Deuteron NMR Relaxometry
Applied to Confined Liquid Crystals

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Abstract. We discuss the capability of deuteron nuclear magnetic resonance (NMR) spectroscopy and relaxometry to reveal molecular ordering and dynamics in confined liquid crystals. The attention is focused on the high-temperature phase above the nematic-isotropic transition, which is – in the absence of the long-range orientational order – very suitable for the study of surface interactions. Deuteron NMR spectra and relaxation rates are presented for two representatives of confined liquid-crystal systems: 8CB in cylindrical cavities of Anopore membranes and 5CB with an embedded polymer network. A substantial increase in the transverse spin relaxation rate, stimulated by the surface-induced order in enclosures, has been observed. In cylindrical cavities, it exhibits a strong temperature dependence on approaching the phase transition, whereas in the polymer network dispersion it is temperature-independent. The increase of T_2^{-1} provides information on the effect of spatial constraints on molecular mobility and on the surface orientational order parameter. Using deuteron relaxometry, one can measure the degree of orientational order in the isotropic phase not only in cylindrical but also in spherical cavities and enclosures of irregular shape, where the standard approach based on quadrupolar splitting of the NMR spectrum fails.

1 Introduction

Deuterium nuclei have been used frequently as a nuclear magnetic resonance (NMR) probe in studies of molecular structure and dynamics in solids [1], liquids [2, 3], and various mesophases [3, 4]. In liquid crystals, in particular, deuteron NMR is one of the most accurate methods of determination of the orientational order parameter. It has been applied to calamitic as well as discotic liquid crystals [4–7]. In contrast to optical methods, which yield the order parameter of a molecule as one entity, deuteron NMR spectra provide order parameters selectively for different atomic groups. In addition, deuteron NMR relaxometry gives an insight into the mobility of liquid-crystal molecules in a broad frequency range from about 10^5 to 10^{11} Hz. With this method, correlation times associated with

fast molecular reorientations and conformational changes were determined [8–12] as well as collective orientational order fluctuations, specific for the liquid-crystalline state [13].

In 1986 Doane et al. [14] discovered polymer-dispersed liquid crystals (PDLCs). These dispersions, consisting of spherical nematic droplets within a solid polymer, are nowadays widely used in the optical shutter technology. The size of droplets ranges from about 100 nm to 10 μm, depending on the concentration of the liquid crystal. In the years to come, liquid crystals were confined into other types of enclosures: cylindrical cavities in organic and inorganic membranes [15, 16], porous glasses [17], aerogels [18], soft gels [18, 19], and low-concentration polymer networks [18]. A common feature of all microconfined liquid crystals is a large surface-to-volume ratio. This produces a striking effect of surface interactions and geometrical constraints on the liquid-crystalline ordering. The nematic director – the local average molecular orientation – assumes a number of different configurations within the enclosures. They depend on the surface interaction, on the shape and size of the cavities, on elastic properties of the liquid crystal, and on the temperature. Deuteron NMR discriminates unambiguously between various director configurations and is sensitive to the structural transitions [15, 20, 21]. It is also used to obtain information on the interaction of liquid crystal molecules with the substrate [22], which is very important for the technology of electrooptic devices.

In this paper we present the deuteron NMR spectra, spin-lattice relaxation times (T_1), and transverse relaxation times (T_2) for two representative confined liquid-crystal systems. Throughout the paper, the results are compared to the behaviour of the experimental observables in bulk and in other liquid crystal dispersions. Our attention is focused to the isotropic phase of mesogenic compounds, which is more convenient for the study of surface interactions than the nematic phase. In fact, the high-temperature phase is not truly isotropic, as the internal surfaces impose a weak orientational order to liquid-crystal molecules. Nevertheless, the term "isotropic" is usually retained as long as the nematic-isotropic transition is discontinuous and the surface-induced order much smaller than in the nematic phase. It should be stressed that the surface-induced order is limited to a thin boundary layer at the liquid crystal-solid interface. Therefore any effect of the confinement observed in the isotropic phase is directly related to the interactions of liquid-crystal molecules with the solid boundary.

In Sect. 2 we address two types of confined liquid crystals used in the present study and the experimental techniques applied. Section 3 includes a discussion on deuteron spectra in the isotropic phase. We show that the degree of surface-induced orientational order can be estimated from the spectra corresponding to liquid crystals confined to cylindrical cavities but not for other types of dispersions. Section 4 is devoted to deuteron spin-lattice relaxation measurements. Section 5 contains transverse spin relaxation data, which have been recorded in a wide temperature range above the nematic-isotropic transition. Relaxation mechanisms, characteristic for confined liquid crystals, are discussed and used for the interpretation of the experimental data. The last section summarizes the infor-

mation concerning molecular order and dynamics obtained by deuteron NMR relaxometry. In particular, we show that NMR relaxometry can yield information on the surface-induced order even in systems where the standard NMR spectroscopy fails.

