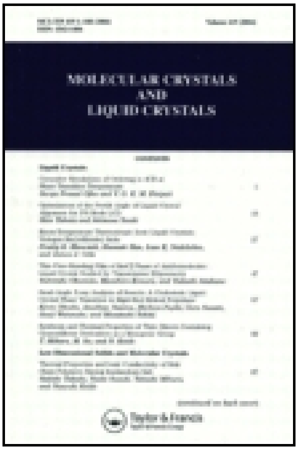

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Disc-Like Liquid Crystals: Molecular Motions and Nuclear Magnetic Relaxation

S. žumer [a] & M. Vilfan [b]

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

[b] J. Stefan Institute, E. Kardelj University of Ljubljana, Jamova 39, 61000, Ljubljana, Yugoslavia

Version of record first published: 14 Oct 2011.

To cite this article: S. žumer & M. Vilfan (1981): Disc-Like Liquid Crystals: Molecular Motions and Nuclear Magnetic Relaxation, Molecular Crystals and Liquid Crystals, 70:1, 39-56

To link to this article: http://dx.doi.org/10.1080/00268948108073578

Mol. Cryst. Liq. Cryst., 1981, Vol. 70, pp. 39-56
0026-8941/81/7001-0039 $06.50/0

Printed in the United States of America

Disc-Like Liquid Crystals: Molecular Motions and Nuclear Magnetic Relaxation†

S. ŽUMER

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

and

M. VILFAN

J. Stefan Institute, E. Kardelj University of Ljubljana, Jamova 39, 61000 Ljubljana, Yugoslavia

(*Received, July 29, 1980*)

The theory of nuclear spin relaxation in the liquid crystal phases formed by disc-like molecules is developed. Both nematic and columnar phases are treated. The following relaxation mechanisms are taken into account: translational self-diffusion, order director fluctuations and molecular rotations. For the description of the diffusion process in both phases, two random jump motions are proposed. A simple description of the bend mode in the columnar phase is also developed. The angular and the frequency dependence of T_1 is evaluated for each contribution separately and for both phases. Most of the results which are calculated numerically are presented graphically. The results are briefly compared with those of liquid crystals consisting of rod-like molecules.

I INTRODUCTION

Liquid crystals formed by disc-like molecules have attracted considerable interest since their discovery in 1977.[1] Up to now, several disc-like compounds[1-6] which exhibit thermotropic mesophases have been found. Most investigations have been focused upon their basic structure,[7-9] and only a few facts[8] are known concerning the molecular dynamics in disc-like systems.

As nuclear magnetic resonance and relaxation have proved to be convenient methods for the study of the molecular orientational[10] ordering and dy-

---

† Presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

namics[11] of rod-like molecules, it is expected that they could provide an insight into the dynamics of disc-like molecules as well.

The aim of this contribution is to study the nuclear spin relaxation due to molecular motions which are expected to contribute most to the relaxation rate in systems consisting of disc-like molecules. These motions are:

i) translational self-diffusion of the molecules (SD);

ii) collective modes associated with the orientational fluctuations of disc-like molecules (ODF);

iii) rotational diffusion of the molecule around the symmetry axis normal to the disc plane (R).

Fast local orientational and translational motions of the whole molecule or its alkyl chains are taken into account only as interaction averaging effects.

We are going to consider both the mesophases with disc-like molecules stacked in parallel columns[1,7,8] and those with a nematic structure.[5]

The proton spin relaxation rates due to each of these motions are estimated separately. Their relative importance is discussed for nuclei in the rigid central part of the disc and for nuclei in the alkyl chains.

II NUCLEAR MAGNETIC RELAXATION

We consider a system where each molecule carries N_0 nuclei (protons) with spin $I = \frac{1}{2}$. Other nuclei have negligible dipolar and quadrupolar moments. Our treatment is based upon the assumption that the rate of the translational diffusion is fast compared with the dipolar frequency ω_D (intermolecular dipolar interactions in frequency units), as is the case in ordinary nematic and smectic A liquid crystals.[12,13] Therefore we define longitudinal proton spin relaxation rate T_1^{-1} in the same way as was done for polyatomic liquids.[14] The effect of three-spin correlations is omitted. In addition the spin diffusion in one molecule is assumed to be fast enough to spread the Zeeman energy uniformly among all protons on the same molecule in a time much shorter than T_1. The relaxation rate is thus mono-exponential and given by[15]

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

where

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

Here N is the total number of nuclei with spin I, $F_{ij}^{(k)}(t)$ are the spatial parts of the dipolar interactions.

Although the natural orientation of the molecular plane is parallel to the magnetic field **B**, we shall for the sake of simplicity evaluate $J^{(k)}(\omega)$ for the case when **B** is parallel to the average disc normal. The results for other orientations follow simply by applying the transformation properties of the spherical harmonics[17,18]

$$J^{(1)}(\omega, \Delta) = \tfrac{1}{4}(\sin^2 \Delta - \sin^4 \Delta) J^{(0)}(\omega, 0°) + (1 - \tfrac{5}{2} \sin^2 \Delta + 2 \sin^4 \Delta) J^{(1)}(\omega, 0°) + \tfrac{1}{8}(2 \sin^2 \Delta - \sin^4 \Delta) J^{(2)}(\omega, 0°) \tag{3}$$

and

$$J^{(2)}(\omega, \Delta) = \tfrac{1}{4} \sin^4 \Delta J^{(0)}(\omega, 0°) + 2(2 \sin^2 \Delta - \sin^4 \Delta) J^{(1)}(\omega, 0°) + (1 - \sin^2 \Delta + \tfrac{1}{8} \sin^4 \Delta) J^{(2)}(\omega, 0°), \tag{4}$$

where 90° $- \Delta$ is the angle between the average disc normal and the external magnetic field.

The contribution of several motions to T_1 can be treated separately when the corresponding correlation times are sufficiently different. We hope that in our case this situation is realized, so that we can write:

$$T_1^{-1} = (T_1^{-1})_{\mathrm{SD}} + (T_1^{-1})_{\mathrm{ODF}} + (T_1^{-1})_{\mathrm{R}} + (T_1^{-1})_{\mathrm{residual}}. \tag{5}$$

In the following, we shall deal with each mechanism separately.

