

Nuclear Magnetic Relaxation by Hindered Rotations*

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The problem of the nuclear magnetic relaxation (NMR) due to hindered rotations in a crystal is treated considering the simple case of diatomic molecules assuming two antiparallel equilibrium orientations. An average time, τ_0 , during which the molecule oscillates around an equilibrium orientation, and a constant jumping time, τ_1 , are introduced. The spectral density is calculated as a function of τ_1 and of $\tau = \tau_1 + \tau_0$. For $\tau_1 = 0$ the spectral density introduced by Bloembergen *et al.* is found if one assumes $\tau/2 = \tau_0$. For $\tau_1 \neq 0$ and for $\omega\tau \ll 1$ the spectral density diminishes as τ_1 increases. Correspondingly, the calculated T_1 's are, in general, longer than those calculated according to Bloembergen *et al.*

1. INTRODUCTION

IN the theory of nuclear magnetic relaxation it is generally assumed that the fluctuations of the local field are due to particular random motions which justify the assumption of exponential correlation functions characterized by a correlation time τ_c .

Such an assumption was introduced for the first time in the theory of Bloembergen *et al.* on nuclear magnetic relaxation.¹

By making substantially equivalent assumptions on the random processes which determine the correlation, Torrey² considered the processes of self-diffusion in crystalline lattices and Gutowsky and Pake³ the hindered rotations in solids.

The theory of Bloembergen *et al.* has been re-examined by Kubo and Tomita⁴ who, although they accept the assumptions of Bloembergen *et al.* on the random processes, introduce some corrections in the expressions for the relaxation times.

However, if one takes some dynamic details of the molecular movements responsible for the relaxation into account, it may be justifiable to introduce two characteristic times instead of one into the correlation functions.

The purpose of this work is to see what modifications of the previous theories are brought about by the introduction of two characteristic times into the random processes.

2. THE PRESENCE OF TWO CHARACTERISTIC TIMES IN SOME RELAXATION PROCESSES

The possibility of introducing two characteristic times into the theory of relaxation is evident if we consider two typical processes which may produce relaxation, i.e., hindered rotation of a molecule in a crystal and self-diffusion in a solid.

In the case of a hindered rotation the local field

oscillates with the frequency of the pendular motions of a molecule until the molecule rotates through a certain angle and crosses a potential barrier. Since, in general, the pendular motion of a molecule does not come into play in the relaxation process, when calculating the spectral density we can assume that the local field maintains a constant value until a change in the orientation of the molecule takes place.

Let τ_0 be the average time during which the molecule oscillates around its equilibrium position and τ_1 be the time spent by the molecule in performing a reorientation.

It seems reasonable to assume that τ_1 has about the same value for each jump of the molecule. In fact, τ_1 is, in general, of the order of the period of the pendular oscillations of the molecule. The validity of such an assumption will be discussed later.

So if the relaxation is due to self-diffusion in a crystal, we may assume that the local field experienced by a spin remains approximately constant during an average time τ_0 until an atom jumps from one crystal site to another; also in this case the time τ_1 required for the jump may be assumed to be about the same for all jumps. It should, in fact, be of the order of the reciprocal of the Debye frequency of the lattice.

So, in general, if relaxation is due to hindered rotation or self-diffusion it may be assumed that a particular component of the local field may take stationary values for an average time τ_0 . The number of such possible stationary values and their probability depends on the particular conditions, and the jump from one stationary value to another takes place during a time τ_1 which is approximately constant.⁵

Such an assumption corresponds well enough to reality in the case where motions which cause the relaxation are characterized by a well-defined activation energy as in the case of a crystal. However, in the case of liquids which exhibit a quasicrystalline structure the

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

² H. C. Torrey, *Phys. Rev.* **92**, 962 (1953).

³ H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **18**, 162 (1950).

⁴ R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954); *Suppl. Nuovo Cimento* **10**, 1063 (1957).

