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Effects of eccentricity on nuclear magnetic relaxation by intermolecular dipole-dipole interactions: ^{13}C relaxation of neopentane

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In order to study the eccentricity effects on the nuclear magnetic relaxation by intermolecular dipole-dipole interactions, we measured the relaxation times T_1 of the center and off-center ^{13}C nuclei in neopentane $\text{C}(\text{CH}_3)_4$. To eliminate a competition between several relaxation mechanisms, mainly with the protons, di-*t*-butylnitroxide free radicals were included with concentrations varying up to 5.6×10^{20} paramagnetic centers $\times \text{cm}^{-3}$. Under these conditions, the dominant relaxation mechanism for the resonating ^{13}C nuclei spins arises from their interactions with the electronic spins of the free radicals. A difference of 15% between the relaxation times of the central ^{13}C and of the off-center carbons is observed. These results are partially interpreted by using the spectral densities $j_2(\omega)$ resulting from translational and rotational motions as established in our previous work. It is shown that pair correlation effects must also be taken into account to improve the fit with the experimental data.

I. INTRODUCTION

Recently considerable interest has been shown in the nuclear magnetic relaxation of spin carrying nuclei in liquids. This is a powerful method of investigation for understanding the dynamical effects of molecules. Since the pioneering work of Bloembergen¹ it is known that when the spins under consideration are coupled by the magnetic dipolar interaction, the relaxation times are simply expressed in terms of the spectral densities, which are the Fourier transforms of the correlation functions of $r^{-3}Y_{2,q}(\theta, \phi)$ where r , θ , ϕ are the coordinates of the vector joining the two coupled spins. The spectral densities are usually evaluated by assuming that the molecules have continuous Brownian translational and rotational motions as described by the solutions of the usual diffusion equations.²

In a previous study³ we improved the treatment of the translational diffusion motion of the molecules by correctly taking into account their impenetrability. This model, which is valid for spherical molecules where the spins are at the center of the molecule, was then extended⁴ to the more general case where the spins are off center. In the latter case, the spectral densities resulting from the intermolecular coupling depend on both the translational and rotational motions of the molecules. This model has shown the importance of the effects of eccentricity.

Harmon and Muller⁵ were the first to introduce pair correlation functions to consider a nonuniform relative

radial distribution of the spherical molecules in equilibrium. But in their treatment, they used a description of the translational motion leading to a uniform radial distribution of the molecules in the long-time limit. This was shown by Hwang and Freed⁶ who greatly improved this model by describing the relative translational motions by the Smoluchowski equation. In this approach, the effective forces acting on the molecules are derived from an effective potential directly correlated with the pair correlation function. However, this theory may only be applied to monoatomic liquids or to interacting spins located at the center of the molecules approximated as rigid spheres.

The effects of eccentricity of the spins were first studied by Hubbard,⁷ assuming a uniform spin distribution and a translational motion of the molecules described by a diffusion equation; however, the treatment of the boundary conditions was incorrect. Furthermore, Hubbard's calculations were done only for nuclei in identical molecules and for $\omega\tau \ll 1$, ω being the Larmor frequency of the nuclei and τ the translational correlation time. Zeidler⁸ has also studied the effects of eccentricity, taking into account the nonuniform distribution of the molecules, but this author has used the approximate classical solution of the diffusion equation which is not valid, particularly when $\omega\tau \gg 1$.^{3,6} Furthermore, his expressions of the spectral densities are given in terms of some coefficients for which there is little information, even in the extreme narrowing case $\omega\tau \ll 1$.

Recently we have extended the general model of Hwang and Freed to the case of polyatomic molecules in which

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the interacting spins are almost always off center. In order to include the effects of eccentricity, we have taken into account the rotation of the molecules and the pair correlation effects on their translational diffusion. General formulas allowing an explicit calculation of the relevant spectral densities have been obtained by using the Verlet and Weiss¹⁰ pair correlation function. The parameters involved in these expressions are the radii of the molecules, the distance of the interacting spins from the center of their own molecule, the translational and rotational diffusion constants and the number density of the molecules in the liquid. It must be underlined that the spectral densities were derived for arbitrary eccentricities of the interacting spins and for all values of $\omega\tau$ compatible with a diffusion equation $0 < \omega\tau < 10^2$. To our knowledge, our formulas^{4,9} are the only available expressions for this kind of situation. In this work, the nuclear spins being coupled with electronic spins, we shall have to evaluate the spectral densities for the electronic frequency ω_s , i. e., for values $\omega_s\tau \sim 20$.