I Translational diffusion

This relaxation mechanism will be treated in a basically similar way to that for ordinary nematic liquid crystals in our first paper[18] (hereafter called I) and for smectic A liquid crystals in our second paper.[19]

The translational self diffusion modulates only intermolecular dipolar interactions, so one must take into account the position of interacting nuclei on the corresponding molecules as well as relative molecular positions. Therefore it is instructive to separate the interproton vector $\mathbf{r}_{ij}$ into the vector $\mathbf{r}$ connecting the centers of the interacting molecules and vectors ζ_i and ζ_j describing the positions of nuclei on the corresponding molecules (see Figure 1!)

$$\mathbf{r}_{ij} = \mathbf{r} + \zeta_i + \zeta_j. \tag{6}$$

As disc-like molecules are relatively thin, we assume that all protons lie in the disc plane. Fast alkyl chain motions which partly average out the dipolar interactions also justify the above approximation. Introducing the difference

$$\zeta = \zeta_i - \zeta_j \tag{7}$$

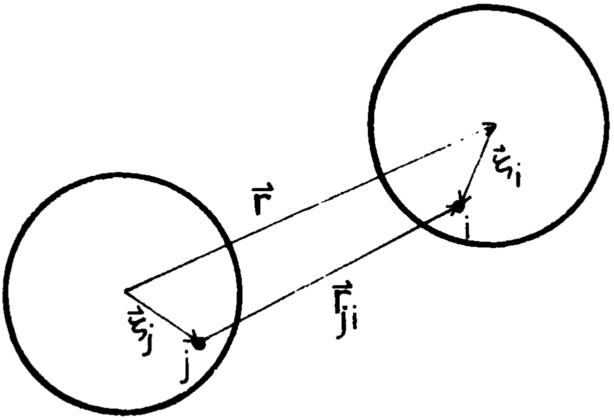

FIGURE 1 Schematic presentation of two molecules with all the notations used in text.

we define the following notation for the spatial part of the intermolecular dipolar interactions:

$$F^{(k)}(\mathbf{r}_{ij}(t)) = F^{(k)}_{\zeta}(\mathbf{r}(t)), \tag{8}$$

where

$$F^{(k)}_{\zeta}(\mathbf{r}) = \frac{e^{ik\varphi}}{(|\rho+\zeta|^2+z^2)^{5/2}}\begin{cases}(\rho+\zeta)^2-2z^2 & k=0\\ |\rho+\zeta|z & k=1.\\ (\rho+\zeta)^2 & k=2\end{cases} \tag{9}$$

Here $|\rho + \zeta|, z, \varphi$ are the cylindrical coordinates of the vector $\mathbf{r} + \zeta$. The distribution $W(\zeta)$ of the vector ζ is related by:

$$W(\zeta) = \int w(\zeta_1)w(\zeta - \zeta_1)d^2\zeta_1 \tag{10}$$

to $w(\zeta)$—the proton distribution projected on the disc plane.

With the help of the two particle dynamical correlation function $P(\mathbf{r}', \mathbf{r}, t)$ and following the procedure of the paper **I**, we can now write:

$$J^{(k)}_{\mathrm{SD}}(\omega) = n\iiint (F^{(k)}_{\zeta}(\mathbf{r})F^{(k)}_{\zeta}{}^{*}(\mathbf{r}'))_{\zeta}P(\mathbf{r}', \mathbf{r}, t)g(\mathbf{r})e^{i\omega t}d^3\mathbf{r}\, d^3\mathbf{r}'\, dt. \tag{11}$$

Here n is the density of protons in the sample, $g(\mathbf{r})$ is the static pair correlation function, and $(\ \ )_{\zeta}$ stands for the average over the distribution $W(\zeta)$.

Neglecting two particle correlations and taking into account some properties of the diffusion process one can express (see I) $P(\mathbf{r}', \mathbf{r}, t)$ as the product:

$$P(\mathbf{r}', \mathbf{r}, t) = g_0(\mathbf{r}')\,G_s(\mathbf{r}' - \mathbf{r}, 2t), \tag{12}$$

where $G_s(\mathbf{r}, t)$ is the one particle dynamical auto-correlation function, and $g_0(\mathbf{r})$ is the short range part of the static pair correlation function. So one can write:

$$J_{\mathrm{SD}}^{(k)}(\omega) = \frac{n}{16\pi^2}\int (Re[\mathfrak{F}_{\zeta}^{(k)}(\mathbf{q})\mathfrak{F}_{0\zeta}^{(k)*}(\mathbf{q})])_{\zeta} S_s\left(\mathbf{q}, \frac{\omega}{2}\right) d^3\mathbf{q}, \tag{13}$$

where

$$\mathfrak{F}_{\zeta}^{(k)}(\mathbf{q}) = \int F_{\zeta}^{(k)}(\mathbf{r}) g(\mathbf{r}) d^3\mathbf{r}, \tag{14}$$

$$\mathfrak{F}_{0\zeta}^{(k)}(\mathbf{q}) = \int F_{\zeta}^{(k)}(\mathbf{r}) g_0(\mathbf{r}) d^3\mathbf{r}, \tag{15}$$

and

$$S_s(\mathbf{q}, \omega) = \iint G_s(\mathbf{r}, t) e^{i\omega t} e^{i\mathbf{q}\cdot\mathbf{r}} dt\ d^3\mathbf{r}. \tag{16}$$

To evaluate the dynamical structure factor $S_s(\mathbf{q}, \omega)$ we shall idealize the mesomorphic structures as follows: Consider a system where each molecule is a rigid cylinder with diameter d and height $l \ll d$, an assumption which is justified especially for the derivatives of the triphenylene. Further, we assume that the average local orientational order of the molecules is perfect. On the other hand, the molecular centers are disordered in the nematic case, while in the columnar phase, the molecules are stacked (in a liquid-like way[1] or regularly[8]) in a hexagonal net of columns whose longitudinal positions are uncorrelated. The (average) stacking distance L is comparable with the molecular height ($L \gtrsim l$). According to the above simplifications we can write:

for the disc nematic phase

$$g_n = g_0(\mathbf{r}) = \begin{cases} 1 \ \ldots \ z > l \quad \text{or} \quad \rho > d \quad \text{for} \quad z \leq l \\ 0 \ \ldots \ z < 1 \quad \text{and} \quad \rho < d \end{cases} \tag{17}$$

for the columnar phase

$$g_c = g_0(\mathbf{r}) \pi d^2 \sum_{i=1}^{N} \delta(\rho - \rho_i), \tag{18}$$

where ρ_i points to the center of the i-th column.

