PHYSICAL REVIEW E **66**, 021710 (2002)

Deuteron NMR study of molecular ordering in a holographic-polymer-dispersed liquid crystal

Marija Vilfan,[1] Boštjan Zalar,[1] Adam K. Fontecchio,[2] Mojca Vilfan,[1] Michael J. Escuti,[2] Gregory P. Crawford,[2] and Slobodan Žumer[1,3]

[1]*Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

[2]*Department of Physics and Division of Engineering, Brown University, Providence, Rhode Island 02912*

[3]*Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia*

(Received 30 April 2002; published 23 August 2002)

Using deuteron nuclear magnetic resonance (NMR) and dynamic light scattering, we study the orientational order and dynamics of a BL038-5CB liquid-crystal mixture in a holographic polymer dispersed liquid-crystal material (HPDLC) as used for switchable diffractive optical elements. At high temperatures, where the liquid crystal is predominantly in the isotropic phase, the HPDLC deuteron NMR linewidth and transverse spin-relaxation rate T_2^{-1} are two orders of magnitude larger than in the bulk. The analysis shows that the surface-induced order parameter in HPDLC is significantly larger than in similar confining systems and that translational diffusion of molecules in the surface layer is at least two orders of magnitude slower than in the rest of the cavity. The unusual temperature dependence of T_2^{-1} upon cooling suggests the possibility of a partial separation of the 5CB component in the liquid-crystal mixture. The onset of the nematic phase in HPDLC occurs at considerably lower temperature than in the bulk and takes place gradually due to different sizes and different content of non-liquid-crystalline ingredients in droplets. Parts of the droplets are found isotropic even at room temperature and the structure of the nematic director field in the droplets is only slightly anisotropic. We point out the capability of NMR to detect the actual state of liquid-crystalline order in HPDLCs and to contribute in this way to the improvement of the switching efficiency of diffraction gratings.

DOI: 10.1103/PhysRevE.66.021710 PACS number(s): 61.30.−v, 65.20.+w, 76.60.−k

I. INTRODUCTION

Holographic polymer dispersed liquid crystals (HPDLCs) are an important stratified optical material consisting of periodic liquid-crystal-rich layers separated by pure polymer layers [1–4]. The liquid-crystal-rich layers exhibit either a discrete or bicontinuous droplet morphology. Owing to the periodically modulated refractive index generated by the layered structure, the HPDLC film behaves as a transmissive or reflective spatial diffraction grating in the zero-voltage state. Its advantage compared to static holograms is the ability to modify the diffraction efficiency by applying the electric field across the film. As the liquid-crystal molecules reorient in the direction of the electric field, the ordinary refractive index of the liquid crystal matches that of the surrounding polymer, and a transparent state with practically zero diffraction efficiency is obtained. Currently, multiple reflection gratings in a single film are being developed [5], and photonic applications of HPDLC materials, particularly switchable optical waveguide devices, are under way [6].

In the production of HPDLC films, a homogeneous prepolymer/liquid-crystal/photosensitive-dye mixture is illuminated by two coherent laser beams forming an interference fringe pattern within the sample. In bright fringes the polymerization takes place more rapidly than in the dark regions. Consequently, the polymer molecules concentrate in the bright regions whereas the liquid-crystal molecules presumably diffuse into dark regions, where they separate from the polymer in the form of nanodroplets or small interconnected pores [7]. The creation of holographic gratings under uniform illumination but with a polarization-state modulation was reported as an alternative way for their production [8]. Investigating the process of formation of a spatial grating, Sutherland *et al.* [9] found that during the holographic illumination first a locally isotropic grating forms but converts later to an anisotropic grating. The final optical anisotropy of the liquid-crystal-rich layers has been demonstrated by the dependence of the diffraction efficiency on the polarization of the incident light beam [9,10]. Very little is known, however, on the actual orientational ordering of the liquid crystal in droplets or voids. A deuteron nuclear magnetic resonance (NMR) study of pentyl-cyanobiphenyl (5CB) in an HPDLC material indicated that the orientation of the liquid-crystal molecules at the inner polymer surfaces is homeotropic, resulting in a radial-like configuration with a line segment defect along the major axis of the ellipsoidal void [11]. It was also conjectured that the orientational order is reduced throughout the pore volume as the splitting of the NMR spectrum was found to be about one order of magnitude smaller than in the bulk liquid crystal.

In the present study we decided to investigate, using NMR and dynamic light scattering, an HPDLC material of composition as close as possible to that prepared for the switchable diffractive optical elements. The purpose of the study is to obtain information on the actual state of liquid-crystalline order in a standard HPDLC material. The knowledge of this parameter, which affects the switching efficiency and contrast, may contribute to the improvement of such materials. Instead of the pure liquid crystal, used in the previous NMR study [11], we report here on the HPDLC containing the commercial liquid crystal BL038, which is frequently chosen for optical applications because of its large birefringence, and selectively deuterated 5CB. In the following, the term LC mixture will denote the BL038(70%)-5CB(30%) mixture, which was used as the liquid-crystal material in our study. This mixture contains a sufficient amount of deuteron nuclei, which are—owing to the interaction of their quadrupole moment with the electric

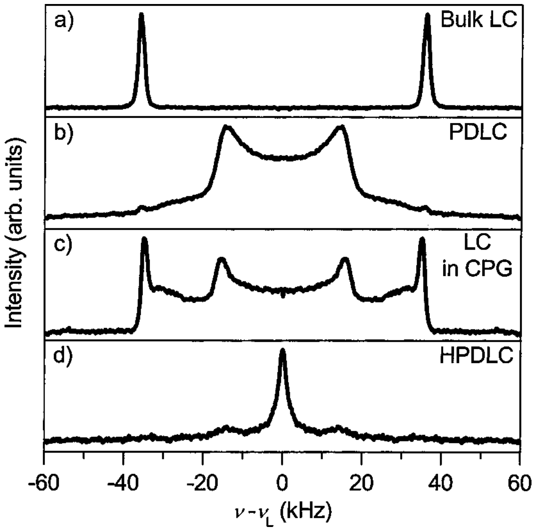

FIG. 1. Deuteron NMR spectra of the BL038-5CB mixture in the bulk sample (a), in the ordinary PDLC material (b), in porous glass CPG (c), and in the HPDLC (d) at roughly the same temperature ~290 K.

field gradient of surrounding electrons—a more suitable NMR probe of molecular orientational order than protons.

