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Reorientations Mediated by Translational Displacements in Confined Liquid Crystals Studied by Field Cycling NMR Relaxometry and Monte Carlo Simulations

Farida Grinberg

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Germany

Corresponding author:
Farida Grinberg
University of Leipzig, Department of Physics,
Linnéstrasse 5, 04103 Leipzig, Germany
E-Mail: grinberg@uni-leipzig.de

Abstract

Ordering effects and low-frequency molecular dynamics in the nematic liquid crystals confined in mesoscopic pores was studied with the help of field cycling (FC) Nuclear Magnetic Resonance (NMR) relaxometry and Monte Carlo simulations. Proton relaxation rates were measured above the bulk isotropisation temperature in the broad frequency range between 2 kHz and 7 MHz. The average pore radii of confinements were between 1.5 and 15 nanometers. The relaxation dispersion curves in the confined materials exhibited strong deviations from the behaviour in bulk. In a few kHz range, a dramatic enhancement of the relaxation rates exceeding two orders of magnitude compared to the bulk sample was observed. The low-frequency value of the relaxation rate exhibited a strong dependence on the pore size. Experimental findings were interpreted in terms of the surface induced orientational order and diffusion between the sites with different orientations of local directors. The analysis was supported by Monte Carlo simulations of the reorientations mediated by translational displacements (RMTD) in spherical cavities.

1. Introduction

In recent years, molecular ordering of soft systems on the meso- and macroscopic length scales has been successfully exploited in molecular engineering and in production of new materials with predefined properties. Molecular ordering is in turn accompanied by multiple molecular (individual or collective) dynamic processes that tend to range over many time decades. While structure properties of these materials are rapidly getting more and more accessible due to advances in optical and scattering techniques, one of the challenging related problems refers to understanding of their complex dynamic features at the molecular level and addressing the relationship between structure, dynamics and function with a predictable power.

Specific functionalities of new materials often exploit self-assembling and molecular ordering properties on the meso- and macroscopic length scales. This also refers to liquid crystals confined in nano-structured materials used in electro-optical applications and in sensors. In particular, liquid crystalls constrained in micro- or nanoscaled environments with solid interfaces, tend to exhibit partial orientational order [1, 2] induced by surface interactions. This type of ordering can extend over mesoscopic length scales and persists well above the bulk isotropisation temperature, T_{NI}.

NMR has proven to provide powerful tools for studying confined liquid crystals [3]. Especially informative in this context are the methods permitting one to access molecular dynamics in the low-frequency limit down to a few kHz. In soft materials, the low frequency scale is characteristic of the unique mechanisms of (collective or individual) molecular motions that are not observed in liquids of low viscosity. The prominent examples are given by the so-called Orientational Director Fluctuations in nematics or long back-bone reptation-like motions of macromolecular chains. Another example is given by the so-called RMTD mechanism observed in polar liquids [4, 5] and liquid crystals confined in mesoscopic pores. In the case of polar liquids under strong adsorption conditions, diffusive displacements along the surface are described with non-Gaussian propagators and are characteristic of the super-diffusive time dependence of the mean-square displacement values. In the case of liquid crystals, molecular ordering occurring at the interfaces gives rise to the long-lived correlations in re-orientational dynamics of molecules.

One of the most powerful NMR techniques which permits one to probe low frequency dynamics in the range covering several orders of magnitude is given by the field cycling relaxometry [4]. The natural extension of the FC relaxometry to even longer time scales is provided by the technique known as the Dipolar Correlation Effect on the stimulated echo [6, 7]. Also, the long time scale translational molecular dynamics can efficiently be probed in diffusion studies using strong pulsed magnetic field gradients [8, 9]. Worth noting is, however, that the surface-layer molecules in confined systems are not easily accessible in direct diffusion studies because typically their relative fraction in the whole sample tends to be too small for a direct detection.

In this contribution, I am going to examine ordering effects in confined liquid crystals with the help of FC NMR relaxometry and Monte Carlo computer simulations. Confining materials were porous glasses with pore sizes in the mesoscopic range where the surface constraints are the strongest.

2. Materials and methods

Samples studied were Controlled Porous Glasses (CPG) and Bioran Glasses filled with nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl (5CB). T_{NI} of 5CB is 308.5 K. The mean pore radii of the CPG samples denoted as CPG-1.5 and CPG-4 were 1.5 nm and 4 nm, respectively. The mean pore radii of the Bioran samples denoted as Bioran-5 and Bioran-15 were 5 nm and 15 nm, respectively. Frequency dependences of the spin-lattice relaxation rates, T_1^{-1}, were measured at 323 K with the help of a home-built FC relaxometer at the University of Ulm, Germany.