Translational diffusion in systems with disc-like molecules is strongly affected by molecular shape (nematic) and also by the long range two-dimensional order (columnar phase). In our treatment, we are going to use a random jump model[20] which seems to be justified for the NMR frequency region in classical liquids[21] and in rod-like systems.[18,19] In this approximation, the Fourier transform $\mathcal{G}(\mathbf{q}, t)$ of the correlation function $G(\mathbf{r}, t)$ has a simple exponential form

$$\mathcal{G}(\mathbf{q}, t) = e^{-t/\tau_{\mathbf{q}}} \tag{19}$$

with

$$\tau_{\mathbf{q}} = \frac{\tau}{(1 - A(\mathbf{q}))}, \tag{20}$$

where $A(\mathbf{q})$ is the Fourier transform of $P_1(\mathbf{r})$-positional distribution after a single jump-which depends on the type of the liquid crystal and τ the average jump time. With Eq. 19, the dynamical structure factor becomes:

$$S_s\left(\mathbf{q}, \frac{\omega}{2}\right) = \frac{\tau(1 - A(\mathbf{q}))}{(1 - A(\mathbf{q}))^2 + \left(\frac{\omega\tau}{2}\right)^2}. \tag{21}$$

Now we are going to specify $A(\mathbf{q})$ for both kinds of order.

Nematic phase of disc-like molecules

We are going to use the same model for diffusion as in our paper I: a molecule is in a potential well, it is then thermally activated and makes a fast jump to a new position where on average it stays for a time τ. The jump is assumed to be of the diffusion type with a strong directionally dependent average length. The corresponding Fourier transform of the distribution P_1 is given by the expression:

$$A(\mathbf{q}) = \frac{1}{1 + D_\parallel^0 \tau q_\parallel^2 + D_\perp^0 \tau q_\perp^2}, \tag{22}$$

where the principal values of the diffusion tensor $D_\parallel^0$ and $D_\perp^0$ in the perfectly oriented liquid crystal are related to the average of squares of the corresponding jump lengths by

$$D_\parallel^0 = \frac{\langle r_\parallel^2 \rangle}{2\tau} \quad \text{and} \quad D_\perp^0 = \frac{\langle r_\perp^2 \rangle}{4\tau}. \tag{23}$$

The sign $\parallel$ stands for the direction parallel to the average disc normal and $\perp$ for the direction orthogonal to it.

Columnar phase

Here one should distinguish between two independent translational motions: intercolumnar diffusion which is a kind of permeation, and one-dimensional intracolumnar motions.

The intercolumnar motion is a random jump motion where molecules exchange columns. The orthogonal component of the molecular position vector ρ changes at a discrete value which is equal to the diameter of the molecule d. The one-jump change of $r_\parallel$ is due to the uncorrelated position of the adjacent columns restricted to the interval $(+L, -L)$, where L is the average distance between two successive molecules in the column. Therefore, for the hexagonal arrangement of columns, the positional distribution of molecular centers after one jump P_1, has the following form:

$$P_1(\rho, z) = \frac{1}{6}\sum_{i=1}^{6}\delta(\rho - \rho_i)\,\frac{1}{2L}\begin{cases}1 \ldots |z| \leq L\\ 0 \ldots |z| > L\end{cases}, \tag{24}$$

where ρ_i are positional vectors of the centers of 6 adjacent columns. Performing a Fourier transform of P_1 we get:

$$A(\mathbf{q}) = \sum_{i=1}^{6}(\cos \mathbf{q}\rho_i \sin q_\parallel L)/6q_\parallel L. \tag{25}$$

The diffusion constants are, according to the relations (23), related by:

$$D_\perp^0 / D_\parallel^0 = \frac{d^2}{2\langle r_\parallel^2\rangle} \simeq \frac{3}{2}\left(\frac{d}{L}\right)^2. \tag{26}$$

The above treatment can be easily adapted to other columnar arrangements.[9] In our further treatment, only $\mathfrak{F}_\zeta^{(k)}(\mathbf{q})$ and $\mathfrak{F}_{0\zeta}^{(k)}(\mathbf{q})$ can be calculated analytically, while the integration over the q-space and the averaging over the distribution $W(\zeta)$ must be performed numerically. For the evaluation of $(\quad)_\zeta$ one also needs $W(\zeta)$ which depends on the type of molecules. In our approximate treatment, we characterize $W(\zeta)$ only by a parameter ϵ defined by

$$\epsilon^2 = \int W(\zeta)\,\zeta^2\,d^2\zeta. \tag{27}$$

Introducing the dimensionless function R_n for the nematic phase and R_c for the columnar phase we can write:

$$(T_1^{-1})_{SD} = \frac{9}{8}\gamma_I^4\hbar^2\frac{n\tau}{d^3}\begin{cases}R_n\left(\frac{l}{d}, \frac{D_\perp^0}{D_\parallel^0}, \frac{\langle r^2\rangle}{d^2}, \epsilon, \Delta, \omega\tau\right)\\ R_c\left(\frac{l}{d}, \frac{D_\perp^0}{D_\parallel^0}, \epsilon, \Delta, \omega\tau\right)\end{cases} \tag{28}$$

Explicit relations between R and $J^{(k)}$ can be easily obtained using Eqs. (1-4). Numerical calculations of R_n and R_c have been performed for a number of different values of parameters. The spin distribution has an effect mainly on the value of the relaxation rate, but only weakly on the angular and frequency dependencies of T_1. Therefore, we shall postpone this problem until the experimental data are available. The frequency dependence, normalized to one at zero Larmor frequency, is presented in Figure 2 for both phases, using the following values of the parameters $\epsilon = 0.7$, $\Delta = 90°$, $l/d = 0.25$, while $D_\perp^0/D_\parallel^0 = 3$ and $\langle r_\perp^2\rangle/d^2 = 0.1$ for the nematic phase, and $D_\perp^0/D_\parallel^0 = 24$ (Eq. 26) for the columnar phase. For comparison, there is Torrey's dispersion, which describes $(T_1^{-1}(\omega))_{SD}$ for isotropic liquids. One can conclude that discotic nematic dispersion in the low frequency region $\omega\tau \lesssim 0.2$, obeys the well known $J(\omega) = C - C'\sqrt{\omega}$ law, which is valid for isotropic liquids and rod-like nematics. On the other hand, the columnar dispersion is completely different—Lorentz like—and this can be explained by a relatively well defined permeation jump length.