The deuteron NMR spectrum of a nematic liquid crystal in bulk consists of two well resolved lines [Fig. 1(a)], separated by [12,13]

$$\Delta\nu=\frac{3}{2}\,\frac{\overline{e^2qQ}}{h}\,\frac{1}{2}(3\cos^2\theta_B-1)S, \tag{1}$$

where $\overline{e^2qQ/h}$ is the quadrupole coupling constant averaged by molecular conformational changes and fast reorientations around the long axis, θ_B denotes the angle between the nematic director and the external magnetic field, and S is the orientational order parameter. Small effects of director fluctuations and molecular biaxiality have been neglected. At the nematic-isotropic transition temperature T_{NI}, the two lines of the spectrum discontinuously merge into one single line as the fast isotropic molecular reorientations completely average out the quadrupole interaction of deuterons.

The spectra of microconfined liquid crystals differ significantly from those of the bulk [14]. Here, the director field is not spatially uniform but configures itself to the restrictions imposed by the inner solid boundaries. Each director field configuration is characterized by a specific spectral pattern. For an isotropic distribution of director orientations found, for example, in spherical droplets of a PDLC material, the NMR spectrum is a powder pattern with two peaks at half of the bulk splitting and two outer shoulders [15], though its shape might be slightly "blurred" by the translational difusion of molecules [Fig. 1(b)]. The BL038-5CB mixture confined into ~70-nm-wide pores of irregular shape within the controlled-size porous glass (CPG) yields a powder pattern as well [16]. The two superimposed outer peaks originate from the remains of the bulk material in the sample [Fig. 1(c)]. However, much to our surprise, we found that the deuteron spectra of the same LC mixture in the HPDLC material do not show a clear structure down to very low temperatures. As shown in Fig. 1(d), the HPDLC deuteron spectrum at about 290 K exhibits clearly a strong central line, whereas the spectra of bulk, ordinary PDLC material and CPG have the shape characteristic for the nematic phase. To understand the origin of such unusual behavior in HPDLC, simultaneous measurements of the NMR spectra and of the spin relaxation of deuterons were performed. It should be noted, however, that using deuteron NMR we could observe only the behavior of one component in the LC mixture. Therefore a dynamic light scattering experiment was carried out with the same sample to provide an insight into the LC mixture as a whole.

In Sec. II, the preparation of the sample and experimental methods used in the present study are briefly described. In Sec. III, experimental results obtained by NMR and dynamic light scattering are presented; the analysis is focused on the surface-induced order and molecular dynamics in the isotropic phase and on the transition into the nematic state. A plausible scenario of the development of nematic order upon cooling is proposed and its possible impact on the operational capability of HPDLC in switchable gratings is considered.

II. EXPERIMENT

The HPDLC sample under study was prepared in the form of 50-μm-thick films from the homogeneous mixture of liquid crystal BL038 (EM Industries, 22.7 wt %), deuterated liquid crystal 5CB (9.7%), monomeric urethane resin (No. 8301 and No. 4866 UCB Radcure, total 45%), coinitiator *N*-Phenylglycine (Sigma Aldrich, 1.3%), photoinitiator Rose Bengal (Sigma Aldrich, 0.3%), chain-terminator *N*-Vinyl-Pyrrolidinone (Sigma Aldrich, 11%), and surfactant S271 (Chem. Service, 10%). 5CB was selectively deuterated in the first position of the alkyl chain. The details of the preparation can be found elsewhere [17]. We deliberately chose this complex system since its composition is close to that of HPDLCs considered for application in display and telecommunication devices. The reason for using the BL038-5CB mixture in our sample is twofold. First, pure 5CB alone, which is the deuterated component required for NMR measurements, will not phase separate from the polymer used in the regular HPDLC devices. Second, BL038 is a material very suitable for optical applications since it has a large birefringence ($\Delta n=0.28$ at wavelength 589 nm). The prepolymer emulsion was cured by two coherent Ar-laser beams (514 nm wavelength). The final morphology of the HPDLC film is visualized in the scanning electron micrograph (SEM) (Fig. 2). The dark areas are voids left in the polymer after the liquid crystal has been removed by a solvent for the SEM photography. It is seen that the dark liquid-crystal-rich regions consist of a dense network of LC droplets with sizes ranging roughly from 50 nm to 300 nm. The layers with dark patches are clearly separated by the bright pure-polymer layers with the average periodicity of the grating being 1.3 μm.

Using such an HPDLC sample in the form of a 50-μm-thick film, the dynamic light scattering measurements were performed by the standard photon correlation spectroscopy setup with a He:Ne laser source. The intensity

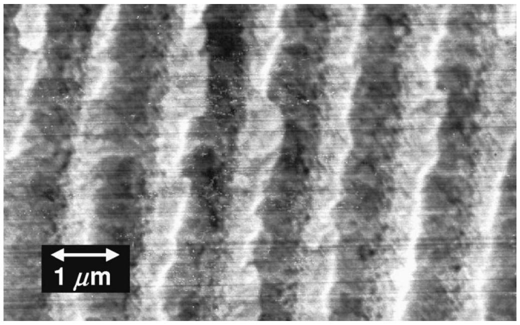

FIG. 2. Scanning electron micrograph (SEM) of the HPDLC grating used in the NMR experiment. Black areas in the figure represent enclosures containing liquid crystal (which was removed before making the micrograph). One can clearly discern liquid-crystal-rich layers from the bright pure polymer layers in the HPDLC grating.

autocorrelation function $g^{(2)}$ of the scattered light was measured by an ALV-5000 correlator and its characteristic decay time was determined as a function of temperature. For the NMR measurements, 20 identically prepared HPDLC films were stacked on top of each other to attain a sample giving a sufficiently large signal-to-noise ratio in the NMR experiment. The stack was carefully controlled to maintain the planar alignment of the films when sealed in a thin-walled NMR tube. The spectra and the transverse spin-relaxation time T_2 were measured using the quadrupolar echo pulse sequence improved by an eight-step-phase-cycling scheme [18,19]. The spin-lattice-relaxation time T_1 was determined by the standard inversion-recovery technique. In order to achieve a reasonably good signal-to-noise ratio, ≈ 1000 accumulations were typically acquired. All data were obtained on cooling the sample from 383 K to 270 K in the magnetic field of the NMR spectrometer operating at the deuteron Larmor frequency of 58.3 MHz. The observed relaxation of magnetization was monoexponential over at least 1 decade and the experimental error of the measured linewidths and relaxation times was less than 5%.

