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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Ronald Y. Dong^a

^a Department of Physics and Astronomy, Brandon University, Brandon, Canada

To cite this Article Dong, Ronald Y.(1994) 'Nuclear spin relaxation in biaxial liquid crystal phases', *Liquid Crystals*, 16: 6, 1101 – 1104

To link to this Article: DOI: 10.1080/02678299408027879

URL: <http://dx.doi.org/10.1080/02678299408027879>

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Nuclear spin relaxation in biaxial liquid crystal phases

by RONALD Y. DONG

Department of Physics and Astronomy, Brandon University,
Brandon, Manitoba R7A 6A9, Canada

(Received 31 January 1994; accepted 18 February 1994)

The orientation-dependent spin-lattice relaxation rates for biaxial liquid crystal phases are given explicitly in terms of spectral densities $J_{m_L m_L'}(\omega)$ described by Berggren *et al.* (1993, *J. chem. Phys.*, **99**, 6180). It is recognized that the 'biaxial' spectral densities are not observed in biaxial phases unless the director is oriented away from the external magnetic field.

Nuclear spin relaxation is a proven experimental technique [1] for studying dynamic properties of liquid crystals. The internal dynamics of flexible mesogens has attracted [2, 3] much attention in recent years. Most spin relaxation studies have been limited to uniaxial nematic and smectic phases. The smectic C phase was probably the first mesophase to be recognized as biaxial. When treating spin relaxation in smectic C phases, it was assumed [4] that effects of phase biaxiality are small and may be neglected. Biaxial smectic phases have been known for a long time, and biaxial nematic phases are now found in lyotropics and thermotropics, including polymer liquid crystals. Deuterium NMR has played [5, 6] an important role in detecting phase biaxiality via motionally-induced asymmetry parameters η in quadrupolar spin interactions. This is possible only by observing spectral patterns in biaxial liquid crystal phases when the director is not aligned along the external magnetic field. We will see below that phase biaxiality can be important to nuclear spin relaxation only when the sample director is oriented at an angle with the magnetic field.

Recently there have been two important developments that may lead to a better understanding of effects of phase biaxiality in nuclear spin relaxation. Berggren *et al.* [7] have chosen to calculate orientational correlation functions and spectral densities that are needed to interpret spin relaxation data, based on the rotational diffusion model of uniaxial probes in biaxial liquid crystal phases. They showed that some spectral densities in biaxial phases vanish, while others change continuously at the biaxial–uniaxial phase transition. However, they have not commented on the spin-lattice relaxation time T_1 and how these 'biaxial' (or cross-correlation) spectral densities could be experimentally observed. Morrison and Bloom [8] have considered the orientation dependence of T_1 for spin-1 nuclei relaxing via fluctuating quadrupolar interactions within the Redfield approximation. They found a general expression for the orientation-dependent relaxation rates

$$[T_{1i}(\beta, \alpha)]^{-1} = \sum_{l=0}^4 \sum_{m=-l}^l b_{lm}^{(i)} Y_{lm}(\beta, \alpha), \quad (1)$$

where Y_{lm} are spherical harmonics of rank l ($l = \text{even}$), (β, α) are the polar angles of the magnetic field in the motionally averaged electric-field gradient tensor frame, i represents either the Zeeman ($i = Z$) or quadrupolar ($i = Q$) spin-lattice relaxation time, and $b_{lm}^{(i)}$ are complicated expressions involving orientational order parameters and reduced spectral densities. They have not commented explicitly on the role of phase symmetry in this general equation. Their orientation-dependent relaxation rates contain both uniaxial order parameters $\langle D_{00}^l \rangle$ (i.e. \bar{P}_2 and \bar{P}_4) and biaxial order parameters $\langle D_{m0}^l \rangle$. They also assume that the molecular symmetry is uniaxial. It is noted that these phase biaxial order parameters do not appear in equation (1) unless the β angle is non-zero. Although equation (1) is particularly suitable for powder samples such as those of biomembranes, it is not a useful form for aligned liquid crystal samples. Furthermore, if a particular motional model is chosen, it is more useful to express $[T_{1i}(\beta, \alpha)]^{-1}$ explicitly in terms of all non-zero spectral densities whose coefficients are known functions of β and α . Such expressions for uniaxial phases are well known [9] in the literature. In this communication, we derive equation (1) in terms of spectral densities $J_{m_L m_L}(\omega)$ [7]

$$J_{m_L m_L}(\omega) = \frac{3\pi^2}{2} \left(\frac{e^2 q Q}{h} \right)^2 \sum_{m_M} [d_{m_M 0}^2(\theta)]^2 \int_0^\infty \phi_{m_L m_L m_M}^{22}(t) \exp[-i\omega t] dt, \quad (2)$$

where $\phi_{m_L m_L m_M}^{22}(t)$, the correlation function for a uniaxial molecule in a medium of biaxial symmetry, may be found based on the rotational diffusion model as a sum of decaying exponentials, and θ is the angle between the C–C bond and the molecular z axis. In a uniaxial phase, the above spectral densities reduce to $J_{m_L}(\omega)$ due to $\delta_{m_L m_L}$, i.e. axial symmetry about the z axis of the laboratory (director) frame. The general theory of spin-lattice relaxation for spin-1 nuclei gives [10]

