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Diffusion studies in confined nematic liquid crystals by MAS PFG NMR

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ABSTRACT

Pulsed field gradient (PFG) NMR and magic-angle spinning (MAS) NMR have been combined in order to measure the diffusion coefficients of liquid crystals in confined geometry. Combination of MAS NMR with PFG NMR has a higher spectroscopic resolution in comparison with conventional PFG NMR and improves the application of NMR diffusometry to liquid crystals. It is found that the confinement of the liquid crystal 5CB in porous glasses with mean pore diameters of 30 and 200 nm does not notably change its diffusion behavior in comparison with the bulk state.

1. Introduction

Liquid crystals (LC) in confined geometries attracted much attention of scientists due to their application in electro-optical devices and sensors [1–3]. In contact with solid surfaces, the LCs gained a significant importance also in biomedical applications [4]. A rapidly growing interest in these systems during the last decade was caused by their exploitation in synthesis of novel nanostructured materials using a procedure called "liquid crystal templating" [5–7]. Fabrication of these materials with tailored functionalities is based on the use of ordering properties of the LCs which serve as the self-organized templates for a specific alignment of the material particles.

Molecular dynamical and transport properties of the LCs and their interactions with solid interfaces play an important role for final material properties both in electro-optics and in guided synthesis. However, whereas re-orientational dynamics of the confined LCs was extensively probed by various NMR techniques [8–10], their self-diffusion remains very poorly investigated. One of the main difficulties of performing diffusion experiments is due to the relatively strong residual dipolar interactions remaining in these systems. The general problem is that although the internal molecular dynamics is fast, anisotropic orientation of molecules along the local symmetry axis prevents a complete averaging of dipolar couplings on the time scale of the NMR experiments [11]. This in turn leads to fast attenuation of the transverse magnetization which hinders an application of the conventional diffusion techniques, such as Pulsed Field Gradient (PFG) NMR [12–14]. The latter technique relies on the implementation of the field gradient pulses between the r.f. pulses which should have a time separation of at least a few milliseconds [15]. If transverse relaxation time is below this limit, as it is typically the case in many LCs, measuring diffusion with the help of pulsed field gradients becomes difficult and demands implementation of sophisticated line-narrowing techniques [16,17]. The application of the alternative NMR diffusometry technique employing the fringe magnetic field gradient [18] and allowing for short r.f. pulse separations is hindered by the so-called Dipolar Correlation Effect [19,20] which becomes the dominating mechanism of echo attenuation and masks any effect caused by translational diffusion.

Several modifications of the PFG NMR method including nematic and solid echoes [15,21], dipolar decoupling [15,21,22], magic-angle sample orientation [15,23], and a combination of multipulse dipolar decoupling in addition to the stimulated echo [17,24] were suggested to overcome the above-mentioned difficulties. The most accurate value of the diffusion coefficient in liquid crystals was obtained by using a gradient slice selection, stimulated echoes and a multipulse homonuclear decoupling [16,17,25].

An alternative novel technique, usually abbreviated as MAS PFG NMR, combines magic-angle spinning (MAS) with the pulsed field gradients [26–31]. MAS implies the orientation of the axis of a fast spinning sample in an angle of $\theta_m \approx 54.7^\circ$ with respect to the external magnetic field. This has two advantages. First, the

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increased resolution in the ppm-scale permits one to observe separately each individual group with identical electronic surroundings. Second, the enhanced transverse relaxation time under MAS conditions allows for a sufficient time for the implementation of the pulsed magnetic field gradients. The application to liquid systems should be performed carefully since the measured self-diffusion coefficient tends to deviate from its intrinsic value at higher MAS frequencies [32].

In this work we apply the MAS PFG NMR technique to a confined liquid crystal 4′-pentyl-4-cyanobiphenyl (5CB). This nematic LC has been most extensively studied in the literature and established itself as the classical model system for investigation by NMR. Dynamic properties of the confined nematic liquid crystal 5CB has been studied by several NMR techniques, including NMR deuterium spectrometry and relaxometry [8,33], the Dipolar Correlation Effect [20] and Field Cycling Relaxometry [34–36]. However, no NMR diffusion measurements were performed so far rather than that above the isotropization temperature [37] where the relaxation times become long again. The primary aim of the current study is an extension of the novel MAS PFG NMR method to the class of systems with short relaxation times where conventional pulsed field gradient diffusometry would fail. This application is exemplified for the confined nematic 5CB which exhibits particularly short relaxation times, of the order of a few hundreds of microseconds [35].