⁵ We have presented this model and some preliminary conclusions at the 11th Colloque Ampère, Eindhoven, 1962, *Compte Rendu du 11^e Colloque* (North-Holland Publishing Company, Amsterdam). Recently R. J. C. Brown, H. S. Gutowsky, and K. Shimomura, *J. Chem. Phys.* **38**, 76 (1963), assumed a similar model for spin-rotational interaction in liquid CHFCl_2 . Nevertheless, the question is treated by these authors in a different way by assuming that relaxation can be attributed to the contributions of a step function and of a pulse function.

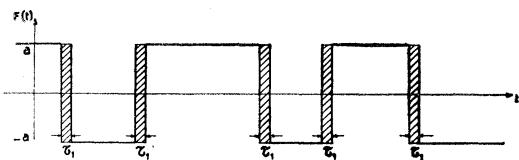


FIG. 1. Local field experienced by a nucleus of a diatomic molecule which jumps between two antiparallel orientations.

assumption we made, i.e., the presence of two characteristic times, should hold also to a certain extent.

3. CALCULATION OF THE SPECTRAL DENSITY IN A PARTICULAR CASE OF HINDERED ROTATION

For the sake of simplicity we shall limit ourselves to the case of hindered rotation and shall assume that the local field may take only two fixed values.

Such an assumption may correspond, for example, to the case of a diatomic molecule or diatomic molecular group which can take only two opposite equilibrium orientations in the crystal.

During a jump, the local field changes with a finite rate; nevertheless, in the present approximation we assume the local field to be a step function of the time, with the condition that τ_1 represents the shortest time between two subsequent jumps. We think that simplifications inherent in the present approach could not affect appreciably the main features of the results.

Let $AF(t)$ denote a perturbation on the spin system due to nuclear motion, where A is a spin operator and $F(t)$ a random function of time.

According to the above assumption we take

$$F(t) = ax(t), \quad (1)$$

where a is a positive constant and $x(t)$ a random function of time which follows the random process discussed above, with constant value 1 and -1 (see Fig. 1).

The mathematical problem consists in finding the spectral density associated with $F(t)$.

We consider a sequence of events defined by assuming that, when a time τ_1 is spent after the occurrence of given event [a change in value of $F(t)$], the process is regenerated following a Poisson distribution with

parameter $\alpha_0 = (\tau_0)^{-1}$. The average time between successive events will then be $\tau = \tau_0 + \tau_1$.

Let $\Upsilon(t)$ be a random variable denoting the number of events taking place in the interval $(0, t)$. We assume that a stationary distribution of $Y(t)$ exists. Let $\{t_i\}_{i \geq 1}$ denote the sequence of times corresponding to the occurrence of the events, and let $T_i = t_{i+1} - t_i (i \geq 1)$ denote the time between the i and the $(i+1)$ events. Denote by T_0 the time up to the first event.

The time differences $\{T_i\}_{i \geq 1}$ are positive-independent random variables having the common distribution function,

$$P(T_i \leq t) = \Phi(t) = 1 - \exp[-\alpha_0(t - \tau_i)], \quad t \geq \tau_i, \quad (2) \\ = 0, \quad t \leq \tau_i.$$

A critical point is the choice of the distribution function for the positive random variable T_0 ; for $\tau_1 \leq \tau_0$ we think a Poisson distribution with parameter $\alpha = (\tau)^{-1}$ will be a reasonable approximation:

$$P(T_0 \leq t) = \Phi(t) = 1 - \exp[-\alpha t]. \quad (3)$$

From the definition of the T_i , the time up to the y th event is given by

$$\Theta_y = \sum_{i=0}^{y-1} T_i,$$

and let $P(\Theta_y \leq t) = \Phi_y(t)$ denote the distribution function of Θ_y .

