PHYSICAL REVIEW E VOLUME 59, NUMBER 5 MAY 1999

Measurement of the surface-induced order in polymer dispersed liquid crystals: An approach by NMR relaxometry

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(Received 14 December 1998)

A method based on NMR relaxometry is introduced to study surface-induced order in the isotropic phase of confined liquid crystals. We show that the magnitude of the surface order parameter S_0 can be obtained from an increase in the deuteron transverse relaxation rate T_2^{-1}. The increase originates in the molecular diffusion between the weakly ordered surface region and disordered area in the rest of the cavity. No assumptions concerning the residence time of molecules at the surface are needed. We apply the approach to a polymer dispersed liquid crystal and find a temperature independent S_0 of magnitude $\cong 0.08$. This indicates that short range interactions at the interface dominate the behavior of S_0, and that only a partial orientational wetting occurs. [S1063-651X(99)51205-1]

PACS number(s): 61.30.Gd, 76.60.Es

A liquid crystal in contact with an orienting substrate is partially ordered even above the nematic-isotropic transition temperature $T_{\rm NI}$. This phenomenon can be regarded as the orientational wetting of the substrate by the nematic phase in the temperature range where the isotropic phase is stable in bulk [1,2]. On approaching $T_{\rm NI}$ from above, the thickness of the ordered surface layer assumes either a finite or infinite limiting value, corresponding to partial or complete orientational wetting. The nature of the wetting depends on the strength of anisotropic interactions between the liquid crystal molecules and the solid substrate. Neglecting a possible biaxiality, the surface-induced ordering in the isotropic phase can be described by the scalar orientational order parameter $S(\mathbf{r})$ and preferred molecular direction $\mathbf{n}(\mathbf{r})$ in the boundary layer. The value of the surface-induced order parameter at the interface, S_0, is closely related to the wetting behavior. If the surface order parameter at $T_{\rm NI}$ exceeds a certain threshold value S_c, complete wetting occurs, whereas the wetting is only partial for S_0 smaller than S_c. Within an estimate based on the Landau–de Gennes theory, the threshold value S_c equals the bulk nematic order parameter at the transition [1,2].

The experimental evidence of surface-induced orientational order above $T_{\rm NI}$ was provided by Miyano, who measured the pretransitional birefringence [3]. Further experimental studies include second harmonic generation [4], field-induced twist [5], and evanescent wave ellipsometry techniques [6]. A systematic investigation of surface-induced order in cylindrical cavities—coated with various surfactants—was performed by Crawford *et al.* by means of deuterium NMR [7–9]. In contrast to the intensive efforts devoted to liquid crystals in planar and cylindrical geometries, surface parameters of polymer dispersed liquid crystals (PDLCs) have been only scarcely investigated. Golemme *et al.* [10] studied the deuterium NMR spectra of spherical liquid crystal droplets in a PDLC material. Measuring the linewidth, they showed that for sufficiently small droplets the nematic-isotropic transition is replaced by a continuous evolvement of order, in agreement with theoretical predictions [1,2,11]. However, the experimental results of Golemme *et al.* do not quantitatively reveal the details of the surface-induced ordering. In this paper we present an approach, based on deuteron NMR relaxometry, which yields information on the surface order parameter also for systems where the previously mentioned NMR method fails. Applying the approach to a PDLC material, we present an experimental determination of the surface order parameter in its isotropic phase. In view of the widespread application of PDLC materials in optical shutters, we find that it is worth shedding light on their microscopic properties.

The deuteron NMR spectrum of a bulk liquid crystal, recorded in the isotropic phase, consists of a single narrow line, as a fast and isotropic molecular tumbling completely averages out the quadrupolar interaction of deuterons. On the other hand, the NMR line in the confined isotropic phase might be either broadened or resolved into a doublet as a consequence of the surface-induced orientational order in a thin boundary layer. The residual quadrupolar interaction of a deuteron thus depends on the position of the spin-bearing molecule in the cavity. It is zero in the isotropic region and different from zero in the boundary layer where its value also depends on the orientation of the local director. If molecular translational self-diffusion provides a complete exchange of molecules in the cavity within the time of the NMR experiment, the corresponding splitting $\Delta\nu$ of the spectrum is given by [8,12]

$$\Delta\nu = \frac{3}{2}\frac{e^2qQ}{h}\left[\frac{1}{2}\overline{(3\cos^2\gamma - 1)}\right]\langle S(\mathbf{r})\rangle \times \left\langle \frac{1}{2}(3\cos^2\theta_B(\mathbf{r}) - 1)\right\rangle . \qquad (1)$$