2. Experimental

NMR measurements were performed on a Bruker AVANCE spectrometer operating at 750 MHz with a wide-bore magnet and a 4-mm-MAS-probe with pulsed field gradient capabilities. The MAS frequency was ν_{rot} = 10 kHz and the nutation frequency of the radio frequency (r.f.) power was $\nu_{r.f.}$ = 100 kHz. The maximum gradient strength in this system is 0.54 T m^{-1}. Diffusion measurements were performed using the stimulated-echo sequence with bipolar sin-gradient pulses and eddy current delay before detection, see Fig. 1. The signal attenuation for single-component isotropic diffusion is given by [38]

$$S = S_0 \exp\left[-D\left(\frac{4\delta g\gamma}{\pi}\right)^2\left(\Delta - \frac{\tau}{2} - \frac{2\delta}{3} - p_\pi\right)\right] = S_0 \exp(-Dk)$$

where D denotes self-diffusion coefficient, γ the gyromagnetic ration, δ the gradient pulse width, Δ the observation time, τ the inter-gradient delay, and p_π the duration of the π-pulse. The factor k is defined by the equation above. The delay between gradient pulse and subsequent r.f. pulse was 500 μs. The durations of the dephasing and rephasing periods and the spacings between alternating pulses are multiples of the rotor period. Sine-shaped gradients with 2 ms duration were applied.

Diffusion experiments were carried out by varying the strength of the gradient pulses in the linear range between 10% and 90% of their maximum value (0.54 T m^{-1}).

The MAS-induced temperature gradient was determined by means of a ^{207}Pb NMR thermometer [39]. Fig. 2 shows two signals measured at T = 300 K. The dashed spectrum in Fig. 2 corresponds to a 4-mm-rotor filled with a 1.5 mm thick layer of $Pb(NO_3)_2$ in the middle and ^{207}Pb NMR insensitive material (zeolite powder) above and below. The solid spectrum corresponds to a fused glass sample, which was filled with $Pb(NO_3)_2$ in a length of 8 mm. A temperature gradient of about 5 K over a length of 8 mm is obtained from the shift/temperature equation 0.775 ± 0.007 ppm K^{-1} [40]. Therefore, our measurements of samples in fused glass ampoules were performed with a large temperature gradient. The consequence is that, as a matter of principle, a sharp jump of the NMR parameter (at the phase transition temperature) cannot be observed by MAS NMR of larger samples. Therefore, we focus our studies to temperatures, which are about 10 K above or below the well-known phase transition temperature. Some measurements of the bulk material were performed with 5CB in a half full 12 μL-rotor. The temperature gradient is less than ±0.5 K for the volume in this rotor, which is small compared to the volume of about 35 μL in the fused glass ampoules with an outer diameter of 3 mm, and a length of 10 mm.

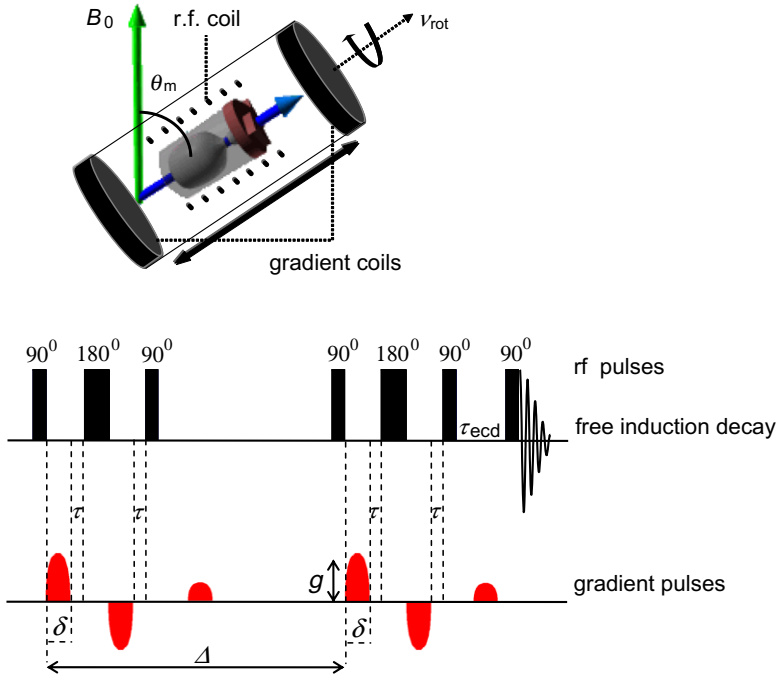

Fig. 1. The MAS design combined with two coils for the pulsed field gradients in a high-resolution MAS NMR probe (top). Radio frequency (r.f.) and gradient pulse scheme of the MAS PFG NMR experiment is shown below. The parameters are diffusion time Δ, gradient pulse width δ, gradient pulse strength g, eddy current delay τ_{ecd}, inter-gradient delay τ. Two weak sine-shaped spoiler gradients (about 0.15 T m^{-1}) average undesirable coherences.