The probability

$$P(y(t) = y) = p(y, t)$$

that y events take place in a time interval $(0, t)$ is found to be

$$p(0, t) = 1 - \Phi_0(t) = \exp(-\alpha t), \quad (4) \\ p(y, t) = \Phi_y(t) - \Phi_{y+1}(t), \quad (y \geq 1),$$

where for $y \geq 2$, the $\Phi_y(t)$ can be determined by the recurrence formula

$$\Phi_{y+1}(t) = \Phi_y(t) * \Phi(t) = \int_0^t \Phi_y(t-u) d\Phi(u)$$

starting from $\Phi_1(t) = \Phi_0(t)$.⁶

Neglecting those terms in the development of the series for $e^{-(\alpha-\alpha_0)t}$ which are higher than first order we obtain the following expression for $\Phi_y(t)$.

$$\Phi_y(t) = \exp\{-\alpha_0[t - (y-1)\tau_1]\} \left(\sum_{n=y}^{\infty} \frac{\alpha_0^n [t - (y-1)\tau_1]^n}{n!} \frac{(\alpha_0 - \alpha) d_0^y [t - (y-1)\tau_1]^y}{\alpha_0 y!} \right) \mathcal{H}(t - (y-1)\tau_1), \quad (5)$$

where $\mathcal{H}(t)$ is the Heaviside step function.

Let $G(t)$ be a correlation function associated with $F(t)$ given by

$$G(t) = \sum_{xx'} p_1(x) p_2(x', t | x) F^*(x) F(x'), \quad (6)$$

where $p_1(x)$ and $p_2(x', t | x)$ are, respectively, the frequency function and the conditional frequency function associated with random processes.

⁶ W. Feller, *An Introduction to Probability Theory and its Applications* (John Wiley & Sons, Inc., New York, 1957), 2nd ed., Vol. I.

In the present case we have

$$p_1(x) = \frac{1}{2}(\delta_{x,1} + \delta_{x,-1}),$$

$$p_2(x',t|x) = \sum_{y=0}^{\infty} [p(2y,t)\delta_{x,x'} + p(2y+1,t)\delta_{x,-x'}]. \quad (7)$$

Inserting (1) and (7) in the right-hand member of (6), remembering (4), we obtain

$$G(t) = a^2 \left\{ \exp(-\alpha_0 t) (1 + (\alpha_0 - \alpha)t) + \sum_{y=1}^{\infty} (-1)^y [\Phi_y(t) - \Phi_{y+1}(t)] \right\}. \quad (8)$$

Taking into account the asymptotic behavior of $\Phi_y(t)$ and the expression of the first derivative of $\Phi_{y+1}(t)$ and integrating by parts, we get

$$J(\omega) = 2a^2\tau \left\{ \frac{2(1-\chi - \sin\chi\omega\tau/\omega\tau)}{(1 + \cos\chi\omega\tau)^2 + (1-\chi - \sin\chi\omega\tau/\omega\tau)^2(\omega\tau)^2} - 2\frac{\chi}{1-\chi} \left[\frac{1 - (1-\chi)^2(\omega\tau)^2}{[1 + (1-\chi)^2(\omega\tau)^2]^2} - \frac{\cos\chi\omega\tau + (1-\chi)\omega\tau \sin\chi\omega\tau}{1 + (1-\chi)^2(\omega\tau)^2} + \frac{(1 + \cos\chi\omega\tau)\cos\chi\omega\tau + (1-\chi - \sin\chi\omega\tau/\omega\tau)\omega\tau \sin\chi\omega\tau}{(1 + \cos\chi\omega\tau)^2 + (1-\chi - \sin\chi\omega\tau/\omega\tau)^2(\omega\tau)^2} \right] \right\}, \quad (9)$$

where $\chi = \tau_1/\tau$. In (9), a^2 may be interpreted as the quadratic quantity $G(0) = \langle F^*(t)F(t) \rangle$. Figure 2 shows the behavior of $J(\omega)$ for some values of τ_1/τ .

It will be recognized that (9), when $\tau_1 \rightarrow 0$, i.e., $\tau = \tau_0$, has the well-known form appropriate to an exponentially decaying correlation function, according to

a Poisson process, and the spectral density coincides with the expression given by Bloembergen *et al.*¹ taking $\tau/2 = \tau_c$. For $\tau_1/\tau \neq 0$ $J(\omega)$ exhibits a maximum in the neighborhood of $\omega\tau = 1$ becoming more and more sharp as the ratio τ_1/τ increases and correspondingly in the range $\omega\tau \ll 1$ becomes more and more small.

