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Xenon NMR Study of a Nematic Liquid Crystal Confined to Cylindrical Submicron Cavities

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NMR studies of xenon gas dissolved in the liquid crystal ZLI 1132 confined to submicron cylindrical cavities are reported. Spectra taken as a function of temperature yield a clear indication of the nematic to isotropic phase transition of the confined liquid crystals. In the nematic phase at 21 °C, the resonance line of dissolved ^{129}Xe exhibits a chemical shift anisotropy of 15 ppm due to a random distribution of director axes in the plane perpendicular to the long axis of the cylinder. The anisotropy and temperature dependence of the confined system are compared to control experiments that use the bulk liquid crystal. The quadrupolar splitting observed in the ^{131}Xe NMR spectrum of the confined liquid crystalline solution of xenon gas is slightly greater than that found in the bulk. Two-dimensional exchange NMR demonstrates that the xenon atoms probe different average liquid crystal directors within a single cavity on a 20 ms time scale and that interpore exchange occurs on a time scale of 400 ms. The exchange data indicate that changes in the orientation of the director within individual cavities occur on a length scale of about 2 μm.

Introduction

Liquid crystals are technologically important due to their widespread use in displays (LCDs) and their potential applicability in nonlinear optical devices.[1−3] Liquid crystalline phases exhibit long-range molecular orientational order, in contrast to normal liquids which lack positional and orientational order. Devices based on liquid crystals are able to exploit the anisotropy of the medium for the control of alignment and switching of the director axis formed by the liquid crystalline phases. Characterization of the orientational order and the factors which govern it are therefore of considerable scientific and commercial interest.

Nuclear magnetic resonance (NMR) is useful for studying liquid crystals[4] due to the sensitivity of the NMR spectrum to orientational order. Anisotropic interactions such as chemical shift anisotropy, quadrupolar interactions, and magnetic dipolar couplings make it possible to measure the degree of orientational order. However, spectra can be extremely complicated and intractable for abundant spins in multiple sites, e.g., protons in the liquid crystal molecules. A common simplifying approach is to study small probe molecules dissolved in the liquid crystal or to use liquid crystal molecules which have been isotopically labeled at specific sites. For solute molecules within a liquid crystalline environment, the ordering of the solute by dispersive and steric forces can be described by an order tensor that relates the average alignment of the solute molecular frame to the liquid crystal director frame.[5] A particularly simple example is the case of an atom dissolved in a liquid crystal solvent; in this case the principal axis system of the probe is completely determined by the liquid crystal director field.

The use of xenon as a microscopic probe of various materials has rapidly developed since the pioneering work in the early 1980s by Fraissard in zeolites, Williamson in liquids, and Ripmeester in clathrates.[6−11] In a nematic liquid crystal, ^{131}Xe was observed to have a spectrum composed of a sharp triplet indicative of a quadrupolar splitting from an orientationally ordered, homogeneous average electric field gradient at the nucleus.[12] More recently Diehl, Jokassari, and co-workers have used several noble gases[13,14] possessing quadrupolar nuclei to perform a systematic study of several nematics and have attempted to explain the observed electric field gradients in bulk liquid crystals and mixtures.[13] Similarly, several NMR studies have attempted to exploit the high sensitivity of the ^{129}Xe chemical shift to its local environment and structure. These studies have sought to correlate various contributions to the total chemical shift to liquid crystal environments by following the temperature dependence of chemical shift of ^{129}Xe dissolved in various liquid crystals and liquid crystalline mixtures.[15,16] The area of noble gas studies of isotropic and anisotropic fluids has recently been reviewed.[17]

An interesting and potentially important aspect of liquid crystal behavior is the effect of confined geometry.[18] In this paper we report the application of xenon NMR to the study of a liquid crystal (ZLI 1132) confined to cylindrical cavities of submicron diameter. Both NMR-active isotopes of xenon ^{129}Xe ($I = {}^1/_2$) and ^{131}Xe ($I = {}^3/_2$) are used, and spectra of xenon dissolved in the confined liquid crystal are compared to the spectra of xenon dissolved in the bulk liquid crystal. The examination of the surface-induced alignment effects is facilitated by the ability to control the orientation of the long axis of the cylinders with respect to the field. Additionally, two-dimensional NMR of ^{129}Xe is used to probe the translational motion on time scales from milliseconds to seconds, revealing additional details about the director structure within the cavities.

