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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Online publication date: 06 August 2010

**To cite this Article** Blinc, R.(1999) 'The impact of NMR on the field of liquid crystals', *Liquid Crystals*, 26: 9, 1295 – 1300

**To link to this Article:** DOI: 10.1080/026782999203959

**URL:** <http://dx.doi.org/10.1080/026782999203959>

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# The impact of NMR on the field of liquid crystals†

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(Received 28 December 1998; accepted 25 March 1999)

In the fifty years that it has been available as an investigative technique, NMR has strongly promoted the advancement of knowledge in the field of liquid crystals. This article provides a brief overview of its contributions to the subject.

## 1. Introduction

Since its discovery in the fifties, nuclear magnetic resonance (NMR) has been intensively used in liquid crystal research. The most important aspect of NMR for the study of liquid crystals is that the splitting of the proton or deuteron NMR line is directly related to the nematic orientational order parameter  $S$  and to the orientation of the nematic director  $\mathbf{n}$ .

The interaction of the nuclear magnetic moment with the external magnetic field results in several equidistant Zeeman energy levels. The Zeeman levels in liquid crystals are perturbed by the interaction of the nuclear spins with the surroundings. In the case of protons with a spin  $I = 1/2$ , magnetic dipole–dipole interactions with neighbouring spins are the main perturbation. For deuterons with a spin  $I = 1$ , the electrical quadrupole interactions with the electric field gradient (EFG) tensor at the nuclear site is dominant.

For an isolated rigid proton pair, dipole–dipole interactions split the NMR line into a doublet separated by:

$$\Delta\nu_d = \frac{3}{2\pi} \frac{\gamma^2 h}{r^3} \frac{1}{2} (3 \cos^2 \theta_0 - 1) \quad (1)$$

where  $\gamma$  denotes the proton gyromagnetic ratio,  $r$  the inter-proton distance and  $\theta_0$  the angle between the inter-proton vector and the external magnetic field  $B_0$ .

For rigid deuterons we find a similar splitting of the deuteron NMR line

$$\Delta\nu_q = \frac{3}{2} \frac{e^2 q Q}{h} \frac{1}{2} (3 \cos^2 \theta_0 - 1) \quad (2)$$

where  $e^2 q Q/h$  stands for the static deuteron quadrupole coupling constant (which is  $\approx 165$  kHz for alkyl chain deuterons and 185 kHz for aromatic deuterons) and where  $\theta_0$  is the angle between the largest principal axis

of the EFG tensor (usually parallel to the C–D bond) and the direction of the magnetic field.

In a liquid crystal the angular factor  $1/2(3 \cos^2 \theta_0 - 1)$  is averaged over all molecular motions which are faster than  $(2\pi\Delta\nu_d)^{-1}$  or  $(2\pi\Delta\nu_q)^{-1}$ , respectively. It is thus averaged over conformational changes of molecules, molecular rotations around the long axis and fluctuations of the long axis around the preferred direction  $\mathbf{n}$ .

For a uniaxial nematic phase we thus find

$$\Delta\nu_d = \frac{3}{2\pi} \frac{\gamma h}{r^3} \frac{1}{2} S (3 \cos^2 \theta_B - 1) \left\langle \frac{1}{2} (3 \cos^2 \beta - 1) \right\rangle \quad (3)$$

and

$$\Delta\nu_q = \frac{3}{2} \frac{e^2 q Q}{h} \frac{1}{2} S (3 \cos^2 \theta_B - 1) \left\langle \frac{1}{2} (3 \cos^2 \beta - 1) \right\rangle. \quad (4)$$

Here  $\theta_B$  describes the orientation of the nematic director with respect to the magnetic field direction,  $\beta$  describes the angle between the inter-proton vector (or the largest principal axis of the EFG tensor) with respect to the molecular long axis and  $S$  represents the nematic orientational order parameter.

$$S = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle \quad (5)$$

where  $\theta$  stands for the angle between the instantaneous direction of the molecular long axis and the local director  $\mathbf{n}$ .  $\langle \rangle$  stands for the ensemble average. It should be noted that  $S = S_{zz}$  and that in deriving equations (3) and (4) the biaxiality term

$$\frac{1}{2} (S_{xx} - S_{yy}) \langle \sin^2 \beta \cos 2\alpha \rangle \frac{3}{2} \frac{e^2 q Q}{h} \frac{1}{2} (3 \cos^2 \theta_B - 1)$$

in equation (4) has been neglected. Here  $\alpha$  would describe the azimuthal angle of the inter-proton vector (or EFG direction) with the molecular long axis.