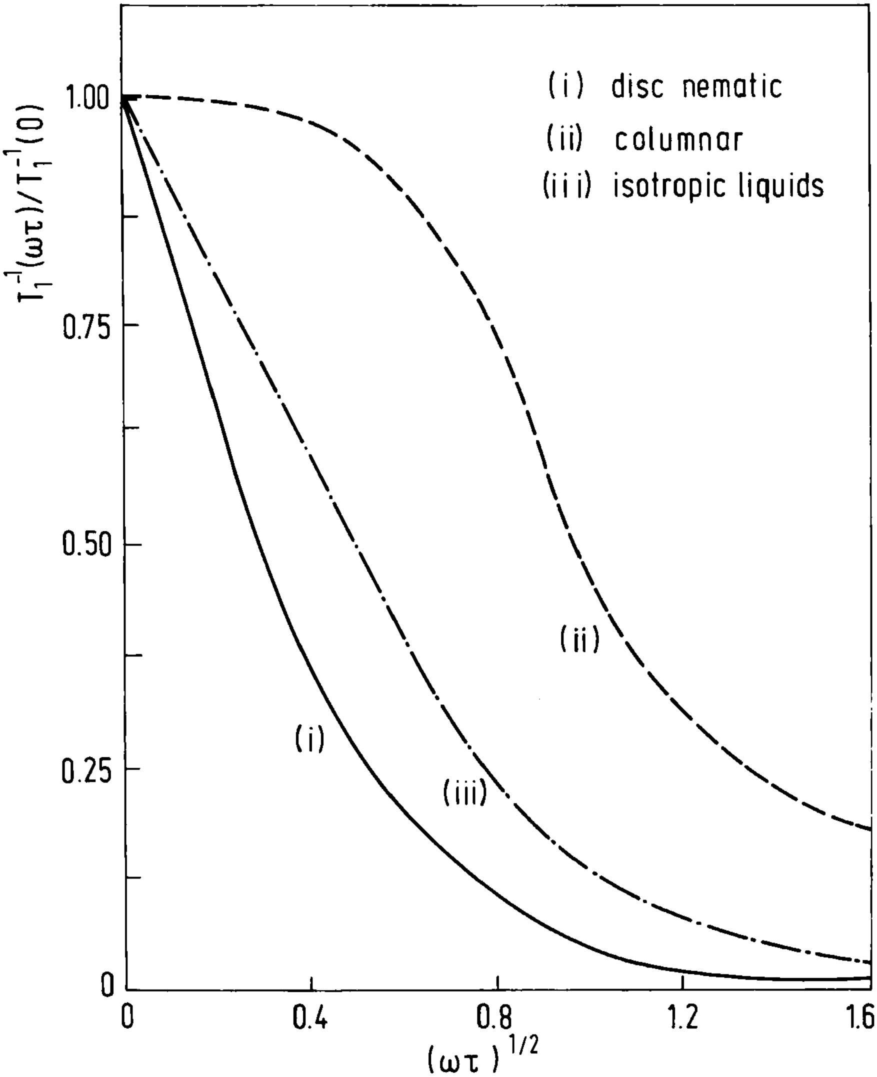

FIGURE 2 Frequency dependence of the translational diffusion contribution to T_1^{-1} for: i) the nematic phase formed by disc-like molecules, ii) the columnar phase, and iii) isotropic liquids.

The angular dependence of the nematic $(T_1^{-1})_{SD}$ (normalized to one at $\Delta = 0°$) presented in the Figure 3 for several $\omega\tau$ shows a weak anisotropy. For $D_\perp^0 / D_\parallel^0 = 3$, $(T_1^{-1})_{SD}$ decreases with increase of Δ from 0° to 90° for about 20% in the low frequency region. At higher frequencies, the anisotropy is even weaker, while the increase of $D_\perp^0 / D_\parallel^0$ enhances the anisotropy.

The columnar angular dependence presented in Figure 4 shows that $(T_1^{-1})_{SD}$

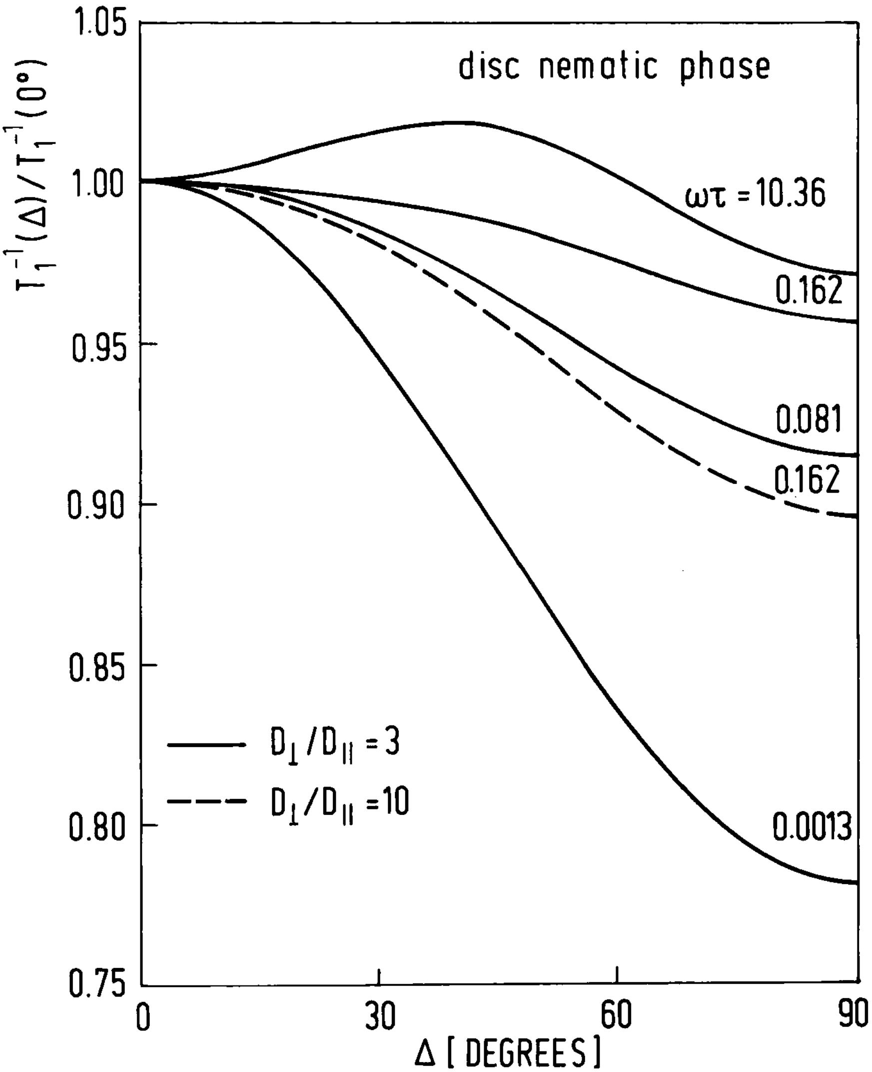

FIGURE 3 Angular dependence of the relaxation induced by translational diffusion in the disc-like nematic phase for several values of $\omega\tau$ and two different values of $D^0_\perp / D^0_\parallel$.

increases on going from $\Delta = 0°$ to $90°$. The anisotropy is again about 20%, but with even less pronounced frequency dependence.