III. RESULTS AND DISCUSSION

A. Experimental results

First, the deuteron NMR spectra of the bulk BL038-5CB mixture were recorded in a broad temperature range between 383 K and 270 K. They exhibit the same characteristic temperature dependence as those of any other nematic liquid crystal [13]. In the isotropic phase, the spectrum consists of one single line, its full width at half maximum (FWHM) being less than 100 Hz (Fig. 3). The transition between the isotropic and nematic phases occurs at $T_{\mathrm{NI}}=358$ K, taking place between the transition temperature of pure BL038 at 373 K and that of pure 5CB at 308 K. In a narrow temperature interval of about 3 K both phases coexist in the sample. In the nematic phase, the spectrum reflects the onset of orientational order as it splits abruptly into a quadrupolar doublet separated by ~ 30 kHz (Fig. 3). The splitting increases with decreasing temperature up to 75 kHz at 273 K.

The same LC mixture in the HPDLC material shows a completely different behavior. At high temperatures, one single line of Lorentzian shape, characteristic of the isotropic phase, is observed as expected. However, its FWHM is at least ten times larger than in the bulk (Fig. 4). Moreover, the FWHM considerably exceeds not only the bulk linewidth but also those of the same LC mixture in the ordinary PDLC with a uniform dispersion of droplets and in the porous glass (Fig. 3). On cooling, the linewidth increases, but the expected line splitting or an abrupt broadening at the bulk isotropic-nematic transition temperature does not occur. The HPDLC deuteron spectrum (Fig. 5) consists of a single central line and does not show any resolved structure over a broad temperature interval of about 50 K below T_{NI}, apart from a weak (less than a few percent of total intensity) broad background, detectable below ~ 330 K, and possibly originating from domains with nematic order. The FWHM of the prevailing narrow part passes the bulk T_{NI} without any noticeable change, levels off, and shows then even a slight decrease (Fig. 4). At $T_a \sim 317$ K a broadening of the central line starts again. Simultaneously, the broad background is

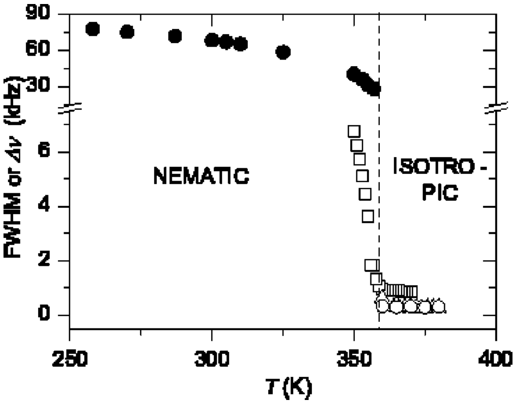

FIG. 3. Full width at half maximum (FWHM) (open symbols) and splitting (solid symbols) of the deuteron NMR spectra for the BL038-5CB mixture in the bulk (circles), confined into the ordinary PDLC material (squares), and into the porous glass CPG with pore diameter ~ 70 nm (triangles).

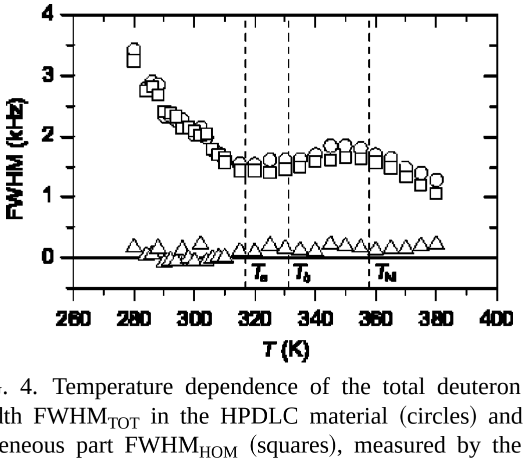

FIG. 4. Temperature dependence of the total deuteron NMR linewidth $\mathrm{FWHM_{TOT}}$ in the HPDLC material (circles) and of its homogeneous part $\mathrm{FWHM_{HOM}}$ (squares), measured by the transverse spin relaxation. It is seen that the linewidth results mostly from the homogeneous broadening, apart from a small contribution of magnetic field inhomogeneity ($\mathrm{FWHM_{INHOM}}$, triangles). $T_a \sim 317$ K denotes the beginning of the onset of the nematic phase in the droplets as clearly determined by dynamic light scattering.

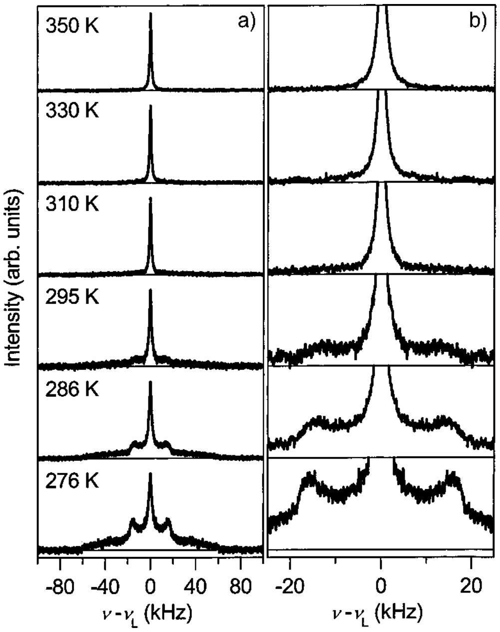

FIG. 5. Deuteron NMR spectra of the BL038-5CB mixture in the HPDLC material at a few selected temperatures. Each spectrum is shown in two frequency intervals, 200 kHz (a) and 50 kHz (b), respectively. The spectra in (b) have been scaled up by a factor of 2.5.

gaining the intensity, eventually developing into a powder pattern typical of the nematic phase with an isotropic distribution of directors. The central line is getting weaker until it almost disappears below 273 K. It is obvious that the appearance of nematic ordering upon cooling is profoundly affected by the confinement of the LC mixture into the HPDLC film.

Complementary to NMR, we used dynamic light scattering measurements to study the phase transition and the onset of nematic ordering in the same HPDLC material. The time dependence of the autocorrelation function of the scattered light was measured in the same broad temperature interval as NMR spectra (Fig. 6). The characteristic decay time of the autocorrelation function is determined by the relaxation time of collective orientational fluctuations in the nematic phase. One important point observed with the HPDLC sample is the absence of dynamic light scattering above $T_b = 332$ K, which clearly shows that the confined LC mixture is in the isotropic phase (apart from the surface layer) at temperatures at which the bulk has already passed into the nematic phase. This observation is in agreement with the appearance of a single line in the NMR spectrum.