† Written to mark the 70th birthday of G. W. Gray in 1996.

In the isotropic phase,  $S=0$  and the splitting of the NMR line vanishes (figure 1). Here the spin interactions are averaged out by fast and isotropic molecular reorientations.

In a bulk nematic,  $\theta_B$  is spatially uniform. For compounds with a positive diamagnetic anisotropy,  $\Delta\chi > 0$ ,  $\theta_B = 0$ .

In a spatially confined or chiral liquid crystal, on the other hand, the director field is space dependent,  $\mathbf{n} = \mathbf{n}(\mathbf{r})$ . In some, for example confined systems, the magnitude of the nematic order parameter may also vary over the sample  $S = S(\mathbf{r})$ . The deuteron NMR line splitting thus becomes

$$\Delta\nu_q(\mathbf{r}) = \Delta\nu_{q0} \frac{1}{2} [3 \cos^2 \theta_B(\mathbf{r}) - 1] S(\mathbf{r}) \quad (6)$$

where  $\Delta\nu_{q0}$  denotes the splitting in the perfectly oriented nematic phase ( $S = 1$ ) with the director oriented along the magnetic field ( $\theta_B = 0$ ). In view of the spatial dependence of  $\Delta\nu(\mathbf{r})$  we have here a frequency distribution rather than a line splitting.

In the case of fast translational diffusion,  $\mathbf{n}(\mathbf{r})$  is also time dependent and additional motional averaging may occur.

## 2. Bulk and confined nematics

NMR has been extensively used to study director configurations and phase transition behaviour in both bulk and confined nematics. The ordering effect of the nematic phase on dissolved organic molecules also allows for structural determinations via high resolution NMR.

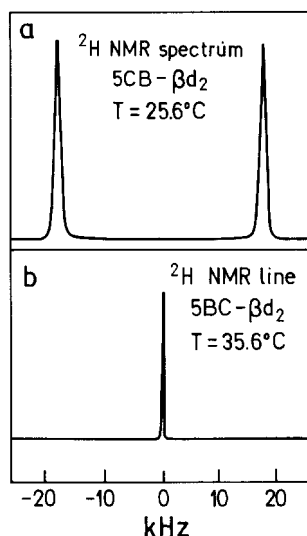


Figure 1. Deuteron NMR spectra of 5CB: (a) deuteron NMR spectrum of 5CB- $\beta d_2$ , in the nematic phase [8]; (b) deuteron NMR spectrum of 5CB- $\beta d_2$  in the isotropic phase.

Using selectively deuterated compounds, the decrease of orientational order along the hydrocarbon chain in thermotropic nematic liquid crystals has been observed by Boss *et al.* [1]. Similar effects were then seen in lyotropic membranes by Charvolin and Hendricks [2]. The even-odd variation of  $S$  along the hydrocarbon chain in nematics has been observed as well, and NMR measurements also allowed the observation of biaxiality in cholesteric liquid crystals by Doane *et al.* [3] and in lyotropic liquid crystals by Yu and Saupe [4]. The gradual increase of the orientational order  $S$  on cooling through the various smectic phases was also clearly seen by Figueirinhas *et al.* [5].

In nematic polymer dispersed liquid crystal (PDLC) materials, NMR has confirmed the bipolar director configuration in droplets with parallel anchoring at the wall [6]. It was also shown by Vilfan *et al.* [7] that in droplets below a critical size  $\approx 0.13 \mu\text{m}$ , the first order isotropic-nematic transition is replaced by a continuous evolution of the orientational order.

