PHYSICAL REVIEW A VOLUME 21, NUMBER 2 FEBRUARY 1980

Theory of nuclear-spin relaxation by translational self-diffusion in liquid crystals: Smectic *A* phase

M. Vilfan

J. Stefan Institute, University E. Kardelj of Ljubljana, 61000 Ljubljana, Yugoslavia

S. Žumer

Physics Department, University E. Kardelj of Ljubljana, 19 Jadranska, 61000 Ljubljana, Yugoslavia

(Received 5 July 1979)

The general theory of nuclear-spin relaxation induced by translational self-diffusion in liquid crystals developed in a previous paper is applied to the smectic *A* phase. The inter- and intralayer molecular jumps, the spin distribution, and the elongated shape of the molecules are taken into account. Results are obtained for the frequency and angular dependence of T_1 and presented graphically for a variety of parameters. The results for the smectic *A* phase are compared with those for the nematic and isotropic phase. The theory reproduces the proton relaxation rate in terephtal-bis-butylaniline very well.

I. INTRODUCTION

Nuclear magnetic relaxation is a widely used method for the study[1] of molecular motions in the liquid-crystalline state. Its importance has increased with new experimental methods which allow accurate measurements of T_1 dispersion in a wide frequency range[2-6] and measurements of the angular dependence of T_1.[7-9] In liquid crystals, where several molecular motions take place, the nuclear-magnetic-relaxation data can lead to a conclusive information on molecular dynamics only if contributions of all different motions to the relaxation rate are quantitatively evaluated. So far a number of studies have been devoted to the effects of "order director fluctuations,"[2,7,10-20] local molecular reorientations,[3,15-17] self-diffusion,[3,21-23] motions of separate molecular groups,[24] and layer sliding.[25] It has been shown in particular that the contribution of self-diffusion in the smectic phases is appreciable, especially at high frequencies.[6,26] Since no theory on the diffusion-induced relaxation in smectic phases is available, Torrey's theory[27] for isotropic liquids has been used to fit the experimental data.

In our first paper,[23] hereafter called I, we have developed a general theory of the longitudinal spin relaxation due to translational self-diffusion in liquid-crystalline phases, and applied it to a quantitative calculation of the relaxation rate in the nematic phases. It has been shown that slightly modified Torrey's theory for classical liquids can be used as a good approximation for the calculation of the frequency dependence of T_1 caused by translational diffusion in nematics, while, for the evaluation of the angular anisotropy of T_1, our specific approach should be used.

The purpose of this paper is to calculate—on the basis of the general theory from I—the nuclear magnetic relaxation rate caused by molecular self-diffusion in the smectic *A* phase. This phase[28] is characterized by layered structure; the centers of elongated molecules lie on parallel equidistant planes, thus resembling a two-dimensional fluid. Within each plane the preferred direction of the long axis is perpendicular to the smectic plane.

The idealized structure of the smectic *A* phase and the model of molecular diffusion in it are described in Sec. II. They are used together with results of I to evaluate the diffusion-induced T_1 appropriate for the smectic *A* phase. Final results were obtained numerically and are presented graphically in Sec. III. A comparison with the experimental data in terephtal-bis-butylaniline (TBBA) from Ref. 5 is given.

II. THEORY

A. Idealized smectic *A* phase

A somewhat idealized model of the smectic *A* phase was assumed as follows. We consider a system where each molecule of the length l and diameter d ($d/l \ll 1$) has N_0 equal nuclei with spin $I=\frac{1}{2}$ (protons), while other nuclei have negligible magnetic dipole and electric quadrupole moments. The resonant spins are distributed on the long molecular axis. This approximation is justified only when the rotations of molecules around their long axes are fast.[23] Experimental results[29-31] show that this is a common situation in smectic *A* phases.

Further, we assume that orientational order of long molecular axes is perfect. This is a good approximation for the smectic *A* phase, since the value of the nematic order parameter is close to 1.[32]

Translational diffusion of molecules in the smectic A phase, which is assumed to be faster[33,34] than ω_D, is described by two independent thermally activated jump motions[23,27]:

(i) The isotropic intralayer motion is two-dimensional liquidlike. Each molecule stays in a potential well until it is thermally excited and makes a fast diffusive jump into another potential well. The time spent for a jump is much shorter than the average time interval $\tau_\perp$ between two succesive jumps. The motion between two potential wells is considered to be a fast two-dimensional isotropic diffusion.

(ii) The interlayer motion is described also by a thermally activated random jump process. Molecules can jump only to one of the two adjacent layers. The jump length is always equal to the interlayer distance. The time spent for a jump is assumed to be much shorter than $\tau_\parallel$—the average time between two succesive interlayer jumps.

B. Nuclear magnetic relaxation

We assume that nuclear magnetic relaxation due to self-diffusion can be treated separately from the rest of the molecular motions. This is justified by their characteristic rates being significantly different from the rate of the diffusion. The longitudinal spin relaxation of the nuclei with spin I due to the translational self-diffusion, which is fast compared to ω_D, can be described by a single relaxation rate[35,23]:

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

where Δ is the angle between molecular director and magnetic field. Using the transformation properties of spherical harmonics one can relate[23] $J^{(k)}(\omega,\Delta)$ to $J^{(k)}(\omega)$ (which stands for $\Delta = 0$). Therefore we shall restrict our calculations to this orientation and recall the expression for $J^{(k)}(\omega)$ from I:

$$J^{(k)}(\omega) = \frac{n}{16\pi^3}\int \mathrm{Re}[\mathfrak{F}_\xi^{(k)*}(\vec{q})\,\mathfrak{F}_{0\xi}^{(k)}(\vec{q})] \times S_s(\vec{q},\tfrac{1}{2}\omega)\,d^3q\,. \tag{2}$$

