PHYSICAL REVIEW A VOLUME 17, NUMBER 1 JANUARY 1978

Theory of nuclear spin relaxation by translational self-diffusion in liquid crystals: Nematic phase

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(Received 17 May 1977)

The theory of intermolecular nuclear spin relaxation by translational self-diffusion in liquid crystals is developed. Torrey's treatment of simple liquids is extended and modified for the liquid-crystalline phases by taking into account the anisotropy of the molecular motion, the elongated molecular shape, and the spin distribution on a molecule. Results, obtained for the frequency and angular dependence of T_1 in the nematic phase, are presented graphically for a variety of parameters and are compared with Torrey's results for classical liquids. A brief comparison with the available experimental data is presented.

I. INTRODUCTION

Liquid crystals have a lower order than ordinary crystals and also a lower symmetry than normal liquids. Such complex systems cannot be treated by conventional methods used for solids or liquids. We shall deal with nuclear magnetic relaxation which is a powerful tool for the study of molecular motions. In liquid crystals this relaxation can be caused by orientational order fluctuations,[1] local molecular reorientations,[2,3] or translational self-diffusion of molecules.[3,4] The relative effectiveness of these relaxation mechanisms depends on the temperature and on the Larmor frequency at which the relaxation is observed.

In this paper we shall deal with the spin relaxation due to translational self-diffusion. This motion affects relaxation by modulating the dipolar interactions between the spins belonging either to different molecules or to the same molecule. As the intramolecular contribution to the total relaxation rate has been evaluated already,[5] we shall restrict our treatment to the intermolecular contribution.

The theory of intermolecular longitudinal spin relaxation for isotropic liquids has been developed by Torrey.[6] Later, his theory was improved by taking into account the effect of a radial distribution function,[7] which has essentially no influence on the frequency dependence, but increases the absolute value of the relaxation rate by ~20%. The validity of Torrey's theory has been verified experimentally on many liquids, e.g., ethane,[7] glycerol,[8] and water.[9] It has also been used, without modifications, for liquid crystals.[3,4,10]

Recently, new experimental methods have been developed which allow accurate measurements of the T_1 dispersion in a wide frequency range,[11,3] as well as measurements of the dependence of the relaxation rate on the angle between the molecular order director and the external magnetic field.[2,12,13] There is no theory of intermolecular relaxation by self-diffusion appropriate for liquid crystals. In this paper Torrey's theory is being extended by taking into account the specific properties of liquid crystalline phases; such as the *anisotropy of molecular diffusion, the elongated molecular shape*, and *the distribution of spins* on the molecule.

In Sec. II the basic expressions for the longitudinal spin relaxation rate are derived. In the derivation it is assumed that spins are distributed on cylindrically shaped molecules which undergo a translational diffusive motion. In Sec. III, a model for the particle diffusion in nematic liquid crystals is described and the nuclear spin relaxation rate for nematic liquid crystals evaluated. Final results are obtained numerically and presented graphically in Sec. IV. A brief comparison with the available experimental data is also made.

II. GENERAL THEORY

Consider a system where each molecule carries N_0 equal nuclei with spin $I=\frac{1}{2}$. Other nuclei have negligible dipolar and quadrupole moments. For the sake of simplicity, we assume that the molecules can be represented by cylinders having length l and diameter d. It may be mentioned that the assumption of ellipsoidal rather than cylindrical shape has no appreciable influence on relaxation rates.

Further we assume that the orientational order of the long molecular axes is perfect. This is achieved when the oscillations of the molecules around their short axes are small in magnitude or fast compared to the process of self-diffusion. The molecular rotations around the long molecular axes are also usually[14] fast. As a consequence, the dipolar interactions are partly averaged out so that spins lie effectively on the long molecular axes.

Now translational diffusion is, except in some smectic phases with two dimensional order, fast compared to the dipolar frequency ω_D. This means that molecules are not coupled magnetically. Their coupling to the "lattice" is stronger similarly as in isotropic liquids. Therefore the spin temperature concept cannot be applied. We shall define the relaxation rate T_1^{-1} in the same way as it was done for polyatomic liquids.[15] The effect of three spin correlations will be omitted. In addition the spin diffusion along one molecule is assumed to be fast enough to spread, in a time much shorter than T_1, the Zeeman energy uniformly among all spins on the same molecule. The longitudinal spin relaxation is thus monoexponential and described by[16]

$$T_1^{-1}=\tfrac{3}{2}\gamma^4\hbar^2 I(I+1)[J^{(1)}(\omega)+J^{(2)}(2\omega)]. \tag{1}$$

Using the equivalence of all molecules, one has

$$J^{(k)}(\omega)=N\int_{-\infty}^{\infty}\frac{1}{N_0^2}\sum_{i,j}^{N_0}\langle F_{ij}^{(k)*}(0)F_{ij}^{(k)}(t)\rangle e^{i\omega t}\,dt. \tag{2}$$

Here N is the total number of nuclei with spin I in the sample, N_0 the number of spins on one molecule, and $F_{ij}^{(k)}$ the spacial parts of the dipolar interactions. In what follows we will assume that the external magnetic field $\vec{B}$ is parallel to molecular order director. The results for any other orientation of the magnetic field can be easily obtained using the transformation properties of spherical harmonics.[14]

The functions $J^{(k)}(\omega)$ depend only on the relative position $\vec{r}_{ij}$ of nuclei. To emphasize the difference between the effect of the position of the nuclei on a molecule and the effect of the relative position of two molecules, we shall write (see Fig. 1)

$$\vec{r}_{ij}=\vec{r}+\vec{\xi}_j-\vec{\xi}_i. \tag{3}$$

Here $\vec{r}$ is the vector connecting the centers of the molecules 1 and 2 while $\vec{\xi}_i$ and $\vec{\xi}_j$ are vectors from the molecular centers to the ith and jth nucleus. Because of the rotational averaging, the nuclear position vectors $\vec{\xi}_i$ lie on the long molecular axes. If we write

$$\vec{\xi}_j-\vec{\xi}_i=\vec{\xi}, \tag{4}$$

we can introduce the following notation:

$$F^{(k)}[\vec{r}_{ij}(t)]=F_\xi^{(k)}[\vec{r}(t)] \tag{5}$$

where

$$F_\xi^{(k)}(\vec{r})=\frac{e^{ik\varphi}}{[\rho^2+(z+\xi)^2]^{5/2}}\times\begin{cases}\rho^2-2(z+\xi)^2, & k=0\\ \rho(z+\xi), & k=1\\ \rho^2, & k=2.\end{cases} \tag{6}$$