Here e^2qQ/h is the static quadrupole coupling constant of deuterium nuclei, γ is the angle between the C-D bond and the long molecular axis, and the bar denotes the average over different conformational states of the molecule. $\theta_B(\mathbf{r})$ is the angle between the local director at the surface and magnetic field, $S(\mathbf{r})$ is the local orientational order parameter, and $\langle \rangle$ stands for the spatial averaging over all positions in the cavity. In systems with uniform orientation of the surface director with respect to the magnetic field, i.e., with the same θ_B everywhere at the walls, the term $\langle 3\cos^2\theta_B(\mathbf{r})-1\rangle$ is relatively large and the spectrum is a well resolved doublet. The measurement of $\Delta\nu$ yields $\langle S(\mathbf{r})\rangle$ directly according to Eq. (1). Such a system is cylindrical cavities oriented parallel to the magnetic field as used by Crawford *et al.* [7–9].

The situation is much more complex in systems where the orientation of the director with respect to the magnetic field varies along the wall. This applies for liquid crystals in spherical cavities, porous glasses, aerogels, and liquid crystals with an embedded polymer network. Here the average $\langle 3\cos^2\theta_B(\mathbf{r})-1\rangle$ is considerably diminished by molecular translational displacements and would be zero for a completely isotropic distribution of θ_B in small cavities. In fact, no splitting of the NMR spectrum has been observed in either of the above systems.

The hampering effect of molecular translational displacements has a different impact in NMR relaxometry [13]. The nuclear spin relaxation is in fact caused by the time modulation of quadrupolar interaction induced by molecular motion. Whereas the line splitting depends on the mean value of the residual quadrupolar interaction in the cavity, the spin relaxation rates depend basically on the mean-square value, which does not average out to zero. Although a relationship between the deuteron relaxation rates and surface order parameter has been suggested earlier [12], we show how the surface order parameter can be obtained directly, without knowledge of the residence time of molecules at the surface. With this purpose we measured and analyzed the transverse spin relaxation rate T_2^{-1} of deuterons in the isotropic phase of a PDLC material.

Liquid crystal 4′-pentyl-4-cyanobiphenyl (5CB-αd_2), deuterated in the α position of the hydrocarbon chain, was dispersed in the form of spherical droplets within a two-component epoxy polymer (Bostik brand). The droplets' diameters are between 500 and 600 nm. Due to the parallel anchoring of liquid crystal molecules at the surface, the structure of the director field in the nematic phase is bipolar, i.e., with two point defects at the poles of the sphere. A discontinuous transition from the nematic into the isotropic phase takes place at nearly the same temperature as in the bulk 5CB ($T_{\mathrm{NI}}\approx 34.5\,^\circ\mathrm{C}\pm 0.5\,^\circ\mathrm{C}$). The measurements of the deuteron transverse and spin-lattice relaxation times, T_2 and T_1, respectively, were performed on a Bruker spectrometer at a Larmor frequency of 58.3 MHz on cooling the samples in the isotropic phase. Transverse spin relaxation time T_2 was measured by the quadrupolar echo pulse sequence, $(\pi/2)_x$-τ-$(\pi/2)_y$-τ-$(acquisition)$, improved by an eight step phase cycling scheme, and T_1 by the standard pulse sequence. The observed relaxation processes are monoexponential over at least one decade and the experimental errors are less than 10%.

The temperature dependences of the deuteron T_2^{-1} in the isotropic phase of 5CB-αd_2 droplets and of the bulk 5CB-αd_2 are shown in Fig. 1. There is a pronounced difference between the relaxation rates of the two samples. T_2^{-1} for the confined liquid crystal is larger for at least a factor of $\sim$2.5 compared to the bulk, and shows a well expressed pretransitional increase as T_{NI} is approached from above. In contrast to the transverse spin relaxation, the spin-lattice relaxation rate T_1^{-1} hardly experiences any effect of the confinement. The lack of any significant difference in T_1^{-1} between the PDLC material and bulk leads to the conclusion that fast local molecular reorientations (they determine T_1^{-1} in the MHz regime [14]) are not affected by the confinement. A large difference in the transverse relaxation rates, however, clearly indicates that, in addition to the fast local reorientations, there exists in droplets a slower modulation of the quadrupolar interaction as well, which is not present in the bulk.