Here n is the density of nuclei with spin I in the sample, and $S_s(\vec{q},\omega)$ the space-time Fourier transform of the one-particle dynamical autocorrelation function $G_s(\vec{r},t)$. The product $G_s(\vec{r},t)d^3r$ is the probability that the molecule, which is initially at the origin, is located in d^3r at $\vec{r}$ after a time t. Functions

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

and

$$\mathfrak{F}_{0\xi}^{(k)}(\vec{q}) = \int F_\xi^{(k)}(\vec{r})g_0(\vec{r})e^{i\vec{q}\cdot\vec{r}}\,d^3r \tag{4}$$

are the weighted Fourier transforms of the spatial part of the dipolar interaction

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

where ρ, z, φ are cylindrical coordinates of the vector connecting the centers of the two molecules, which are carrying the interacting spins; ξ is the difference of ξ_1 and ξ_2, which measures the relative position of the spins on the molecule (see Fig. 1). The average $(\;)_\xi$ is performed over $W(\xi)$ (the distribution of differences ξ), which is related to $w(\xi_1)$ (the distribution of spins along the molecular axis) by the convolution

$$W(\xi) = \int w(\xi_1)w(\xi-\xi_1)\,d\xi_1\,. \tag{6}$$

Our next step is to calculate $S_s(\vec{q},\omega)$ specific for the smectic A phase.

C. Dynamical structure factor $S_s(\vec{q},\omega)$

The dynamical autocorrelation function $G_s(\vec{q},t)$, which is related to $S_s(\vec{q},\omega)$ by

$$S_s(\vec{q},\omega) = \iint_{-\infty}^{\infty} G_s(\vec{q},t)e^{i\omega t}e^{i\vec{q}\cdot\vec{r}}\,dt\,d^3r\,, \tag{7}$$

is written—in accord with our model, which assumes the independence of the intralayer and interlayer diffusion—as

$$G_s(\vec{r},t) = G_{s\parallel}(z,t)G_{s\perp}(\vec{\rho},t)\,; \tag{8}$$

$G_{s\perp}(\vec{\rho},t)$ describes the intralayer motion and $G_{s\parallel}(z,t)$ the interlayer motion. Following Chandrasekhar,[36] the autocorrelation functions for both random jump processes can be written as

$$G_{s\parallel}(z,t) = \sum_{n_\parallel} P_{n_\parallel}(z)W_{n_\parallel}(t) \tag{9}$$

and

$$G_{s\perp}(\vec{\rho},t) = \sum_{n_\perp} P_{n_\perp}(\vec{\rho})W_{n_\perp}(t)\,, \tag{10}$$

where $P_{n_\perp}(\vec{\rho})$ is the distribution of the intralayer molecular position vectors $\vec{\rho}$ after $n_\perp$ jumps and $P_{n_\parallel}(z)$ is the distribution of the z component of the molecular position vector after $n_\parallel$ jumps. $W_{n_\parallel}(t)$ and $W_{n_\perp}(t)$ are the probabilities that correspondent number of jumps; i.e., $n_\parallel$ and $n_\perp$ occur in a time interval t. They are assumed to be of the

Poisson type characterized by $\tau_\parallel$ and $\tau_\perp$ (the characteristic times between two successive jumps). In the random-flight approximation one easily gets[36]

$$G_{s\perp}(\vec{\rho},t)=\frac{1}{(2\pi)^2}\int \exp\{-i\vec{q}_\perp\cdot\vec{\rho}-[1-A_\perp(\vec{q}_\perp)]t/\tau_\perp\}d^2q_\perp \tag{11}$$

and

$$G_{s\parallel}(z,t)=\frac{1}{2\pi}\int \exp\{-iq_\parallel z-[1-A_\parallel(q_\parallel)]t/\tau_\parallel\}dq_\parallel\,, \tag{12}$$

where

$$A_\perp(\vec{q}_\perp)=\int P_{1_\perp}(\vec{\rho})\exp(i\vec{q}_\perp\cdot\vec{\rho})\,d^2\rho \tag{13}$$

and

$$A_\parallel(q_\parallel)=\int P_{1_\perp}(z)\exp(iq_\parallel z)\,dz\,. \tag{14}$$

Taking into account that the 2D intralayer motion is described by the model (i), the results of Torrey[27] and of I can be used, giving

$$A_\perp(\vec{q}_\perp)=1/(1+D_\perp^0\tau_\perp q_\perp^2) \tag{15}$$

Here $D_\perp^0$ is the macroscopic interlayer diffusion constant, which is related to the mean-square intralayer jump length by

$$\langle r_\perp^2\rangle=4D_\perp^0\tau_\perp\,. \tag{16}$$

It should be noted that $D_\perp^0$ is the diffusion tensor of the perfectly ordered liquid-crystalline phase, while the experimentally determined tensor $D_\perp$ in real liquid crystals is slightly smaller.[33]

For the interlayer motions where the length of all jumps is l, the distribution function $P_{1_\perp}(z)$ of the molecular positions after one interlayer jump is

$$P_{1_\perp}(z)=\tfrac{1}{2}[\delta(z+l)+\delta(z-l)]\,. \tag{17}$$

Its Fourier transform is

$$A_\parallel(q_\parallel)=\cos q_\parallel l\,. \tag{18}$$

Thus in our model, the smectic A dynamical structure factor is of the same Lorenzian form as for the nematics and classical liquids:

$$S_s(\vec{q},\omega)=2\tau_{\vec{q}}/[1+(\omega\tau_{\vec{q}})^2]\,. \tag{19}$$

The difference occurs in the structure of the correlation time $\tau_{\vec{q}}$, which for the smectic A phase is

$$\tau_{\vec{q}}^{-1}=[1-A_\parallel(q_\parallel)]/\tau_\parallel+[1-A_\perp(\vec{q}_\perp)]/\tau_\perp\,. \tag{20}$$