II Order director fluctuations

The molecular director $\mathbf{n}(\mathbf{r},t)$ is defined as the unit vector pointing in the locally preferred direction of the normal to the molecular plane. Its orientation

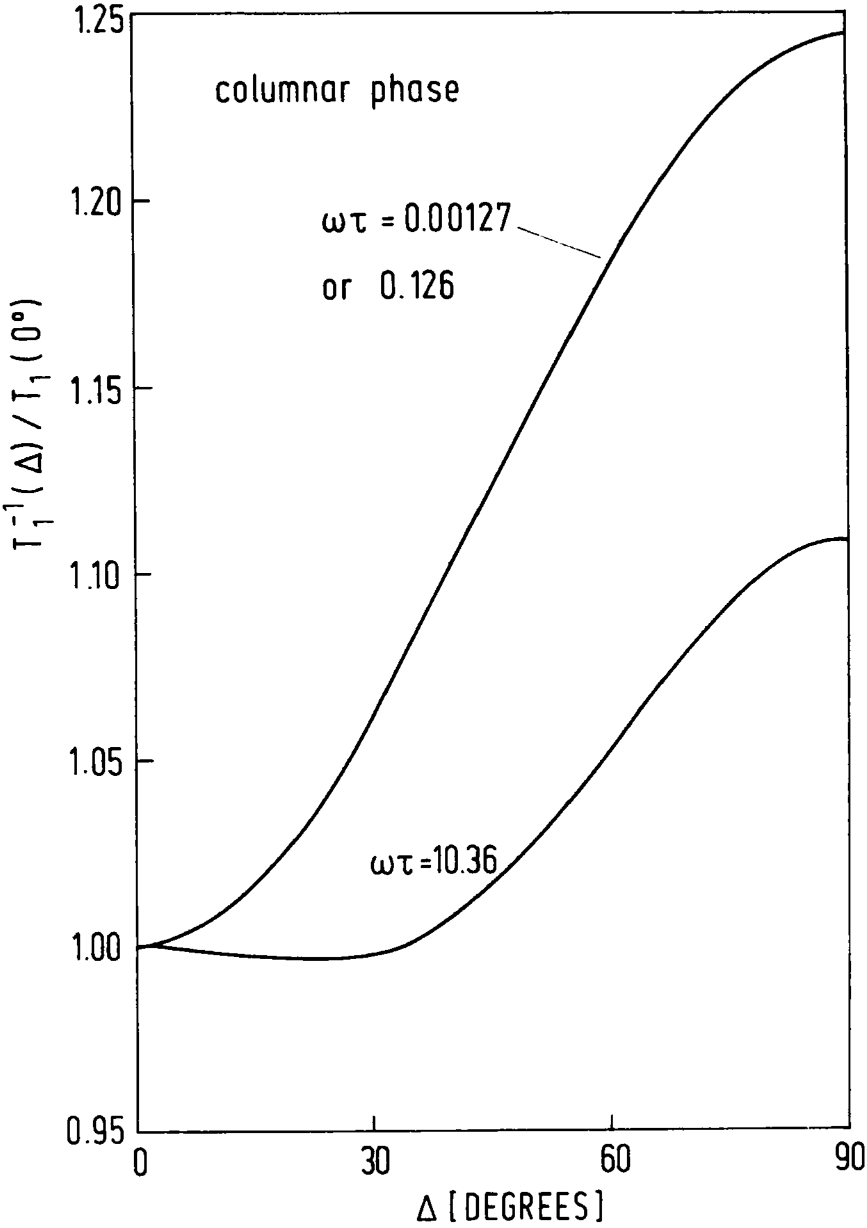

FIGURE 4 Angular dependence of the relaxation induced by translational diffusion in the columnar phase for three values of $\omega\tau$.

is expected to change slightly in space and time as has been found in liquid crystals with rod-like molecules. These orientational fluctuations (usually called order director fluctuations—ODF) are in fact collective modes associated with the bend, twist or splay elastic deformation of a liquid crystal. They have been shown to be the most important relaxational mechanism for protons in both nematic and smectic A (rod-like) liquid crystals,[22] with however a few exceptions. It is thus expected that order director fluctuations could play an important role in the proton relaxation in discotic liquid crystal phases as well. However, their importance is strongly limited by the fact that probably only the protons attached to the central part of the molecule, i.e. to the benzene or triphenylene ring, can be relaxed directly *via* order director fluctuations. Relatively long and flexible alkyl chains are not expected to play an important part in this type of motion.

The proton spin relaxation rate due to order director fluctuations in a discotic nematic phase can be theoretically determined in the same way as for the rod-like nematic phase. The relaxation is caused by the modulation of dipolar interaction between adjacent protons of the same molecule. Order director fluctuations do not influence the distance between two protons; they only change the angle between the direction of inter-proton vectors, which lie approximately perpendicular to the director in the plane of the molecule. For such a case, the spectral densities (Eq. 2) which are needed to calculate $(T_1^{-1})_{\mathrm{ODF}}$ (Eq. 1) can be written as[23]

$$J^{(1)}_{\mathrm{ODF}}(\omega) = \frac{1}{2r_{12}^6}\int_{-\infty}^{\infty} \langle \mathbf{n}_\perp(\mathbf{r}, 0)\,\mathbf{n}_\perp(\mathbf{r}, t)\rangle\, e^{i\omega t}\, dt. \tag{29}$$

Here $\mathbf{n}_\perp$ denotes the component of $\mathbf{n}\,(\mathbf{r},t)$ perpendicular to the average direction of the disc-normal. $\mathbf{n}_\perp$ is zero at equilibrium and different from zero when fluctuations in the orientation take place; r_{12} denotes the inter-proton distance. For small fluctuations of $\mathbf{n}$, $J^{(2)}$ and $J^{(0)}$ are zero in the first approximation.

It is easy to show—in the same way as for rod-like nematics[22]—that by introducing the Fourier components of $\mathbf{n}_\perp(\mathbf{r}, t)$, and replacing the summation over all wave vectors by an integration from zero to infinity, $J^{(1)}(\omega)$ becomes:

$$J^{(1)}_{\mathrm{ODF}}(\omega) = \frac{1}{r_{12}^6}\,\frac{kT\sqrt{2}}{8\pi}\sum_{\alpha=1}^{2}\frac{1}{K_\alpha}\,\frac{\sqrt{\eta_\alpha}}{K_3}\,\frac{1}{\sqrt{\omega}}. \tag{30}$$