2 Experimental

The present study includes: (i) liquid crystal 8CB (4′-n-octyl-4-cyanobiphenyl), confined to cylindrical cavities of Anopore membranes, and (ii) liquid crystal 5CB (4′-n-pentyl-4-cyanobiphenyl) with an embedded polymer network. Both liquid crystals are selectively deuterated in the first position of the hydrocarbon chain.

i. Anopore membranes are commercially available inorganic filters, fabricated by anodic oxidation of aluminum that results in a porous structure with cylindrical cavities. The pores are 200 nm in diameter and oriented perpendicular to the surface of 60 μm thick membranes. In preparing NMR samples, Anopore membranes are permeated with the liquid crystal, heated, pressed, and stacked one upon the other to obtain a large enough sample suitable for NMR measurements. Within an Anopore cavity, the liquid crystal is oriented parallel to the cylinder axis if no special treatment has been applied.

ii. The sample of liquid crystal with an embedded polymer network was prepared by dissolving 6 wt.% of the monomeric 4,4′-bis-acryloybiphenyl (BAB) and photoinitiator in the liquid crystal 5CB-αd_2. By exposing the sample to the ultraviolet (UV) irradiation, the monomer molecules of BAB are linked together into tiny fibers. The fibers and bundles of the polymer grow in the nematic environment fairly parallel to the director but interconnect mutually to form a strong network. The structure of the network is retained even upon heating the liquid crystal into the isotropic phase. This was proved by optical birefringence measurements [18].

The confinement of liquid crystals to Anopore cavities and the constraints imposed by polymer networks do not affect the transition from the nematic into the isotropic phase considerably. The phase transition in the two systems described above is discontinuous and takes place at nearly the same temperatures (within 1 K) as in bulk samples, i.e., about 40°C for 8CB and about 34°C for 5CB. A continuous evolution of nematic ordering instead of the discontinuous phase transition was observed in cavities of much smaller sizes [17, 20].

The measurements of the deuteron NMR spectra, spin-lattice relaxation times T_1, and transverse relaxation times T_2 were performed at Larmor frequency 13.8 MHz (and partially at 58.3 MHz) as a function of temperature on cooling the samples in the isotropic phase. The spin-lattice relaxation time T_1 was measured by the π–τ–$(\pi/2)_x$–δ–$(\pi/2)_y$–δ–$(acquisition)$ pulse sequence with an alternation of phases in subsequent cycles. The spectra and the transverse spin-relaxation time T_2 were obtained from the ω_2 and ω_1 domains of two-dimensional spectra. The basic pulse sequence used was that of the quadrupolar echo, i.e., $(\pi/2)_x$–τ–$(\pi/2)_y$–τ–$(acquisition)$. It was improved by an eight-step phase cycling scheme

to eliminate the contributions of free induction decays following the first and the second pulse. The temporal evolution of the echo turned out to be mono-exponential over more than one decade. The monoexponential behaviour indicates that the translational diffusion of molecules is fast enough to yield a single relaxation time T_1 or T_2 although the relaxation process might not be equally fast in all parts of the cavity. The experimental error in the evaluation of T_1 and T_2 data was reduced to less than 10% by averaging typically a few thousand times.

3 Spectra of Confined Liquid Crystals above T_{NI}

The deuteron NMR spectrum of a selectively deuterated compound in the bulk nematic phase consists of two sharp lines as a result of the coupling of the deuteron quadrupole moment with the electric field gradient (EFG) tensor at the site of the nucleus. The static quadrupole coupling tensor is partly diminished by fast molecular conformational changes and reorientations. If the liquid-crystalline phase is microscopically uniaxial, the splitting $\Delta \nu_Q$ of the two lines in the spectrum is given to a good approximation by [5]

$$\Delta \nu_Q = \frac{3}{2} \frac{e^2 qQ}{h} \frac{1}{2} \overline{(3\cos^2\gamma - 1)} \frac{1}{2}(3\cos^2\Theta_B - 1) S . \qquad (1)$$

Here $e^2 qQ/h$ is the static deuteron quadrupole coupling constant, EFG tensor is considered to be axially symmetric, γ stands for the polar angle of the EFG tensor symmetry axis with respect to the long molecular axis, and the bar denotes an average over conformational states of the molecule. The diminution of the splitting caused by the fluctuations of the long molecular axis around the director is described by the orientational order parameter S defined as $(1/2)\langle 3\cos^2\vartheta - 1 \rangle$, where ϑ is the instantaneous deviation of long molecular axis from the local director, and $\langle ... \rangle$ is the ensemble average. An additional diminution of the quadrupolar splitting $\Delta \nu_Q$ due to collective order director fluctuations is usually smaller than a few percent [23] and has been neglected in evaluating Eq. (1). Finally, the quadrupolar splitting also depends on the orientation of the liquid crystal in the magnetic field: Θ_B is the angle between the director of the nematic phase and the magnetic field. An important point to be recognized in Eq. (1) is the fact that the splitting $\Delta \nu_Q$ of the deuteron spectrum is directly proportional to the degree of orientational order S and depends on the orientation of the director in the magnetic field.

If a bulk nematic sample is heated above the clearing point T_{NI}, fast and isotropic molecular reorientations average out the quadrupolar interaction of the deuterons. The splitting of the deuteron NMR spectrum disappears, which reflects the fact that the order parameter vanishes in the isotropic phase (Fig. 1a). However, on approaching T_{NI}, the linewidth slightly increases due to the growing short-range anisotropy and thermal fluctuations of the orientational order. The
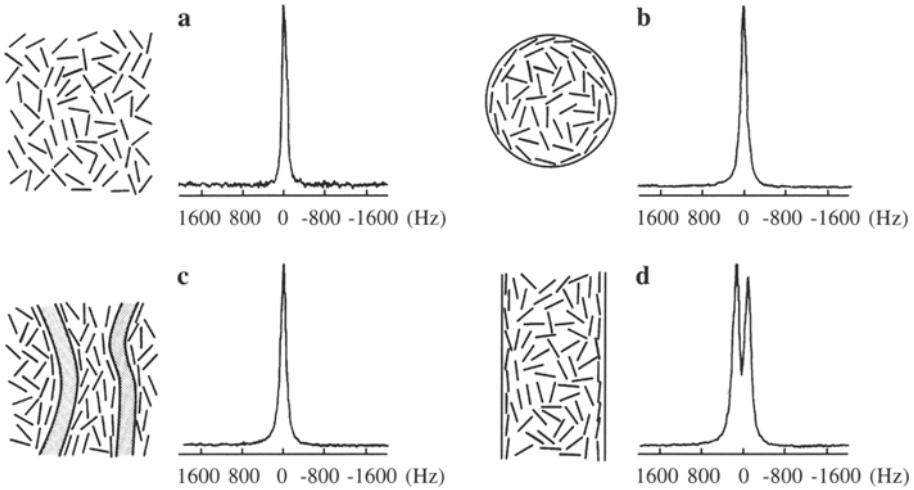
Fig. 1. Deuteron NMR spectrum in the isotropic phase at $T = T_{NI} + 4$ K: **a** bulk 5CB sample, **b** 5CB with embedded polymer network, **c** 5CB in a PDLC, and **d** 8CB in cylindrical cavities.