ρ, z, and φ are cylindrical coordinates of $\vec{r}$ with z axis parallel to the long molecular axis. The correlation function $\langle F_\xi^{(k)*}[\vec{r}(0)]F_\xi^{(k)}[\vec{r}(t)]\rangle$ is the same for each pair of molecules and depends only on the position of the nuclei i and j. The sum

$$\frac{1}{N_0^2}\sum_{i,j}$$

in Eq. (2) can be substituted by the integral $\int_{-l}^{l}d\xi\,W(\xi)\cdots$, which we shall for brevity write as the average $(\;)_\xi$. $W(\xi)$ is the distribution of ξ and is related to $w(\xi_i)$—the distribution of spins along the molecular axis—by the following convolution:

$$W(\xi)=\int w(\xi_1)w(\xi-\xi_1)\,d\xi_1. \tag{7}$$

Next we express the ensemble average in Eq. (2) in terms of a probability function, $P(\vec{r}',\vec{r},t)$, and a static pair correlation function $g(\vec{r})$. Following Torrey[6,18] we can, using all previously mentioned notations, write

$$J^{(k)}(\omega)=n\int\int\int(F_\xi^{(k)*}(\vec{r})F_\xi^{(k)}(\vec{r}'))_\xi \times P(\vec{r}',\vec{r},t)\,d^3\vec{r}'\,g(\vec{r})\,d^3\vec{r}\,e^{i\omega t}\,dt. \tag{8}$$

Here n is the density of the nuclei with spin I in the sample. To understand the meaning of the functions $P(\vec{r}',\vec{r},t)$ and $g(\vec{r})$, we consider two molecules 1 and 2 and observe them at time zero and at time t (see Fig. 2). $g(\vec{r})d^3\vec{r}/V$, where V is the volume of the sample, is the probability that at time zero molecule 2 is in a volume $d^3\vec{r}$ at a position $\vec{r}$ from molecule 1. $P(\vec{r}',\vec{r},t)d^3\vec{r}$ is the

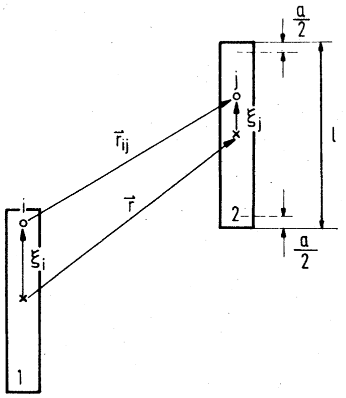

FIG. 1. Schematic presentation of two molecules with all notations used in Sec. II.

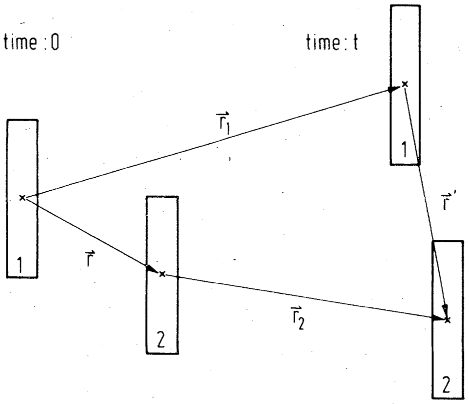

FIG. 2. Relative positions of two molecules at time zero and at time *t*.

probability that, if at time zero the relative distance between the two molecules was $\vec r$, at time t molecule 2 will be in a volume $d^3\vec r'$ located at $\vec r'$ from the new position of molecule 1.

Unfortunately, the joint probability function for diffusive motion $P(\vec r', \vec r, t)$ is not known even for simple liquids. It is therefore usually approximated with two one-particle autocorrelation functions $G_s(\vec r_1, t)$ and $G_s(\vec r_2, t)$, neglecting the two-particle correlations. In the theory of simple liquids $G_s(\vec r, t)$ is called the self-part of the van Hove dynamical pair correlation function. $G_s(\vec r_1, t)$ multiplied by $d^3\vec r_1$ gives the probability that molecule 1, initially at the origin, is after a time t located in $d^3\vec r_1$ at $\vec r_1$.

The diffusion in liquid crystals has some features of liquid phase and some of the solid phase.[19] The above approximation which is justified for the calculation of T_1 due to self-diffusion in simple liquids is often used even for crystals.[6] Therefore we expect that collective features of the translational diffusion can be neglected in the liquid crystalline phases as well. So the probability that molecule 1 moves to $\vec r_1$ in a time t, when molecule 2 has moved to $\vec r_2$, can be written simply as

$$G_s(\vec r_1, t)d^3\vec r_1 G_s(\vec r_2, t)d^3\vec r_2 . \tag{9}$$

As we have omitted all correlations, this product also allows for situations when both molecules move into the same space. To avoid this we shall multiply (9) by a kind of static pair correlation function $g_0(\vec r)$, which partly correlates the final positions of the two molecules. It can be seen that in the case of the positionally ordered smectic structures (periodical structure in the direction normal to the planes), some information which is hidden in $g(\vec r)$ is also in $G_s(\vec r_2, t)$ and $G_s(\vec r_1, t)$. To exclude this interference, we assume that $g_0(\vec r)$ includes only short-range positional order. For nematics $g_0(\vec r)$ coincides with $g(\vec r)$.

