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

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Version of record first published: 20 Apr 2011.

To cite this article: Vladimir Andreev (1982): Influence of Molecular Self-Diffusion on Spin-Lattice Relaxation in Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 82:8, 289-294

To link to this article: http://dx.doi.org/10.1080/01406568208247019

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 289-284
0140-6566/82/8208-0289$06.50/0

INFLUENCE OF MOLECULAR SELF-DIFFUSION ON SPIN-LATTICE RELAXATION IN CHOLESTERIC LIQUID CRYSTALS

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(Submitted for Publication May 3, 1982)

Abstract: A new mechanism of spin-lattice relaxation (SLR) due to modulation of the dipole-dipole nuclear spin interaction by the rotation of the molecular preferential direction under diffusion along the pitch axis is suggested. The time of longitudinal relaxation (T_1) is calculated for the pair of protons in the rapid diffusion limit. The estimate shows that this mechanism of SLR should be important in the low frequency experiments (10kHz-1MHz).

In liquid crystals a characteristic molecular motion combines with orientational anisotropy to create special mechanisms for nuclear SLR. These have been studied intensively in the nematics for which, in the low frequency region (0.5-1MHz), the dominant source of SLR is known to be the modulation of intramolecular dipole-dipole interaction by fluctuations in orientation of the director field which results in a frequency dependence in SLR time of $T_1 \sim \sqrt{\omega}$.[1] One may infer from the work of Dong et al[2] and Tarr et al[3] that such a mechanism also contributes to SLR in cholesteric liquid crystals (ChLC) but here the more complicated structure admits a wider range of possibilities. One of these, the dipolar modulation induced by the rotation of molecular preferential direction under diffusion along the pitch axis is the subject of the present report.

The mechanism is readily understood in qualitative terms. First, the ChLC may be regarded as a set of nematic layers turned relative to one another about the axis of the cholesteric helix, so that the director field $\vec{n}(\vec{r})$ is given by

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$$\vec{n}(\vec{r}) = \vec{n}(o)\cos\phi\,(\vec{r}) + (\vec{h}\times\vec{n}(o))\sin\phi\,(\vec{r}) \qquad (1)$$

where $\vec{n}(o)$ is the unit vector of director field at the point $r = 0$, $\vec{h}$ is the unit vector characterizing the direction of the helix axis ($\vec{h} \perp \vec{n}(\vec{r})$) and

$$\phi\,(\vec{r}) = \frac{2\pi}{p}(\vec{h}\cdot\vec{r}) \qquad (2)$$

is the angle between $\vec{n}(\vec{r})$ and $\vec{n}(o)$ (see Fig. 1) which is dependent on the value of helix pitch p and $\vec{r}$.

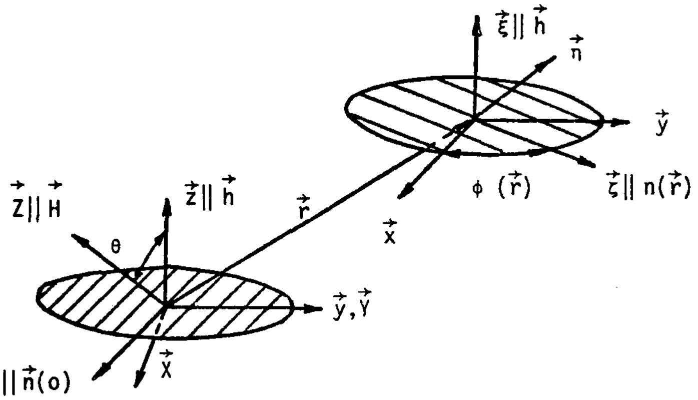

Fig. 1. Configuration of the coordinate system axes used for the calculation of T_1: $\vec{x},\vec{y},\vec{z}$ and $\vec{\xi},\vec{\eta},\vec{\zeta}$ are connected with the local ChLC axes at the different points of sample, $\vec{X},\vec{Y},\vec{Z}$ axes are associated with the external magnetic field direction.

Molecular tumbling about this local $\vec{n}$ occurs with a high frequency (10^4-10^5MHz) compared with the frequency of Pake splitting ($\delta\omega \sim$ 10KHz) and therefore the dipole-dipole interaction is averaged. Since the tumbling is anisotropic, the averaging is incomplete, leaving a residual value that depends on the local direction of $\vec{n}(\vec{r})$. Consider now a molecular diffusing along the cholesteric helix axis. The motion along $\vec{h}$ is accompanied by a rotation of $\vec{n}$, which, by inducing a time dependence in the residual interaction, couples the self-diffusion to the relaxation mechanism in question.