Background

The ordering of a liquid crystal confined to a small volume is a consequence of the competition between the elastic forces within the liquid crystal and the molecular interactions with the

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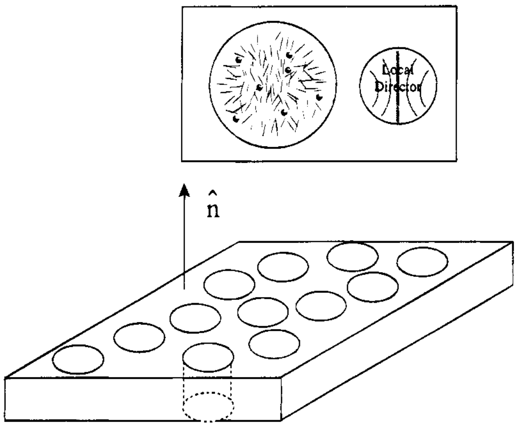

Figure 1. Schematic picture of an anopore membrane whose unit normal is denoted **n̂**. The lecithin-induced "planar polar" director field within the pores is sketched above the membrane. The membrane size is 15 × 10 × 0.06 mm, and the cylinder diameters are 0.2 μm.

surface, in addition to alignment induced by externally applied electric or magnetic fields. A grooved surface can strongly anchor the molecules in a preferred direction, and various surface coatings can also exert effects on the alignment of the molecules by changing the surface interaction energy.[19] Optical techniques, such as surface ellipsometry, have long been used to investigate these effects,[20] but NMR, lacking sufficient sensitivity to probe a surface area which is generally a few square centimeters, has typically been relevant only to studies of bulk phases. Liquid crystals confined in submicron structures, however, are high surface area systems in which sufficient liquid crystalline material can be loaded to allow NMR studies. Surface orientation effects in these systems have previously been observed using NMR of site-selectively deuterated liquid crystals.[21] It has been shown that, in these submicron-sized systems, liquid crystals behave quite differently than in the bulk, as might be anticipated from the potential for strong liquid crystal–surface interactions. Xenon NMR has the advantage over previous deuterium NMR studies of microconfined liquid crystals in that no special synthesis is required for the liquid crystal.

Although magnetic fields also are capable of orienting liquid crystals, in these confined systems the effect is expected to be much weaker than effects due to surface interactions. The magnetic coherence length, ξ_m,[22] is determined by the magnetic field strength B, the susceptibility anisotropy $\Delta\chi$, and the elastic constant of the medium K through $\xi_m = [K/\Delta\chi]^{1/2}/B$. In a field of 11.7 T, the magnetic coherence length is on the order of 1 μm. Since the magnetic field coherence length is larger than the cavity diameter (0.2 μm), the formation and orientation of the local director axis are dominated by the surface interactions in these confined systems, with the magnetic field playing only a secondary role. The dominance of the surface effects enables observations to be made with different angles of the director axis with respect to the magnetic field, which is typically not possible in the bulk because of fast realignment of the director relative to the magnetic field.

The liquid crystal studied here is loaded into a high-surface area anopore membrane shown schematically in Figure 1. These membranes are composed of aluminum oxide that has been electrochemically treated to create a noninterconnected set of highly parallel pores through the membrane. The membranes have a very narrow distribution of pore diameters, with an average diameter of 0.2 μm.[18] The extremely high pore density (up to 10^9 pores/cm^2) results in BET surface areas of approximately 10 m^2/g.[18] Each membrane is 60 μm thick and may be cut into square sheets.