Here K_1, K_2, and K_3 stand for three different elastic constants and η_α are the corresponding viscosities.[24] Values of the elastic constants can be, in the case of disc-like nematics, significantly different from those in a classic nematic. This difference does not influence the frequency and angular dependence of the relaxation rate. It is obvious that $(T_1^{-1})_{\mathrm{ODF}}$ in the discotic nematic phase is inversely proportional to the square root of the Larmor frequency, $(T_1^{-1})_{\mathrm{ODF}} \propto 1/\sqrt{\omega}$. In a calculation, where the low and high frequency cut-offs of the wave vector are taken into account $(T_1^{-1})_{\mathrm{ODF}}$ becomes independent of frequency at very low frequencies and proportional to $1/\omega^2$ at very high frequencies. $(T_1)_{\mathrm{ODF}}$ for a 100 MHz cut-off frequency is shown for the nematic in Figure 5. The angular dependence of $(T_1^{-1})_{\mathrm{ODF}}$, presented in Figure 6 shows that the relaxation rate decreases for about 50% when the sample is turned from its

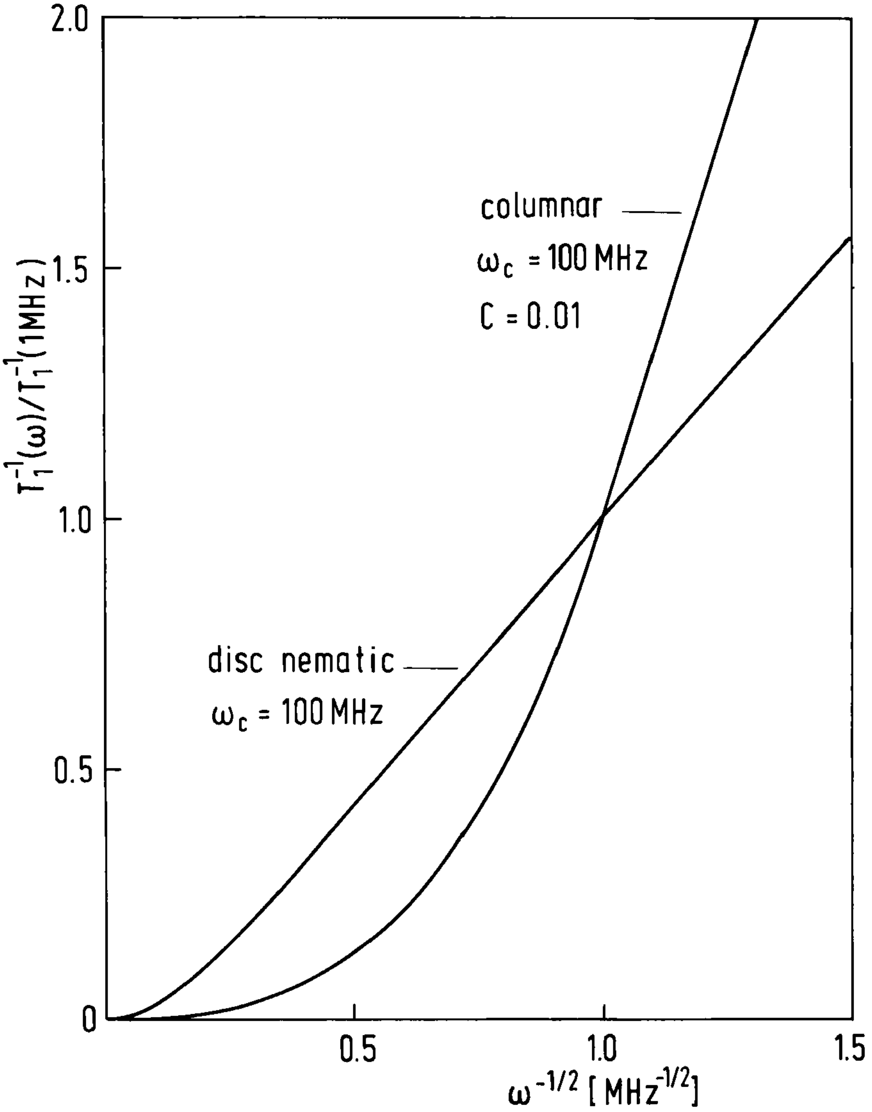

FIGURE 5 Frequency dependence of the contribution of director order fluctuations to T_1^{-1} for nematic and columnar phases consisting of disc-like molecules.

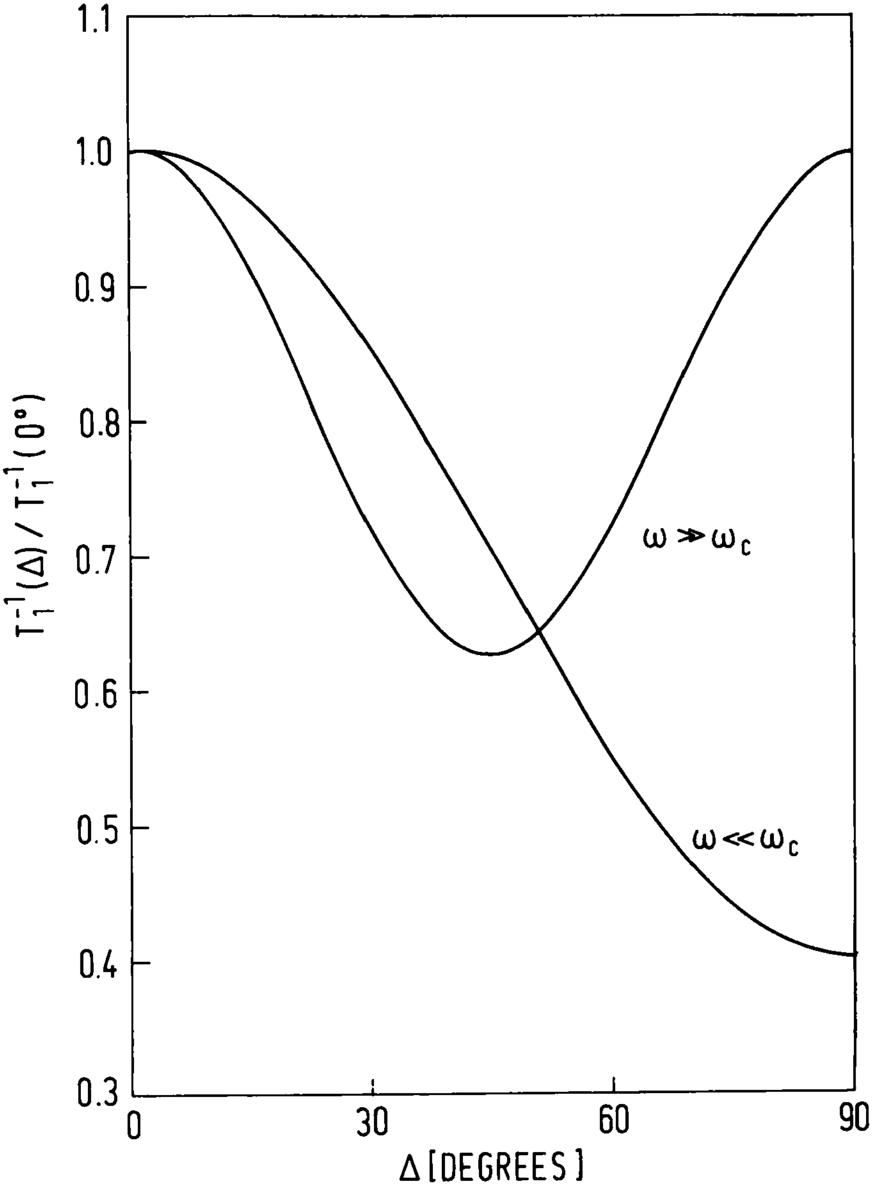

FIGURE 6 Angular dependence of the relaxation rate induced by director order fluctuations for $\omega \gg \omega_c$ and $\omega \ll \omega_c$.