3. Monte Carlo Simulations

Simulated dipolar correlation functions are defined as

$$G_k^{red}(t) \equiv \frac{\left\langle Y_{2,k}(0) Y_{2,k}{}^*(t) \right\rangle}{\left\langle Y_{2,k}^2(0) \right\rangle}, \qquad (1)$$

where $Y_{2,k}$ (k=0,1,2) are second order spherical harmonics describing the instantaneous orientation of the internuclear vector relative to the external magnetic field. Random-walk Monte Carlo simulations were performed for a spherical cavity of a given radius, R. In each cycle time, $\Delta t << t$, a random step of a fixed length, $\Delta l << R$, was generated and $G_k^{red}(t)$ was evaluated as described in References [10, 11]. All relevant time and length scales are expressed in terms of the predefined values of Δl and the diffusion coefficient, D. The (predefined) value of the diffusion coefficient was equal to 10^{-10} m^2s^{-1}, the step length was set to 0.2 nm.

The simulated correlation functions were used to evaluate the laboratory frame spin-lattice relaxation rates [12]:

$$\frac{1}{T_1(\omega_0)} = K\left[I_1(\omega_0) + 4I_2(2\omega_0)\right], \qquad (2)$$

where ω_0 is the Larmor frequency, $K = \frac{3}{20}\gamma^4\hbar^2 r^{-6}\left(\frac{\mu_0}{4\pi}\right)^2$, γ is the gyromagnetic ratio of the nuclei, $\hbar$ is the Planck constant divided by 2π, r is the internuclear distance, and

$$I_k(\omega) = \int G_k(t)\exp(i\omega t)dt. \qquad (3)$$

4. RMTD and the exchange model

Effects of surface ordering on nuclear magnetic relaxation were analysed for a simple spherical geometry under consideration of the two-phase exchange and RMTD processes. Within the sphere, two areas are distinguished: a) the isotropic bulk-like area inside the sphere and b) the surface-ordered layer of thickness δr. Generally, the total correlation function $G_k^{red}(t)$ can be decomposed in four partial correlation functions [10] related to the two fractions of molecules initially and finally in the same phase (surface layer or bulk) and the two fractions of molecules initially and finally in different phases. Any correlations occurring in the bulk-like area were not considered, anticipating that molecular reorientations in this phase are isotropic and fast and thus do not contribute to the observed relaxation. In practice, this was realized by replacing the spherical harmonics by zero any time when a spatial position of the molecule was in the bulk-like area. Within the surface-ordered layer, the current value of Y_{2k} was determined by the preferential orientation (in this case, perpendicular) relative to the surface at the instantaneous position of the random walker. Under these conditions, $G_k^{red}(t)$ reduces to [10]:

$$G_k^{red}(t) = f_{s,s}\left\langle Y_{2.k}(0)Y_{2.-k}(t)\right\rangle_{RMTD}, \qquad (4)$$

where $f_{s,s}$ is the fraction of molecules being initially and finally in the surface layer. The abbreviation RMTD stands for the mechanism [4, 5] describing molecular reorientations due to diffusion between the surface sites with different preferred molecular orientations (different directors of the surface order). Between times 0 and t, the correlation to the initial molecular orientation in the surface layer may temporarily be lost, as molecules perform extended excursions to the bulk-like area, but it tends to restore at much longer times, as molecules repeatedly return to the ordered layer and adopt the preferential orientations again. The correlation function for the RMTD process thus depends on such factors as the surface topology, geometry of the pore space, molecular diffusivity and interactions with the surface.

