t and $g_2(t)$ is given by Eq. (9b). However, as no deviations from the law expressed by Eq. (4) are found⁴ down to $\omega_I\tau \approx 10^{-6}$, i. e., down to $\omega_S\tau \approx 10^{-3}$ for $N_S = 0.5 \times 10^{20} \text{ cm}^{-3}$, an upper limit of $(\tau/\tau_S) = 0.01$ is obtained for that concentration. This means that even at the highest concentrations ($N_S = 6.10^{20} \text{ cm}^{-3}$), $(\tau/\tau_S) < 0.1$. As we are interested by the variation of $\omega_S\tau$ in a range up to $\omega_S\tau \approx 50$, this effect is negligible.

IV. THEORY

A. Simple diffusion model

We consider first a very simple theory in which the random translational motions of the molecules are described by the usual diffusion equation

$$\frac{\partial}{\partial t} \rho(\mathbf{R}_0, \mathbf{R}, t) = D \nabla_{\mathbf{R}}^2 \rho(\mathbf{R}_0, \mathbf{R}, t), \quad (15a)$$

where $\rho(\mathbf{R}_0, \mathbf{R}, t)$ is the conditional probability satisfying the hard sphere condition

$$\frac{\partial}{\partial R} \rho(\mathbf{R}_0, \mathbf{R}, t) \Big|_{R=b} = 0. \quad (15b)$$

In the model called (A_c),^{2,8} we neglect the eccentricity of the spins I and S assumed to be at the center of the molecules. The time correlation function $g_2(t)$ defined by Eq. (9b), written here $G_2(t)$ because r is replaced by \mathbf{R} , is given by

$$G_2(t) = N_S \iint g(R_0) \rho(\mathbf{R}_0, \mathbf{R}, t) f_2^{(a)}[\mathbf{R}(0)] f_2^{(a)*}[\mathbf{R}(t)], \quad (16)$$

$$J_2(\omega\tau) = \frac{4 + \frac{5}{\sqrt{2}} (\omega\tau)^{1/2} + \omega\tau}{27 + 27\sqrt{2}(\omega\tau)^{1/2} + 27\omega\tau + 9\sqrt{2}(\omega\tau)^{3/2} + \frac{16}{3}(\omega\tau)^2 + \frac{4\sqrt{2}}{3}(\omega\tau)^{5/2} + \frac{1}{3}(\omega\tau)^3}. \quad (17)$$

For $\omega\tau \ll 1$ we obtain

$$J_2(\omega\tau) = \frac{4}{27} - \frac{\sqrt{2}\omega\tau}{18}. \quad (17a)$$

By comparison with the general Eq. (12), we obtain $\bar{J}_2(0) = \frac{4}{27} = 0.148$ instead of 0.210 [see Eq. (13)].

In Fig. 3 we have drawn the variation of $(\frac{4}{27}) \bar{J}_2(\omega_S\tau)$ vs $\omega_S\tau$ with this model and we observe a large discrepancy with experiment.

B. Effects of eccentricity

The next step is to take into account the effects of eccentricity of the spins. In this model called (A_e),⁹ $\bar{J}_2(\omega\tau)$ is obtained from Eqs. (9) and (10) by assuming that the translational and rotational motions of the molecules are stochastically independent and $\rho(\mathbf{R}_0, \mathbf{R}, t)$ obeys the same Eqs. (15a) and (15b) as the A_c model.