Our model was first used⁹ to calculate the relevant spectral density $j_2(\nu_p)$ and the proton intermolecular relaxation rate of benzene and some of its monohalogen derivatives under a pressure up to 2 kbar, as a function of the proton resonance frequency ν_p .^{11,12} From these calculations it has been possible⁹ to estimate the relative importance of the eccentricity effects and of the nonuniform equilibrium distribution of the molecules. Our calculations show clearly that both these effects have an increasing magnitude with frequency. However, as the only available data were obtained at a fixed frequency $\nu_0 = 60$ MHz, it was not possible to check the accuracy of our theoretical predictions. Furthermore, the two effects of interest in the theory were only approached in an indirect way.

In order to obtain more direct experimental evidence of the effects of eccentricity on the intermolecular spin relaxation rate in polyatomic molecules, we selected neopentane $\text{C}(\text{CH}_3)_4$, which is approximately spherical and possesses ^{13}C nuclei with different eccentricities.

The nuclear magnetic resonance signals of ^{13}C isotopes from the central and the four equivalent off-center sites of the molecule are easily distinguished as they show a chemical shift difference of 3.5 ppm. A large difference in the relaxation rates of the two kinds of ^{13}C is observable in neat neopentane, but the effects of eccentricity on the ^{13}C intermolecular interactions cannot be easily separated because several competing relaxation mechanisms have to be taken into account, i. e., spin rotational effects and dipolar intra- and intermolecular interactions with the protons. To overcome this problem, we studied the ^{13}C relaxation of neopentane in the presence of DTBN, the paramagnetic free radical, di-tert-butyl nitroxide $[(\text{CH}_3)_3\text{C}]_2\text{NO}$. The inclusion of this free radical in relatively high concentration (5%–12% of the number of molecules) provides an efficient intermolecular dipolar relaxation mechanism which renders all the other mechanisms negligible.

In the next section, we present experimental results for this system. They provide direct evidence of the effects of eccentricity on the dipolar intermolecular

relaxation. It must be noted that these effects are also enhanced by the presence of electronic spins because the relevant frequency in some of the spectral densities will be the electronic instead of the nuclear resonance frequency. These results will be discussed from a theoretical point of view in Sec. III.

II. EXPERIMENTAL

A. Apparatus and procedure

^{13}C spin-lattice relaxation times T_1 were measured with the standard $180-\tau-90$ pulse sequence using a Varian XL-100-15 spectrometer operating at a frequency of 25.16 MHz (which corresponds to a frequency of 100.01 MHz for the proton). Field frequency stabilization was achieved using the ^{19}F external lock capability of the system. ^{13}C N. M. R. spectra were obtained in the Fourier transform mode with proton noise decoupling. The temperature was regulated by using the standard Varian temperature unit and measured with a thermocouple before and after each experiment. (For monitoring the experiments, an Informatek Matek-1026 data system with 64×10^3 bytes core memory, a hard disk and a magnetic tape unit was connected to the spectrometer. Modifications of the Varian software were made to allow acquisition and Fourier transformation of the signal up to 16×10^3 points and to permit temporary storage of the data for twenty different values of τ in the pulse sequence.

Neopentane was obtained from Fluka A. G. and was purified by fractionation on a vacuum line. DTBN was obtained from Lancaster Synthesis Ltd. and used without further purification. In order to confine the sample within the NMR detection coil, special cylindrical cells (" T_1 cells" Wilmad No. 529 E-12) were used. Samples with different concentrations of DTBN were prepared by weighing the amount of radicals in the cell and then condensing the required amount of neopentane from the vacuum line. The cells were then sealed *in vacuo* as near the reservoir as possible to prevent reflux in the capillary part of the cell and to minimize the contribution of the gaseous phase to the relaxation. It may be noted that, at the experimental temperature $T = 303^\circ\text{K}$, the vapor pressure of liquid neopentane does not exceed 3 bar.¹³ Under these conditions, the pressure effects are negligible.