Below ~ 332 K the dynamic scattering of light is observed. The time decay of the autocorrelation function in the millisecond range results from nematic director fluctuations, but incoherent dynamic events on the time scale of seconds are observed as well. Such a scattering might arise from defects exhibiting nematic order, even if less than 1% of the total LC material is trapped within. In these regions, the isotropic and nematic phases can coexist in a certain temperature range. The director fluctuations within the nematic parts account for the fast decay of the autocorrelation function, whereas the variation of their shape and position with time gives rise to the slow incoherent events. The indication for the existence of nematically ordered regions has been already obtained by NMR as the weak broad background, though it becomes clearly visible only at lower temperatures.

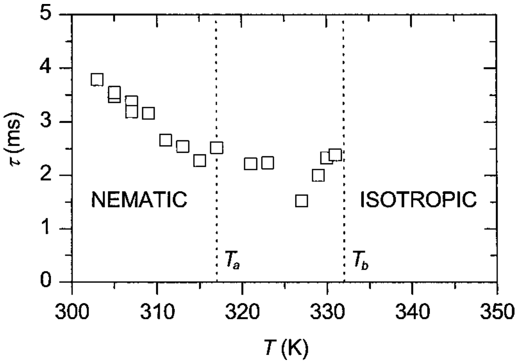

FIG. 6. Temperature dependence of the relaxation times of the autocorrelation function $g^{(2)}$ in the dynamic light scattering experiment on the HPDLC film. T_b denotes the temperature at which, upon cooling, the dynamic light scattering appears, and T_a denotes the beginning of the formation of the nematic phase in the grating's droplets.

Finally, at $T_a \sim 317$ K the onset of strong elastic light scattering on collective orientational fluctuations alone appears. This scattering is characteristic of the nematic phase and obviously shows that at this temperature the LC mixture in many droplets in the HPDLC grating has turned into the nematic phase. The measured relaxation time of the slowest director fluctuations, which is of the order of a few milliseconds, starts here to increase with decreasing temperature and so does the NMR linewidth. It should be stressed that the overall transition into the nematic phase is not sharp but gradual. With decreasing temperature the amplitude of the autocorrelation function increases indicating that more and more droplets turn into the nematic phase and contribute to the elastic light scattering. The same fact, though less obvious, is reflected by the growing "wings" and emerging powder pattern in the NMR experiment. The time decay of the autocorrelation function is a stretched exponential indicating slightly different relaxation times and therefore a distribution in droplet sizes. The stretching exponent is about 0.9 instead of 1 as would be in the bulk liquid crystal. Different sizes of droplets in the grating may be one of the reasons for a gradual evolution of the nematic order in HPDLC [20].

The observed shift of the isotropic-nematic transition for ~ 40 K towards lower temperatures can be explained by the presence of non-liquid-crystalline ingredients in the confined LC mixture, which act as impurities. The candidates are the photosensitive dye, a small amount of dissolved polymer, and/or remains of the monomer. On the other hand, the surfactant that is added to lower the switching voltage of the HPDLC film [21] was found nonsoluble in the LC mixture in the absence of other constituents. For this reason it is highly improbable that a fair amount of the surfactant would be dissolved in the liquid-crystal droplets. No significant shift in the transition temperature has been observed in the BL038-5CB mixture constrained either in the spherical droplets of an ordinary PDLC material or in the CPG with comparable pore sizes ~70 nm (Fig. 3). In both cases a sharp transition from the isotropic into the nematic phase at nearly the same temperature T_{NI} as in the bulk takes place. On the other hand, the commercial liquid-crystal mixture BL038 without added 5CB experiences in the HPDLC material an equally strong reduction of the isotropic-nematic transition temperature [10]. These observations lead to the conclusion that the gradual formation of the nematic phase results, to a minor extent, from the spread in droplet sizes and mainly from a different amount of non-liquid-crystalline ingredients in different droplets.

B. NMR linewidth in the high-temperature phase

NMR data and dynamic light scattering show that the LC mixture in the HPDLC grating is mainly in the isotropic phase above 317 K. But even in the isotropic phase, a tiny surface layer located at the LC-polymer interface is expected to possess a weak orientational order far above the transition temperature [22–25]. Though the fluctuations of the surface-induced order in the high-temperature phase are too weak to be observed by dynamic light scattering, the orientational order at the surface is clearly demonstrated by the broadening of the deuteron NMR line. The surface-induced order parameter, inherent to the surface layer, is expected to be the largest at the liquid-crystal–polymer interface and to decrease exponentially with increasing distance from the wall. The characteristic decay length is the nematic correlation length introduced by de Gennes [26]. It describes to a good approximation the thickness of the ordered surface layer. If there would be no translational diffusion of molecules, the deuteron NMR spectrum would be a powder pattern, resulting from the molecules in the surface layer, superimposed on the narrow central line originating from the isotropic region of the droplet. The presence of translational diffusion, however, gives rise to a motional narrowing of the spectrum, though the narrowing might not be complete [27,28]. In the case of partial narrowing, the observed broadening of the line is inhomogeneous and is caused by the residual static quadrupolar interaction of deuterons in the surface layer. It is proportional to the orientational order parameter S_0 at the surface. On the other hand, the broadening of the line might be also dynamic, i.e., induced by the time modulation of the quadrupolar interaction [16,25]. This homogeneous contribution to the linewidth equals T_2^{-1}/π, where T_2^{-1} is the transverse deuteron spin-relaxation rate, and is proportional to the square of the surface order parameter. In order to separate the homogeneous and inhomogeneous contributions to the linewidth, the measurements of T_2^{-1} were performed independently. The comparison of the homogeneous and total linewidths in Fig. 4 clearly shows that the broadening of the central line in the HPDLC film is almost entirely homogeneous and should be therefore analyzed in terms of the transverse spin-relaxation time.

C. Effect of confinement on T_1^{-1} and T_2^{-1} in the isotropic phase

In the isotropic phase of a bulk liquid crystal, T_1^{-1} and T_2^{-1} of deuterons result from the time modulation of quadrupole interaction by fast local molecular reorientations of the spin-bearing molecules. Similarly as in the isotropic phase of pure liquid crystals, the values of T_1^{-1} and T_2^{-1} in the bulk LC mixture high above T_{NI} are almost equal $(\sim 30\ \mathrm{s}^{-1}$ at 383 K$)$. Within the simple theory of Woessner and co-workers for the relaxation induced by isotropic rotation of elongated molecules [29,30], the correlation time associated with the reorientations of the long molecular axes is evaluated to be $\sim 4\times 10^{-10}$ s at ~383 K. A more elaborated theory that includes conformational changes of the alkyl chains was developed and applied to 5CB by Dong and co-worker [31,32]. Upon confinement into the HPDLC material, the spin-lattice-relaxation rate increases only by a factor of ~2, whereas the transverse spin-relaxation rate experiences a dramatic growth resulting in T_2^{-1} about hundred times larger than in the bulk.