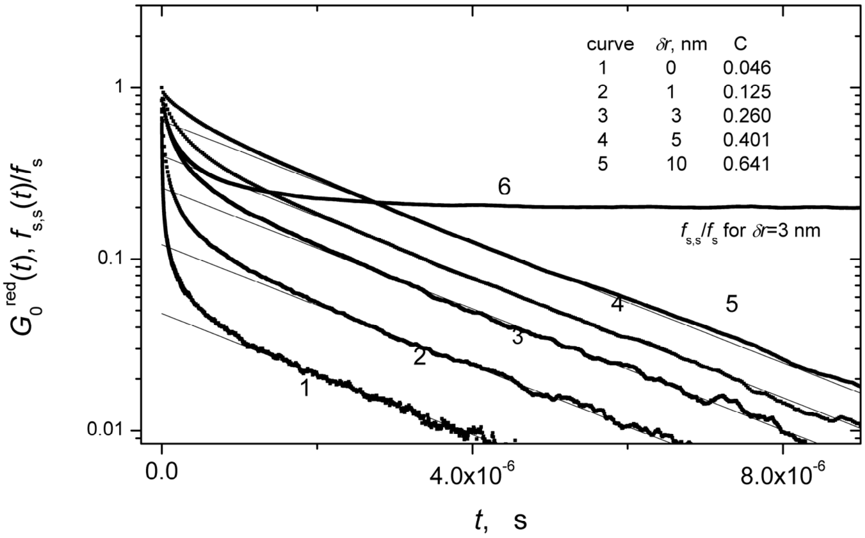

Figure 1. Monte Carlo simulations of the correlation function, Eq. (1), for k=0, curves 1-5. The straight lines are fits of the function $C\exp(-t/\tau_{RMTD})$ to the long tails of the simulated functions. The values of C and δr are indicated in the inset. Curve 6 represents the (normalized) exchange-loss factor, $f_{s,s}(t)/f_s$, for δr = 3 nm.

The fraction $f_{s,s}$ is generally a function of time. At very short times, for which the probability of the exchange between the ordered and the bulk-like populations tends to zero, $f_{s,s} \approx f_s$, where f_s is the (constant) population of the surface layer. At long times, for which the initial and final probabilities to be in the surface layer become independent of each other, $f_{s,s}(t) \approx f_s^2$. The function $f_{s,s}(t)$ in Eq. (4) thus decays from the initial value f_s to the value f_s^2 and resembles an exchange-loss process, that is, the loss of molecules populating the surface phase at time 0 but being rather in the bulk-like phase at time t.

3. Results and Discussion

Figure 1 shows typical shapes of the reduced correlation functions, Eq. (1), simulated for a sphere of R = 50 nm and different values of δr, curves 1-5. The correlation functions clearly exhibit two components with different characteristic decay rates. The initial fast loss of correlations ($t < 10^{-6}$ s) is due to the exchange losses represented by the factor $f_{s,s}(t)$. The long-time tails of the correlation functions are not affected by the exchange losses and are governed entirely by the RMTD process, that is, they are controlled by orientations adopted by the random walker in the surface ordered layer.

Two components of the correlation function can be distinguished by repeating the simulation with the RMTD mechanism inactivated, i. e., assuming a constant fixed molecular orientation at any position of the surface layer. In this case, the simulation results, Eq. (4), represent merely the function $f_{s,s}(t)$. The latter is demonstrated in Fig. 1 by curve 6 for δr equal to 3 nm. The crossover from the initial value to the constant value in the long-time limit is clearly distinguishable and gives an estimate of the mean exchange time between two phases. For the simulation conditions used in Fig. 1, the mean exchange time is of the order of 10^{-6} s.

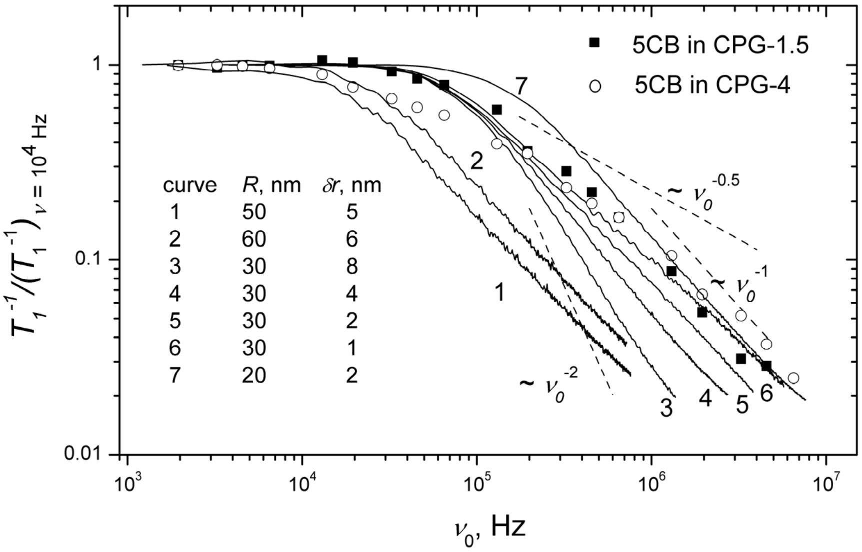

Figure 2. Normalised frequency dependencies of the spin-lattice relaxation rates, curves 1-7, evaluated from the simulated correlation functions. The curve parameter refers to different values of δr and R. The experimental data points refer to 5CB in CPG-1.5 and CPG-4 at 323 K.

