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Biaxial Order Parameters in Liquid-Crystals - Their Meaning and Determination With Nuclear-Quadrupole Resonance

David W. Allender
Kent State University - Kent Campus, dallende@kent.edu

J. William Doane
Kent State University - Kent Campus, jdoane@neo.rr.com

Biaxial order parameters in liquid crystals: Their meaning and determination with nuclear quadrupole resonance

David W. Allender and J. William Doane

Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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A simple formulation is presented for the analysis of nuclear quadrupole spectra in biaxial liquid crystals based on orientational order parameters. The analysis contains no tilt angle or other model-dependent parameters not directly measured in NMR experiments. The observability and effect of various order parameters on the asymmetry of the electric field gradient η is discussed. It is shown that η is insensitive to rotational freeze-out of the variety expected to be observed in some biaxial phases. Nuclear quadrupole resonance experiments are described which are expected to yield rotational freeze-out parameters.

INTRODUCTION

Biaxiality in liquid crystals is most commonly identified optically by a distortion of the familiar Maltese cross figure seen in the conoscopic observation of an aligned sample when placed between crossed polaroids.[1] In nuclear quadrupole resonance (NQR) it is observed by an asymmetry of the nuclear quadrupole spin interaction. A measurable parameter in this observation is the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where the V_{ii} are the principal values of the time-averaged electric field gradient at the nuclear site. This electric field gradient is created within the molecule and depends, not only on the molecular structure and the local bonds, but also on molecular motion since it is the time-averaged value which is observed in liquid crystals. In uniaxial phases $\eta = 0$ but in biaxial phases the molecular orientational order is always such that η is finite. The central question is: what kind of order? Seliger *et al.*[2] have discussed this question in terms of parameters which were model based. In their calculations, a tilted smectic-C-type model was assumed and parameters containing the tilt angle were used in the discussion. A recent comment on their work used a similar type of approach.[3] There are several problems with these model-based approaches. First, they do not allow one to see clearly the sensitivity of η to the various kinds of biaxial orientational order. Second, NQR is not sensitive to translational order and the tilt angle is ordinarily not an observable quantity with NMR.[4]

In this paper we show a simple but direct calculation for η which is not model based. The order parameters are those which describe the preferential order of the molecular axes in the principal-axis system of the quadrupole interaction. We then discuss the sensitivity of η to various kinds of biaxial molecular-order and rotational-diffusion processes.

MOTIONAL AVERAGING OF THE QUADRUPOLE INTERACTION

In the principal-axis system the quadrupole Hamiltonian takes on the form[5]

$$H_Q = \frac{eQ}{2I(2I-1)} \sum_{m_0=-2}^{2} (-1)^{m_0} \langle R^p_{2,-m_0} \rangle T^p_{2,m_0}, \tag{1}$$

where

$$\langle R^p_{2,0} \rangle = \sqrt{\tfrac{3}{2}} V_{zz} \equiv \sqrt{\tfrac{3}{2}} eq^p, \quad T^p_{2,0} = (3I_z^2 - \vec{I}^2)/\sqrt{6},$$

$$\langle R^p_{2,\pm1} \rangle = 0, \quad T^p_{2,\pm1} = I_\pm I_z + I_z I_\pm,$$

$$\langle R^p_{2,\pm2} \rangle = \tfrac{1}{4}(V_{xx} - V_{yy}) \equiv \tfrac{1}{4} eq^p \eta^p, \quad T^p_{2,\pm2} = I_\pm^2,$$

where I_z, $I_\pm$, and $\vec{I}$ are the usual spin operators.[5]

The values of the coupling constant $e^2 q^p Q/h$ and the asymmetry parameter η^p are the quantities measured in an NQR experiment. The x, y, z coordinate frame is that of the principal-axis system. It is fixed with respect to the liquid-crystal sample. If we use the director concept for the liquid-crystal phase, the director frame is fixed with respect to the quadrupole principal axes. The two frames may or may not coincide. In an appropriate experiment the quadrupole principal-axis system can be determined. In a "pure" quadrupole-resonance experiment such as that performed by Seliger *et al.* the principal-axis system is not known. For the purpose of our discussion in this paper, its location is not important, but, as will be discussed later, its location can provide additional and useful order parameters.