$$\text{and} \quad \left. \begin{aligned} [T_{1Q}(\Omega)]^{-1} &= 3J_1(\omega_0, \Omega), \\ [T_{1Z}(\Omega)]^{-1} &= J_1(\omega_0, \Omega) + 4J_2(2\omega_0, \Omega), \end{aligned} \right\} \quad (3)$$

where $\Omega \equiv (\beta, \alpha)$. Now $\omega_0/2\pi$ is the Larmor frequency and $J_m(m\omega_0, 0^\circ) = J_m(m\omega_0)$ when the director is aligned along the magnetic field. This is the case when the liquid crystal sample has a positive diamagnetic susceptibility anisotropy ($\Delta\chi > 0$). When the sample exhibits certain smectic phases, it could be rotated in the magnetic field to give a non-zero β angle. Electric field or surface alignment could also be used to orient the director away from the external magnetic field. In order to interpret the observed spin-lattice relaxation rates in equation (3), explicit expressions for $J_m(m\omega_0, \Omega)$ in terms of $J_{m_L m_L}(\omega_0)$ are required and a motional model must be chosen. Now $J_m(m\omega, \Omega)$ expressions are given by equation (11) of [8] in terms of order parameters, Clebsch–Gordon coefficients and reduced spectral densities. These expressions can be written [8, 11] in terms of $J_{m_L m_L}(\omega_0)$ to give

$$\begin{aligned} J_1(\omega, \Omega) &= \frac{3}{2} \cos^2 \beta \sin^2 \beta J_{0,0}(\omega) + \frac{1}{2} (1 - 3 \cos^2 \beta + 4 \cos^4 \beta) J_{1,1}(\omega) \\ &\quad + \frac{1}{2} (1 - \cos^4 \beta) J_{2,2}(\omega) + \cos 2\alpha \cos^2 \beta \sin^2 \beta J_{2,0}(\omega) \\ &\quad - \frac{1}{8} \cos 2\alpha [1 - 29 \cos^2 \beta + 28 \cos^4 \beta] J_{1,-1}(\omega) \\ &\quad - \frac{1}{2} \cos 4\alpha [1 - \cos^2 \beta]^2 J_{2,-2}(\omega), \end{aligned} \quad (4)$$

and

$$\begin{aligned}
 J_2(2\omega, \Omega) = & \frac{3}{8}(1 - \cos^2 \beta)^2 J_{0,0}(2\omega) + \frac{1}{2}(1 - \cos^4 \beta) J_{1,1}(2\omega) \\
 & + \frac{1}{8}(1 + 6 \cos^2 \beta + \cos^4 \beta) J_{2,2}(\omega) \\
 & + \frac{1}{4} \cos 2\alpha [1 - \cos^4 \beta] J_{2,0}(2\omega) \\
 & + \frac{1}{28} \cos 2\alpha [5 + 2 \cos^2 \beta - 7 \cos^4 \beta] J_{1,-1}(2\omega) \\
 & + \frac{1}{8} \cos 4\alpha [1 - \cos^2 \beta]^2 J_{2,-2}(2\omega), \tag{5}
 \end{aligned}$$

where spectral densities $J_{1,0}(\omega)$, $J_{1,2}(\omega)$ and $J_{2,-1}(\omega)$ are identical to zero when we follow Berggren *et al.* [7], by adopting a D_{2h} symmetry for biaxial mesophases. These two equations reduce to the familiar expressions for uniaxial phases [9]. The reason is that the 'biaxial' spectral densities $J_{2,0}(m\omega)$, $J_{1,-1}(m\omega)$ and $J_{2,-2}(m\omega)$ are non-zero only in biaxial phases. In particular, these spectral densities involve amplitudes that depend on biaxial order parameters $\langle D_{2,0}^4 \rangle$, $\langle D_{2,0}^2 \rangle$ and/or $\langle D_{4,0}^4 \rangle$ (see table 2 of [7]). From equations (4) and (5), it is obvious that in biaxial mesophases when the director is aligned along the magnetic field ($\beta = 0$), the spin-lattice relaxation rates are insensitive to the 'biaxial' spectral densities. Thus in this case, a biaxial phase behaves like a uniaxial phase as far as spin-lattice relaxation is concerned. Preliminary experiments [12] at the S_B - S_C phase transition of 4-*n*-pentyloxybenzylidene-4'-*n*-heptylaniline (5O.7- d_1 and 5O.7- d_4) show no discontinuity in both $J_1(\omega_0)$ and $J_2(2\omega_0)$. This is expected since, in the smectic G phase of 5O.7, the director is aligned along the field, while the layers are tilted with respect to the field [13]. It is also known [14] that the director is aligned by the external magnetic field in smectic C phases. Thus no discontinuities are observed in $J_1(\omega_0)$ and $J_2(2\omega_0)$ at the S_A - S_C phase transition in 5O.7 [15]. The earlier assumption that phase biaxiality of the S_C phase may be ignored in treating spin relaxation is now justified. To detect uniaxial-biaxial phase transitions in liquid crystals, one should therefore perform spin relaxation studies as a function of temperature for samples in which the director is oriented away from the external field, for example, $\beta = 90^\circ$. Angular dependence studies of biaxial liquid crystal phases are currently in progress in our laboratory. We hope that the present communication will encourage further experimental spin relaxation study of phase biaxiality in liquid crystals by rotation of samples. The prediction of the rotational diffusion model [7] and other motional models [1] in biaxial phases may hopefully be tested experimentally.

The financial support of the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. We thank Professor Myer Bloom for stimulating discussions.

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