For liquid crystals confined in sub-micron size cylindrical cavities, deuteron NMR was used by Crawford *et al.* [8] to discriminate between various different nematic director field configurations (figure 2) resulting from an interplay of elastic forces, surface interactions, and also the morphology and size of the cavity. NMR also allows for a determination of the strength of surface anchoring and measurement of the surface elastic constants.

NMR has also been used for the study of nematics confined in a random network of pores in Vycor glasses (Iannacchione *et al.* [9]) and in silica aerogel matrices (Kralj *et al.* [10] and Zidanšek *et al.* [11]). Liquid crystals embedded in a low concentration polymer network have been also studied (Vilfan and Vrbančič-Kopač [12]) and valuable information on the polymer-liquid crystal interactions and the ordered surface layer were obtained (figure 3).

Very recently deuteron NMR demonstrated the existence of nematic biaxiality (figure 4) in a homeotropically aligned  $\alpha$ -deuterated 5CB surface layer in Anapore cylindrical cavities (Kopač, Zalar, and Blinc [13]). For  $\theta_B = \pi/2$  four peaks in the frequency distribution are found:

$$\Delta\nu_{1\pm} = \pm \frac{3}{2} \frac{e^2 q Q}{h} S \quad (7a)$$

and

$$\Delta\nu_{2\pm} = \pm \frac{3}{4} \frac{e^2 q Q}{h} [S(1 - \eta)]. \quad (7b)$$

The results yield at  $T = 293 \text{ K}$ :  $S = 0.22$  and  $\eta = 0.142$ . Here  $\eta = (S_{xx} - S_{yy})/S$ .

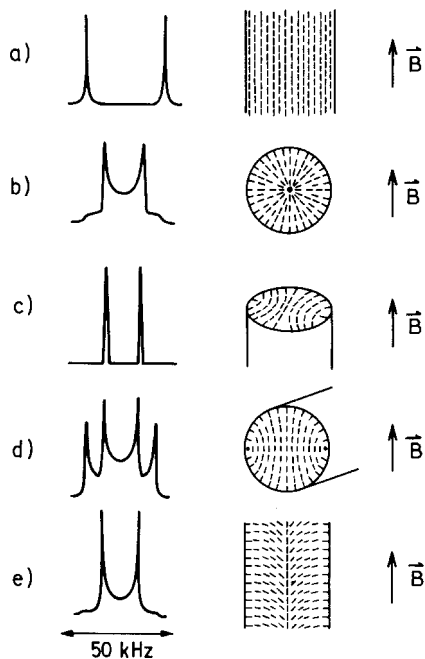


Figure 2. Deuteron NMR spectra for different nematic director fields in sub-micron size cylindrical cavities [8]: (a) nematic phase with parallel-axial structure in the cylindrical cavity and splitting  $\Delta v_{q\text{bulk}}$ ; (b) Pake-type powder spectrum for isotropic spatial distribution of directors in a spherical cavity with radial structure; (c) spectrum of a planar-polar structure in cylindrical cavities with all directors perpendicular to the magnetic field and splitting  $1/2\Delta v_{q\text{bulk}}$ ; (d) spectral pattern for the isotropic distribution of nematic directors in a plane parallel to the magnetic field; (e) escaped-radial structure in a cylindrical cavity.

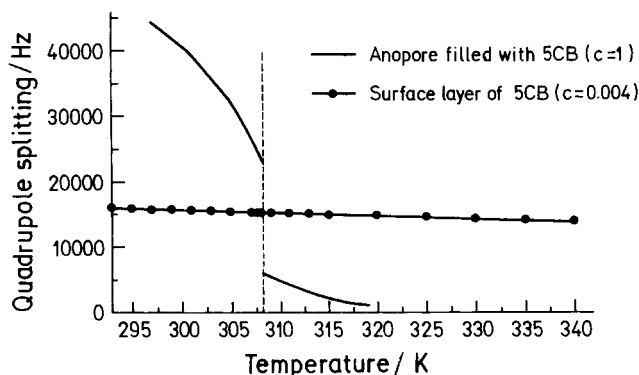


Figure 3. Temperature dependence of the nematic order parameter  $S$  of 5CB in Anopore membranes with filled cylindrical cavities and a thin surface layer on the walls of the cylindrical cavities.