After a summation over all pair configurations which result in the same $\vec r'$ and $\vec r$, we find

$$P(\vec r', \vec r, t) = g_0(\vec r') \int G_s(\vec r_1, t) G_s(\vec r_1 + \vec r - \vec r', t)\, d^3\vec r_1 . \tag{10}$$

It is convenient to express $G_s(\vec r, t)$ with its space Fourier transform

$$G_s(\vec r, t) = \frac{1}{(2\pi)^3} \int \mathcal{G}_s(\vec q, t) e^{i\vec q\cdot\vec r} d^3\vec q . \tag{11}$$

This gives

$$P(\vec r', \vec r, t) = g_0(\vec r') \frac{1}{(2\pi)^3} \int \mathcal{G}_s(\vec q, t)^2 e^{i\vec q\cdot(\vec r' - \vec r)} d^3\vec q . \tag{12}$$

The spectral density of $\mathcal{G}_s(\vec q, t)$ is the self-part of the dynamic structure factor

$$S_s(\vec q, \omega) = \int_{-\infty}^{\infty} \mathcal{G}_s(\vec q, t) e^{i\omega t} dt . \tag{13}$$

We shall follow the treatment of simple liquids[20] where $S_s(\vec q, \omega)$ can be quite generally written as

$$S_s(\vec q, \omega) = 2\,\mathrm{Re} \frac{1}{-i\omega + M_s(\vec q, \omega)} . \tag{14}$$

This relation defines a memory function $M_s(\vec q, \omega)$, which is in fact a generalized diffusion coefficient multiplied by q^2. In the limit of small q and ω the memory function becomes

$$\lim_{\vec q,\, \omega \to 0} M_s(\vec q, \omega) = \vec q \cdot \underline{D} \cdot \vec q , \tag{15}$$

where $\underline{D}$ is the conventional diffusion tensor. Even for classical liquids there is no general solution for $M_s(\vec q, \omega)$. However, a number of phenomenological expressions[20] have been developed, which describe well the results of computer experiments on simple liquids.

Compared to a typical NMR frequency the kinetic frequency kTq^2/m is high even for q as small as to 10^{-3} Å^{-1} also in liquid crystals. Therefore one can see[20] that in the NMR frequency region the only important part of the memory function is real and independent of frequency, except for very small $\vec q$ the contributions of which are in any case negligible. Thus the memory function may be written as $\tau_{\vec q}^{-1}$, and we immediately see that

$$S_s(\vec q, \omega) = 2\,\mathrm{Re} \frac{1}{-i\omega + \tau_{\vec q}^{-1}} = \frac{2\tau_{\vec q}}{1 + (\omega\tau_{\vec q})^2} \tag{16}$$

has a Lorentzian shape in the frequency region of interest.

Since $\mathcal{G}_s(\vec q, t)$ has an exponential form $e^{-t/\tau_{\vec q}}$ and we can write

$$\mathcal{G}_s(\vec{q}, t)^2 = \mathcal{G}_s(\vec{q}, 2t)\,. \tag{17}$$

This enables us to simplify expression (12) to

$$P(\vec{r}', \vec{r}, t) = g_0(\vec{r}')G_s(\vec{r}' - \vec{r}, 2t)\,. \tag{18}$$

Introducing the Fourier transforms

$$\mathfrak{F}_\xi^{(k)}(\vec{q}) = \int F_\xi^{(k)}(\vec{r})g(\vec{r})e^{i\vec{q}\cdot\vec{r}}\,d^3\vec{r} \tag{19}$$

and

$$\mathfrak{F}_{0\xi}^{(k)}(\vec{q}) = \int F_\xi^{(k)}(\vec{r})g_0(\vec{r})e^{i\vec{q}\cdot\vec{r}}\,d^3\vec{r}\,, \tag{20}$$

we can write expression (8) in the following form:

$$J^{(k)}(\omega) = \frac{n}{16\pi^3}\int \mathrm{Re}(\mathfrak{F}_\xi^{(k)*}(\vec{q})\mathfrak{F}_{0\xi}^{(k)}(\vec{q}))_\xi S_s(\vec{q}, \omega/2)d^3\vec{q}\,. \tag{21}$$

The expression for $S_s(\vec{q}, \omega)$ can be obtained from dynamical computer experiments, but until now such calculations have not been done for liquid crystals.

In the next section we shall therefore derive some approximate expressions for $S_s(\vec{q}, \omega)$ using the random flights model.[21] Because of some essential differences between nematic and smectic liquid crystals, these two phases must be treated separately. In this paper we shall deal only with nematics.

III. NEMATIC LIQUID CRYSTALS

For the description of the translational self-diffusion of molecules in the nematic phase we choose a jump model, which will be treated in the random walk approximation.[21] This is similar to Torrey's[6] treatment of isotropic liquids, where the application of this relatively crude model gave quite a satisfactory agreement with nuclear magnetic relaxation data.[7,8,9]

We adopt the following model for the molecular motions: the molecule is in a potential well, it is then thermally excited and makes a fast diffusive jump into another potential well. The time spent for a jump is much shorter then the average time interval between two successive jumps. The motion during the jump is described by a fast anisotropic diffusion.

A. Random-walk model with anisotropic diffusive jumps

Following Chandrasekhar[21] we can express $G_s(\vec{r}, t)$ for a random jump process as

$$G_s(\vec{r}, t) = \sum_{n=1}^{\infty} P_n(\vec{r})W_n(t)\,, \tag{22}$$

where $P_n(\vec{r})$ is a distribution of the molecular position vector $\vec{r}$ after n jumps and $W_n(t)$ is the probability that n jumps occur in a time interval t. Following the theory of random flights[21] one can write

$$P_n(\vec{r}) = \frac{1}{(2\pi)^3}\int A^n(\vec{q})e^{-i\vec{q}\cdot\vec{r}}d^3\vec{q}\,, \tag{23}$$

where $A(\vec{q})$ is the Fourier transform of the distribution of $\vec{r}$ reached after only one jump:

$$A(\vec{q}) = \int P_1(\vec{r})e^{i\vec{q}\cdot\vec{r}}d^3\vec{r}\,. \tag{24}$$

Further we assume a Poisson distribution for the number of jumps which occur in a time interval t,

$$W_n(t) = \frac{1}{n!}\left(\frac{t}{\tau}\right)^n e^{-t/\tau}\,, \tag{25}$$

where τ is the mean time between two successive jumps. Inserting expressions (23) and (25) into (22), we get

$$G_s(\vec{r}, t) = \frac{1}{(2\pi)^3}\int \exp\{-i\vec{q}\cdot\vec{r} - [1 - A(\vec{q})]t/\tau\}\,d^3\vec{q}\,. \tag{26}$$

If we write

$$\tau/[1 - A(\vec{q})] = \tau_{\vec{q}}\,, \tag{27}$$

it follows

$$\mathcal{G}_s(\vec{q}, t) = e^{-t/\tau_{\vec{q}}}\,, \tag{28}$$

which is in agreement with our statement about the exponential nature of $\mathcal{G}_s(\vec{q}, t)$.