In order to understand such behavior one should be aware that the relaxation efficiency of a specific dynamic process depends on its intensity and frequency distribution. The spin-lattice relaxation is determined by the spectral densities of the correlation functions, related to the deuteron quadrupolar interaction, at Larmor and double Larmor circular frequencies. It is therefore sensitive particularly to motions with frequencies in the high megahertz and low gigahertz regime [13,24]. The transverse spin relaxation, on the other hand, contains also the spectral density at zero Larmor frequency. For this reason a substantial contribution to T_2^{-1} might arise from slow dynamic processes with frequencies smaller than the Larmor frequency but larger than the static NMR linewidth. In practice, this implies that T_2^{-1} is suitable for detecting not only fast molecular motions but also dynamic processes in the kilohertz frequency range.

A relatively small increase in T_1^{-1} of the LC mixture in the HPDLC indicates that individual molecular reorientations have not been significantly affected by the confinement. An increase by the factor of ~2 in the spin-lattice-relaxation rate means roughly an increase in the correlation time by the same factor. Such an increase is not surprising taking into account that a small amount of polymer dissolved in the liquid crystal significantly increases its rotational viscosity [33,34]. It is therefore highly probable that the dissolved polymer affects the translational and rotational diffusion of molecules in the same way.

The huge T_2^{-1} in the HPDLC material is of a different origin. It results from the surface-induced order close to the cavity walls. The correlation function of quadrupolar interaction related to molecules in the ordered surface layer does not decay to zero due to fast molecular reorientations alone because of the finite value of the orientational order parameter in this layer. The residual quadrupolar interaction is further modulated on the kilohertz frequency scale by molecular translational displacements between regions with different orientational order within the void. The slow time decay of the residual correlation depends on the rate of molecular exchange between the surface layer and the isotropic region, and on the so-called RMTD process (reorientations mediated by translational displacements). The latter process is caused by molecular diffusion in a cavity where different surface sites impose different orientation to molecules in the surface layer. The director at the surface is assumed to be everywhere perpendicular to the local surface direction, as the surfactant, added to the HPDLC mixture, promotes the homeotropic orientation of liquid-crystal molecules. Both relaxation mechanisms, exchange and RMTD, are interconnected; their relative importance depends on the frequency of the NMR experiment and on the nature of the system [25,35–38]. A comprehensive treatment of both contributions to the spin relaxation can be performed by simulating numerically the time dependence of the correlation functions [35]. In the first approximation, however, the two mechanisms may be addressed separately in view of a considerable difference in their time scales. In the following section their basic characteristics will be discussed.

D. Relaxation mechanisms in the kilohertz range

If the translational diffusion coefficient D of liquid-crystal molecules is almost uniform throughout the cavity, the RMTD relaxation mechanism prevails in determining the increase in T_2^{-1} upon confinement. The time decay of the correlation function due to the RMTD process is not monoexponential. It cannot be described by a single correlation time, but rather by a discrete set of characteristic times related to the topologically restricted translational diffusion [25,36]. As the RMTD process involves only the molecules that are in the surface layer at the beginning as well as at the end of the observed correlation decay, the resulting relaxation rate $(T_2^{-1})_{\mathrm{RMTD}}$ becomes proportional to the square of the relative number of molecules in the ordered surface layer f_S. The complex expression describing this situation in a spherical cavity [25] can be to a good approximation—the discrepancy being only a few percent—replaced by the relaxation rate calculated for a simple two-phase model in the form [37,38]

$$(T_2^{-1})_{\mathrm{RMTD}}=\frac{9}{20}\ \pi^2 f_S^2\left(\frac{\overline{e^2qQ}}{h}\right)^2 S_0^2\ \ \tau. \tag{2}$$

S_0 denotes here the order parameter at the surface and $\tau=R^2/(6D)$, where R is the radius of the cavity and D the self-diffusion coefficient. The relaxation rate induced by the RMTD relaxation mechanism shows a pretransitional increase due to the critical behavior of the nematic correlation length ξ on approaching T_{NI} from above [26]:

$$\xi=\xi_0\sqrt{\frac{T^*}{T-T^*}}, \tag{3}$$

where ξ_0 is of the order of molecular dimension ($\sim$0.65 nm for 5CB) and T^* is the bulk supercooling limit of the isotropic phase (about 1 K below T_{NI}). In large spherical cavities, where the thickness of the surface layer is small compared to the cavity radius, this leads to

$$(T_2^{-1})_{\mathrm{RMTD}}\propto f_S^2\sim\left(\frac{3\xi}{R}\right)^2=\left(\frac{3\xi_0}{R}\right)^2\frac{T^*}{T-T^*}. \tag{4}$$

Such pretransitional temperature behavior of the transverse spin-relaxation rate was found in 5CB confined into controlled porous glass [16]. In some cases the surface order parameter is temperature dependent as well [24]. It increases on approaching T_{NI} and makes the pretransitional increase in $(T_2^{-1})_{\mathrm{RMTD}}$ even more significant.

The situation is quite different in systems where a considerable slowing down of molecular translational displacements at the surface takes place. In this case, the increase in the transverse relaxation rate upon confinement is mainly due to the exchange of molecules from the ordered into the disordered region. The slowing down of molecules concerns basically only the first monomolecular layer at the interface, which has a roughly fixed number of molecules. In the case that the surface order parameter is determined by short-range surface interactions and therefore is not much affected by the isotropic-nematic transition, the exchange induced relaxation would be only weakly temperature dependent. Within the two-phase model, the relaxation rate $(T_2^{-1})_{\mathrm{exch}}$ is given by [24,37,38]

$$(T_2^{-1})_{\mathrm{exch}}=\frac{9}{20}\ \pi^2\eta(1-\eta)\left(\frac{\overline{e^2qQ}}{h}\right)^2 S_0^2\ \ \tau_{\mathrm{exch}}, \tag{5}$$

where η denotes the fraction of molecules in the first monomolecular layer at the surface and τ_{exch} denotes their approximate average lifetime within it. In the ordinary PDLC material the two relaxation mechanisms, RMTD and exchange, could be clearly separated [25]. The exchange contribution prevails farther from the phase transition and the RMTD takes over closer to T_{NI}.