### 3. Dynamics of bulk and confined nematics

Whereas static dipole-dipole or electric quadrupole interactions give rise to a splitting of the NMR spectrum, the time variations of these interactions induce spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation processes [14].

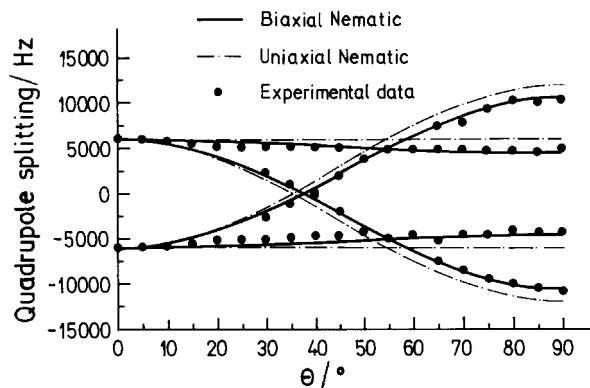


Figure 4. Angular dependence of the deuteron quadrupole splitting of a thin surface layer of  $\alpha$ -deuterated 5CB ( $C=0.4\%$ ) on the walls of the cylindrical cavities of Anopore membranes.

Soon after de Gennes in 1968 stressed the importance of collective order director fluctuations

$$\mathbf{n}(\mathbf{r}, t) = \mathbf{n}_0(\mathbf{r}) + \delta\mathbf{n}(\mathbf{r}, t) \quad (8a)$$

in nematics, it was realized by Pincus [15], and by Blinc *et al.* [16] that these fluctuations lead to a characteristic square root type dependence of the spin-lattice relaxation rate  $(T_1^{-1})_{\text{ODF}}$  on the nuclear Larmor frequency:

$$(T_1^{-1})_{\text{ODF}} \propto 1/\omega_L^{1/2}. \quad (8b)$$

This characteristic frequency dependence is due to the gapless nature of the two director modes which are the Goldstone modes of the isotropic-nematic transition. These are the modes responsible for the strong scattering of light in the nematic phase.

Director fluctuations are however not the only spin-lattice relaxation mechanism in bulk nematics. Translational self-diffusion, individual molecular rotations around the molecular long axis and internal conformational changes all contribute to the spin-lattice relaxation process [17] so that:

$$T_1^{-1} = (T_1^{-1})_{\text{ODF}} + (T_1^{-1})_{\text{SD}} + (T_1^{-1})_{\text{R}} \quad (9)$$

These contributions may be separated (figure 5) due to their different Larmor frequency, angular and temperature dependences. Order director fluctuations dominate  $T_1^{-1}$  in the bulk nematic phase below  $10^5$ – $10^6$  Hz, i.e. in the kHz region. Above a few MHz translational self-diffusion,  $(T_1^{-1})_{\text{SD}}$ , and molecular rotation  $(T_1^{-1})_{\text{R}}$  take over [18].

The absence of order director fluctuations in the bulk isotropic phase results in a smaller and Larmor frequency independent spin-lattice relaxation rate in the kHz range. On approaching the isotropic-nematic transition temperature  $T_c$  from above, nematic fluctuations appear within the isotropic phase. In 5CB, for instance, regions

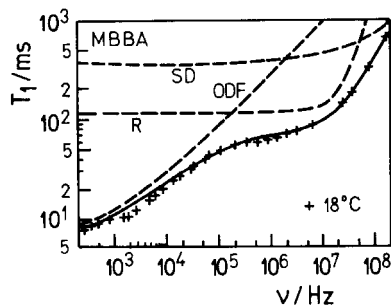


Figure 5. Dispersion of the proton  $T_1$  in the nematic phase of MBBA. The solid line is the fit to equation (9) where ODF denotes the contribution of director fluctuations, SD the contribution of translational self-diffusion, and R the contribution of molecular reorientations about the short axis.

with nematic order appear a few degrees above  $T_c$ . The size of these regions is  $\approx 0.65$  nm. As a molecule diffuses from the ordered into the disordered region, the deuteron quadrupole interaction is modulated. It is zero in the disordered region and small but non-zero in the ordered islands of the nematic phase. This slow modulation is characterized by the exchange time,  $\tau_{\text{exch}}$ , of the molecules which depends on the size of the ordered regions [19].