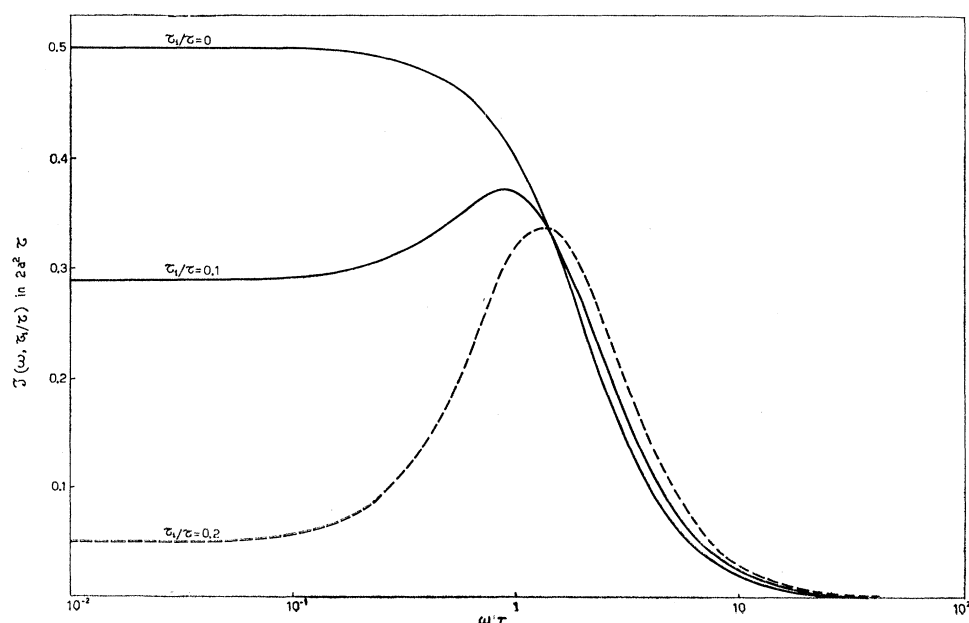
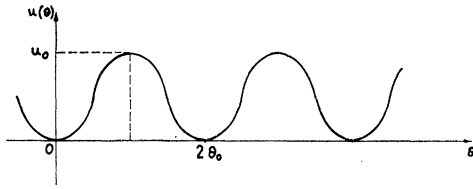


FIG. 2. $J(\omega)$ versus $\omega\tau$ for different values of τ_1/τ .

FIG. 3. The potential function $U(\theta)$.

4. THE VALIDITY OF THE ASSUMPTION $\tau_1 = \text{CONST}$

We wish to investigate the limits of validity of the assumption of a constant jumping time; let us, therefore, examine what the distribution of the jumping time might be by assuming a simple model. We, therefore, consider a statistical ensemble of particles each of them moving in a potential field $U(\theta)$ of the periodic type shown in Fig. 3, where

$$U(\theta) = \frac{1}{2}\Omega^2\theta^2 \quad \text{for } -\frac{1}{2}\theta_0 \leq \theta \leq \frac{1}{2}\theta_0,$$

$$U(\theta) = U_0 - \frac{1}{2}\Omega^2(\theta - \theta_0)^2 \quad \text{for } \frac{1}{2}\theta_0 \leq \theta \leq \frac{3}{2}\theta_0.$$

In the case we have considered, of a molecule with two opposite equilibrium orientations, we have $\theta_0 = \frac{1}{2}\pi$. Classical mechanics can be a sufficient approach to this problem.