D. Static pair correlation function

The positional order of the molecules in the smectic A phase has a long range in the direction normal to the layers, and a short liquidlike range in the layers. Therefore the static pair correlation function $g(\vec{r})$ used in Eqs. (3) and (4) has a discrete periodic structure in the direction normal to the smectic planes, and a 2D liquidlike structure in the layer. We can write it as the product of two parts,

$$g(\vec{r})=g_1(\vec{r})g_0(\vec{r})\,, \tag{21}$$

where $g_1(\vec{r})$ corresponds to the long- and $g_0(\vec{r})$ to the short-range positional order. Within our model of the idealized smectic A phase, g_1 is the sum of δ functions:

$$g_1(\vec{r})=g_1(z)=l\sum_{m=0}^{+\infty}\delta(z-ml)\,, \tag{22}$$

while for $g_0(\vec{r})$ the "square-well" form is used:

$$g_0(\vec{r})=g_0(\vec{\rho})=\begin{cases}1, & \rho>d \text{ and } |z|\leq l \text{ or } |z|>l\,,\\ 0, & \rho\leq d \text{ and } |z|\leq l\,.\end{cases} \tag{23}$$

E. Distribution of spins

As in the nematic case, we shall treat three different spin distributions:

(a) Spins are concentrated in the center of each molecule. Such a situation is described by

$$w(\xi_i)=\delta(\xi_i)\,, \tag{24}$$

which greatly simplifies the calculations and has proved to be quite satisfactory for the nematic case.[23] However, for layered structures this approximation is too rough, as will be shown later.

(b) Spins are uniformly distributed along the molecular axis except on both ends (with the length $\frac{1}{2}a$), which are assumed to be free of spins.[23] This gives

$$w(\xi_i)=\begin{cases}1/(l-a), & |\xi_i|<\frac{1}{2}(l-a)\,,\\ 0, & |\xi_i|\geq\frac{1}{2}(l-a)\,.\end{cases} \tag{25}$$

(c) The spin density increases with the distance from the center of the molecule quadratically. It is zero on both ends of the molecule (length $\frac{1}{2}a$):

$$w(\xi_i)=\begin{cases}\alpha+\beta\xi_i^2, & |\xi_i|<\frac{1}{2}(l-a)\,,\\ 0, & |\xi_i|\geq\frac{1}{2}(l-a)\,.\end{cases} \tag{26}$$

By properly adjusting the constants α and β, this contribution can take into account the increasing number of spins when going from the benzene protons along the CH_2 chain to the CH_3 end group. It is applicable to relatively short molecules.

F. Expression for the longitudinal spin relaxation rate

To get finally the expression for T_1^{-1}, the integrations in Eq. (3) and (4) for $\mathfrak{F}_\xi^{(k)}(\vec{q})$ and $\mathfrak{F}_{\xi 0}^{(k)}(\vec{q})$ should be performed.

$\mathfrak{F}_{\xi 0}^{(k)}(\vec{q})$ has the same form as in the nematic case and the expression derived in I can be used directly by

$$\mathfrak{F}_{\xi 0}^{(k)}(\vec{q}) = 2\pi i^k e^{ik\varphi} e^{-iq_\parallel \xi}[\mathfrak{A}^{(k)}(\vec{q}) + \mathfrak{B}^{(k)}(\vec{q},\xi)], \tag{27}$$

where

$$\mathfrak{A}^{(k)}(\vec{q}) = 2\begin{Bmatrix} 1 \\ \frac{1}{3} \\ \frac{1}{3} \end{Bmatrix} \frac{q_\parallel^2}{q_\parallel^2 + q_\perp^2}[q_\parallel d K_{k-1}(q_\parallel d) J_k(q_\perp d) + q_\perp d J_{k-1}(q_\perp d) K_k(q_\parallel d)] \tag{28}$$

and

$$\mathfrak{B}^{(k)}(\vec{q},\xi) = \int_0^d J_k(\rho q_\perp)\int_{l+\xi}^{\infty} + \int_{-\infty}^{\xi - l} e^{iq_\parallel z} \times f^{(k)}(\rho, z)\rho\, d\rho\, dz, \tag{29}$$

with

$$f^{(k)}(\rho, z) = \frac{1}{(\rho^2 + z^2)^{5/2}}\begin{Bmatrix} \rho^2 - 2z^2, & (k=0) \\ \rho z, & (k=1) \\ \rho^2, & (k=2) \end{Bmatrix}. \tag{30}$$