Each point of the curve giving the relaxation rate versus the DTBN concentration was obtained from a least square fit of an exponential with the values of the ^{13}C magnetization for at least fifteen values of τ in the pulse sequence. Furthermore, each determination was repeated four times and the corresponding T_1 values averaged.

B. Results

In Fig. 1 we give the variation of the measured relaxation times of the center and off-center ^{13}C nuclei of neopentane versus the number density N_s of paramagnetic centers DTBN in the range $0 \leq N_s \leq 5.6 \times 10^{20} \text{ cm}^{-3}$, at a temperature $T = 303^\circ\text{K}$ and for a ^{13}C resonance frequency $\nu = 25.16$ MHz.

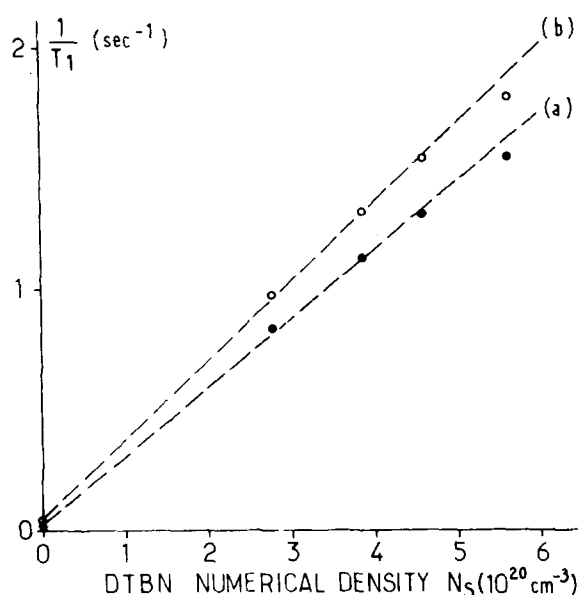


FIG. 1. Experimental values of the observed relaxation rates $(1/T_1)_{\text{obs}}$ of: (a) the ^{13}C nuclei at the center of neopentane and (b) the off-center ^{13}C nuclei versus the number N_s of molecules of DTBN/cm 3 at 303°K and $\nu=25.16$ MHz. For pure neopentane ($N_s=0$) the respective values of T_1 are (a) $(T_1)_{\text{obs}}=86.3$ sec, (b) $(T_1')_{\text{obs}}=23.0$ sec. Dashed lines represent the linear laws expressed by Eqs. (2) and (3).

As expected for a number density N_s of DTBN $\geq 2 \times 10^{20}$ cm $^{-3}$, the measured relaxation rates are enhanced by more than one order of magnitude compared with those of pure neopentane. The difference between both curves is, to our knowledge, the first direct experimental evidence of the effects of eccentricity on the intermolecular magnetic dipolar relaxation in liquids.

Both curves in Fig. 1 show a linear variation of $(1/T_1)_{\text{obs}}$ versus N_s up to $N_s \sim 5 \times 10^{20}$ cm $^{-3}$.

The general expression of the relaxation rate for the central ^{13}C nuclei,

$$\left(\frac{1}{T_1}\right)_{\text{obs}} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}}^n + \left(\frac{1}{T_1}\right)_{\text{inter}}^e, \quad (1)$$

where $(1/T_1)_{\text{intra}}$ is the intramolecular relaxation rate in neopentane, $(1/T_1)_{\text{inter}}^n$ and $(1/T_1)_{\text{inter}}^e$ are the intermolecular relaxation rates with the nuclear spin of the other neopentane molecules, and with the electronic spins of the free radical, respectively. $(1/T_1)_{\text{intra}}$ is, with an excellent approximation, independent of the number densities N_n and N_e of neopentane and DTBN molecules. $(1/T_1)_{\text{inter}}^n$ and $(1/T_1)_{\text{inter}}^e$ are proportional to N_n and N_e respectively. We have then:

$$\left(\frac{1}{T_1}\right)_{\text{obs}} = \alpha + \beta N_s, \quad (2)$$

with

$$\alpha = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}}^n \quad (2a)$$

and

$$\beta N_s = \left(\frac{1}{T_1}\right)_{\text{inter}}^e. \quad (2b)$$

In Eq. (2a) $(1/T_1)_{\text{inter}}^n$ is the intermolecular relaxation rate $(1/T_1)_{\text{inter}}^n$ previously defined for pure neopentane; in the definition (2b) of the parameter β we have neglected the negative contribution proportional to $N_e/N_n \times (1/T_1)_{\text{inter}}^n$ arising from the decrease of N_n due to the inclusion of DTBN molecules. This error is always less than 1% in the studied concentration range. We have a similar expression giving the relaxation rate for the off-center ^{13}C nuclei:

$$\left(\frac{1}{T_1}\right)_{\text{obs}} = \alpha' + \beta' N_s. \quad (3)$$

From Fig. 1, where the dashed lines are obtained from a least squares fit, we obtain:

$$\begin{aligned} \alpha &= 0.022 \text{ sec}^{-1}, & \alpha' &= 0.049 \text{ sec}^{-1} \\ \beta &= 0.285 \times 10^{-20} \text{ sec}^{-1} \text{ cm}^3, & \beta' &= 0.328 \times 10^{-20} \text{ sec}^{-1} \text{ cm}^3. \end{aligned}$$

The magnitude of the eccentricity effect under investigation is given by

$$\epsilon = \frac{\beta'}{\beta} - 1 = 15\%. \quad (4)$$

In Fig. 1 a slight departure from the linear variation of the measured relaxation rates can be observed for high concentrations of free radicals ($N_s \geq 5 \times 10^{20}$). Two arguments, at least may be given in order to explain these features: with increasing concentrations of DTBN, the characteristics of the liquid sample such as viscosity are appreciably modified, also the interactions between the electronic spins of DTBN molecules, mainly exchange interactions, modify their quantum states.

III. THEORY

A. Physical data

We give here the various geometrical parameters (see Fig. 2) and the physical constants relevant to this study.

Let I and S be the spin of the ^{13}C nuclei and of the free electron of DTBN, γ_I and γ_S their gyromagnetic ratios. We have

$$\gamma_I = 6.7263 \times 10^3 \text{ rad sec}^{-1} \text{ Gauss}^{-1},$$

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

The radius a_I of the neopentane molecule considered as

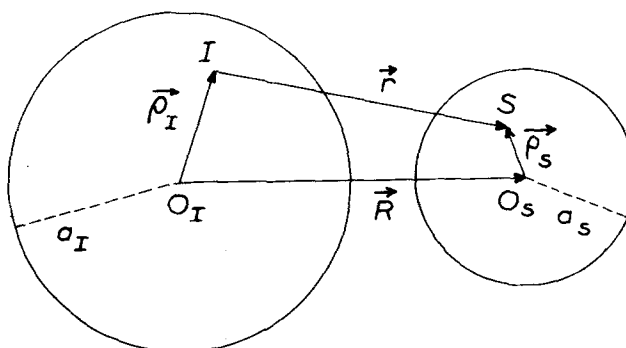


FIG. 2. Characteristic parameters of the intermolecular dipolar interaction between the spins I and S .

a hard sphere was estimated from its van der Waals volume V_I^W ¹⁴:

$$V_I^W = 58.0 \text{ cm}^3 \text{ mol}^{-1},$$

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

The distance between the off-center ^{13}C nuclei and the center of the neopentane molecule (C-C bond) is

$$\rho_I = 1.54 \times 10^{-8} \text{ cm}.$$

Similarly, the van der Waals volume V_S^W of the DTBN molecule is¹⁴

$$V_S^W = 99.7 \text{ cm}^3 \text{ mol}^{-1},$$

from which the following hard sphere radius a_S of this molecule may be deduced:

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

It may be noted that the DTBN molecule looks more like an ellipsoid than a sphere, the three principal axes of this ellipsoid having the following respective dimensions^{15,16}; 4.1, 3.1, and 3.1 Å, and that the volume of this ellipsoid is exactly equal to V_S^W .

The average position of the free electron in DTBN is not accurately known. However, it may be assumed that it is localized in the middle of the NO bond,¹⁷ which would give a distance ρ_S between the spin S and the center of the DTBN molecule considered as a hard sphere,

$$\rho_S = 1.6 \times 10^{-8} \text{ cm}.$$

Thus, the minimum distance of approach of the centers of both kinds of molecules is

$$b = a_I + a_S = 6.2 \times 10^{-8} \text{ cm}. \quad (5)$$

The parameters of eccentricity of the spins I and S are given by

$$\left(\frac{\rho_I}{b}\right)^2 = 0.062, \quad \left(\frac{\rho_S}{b}\right)^2 = 0.067.$$

The absolute translational diffusion constants D_I^t and D_S^t of neopentane and DTBN molecules were determined in the following way.