"natural" orientation in the magnetic field through 90°. In the high frequency limit the relaxation rate has its minimum value at $\Delta = 45°$.

To calculate $(T_1^{-1})_{\mathrm{ODF}}$ in the columnar phase, we must first derive a description of its order director fluctuations. It has been found by Levelut[8] that bending of the columns definitely takes place. For a wave length > 15 Å, the frequency is low, so that bending is potentially an efficient mechanism for the proton relaxation. Other elastic deformations are not expected to be important in the columnar phase. We write the expression for the free energy density in its simplest form:

$$F = F_0 + \frac{1}{2} B\left(\frac{\partial \mathbf{u}}{\partial \rho}\right)^2 + \frac{1}{2} K_3\left(\frac{\partial^2 \mathbf{u}}{\partial z^2}\right)^2, \tag{31}$$

where $\rho = \sqrt{x^2 + y^2}$, and $\mathbf{u}$ denotes the displacement of the column perpendicular to its long axis. This distortion is related to $\mathbf{n}_\perp$ through $\partial \mathbf{u}/\partial \rho = \mathbf{n}_\perp$. The last term in Eq. (31) describes the bending of the columns, while the second takes into account the eventual compressibility of the columns. By expanding $\mathbf{u}(\mathbf{r})$ in a Fourier series

$$\mathbf{u}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{u}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{32}$$

applying the RPA approximation, and using the equipartition theorem one can get:[24]

$$\langle n_\perp(\mathbf{q}, 0) n_\perp(\mathbf{q}, t)\rangle = \langle |n_\perp(\mathbf{q})|^2\rangle e^{-t/\tau_{\mathbf{q}}} \tag{33}$$

with

$$\langle |n_\perp(\mathbf{q})|^2\rangle = \frac{kT}{B\dfrac{q_\perp^2}{q_\parallel^2} + K_3 q_\parallel^2} \tag{34}$$

and

$$\tau_{\mathbf{q}} = \frac{\eta}{B\dfrac{q_\perp^2}{q_\parallel^2} + K_3 q_\parallel^2}, \tag{35}$$

where η is the corresponding viscosity coefficient. Inserting these equations into the expression for the spectral density $J^{(1)}(\omega)$ we obtain:

$$J^{(1)}_{\mathrm{ODF}}(\omega) = \frac{kT\eta}{2\pi^2} \int_0^{q_{\perp c}} \int_0^{q_{\parallel c}} \frac{q_\perp dq_\perp q_\parallel^4 dq_\parallel}{(Bq_\perp^2 + K_3 q_\parallel^4)^2 + \omega^2\eta^2 q_\parallel^4}. \tag{36}$$

Also here the high frequency cut-off is taken into account so that the integration over $\mathbf{q}$ is performed only up to the cut-offs $q_{\parallel c}$ and $q_{\perp c}$ which are of the order of the reciprocal molecular dimension. Evaluating the spectral density $J^{(1)}_{\rm ODF}(\omega)$, the low and high frequency limits can be obtained analytically. The values in the intermediate region must be evaluated numerically. In the low-frequency limit $(T_1^{-1})_{\rm ODF}$ is frequency independent, while it behaves like $1/\omega^2$ in the high frequency region. Figure 5 also represents the frequency dependence of the columnar $(T_1^{-1})_{\rm ODF}$ for a 100 MHz cut-off frequency and $C = BK_3 q^2_{\perp c}/\eta^2 = 0.01$. The region where the relaxation rate is a linear function of $1/\sqrt{\omega}$, is limited to low frequencies $\omega < 1$ MHz. The angular dependence is similar to that in a disc-like nematic.

It should be stressed that the value of $(T_1^{-1})_{\rm ODF}$ depends on the number of proton pairs which are involved in this relaxation process.

iii Rotational diffusion

The disc-like molecules have large moments of inertia around their symmetry axes, so it is expected that corresponding molecular rotations are relatively slow and therefore can play an important role in the proton spin relaxation. However translational self-diffusion and fast alkyl chain motions average out the intermolecular interactions and a part of the intramolecular interactions, respectively. That reduces the relaxation effectiveness of the rotation. As the relaxation due to molecular rotations has already been treated many times,[15] we shall deal with the problem only briefly. Introducing the rotational correlation time τ_r, one can easily estimate the magnetic relaxation of a proton pair lying in the plane normal to the rotational axis. For **B** parallel to the molecular director the spectral densities are $J_R^{(0)} = J_R^{(1)} = 0$ and

$$J_R^{(2)}(\omega) = \frac{1}{2r_{12}} \frac{\tau_r/4}{1+(\omega\tau_r/4)^2} . \tag{37}$$

The resulting $(T_1^{-1})_R$ has a well known Lorentzian frequency dependence. Its value depends on the number of the proton pairs with a non-averaged dipolar interaction. The angular dependence is for comparison presented in Figure 7.

III CONCLUSIONS

In this paper some relaxational mechanisms for disc-like mesophases are treated theoretically.

i) The general theory of the translational diffusion-induced nuclear spin relaxation in rod-like liquid crystals developed in I is extended to disc systems. The disc nematic phase is treated similarly to the corresponding rod-like case, while for the columnar phase, a jump model for the molecular permeation is introduced.