In confined liquid crystals or liquid crystals with an embedded polymer network, the nematic orientational order persists in a thin surface layer far above the nematic–isotropic transition temperature. This results in an additional exchange-induced contribution to the spin–spin relaxation rates  $(T_2^{-1})_{\text{exch}}$  which extends over a much wider temperature interval than pretransitional fluctuations in the bulk phase, as shown by Dolinšek *et al.* [20] and Vrbančič *et al.* [21].

If the biaxiality effects are neglected, one finds

$$(T_2^{-1})_{\text{exch}} = \tilde{\eta} \frac{1}{4} \left( 2\pi \Delta v_{q,\text{nem}} \frac{S_0}{S_{\text{nem}}} \right)^2 \left[ \frac{1}{2} (3 \cos^2 \theta_B - 1) \right] \tau_s. \quad (10)$$

Here  $\tau_s \approx \tau_{\text{exch}}$  is the average life-time of the molecules at the surface and  $S_0$  is the surface order parameter, whereas  $S_{\text{nem}}$  and  $\Delta v_{q,\text{nem}}$  are the values of the nematic order parameter and quadrupole splitting in the bulk nematic phase.  $\tilde{\eta}$  is the surface to volume ratio measuring the fraction of molecules temporally bound to the surface.

Typical values  $\tilde{\eta} = 0.06$ ,  $S_0 = 0.05$  and  $\tau_s = 2 \times 10^{-5}$  s are obtained, whereas  $S_{\text{nem}} \approx 0.45$  and  $\Delta v_{q,\text{nem}} = 51$  kHz at 28°C. These values refer to a 3% polymer dispersion in 5CB- $\alpha_2$  in the isotropic phase. Molecular exchange with the ordered surface layer is thus the dominant spin relaxation mechanism in confined or polymer dispersed systems in the isotropic phase in the 30–200 kHz range. In the MHz regime on the other hand, the proton and

deuteron spin relaxation times in these systems differ only modestly from those in pure bulk nematic or isotropic phases.

#### 4. Ferroelectric and antiferroelectric liquid crystals

In ferroelectric (FE) liquid crystals, the direction of the average molecular tilt slowly varies in space as one goes from one smectic layer to another in the chiral  $\text{SmC}^*$  phase. In antiferroelectric (AFE) liquid crystals, on the other hand, the average molecular tilt direction alternates as one goes from one smectic layer to the next:  $\theta_0 \rightarrow -\theta_0$ ,  $\vec{P} \rightarrow -\vec{P}$  or what is the same  $\phi \rightarrow \phi + \pi$  (figure 6) where  $\phi$  is the azimuthal angle of the average direction of the molecular long axis. Superimposed on this rapid alternation of the sign of the tilt we have in the AFE  $\text{SmC}_A^*$  phase a chirality-induced slow precession of each of the two sub-lattice tilts resulting in a double helicoidal structure (figure 6).

The deuteron NMR frequency  $\nu$  for a tilted molecular layer where the angle between the external magnetic field and the normal to the smectic layers is  $\theta \neq 0$  is given by

$$\nu = \nu_L \pm \frac{3}{8} \frac{e^2 q Q}{h} S [3(\sin \theta \sin \theta_0 \sin \phi + \cos \theta \cos \theta_0)^2 - 1]. \quad (11)$$

In view of the distribution of azimuthal angles in the multi-layer sample we have a frequency distribution

$$f(\nu) = \frac{\text{const}}{d\nu/dz} = \frac{\text{const}}{\frac{d\nu}{d\phi} \frac{d\phi}{dz}}. \quad (12)$$

In the plane wave limit  $d\phi/dz = \text{const}$ . The frequency distribution has intensity singularities at frequencies where

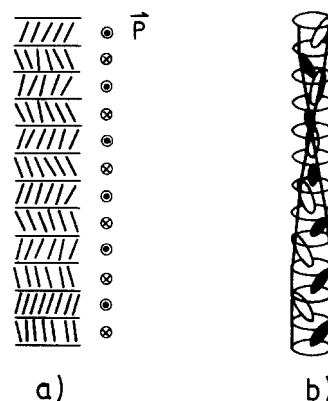


Figure 6. (a) The alternating-tilt model of the homogeneous antiferroelectric smectic  $\text{C}_A^*$  phase of liquid crystals, (b) the antiferroelectric double helix.