If E is the energy of the molecule and I its inertial moment, in the passage from an equilibrium position characterized by a minimum of potential energy to another equilibrium position the molecule spends a time τ_1 given by

$$\tau_1 = \left(\frac{I}{2}\right)^{1/2} \int_0^{2\theta_0} \frac{d\theta}{[E - U(\theta)]^{1/2}}.$$

It can be assumed that most of the particles that overcome the potential barrier have energies a little greater than U_0 . Taking $E = (\eta + 1)U_0$, for $\eta \rightarrow 0$, τ_1 is given by

$$\tau_1 = (2.3 - \ln \eta)\tau_v,$$

where $\tau_v = (I\theta_0^2/4U_0)^{1/2}$ is the period of the pendular motions of the molecule.

The function $f(\tau_1, U_0/kT)d\tau_1$, which is the probability that the jumping time τ_1 lies between τ_1 and $\tau_1 + d\tau_1$, can be evaluated by assuming that the distribution of molecular energies is governed by Maxwell-Boltzmann statistics

$$f\left(\tau_1, \frac{U_0}{kT}\right) = 9.58 \frac{U_0}{kT} \exp\left(-\frac{\tau_1}{\tau_v}\right) \times \exp\left[-9.58 \frac{U_0}{kT} \exp\left(-\frac{\tau_1}{\tau_v}\right)\right] \frac{1}{\tau_v} d\tau_1. \quad (10)$$

On the other hand, if $\langle \tau_1 \rangle$ is the mean value of τ_1 , it seems reasonable to suppose that τ_1/τ_0 is equal to the ratio of the number of particles whose energy is greater

than U_0 to the number of particles whose energy is less than U_0 , that is:

$$\frac{\langle \tau_1 \rangle}{\tau_0} = \frac{\exp(-U_0/kT)}{1 - \exp(-U_0/kT)}.$$

It is, thus, possible to find the distribution functions $f(\tau_1; \langle \tau_1 \rangle/\tau)$ for some values of $\langle \tau_1 \rangle/\tau$. The graph of the distribution function $f(\tau_1/\tau_0, \langle \tau_1 \rangle/\tau)$ for some values of $\langle \tau_1 \rangle/\tau$ as a function of τ_1 is shown in Fig. 4.

As in the calculation of the spectral density it has been assumed $\tau_1 = \text{const}$ we may verify the validity of such a hypothesis for a particular value τ_1/τ by comparing the spectral densities as calculated for $\tau_1 = \text{const} = \langle \tau_1 \rangle$ with that calculated by performing a weighted average of the spectral density corresponding to a distribution $f(\tau_1, \langle \tau_1 \rangle/\tau)$.

We were able to verify that the assumption $\tau_1 = \text{const} = \langle \tau_1 \rangle$ does not introduce a substantial error in the calculation of the spectral density for $0 \leq \tau_1/\tau \leq 0.15$; the spectral density calculated for $\tau_1/\tau = 0.2$ and shown in Fig. 2 (dashed line) can be accepted only with a certain approximation.

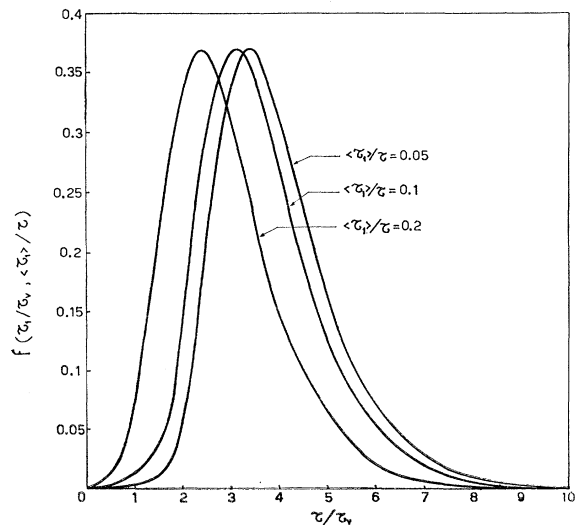
5. SPIN-LATTICE RELAXATION TIME

The relaxation due to the hindered rotations depends on the orientation of the molecules. If we assume that the axes of rotation are isotropically distributed we may perform a comparison with the Bloembergen theory. In this hypothesis the spin-lattice relaxation time T_1 is given by

$$1/T_1 = K[J(\omega) + 4J(\omega)], \quad (11)$$

where K is a constant depending on the nuclear spins and on the nuclear gyromagnetic ratios.