Previous deuterium NMR studies have shown that the alignment axis of the director is perpendicular to the wall.[23] Although several director configurations are possible, in this case it is known that a lecithin coating reduces the surface interaction energy, making a planar–polar configuration a relative energy minimum.[23] This structure is sketched above the membrane in Figure 1. Deuterium NMR has shown that in lecithin-treated anopores the director axis of the configurations do not align along the magnetic field but instead remain pinned at random orientations within the plane perpendicular to the cylinder axis.

Since the xenon resonance is sensitive to the director orientation, further information about the spatial proximity of different orientations can be obtained by following xenon magnetization exchange between the different components of the xenon spectrum. Two-dimensional xenon NMR spectroscopy is well suited to such studies of xenon dynamics,[24–27] as it allows the observation of xenon atomic motion on time scales that exceed the free induction decay time. Motion between distinct environments can be studied over times up to the order of the spin–lattice relaxation time, T_1.

Experimental Section

The anopore membranes were cut into square strips (2.0 × 1.0 cm) and treated with lecithin before being loaded with ZLI 1132 (Merck, a mixture of *trans*-4-*n*-alkyl-(4′-cyanophenyl)-cyclohexanes and *trans*-4-*n*-pentyl-(4′-cyanobiphenyl)cyclohexane). The coating and loading procedure have been described in detail.[18] ZLI 1132 was chosen due to its convenient nematic range and since it has been previously characterized in the bulk by xenon NMR.[16,28] Several glass sample cells were constructed from square tubing (1.0 × 1.0 cm i.d.) to accommodate the membranes tightly and facilitate orientational studies. Approximately 100 membranes were stacked into each cell. One cell was loaded with 6 atm of enriched ^{129}Xe (EG+G Mound, 80%) and another with 5 atm of enriched ^{131}Xe (EG+G Mound, 70%) and flame-sealed. Before starting the experiments, the cells were briefly heated to above 100 °C to allow the xenon to dissolve rapidly into the isotropic phase of the liquid crystal. For comparison, samples of bulk ZLI 1132 were also prepared with 3–5 atm of enriched ^{131}Xe and ^{129}Xe.

The spectra were recorded on a 500 MHz (11.7 T) CMX spectrometer operating at 138 MHz for ^{129}Xe and 41 MHz for ^{131}Xe nuclei and a 400 MHz (9.4 T) Bruker with a ^{129}Xe frequency of 110 MHz. The 90° pulse for ^{129}Xe was 10 μs. Typical relaxation delays were 30 s for ^{129}Xe and 50 ms for ^{131}Xe, and sufficient signal-to-noise was achieved with 200–400 and 100 000–500 000 scans, respectively. All reported chemical shifts are referenced to an external standard of low-pressure Xe gas.[29]

For the 2D exchange experiments, a standard pulse sequence and the method of States *et al.*[30] or TPPI[31,32] were used to obtain pure phase absorption spectra. Typically, 128 and 256 points were acquired in t_1 and t_2, respectively, with 8 scans per t_1 value. During data processing, the t_1 dimension was zero-filled to 256 points and 100 Hz Gaussian line broadening was applied in both dimensions.

Diffusion measurements of xenon in ZLI 1132 at room temperature were performed using a pulsed field gradient spin echo technique on a sample of ZLI 1132 sealed with 5 atm of 80% ^{129}Xe (EG+G Mound) and ~50 Torr of O_2 (Matheson). The experiments were performed with a 180 MHz (4.3 T) microimaging spectrometer (Quest 4300, Nalorac Cyrogenics Inc.) operating at 51 MHz for ^{129}Xe and using cylindrical microimaging gradients (Nalorac Cryogenics Inc.) and a home-