It is important to make a proper choice of $P_1(\vec{r})$, which is determined by the motion during the jump. As mentioned above we assume that this motion is an anisotropic diffusion which can be described by the solution

$$\frac{1}{4\pi(D_\perp'^2 D_\parallel' t^3)^{1/2}}\exp\left(-\frac{z^2}{4D_\parallel' t} - \frac{\rho^2}{4D_\perp' t}\right) \tag{29}$$

of the diffusion equation characterized by the diffusion tensor

$$\underline{D}' = \begin{pmatrix} D_\perp' & 0 & 0 \\ 0 & D_\perp' & 0 \\ 0 & 0 & D_\parallel' \end{pmatrix}. \tag{30}$$

$D_\parallel'$ and $D_\perp'$ describe the diffusion in the direction parallel and perpendicular to the order director, respectively.

The probability that a molecule finishes its jump after a time t can be described by

$$e^{-t/\tau'}dt/\tau'\,, \tag{31}$$

where τ' is the mean time spent for a jump. It does not depend on the direction of the motion, because in the moment when a molecule is trapped after performing a diffusive jump, both otherwise independent motions, || and ⊥ to the order director, cease.

Using (29) and (31) and averaging over all possible jump time periods, we get

$$P_1(\vec{r}) = \frac{1}{4\pi D_\perp' \tau'}\left(\rho^2 + \frac{D_\parallel'}{D_\perp'} z^2\right)^{-1/2} \times \exp\left[-\left(\frac{\rho^2}{D_\perp'\tau'} + \frac{z^2}{D_\parallel'\tau'}\right)^{1/2}\right] \tag{32}$$

and for its Fourier transform

$$A(\vec{q}) = (1 + D_\perp'\tau' q_\perp^2 + D_\parallel'\tau' q_\parallel^2)^{-1}. \tag{33}$$

We do not need quantities $\underline{D'}$ and τ' separately because in our treatment only the product $\underline{D'\tau'}$ occurs. This product is related to the mean square of the jump length $\langle r_0^2\rangle$ in the following way:

$$\langle r_0^2\rangle = \langle \rho_0^2\rangle + \langle z_0^2\rangle = 4D_\perp'\tau' + 2D_\parallel'\tau', \tag{34}$$

where $\langle \rho_0^2\rangle$ and $\langle z_0^2\rangle$ are the mean-square displacements in ⊥ and || direction, respectively. On the other hand, the mean square displacement in an arbitrary time t, obtained from (26) and (33) is

$$\langle r^2(t)\rangle = (4D_\perp'\tau' + 2D_\parallel'\tau')t/\tau. \tag{35}$$

We can now introduce effective diffusion constants

$$D_\perp^0 = D_\perp' \frac{\tau'}{\tau}, \quad D_\parallel^0 = D_\parallel' \frac{\tau'}{\tau} \tag{36}$$

and derive the relation

$$\langle r^2(t)\rangle = (4D_\perp^0 + 2D_\parallel^0)t \tag{37}$$

which describes the overall motion of the molecules even for time periods longer than the time interval between two successive jumps. $D_\perp^0$ and $D_\parallel^0$ are the macroscopic self-diffusion constants of the perfectly oriented liquid crystalline phase, while in the real liquid crystal they are related[22] to measurable constants $D_\perp$ and $D_\parallel$.

Now we write $A(\vec{q})$ using (36):

$$A(\vec{q}) = (1 + D_\perp^0\tau q_\perp^2 + D_\parallel^0\tau q_\parallel^2)^{-1}. \tag{38}$$

Thus both $A(\vec{q})$ and $P(\vec{r}\,', \vec{r}, t)$ are determined. Before we proceed with the main calculation of the spectral densities $J^{(k)}(\omega)$, the static pair correlation function $g(\vec{r})$ and the distribution of spins on each molecule should be discussed.

B. Static pair correlation function

The positional order of molecular centers in a nematic phase has only a short range. As a result the long-range part of the static pair correlation function $g(\vec{r})$ is zero, and $g(\vec{r}) = g_0(\vec{r})$. The detailed structure of $g(\vec{r})$ is unknown in the nematic liquid crystalline phase. We shall use the most simple "square well" form

$$g(\rho, z) = \begin{cases} 1, & |z| < l \text{ and } \rho > d, \text{ or } |z| > l \\ 0, & \rho \leqslant d \text{ and } |z| \leqslant l. \end{cases} \tag{39}$$

A better approximation could be obtained by a "square well" surrounded with a δ function whose strength can be determined by a well-known relation between $g(\vec{r})$ and the compressibility of the substance.

C. Distribution of spins

We shall treat three different spin distributions (Fig. 3):

(i) Spins are concentrated in the center of the molecule. This is described by $w(z) = \delta(z)$, a description which greatly simplifies the calculations. It will be shown later that this distribution yields results which do not differ appreciably from those obtained for a more realistic spin distribution, provided one deals with elongated molecules, i.e., $l \gg d$.

(ii) Spins are uniformly distributed along the molecular axis except on both ends which are assumed to be free of spins.

$$w(z) = \begin{cases} \dfrac{1}{l-a}, & |z| < (l-a)/2 \\ 0, & |z| \geqslant (l-a)/2, \end{cases} \tag{40}$$

where $a/2$ is the length of molecular ends without spins. We must introduce these free ends because in our picture the molecules may touch one another.