size of clusters with nematic ordering is roughly given by the nematic correlation length ξ defined by [24]:

$$\xi = \xi_0 \sqrt{\frac{T^*}{T - T^*}} , \qquad (2)$$

where ξ_0 is of the order of one molecular length and T^* is the bulk supercooling limit (usually about 1 K below T_{NI}).

In a confined liquid crystal, the onset of order above T_{NI} is not induced only by thermal fluctuations but also – and to a larger extent – by the aligning effect of the internal surfaces of cavities or networks. According to the theory of Sheng [25], the surface-induced orientational order assumes the largest value S_0 at the boundary and decays exponentially with increasing distance z from the surface

$$S(z) = S_0 \exp(-z/\xi). \qquad (3)$$

In more realistic models, the finite size of molecules should also be taken into account. This can lead to spatial profiles of the order parameter such that S is constant and equal to S_0 over a distance l_0 from the boundary, whereas for $z > l_0$ S decreases exponentially according to Eq. (3).

The effect of the surface-induced order can clearly be seen in the spectra of a liquid crystal confined into cylindrical cavities. In Fig. 1d a quadrupolar splitting is quite distinct although it is much smaller than in the nematic phase. The absence of a central line, which would originate from the isotropic part far away from the walls, is a signature of a fast exchange of molecules between the or-
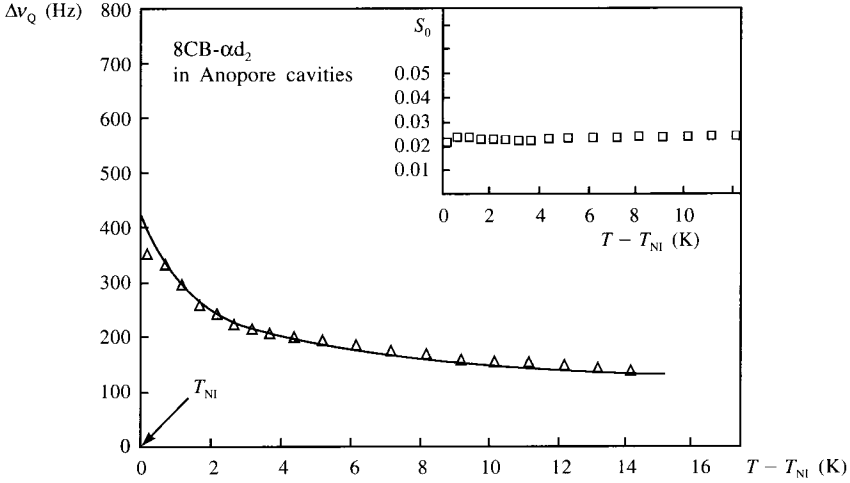
Fig. 2. Deuteron line splitting in 8CB in nontreated cylindrical cavities vs. temperature: experimental data and fit on the basis of Eq. (7). Inset: temperature dependence of the surface order parameter.

dered and disordered regions. The exchange is faster than the time of the NMR measurement. The splitting is therefore proportional to the average order parameter in the cavity $\langle S \rangle$:

$$\Delta v_Q = \frac{3}{2} \frac{e^2 qQ}{h} \frac{1}{2} \overline{(3 \cos^2 \gamma - 1)} \frac{1}{2} \langle 3 \cos^2 \Theta_B - 1 \rangle \langle S \rangle , \qquad (4)$$

or

$$\Delta v_Q = \Delta v_0 \frac{1}{2} \langle 3 \cos^2 \Theta_B - 1 \rangle \langle S \rangle , \qquad (5)$$

where Δv_0 corresponds to the splitting of the perfectly ordered nematic phase ($S = 1$, $\Theta_B = 0$). For cylinders parallel to the magnetic field and the director in the surface layer parallel to the cylinder axis, the term $(1/2)\langle 3 \cos^2 \Theta_B - 1 \rangle \approx 1$. Since in Anopore cavities the approximate thickness of the ordered layer $\xi + l_0$ is much smaller than the radius of the cavity R, the average order parameter $\langle S \rangle$ is to a good approximation given by [16]:

$$\langle S \rangle \approx \frac{2 l_0 S_0}{R} + \frac{2 \xi S_0}{R} , \qquad (6)$$

which reduces the quadrupolar splitting to

$$\Delta v_Q = \Delta v_0 \frac{2 S_0}{R} \left(l_0 + \xi_0 \sqrt{\frac{T^*}{T - T^*}} \right) . \qquad (7)$$

The temperature dependence of Δv_Q for 8CB-αd$_2$ in nontreated cylindrical cavities of Anopore membranes is presented in Fig. 2. A good fit of Eq. (7) to the experimental data (solid line in Fig. 2) is obtained if the surface order parameter S_0 is assumed to be temperature-independent. The values of the two fitting parameters are $S_0 = 0.024 \pm 0.005$ (Fig. 2, inset) and $l_0 = 0.8$ nm, whereas $\Delta v_0 = 92$ kHz, $\xi_0 \approx 0.5$ nm, and $T^* \approx T_{NI} - 1$ K [26]. It turns out that the contribution of the first term in Eq. (7) is small (only about 35 Hz) compared to the second term, which arises from the ordered layer of thickness ξ and is responsible for the pretransitional increase of Δv_Q.