The exchange relaxation mechanism loses its efficiency upon cooling the sample below the isotropic-nematic transition temperature. Except in the close proximity of T_{NI} and at the disclination lines and point defects in the structure, the magnitude of the orientational order in the nematic phase is homogeneous throughout the enclosure. The effect of the exchange relaxation mechanism is therefore negligible. On the other hand, the importance of the RMTD mechanism might increase below T_{NI}. The director field in the cavity is not homogeneous, and the translational diffusion of all molecules (not only of those in the surface layer) contributes to the deuteron spin relaxation by modulating the quadrupolar interaction. The discrete set of characteristic times involved in this process depends on the structure of the director field [36]. Finally, it should be noted that the thermal fluctuations of the director also represent a strong relaxation mechanism at low frequencies in the nematic phase.

E. Discussion of experimental T_2^{-1} and NMR linewidth data

Already a brief inspection of Fig. 4, where $\mathrm{FWHM}_{\mathrm{HOM}}$ represents T_2^{-1}/π, demonstrates that the transverse spin-relaxation rate T_2^{-1} does not show a simple pretransitional increasing on approaching the temperature where the onset of the nematic phase takes place ($\sim$317 K). Between 380 K and 353 K a smooth increase in T_2^{-1} is observed but, on cooling further, the T_2^{-1} vs T curve levels off, turns into a flat plateau, and even slightly decreases before the transition

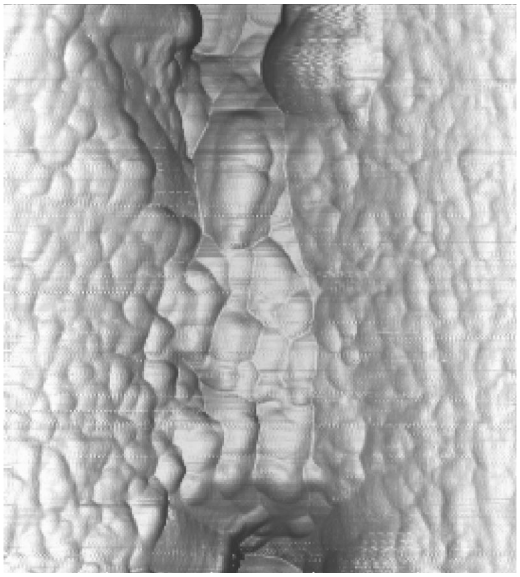

FIG. 7. Atomic force microscopy (AFM) photography of the inner surface of the cavity enclosing the liquid crystal in the HPDLC material. Hemispherical polymer blobs protruding from the cavity walls are clearly seen. The area in the figure is 1 $\mu\mathrm{m}^2$.

into the nematic phase is attained. As mentioned earlier, the RMTD relaxation mechanism predicts a strong pretransitional increase in the transverse relaxation rate, which has not been observed in HPDLC. Besides, $(T_2^{-1})_{\mathrm{RMTD}}$ calculated for uniform diffusion throughout the cavity according to Eq. (2), amounts—for a set of reasonable parameters—only to $\sim 90\ \mathrm{s}^{-1}$. This is much less than the huge experimentally determined value $\sim 4500\ \mathrm{s}^{-1}$ (at 360 K). In this estimate the following values of the relevant parameters have been used: $\overline{e^2qQ/h} \sim 60$ kHz [25], the correlation length ~ 2 nm leading to $f_S \sim 0.12$ in a spherical enclosure with smooth walls and radius of about 50 nm, diffusion coefficient $D \sim 1\times 10^{-10}\ \mathrm{m}^2\,\mathrm{s}^{-1}$, and $S_0 \sim 0.3$. However, S_0 might be larger and the relative number of orientationally ordered molecules might be higher for cavities with rugged walls. But even the largest theoretically allowed value of $S_0 = 1$ and a two times larger f_S do not account, when applied to Eq. (2), for the huge T_2^{-1} in HPDLC, which is much larger than T_2^{-1} of pure 5CB in the normal PDLC and in the porous glass [16,25].

On the other hand, the predicted magnitude of the relaxation rate is considerably enhanced if a slowing down of the molecular translational motion in the immediate vicinity of the surface is assumed. In a thorough treatment, the resulting relaxation rate should be calculated by numerically simulating the time dependence of the interaction correlation functions to include both the RMTD and exchange losses of correlation [35,39]. To get only a rough estimate of the dynamical parameters involved in this process, Eq. (5) can be used as the first approximation, yielding $T_2^{-1} \sim 4500\ \mathrm{s}^{-1}$ for $\eta \sim 0.12$ (spherical cavity with smooth walls) and the factor $S_0^2\ \tau_{\mathrm{exch}} \sim 2.6\ \mu\mathrm{s}$. However, an atomic force microscopy (AFM) photograph indicates a rugged inner polymer surface with hemispheres protruding from the cavity walls, all with similar radii of curvature (Fig. 7) [40]. Such a structure yields $\eta \sim 0.24$ and correspondingly the value $\sim 1.5\ \mu\mathrm{s}$ for $S_0^2\ \tau_{\mathrm{exch}}$. In the attempt to specify the last two parameters, S_0 and τ_{exch}, separately, we take into account the fact that the exchange of molecules between the surface layer and isotropic region is fast enough to provide a motional narrowing of the residual quadrupole interaction, which is reflected in a single and structureless NMR line at high temperatures. Therefore the condition [13,24,28]

$$\pi(\overline{e^2qQ/h})S_0\tau_{\mathrm{exch}} \lesssim 1 \tag{6}$$

must be fulfilled. This additional requirement limits S_0 in the high-temperature phase to values larger than ~ 0.2 (for the rugged surface), and yields an exchange time of the order of $\sim 10\ \mu\mathrm{s}$. The exchange time is roughly equal to the dwell time of molecules in the surface layer and of the same order of magnitude as in the ordinary PDLC.

In view of the simple model used to describe a complex relaxation process, the above values should be treated as merely indicative. Moreover, any polymer strands stretched across the cavity might increase the inner surface and decrease the estimated surface order parameter. The fact, however, remains that the magnitude of the surface order parameter in HPDLC is larger than in the ordinary PDLC materials ($S_0 \sim 0.08$) [16]. This might be due to the presence of surfactant molecules that attach to the polymer surface and promote homeotropic, i.e., perpendicular orientation of liquid-crystal molecules at the interface. The surfactant usually promotes a larger degree of surface order as was observed for 5CB in Anopore cavities with treated walls [41,42]. However, the surface order parameter in treated Anopore exhibits a strong pretransitional increase, which has not been observed in HPDLC. It should be also stressed that the large T_2^{-1} in HPDLC cannot be explained without assuming a slowing down of the translational diffusion of liquid-crystal molecules in contact with the polymer/surfactant. The diffusion coefficient of liquid-crystal molecules in the surface layer is at least two orders of magnitude smaller than in the isotropic region. Besides, the polymer surface is—irrespective of the surfactant molecules—far from being smooth. A rough and blobbed structure that increases the inner surface area has a larger effect on the liquid crystal at the same concentration ratio of ingredients in the HPDLC material.