The additional relaxation-inducing process with a frequency in the kHz range could be either *order fluctuations* in the boundary layer or *molecular translational displacements*. The first possibility can be ruled out on the basis of the work of Ziherl and Žumer on order fluctuations in the confined isotropic phase [15]. They showed that, in the case of complete wetting of the substrate by the nematic phase, the slowest mode, which would provide the largest contribution to T_2^{-1}, is associated with fluctuations in the thickness of the ordered layer. It is slower than the bulk modes only in a narrow temperature interval of about 1 K above the transition and diverges at T_{NI}. No such divergence in T_2^{-1} has been observed experimentally in the examined system (Fig. 1). In addition, the increase in T_2^{-1} upon confinement is not limited to the intermediate vicinity of the transition. This leads to the conclusion that molecular translational motion should be responsible for the enhancement of T_2^{-1}. That fact is not surprising since molecular translational displacements provide an effective relaxation mechanism in many heterogeneous systems [16–21]. The quadrupolar interaction of deuterons, averaged by fast local molecular reorientations, is *additionally* modulated on a much slower time scale as a spin-bearing molecule changes its position from the isotropic region in the inside of the droplet into the ordered surface layer and out. The angular part of the quadrupolar Hamiltonian also varies along the curved surface.

The contribution of molecular translational displacements (TD) to the deuteron T_2^{-1} is quantitatively given by [13,14]

$$(T_2^{-1})_{\mathrm{TD}}\cong \frac{9}{4}\pi^2\left(\frac{e^2qQ}{h}\right)^2 J_0(0), \tag{2}$$

where $J_0(0)$ is the spectral density of the quadrupolar autocorrelation function of zero order at zero Larmor frequency. The spectral densities at Larmor and the double Larmor frequencies have been omitted in Eq. (2), their contributions being negligible for fluctuations that are much slower than the inverse Larmor frequency. The spectral density $J_0(0)$ is expressed in terms of the angular part $\overline{F_0(\mathbf{r})}$ of the quadrupolar interaction for a nucleus at position r in the droplet and averaged over fast molecular reorientations, and in terms of $P(\mathbf{r}_0,\mathbf{r},t)$ [18]:

$$J_0(0)=\frac{2}{V}\int_0^\infty\int_V\int_{V_0}\overline{F_0(\mathbf{r}_0)}P(\mathbf{r}_0,\mathbf{r},t)\overline{F_0(\mathbf{r})^*}d\mathbf{r}\,d\mathbf{r}_0dt \tag{3}$$

with

$$\overline{F_0(\mathbf{r})}=\frac{1}{\sqrt{2}}\left[\frac{1}{2}\overline{(3\cos^2\gamma-1)}\right]S(\mathbf{r})\,\frac{1}{2}[3\cos^2\theta_B(\mathbf{r})-1]. \tag{4}$$

$P(\mathbf{r}_0,\mathbf{r},t)$ is the conditional probability density that a molecule at position $\mathbf{r}_0$ at time zero migrates to $\mathbf{r}$ in time t. In evaluating $P(\mathbf{r}_0,\mathbf{r},t)$ we use a simple model and describe molecular translational displacements in the droplet as ordinary isotropic diffusion with coefficient D, which is restricted to a spherical volume V with reflecting boundaries. The conditional probability density for such motion was calculated in the appendix of Ref. [18]. The local order parameter S at position $\mathbf{r}$, which enters into Eq. (4), is calculated by minimizing Landau–de Gennes free energy for the isotropic phase within a cavity with orienting walls [1,8]. It was found that

$$S(r)=S_0\exp[-(R-r)/\xi], \tag{5}$$

where $R-r$ denotes the distance from the wall and ξ denotes the characteristic decay constant. The decay constant has a critical temperature behavior, $\xi=\xi_0(T^*/(T-T^*))^{1/2}$, where ξ_0 is of the order of molecular length ($\xi_0\approx 0.65\,\text{nm}$ for 5CB) and T^* is the bulk supercooling limit (about 1 K below T_{NI}). In deriving Eq. (5), the spherical symmetry of $S(\mathbf{r})$ was assumed as well as $S_0 \ll 1$ and the decay constant ξ much smaller than the radius R the droplet.