While the principal-axis frame is fixed, the molecule is not. A molecular frame is normally chosen with the z axis parallel to the long axis of the molecule (a line through the center of the aromatic rings) and the x axis is often chosen to be normal to the aromatic rings. The y axis completes a right-handed system. The molecular axes fluctuate about the principal axes. We therefore transform to the molecular frame, in which case

$$\langle R^p_{2,m_0}\rangle = \sum_{m_1=-2}^{2} \langle D^{(2)*}_{m_0,m_1}(\phi,\theta,\psi)\rangle R^M_{2,m_1}, \qquad (2)$$

where ϕ, θ, and ψ are the Euler angles[6] that take the P frame into the M frame. The molecule contains the spin interaction of interest. If the molecule were in the solid phase, where the molecular axes do not fluctuate appreciably, the principal axes of the spin interaction would not necessarily correspond to the molecular axes as defined above. We must, therefore, make an additional transformation to where the principal axes of the interaction are known to be in the "frozen" molecule (local frame) and

$$\langle R^p_{2,m_0}\rangle = \sum_{m_1,m_2=-2}^{2} \langle D^{(2)*}_{m_0,m_1}(\phi,\theta,\psi)\rangle$$
$$\times D^{(2)*}_{m_1,m_2}(\alpha,\beta,\gamma) R^L_{2,m_2}, \qquad (3)$$

where

$$R^L_{2,0} = \sqrt{\tfrac{3}{2}} V_{ZZ} = \sqrt{\tfrac{3}{2}} eq^L,$$

$$R^L_{2,\pm1} = 0,$$

$$R_{2,\pm2} = \tfrac{1}{4}(V_{XX} - V_{YY}) = \tfrac{1}{4} eq^L \eta^L,$$

where the X, Y, Z frame is the principal-axis frame of

the local interaction in the molecule. The Euler angles α, β, and γ take the M frame into the L frame. The quantities $e^2 q^L Q/h$ and η^L, as well as the local principal-axis system relative to the molecular frame, are often known from solid-state experiments. The quantity η^L is normally small, $\lesssim 0.1$, and we shall neglect it in the remaining discussion. Combining Eqs. (3) and (1), we get

$$\eta^P = \sqrt{\tfrac{3}{2}} \langle S^p_{2,-2} + S^p_{2,2}\rangle / \langle S^p_{2,0}\rangle, \qquad (4)$$

where

$$\langle S^p_{2,m_0}\rangle = \sum_{m_1=-2}^{2} \langle D^{(2)*}_{m_0,m_1}(\phi,\theta,\psi)\rangle D^{(2)*}_{m_1,0}(\beta,\alpha). \qquad (5)$$

There are nine terms and consequently nine order parameters in the above expression which can be considerably simplified by considering apolar phases in which a molecule may exchange end-for-end. However, in some models[7-10] this exchange may only occur about one axis. If we define our molecular system such that this is the x axis, M_x, such an exchange would give the invariant operations $\phi \to \pi + \phi$, $\theta \to \pi - \theta$, and $\psi \to -\psi$ in which case Eq. (4) becomes[11]

$$\eta = \tfrac{3}{2}\{\sin^2\beta\cos2\alpha[\langle\cos2\phi(1+\cos^2\theta)\cos2\psi\rangle - 2\langle\sin2\phi\cos\theta\sin2\psi\rangle]$$

$$- 2\sin2\beta\sin\alpha[\langle\cos2\phi\sin\theta\cos\theta\sin\psi\rangle + \langle\sin2\phi\sin\theta\cos\psi\rangle]$$

$$+ \langle\sin^2\theta\cos2\phi\rangle(3\cos^2\beta - 1)\}\{\langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle(3\cos^2\beta - 1)\}^{-1}. \qquad (6)$$

It is useful to note two special cases in connection with the smectic C phase. One is the case where the molecular long axis is a threefold or greater axis of rotation. In fact, some models[12,13] consider the molecule to rotate in a nearly unhindered fashion about the long axis in which case all values of ψ are equally probable, independent of ϕ and θ, and Eq. (6) averages to

$$\eta = \tfrac{3}{2}\langle\sin^2\theta\cos2\phi\rangle / \langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle. \qquad (7)$$

In another model it is assumed that the long axis of the molecule is well ordered (i.e. $\theta \approx 0$) but that there is partial rotational freeze-out in which case the first term dominates and the asymmetry parameter becomes

$$\eta \approx 3\frac{\sin^2\beta\cos2\alpha}{(3\cos^2\beta - 1)}\langle\cos2(\phi+\psi)\rangle. \qquad (8)$$

In this last expression we note the absence of the order parameter $\langle\cos(\phi+\psi)\rangle$ which describes rotational freeze-out. The parameter $\langle\cos2(\phi+\psi)\rangle$ is, however, present but its value would be negligibly small for the mean-field potentials expected for some models. This is easily verified within the context of a simple mean-field approach.