The J_k are Bessel functions and the K_k modified Bessel functions. The function $\mathfrak{F}_\xi^{(k)}(\vec{q})$ contains $g(\vec{r})$, appropriate for the smectic A phase, and had to be calculated. The integration over z and ρ yields

$$\mathfrak{F}_\xi^{(k)}(\vec{q}) = 2\pi i^k e^{ik\varphi}[\mathcal{E}^{(k)}(\vec{q},\xi) + \mathfrak{D}^{(k)}(q_\perp,\xi)], \tag{31}$$

where

$$\mathcal{E}^{(k)}(\vec{q},\xi) = 2\begin{Bmatrix} -1 \\ \frac{1}{3} \\ \frac{1}{3} \end{Bmatrix} q_\perp l e^{-lq_\perp} \times \left[\cos q_\parallel l \begin{Bmatrix} \cosh \xi q_\perp \\ -\sinh \xi q_\perp \\ \cosh \xi q_\perp \end{Bmatrix} + i \sin q_\parallel l \begin{Bmatrix} -\sinh \xi q_\perp \\ \cosh \xi q_\perp \\ -\sinh \xi q_\perp \end{Bmatrix}\right] \tag{32}$$

and

$$\mathfrak{D}(q_\perp,\xi) = \int_d^\infty f^{(k)}(\rho,\xi) J_k(\rho q_\perp)\rho\, d\rho \tag{33}$$

The integrations in the terms $\mathfrak{B}^{(k)}(\vec{q},\xi)$ and $\mathfrak{D}^{(k)}(q_\perp,\xi)$ had been performed after the expansion of the integrand in the power series (one for $\rho/z > 1$ and another for $\rho/z < 1$).

Combining expressions (27)–(33) with expressions (1) and (2), and introducing a dimensionless function $R(\omega\tau_\perp, \langle r_\perp^2\rangle/d^2, D_\parallel/D_\perp, l/d, \Delta)$, we can write the relaxation rate T_1^{-1} caused by translational diffusion in the smectic A phase

$$T_1^{-1} = \frac{9}{8}\gamma^4 \hbar^2 \frac{n\tau_\perp}{d^3} R\left(\omega\tau_\perp, \frac{\langle r_\perp^2\rangle}{d^2}, \frac{D_\parallel}{D_\perp}, \frac{l}{d}, \Delta\right). \tag{34}$$

The function R has been calculated for different parameters by integrating numerically over $q_\parallel, q_\perp$, and ξ.

III. RESULTS AND DISCUSSION

Values of the function R from the Eq. (34) have been obtained numerically for a number of different values of $\omega\tau_\perp$, $\langle r_\perp^2\rangle/d^2$, $D_\parallel/D_\perp$, and Δ. Some results have been evaluated for three different distributions of spins along the molecule, as indicated in Sec. II.

The distribution with one spin in the middle of the molecule is the easiest for a numerical treatment. Some relaxation rates calculated with this distribution have already been presented in Ref. 37. Therefore in this paper the main emphasis is on the remaining two more realistic distributions. It has been found, however, that the values of R are nearly the same—within the limits of the numerical accuracy—for both the uniform and quadratic spin distribution. If not specially indicated, the values of T_1^{-1} presented in this section are calculated for the uniform spin distribution.

The value of the ratio of the molecular length to its diameter has been set at 5, and the closest distance a between two spins belonging to adjacent layers at 2 Å (see Fig. 1).

The frequency dependence of the relaxation rate caused by translational diffusion in layered phases is presented in Fig. 2. The function R, which is proportional to T_1^{-1}, exhibits a characteristic frequency dependence, and depends on the orientation of the sample in the external magnetic field. The dispersion curves in Fig. 2 are plotted for two extreme orientations, $\Delta = 0°$ and 90°. The relaxation rate for isotropic fluid, with the diameter of spherical molecules d_{sph} equal to d and with

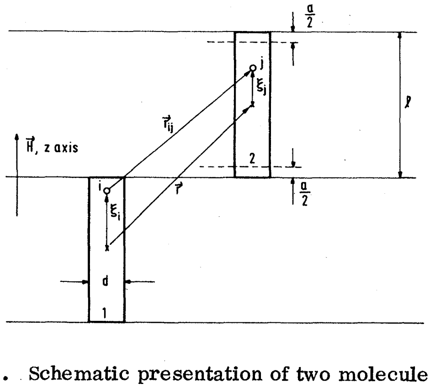

FIG. 1. Schematic presentation of two molecules with all notations used in text.

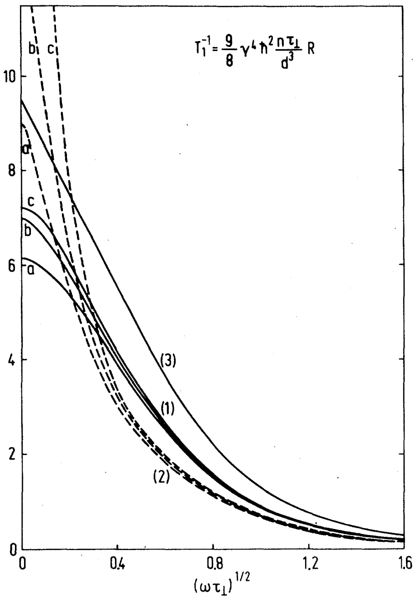

FIG. 2. Frequency dependence of $R \propto T_1^{-1}$ at $\vec{H} \parallel \vec{N}_0$ (1) and $\vec{H} \perp \vec{N}_0$ (2) for $\langle r_\perp^2\rangle/d^2 = 1$ and for three different ratios: $D_\parallel/D_\perp = 1$ lines denoted by (a), $D_\parallel/D_\perp = \frac{1}{3}$ (b), and $D_\parallel/D_\perp = 0$ (c). Torrey's function with parameters as described in text. (3) is added for comparison.

$\tau_{\text{iso}} = \tau_\perp$, is plotted for comparison (Torrey's function).