Introducing the time correlation functions

$$G_I(t) = \langle F_I^{(a)}[\mathbf{R}(0)] \times F_I^{(a)*}[\mathbf{R}(t)] \rangle \quad (18a)$$

of the random functions

$$F_I^{(a)}(\mathbf{R}) = R^{-(l+1)} Y_{l,a}(\Theta, \Phi), \quad (18b)$$

where $\mathbf{R}(R, \Theta, \Phi)$ is the vector joining the centers of the molecules, it was shown⁹ that $\bar{J}_2(\omega\tau)$ may be expanded as a series in ascending powers of the parameters of eccentricity defined by Eq. (3):

$$\bar{J}_2(\omega_S\tau) = \text{Re}[\bar{G}_2(i\omega\tau)] \times \left[1 + \sum_{\lambda=1}^{\infty} \sum_{\lambda=0}^l C_{l,\lambda}(\omega\tau, D_I^r\tau, D_S^r\tau) \left(\frac{\rho_I}{b_e}\right)^{2\lambda} \left(\frac{\rho_S}{b_e}\right)^{2(l-\lambda)} \right], \quad (19a)$$

with

$$C_{l,\lambda}(\omega\tau, D_I^r\tau, D_S^r\tau) \equiv \frac{1}{24} \frac{(2l+4)!}{(2\lambda+1)! [2(l-\lambda)+1]!} \times \frac{\text{Re}\{\bar{G}_{l+2}[i\omega\tau + \lambda(\lambda+1)D_I^r\tau + (l-\lambda)(l-\lambda+1)D_S^r\tau]\}}{\text{Re}[\bar{G}_2(i\omega\tau)]}. \quad (19b)$$

The functions $\bar{G}_l(\sigma\tau)$ appearing in Eqs. (19a) and (19b) are given by

$$\bar{G}_l(\sigma\tau) = \frac{b^{2l-1}}{N_S\tau} \bar{G}_l(\sigma), \quad (19c)$$

where R is the distance between the centers of a given pair of molecules of neopentane and DTBN (see Fig. 2). This model assumes a uniform equilibrium distribution of the molecules

$$g(R_0) = 1 \quad \text{if } R_0 > b, \\ g(R_0) = 0 \quad \text{if } R_0 < b. \quad (16a)$$

We obtain by solving Eq. (15) the exact expression of $J_2(\omega\tau)$, the symbol J_2 replacing j_2 for the same reason as above:

where the $\bar{G}_l(\sigma)$ are the Laplace transforms

$$\bar{G}_l(\sigma) = \int_0^\infty G_l(t) e^{-\sigma t} dt \quad (19d)$$

of the correlation functions $G_l(t)$ defined by Eqs. (18a) and (18b).

Model (A_e) is slightly better than model (A_c) leading to a value of $\bar{J}_2(0) = 0.158$. Furthermore, the effects of eccentricity appear to be more important for the large values of $\omega_S\tau$, but this model is not sufficient to describe the experimental variation of $\bar{J}_2(\omega_S\tau)$ correctly.

C. Local molecular order and effects of eccentricity

We now consider a more realistic model, denoted F_e ,¹² in which we take into account the nonuniform equilibrium distribution of the molecules.

In this theory, the conditional probability $\rho(\mathbf{R}_0, \mathbf{R}, t)$ obeys the Smoluchowski equation

$$\frac{\partial}{\partial t} \rho(\mathbf{R}_0, \mathbf{R}, t) = D \nabla_{\mathbf{R}} \cdot \left[\nabla_{\mathbf{R}} \rho(\mathbf{R}_0, \mathbf{R}, t) + \frac{1}{k_B T} \rho(\mathbf{R}_0, \mathbf{R}, t) \nabla_{\mathbf{R}} V(R) \right], \quad (20a)$$

where the local effective potential $V(R)$ is related to the radial distribution $g_{IS}(R)$ by

$$\log g_{IS}(R) \equiv - \frac{V(R)}{k_B T}. \quad (20b)$$

Here the reflecting boundary conditions (15b) must be rewritten as

$$\mathbf{R} \cdot \left[\nabla_{\mathbf{R}} \rho(\mathbf{R}_0, \mathbf{R}, t) + \frac{1}{k_B T} \rho(\mathbf{R}_0, \mathbf{R}, t) \nabla_{\mathbf{R}} V(R) \right] \Big|_{R=b} = 0. \quad (20c)$$