The long-time tails representing the correlation function of the RMTD mechanism, $\langle Y_{2,k}(0)Y_{2,-k}(t)\rangle_{RMTD}$, can be well fitted by an exponential function, $C\exp(-t/\tau_{RMTD})$, where the time constant, τ_{RMTD}, was fitted to $2.4 \pm 0.24 \times 10^{-6}$ s. The fits are shown as the straight lines in Fig. 1. The values of the pre-factor C depend on the thickness of the oriented layer (or on the population of the ordered molecules) as shown in the inset of Fig. 1.

Figure 2 shows the simulated frequency dependences of T_1^{-1} normalized by the low-frequency values, curves 1-7. Simulation data are shown for various thicknesses δr within a cavity of the same size (R = 30 nm), curves 3-6, and for the cavities of different sizes (R = 60 nm, 50 nm, 20 nm), curves 1, 2 and 7. Figure 2 shows that, given the same cavity size, the width of the surface-ordered layer strongly affects the dispersion slopes, compare curves 1-4, but not the cut-off frequency of the dispersion (the cross-over between the plateau and the power-law dependence). As demonstrated in Fig. 2, the slopes "span" the power laws between ν_0^{-2} and $\nu_0^{-0,5}$ represented graphically by the straight lines. Thinner layers are characteristic of flatter slopes as a result of the increasing relative fraction of the bulk-like phase. Increasing the pore radius shifts the cut-off frequency towards lower values but does not considerably affect the slope, provided that the thickness of the ordered layer remains in the same proportion to the pore size.

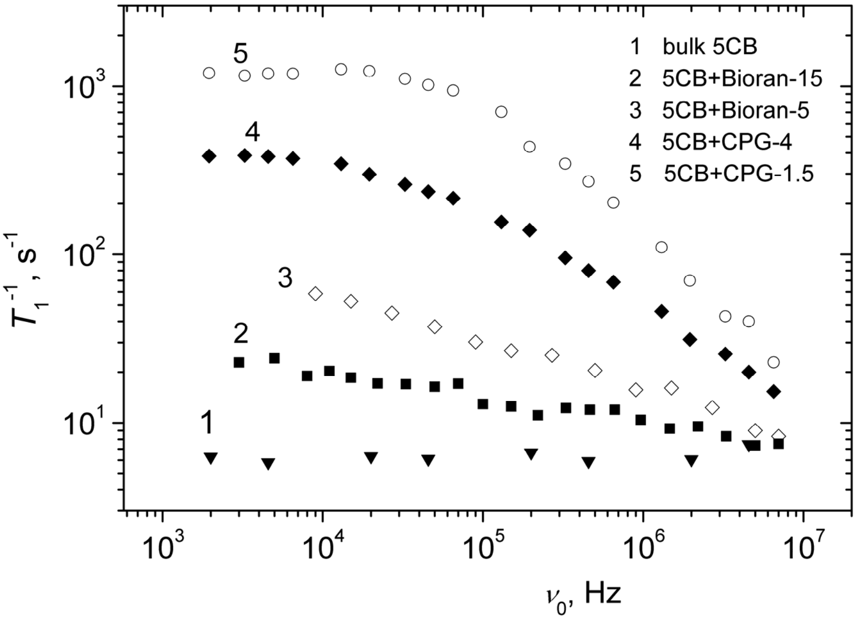

Figure 3. Experimental frequency dependencies of the spin-lattice relaxation rates of bulk 5CB and 5CB confined in CPG-1 and CPG-4 and in Bioran-5 and Bioran-15.

Experimental relaxation rates of 5CB confined in CPG and Bioran glasses are shown as a function of the Larmor frequency in Fig. 3 in the range between 2 kHz and 7 MHz. The measuring temperature was 323 K well above T_{NI}. A strong impact of confinements on the low-frequency behavior of the relaxation rates was observed. That means, in contrast to bulk 5CB where the relaxation rates are practically independent of the frequency (as typically expected for ordinary liquids below the megahertz range), the confined samples exhibit a pronounced dispersion. At the lowest frequency limit, the values of T_1^{-1} were the highest for the sample with the smallest pore size (1.5 nm) and exceeded that of bulk 5CB by more than two orders of magnitude. Increasing the pore size resulted in a dramatic decrease of the relaxation rates.