Several facts concerning the dispersion in layered structures should be noted:

(i) In the frequency range studied, from $\omega\tau_\perp = 0$ to $\omega\tau_\perp \sim 2.5$, the diffusion induced relaxation rate depends on the orientation of the smectic planes in the magnetic field. At low frequencies ($\omega\tau_\perp < 0.3$), the difference in the dispersion behavior of T_1^{-1} at $\Delta = 0°$ and $90°$ is significant; the decrease of T_1^{-1} with increasing $\omega\tau_\perp$ is much steeper at the perpendicular orientation. When $\omega\tau_\perp$ increases above 0.3 this difference in behavior rapidly disappears. The value of $\omega\tau_\perp = 0.3$ at the proton Larmor frequency $\nu_L = 30$ MHz in a typical smectic A phase [with $D_\perp \approx D_\parallel = 10^{-6}$ cm^2/sec and $(\langle r_\perp^2\rangle)^{1/2} \approx d = 6$Å] corresponds to the jump time $\tau_\perp = \langle r_\perp^2\rangle/4D_\perp \approx 10^{-9}$ sec.

(ii) The dispersion curves at low frequencies do not follow the well-known $J^{(k)}(\omega) = C - F\omega^\nu$ law with $\nu = \frac{1}{2}$, which is valid for isotropic liquids[27] and nematics.[23] In the smectic A phase the exponent ν has values from 0.5 to 1, depending on the index k. Thus the above analytic expression is of no practical use in the smectic case.

(iii) Only in the low-frequency region, where $\omega\tau_\perp < 0.3$, does the value of T_1^{-1} depend on the ratio $D_\parallel/D_\perp$. The experimentally determined ratio $D_\parallel/D_\perp$ in the smectic A phase is either close to unity (in TBBA), or smaller than unity.[33,34] We have calculated R for $D_\parallel/D_\perp = 1$, $\frac{1}{3}$, and 0. The value of R increases with the slowing down of the interlayer diffusion ($D_\parallel/D_\perp \to 0$) and reaches its maximum value in the limiting case where only the diffusion within layers takes place. Since at low frequencies T_1^{-1} is proportional to $\tau_{\vec{q}} = [1/\tau_\perp(\vec{q}) + 1/\tau_\parallel(\vec{q})]^{-1}$, slowing down of one motion increases the relaxation rate. At higher frequencies, with $\omega\tau_\perp > 0.3$, the influence of the anisotropy of the jump diffusion on the relaxation disappears, and the three curves, calculated for three different $D_\parallel/D_\perp$ ratios, fuse into one. The T_1^{-1} dispersion for $D_\parallel/D_\perp = 0$, presented in Fig. 2, is similar in its behavior to that calculated for the planar diffusion of spherical molecules.[38] However, these earlier results cannot be directly compared with ours, because the distribution of spins on the elongated molecules which we have taken into account, has an appreciable effect.

(iv) In the frequency range between $\omega\tau_\perp = 0.3$ and 1, which is of practical importance for many NMR studies, the anisotropic relaxation rate for the usual orientation, in which the molecules lie along the direction of the magnetic field, depends on the Larmor frequency in a similar way as that calculated for the nematic phase with the same molecular dimensions. This confirms the earlier suggestion that at $\omega\tau_\perp > 0.3$ the anisotropy of the diffusion becomes irrelevant. The anisotropy in the relaxation rate is then induced by the elongated shape of the molecules. For the description of the dispersion of the T_1^{-1} ($\omega\tau_\perp > 0.3$) it is a good approximation to use Torrey's T_1^{-1} with $d_{\text{sph}} = d$ and $\tau_{\text{iso}} = \tau_\perp$, diminished by an appropriate factor (in our case about 1.4) for both, the nematic and the smectic A phase when $\vec{N}_0 \parallel \vec{H}$.

(v) The effectivness of the diffusion-induced relaxation rate depends as well on the mean-square jump lengths $\langle r_\perp^2\rangle$ and $\langle r_\parallel^2\rangle$. As the latter is fixed in the smectic A phase with the thickness of the layer, only the variations in $\langle r_\perp^2\rangle$ need be considered. We have therefore also calculated R for a small jump length $\langle r_\perp^2\rangle/d^2 = 0.04$ with $D_\parallel/D_\perp = 1$, and $\omega\tau_\perp = 0.01$ and 0.02. The calculated value is smaller for $\approx 40\%$ as that with $\langle r_\perp^2\rangle/d^2 = 1$ at the same ω. Otherwise its dispersion and angular dependence do not show any different features.

(vi) In the high-frequency limit ($\omega\tau_\perp \to \infty$), which is not shown in Fig. 2, the relaxation rate decreases proportional to ω^{-2}, as has been already pointed out for the nematic and isotropic case.

(vii) It should be mentioned that the values of R, if calculated for the distribution with all spins located in the center of the molecule, exceed those for a realistic distribution by a factor of 3, but exhibit roughly the same general dispersion behavior.[37]

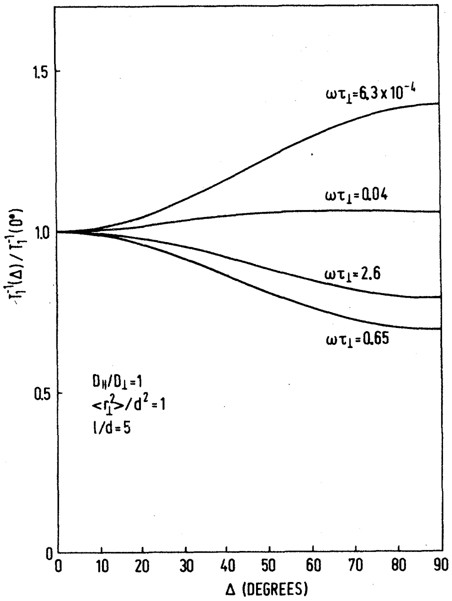

FIG. 3. Angular dependence of T_1^{-1} for four different values of $\omega\tau_\perp$.