A similar result – a small and temperature-independent surface order parameter S_0 – was obtained by Crawford et al. [16] for the liquid crystal 5CB-βd$_2$ in the same type of cavities. A temperature-independent surface order parameter is an indication that S_0 is determined primarily by the short-range interactions between liquid-crystalline molecules and solid surface rather than by the interactions between liquid-crystalline molecules themselves.

The study of surface-induced order in liquid crystals with embedded polymer networks, in PDLC materials, and in liquid crystals within porous glasses and aerogels is somewhat more complicated. The deuteron NMR spectra of these systems consists of a single line which is broadened but not split (Fig. 1b and c). The average value of the factor $(1/2)\langle 3\cos^2\Theta_B - 1\rangle$ is considerably diminished by molecular diffusion along the curved internal surface and would be zero for a completely isotropic distribution of Θ_B in small cavities. Though a broadening of the linewidth is observed in a wide temperature range (Fig. 3), one cannot tell from the spectra whether the broadening is homogeneous and produced by the fluctuating part of the quadrupolar interaction or whether it is due to a distribution of the residual static quadrupolar splittings. In such confined systems the measurements of relaxation rates are of great importance. We deal with them in the following.
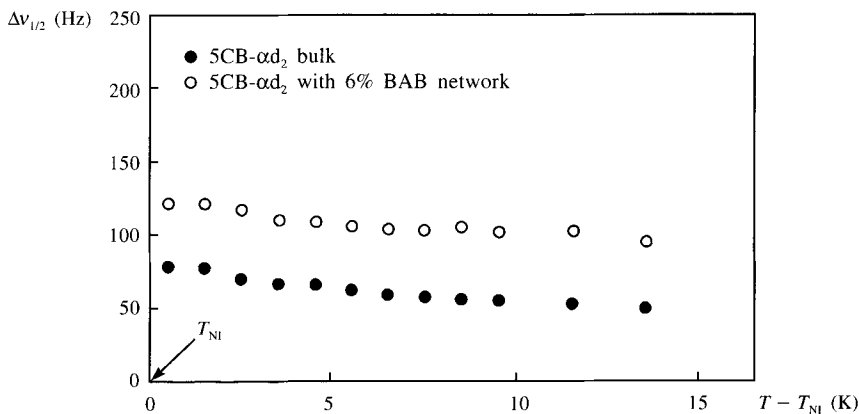

Fig. 3. Broadening of the deuteron NMR linewidth in bulk 5CB and in 5CB with embedded polymer network as a function of temperature.

4 Deuteron Spin-Lattice Relaxation

First of all, deuteron spin relaxation measurements provide an insight into the molecular dynamics in confined liquid crystals. The temporal modulation of the quadrupolar interaction, which gives rise to the spin relaxation processes, is caused by the motion of spin-bearing molecules. The relaxation efficiency of a specific dynamic process depends on its intensity and frequency distribution, which both appear in the spectral densities of the autocorrelation functions of the quadrupolar interaction. For deuterons (and other nuclei with spin 1), the spin-lattice relaxation rate T_1^{-1} for the Zeeman order and the transverse spin relaxation rate T_2^{-1} are given by the well-known relations [27]

$$T_1^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2 [J_1(\omega_L) + 4J_2(2\omega_L)] \tag{8}$$

and

$$T_2^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left[\frac{3}{2}J_0(0) + \frac{5}{2}J_1(\omega_L) + J_2(2\omega_L)\right], \tag{9}$$

where J_k denotes the spectral densities of zero, first, and second order. It should be mentioned that T_2^{-1}, given by Eq. (9), corresponds to the quantity measured by the nonselective spin-echo experiment [3, 4].

According to Eq. (8), the spin-lattice relaxation rate T_1^{-1} is determined by the spectral densities at Larmor and double Larmor circular frequencies and is therefore sensitive particularly to motions with frequencies in the high megahertz regime. On the other hand, T_2^{-1} also contains the term $J_0(0)$ at zero Larmor frequency. This term implies that a substantial contribution to T_2^{-1} might arise from motions at a frequency smaller than the Larmor frequency but larger than the NMR linewidth in the absence of molecular motions. In liquid crystals this means that T_2^{-1} probes the dynamics in the kilohertz range. The same frequency window can be studied by T_1^{-1} if the NMR field-cycling technique is applied [13].

Deuteron spin-lattice relaxation in the bulk isotropic phase is caused by local molecular reorientations which have at least one correlation time in the nanosecond range. Its temperature dependence is well described by a thermally activated process of Arrhenius type. On going to the nematic phase, T_1^{-1} decreases abruptly as orientational ordering takes place and imposes limitations to molecular rotational mobility. In the nematic phase, T_1^{-1} depends on the orientation of the director in the magnetic field: it is smallest for the director parallel to the magnetic field and increases as the director departs from this direction.