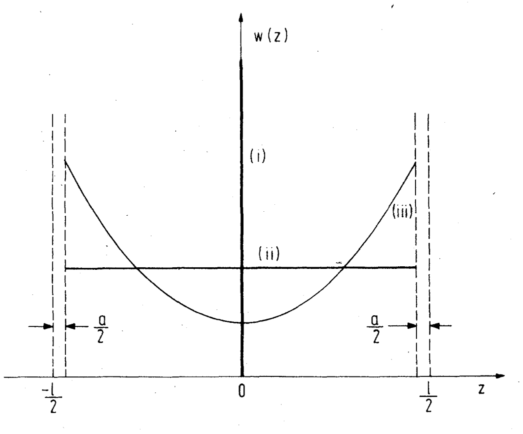

FIG. 3. The spin density along the molecular axis $w(z)$: (i) spins are concentrated in the center of the molecule, (ii) uniform distribution of spins, and (iii) spin density increasing toward molecular ends like in real molecules.

Performing the convolution (7) with (40), we get

$$W(\xi)=\begin{cases}\dfrac{1-|\xi|/(l-a)}{(l-a)}, & |\xi|<l-a\\ 0, \quad |\xi|\geq l-a. & \end{cases} \tag{41}$$

(iii) The spin density is increasing from the center toward the ends of the molecule and, for the same reason as before, it drops to zero at $z=(l-a)/2$. We assume

$$w(z)=\begin{cases}\alpha+\beta z^2, & |z|<(l-a)/2\\ 0, & |z|\geq(l-a)/2,\end{cases} \tag{42}$$

which roughly describes the increase of the spin density on a molecule when going from the benzene protons along the CH_2- chain to the CH_3-end groups. The constants α and β depend on the nature of the molecule.

D. $J^{(k)}(\omega)$ due to translational self-diffusion in nematics

Using the above model one can easily show that (21) yields

$$J^{(k)}(\omega)=\frac{n}{8\pi^2}\int\int\left(|\mathfrak{F}_\xi^{(k)}(\vec{q})|^2\right)_\xi S_s(\vec{q},\omega/2)\,dq_\parallel\, q_\perp\, dq_\perp, \tag{43}$$

where

$$S_s(\vec{q},\omega/2)=\frac{2\tau_{\vec{q}}}{1+(\omega\tau_{\vec{q}}/2)^2} \tag{44}$$

and

$$\mathfrak{F}_\xi^{(k)}(\vec{q})=2\pi i^k e^{ik\phi}e^{-iq_\parallel\xi}\times[\mathcal{A}^{(k)}(\vec{q})+\mathcal{B}^{(k)}(\vec{q},\xi)] \tag{45}$$

with

$$\mathcal{A}^{(k)}(\vec{q})=\int_d^\infty J_k(\rho q_\perp)\int_{-\infty}^\infty e^{iq_\parallel z}f^{(k)}(\rho,z)\,dz\,\rho\,d\rho\;, \tag{46}$$

$$\mathcal{B}^{(k)}(\vec{q},\xi)=\int_0^d J_k(\rho q_\perp)\left(\int_{l+\xi}^\infty+\int_{-\infty}^{\xi-l}\right)e^{iq_\parallel z}f^{(k)}(\rho,z)\,dz\,\rho\,d\rho. \tag{47}$$

Here $f^k(\rho,z)$ are

$$f^{(k)}(\rho,z)=\frac{1}{(\rho^2+z^2)^{5/2}}\times\begin{cases}\rho^2-2z^2, & k=0\\ \rho z, & k=1\\ \rho^2, & k=2.\end{cases} \tag{48}$$

$\mathcal{A}^{(k)}(\vec{q})$ includes contributions of all molecules which lie in the region with $\rho>d$, while $\mathcal{B}^{(k)}(\vec{q})$ describes the contribution of the molecules which are in the region where $\rho<d$ and $|z|>l$. $\mathcal{A}^{(k)}(\vec{q})$ is thus independent of the position of spins on molecule (ξ). It alone describes rigorously only long molecules ($l\gg d$), with spins concentrated in the center of the molecule. After the evaluation of the integrals, one gets

$$\mathcal{A}^{(k)}(\vec{q})=2c_k\frac{q_\parallel^2}{q_\parallel^2+q_\perp^2}[q_\parallel dK_{k-1}(q_\parallel d)J_k(q_\perp d)+q_\perp dJ_{k-1}(q_\perp d)K_k(q_\parallel d)], \tag{49}$$

with

$$c_k=\begin{cases}1, & k=0\\ \tfrac{1}{3}i, & k=1\\ \tfrac{1}{3}, & k=2.\end{cases}$$

The term $\mathcal{B}^{(k)}(\vec{q})$, which cannot be written analytically in a closed form, must be taken into account if molecules are not appreciably elongated ($l\sim d$) or if spins are distributed along the whole molecule.

Introducing a dimensionless function $Q(\omega\tau,\langle r_\perp^2\rangle/d^2, D_\parallel^0/D_\perp^0)$ we can write the relaxation rate in the form

$$T_1^{-1}=\tfrac{9}{8}\gamma^4\hbar^2\frac{n\tau}{d^3}\,Q(\omega\tau,\langle r_\perp^2\rangle/d^2, D_\parallel^0/D_\perp^0). \tag{50}$$

The function Q must be calculated numerically. A double integration over $\vec{q}$ space must be performed, if one includes only the $\mathcal{A}^{(k)}(\vec{q})$ term in Eq. (45). On the other hand, the addition of $\mathcal{B}^{(k)}(\vec{q})$ requires its numerical evaluation, followed by a double integration over $\vec{q}$ space and an averaging over the distribution $w(\xi)$.