$d\nu/d\phi = 0$ , i.e. at

$$v_0 = \pm \frac{3}{8} \frac{e^2 q Q}{h} S \quad (13a)$$

$$v_- = \pm \frac{3}{8} \frac{e^2 q Q}{h} S [3 \cos^2(\theta - \theta_0) - 1] \quad (13b)$$

$$v_+ = \pm \frac{3}{8} \frac{e^2 q Q}{h} S [3 \cos^2(\theta + \theta_0) - 1]. \quad (13c)$$

A measurement of the  $\theta$ -dependence of these singularities allows for a determination of the molecular tilt angle  $\theta_0$  [22] in the FE SmC\* phase (figure 7).

In the AFE SmC<sub>A</sub>\* phase, on the other hand, the  $\theta$ -dependence of the positions of the singularities gives  $\theta_0 = 0$ . This is due to the fact that rapid molecular diffusion between two adjacent smectic layers averages out the  $+\theta_0$  tilt in one layer and the  $-\theta_0$  tilt in the other layer so that the largest principal axis of the deuteron EFG tensor is effectively normal to the smectic layer. Self-diffusion is too slow to have a similar effect in the FE SmC\* phase where the tilt does not reverse on a scale of 30 Å as in AFE liquid crystals, but on a scale of 10 μm.

Deuteron NMR thus provides direct microscopic evidence for the alternating tilt model of AFE liquid crystals.

Deuteron NMR has also allowed for a determination (figure 8) of the  $2\pi$ -symmetry of the magnetic field induced multi-soliton lattice in FE liquid crystals for a general orientation of the magnetic field, as well as for a measurement of the anisotropy of the critical field for the unwinding of the SmC\* helix [22].

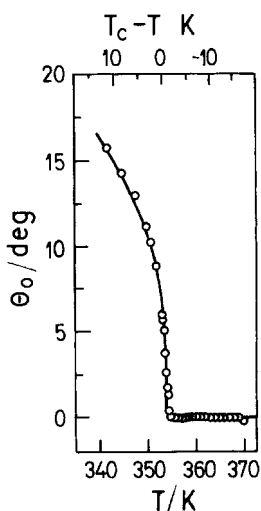


Figure 7. Temperature dependence of the molecular tilt angle  $\theta_0$  of  $\alpha$ -deuterated FE CE-8 deduced from deuteron NMR. The solid line represents the best fit to a power law  $\theta_0 = \theta'_0 [(T_c - T)/T_c]^p$  with  $\theta'_0 = 43^\circ \pm 4^\circ$ ,  $T_c = 353.7 \text{ K} \pm 0.3 \text{ K}$ .

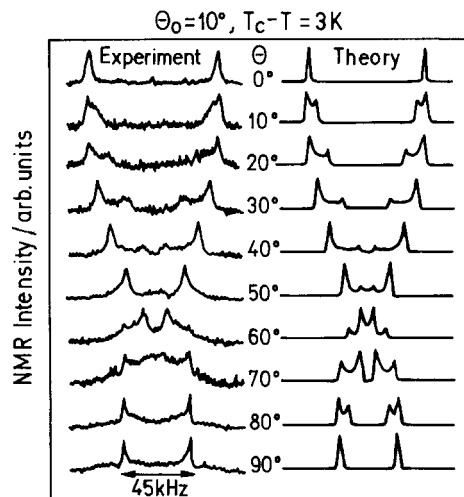


Figure 8. Angular dependences of the quadrupole-perturbed deuteron NMR spectra of CE8 at  $T_c - T = 3 \text{ K}$  ( $\theta_0 = 10^\circ$ ). The theoretical spectra are derived by taking into account the magnetic field induced soliton structure in a 9 T magnet.