The temperature dependence of the linewidth and T_2^{-1} in the high-temperature phase of HPDLC is most unusual. A broad peak appearing in the linewidth vs temperature curve (Fig. 4) has not been observed in any other confining system. One possible scenario of such behavior could be built on the conjecture that the concentration of BL038 and 5CB in the LC mixture is not homogeneous in the whole temperature interval under study. Bearing in mind that the clearing point of BL038 is at 373 K whereas 5CB clears at 308 K, it would not be surprising if a partial separation of 5CB molecules from other liquid-crystal compounds in the mixture took place. In such a case, the surface-induced order and correspondingly the linewidth of 5CB molecules, which represent the only liquid-crystal component seen by NMR, would first increase with decreasing temperature as long as their ordering matches the order of the entire LC mixture. If, however, a formation of 5CB-richer areas, stimulated by the proximity of polymer surfaces, started below ~ 353 K, the molecules of this particular liquid crystal would now behave as being far above their bulk transition temperature. An effective diminishing of their ordering might occur in this way and cause a decrease in the relaxation rate in a certain temperature interval. Whether the diminishing of the ordering means a smaller value of the surface order parameter S_0, a smaller fraction of 5CB molecules in the surface layer η, or even a shorter τ_{exch} cannot be stated in the present study. The partial separation could also account for incoherent dynamic light scattering observed at temperatures between 332 K and 317 K (Fig. 6).

The onset of the nematic phase at 317 K, although clearly visible in dynamic light scattering experiments, is marked by a gradual increase in the NMR spectral FWHM. Obviously some of the droplets, probably the larger ones, become nematic throughout their volume whereas the others still persist in the partly isotropic phase with an oriented surface layer. The nematic droplets are the source of director fluctuations causing the decay of the autocorrelation function in the dynamic light scattering experiment and appearing as a weak powderlike pattern (first only as the ‘‘wings’’ to the Lorentzian) in the NMR spectra. The isotropic droplets are invisible in the optical experiment though they produce the strong central line in the NMR spectrum. With decreasing temperature, the relaxation time of director fluctuations increases (Fig. 6). The amplitude of the autocorrelation function increases as well, indicating a growth in the fraction of droplets in the nematic phase, which shows up also in the increasing intensity of the powder pattern in the NMR spectrum. It is interesting to note that the broadening of the central line up to 3 kHz is still completely homogeneous (Fig. 4). Obviously the ordering of 5CB in the surface layer—even if partly separated from the BL038—increases in the vicinity of the intrinsic 5CB transition temperature and induces a larger transverse spin-relaxation rate.

A point that certainly deserves attention is the surprisingly large amount of liquid crystal that is still in the isotropic phase at room temperature and yields the central line in the NMR spectrum (see Fig. 5). It shows that a considerable number of droplets is not effective in producing the contrast between the on and off state in the switchable Bragg grating. Another reason for the appearance of the central line could be that in very small pores the surface dictates a lower degree of orientational order than expected in the nematic phase. In such pores the fast molecular translational diffusion among sites with varying director orientation could still average out the quadrupole interaction of deuterons and produce a central line in the spectrum albeit the liquid crystal is in the nematic phase. But the question remains whether such droplets are capable of being oriented with the external electric field in the switching procedure.

In order to check the macroscopic anisotropy of the HPDLC grating, the low-temperature NMR spectrum was recorded for different orientations of the stacked sample in the magnetic field. Apart from a small difference in the intensity of peaks in the powder-pattern-like spectrum, no effect of the rotation was observed. The anisotropy of the droplets in the sample under study is obviously very small.

IV. CONCLUSIONS

In this paper we presented a deuteron NMR and dynamic light scattering study of the BL038-5CB liquid-crystal mixture in a standard HPDLC material with an alternating structure of LC-rich and polymer layers. We found that the behavior of the BL038-5CB mixture in the HPDLC differs drastically from the bulk. First, the nematic temperature range of the LC mixture is shifted towards lower temperature almost by 40 K and the formation of the nematic phase in the sample is gradual. Most of the droplets are too large to experience a continuous evolution of nematic order individually [16,22], but the onset of the nematic phase in the whole sample is gradual, as different droplets turn into the nematic phase at different temperatures. One of the reasons for such behavior may be the distribution of droplet sizes between ~ 50 nm and ~ 300 nm, but the overwhelming factor is the different amount of non-liquid-crystalline ingredients in different droplets. Additionally, the concentration of 5CB is probably not exactly equal in all droplets giving another reason for a spread in transition temperatures; droplets with higher 5CB content would turn into the nematic phase at lower temperature.

The huge transverse deuteron spin-relaxation rate in the high-temperature phase of HPDLC unveils a strong effect of polymer and/or surfactant on the liquid-crystal molecules at the surface. The surface order parameter is found larger than in other confining systems (PDLC, CPG). Additionally, the translational mobility of molecules in the surface layer is hindered and slower for at least two orders of magnitude compared to the bulk. Albeit we could estimate only the lower limit of the surface order parameter ($S_0 \gtrsim 0.2$ for droplets of radius ~ 50 nm), it is reasonable to assume that its actual value is close to this limit. The orientational order in smaller droplets might be diminished and probably surface dictated even in the nematic phase. The strong influence of the surface on the orientational order of liquid crystal in the HPDLC is thus demonstrated by the orienting effect in the isotropic phase and probably by a disorienting effect in the nematic phase. The strong influence of the surface might be due to the surfactant added to the polymer, but its capability seems to concern only the static orientational effect, whereas it reduces the switching voltage required to reorient the liquid crystal along the electric field [21].

The observed reduction of the nematic-isotropic transition temperature brings the isotropic phase much closer to the operative temperature range of the HPDLC material than expected. Moreover, a considerable amount of liquid crystal is found in a quasi-isotropic phase even at room temperature. Such diminishing of the overall orientational order in the sample could unfavorably influence the switching efficiency of HPDLC gratings. The drawbacks of the HPDLC material as pointed out in this study might be exaggerated in our sample, as the deuterated 5CB had been added to the liquid-crystal mixture, which is standardly used in the production of switchable gratings. On the other hand, 5CB is a constituent of many commercial mixtures as well. It would be reasonable to take into account this observation in planning the HPDLC chemical constituents. One of the purposes of our study was also to check the suitability of NMR as a supporting method in the optimization of switchable gratings in the future. Our results show that deuteron NMR combined with optical experiments is a well-suited method for this purpose and could successfully be exploited in future experiments to improve the switching performance of different HPDLC materials.