Equation (20a) is constructed in such a way that its solutions $\rho(\mathbf{R}_0, \mathbf{R}, t)$ satisfy the detailed balance principle expressed by

$$g_{IS}(R_0) \rho(\mathbf{R}_0, \mathbf{R}, t) = g_{IS}(R) \rho(\mathbf{R}, \mathbf{R}_0, t). \quad (21)$$

If we include simultaneously in our model the effects of eccentricity of the spins, the spectral densities $\bar{J}_2(\omega\tau)$ are still given by Eqs. (19a), (19b), (19c), and (19d) but the correlation function $G_I(t)$ defined by Eqs. (18a) and (18b) becomes

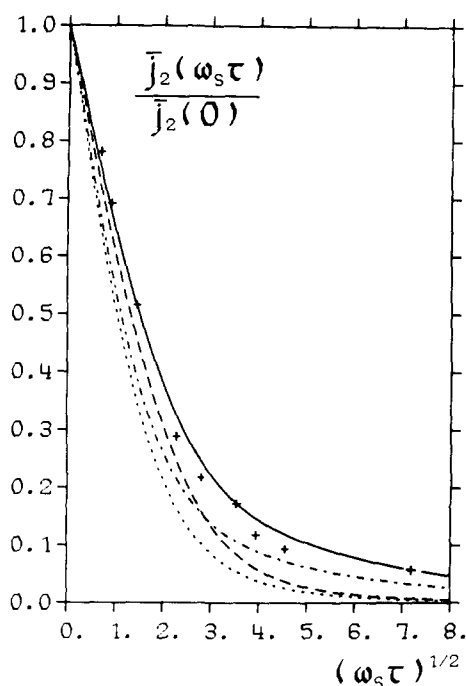


FIG. 4. Variation of the ratio $\bar{j}_2(\omega_s \tau) / \bar{j}_2(0)$ vs $(\omega_s \tau)^{1/2}$ for a liquid mixture of neopentane molecules with DTBN free radicals at $T=303$ K. Experimental values (+) and theoretical models: (A_c ···); (A_e — · — ·); (F_c — — —); (F_e continuous line).

$$G_I(t) = N_S \iint g_{IS}(R_0) \rho(\mathbf{R}_0, \mathbf{R}, t) F_I^{(a)}(\mathbf{R}_0) F_I^{(a)*}(\mathbf{R}) d^3 \mathbf{R}_0 d^3 \mathbf{R}, \quad (22)$$

where $g_{IS}(R)$ is the pair correlation function introduced in Eq. (20). This function was calculated in the approximation of Lee and Levesque.²² These authors have evaluated the partial radial distributions $g_{ij}(R)$ for various binary liquid mixtures of hard spheres by Monte Carlo simulation. They have shown that each distribution $g_{ij}(R)$ may be written to good approximation as an analytical solution of the Percus-Yevick equation^{23,24} derived by Lebowitz²⁵ and Leonard *et al.*²⁶ to which must be added a short range oscillating corrective term.

A typical pair correlation function $g_{IS}(R)$ for a liquid mixture of neopentane with DTBN has been given in Ref. 15.

The computation of the spectral density $\bar{j}_2(\omega_s \tau)$ is essentially based on automated calculations of the various derivatives entering the expression of $g_{IS}(R_0)$ and on finite difference methods for solving the Smoluchowski equation.^{8,12,27}

The corresponding variation of $\bar{j}_2(\omega_s \tau)$ as a function of $(\omega_s \tau)^{1/2}$ is shown in Fig. 3. It is seen that a rather good agreement with the experimental spectral densities is obtained. It must be pointed out that we use only the physical data of Sec. III and that there is *no adjustable* parameter in this model.

For the sake of completeness we also show in Fig. 3, the results of the model called (F_c) in which the pair correlation effects are taken into account but the effects of eccentricity are neglected. One can see that at

low frequencies, the results are intermediate between the models (A_c), (A_e) on one side and the right model (F_e) on the other side but at higher frequencies, the spectral densities obtained with this model are much too weak. Thus pair correlation effects cannot alone explain the experimental behavior of the spectral densities.