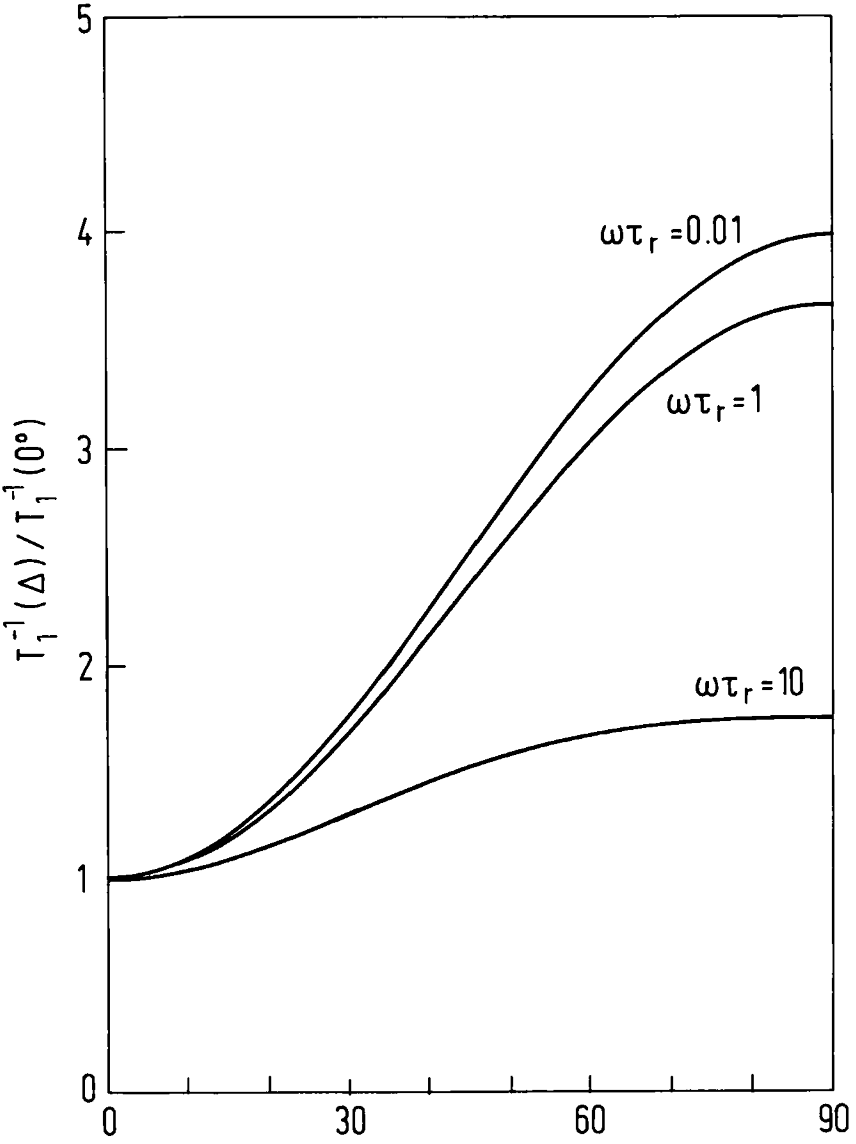

FIGURE 7 Angular dependence of the relaxation induced by molecular rotations for three values of $\omega\tau_r$.

ii) The relaxation due to order director fluctuations developed for the ordinary nematic phase is applied to the disc-like nematic, while for the columnar phase a simple elastic continuum theory for the bend mode is developed.

iii) For the rotational contribution, the well known expressions (developed for simple liquids) are used.

The first relaxation mechanism which modulates the intermolecular dipolar interactions involves all protons. The other two mechanisms modulate the intramolecular interaction, which is on the other hand partly averaged out by the fast motions of alkyl chains. That means that especially the protons which are in the rigid part of the disc molecule contribute to these two relaxation processes.

Numerical results for the frequency and angular dependence of T_1 show that they are characteristic for each relaxation mechanism. So an analysis of the experimental data should give an insight into the dynamics of disc-like molecules. However only if data were available in a wide frequency range (a few kHz to 100 MHz) and for the angles Δ in the whole interval (0°, 90°) could the conclusions be decisive. Additional information can be obtained by partial deuteriation of the alkyl chains.

Acknowledgments

The authors wish to thank M. Kogoj for his help in numerical calculations.

References

1. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. J. Billard, J. C. Dubois, H. T. Nguyen and T. A. Zann, *Nouv. J. Chemie*, **2**, 535 (1978).
3. J. C. Dubois, *Ann. Phys.*, **3**, 131 (1978).
4. C. Destrade, M. C. Mondon and J. Malthete, *J. Phys. (Paris)*, **40**, 17 (1979).
5. H. T. Nguyen, C. Destrade and H. Gasparoux, *Phys. Lett.*, **72A**, 251 (1979).
6. C. Destrade, J. Malthete, H. T. Nguyen and H. Gasparoux, Proceedings of the Eighth International Liquid Crystal Conference, Kyoto, Japan, 1980, to be published.
7. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Mathusudana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys. (Paris)*, **40**, 120 (1979).
8. A. M. Levelut, *J. Phys. Lett.*, **40**, L81 (1979).
9. A. M. Levelut, Proceedings of the Int. Liq. Cryst. Conf., Bangalore (1979).
10. J. W. Doane, *Magnetic Resonance of Phase Transitions*, editors F. J. Owens, C. P. Poole, Jr., H. A. Farach, Academic Press, New York (1979), p. 172–246; M. Vilfan, R. Blinc and J. Seliger, to be published.
11. G. Wade, *Ann. Rev. Phys. Chem.*, **28**, 47 (1977); and references 1–26 in paper 19.
12. R. Blinc, M. Burgar, M. Luzar, J. Pirš, I. Zupančič and S. Žumer, *Phys. Rev. Lett.*, **33**, 1192 (1974).
13. G. J. Kruger, H. Speisecke and R. Steenwinkel, *J. Phys. (Paris)*, **37**, 123 (1976).
14. P. S. Hubbard, *Phys. Rev.*, **128**, 650 (1962).
15. A. Abragam, *The principles of Nuclear Magnetism*, Clarendon Press, Oxford (1962).

16. W. W. Warren, *Phys. Rev.*, **A10**, 657 (1974).
17. D. M. Brink and G. R. Satchler, *Angular Momentum*, Clarendon Press, Oxford (1962).
18. S. Žumer and M. Vilfan, *Phys. Rev.*, **A17**, 424 (1978).
19. M. Vilfan and S. Žumer, *Phys. Rev.*, **A21**, 672 (1980).
20. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).
21. H. C. Torrey, *Phys. Rev.*, **92**, 962 (1953); F. Harmon and B. N. Muller, *Phys. Rev.*, **182**, 400 (1969).
22. R. Blinc, M. Luzar, M. Vilfan and M. Burgar, *J. Chem. Phys.*, **63**, 3445 (1975).
23. W. Wöptel, I. Noack and M. Stohrer, *Z. Natunfonsch*, **A30**, 937 (1975); J. W. Doane, C. E. Tarr and M. A. Nickerson, *Phys. Rev. Lett.*, **33**, 622 (1974).
24. P. G. de Gennes, *Physics of Liquid Crystals*, Clarendon Press, Oxford (1974).