ACKNOWLEDGMENTS

The authors would like to thank Professor Martin Čopič for helpful discussions. The financial support of the Slovenian Office of Science (Grant Nos. PO-0524-0106, PO-0523-0106, and PO-0528-0106) and of the USA-Slovenia Joint Project (NSF Grant No. 9815313) is gratefully acknowledged. A.K.F. and M.J.E. also acknowledge the support from the NASA Graduate Student Research Program.

[1] R.L. Sutherland, V.P. Tondiglia, L.V. Natarajan, T.J. Bunning, and W.W. Adams, Appl. Phys. Lett. **64**, 1074 (1994).

[2] T.J. Bunning, L.V. Natarajan, V.P. Tondiglia, and R.L. Sutherland, Annu. Rev. Mater. Sci. **30**, 83 (2000).

[3] C.C. Bowley, G.P. Crawford, and H. Yuan, Appl. Phys. Lett. **74**, 3096 (1999).

[4] C.C. Bowley, A.K. Fontecchio, G.P. Crawford, J.J. Lin, L. Li, and S. Faris, Appl. Phys. Lett. **76**, 523 (2000).

[5] A.K. Fontecchio, C.C. Bowley, S.M. Chmura, Le Li, S. Faris, and G.P. Crawford, J. Opt. Technol. **68**, 652 (2001).

[6] L.H. Domash, P. Haugsjaa, and B.E. Little, Proc. SPIE **3234**, 146 (1998).

[7] C.C. Bowley and G.P. Crawford, Appl. Phys. Lett. **76**, 2235 (2000).

[8] G. Cipparrone, A. Mazzulla, and G. Russo, J. Opt. Soc. Am. B **18**, 1821 (2001).

[9] R.L. Sutherland, V.P. Tondiglia, L.V. Natarajan, and T.J. Bunning, Appl. Phys. Lett. **79**, 1420 (2001).

[10] M. Jazbinsek, I. Drevensek Olenik, M. Zgonik, A.K. Fontecchio, and G.P. Crawford, J. Appl. Phys. **90**, 3831 (2001).

[11] G.S. Iannacchione, D. Finotello, L.V. Natarajan, R.L. Sutherland, V.P. Tondiglia, T.J. Bunning, and W.W. Adams, Europhys. Lett. **36**, 425 (1996).

[12] J.W. Doane, in *Magnetic Resonance of Phase Transitions*, edited by F. J. Owens *et al.* (Academic, New York, 1979), Chap. 4.

[13] R.Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals* (Springer, Berlin, 1994).

[14] G.P. Crawford, M. Vilfan, J.W. Doane, and I. Vilfan, Phys. Rev. A **43**, 835 (1991).

[15] A. Golemme, S. Zumer, D.W. Allender, and J.W. Doane, Phys. Rev. Lett. **61**, 2937 (1988).

[16] M. Vilfan, T. Apih, A. Gregorovic, B. Zalar, G. Lahajnar, S. Zumer, G. Hinze, R. Boehmer, and G. Althoff, Magn. Reson. Imaging **19**, 433 (2001).

[17] C.C. Bowley, A.K. Fontecchio, G.P. Crawford, and H. Yuan, Society for Information Display Dig. Tech. Pap. **30**, 958 (1999).

[18] R. Kimmich, *NMR Tomography, Diffusometry, Relaxometry* (Springer, Berlin, 1997).

[19] M. Vilfan, N. Vrbancic-Kopac, P. Ziherl, and G.P. Crawford, Appl. Magn. Reson. **17**, 329 (1999).

[20] I. Vilfan, M. Vilfan, and S. Zumer, Phys. Rev. A **40**, 4724 (1989).

[21] S.S. Patnaik and R. Pachter, Polymer **40**, 6507 (1999).

[22] G.S. Iannacchione, G.P. Crawford, S. Zumer, J.W. Doane, and D. Finotello, Phys. Rev. Lett. **71**, 2595 (1993).

[23] G.S. Iannacchione, G.P. Crawford, S. Qian, J.W. Doane, D. Finotello, and S. Zumer, Phys. Rev. E **53**, 2402 (1996).

[24] M. Vilfan and N. Vrbancic-Kopac, in *Liquid Crystals in Complex Geometries*, edited by G.P. Crawford and S. Zumer (Taylor & Francis, London, 1996), Chap. 7.

[25] M. Vilfan, N. Vrbancic-Kopac, B. Zalar, S. Zumer, and G.P. Crawford, Phys. Rev. E **59**, R4754 (1999).

[26] P.G. de Gennes, *Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[27] S. Kralj, M. Vilfan, and S. Zumer, Liq. Cryst. **5**, 1489 (1989).

[28] C. Chiccoli, P. Pasini, G. Skacej, C. Zannoni, and S. Zumer, Phys. Rev. E **60**, 4219 (1999).

[29] D.E. Woessner, J. Chem. Phys. **36**, 1 (1962).

[30] N. Vrbancic-Kopac, M. Vilfan, R. Blinc, J. Dolinsek, G.P. Crawford, and J.W. Doane, J. Chem. Phys. **98**, 3540 (1993).

[31] R.Y. Dong and G.M. Richards, Chem. Phys. Lett. **200**, 541 (1992).

[32] R.Y. Dong, Phys. Rev. A **43**, 4310 (1991).

[33] H.J. Coles and M.S. Bancroft, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **237**, 97 (1993).

[34] M. Vilfan, I. Drevensek Olenik, A. Mertelj, and M. Copic, Phys. Rev. E **63**, 061709 (2001).

[35] F. Grinberg and R. Kimmich, Magn. Reson. Imaging **19**, 401 (2001).

[36] S. Zumer, S. Kralj, and M. Vilfan, J. Chem. Phys. **91**, 6411 (1989).

[37] E.E. Burnell, M.E. Clark, J.A.M. Hinke, and N.R. Chapman, Biophys. J. **33**, 1 (1981).

[38] R. Kimmich, T. Gneiting, K. Kotitschke, and G. Schnur, Biophys. J. **58**, 1183 (1990).

[39] E. Anoardo, F. Grinberg, M. Vilfan, and R. Kimmich (unpublished).

[40] A.K. Fontecchio and G.P. Crawford, presented at European Conference on Liquid Crystals, Halle, Germany, 2001 (unpublished).

[41] G.P. Crawford, R. Ondris-Crawford, S. Zumer, and J.W. Doane, Phys. Rev. Lett. **70**, 1838 (1993).

[42] G.P. Crawford, R. Ondris-Crawford, S. Zumer, and J.W. Doane, Phys. Rev. E **53**, 3647 (1996).