IV. RESULTS AND DISCUSSION

Values of the function Q have been calculated for the frequency range $\omega\tau=0$ to $\omega\tau\approx 10$ for a number of different values of the parameters which determine the ratio $D_\parallel^0/D_\perp^0$ and the average squared jump length. In most of these calculations the $\mathcal{A}^{(k)}(\vec{q})$ term only was used since the inclusion of the $\mathcal{B}^{(k)}(\vec{q})$ term required much more computing time. However, fortunately, the cases, in which the $\mathcal{B}^{(k)}(\vec{q})$ term was included, showed that its effect on the final value of Q was negligible, provided that there were one or more spins at the center of the elongated molecule. This result is obvious (see the definition of $\mathcal{B}^{(k)}(\vec{q})$!), because the distance between the molecular centers is much larger in the direction of the long molecular axes than in the direction perpendicular to the latter. Much more surprising is the fact that the inclusion of the $\mathcal{B}^{(k)}(\vec{q})$ term in the calculation of the overall relaxation rate $T_1^{-1}\propto Q$ is still negligible even if a uniform distribution of spins along the molecule is considered, and does not exceed 1% for a spin distribution, in which the density of spins increases toward the ends of the molecule. In these calculations of Q the following molecular dimensions were used: $l=25$ Å, $d=5$ Å, and $a=2$ Å. Results do not change appreciably even if the value of a is further decreased to 1 Å, or if the ratio l/d is increased. The influence of the $\mathfrak{B}^{(k)}(\vec{q})$ term on the angular dependence of T_1 will be later considered in connection with Fig. 7. All other theoretical curves, which are presented, are calculated by retaining in Eq. (45) the $\mathfrak{A}^{(k)}(\vec{q})$ term only. The accuracy of the numerical integration is better than 1%.

The frequency dependence of the relaxation rate is considered next. It is calculated for the case when the molecular director is parallel to the external magnetic field in the entire sample ($\Delta = 0$). The sample acquires this orientation by itself, when placed in the magnetic field. All measurements of the T_1 dispersion up to now were performed on these self-oriented nematics. Figure 4 shows the dispersion of the anisotropic relaxation rate. The function Q, which is directly proportional to T_1^{-1}, is plotted for the low-frequency range from $\omega\tau_0 = 0$ to $\omega\tau_0 = 1$. Here τ_0 is defined with the relation $\tau_0 = d^2/4D_\perp^0$. Typical values of τ_0 are $\sim 6\times 10^{-9}$ sec for MBBA ($T = 18\,^\circ\mathrm{C}$) and $\sim 2\times 10^{-10}$ sec for PAA ($T = 120\,^\circ\mathrm{C}$). The corresponding values for $\omega\tau_0$ are 0.37 and 0.01 at the Larmor frequency $\nu_L = 10$ MHz. In the calculation of Q we used a value of 2 for the ratio $D_\parallel^0/D_\perp^0$, which is taken from the experimental data,[22-24] and does not differ much for different nematic compounds. On the other hand, there is no definite knowledge of the value of $\langle r_\perp^2\rangle/d^2$ which is also involved in the calculation of Q. For this reason three different values, i.e., 1, 0.1, and 0.01 were used for $\langle r_\perp^2\rangle/d^2$.

It can be recognized at first sight that the frequency behavior of the anisotropic relaxation rate is very similar to the isotropic one, calculated by Torrey[6]: (i) the relaxation rate is increased as the ratio $\langle r_\perp^2\rangle/d^2$ increases from 0.01 up to 1, as $\omega\tau$ approaches zero; (ii) at low values of $\omega\tau$, $T_1^{-1} \propto \text{const.} - (\omega\tau)^{1/2}$, which is a well known relation from the isotropic theory[7]; (iii) in the high-frequency limit, the anisotropic relaxation rate is proportional to ω^{-2} [see Eq. (43)!]. This is again the same frequency behavior as predicted by Torrey.

After the establishment of low- and high-frequency limits, we compared isotropic rate with the anisotropic relaxation rate in the whole frequency range. To this end we calculated $R = T_{1\,\text{iso}}^{-1}/T_{1\,\text{aniso}}^{-1}$. This ratio depends appreciably on the relations between the parameters used in the isotropic and anisotropic case. An interesting result is obtained, if we take $D_{\text{iso}} = D_\perp^0$, $r_{\text{iso}} = d$, and τ equal in both cases. With these parameters R becomes independent of the frequency in a wide frequency region, as shown in Fig. 5. R is equal to 1.4 from the lowest values of $\omega\tau_0$ up to $\omega\tau_0 \sim 0.1$. This constant region is followed by a small increase in R until it reaches a slightly higher constant value in the high-frequency regime. The change from the low-frequency to the high-frequency value of R is approximately 15%. It can be further decreased to only 5% by a suitable choice of D. This result seems to be of large practical importance. When a theoretical expression is needed to describe the dispersion of the intermolecular spin-lattice relaxation due to translational diffusion in nematic liquid crystals, Torrey's results, reduced by a factor, can be used instead of tedious numerical calculations for the real anisotropic case. The error incurred by this approximation is rather small especially for low values of $\omega\tau$. Even for the entire frequency range it hardly exceeds the usual experimental error.

In addition to the frequency dependence, the anis-

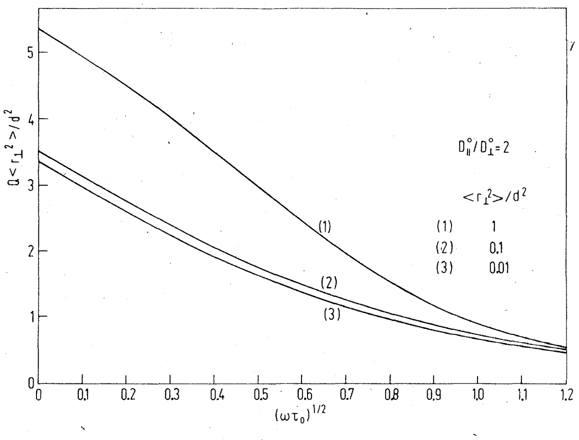

FIG. 4. Frequency dependence of $Q \propto T_1^{-1}$ for three different jump lengths.