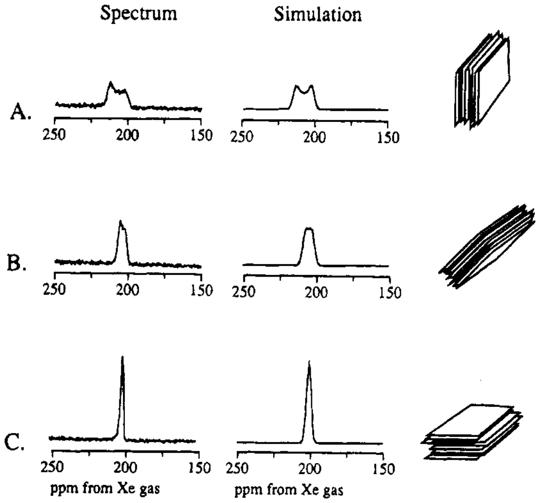

Figure 2. Experimental and simulated ^{129}Xe spectra in ZLI 1132 confined within anopore membranes (T = 19 °C and P = 5 atm) at various orientations with respect to the magnetic field: (a) $\hat{n} \perp \vec{B}$, (b) 45°, (c) $\hat{n} \| \vec{B}$.

built probe. A 500 μs slice-selective pulse was used. Gradients from +5 to −5 kHz/mm in 64 steps were applied for a 1 ms duration with a 500 ms delay between the end of the first gradient pulse and the application of the 180° refocusing pulse. Eight acquisitions were made at each gradient value. Diffusion measurements were made both parallel and perpendicular to the director axis.

Numerical simulations of spectral line shapes were carried out for a random distribution of directors within a plane (transverse isotropy) as a function of the angle between the magnetic field axis and the plane. Line shapes were calculated using an axial chemical shift tensor and were convolved with Gaussian line broadening to mimic the broadening observed in the experimental spectra.

Results

In the bulk sample of ZLI 1132 at 27 °C, the chemical shift of ^{129}Xe was measured to be 222 ppm with a line width of 1.5 ppm, approximately equal to that expected from the magnetic field inhomogeneity. Figure 2 shows the spectrum of ^{129}Xe in ZLI 1132 confined to the cavities of the anopore sample with various orientations of $\hat{n}$. The vector $\hat{n}$ is the normal to the membrane surface; $\hat{n}$ is parallel to the long cylinder axis and perpendicular to the directors (Figure 1). With $\hat{n} \| \vec{B}$ a single line is observed at 201 ppm. With $\hat{n} \perp \vec{B}$ a much broader signal is observed and exhibits a line shape that is characteristic of a random distribution of director axes in a two-dimensional plane, a distribution also known as "transverse isotropy".[33] The simulated line shapes show satisfactory agreement with the experiment; the slight distortions from the theoretical shape are likely due to misalignment of the membranes with respect to the field. The splitting, corresponding to the separation between singularities in the line shape, represents the anisotropy of the chemical shift interaction and is found to be 15 ppm at 21 °C. As in bulk samples,[34] the chemical shift anisotropy of ^{129}Xe within the confined liquid crystal is temperature-dependent, monotonically decreasing with increasing temperature, from 15 ppm at 21 °C to 8 ppm at 90 °C. The isotropic chemical shift moves upfield with increasing temperature at 0.23 ppm K^{-1}, compared to the 0.25 ppm K^{-1} found in bulk studies.[16]

The chemical shift anisotropy has been previously measured in several liquid crystals by observing the change in chemical shift at the nematic−isotropic transition.[15] This method is affected by the temperature and phase dependence of σ_{iso}; however, from the data of Jokisaari and Diehl (Figure 2 in ref 16), the anisotropy near the transition temperature appears to be 11 ppm for bulk ZLI 1132, compared to 8 ppm in the present confined system.

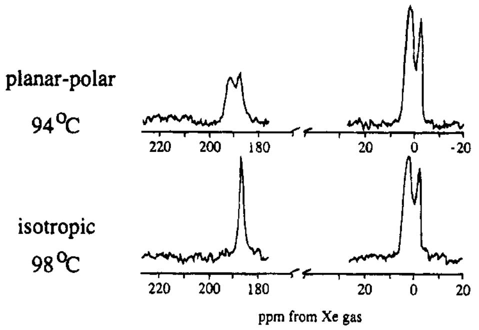

Figure 3. ^{129}Xe spectra of XLI 1132 confined within anopore membranes, at temperatures just below (94 °C) and just above (98 °C) the isotropic to nematic phase transition.