The characteristic time of molecular preferential orientation rotation under diffusion along $\vec{h}$ is given by

$$\tau = \left(\frac{p}{4\pi}\right)^2 D^{-1} \qquad (3)$$

where D is the diffusion constant and for different values of p and D there should exist a distinct averaging regimes. If $\tau\ \delta\ \omega << 1$, then the NMR spectrum is determined by the dipole-dipole interaction averaged over all orientations of the molecule around $\vec{h}$. If $\tau\ \delta\ \omega >> 1$ this averaging does not take place. The dependence of the NMR spectrum on the rate of diffusion and the value of the pitch was predicted by Collings et al,[5] who reported the experimental evidence of a rapid diffusion limit for ChLC with p = 2500Å. An analogous effect on the quadrupole interaction was studied by Luz et al[6] and Doane et al[7]. The change of the lineshape due to transfer between the limiting cases was also observed.[8] In the present study of SLR we restrict ourselves to rapid diffusion limit.

To calculate SLR rates we shall consider a pair of neighboring protons on the same molecule. The spin-Hamiltonian of this pair, averaged for fast molecular tumbling around the local direction of $\vec{n}$ and fast rotation around the long molecular axis can be written in the form

$$\mathcal{H} = \omega_0 I_z - \frac{\delta\omega}{6} \sum_{mn=-2}^{2} T_m^2 D_{mn}^2 (0,\theta,0)\, D_{no}^2 (\phi, \tfrac{\pi}{2}, 0) \qquad (4)$$

where the first term is the Zeeman interaction of the total spin $\vec{I}(I-1)$ for a magnetic field $\vec{H} \| Z$ and $\omega_0 = \gamma H$ is the Larmor frequency of the proton. The second term describes the residual part of the proton spin dipole-dipole interaction. $\delta\omega$ is the maximum value of the Pake splitting and is given by

$$\delta\omega = \frac{3\hbar^2\gamma^2}{a^3}\ S \cdot P_2 (\cos \alpha) \qquad (5)$$

where a is the interproton distance and α is the angle between $\vec{a}$ and the "long" axis of the molecule, and $P_2(x)$ is a Legendre polynomial. The order parameter S is given by

$$S = \langle P_2 (\cos \beta) \rangle_t \qquad (6)$$

where β is the angle between the "long" molecular axis and local direction of $\vec{n}$, and $\langle \ldots \rangle_t$ denotes the time averaging corresponding to fast molecular tumbling around the local director. T^2_m are the irreducible tensor operators[9] that depend on the components of $\vec{I}$ in the coordinate system with $\vec{Z} \| \vec{H}$ and D^2_{mn} are Wigner functions,[9]

$$D^2_{mn} (\alpha,\beta,\gamma) = e^{im\alpha} d^2_{mn}(\beta) e^{-in\gamma} \qquad (7)$$

these depend on the Euler angles (α,β,γ) describing the coordinate system rotation from $\vec{X}\ \vec{Y}\ \vec{Z}$ $(Z \| H)$ to $\vec{x}\ \vec{y}\ \vec{z}$ $(\vec{z} \| \vec{h},\ \alpha = 0,\ \beta = \theta,\ \gamma = 0)$ and from $\vec{x}\ \vec{y}\ \vec{z}$ to $\vec{\xi},\vec{\eta},\vec{\zeta}$ $(\vec{\xi} \| \vec{h},\ \vec{\zeta} \| \vec{n},\ \alpha = \phi, \beta = \frac{\pi}{2},\ \gamma = 0)$, which are shown on Fig. 1.