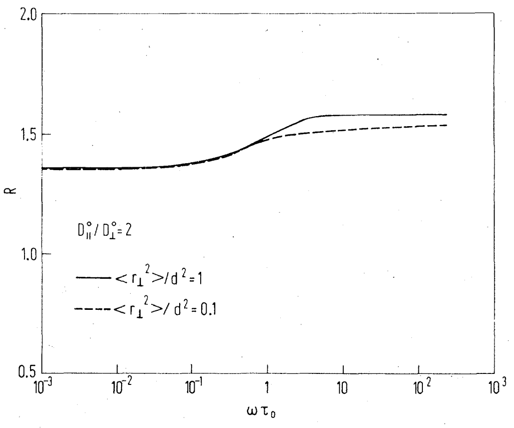

FIG. 5. Frequency dependence of the ratio $R = T_{1\,\text{iso}}^{-1}/T_{1\,\text{aniso}}^{-1}$ for $D_{\text{iso}} = D_\perp^0$, $r_{\text{iso}} = d$ and τ equal in both cases.

otropy, i.e., the dependence of the relaxation rate on the angle Δ between the molecular director and the magnetic field, has also been studied. After the application of the transformations for spherical harmonics[17,6] we obtain spectral densities $J^{(k)}(\omega, \Delta)$ for an arbitrary orientation of the preferred molecular direction in the magnetic field:

$$\begin{aligned} J^{(1)}(\omega, \Delta) = {} & \tfrac{1}{4}(\sin^2\Delta - \sin^4\Delta)J^{(0)}(\omega, 0^\circ) \\ & +(1 - \tfrac{5}{2}\sin^2\Delta + 2\sin^4\Delta)J^{(1)}(\omega, 0^\circ) \\ & + \tfrac{1}{8}(2\sin^2\Delta - \sin^4\Delta)J^{(2)}(\omega, 0^\circ) \end{aligned} \tag{51}$$

and

$$\begin{aligned} J^{(2)}(\omega, \Delta) = {} & \tfrac{1}{4}\sin^4\Delta\, J^{(0)}(\omega, 0^\circ) \\ & + 2(2\sin^2\Delta - \sin^4\Delta)J^{(1)}(\omega, 0^\circ) \\ & + (1 - \sin^2\Delta + \tfrac{1}{8}\sin^4\Delta)J^{(2)}(\omega, 0^\circ)\,. \end{aligned} \tag{52}$$

Here $J^{(k)}(\omega, 0^\circ)$ stands for the spectral densities calculated assuming $\Delta = 0^\circ$. The angular dependence of T_1^{-1} is obtained by inserting the expressions (51) and (52) into expression (1).

Figure 6 shows the angular dependence of the reduced relaxation rate $T_1^{-1}(\Delta)/T_1^{-1}(0^\circ)$ at three different frequencies but for the same ratio $D_\parallel^0/D_\perp^0 = 2$ and $\langle r_\perp^2\rangle/d^2 = 0.1$. The main feature of these dependences is the *decrease* of the relaxation rate as the angle Δ increases from 0° to 90°. This behavior is quite opposite to that caused by order direction fluctuations, where an increase in Δ results in a strong increase in T_1^{-1}.[2,4] A typical value of the calculated decrease is 25% for frequencies with $\omega\tau_0 < 1$, as shown in Fig. 8. In the limit of high frequencies, the decrease is smaller (≈10%). The relative decrease in the calculated relaxation rate seems to be essentially independent of the jump length and the distribution of spins on the molecule. We see that the anisotropy of T_1^{-1} does not depend strongly on the model of spin distribution, Fig. 7. The assumption of uniform spin distribution changes the anisotropy of T_1^{-1} only by 1% compared to the result obtained when spins are assumed to be located at the center of the molecule. The same holds for the assumption of a spin density distribution which increases towards each end of the molecule. In this case the change

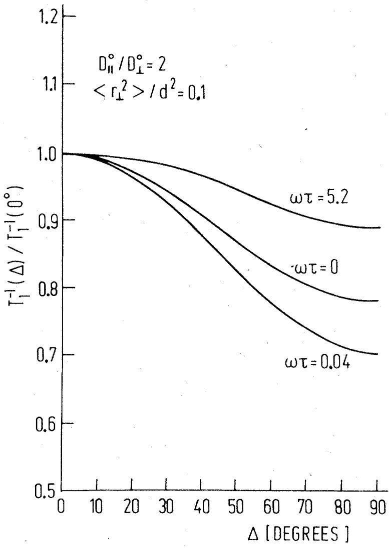

FIG. 6. Angular dependence of T_1^{-1} for three different values of $\omega\tau$.

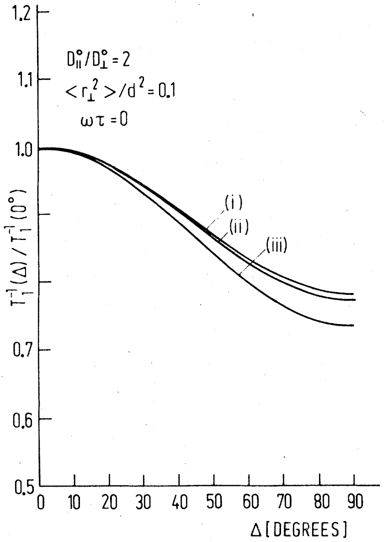

FIG. 7. Angular dependence of T_1^{-1} at $\omega\tau = 0$ for three different spin distributions: (i) spins concentrated in the center of the molecule, (ii) uniform distribution of spins, and (iii) spin distribution $w(z) = \alpha + \beta z^2$.

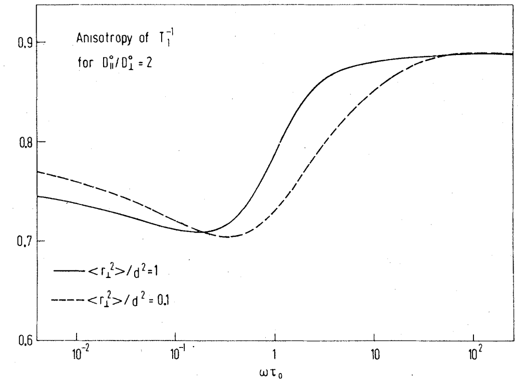

FIG. 8. Frequency dependence of the anisotropy of T_1^{-1} for two different jump lengths and $D_\parallel^0/D_\perp^0 = 2$.