## 5. Conclusion

From this brief review, it is clear that not only has NMR contributed greatly to the establishment of the understanding of liquid crystals that is now regarded as fundamental, but also it continues to play a very significant role in advancing knowledge in developing areas of liquid crystals as those involving anisotropic fluids in confined geometries, polymer LC networks and ferro- and antiferro-electric LC systems.

## References

- [1] BOS, P. J., PIRŠ, J., and DOANE, J. W., 1985, *Phys. Rev. Lett.*, **54**, 438.
- [2] CHARVOLIN, J., and HENDRIX, Y., 1984, *NMR in Liquid Crystals*, edited by J. W. Emsley (Amsterdam: Reidel Publishing Company).
- [3] DOANE, J. W., YANIV, Z., CHIDICHIMO, G., and VAZ, N., 1982, Proceedings of the 7th AMPERE International Summer School, Portorož, edited by R. Blinc and M. Vilfan, J. Stefan Institute, p. 181.
- [4] YU, L. J., and SAUPE, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
- [5] FIGUEIRINHAS, J., ŽUMER, S., and DOANE, J. W., 1987, *Phys. Rev. A*, **35**, 4389.
- [6] GOLEMME, A., ŽUMER, S., ALLENDER, D. W., and DOANE, J. W., 1988, *Phys. Rev. Lett.*, **61**, 2937.
- [7] VILFAN, I., VILFAN, M., and ŽUMER, S., 1989, *Phys. Rev. A*, **40**, 4724.
- [8] CRAWFORD, G. P., VILFAN, M., DOANE, J. W., and VILFAN, I., 1991, *Phys. Rev. A*, **43**, 835.
- [9] IANNACCHIONE, G., CRAWFORD, G. P., ŽUMER, S., DOANE, J. W., and FINOTELLO, D., 1993, *Phys. Rev. Lett.*, **71**, 2595.
- [10] KRALJ, S., LAHAJNAR, G., ZIDANŠEK, A., VRBANČIČ-KOPAČ, N., VILFAN, M., BLINC, R., and KOSEC, M., 1993, *Phys. Rev. E*, **48**, 340.
- [11] ZIDANŠEK, A., KRALJ, S., LAHAJNAR, G., and BLINC, R., 1995, *Phys. Rev. E*, **51**, 3332.

- [12] VILFAN, M., and VRBANČIČ-KOPAČ, N., 1996, *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Žumer (London: Taylor & Francis).
- [13] KOPAČ, P., ZALAR, B., and BLINC, R., 1998 (to be published).
- [14] ABRAGAM, A., 1961, *The Principles of Nuclear Magnetism* (Oxford: Clarendon Press).
- [15] PINCUS, P., 1969, *Solid State Commun.*, **7**, 415.
- [16] BLINC, R., HOGENBOOM, D., O'REILLY, D., and PETERSON, E., 1969, *Phys. Rev. Lett.*, **23**, 969.
- [17] VILFAN, M., BLINC, R., and DOANE, J. W., 1972, *Solid State Commun.*, **11**, 1073.
- [18] NOACK, F., 1986, *Prog. NMR Spectrosc.*, **18**, 171.
- [19] MARTIN, J. F., VOLD, R. R., and VOLD, R. L., 1984, *J. chem. Phys.*, **80**, 2237.
- [20] DOLINŠEK, J., JARH, O., VILFAN, M., ŽUMER, S., BLINC, R., DOANE, J. W., and CRAWFORD, G. P., 1991, *J. chem. Phys.*, **95**, 2154.
- [21] VRBANČIČ, N., VILFAN, M., BLINC, R., DOLINŠEK, J., CRAWFORD, G. P., and DOANE, J. W., 1993, *J. chem. Phys.*, **98**, 3540.
- [22] ZALAR, B., GREGOROVIČ, A., SIMSIČ, M., ZIDANŠEK, A., and BLINC, R., 1998, *Phys. Rev. Lett.*, **80**, 4458.