Averaging the Hamiltonian (4) over all values of ϕ and keeping in mind that $\omega_0 \gg \delta\omega$, we obtain the Hamiltonian for the spectrum of the pair of protons in the rapid diffusion limit to be

$$\mathcal{H} = \hbar\omega_0 I_z - \frac{\hbar\delta\omega}{\sqrt{6}} P_2 (\cos \theta) \cdot T^2_0 \qquad (8)$$

Using eqs. (4) and (8) we find the time-dependent residual interaction

$$V(t) = -\frac{\hbar\delta\omega}{\sqrt{6}} \sum_{mn=2}^{2} T^2_m D^2_{mn} (0,\theta,0)\, D^2_{no} (\phi (t), \tfrac{\pi}{2}, 0)\, (1-\delta_{no}) \qquad (9)$$

and obtain an expression for the probability of relaxation transitions between the energy levels of Hamiltonian (8):

$$W_{\sigma\sigma'} = \frac{5}{48} (\delta\omega C^{1\sigma}_{1\sigma,2\sigma-\sigma'})^2 \sum_{mn=-2}^{2} d^2_{\sigma-\sigma',m}(\theta)\, d^2_{\sigma-\sigma',n}(\theta)\, F_{mn}(\omega_{\sigma\sigma'}) \qquad (10)$$

where $C^{1\sigma}_{1\sigma',2\sigma-\sigma'}$ are the Clebsch-Gordon coefficients, $\sigma,\sigma' = 0, \pm 1$, and

$$F_{mn}(\omega) = \int_{-\infty}^{\infty} \langle \exp \left\{-1 \left[m\phi (t) - n \phi (0) - \omega t \right]\right\} \rangle \, dt \qquad (11)$$

where $\langle \ldots \rangle$ denotes the averaging associated with the diffusion of molecule. This may be performed using the following formula:

$$\left\langle \exp\left\{ i \left[m\phi(t) - n\phi\ (0) \right] \right\} \right\rangle =$$
$$= \int dv_0\ dv\ p(\vec{r}_0)\ p(\vec{r}-\vec{r}_0,t)\ e^{im\phi(\vec{r})-in\phi(\vec{r}_0)} \qquad (12)$$

where $p(\vec{r}_0) = \frac{1}{V}$ is the probability of finding the molecule at the point $\vec{r}_0$ in volume V at time $t = 0$; $p(\vec{r}-\vec{r}_0,t)$ is the probability of finding this molecule at the point $\vec{r}$ in the time interval t, and is determined by the diffusion equation.

In such a way we obtain

$$F_{nm}(\omega) = 2\delta_{nm}\,\tau(1 + \tau^2\omega^2)^{-1} \qquad (13)$$

where the correlation time τ is given by equation (3).

Substituting (13) into (10), and after some algebra, we find an experession for the longitudinal relaxation time:

$$T_1^{-1} = W_{10} + 2W_{1-1} =$$
$$= \frac{\tau\delta\omega^2}{32}\left\{ \frac{\sin^2\theta\ (1+\cos^2\theta)}{1 + \omega_0^2\ \tau^2} + \frac{8(\cos^2\ \theta/2\ \sin^2\ \theta/2)}{1 + 4\ \omega_0^2\ \tau^2} \right\} \qquad (14)$$

which depends on the angle θ between $\vec{h}$ and $\vec{H}$.

For $p \sim 1000\text{-}2000\text{Å}$ and $D \sim 3.10^{-6}\ \text{cm}^2\ \text{sec}^{-1}$, $\tau \sim 10^{-6}$ sec and, for $\omega > 0.1$MHz, $\omega_0^2\ \tau^2 >> 1$. In this case from eq. (14) we get a simpler formula:

$$T_1^{-1} = \frac{D}{8}\left(\frac{\pi}{p}\right)^2\left(\frac{\delta\omega}{\omega_0}\right)^2\ (5 + 6\ \cos^2\theta - 3\ \cos^4\theta) \qquad (15)$$

With these parameters and $\delta\omega \sim 10$KHz a change of ω from 10KHz to 1MHz for this mechanism of SLR changes T_1 from 10^{-4} to 10^{-1} sec. The SLR caused by director-field fluctuation in this region is less frequency dependent and for $\omega \sim 30$MHz a typical experimental value of T_1 is 0.1 sec,[10,11] so one may expect to find a contribution from diffusion to SLR in the low frequency region.

To identify the mechanism of SLR we have discussed, one can use the angular dependence of T_1 in eqs. (14) and (15). Furthermore, the strong dependence of T_1 on the value of pitch, ($T_1 \sim p^2$) points to the value of pressure and temperature studies, since in ChLC these parameters have a distinct influence on the value of pitch. This SLR channel may also be pronounced in twisted nematics and may be sensitive to the distortions of the ideal helical structure induced by an applied magnetic field similar to the case of self-diffusion effects on the lineshape.[4,7]

The author gratefully acknowledges the receipt of preprints from Professor J.W. Doane and useful support and discussions from Professor M. Pope and Dr. J. Rosenthal.

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