In Fig. 4, the temperature dependences of T_1^{-1} in the isotropic and nematic phases of bulk 5CB-αd_2 and of the same compound with an embedded polymer network are shown. The data were obtained at $\nu_L = 13.8$ MHz on cooling. The measurements clearly show, within the limitations imposed by the experimental error, that in the isotropic phase there is no difference in T_1^{-1} between the bulk and the constrained liquid crystal. The lack of impact of confinement upon the
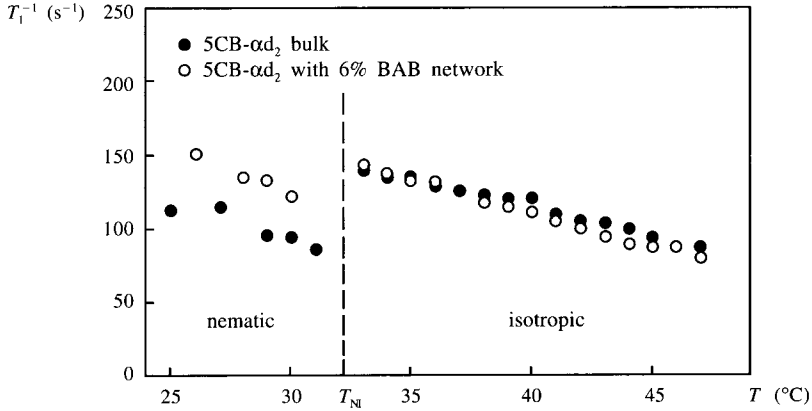
Fig. 4. Temperature dependence of the deuteron spin-lattice relaxation rate in bulk 5CB and in 5CB with embedded polymer network at Larmor frequency 13.8 MHz.

spin-lattice relaxation rate was also found for 8CB-αd_2 in cylindrical cavities [28, 29]. The result is not surprising since the same phenomenon has been observed earlier for 5CB-βd_2 with a less dense network [28] and in a PDLC material [26]. The conclusion drawn from it, however, is far from being trivial. The experiments cited as well as the present study clearly point out that the correlation times of local molecular reorientations are not substantially modified by the spatial constraints.

On the other hand, the spin-lattice relaxation rate of a confined liquid crystal in the nematic phase is characterized by a T_1^{-1} larger than its bulk counterpart. Such an increase might be expected since the network spoils the perfect orientation of liquid crystal along the magnetic field. This creates an ensemble of domains with different director orientation, which gives rise to an increase of T_1^{-1}. The increase in T_1^{-1} confirms indirectly that the polymer network is strong enough to overwhelm the orienting effect of the magnetic field.

5 Deuteron Transverse Relaxation above T_{NI}

In the bulk isotropic phase, the transverse relaxation rate T_2^{-1} of deuterons is equal to the spin-lattice relaxation rate T_1^{-1} at temperatures far above the transition temperature T_{NI}, as expected for a random isotropic motion of molecules. With decreasing temperature, T_2^{-1} increases faster than T_1^{-1} due to the growing short-range anisotropy within the isotropic phase. A pretransitional increase of T_2^{-1} with a characteristic $\sim(T - T^*)^{-1}$ temperature dependence was observed in a narrow interval of a few kelvin above T_{NI} [30]. One might expect that the surface-induced order in confined liquid crystals will enhance this effect. In fact, a striking difference between the T_2^{-1} of a confined liquid crystal and that of the bulk is observed at temperatures as high as 15 K above T_{NI}.

In Figs. 5 and 6, experimental T_2^{-1} data for 8CB-αd$_2$ in nontreated cylindri-
cal cavities of Anopore membranes and for 5CB-αd$_2$ with BAB network are
shown. The difference ΔT_2^{-1} between the relaxation rates T_2^{-1} of confined and
of the bulk liquid crystal is plotted with dashed lines. Its existence itself clearly
demonstrates the appearance of an additional relaxation mechanism in confined
liquid crystals which is not present in bulk systems. Obviously, the residual
quadrupolar interaction – left after the averaging by fast local molecular reori-
entations – is additionally modulated on a much slower timescale. The frequency
of this modulation falls into the kilohertz range. The origin of the modulation,
however, seems to be different for the two systems studied. In cylindrical cavi-
ties ΔT_2^{-1} exhibits a strong pretransitional increase, but in the liquid-crystal dis-
persion with a polymer network it is almost temperature independent.

Cylindrical cavities of radius 100 nm are large enough to be characterized
by a bulk-like isotropic region in the central part and a layer with surface-in-
duced order next to the walls. As seen from the T_1^{-1} data, the local molecular
reorientations are approximately equally fast in both regions. However, the re-
sidual quadrupolar interaction is zero in the isotropic region but different from
zero at the wall. It also varies along the curved or rough wall as the orientation
of the director changes in the magnetic field. The temporal modulation of the
residual quadrupolar interaction and consequently the increase in ΔT_2^{-1} might
occur as a result of two dynamic processes: order fluctuations at a given posi-
tion r in the cavity, or translational displacements of the spin-bearing molecules
through the regions with inhomogeneous degree of order or director orientation.
As a first approximation we consider both processes as statistically independent.