Although many features of the T_1^{-1} dependence on the angle between $\vec{N}_0$ and $\vec{H}$ have been pointed out already in the discussion on the dispersion behavior, it is worthwhile to present some curves showing the angular dependence of T_1^{-1}. The angular dependence usually characterizes a relaxation mechanism very well. In smectic phases it can be determined simply by rotating the sample in the magnetic field, which is much easier than in the nematic phase.

The angular dependence of the relaxation rate caused by translational diffusion in a smectic A phase at different Larmor frequencies is shown in Fig. 3. The ratio $D_\parallel/D_\perp$ has been taken as 1 and the mean-square jump length equals the square of molecular diameter. The smaller value of $\langle r_\perp^2\rangle$ would not influence the results. As the angle Δ is increased from 0° to 90° the relaxation rate increases sharply at very low frequencies. This feature is characteristic for the diffusion in smectic structures. As the frequency is increased, the anisotropy of T_1^{-1} first diminishes and then, at $\omega\tau_\perp \sim 0.1$, a completely different dependence of T_1^{-1} on the angle Δ appears. The relaxation rate decreases with increasing Δ (see Fig. 3). This behavior does not change appreciably at higher frequencies studied. The drop in the relaxation rate from $\Delta=0°$ to 90° is about 25% when uniform or quadratic spin distribution is considered. The more unusual distribution with spins located in the center of the molecule results in an angular dependence of T_1^{-1} with the same main features but with more pronounced anisotropy. At the frequency $\omega\tau_\perp=0.162$ for example, the drop in the relaxation rate amounts to 50% for this specific distribution (see Fig. 4).

A test has been performed to demonstrate how the anisotropy of T_1^{-1} is influenced by the variation of $D_\parallel/D_\perp$ (that is, by the anisotropy of the diffusion process; see Fig. 5). As already suggested

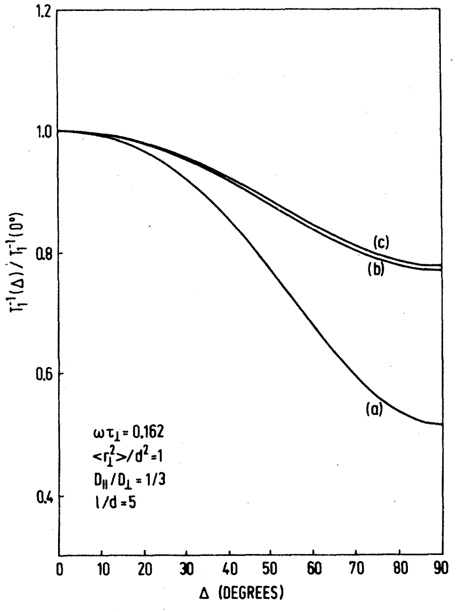

FIG. 4. Angular dependence of T_1^{-1} at $\omega\tau_\perp=0.162$ for (a) spins concentrated in the center of the molecule, (b) uniform distribution of spins, and (c) spin distribution $w(\xi_i)=\alpha+\beta\xi_i^2$ with parameters appropriate for TBBA.

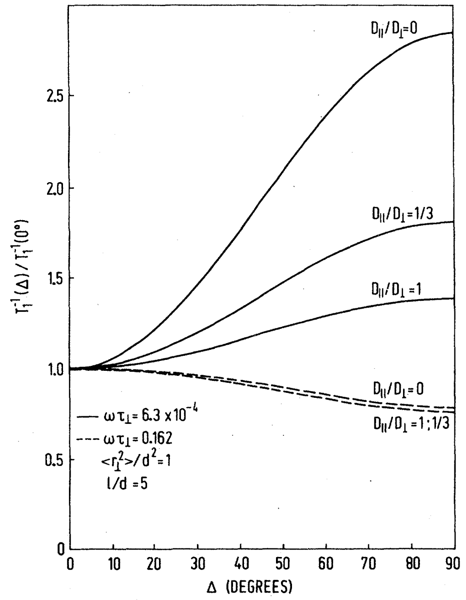

FIG. 5. Angular dependence of $R \propto T_1^{-1}$ at two frequencies for three different ratios $D_\parallel/D_\perp$.

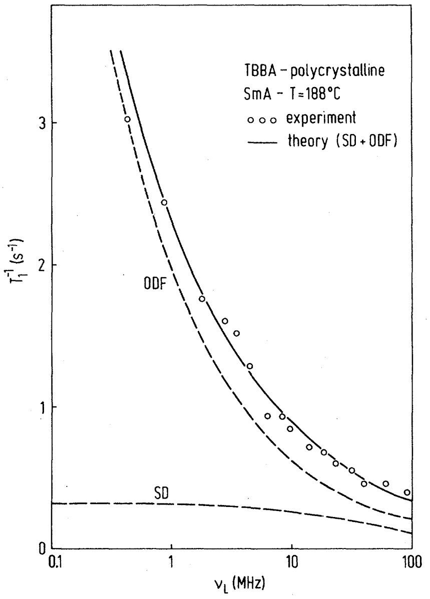

FIG. 6. Frequency dependence of T_1^{-1} in the smectic *A* phase of TBBA. The theoretical curve is the sume of the ODF and SD contributions, which are indicated separately as well.