Kessler *et al.*¹⁸ have studied the temperature dependence of D_I^t using a spin-echo method and give the empirical expression

$$D_I^t = 3.85 \times 10^{-3} \exp\left(-\frac{1355}{T}\right) \text{ cm}^2 \text{ sec}^{-1}.$$

Using this expression, we obtain for $T = 303^\circ\text{K}$,

$$D_I^t = 4.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}.$$

According to the Stokes formula, in a liquid of given viscosity the translational diffusion constants of spherical migrating molecules are inversely proportional to their radii. Assuming here that in the presence of DTBN molecules, the viscosity of the liquid sample is the same as in pure neopentane, we get

$$D_S^t = D_I^t \frac{a_I}{a_S} = 3.6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}.$$

In the study of the intermolecular dipolar relaxation between neopentane and DTBN molecules, it is necessary to introduce the relative diffusional motion of both

kinds of molecules which is characterized by the diffusion constant

$$D^t = D_I^t + D_S^t = 8.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}.$$

We may then introduce a translational correlation time τ defined by

$$\tau = \frac{b^2}{D^t} = 4.8 \times 10^{-11} \text{ sec}. \quad (6)$$

Next we must evaluate the rotational diffusion constants D_I^r and D_S^r of neopentane and DTBN.

From spin-lattice relaxation measurements in neopentane- d_{12} ,¹⁹ the estimated rotational correlation time of this compound at 303°K is $0.64 \times 10^{-12} \text{ sec}$. As the rotational correlation times are roughly proportional to the square root of the moment of inertia of the molecule, a corrective factor of 0.868 is applied to the previous value to obtain the corresponding correlation time τ_2 for pure neopentane;

$$\tau_2 = 0.56 \times 10^{-12} \text{ sec};$$

consequently

$$D_I^r = \frac{1}{6\tau_2} = 3.0 \times 10^{11} \text{ sec}^{-1}.$$

From the Stokes formula for rotation, in a liquid of a given viscosity the diffusion constants of hard sphere molecules are inversely proportional to their volume. From the van der Waals volumes given previously, we get for DTBN,

$$D_S^r = D_I^r \frac{V_I^W}{V_S^W} = 1.75 \times 10^{11} \text{ sec}^{-1}.$$

B. Relaxation times

In this section, we use our previous theoretical results^{4,9} to calculate the intermolecular relaxation rates between the ^{13}C nuclei of neopentane and the electronic spins of DTBN. In general,

$$\left(\frac{1}{T_1}\right)_{\text{inter}}^e = \frac{2}{15} \gamma_I^2 \gamma_S^2 h^2 S(S+1) \times [j_2^{(0)}(\omega_I - \omega_S) + 3j_2^{(1)}(\omega_I) + 6j_2^{(2)}(\omega_I + \omega_S)], \quad (7)$$

where ω_I , ω_S are the Larmor frequencies of the ^{13}C spin nuclei I and of the free radical electronic spin $S = \frac{1}{2}$. The spectral densities $j_2^{(q)}(\omega)$ are the Fourier transforms

$$j_2^{(q)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} g_2^{(q)}(t) e^{-i\omega t} dt \quad (8)$$

of the correlation functions

$$g_2^{(q)}(t) = \langle f_2^{(q)}(\mathbf{r}_0) f_2^{(q)*}(\mathbf{r}) \rangle, \quad (8a)$$

where the

$$f_2^{(q)}(\mathbf{r}) = r^{-3} Y_{2q}(\theta, \phi), \quad (-2 \leq q \leq 2) \quad (8b)$$

are random functions of the relative position \mathbf{r} (r, θ, ϕ) of the interacting spins I and S . It must be stressed that in this theory both translational and rotational random motions of the molecules are taken into account and are considered as stochastically independent. It may be noted that, according to the spherical symmetry of the problem, the $j_2^{(q)}(\omega)$ entering Eq. (7) are independent