Order fluctuations in confined liquid crystals above T_{NI} have been studied
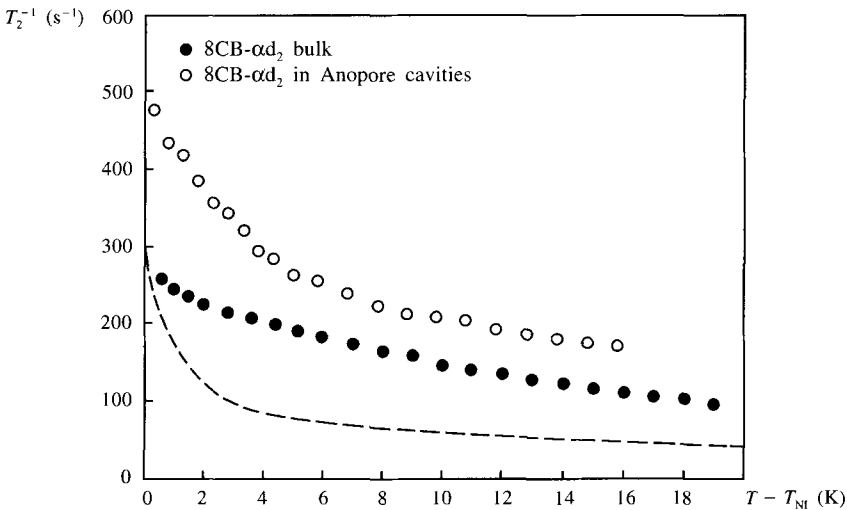by Ziherl and Žumer [31]. They showed that if the degree of the surface orien-

Fig. 5. Deuteron transverse spin relaxation rate for 8CB in cylindrical cavities, for bulk 8CB and
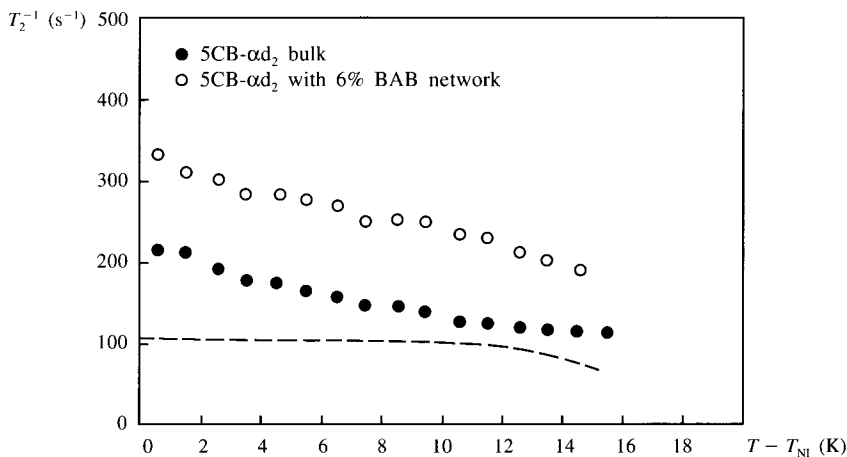their difference (dashed line) vs. temperature.

Fig. 6. Deuteron transverse spin relaxation rate for 5CB with embedded polymer network, for bulk 5CB and their difference (dashed line) vs. temperature.

tational order parameter is nematic-like, i.e., ≈ 0.3, the spectrum of fluctuations is characterized by the appearance of two slow modes which are not present in bulk samples. One of them corresponds to fluctuations of the thickness of the boundary layer and the other to nematic director fluctuations within this region. The characteristic decay time of fluctuations in the thickness of the ordered layer diverges as $(T - T_{NI})^{-1}$ and represents the soft mode responsible for the onset of the nematic phase. The decay time of director fluctuations also diverges but the divergence is not that pronounced. However, the two modes are relevant only in a relatively narrow temperature range up to about 1 K above the transition temperature (Fig. 7). At temperatures higher than $T_{NI} + 1$ K the spectrum of the fluctuations in a confined system does not depart significantly from its bulk counterpart. The transverse spin relaxation rate resulting from order fluctuations is important in a temperature interval even narrower than 1 K, and is large close to the transition but it merges into the bulk relaxation rate at about 0.3 K above T_{NI}. This is illustrated in Fig. 8, where one can see that the relaxation rate T_2^{-1} induced by order fluctuations exceeds that of the bulk liquid crystal (about 100 s^{-1} for 8CB) only up to $T_{NI} + 0.3$ K. In systems with weaker interaction between the wall and the liquid crystal, which results in $S_0 < 0.3$, the pretransitional slowdown of the excitations is less pronounced, and their contribution to the relaxation rate is smaller. This might be the reason that no critical divergence of ΔT_2^{-1} is observed in Fig. 5. Order fluctuations obviously do not contribute to the deuteron relaxation of isotropic 8CB-αd$_2$ in cylindrical cavities. This leads to the conclusion that molecular translational displacements should be responsible for the enhancement in T_2^{-1}.

Molecular translational displacements cause a modulation of the residual deuteron quadrupolar interaction which is proportional to the local order parameter $S(r)$ at the site where the deuteron-bearing molecule momentarily resides.
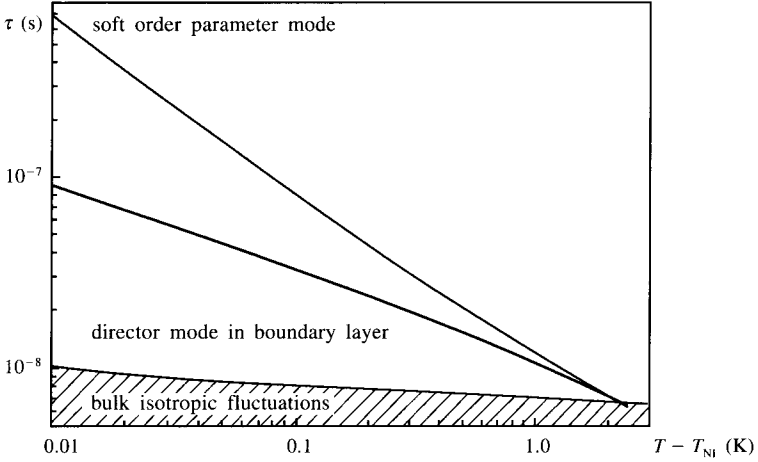
Fig. 7. Typical relaxation times of wetting-specific collective modes in confined nematic liquid crystals as a function of temperature. The material parameters used in the calculation are those of 5CB.