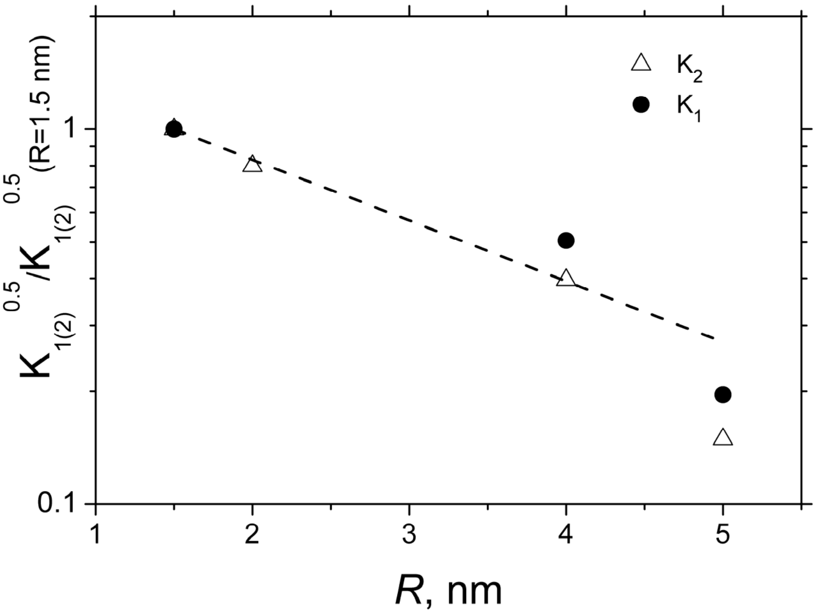

Figure 4. Normalised values of square root longitudinal (K_1) and transverse (K_2) relaxation rates of 5CB in pores as a function of the pore radius.

Strong enhancement of the relaxation rates in the kHz range in the confined samples can be attributed to the orientational ordering at the surface and the RMTD mechanism. The orientational anisotropy stabilized by solid interfaces prevents a complete averaging of dipolar interactions by molecular motions. Diffusion between the regions with different surface orientations and different levels of orientational anisotropy then produces a strong relaxation mechanism in the kilohertz frequency range. This mechanism is also relevant for the transverse relaxation [11, 13].

The Landau-de Gennes theory predicts that the order parameter decreases exponentially with increasing distance, r, from the wall as

$$S(r) \propto \exp\left(-\frac{r}{\xi}\right) \tag{5}$$

where S is a local order parameter, ξ is the characteristic decay constant called the nematic correlation length. The relaxation rates are generally proportional to the square of the (residual) dipolar couplings. As shown in the Reference [2], in confined liquid crystals above T_{NI} the square roots of the relaxation rates then appear to be proportional to S.

The nematic correlation length in the investigated materials was roughly estimated in Reference [13] as approximately 3 nm at 313 K. In CPG-1.5, therefore, the dominating fraction of confined molecules should exhibit a relatively strong ordering. In samples with larger pores, that is, in CPG-4 and Bioran glasses, the interior middle area is essentially less ordered, and the relative fraction of the more "bulk-like" fraction increases for bigger pores. Consequently, the decrease of the relaxation rates with increasing the pore size is due to the averaging effect of translational molecular diffusion between the regions with different degrees of local anisotropies. This finding complies with the earlier reported measurements of the transverse relaxation and cross-relaxation rates [13, 14] in the CPG samples.

Figure 4 shows the pore size dependence of the square roots of the longitudinal relaxation rates in the low frequency limit (at approximately 10 kHz) in comparison to that of the transverse relaxation rates. The latter were earlier used for the estimation of the nematic correlation length [11]. The similarity in the behavior of both relaxation rates as a function of the pore size allows one to conclude that transverse and longitudinal relaxation at low frequencies are governed by the same mechanisms and that the field cycling relaxometry is well suited for the quantitative study of interfacial ordering occurring in confined liquid crystals.

The normalized dispersion curves of the CPG samples at 323 K are shown once again in Fig. 2 together with the simulated data. The low frequency value of T_1^{-1} of the bulk sample was subtracted from the measured values of the relaxation rates of the confined samples in order to account for the contribution of fast bulk-like motions (not taken into account in the simulations). The experimental dispersions cannot be described as a Lorentzian type mechanism (slope –2) but rather exhibit power law frequency dependences with slopes between –1 and –0.5. This correlates with the results reported in the Reference [15] for 5CB confined in much bigger, compared to our samples, pores of 72 nm. As shown in Reference [15], the RMTD mechanism gives rise to the inverse square root frequency dispersion.

The cut-off frequency observed for the CPG glasses corresponds to much bigger radii used in the simulated data than their actual pore sizes. This is, however, not surprising since diffusion in our samples is not restricted to a single cavity. During the typical observation time, the molecules probe much larger distances (exceeding 100 nm) of the random pore space compared to the pore radii. The cut-off frequency, however, permits one to get an estimate of the effective curvature (or the smallest cut-off wave number) probed by diffusing molecules which is of the order of a few tenths of nanometers [14].

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