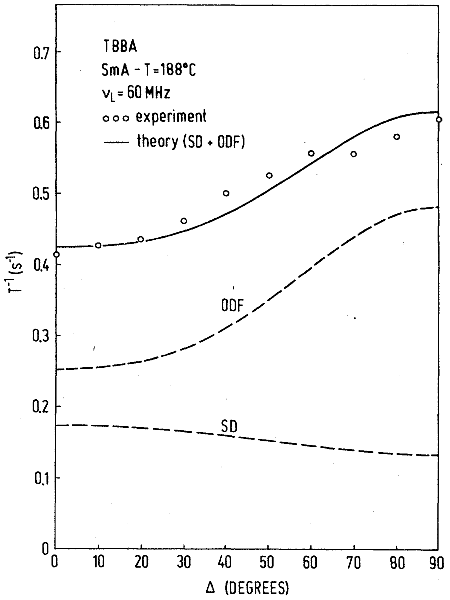

FIG. 7. Angular dependence of T_1^{-1} in the smectic *A* phase of TBBA. The theoretical curve is the sum of the ODF and SD contributions, which are indicated separately as well.

(Fig. 5), only at low frequencies the details of the motion influence the relaxation rate. Its anisotropy in the low-frequency limit is larger by almost a factor of 2 in the case of the diffusion within the layer ($D_\parallel/D_\perp=0$) as compared to that with $D_\parallel/D_\perp=1$. At higher frequencies the difference disappears.

Until now the proton relaxation rates have been determined experimentally in several smectic *A* compounds.[5,20,26] The most exhaustive data exist on relaxation in the smectic *A* phase of the terephtal-bis-butylaniline (TBBA). The dispersion of the proton T_1^{-1} has been determined in the wide frequency range from 0.5 to 90 MHz. The data on the angular dependence are available as well. It has been suggested earlier[6] that there are two contributions to the proton relaxation in this case, one caused by a mechanism similar to the order director fluctuations (ODF) in the nematic phase with $T_{1\text{ODF}}^{-1}=A/\sqrt{\omega}$ and the other caused by translational self-diffusion (SD). We have used the theory developed above to get a comprehensive explanation of the dispersion and of the angular dependence of proton relaxation rates.

It is shown in Fig. 6 that the T_1^{-1} dispersion can be fitted to the sum of an ODF-type contribution with $A=4950$ sec$^{-3/2}$ and of a self-diffusion-induced contribution if the intermolecular distance within the smectic layer is 6.5 Å (which is roughly the diameter of the phenyl ring) and $\langle r_\perp^2\rangle$ is assumed to be equal to d^2. For the other parameters needed in the calculation of T_1^{-1} from Eq. (34), the following well-known values have been used: $l=28.5$ Å, $D_\perp=2.5\times10^{-6}$ cm^2/sec(Ref. 34), $D_\parallel\approx D_\perp$ at 188°C,[34] and $n=0.05$ Å^{-3}. The diminishing of $\langle r_\perp^2\rangle/d^2$ leads to a good fit as well, if a smaller value of the molecular diameter is used ($d\approx5.2$ Å for $\langle r_\perp^2\rangle/d^2\approx0.04$). The value $d=5.2$ Å is in excellent agreement with the value 5.18 Å which has been determined for the intermolecular distance in the smectic *H* phase of TBBA.[39] However, on going from the smectic *H* phase to the smectic *C* and *A* phases, the average intermolecular distance increases slightly owing to enhanced thermal motions. Thus the value of $\langle r_\perp^2\rangle/d^2$, which would fit the experimental T_1^{-1} data in the smectic *A* phase for the real intermolecular distance, should not be much higher than 0.04, but in any case smaller than 1. Similar conclusions have been obtained earlier by Krüger *et al.*[34]

It can be seen from Fig. 6 that the diffusion-induced relaxation in the smectic *A* phase is negligible at frequencies smaller than 1 MHz. At higher frequencies its contribution increases (relative to the ODF mechanism).

The angular dependence confirms the above suggestions. At 60 MHz the diffusion contribution amounts to about one-third of the ODF contribution. Characteristic decreasing of the SD relaxation rate and strong increase of the ODF relaxation rate[20] fit together the experimental data well (Fig. 7). The values of the parameters used in this fit are the same as in the previous one.

IV. CONCLUSIONS

In this paper the theory of the intermolecular longitudinal spin-lattice relaxation due to molecular self-diffusion in the smectic A phase is evaluated. Starting from the general theory for the diffusion-induced spin relaxation in liquid crystals, developed in I, the specific properties of the layered structure have been taken into account. Molecular diffusion is proposed to be a superposition of two jump motions: one intralayer motion (2D liquidlike), and one interlayer motion with the jump length equal to the thickness of the layer.

Numerical results for the frequency and angular dependences of T_1^{-1} show that in the smectic phases the anisotropy of molecular jump motion influences the relaxation rate only in the low-frequency region, where $\omega\tau_\perp \lesssim 0.3$. For higher frequencies the effect of spin distribution and of the elongated molecular shape almost completely determine the behavior of the dispersion and of the angular dependence. This explains the similarity between the relaxation behavior in the nematic and smectic A phases at higher frequencies.

The theory proposed in this paper is applicable to the relaxation in all smectic A systems where the contribution of self-diffusion to the relaxation is not negligible. We have used it to reproduce the proton relaxation in the smectic A phase of TBBA. The limiting case of our theory, with $D_\parallel/D_\perp = 0$, can describe, to a good approximation, also the diffusion-induced relaxation in the lyotropic lamellar phase.

ACKNOWLEDGMENT

The authors wish to thank Professor R. Blinc for constant encouragement in all stages of this work.

---

[1] G. Wade, Ann. Rev. Phys. Chem. 28, 47 (1977). (This excellent review article covers NMR relaxation in thermotropic liquid crystals up to 1977.)