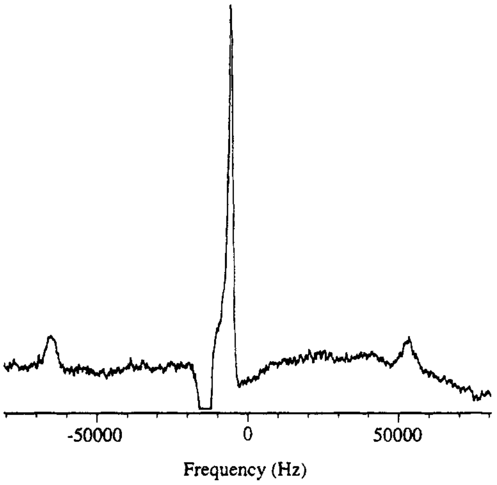

Figure 4. ^{131}Xe spectra in ZLI 1132 within anopore membranes show the entire triplet (and the gas phase peak which is inverted and truncated). T = 49 °C, splitting = 120 kHz, and number of acquisitions = 206 450.

The nematic−isotropic transition in our bulk samples without xenon was measured to be 74 ± 1 °C, by observation of the clearing temperature. It has been observed previously that the transition temperature depends on the total pressure of xenon dissolved.[15] The transition temperature is further altered in the restricted geometry. In the anopores, the transition was found to be 96 ± 3 °C for the sample which includes ^{129}Xe gas dissolved under a pressure of ~6 atm. This transition is shown in Figure 3, where the anisotropic line shape at 190 ppm collapses to a narrow isotropic line. It should be noted that the resonance assigned to the xenon gas near 0 ppm also shows structure. The gas resonance is composed of two partially resolved peaks whose separation is independent of temperature over the range 0−100 °C. There is a very narrow component identified with the gas in regions of the tube that contain no sample and a broader component most likely due to gas that experiences magnetic susceptibility shifts between the plates and interactions with the aluminum oxide surface.

The quadrupolar splitting (defined as the frequency separation of the satellite transitions) of ^{131}Xe in the bulk sample at 29 °C was measured to be 207 kHz, in agreement with the results of previous work.[28] Figure 4 shows the spectrum of ^{131}Xe in ZLI 1132 in the anopore sample at the orientation $\hat{n} \| \vec{B}$. The quadrupolar splitting has been measured as 230 kHz at 49 °C in the bulk.[28] In the anopore membrane at 49 °C the quadrupolar splitting is reduced to 120 kHz. The quadrupolar splitting

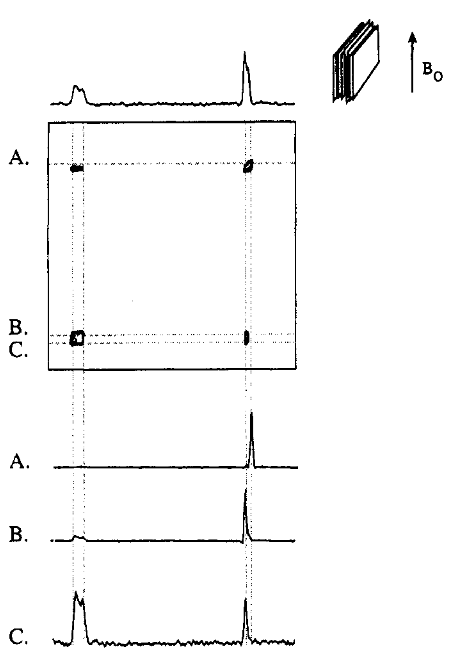

Figure 5. 2D exchange spectrum of xenon in ZLI 1132 loaded into anopore membranes at $T = 33$ °C with $\tau_{mix} = 400$ ms. The projection is shown above the spectrum. (A, B, C) Three different slices indicated by the dashed lines are shown. The largest peaks are normalized to the same height.