For example, if the expected order is a rotational freeze-out, the effective potential felt by each molecule should have the form $V \approx -V_0\alpha\cos(\phi+\psi)$, where $\alpha = \langle\cos(\phi+\psi)\rangle$ is the order parameter and V_0 is a constant. The single-molecule distribution function is then given by

$$f = \exp(-V/kT)\Big/\int_{-\pi}^{\pi} dt \exp[V_0\alpha\cos(t)/kT]. \qquad (9)$$

This leads immediately to

$$\alpha = \int_{-\pi}^{\pi} d(\phi+\psi)\cos(\phi+\psi)f = \frac{I_1(V_0\alpha/kT)}{I_0(V_0\alpha/kT)} \qquad (10)$$

and

$$\beta \equiv \langle\cos2(\phi+\psi)\rangle = \int_{-\pi}^{\pi} d(\phi+\psi)\cos2(\phi+\psi)f$$

$$= \frac{I_2(V_0\alpha/kT)}{I_0(V_0\alpha/kT)},$$

where I_n is the nth modified Bessel function.[14] Figure 1 illustrates this result over the entire temperature range.[15] However, near the transition, $V_0/kT \approx 2$ and $\alpha \ll 1$ so the Bessel functions may be expanded to obtain
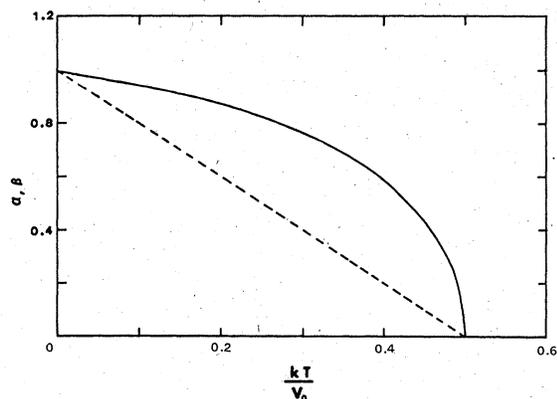
FIG. 1. The temperature dependence of the order parameters is depicted over the entire temperature range under the assumption of a one-body potential proportional to $\cos(\phi+\psi)$. The solid line shows $\alpha = \langle \cos(\phi+\psi)\rangle$ while the dashed line shows $\beta = \langle \cos[2(\phi+\psi)]\rangle$. Transitions typically occur at a few hundred degrees with the solid phase occurring tens of degrees lower. Thus only the region near $kT/V_0 \approx 0.5$ is of interest.

$$\langle \cos2(\phi+\psi)\rangle \simeq \tfrac{1}{2}\langle \cos(\phi+\psi)\rangle^2 \ll \langle \cos(\phi+\psi)\rangle. \quad (11)$$

Thus, the asymmetry parameter η is expected to be insensitive to $\langle \cos(\phi+\psi)\rangle$ (i.e. the observance of a very small $\langle \cos2(\phi+\psi)\rangle$ does not indicate the absence of rotational freeze-out), making it very dif-ficult to resolve the question of the occurrence of rotational freeze-out from a measurement of η alone.

THE NMR OBSERVATION OF ROTATIONAL FREEZE-OUT

There are, however, other NMR measurements which can be made that are sensitive to rotational freeze-out. One of these is an NMR measurement which is sensitive to the orientation of the principal-axis system relative to some other laboratory fixed frame. One such frame could be that of the principal-axis system of the diamagnetic susceptibility. A thermotropic liquid crystal will align itself in a magnetic field so that the principal z axis of the susceptibility tensor is parallel to the field direction. In a biaxial liquid crystal where there is rotational freeze-out this axis will not in general coincide with the principal z axis of the quadrupole interaction.