The residual interaction is zero when the molecule is in the central part of the cavity, increases exponentially as the molecule diffuses closer to the wall, and assumes the largest value when the observed molecule enters the first molecular layer at the boundary. The contribution of molecular translational displacements to the deuteron T_2^{-1} has been calculated recently for liquid-crystal molecules confined to spherical cavities [26]. A simple model for molecular motion – ordinary isotropic diffusion restricted to a spherical volume with reflecting bound-
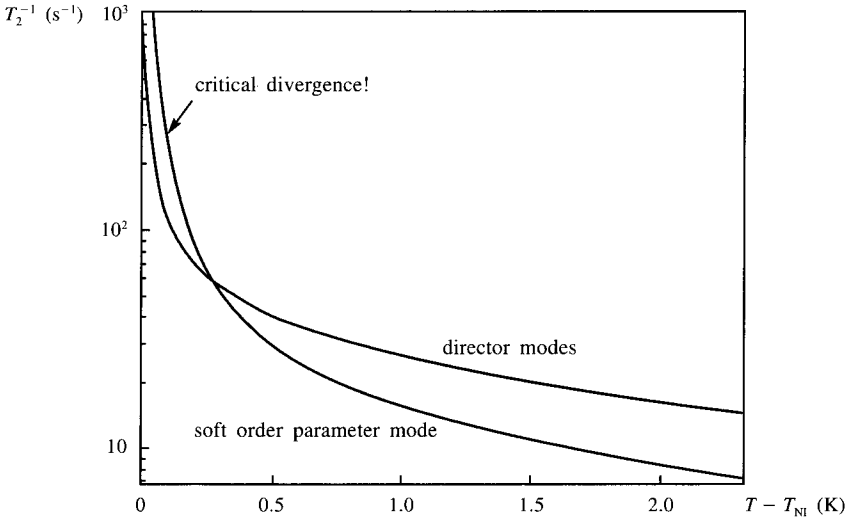

Fig. 8. Calculated temperature dependence of transverse spin relaxation rates due to wetting-specific collective fluctuations within the boundary layer. The material parameters used correspond to 5CB.

aries – was proposed. It was shown that the resulting relaxation rate caused by this mechanism is given by a weighted sum of correlation times corresponding to discrete solutions of the diffusion equation in confined geometry. Though the complete expression must be calculated numerically and is different for each confining geometry, the temperature dependence of ΔT_2^{-1} is to a good approximation given by

$$\Delta T_2^{-1} \approx A\xi^2 S_0^2 + CS_0^2, \tag{10}$$

where the constants A and C include the quadrupole coupling constant, the radius of the cavity, and the translational diffusion coefficient. The first term in Eq. (10) arises from the diffusion of molecules through the region of exponentially decaying order parameter. It is therefore always temperature-dependent and roughly proportional to $(T - T^*)^{-1}$ provided that the surface order parameter S_0 does not depend on the temperature. In such a case, the second term, which originates from the molecular displacements into and from the layer of thickness l_0 at the boundary, negligibly varies with temperature. However, it may be larger than the prediction of the uniform diffusion model since there is a slowing down of molecular translational motion at the boundary [32, 33]. Both terms in Eq. (10) are proportional to S_0^2 as the relaxation rate depends on the square of the residual quadrupolar interaction.

The above theory was used to determine the surface order parameter of 5CB molecules in a PDLC material from experimental T_2^{-1} data [26]. S_0 was determined from the temperature-dependent part of the deuteron ΔT_2^{-1} (the first term in Eq. (10)). A great advantage of this approach is that no assumptions concerning the residence time of molecules at the surface are necessary. A temperature-independent $S_0 = 0.08$ was obtained from the fit of theory to the experimental data as the only adjustable parameter apart from the constant C.

The relaxation behaviour of 8CB-αd_2 in cylindrical cavities resembles considerably that of the PDLC material described above. The dashed line in Fig. 5 is characterized by a temperature dependence which can be well described by Eq. (10). It exhibits a pretransitional increase proportional to $(T - T^*)^{-1}$ and a temperature-independent contribution of 35 s^{-1}. Such behaviour implies that the surface order parameter S_0 is temperature-independent. A rough estimate of S_0 from the temperature-dependent contribution to T_2^{-1} yields a value which agrees within 30% with the one obtained from the splitting Δv_Q. By plotting ΔT_2^{-1} as a function of the square of the line-splitting Δv_Q for different temperatures (Fig. 9), we demonstrate directly that ΔT_2^{-1} is linear in S_0^2 and that molecular translational displacements increase T_2^{-1} of 8CB in cylindrical cavities of Anopore membranes.