The final result for $(T_2^{-1})_{\text{TD}}$ is obtained by inserting Eq. (5) into Eqs. (4) and (3), using $P(\mathbf{r}_0,\mathbf{r},t)$ from Ref. [18], and by performing the time and volume integrations. Generally, at least one of the integrations should be performed numerically. For a special distribution of directors at the surface—with all molecules preferentially oriented perpendicular to the interface—the spherical symmetry simplifies the problem and we find

$$\begin{aligned}(T_2^{-1})_{\text{TD}}=&\frac{27}{10}\pi^2\left(\frac{e^2qQ}{h}\right)^2\left[\frac{1}{2}\overline{(3\cos^2\gamma-1)}\right]^2 S_0^2\\ &\times\sum_s\frac{\tau_S}{(1-6/\beta_s^2)j_2^2(\beta_s)}\\ &\times\left[\int_0^1 j_2(\beta_s x)e^{-[(1-x)R]/\xi}x^2dx\right]^2.\end{aligned} \tag{6}$$

Here j_2 denotes the spherical Bessel function of second order and β_s denotes the sth zero of the first derivative of j_2. The resulting relaxation rate is a weighted sum of a discrete set of times $\tau_s=R^2/(\beta_s^2 D)$ related to the topologically restricted diffusion process. It should be mentioned that parallel surface anchoring of molecules, which is, in view of the bipolar structure in the nematic phase, more probable for our system than the radial one, would give approximately the same $(T_2^{-1})_{\text{TD}}$ for bipolar surface orientation and randomly oriented droplets in the sample.

The comparison of experimental data for 5CB-αd_2 droplets with theory [Eq. (6)] shows that an adequate interpretation is not possible unless a temperature independent term C is added. The bold solid line in Fig. 1 is thus obtained by fitting the expression

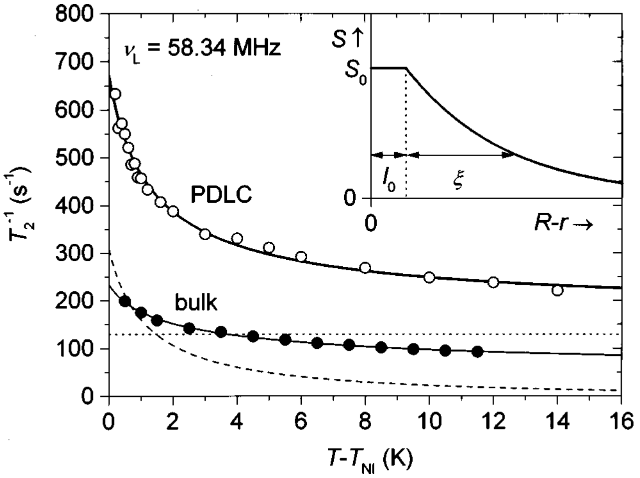

FIG. 1. Temperature dependences of the deuteron T_2^{-1} for 5CB-αd_2 droplets (PDLC) and the bulk sample. The bold solid line represents the fit of Eq. (7) to the experimental data. It is a sum of three contributions: $(T_2^{-1})_{\text{bulk}}$ (thin solid line), $(T_2^{-1})_{\text{TD}}$ (dashed line), and C (dotted line). The inset represents a schematic presentation of the order parameter S versus the distance from the wall $(R-r)$. S is constant in the first molecular layer (l_0) whereas, for $R-r>l_0$, it decays exponentially with the characteristic length ξ.

$$(T_2^{-1})_{\text{PDLC}}=(T_2^{-1})_{\text{bulk}}+(T_2^{-1})_{\text{TD}}+C \tag{7}$$