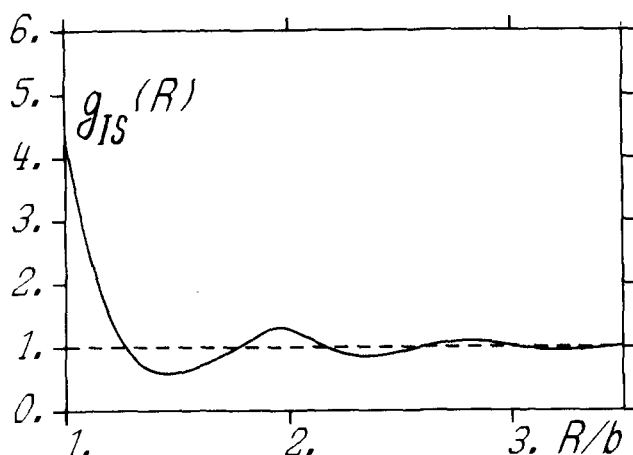


FIG. 3. Typical pair correlation function $g_{IS}(R)$ for a liquid mixture of neopentane with DTBN with the following numerical densities: $N_n = 4.45 \times 10^{21} \text{ cm}^{-3}$; $N_s = 0.277 \times 10^{21} \text{ cm}^{-3}$. The radii a_I , a_S of neopentane and DTBN considered as hard spheres are $a_I = 2.8 \text{ \AA}$, $a_S = 3.4 \text{ \AA}$, $b = a_I + a_S = 6.2 \text{ \AA}$.

of the index q which will be omitted in what follows.

We define, at this point, a dimensionless spectral density $\bar{j}_2(\omega\tau)$ by⁹

$$j_2(\omega) = \frac{N_S \tau}{\pi b^3} \bar{j}_2(\omega\tau), \quad (9a)$$

b and τ being defined by Eqs. (5) and (6), respectively. With the help of the various physical parameters introduced in Sec. IIIA, we have a series expansion in terms of the eccentricity parameters:

$$\bar{j}_2(\omega\tau) = \text{Re}[\bar{G}_2(i\omega\tau)] \times \left\{ 1 + \sum_{l=1}^{\infty} \sum_{\lambda=0}^l C_{l,\lambda}(\omega\tau, D_I^* \tau, D_S^* \tau) \left(\frac{\rho_1}{b}\right)^{2\lambda} \left(\frac{\rho_S}{b}\right)^{2(l-\lambda)} \right\}, \quad (9b)$$

with

$$C_{l,\lambda}(\omega\tau, D_I^* \tau, D_S^* \tau) \equiv \frac{1}{24} \frac{(2l+4)!}{(2\lambda+1)! [2(l-\lambda)+1]!} \times \frac{\text{Re}[\bar{G}_{l+2}(i\omega\tau + \lambda(\lambda+1)D_I^* \tau + (l-\lambda)(l-\lambda+1)D_S^* \tau)]}{\text{Re}[\bar{G}_2(i\omega\tau)]}. \quad (9c)$$

In Eqs. (9b) and (9c) expressions of the form $\bar{G}_l(\sigma\tau)$ are defined by

$$\bar{G}_l(\sigma\tau) = \frac{b^{2l-1}}{N_S \tau} \bar{G}_l(\sigma), \quad (9d)$$

where $\bar{G}_l(\sigma)$ is the Laplace transform

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

of the random functions $F_i^{(q)}(\mathbf{R}) \equiv R^{-(l+1)} Y_{l,q}(\Theta, \Phi)$ of the relative position \mathbf{R} (R, Θ, Φ) between the centers 0_I and 0_S of the interacting neopentane and DTBN molecules. More precisely, we have

$$G_l(t) = N_S \iint g(R_0) \rho(\mathbf{R}_0, \mathbf{R}, t) F_i^{(q)}(\mathbf{R}_0) F_i^{(q)}(\mathbf{R})^* d^3 \mathbf{R}_0 d^3 \mathbf{R} \quad (10)$$

\mathbf{R}_0 and \mathbf{R} referring to the values of \mathbf{R} at time $t=0$ and t respectively. The conditional probability $\rho(\mathbf{R}_0, \mathbf{R}, t)$ is the solution of the generalized diffusion equation (Smoluchowski equation) which takes into account the relative distribution $g(R_0)$ of the molecules at the equilibrium and the effective force

$$\mathbf{F}(\mathbf{R}) = \nabla_{\mathbf{R}} \log g(R) \quad (11)$$

between both kinds of molecules.