In Fig. 5 T_1/ω_0 is plotted versus $\tau\omega_0$ (ω_0 Larmor fre-

FIG. 4. The distribution function $f(\tau_1/\tau_0, \langle \tau_1 \rangle/\tau)$ versus τ_1/τ_0 for different values of $\langle \tau_1 \rangle/\tau$.

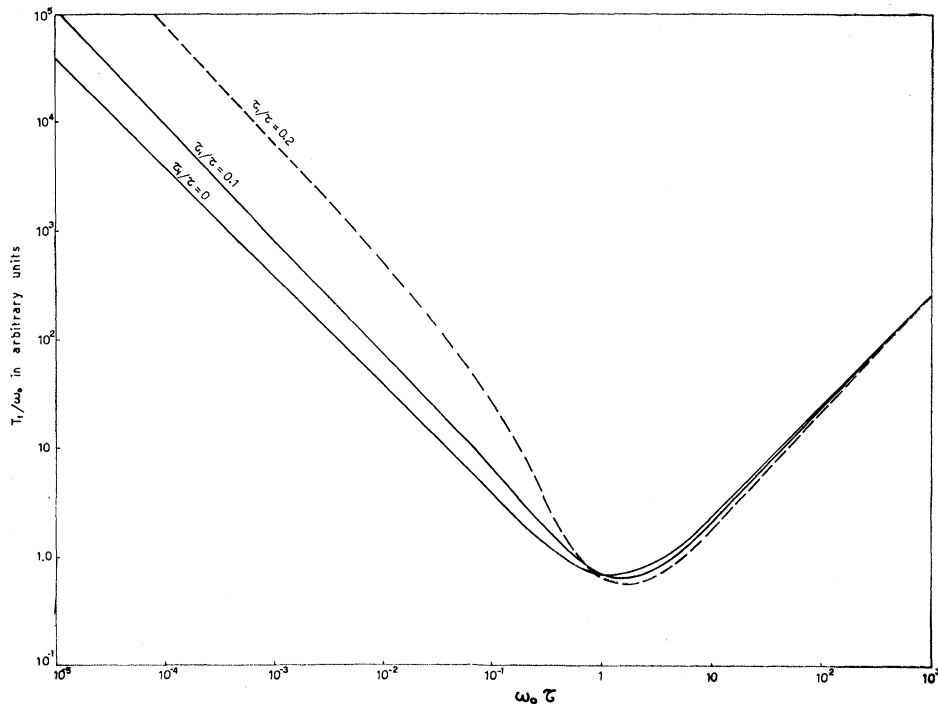


FIG. 5. T_1/ω_0 in arbitrary units versus $\omega_0\tau$ (ω_0 , Larmor frequency) for different values of τ_1/τ .

quency) for different values of τ_1/τ evaluated by assuming for $J(\omega)$ the expression (9). For $\tau_1/\tau=0$ the behavior of T_1 as function of τ coincides with the behavior of T_1 as function of τ_c proposed by Bloembergen assuming $\tau/2=\tau_c$.

For $\tau_1/\tau \neq 0$ and for $\omega\tau \ll 1$ the T_1 's calculated are longer than those calculated by Bloembergen *et al.*

CONCLUSIONS

The spectral density calculated under the assumption that a diatomic molecule jumps between two antiparallel equilibrium orientations with an average semiperiod $\tau = \tau_0 + \tau_1$ (τ_0 average time spent in an equilib-

rium position, τ_1 jump time) is in general different from the spectral density calculated following the theory of Bloembergen *et al.* assuming $\tau/2$ as correlation time.

The T_1 's calculated with the jumping molecule model are higher than the T_1 's calculated following the theory of Bloembergen *et al.* in the range $\omega\tau \ll 1$. It is probable that such an effect may occur in general when the relaxation is due to motions controlled by an activation energy.

ACKNOWLEDGMENT

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