to the experimental data. A good matching is obtained by varying only two adjustable parameters: the surface order parameter S_0, and the temperature independent contribution C. The values of the two fitted parameters are $S_0=0.08 \pm 0.01$ and $C=130\,\text{s}^{-1}$, whereas $e^2qQ/h[\frac{1}{2}\overline{(3\cos^2\gamma-1)}]\approx 62\,\text{kHz}$ is obtained from the bulk nematic phase, $R=275\,\text{nm}$, and $D=D_0\exp(-E_a/k_BT)$, with $D_0=2.83\times 10^{-5}\,\text{m}^2/\text{s}$ and $E_a/k_B=4050\,\text{K}$ [21]. It should be stressed that only a *temperature independent* S_0 reasonably explains the experimental results. Though our data yield the magnitude of S_0, they provide no means of distinguishing between the details of the surface alignment, i.e., whether it is uniform planar, random planar, or homeotropic. As the fitted value of S_0 depends to some extent on these details, we estimate that the error in determining S_0 could be larger than the deviation in the fit and might amount to about 30%. We have also applied the approach described above to determine S_0 in cylindrical geometry, i.e., for 5CB-αd_2 in Anopore membranes, where the surface order parameter is known from NMR spectra [8,9]. A preliminary analysis shows good agreement (within 30%) between both methods.

The necessity to include a temperature independent contribution C *ad hoc* in Eq. (7) arises from the simplicity of our description related to (i) molecular translational diffusion in the cavity, and (ii) the order-parameter profile [Eq. (5)]. In real droplets, a slowing down of molecular translational diffusion occurs in the first molecular layer at the boundary [22]. Besides, taking into account the finite length of the molecules, a more realistic order-parameter profile is found to be constant over a distance l_0 from the wall [7–9], and only then starts to decrease exponentially with the decay constant ξ (inset in Fig. 1). The thickness l_0 of the layer with constant order parameter is roughly one molecular length and does not change with temperature up to about 20 K above T_{NI} [7–9]. The exchange of molecules between this first molecular layer and the rest of the cavity leads to a temperature independent contribution to the relaxation rate T_2^{-1}, which can be interpreted as the term C in Eq. (7). Its value is rather large in view of the slowing down of translational diffusion at the wall. In the total relaxation rate, the temperature independent term C prevails far above T_{NI}, whereas the relative importance of $(T_2^{-1})_{\mathrm{TD}}$, arising from the diffusion of molecules to and from the region of thickness ξ, increases with decreasing temperature. It is roughly proportional to $\xi^2 \propto (T-T^*)^{-1}$, as long as $\xi \ll R$.

The value of the surface order parameter $S_0 \approx 0.08$, obtained from the fit, is temperature independent in the whole range between $T \sim T_{\mathrm{NI}} + 0.2\,\mathrm{K}$ and $T \sim T_{\mathrm{NI}} + 15\,\mathrm{K}$. It is much smaller than the threshold value S_c (≈ 0.27 for 5CB) and, therefore, characteristic of a noncomplete, i.e., partial orientational wetting. The orienting effect of the polymer surface in a PDLC material is thus relatively weak; the surface has an ordering effect at temperatures where bulk is isotropic but a disordering effect in the nematic phase. If the standard Landau–de Gennes free energy density is complemented by two terms that describe the surface free energy density, $(-GS(r) + \frac{1}{2}US^2(r))\,\delta(r-R)$, where G is the orienting surface coupling constant and U is the disorienting one [2], the minimization of the free energy yields $S_0 = G/(U + \sqrt{aL(T-T^*)})$, where a and L are material parameters ($a = 0.13 \times 10^6\,\mathrm{J/m^3K}$ and $L = 1.7 \times 10^{-11}\,\mathrm{J/m}$ for 5CB) [11]. A temperature independent S_0 indicates that the disorienting surface coupling constant U dominates over the term $\sqrt{aL(T-T^*)}$. This imposes limits on the surface coupling constants in our system: U should be larger than $5 \times 10^{-3}\,\mathrm{J/m^2}$ and, consequently, $G < 4 \times 10^{-4}\,\mathrm{J/m^2}$. Obviously, S_0 is determined by short-range interactions at the interface.

In summary, we have shown that NMR relaxometry provides a way to determine the magnitude and temperature behavior of the surface order parameter in confined liquid crystals. S_0 is determined from that part of the deuteron T_2^{-1} that results from the modulation of quadrupolar interaction caused by molecular diffusion to and from the region with exponentially decaying order parameter. With this approach no assumptions concerning the residence time of molecules at the surface are necessary and S_0 is, apart from the constant C, extracted as the only fitted parameter. Our results represent quantitative determination of the surface order parameter in a PDLC material.

This work was supported by the Ministry of Science and Technology of Slovenia (Grant No. J1-7470) and by the U.S.-Slovenia NSF under Grant No. 9815313.

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