Two models will be considered in this study:

(i) The first called A_e is a simplified model⁴ assuming a uniform distribution of the interacting molecules [$\mathbf{F}(\mathbf{R})$ vanishes in this case] for which we have:

$$g(R_0) = 1 \quad \text{if } R_0 \geq b \\ = 0 \quad \text{if } R_0 < b.$$

(ii) In the second, called F_e , we use a pair correlation function introduced by Lebowitz²⁰ and evaluated in some specific cases by Leonard *et al.*²¹ In this model, both kinds of molecules are approximated as rigid spheres with respective numerical densities N_n and N_s . The pair correlation function which depends on the radii a_I , a_S and on these numerical densities N_n , N_s will be denoted $g_{IS}(R_0)$.

In Fig. 3, we give a typical pair correlation function for a liquid mixture of neopentane and DTBN with $N_n = 4.45 \times 10^{21} \text{ cm}^{-3}$ and $N_s = 0.277 \times 10^{21} \text{ cm}^{-3}$.

From Eqs. (7) to (10) we were able to evaluate the theoretical relaxation rates $(1/T_1)_{\text{inter}}^e$ in the framework of the two above forms of $g(R_0)$.

TABLE I. Experimental and theoretical intermolecular relaxation times $(T_1)_{\text{inter}}^e$, $(T_1')_{\text{inter}}^e$ of the central and off center ^{13}C nuclei in neopentane due to the electronic spins of dissolved DTBN with a numerical density N_S . Models A_e and F_e refer respectively to an uniform relative distribution of both kinds of molecules and to a computed pair correlation function $g_{IS}(R_0)$ similar to that given in Fig. 3.

$N_S \text{ (cm}^{-3}\text{)}$	$(T_1)_{\text{inter}}^e$, central ^{13}C (sec)			$(T_1')_{\text{inter}}^e$, off-center ^{13}C (sec)		
	Exptl	A_e model	F_e model	Exptl	A_e model	F_e model
2.77×10^{20}	1.22	1.94	1.45	1.07	1.87	1.36
3.85×10^{20}	0.90	1.40	1.04	0.78	1.35	0.97
4.58×10^{20}	0.77	1.17	0.87	0.67	1.13	0.82
5.60×10^{20}	0.66	0.96	0.71	0.57	0.92	0.67

The computational techniques are essentially based on automatic calculations of the various derivatives entering the expression of $g_{IS}(R_0)$ and on finite difference methods for getting the conditional probability $\rho(\mathbf{R}_0, \mathbf{R}, t)$ solution of the Smoluchowski differential equation.^{9,22}

With the various values of the physical and geometrical parameters given in Sec. III A we obtained the results summarized in Table I.

IV. DISCUSSION

From Table I, a remarkable agreement between the magnitude of the measured relaxation times and their theoretical values is obtained mainly with the F_e model. It must be stressed that there is no adjustable parameter in the theory but that we always used the best estimation of the various physical data of the problem.

The effects of eccentricity are characterized by the number ϵ defined in Eq. (4) and also given by

$$\epsilon = \frac{(T_1)_{\text{inter}}^e}{(T_1')_{\text{inter}}} - 1. \quad (12)$$

With the A_e and F_e models, we obtain $\epsilon = 4\%$ and $\epsilon = 6.5\%$, respectively, instead of 15% experimentally.

Thus, for evaluating the magnitude of the relaxation times and of the effects of eccentricity, the F_e model appears to be more satisfactory than the A_e model which neglects the compact packing of the molecules.

However, there remains a discrepancy between the theoretical and experimental values of ϵ . By analyzing the accuracy of some of the physical data introduced in Sec. III A, this discrepancy may be partially explained. Indeed, there is a first uncertainty concerning the position of the DTBN free electron. We assumed that it is localized in the middle of the NO bond which corresponds to a value $\rho_s = 1.6 \text{ \AA}$. In fact, some theoretical calculations in similar compounds^{17,23,24} show that a reasonable range of values for ρ_s is $\rho_s = 1.6 \pm 0.3 \text{ \AA}$, and it is clear from Eq. (9b) that the effects of eccentricity notably increase with ρ_s .