scales as $P_2(\cos \vartheta)$, where ϑ is the angle between the director and the magnetic field; a scaling of 0.5 is anticipated because, with this macroscopic orientation of the membranes, all of the directors are perpendicular to the field (cf. Figure 1). Since the splitting is slightly more than one-half of the bulk value, it appears that the electric field gradient experienced by the xenon is slightly higher in the confined liquid crystal than in the bulk. The line width is 1.2 kHz for the central transition and 4.5 kHz for the satellites. The satellite transitions are difficult to observe in the ^{131}Xe spectrum since they are broadened by slight misalignments of the membranes, temperature gradients over the sample, and small temperature fluctuations over the acquisition time. The satellites broaden out rapidly upon rotating the sample and are unobservable at more than a few degrees of misalignment from the magnetic field.

Figure 5 shows the two-dimensional ^{129}Xe exchange spectrum obtained with a mixing time of 400 ms. The spectrum has off-diagonal peaks connecting the gas and liquid crystal resonances, indicating that exchange is occurring between these two regions on this time scale. The observed exchange at 400 ms occurs only with the second, broad gas component, associated with xenon near the membranes. The expansion beside the spectrum in Figure 6 shows the detail of the liquid crystal region and displays the effects of exchange among the different components of the inhomogeneous dissolved xenon line shape, indicating that exchange among the different components of the xenon dissolved in the liquid crystal at 25 °C also takes place on a time scale of 20 ms.

The diffusion measurements of xenon within bulk ZLI 1132 yielded a value of (2.0 ± 0.3) × 10^{-10} m^2/s with no observable anisotropy.

Discussion

Liquid crystals confined to the cylindrical cavities with dimensions much less than the magnetic coherence length allow measurements that are not normally possible in bulk liquid crystals. In these systems, rotation of the cylinders with respect to the direction of the magnetic field can provide a direct measurement of anisotropic interactions in these systems. In the case of the lecithin-treated membranes, perpendicular anchoring of the liquid crystal molecules is obtained,[35] and a random distribution of the director configurations in the plane perpendicular to the long cylinder axes has been observed. The anisotropy of the ^{129}Xe chemical shift can be *directly* determined from the splitting of the transverse isotropic powder pattern. This enables a direct determination of the anisotropy of a particular configuration over a broad temperature range, compared to other methods which only infer the anisotropy from the change in chemical shift at the nematic−isotropic transition.

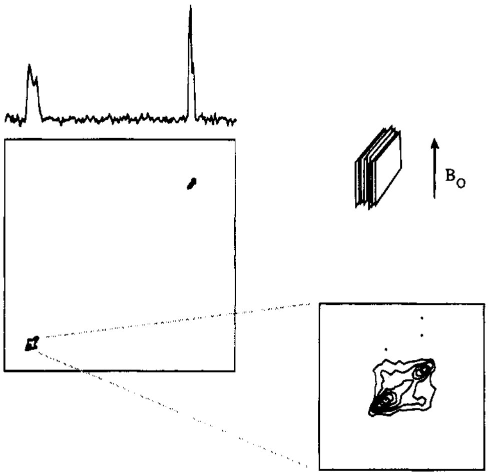

Figure 6. 2D exchange spectrum of xenon in ZLI 1132 loaded into anopore membranes at $T = 25$ °C with $\tau_{mix} = 20$ ms. The lower spectrum is an expansion of the liquid crystal region.

Using the measured diffusion constant of the xenon in ZLI 1132, $D = 2.0 \times 10^{-10}$ m^2/s, it can be estimated that it takes only ~25 μs for the root-mean-square distance traveled by dissolved xenon in the cross-sectional plane of the cylinders to approach the 0.1 μm radius of the cylinder. Given that the observed anisotropy is on the order of 1−2 kHz, this rate of diffusion ensures that the exchange within this plane is in the fast exchange regime and that the observed chemical shift represents the average chemical shift in the cross-sectional plane. Thus, the observed decrease in chemical shift anisotropy with increasing temperature indicates either a temperature-dependent change in planar polar configuration or a reduction in the order parameter of the liquid crystal. The xenon chemical shift line shape can be viewed as a complement to the deuterium line shape analysis previously used to identify and assign liquid crystalline configurations in these systems; whereas deuterium NMR provides a detailed view of individual molecular orientations in the plane, xenon NMR gives an average over the cylinder cross section and makes possible the study of greater length scales.