In the dispersion consisting of 5CB with embedded polymer network, T_2^{-1} does not show a critical pretransitional increase (Fig. 6). The difference between T_2^{-1} in the dispersion and the bulk exhibits hardly any temperature dependence at all. Since the contribution of molecular diffusion through regions with exponentially decaying order parameter is not observed, a simple conclusion can be drawn that such regions do not exist in a well developed form. The tiny fibers
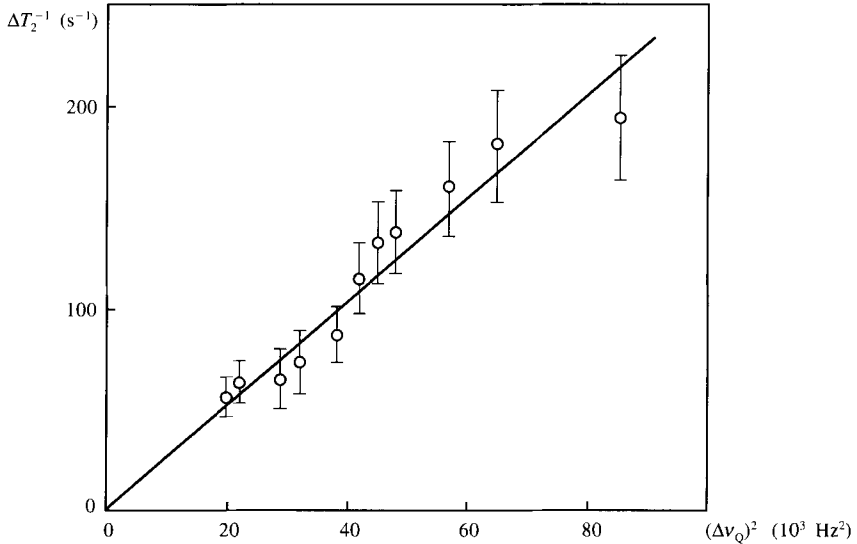
Fig. 9. The difference between transverse spin relaxation rates for 8CB in cylindrical cavities and in bulk is a linear function of the square of the line-splitting: $\Delta T_2^{-1} = (T_2^{-1})_{\text{LC-Anopore}} - (T_2^{-1})_{\text{bulk}}$.

of the polymer network might be so close together – at a distance smaller than the nematic correlation length ξ – that their proximity smears out the characteristic order parameter profile. In this case, the increase of T_2^{-1} might be caused by the molecular translational displacements along the network where the orientation of the long molecular axis adopts the local orientation of the fibers and the interconnecting filaments. On the other hand, a molecule might also stay for a while at the surface of the fiber and still experience orientational modulation because of thermal fluctuations of the network. These fluctuations might be either of one-dimensional type as in polymers or three-dimensional – in view of a great interconnectivity of the network. Frequency dispersion measurements of T_1^{-1} or T_2^{-1} could decide about it. In case of one-dimensional fluctuations the dispersion should obey the $\omega_L^{-3/2}$ law, whereas in case of three-dimensional fluctuations the $\omega_L^{-1/2}$ law should show up. Without additional measurements, we can say on the basis of deuteron relaxometry that a liquid crystal is partially ordered above T_{NI} in the presence of a BAB network (only a residual quadrupolar interaction can produce an increase in T_2^{-1}), and that the surface order parameter is temperature-independent. A complex study of liquid-crystal dispersions with a smaller concentration of polymer that included optical birefringence data, proton relaxometry, and deuteron data yielded a surface order parameter of the order 0.1 [28].

It is interesting to note that the surface order parameter of a liquid crystal in cylindrical cavities with nontreated inorganic walls, in a polymer network, and in spherical droplets of a PDLC material is much smaller than in the nematic phase and does not depend on the temperature. According to Landau-de Gennes theory implemented by adding two terms which describe the coupling of the

liquid crystal with the surface, the surface order parameter in a confined liquid crystal is given by [26]

$$S_0 = \frac{G}{U + \sqrt{a L (T - T^*)}},$$ (11)

where G is the orienting surface constant coupled linearly to S, and U the disorienting one entering in the quadratic term, whereas a and L are bulk material parameters. A temperature-independent S_0 means that the term U prevails in the denominator of Eq. (11) and that short-range surface interactions determine the value of the surface order parameter. Its small magnitude is characteristic of noncomplete wetting of the substrate by the nematic phase in the temperature range where the bulk isotropic phase is stable. The effect of liquid crystalline intermolecular interactions on the surface order parameter, i.e., of the second term in the denominator of Eq. (11), was observed in cylindrical cavities if the wall had been treated by a surfactant that produces homeotropic anchoring.

6 Conclusions

We have shown that deuteron NMR relaxometry in the kilohertz range is a technique very sensitive to both surface-induced order and molecular dynamics in the isotropic phase of confined liquid crystals. An increase in T_2^{-1} has been observed in all confined systems studied so far regardless of the shape and size of the cavities. In cylindrical and spherical cavities with radius of a few hundred nanometers the translational diffusion of molecules between the regions with different degrees of orientational order or different director orientation results in an additional relaxation mechanism in the kilohertz regime. A pretransitional increase of the transverse relaxation rate due to the increase in the thickness ξ of the surface layer is well pronounced. Similar behaviour of the transverse relaxation rate was observed for a liquid crystal in controlled porous glass with cavities of about the same size. In contrast, T_2^{-1} in the liquid-crystal dispersion with a polymer network is temperature-independent – apart from the bulk contribution. This may be due to a fine distribution of fibers on the nanometer scale that smears out the contrast between the ordered and the disordered regions. It should be stressed that the deuteron relaxometry yields information not only on molecular mobility leading to the spin relaxation but also on the surface-induced order parameter. The applicability of this method is not limited to cylindrical cavities but extends to other types of cavities where S_0 cannot be determined from the splitting of the spectrum.

Acknowledgements

during the visit of M.V. in Heidelberg (1987). The research described in this work was supported by the Ministry of Science and Technology of Slovenia (Grant no. J1-0595) and by the U.S.-Slovene NSF Grant no. 9815313.

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