Furthermore, the radius a_s of the DTBN molecule considered as a hard sphere was estimated to 3.4 \AA . But, as was already mentioned, this molecule looks more like an ellipsoid than a sphere and the minimum distance of approach of the centers of neopentane and DTBN molecules is then only 5.9 \AA instead of 6.2 \AA for rigid spheres with the same volume. The eccentricity constant ϵ is also increased by this effect.

With both corrections mentioned above, values of ϵ up to 5.5% and 9% were reached for the A_e and F_e models, respectively. It is thus clear that some improvements must be brought to the theoretical model in order to fit the experiments completely. We believe

that a more satisfactory model for describing the relative translational random motion of the interacting molecules is obtained by the introduction of finite jumps instead of continuous trajectories.²⁵⁻²⁷ We are currently investigating a theory of finite random jumps taking into account the impenetrability of the molecules, their relative nonuniform distribution and the eccentricity of the interacting spins. In a subsequent paper, this theory will be explained and applied to improve the interpretation of the experiments described in this article.

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- ¹N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
- ²A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1951).
- ³Y. Ayant, E. Belorizky, J. Alizon, and J. Gallice, *J. Phys. (Paris)* **36**, 991 (1975).
- ⁴Y. Ayant, E. Belorizky, P. Fries, and J. Rosset, *J. Phys. (Paris)* **38**, 325 (1977).
- ⁵J. F. Harmon and B. H. Muller, *Phys. Rev.* **182**, 400 (1969).
- ⁶L. P. Hwang and J. H. Freed, *J. Chem. Phys.* **63**, 4017 (1975).
- ⁷P. Hubbard, *Phys. Rev.* **131**, 275 (1963).
- ⁸M. D. Zeidler, *Mol. Phys.* **30**, 1441 (1975).
- ⁹P. Fries and E. Belorizky, *J. Phys. (Paris)* **39**, 1263 (1978).
- ¹⁰L. Verlet and J. J. Weis, *Phys. Rev. A* **5**, 939 (1972).
- ¹¹H. J. Parkhurst Jr., Y. Lee, and J. Jonas, *J. Chem. Phys.* **55**, 1368 (1971).
- ¹²R. A. Assink, J. de Zwaan, and J. Jonas, *J. Chem. Phys.* **56**, 4975 (1972).
- ¹³A. H. Narten, *J. Chem. Phys.* **70**, 299 (1979).
- ¹⁴A. Bondi, *Physical Properties of Molecular Crystals, Liquids and Gases* (Wiley, New York, 1968).
- ¹⁵J. Lajzerowicz-Bonnetau in L. Berliner, *Spin Labelling Theory and Applications* (Academic, New York, 1976), p. 239.
- ¹⁶B. Andersen and P. Andersen, *Acta Chem. Scand.* **20**, 2728 (1966).
- ¹⁷P. J. Brown, A. Capiomont, B. Gillon, and J. Schweizer, *J. Magn. & Magn. Mater.* **14**, 289 (1979).
- ¹⁸D. Kessler, A. Weiss, and H. Witte, *Ber. Bunsenges. Phys. Chem.* **71**, 3 (1967).
- ¹⁹B. A. Pettitt, R. E. Wasylshen, R. Y. Dong, and T. P. Pitner, *Can. Chem.* **56**(19), 2576 (1978).
- ²⁰J. L. Lebowitz, *Phys. Rev. Sect. A* **133**, 895 (1964).
- ²¹P. J. Leonard, D. Henderson, and J. A. Barker, *Mol. Phys.* **21**, 107 (1971).
- ²²B. Melloni, thesis, Pontificia Universidad Católica del Peru, Lima, 1980 (to be published).
- ²³B. Burton, T. A. Claxton, and Y. Ellinger, *Comput. Phys. Commun.* **17**, 27 (1979).
- ²⁴J. Schweizer and B. Gillon (private communication).
- ²⁵H. C. Torrey, *Phys. Rev.* **92**, 962 (1953).
- ²⁶J. H. Freed, *J. Chem. Phys.* **68**, 4034 (1978).
- ²⁷P. Fries, thesis, Grenoble, 1977.