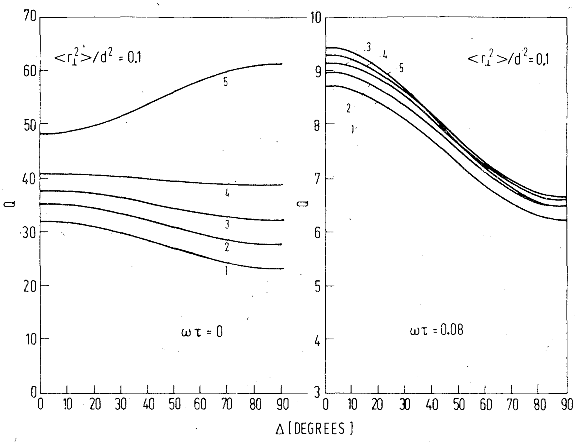

FIG. 9. Angular dependence of $Q \propto T_1^{-1}$ at two different frequencies for: (1) $D_\parallel^0/D_\perp^0=3$, (2) $D_\parallel^0/D_\perp^0=2$, (3) $D_\parallel^0/D_\perp^0=1.5$, (4) $D_\parallel^0/D_\perp^0=1$, and (5) $D_\parallel^0/D_\perp^0=\frac{1}{3}$ using the same value of $D_\perp^0$ in all cases.

amounts to 5%.

Finally, the influence of the parameter $D_\parallel^0/D_\perp^0$ on the angular behavior was studied, Fig. 9. In the zero-frequency limit a decrease in the relaxation rate is observed as long as $D_\parallel^0 > D_\perp^0$. It amounts to 15% at $D_\parallel^0/D_\perp^0=1.5$ and to 28% for $D_\parallel^0/D_\perp^0=3$. All experimental values of the ratio $D_\parallel^0/D_\perp^0$ fall into this region.[22-24] If $D_\parallel^0$ were equal to $D_\perp^0$ the anisotropy of T_1^{-1} would nearly disappear. It would even exhibit quite opposite behavior if $D_\parallel^0$ were smaller than $D_\perp^0$. This indicates that in the zero frequency limit the anisotropy of T_1^{-1} is mainly determined by the anisotropy of the diffusion and less by the molecular shape. On the other hand, the same calculations at higher frequency, $\omega\tau=0.08$, show nearly the same anisotropy of the relaxation rate for various values of the ratio $D_\parallel^0/D_\perp^0$. It seems that at higher frequencies the molecular shape becomes the dominant "anisotropic factor."

As shown above, the relaxation rate caused by translational self-diffusion in nematic liquid crystals exhibits a specific angular dependence—it decreases with increasing Δ—which is essentially independent of the Larmor frequency, the jump length, or the ratio $D_\parallel^0/D_\perp^0$. The measurements of the angular dependence of proton T_1^{-1}, performed up to now, do not exhibit a definite decrease in the relaxation rate. Yet, T_1^{-1} seems to be constant (in MBBA-EBBA mixture)[12] or shows a slight increase (in pure MBBA)[2] which cannot be explained by the usual order director fluctuations relaxation itself. This situation indicates the possibility of "combined" $(1/T_{\text{self-diff}}+1/T_{1\text{ODF}})$ spin relaxation in low temperature nematics which has been already suggested in order to explain the observed T_1 relaxation dispersion.[3]

The only measurements of proton T_1 dispersion, where the intermolecular contribution to the relaxation rate is strictly separated from the intramolecular, are done on PAA-*d*6.[25] The measured frequency dependence of the intermolecular contribution is of the form $T_{1\text{inter}}^{-1}=A'\omega^{-1/2}+B'$, as shown by Wade.[26] The frequency dependent term is characteristic for order director fluctuations. The relaxation rate, caused by translational self-diffusion, should be in PAA-*d*6 nearly frequency independent in the MHz range if the large value of self-diffusion constant ($D\sim 3\times 10^{-6}$ cm^2/sec)[24] in this compound is taken into account. The estimated value of this contribution (0.05 sec^{-1} for the following parameters: $n=0.02$ spins/Å^3, $d=6$ Å, $D_\perp=3\times 10^{-6}$ cm^2/sec (at 120 °C), $\langle r_\perp^2\rangle/d^2 \leq 0.1$, $D_\parallel^0/D_\perp^0=2$) is nearly equal to the experimental value of B', which is about half of the total value of $T_{1\text{inter}}^{-1}$ at 60 MHz or 100 MHz. This indicates that the intermolecular contribution to the relaxation rate in PAA-*d*6 is partly due to the self-diffusion and partly to other relaxation mechanisms.

V. CONCLUSIONS

In this paper the theory of intermolecular longitudinal spin relaxation due to molecular self-diffusion in liquid crystals is developed. It has been assumed that other molecular motions have different rates so that their direct effect on the relaxation can be treated separately. The motional averaging—the indirect effect of fast molecular rotation around the long axes—enables us to treat spins as lying effectively on the long molecular axes. The use of perfect local orientational order of molecules is well established if tumbling of molecules is fast or has small amplitude.

Numerical results are evaluated for the relaxation rate in nematic phase. It is shown that the frequency dependence of T_1 in nematics is similar to that obtained for simple isotropic liquids. We proved that the Torrey's analytic expression for $T_1(\omega)$ can be used, with proper adjustment of parameters, for the treatment of T_1 in nematics in a wide frequency interval. Further, the anisotropy of the relaxation rate in nematic liquid crystals is calculated. The angular dependence is opposite to the one characteristic for the order director fluctuations relaxation mechanism. As the angle between the molecular preferred axis and the external magnetic field is increased from zero to 90°, the relaxation rate decreases. A typical value of the decrease is 25%.

ACKNOWLEDGMENTS

The authors are indebted to Professor R. Blinc for calling their attention to this problem and for many helpful discussions. One of the authors (S. Ž.) acknowledges interesting and stimulating discussions with Professor J. Jeener and Professor P. Résibois. The authors wish to thank E. Zakrajšek for helpful advice on numerical calculations, and M. Žumer for programming.

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