Finally, as there is a weak uncertainty in the experimental value of $\bar{j}_2(0)$ given by Eq. (13) and as we are mainly interested in the variation of the spectral densities with $\omega_s \tau$, we show in Fig. 4 the variation of $\bar{j}_2(\omega_s \tau) / \bar{j}_2(0)$ obtained from experiment [Eq. (14)] and from the models (A_c), (A_e), (F_c), and (F_e) previously described. The improvement brought by simultaneous introduction of pair correlation functions and of the effects of eccentricity is clear.

D. Monte Carlo simulation

The time correlation function characteristic of the intermolecular dipolar spin relaxation in our liquid solution has also been calculated by a Monte Carlo diffusive simulation. We worked on a mixture of 97 neopentane molecules with 11 DTBN molecules in a cubic box of which the size was calculated in such a way as to respect the true packing factor of the solution. The simulation process in order to obtain the random small displacements of the molecule and consequently the different configurations at various times is described in detail in Ref. 14. Neglecting the effects of eccentricity, the correlation function obtained by this process was shown to be the same (within the statistical fluctuations) as the function $G_2(t)$ obtained by solving the Smoluchowski equation with the pair correlation function of Lee and Levesque.²²

V. DISCUSSION

By introducing free radicals with different concentrations in our solution, we have been able to obtain accurate information about the spectral densities characteristic of the dipolar magnetic interactions between the protons and the electronic spins over a large range of values of $\omega_s \tau$: $0 < \omega_s \tau \leq 50$. For higher values of $\omega_s \tau$, $\bar{j}_2(\omega_s \tau)$ becomes too small compared to $\bar{j}_2(0)$ and cannot be determined by this method. Other techniques like nuclear dynamic polarization should be used.²⁸ The molecular dynamics of the liquid are very well described by a diffusive process using the Lee and Levesque approximation for the pair correlation function.²² This result is extremely interesting: In their work on CCl_4 with chromium acetyl-acetonate molecules, Hexem *et al.*⁵ used a jump diffusion model for translational motions with jump distances comparable to the diameter of the solvent molecules. This was necessary because the molecular local order of the molecules was neglected. However, we have shown in our example which is very similar, that a description of the translational motions by small jumps, i.e., by using a diffusion equation, is possible if pair correlation functions are introduced. This may be understood easily in the following way. The simple model (A_c) with Fick's law (15a) for diffusion leads to a value of $\bar{j}_2(0)$ which is too weak as can be seen

in Figs. 3 or 4. The pair correlation function $g_{TS}(R)$ increases the probability of close contact of the interacting molecules and thus the correlation function $g_2(t)$. Consequently, $\bar{f}_2(0)$ is increased and this effect is also considerably enhanced by the effects of eccentricity.^{12,13} On the other hand, with a jump model with uniform equilibrium distribution of the molecules, it is necessary to increase considerably the jump distances in order to increase $\bar{f}_2(0)$ and to fit the values of the relaxation times.

Another point must be mentioned. The description of translational diffusion with pair correlation functions gives a good description of the collective molecular motions in the liquid. This was shown by our simulation process including the many body effects for a liquid solution with a packing factor $\eta = 0.45$. For higher values of η some discrepancies between the description by the Smoluchowski diffusion equation and the Monte Carlo simulation could arise but this point has not yet been studied.

As a conclusion, we have seen that the model (F_0) is extremely successful for describing translational motions of nonviscous liquids at room temperature and we believe that it is the most sophisticated model presently available in the framework of a description by a diffusion equation. It must also be noted that for this model, the very simple $\omega^{1/2}$ law expressed by Eq. (12) is valid in the range $0 < \omega_s \tau < 1$ with an accuracy of 1% and not only for $\omega_s \tau \ll 1$. This remark allows us to extend the range of application of the low frequency nuclear relaxation method for determining the diffusion constants.⁴

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