Two-dimensional exchange experiments as a function of mixing time indicate that exchange between different liquid crystal director axes is faster than gas to liquid crystal exchange. Xenon atoms are therefore exchanging between different environments within a single pore. One possible mechanism for this is that if the observed one-dimensional line shape (Figure 2a) is representative of a single pore, then the xenon may remain bound near the liquid crystal/anopore interface for times around 20 ms and then rapidly diffuse through the pore until binding at another interface site where there is a different director orientation. This possibility relies on unreasonably long surface residence times and thus appears unlikely.

If the distribution of directors were from different pores, the observed exchange would dictate that the average environment experienced by the xenon within each pore must be varying on

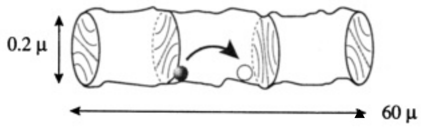

Figure 7. Schematic picture of the director structure within a single pore experienced by the xenon atoms in the 2D exchange experiment.

the time scale of ~20 ms. Director order fluctuations of the liquid crystals within a pore appear unlikely because of the time scale of the slowest reorientation mode, $1/\tau \approx Kq^2/\eta$ where $q \cong \pi/r = 30\ \mu\text{m}^{-1}$.[22] Inserting typical values for $K = 10^{-11}$ N and $\eta = 10^{-2}$ N s/m^2, one obtains $\tau = 10\ \mu$s, which is much too short to account for the appearance of off-diagonal intensity (~20 ms).

A more probable mechanism is a change in the orientation of the symmetry axis of the configuration along the cylinder axis due to random changes in surface roughness and ellipticity of the cylinders. These deviations are thought to be the cause of the random distribution of director axes observed in this study as well as previous deuterium NMR studies.[35] At $\tau_m = 20$ ms an estimated 25% of the xenon has undergone a reorientation of its director axis. Using the diffusion constant of 2×10^{-10} m^2/s, the root-mean-square distance traveled by a xenon atom along the cylinder is 2 μm in 20 ms. This defines the length scale between random variations of director domains within each pore. Such an exchange mechanism is illustrated schematically in Figure 7.

Diffusion is also responsible for the appearance of exchange between the dissolved and gas phase xenon. At a mixing time of 400 ms, about 20% of the dissolved xenon has appeared in the peak assigned to the susceptibility-shifted gas between the membranes. The root-mean-square distance along the cylinder axis during this time interval is calculated to be 9 μm (compared to 60 μm total length), a reasonable estimate given the rough nature of the calculation.

Conclusions

It has been shown that xenon NMR studies of microconfined liquid crystals are feasible and supply new information about such systems. The two xenon isotopes offer different observables with which to probe the liquid crystal system. Additional insight is gained by comparison of confined liquid crystals to bulk studies. In the 1D studies the main difference between confined and bulk liquid crystal is the slightly decreased chemical shift anisotropy of ^{129}Xe at the nematic to isotropic transition and slightly enhanced quadrupolar splitting of ^{131}Xe. The difference in quadrupolar splitting could be due to the additional effects of the cavity walls on the polarization of xenon atoms or a change of the liquid crystal order parameter at the wall.

Multidimensional experiments offer new possibilities for obtaining information on these systems. Two-dimensional exchange spectroscopy allows much longer time scales (and thus length scales) to be probed and suggests the presence of variations of the symmetry axis of the director within a single cavity on a length scale of 2 μm. Finally, the xenon NMR methods in this paper could be used to investigate surface-induced order in the isotropic phase[36] and studies of other confined systems such as liquid crystals loaded in silica aerogels.[37]

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