[2] W. Wölfel, F. Noack, and M. Stohrer, Z. Naturforsch. A 30, 437 (1975).

[3] V. Graf, F. Noack, M. Stohrer, Z. Naturforsch. A 32, 61 (1977).

[4] W. Wölfel, *Kernrelaxationsuntersuchungen der Molekülbewegung im Flüssigkristall PAA* (Minerva, München, 1978).

[5] R. Blinc, M. Luzar, M. Mali, R. Osredkar, J. Seliger, and M. Vilfan, J. Phys. (Paris) 37, C3-73 (1976).

[6] R. Blinc, M. Vilfan, M. Luzar, J. Seliger, and V. Žagar, J. Chem. Phys. 68, 303 (1978).

[7] J. W. Doane, C. E. Tarr, and M. A. Nickerson, Phys. Rev. Lett. 33, 620 (1974).

[8] I. Zupančič, V. Žagar, M. Rožmarin, I. Levstek, F. Kogovšek, and R. Blinc, Solid State Commun. 18, 1591 (1976).

[9] J. Pirš, P. Ukleja, and J. W. Doane, Solid State Commun. 19, 877 (1976).

[10] P. Pincus, Solid State Commun. 7, 415 (1969).

[11] R. Blinc, D. L. Hogenboom, D. E. O'Reilly, and E. M. Peterson, Phys. Rev. Lett. 23, 969 (1969).

[12] B. Cabane, Adv. Mol. Relaxation Processes 3, 341 (1972).

[13] J. W. Doane and D. C. Johnson, Chem. Phys. Lett. 6, 291 (1970).

[14] E. T. Samulski, C. R. Dybowski, and C. G. Wade, Phys. Rev. Lett. 29, 340 (1973); 29, 1050 (1973); B. M. Fung, C. G. Wade, and L. D. Orwoll, J. Chem. Phys. 64, 148 (1976).

[15] P. Ukleja, J. Pirš, and J. W. Doane, Phys. Rev. A 14, 414 (1976).

[16] J. H. Freed, J. Chem. Phys. 66, 4183 (1977).

[17] P. Nordio and U. Segre, Gazz. Chim. Ital. 106, 431 (1976).

[18] T. E. Faber, Proc. R. Soc. A 353, 277 (1977).

[19] (a) R. Y. Dong, W. F. Forbes, and M. M. Pintar, Solid State Commun. 9, 151 (1971); (b) J. J. Visintainer, R. Y. Dong, E. Bock, E. Tomchuk, D. B. Dewey, An-Li Kuo, and C. G. Wade, J. Chem. Phys. 66, 3343 (1977).

[20] R. Blinc, M. Luzar, M. Vilfan, and M. Burgar, J. Chem. Phys. 63, 3445 (1975).

[21] M. Vilfan, R. Blinc, and J. W. Doane, Solid State Commun. 11, 1073 (1972); R. Blinc, M. Vilfan, and V. Rutar, *ibid.* 17, 171 (1975).

[22] M. Vilfan and S. Žumer, *Proceedings XIX Congress Ampère, Heidelberg, 1976* (Groupement Ampere, Heidelberg-Geneve, 1976), p. 189.

[23] S. Zumer and M. Vilfan, Phys. Rev. A 17, 424 (1978).

[24] J. Charvolin and B. Deloche, J. Phys. (Paris) 37, C3-69 (1976); P. J. Bos and J. W. Doane, Phys. Rev. Lett. 40, 1030 (1978).

[25] S. Žumer, Phys. Rev. A 15, 378 (1977).

[26] G. J. Krüger, H. Spiesecke, and R. Van Steenwinkel, Mol. Cryst. Liq. Cryst. 40, 103 (1977).

[27] H. C. Torrey, Phys. Rev. 92, 962 (1953); H. A. Rhesing and H. C. Torrey, *ibid.* 131, 1102 (1963); G. J. Krüger, Z. Naturforsch. A 24, 560 (1969); J. F. Harmon and B. N. Müller, Phys. Rev. 182, 400 (1969); G. Held and F. Noack, *Proceedings XVIII Congress Ampère, Nottingham, 1974* (Nottingham Ampere Committee, 1974), p. 461.

[28] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[29] J. A. Janik, J. M. Janik, K. Otnes, K. Rosciszewski, and S. Wrobel, Pramana, Suppl. No. 1, 253 (1975).

[30] J. A. Janik, J. Krawczyk, J. M. Janik, and K. Otnes, J. Phys. (Paris) 40, C3-169 (1979).

[31] F. Volino, A. Dianoux, and H. Hervet, J. Phys. (Paris) 37, C3-55 (1976).

[32] Z. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys. 61, 1958 (1974); A. J. Dianoux and F. Volino, J. Phys. (Paris) 40, 181 (1979).

[33] R. Blinc, M. Burgar, M. Luzar, J. Pirš, I. Zupančič, and S. Žumer, Phys. Rev. Lett. 33, 1192 (1974).

[34] G. J. Krüger, H. Speisecke, and R. Van Steenwinkel, J. Phys. (Paris) 37, C3-123 (1976).

[35] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1972).

[36] S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

[37] S. Žumer and M. Vilfan, J. Mol. Struct. 46, 475 (1978).

[38] D. Beckert, Ann. Phys. (Leipzig) 23, 98 (1969); A. Avogadro and M. Villa, J. Chem. Phys. 66, 2359 (1977).

[39] J. Doucet, M. Lambert, A. M. Levelut, P. Porquet and B. Dorner, J. Phys. (Paris) 39, 173 (1978).