In a large magnetic field the quadrupole interaction for the ^2D spins or ^{14}N spins will be observed as a perturbation on the Zeeman interaction. For spin-one nuclei such as ^{14}N or ^2D the NMR spectra will appear as a doublet. If we take the case of the smectic phase where the long molecular axis is well ordered ($\langle\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle \approx 1$) the splitting of the doublet $\delta\nu_Q$ becomes[11]

$$\delta\nu_Q \simeq \tfrac{3}{2}e^2q^LQ\{\tfrac{3}{4}\sin^2\theta_0\sin^2\beta\cos2\alpha[\langle\cos2(\phi+\psi)\rangle\cos2\phi_0 + \langle\sin2(\phi+\psi)\rangle\sin2\phi_0]$$

$$-\tfrac{3}{4}\sin2\theta_0\sin2\beta\sin\alpha[\cos\phi_0\langle\sin(\phi+\psi)\rangle - \sin\phi_0\langle\cos(\phi+\psi)\rangle] + P_2(\cos\theta_0)P_2(\cos\beta)\}, \quad (12)$$

where the polar angles θ_0 and ϕ_0 describe the orientation of the magnetic field direction in the principal-axis system of the quadrupole interaction. The coefficient of the $\sin2\theta_0$ term then provides a measure of $\langle\cos(\phi+\psi)\rangle$. An NMR experiment in which θ_0 can be varied is therefore necessary. One such experiment has been reported where electric fields have been used to accomplish this.[16] Other experiments which make use of spinning samples have been used to obtain both the $\langle\cos2(\phi+\psi)\rangle$ and $\langle\cos(\phi+\psi)\rangle$ parameters.[17]

Another experimental NMR order parameter sensitive to rotational freeze-out is finite in an apolar phase, where the molecular z axis M_z prefers an end-for-end exchange about only one axis, M_x or M_y. In the Euler angle notation above, this parameter is $\langle\sin2\theta\sin\psi\rangle$. This parameter shows itself in the coupling constant e^2q^PQ/h. In the sense that the Euler angle ϕ does not appear in this pa-rameter, it is uniaxial in character.[11] As such, it will affect the spectral splittings even when $\theta_0 = 0$ (i.e., the magnetic field is parallel to the principal z axis of the quadrupole interaction).[11] The experimental observation and measurement of this parameter have recently been made in the compound 4-n-octyl-d_{17}-oxybenzoic acid-d where it has been observed to be finite in the smectic C phase but zero in the nematic.[18]

Finally, it is useful to note the dependence of Eq. (6) on the angles β and α. These are the spherical coordinates which describe the orientation of the principal Z axis of the local quadrupole interaction in the molecular frame. It is seen from Eq. (6) that differently oriented Z axes relative to the molecular frame provide different sensitivities to the various kinds of order parameters displayed in the equation. If, for example, we had a situation where the Z axis (often in the direction of a chemical bond)

was parallel to M_z then only the order parameter of Eq. (7) would be observed, since $\beta = 0$. Likewise, for $\beta = 90°$ only the first term of Eq. (6) would be present. If one had available a variety of differently oriented local interactions in the molecule it should then, in principle, be possible to measure all of the parameters in Eq. (6).

Note added in proof. In Eq. (8) we have assumed weak biaxiallity, where the principal z axis nearly

coincides with the director.

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[4] While NMR is sensitive to the orientational order of the molecule relative to a director it is also sensitive to the orientation of the director in a magnetic field (see, for example, Ref. 11). The orientation of the director in a magnetic field can sometimes be governed by the tilt angle in suitably designed experiments such as those by Z. Luz, R. C. Hewitt, and S. Meiboom [J. Chem. Phys. 61, 1758 (1974)] and by R. A. Wise, D. H. Smith, and J. W. Doane [Phys. Rev. A 7, 1366 (1973)]. In a model-based interpretation, the tilt angle can be determined. The parameters discussed in this paper are, however, totally insensitive to translational order and hence to tilt angle.

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[15] Equation 10 applies if only $\cos(\phi + \psi)$ ordering is important (i.e. C, B, or H phases). If both $\cos(\phi + \psi)$ and $\cos[2(\phi + \psi)]$ ordering is relevant (e.g. the VI phase) then the expression must be evaluated numerically. This conclusion has also been independently obtained by R. J. Meyer and related to us by private communication.

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