IDE💥L®

Anisotropic Diffusion in a Nematic Liquid Crystal—
An Electric Field PFG NMR Approach

Peter Holstein, Michael Bender, Petrik Galvosas, Dieter Geschke, and Jörg Kärger

Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstrasse 5, D-04103 Leipzig, Germany

The access to self-diffusion coefficients in anisotropic systems such as thermotropic liquid crystals by means of PFG NMR is complicated by strong dipolar interactions. Additionally, problems arise due to the immediate orientation of low-molar-mass nematic liquid crystals in an external field. The director orientation can be changed by the application of an additional electric field. This can be exploited in order to reduce the dipolar interaction to such an extent that the NMR linewidths change from a solid-state to a liquid-like situation enabling PFG NMR experiments. © 2000 **Academic Press**

Key Words: **PFG NMR; electric fields; self-diffusion coefficient; reorientation; liquid crystals.**

INTRODUCTION

The ^{1}H NMR linewidth of liquid crystals is dominated by the strong dipolar interactions among the protons. Typically, the splitting of the linewidth (PAKE doublet) may be some 10 kHz wide. Nematic liquid crystals tend to orient immediately in the magnetic field B_0 of an NMR spectrometer due to their anisotropic magnetic properties. In the case of a positive diamagnetic susceptibility ($\Delta\chi > 0$) the director of the sample aligns parallel to the external field. Contributions to the linewidth $\Delta\nu$ have, according to the relation

$$\Delta\nu \propto (1 - 3\cos^2\theta), \qquad [1]$$

the largest value if the (averaged) internuclear vector is just parallel to the magnetic field. θ denotes the angle between the director of the nematic phase and the magnetic field. Direct access to self-diffusion coefficients is not possible because of the extremely fast decaying transverse magnetization in the order of 20 μs. There were several promising attempts made to remove dipolar interactions in PFG experiments in order to enable long transverse relaxation times, which are discussed in the review of Krüger (*1*). The orientation achieved in a nematic phase can be maintained by cooling in smectic phases. Because the dipolar interaction is anisotropic a change of the sample orientation relative to the magnetic field can reduce the dipolar interaction to such an extent that PFG NMR experiments become possible (*1*). However, to achieve the necessary accu-

racy, a goniometer for adjusting the "magic" angle is needed. The measurement of the complete anisotropic tensor information requires a change of gradient direction in PFG NMR experiments. A more demanding approach is the combination of PFG NMR experiments with multiple-pulse line narrowing techniques (*2–5*) in order to reduce the dipolar interaction as exemplified for smectic liquid crystals. This would enable, in principle, an access to the diffusion coefficient which is independent of the angular dependent dipolar interaction. In nematic liquid crystals, there remains the possibility of changing the relative orientation between the sample and magnetic field gradient, e.g., by varying the direction of the gradient **G**. In our case the gradient of the probe has a fixed direction $\mathbf{G}_z$. The second option would be a change of the sample orientation, which is difficult in the case of nematic liquid crystals.

In this paper, a technique is reported for the measurement of the diffusion coefficient in nematic liquid crystals which can be simultaneously oriented by means of magnetic and electric fields. Magnetic and electric torques are in competition (*6–8*). The director orientation can be stabilized in any angle relative to the magnetic field or its gradients. The equilibrium angle depends on material parameters ($\Delta\epsilon$, $\Delta\chi$), the strengths of the magnetic and electric field, and the angle between the torques (*8*). This electrically induced orientation can be used to minimize the ^{1}H NMR linewidth to such an extent that PFG NMR experiments seem to be possible.

EXPERIMENTAL

The NMR experiments have been carried out using different spectrometers. Lower magnetic fields would be favorable for experiments with competing magnetic and electric fields. For preparing experiments, a 100-MHz spectrometer (Bruker MSL100) has been used. A probe with short ring-down delays operating only at the proton frequency with improved background conditions (Bruker - HP FF 100WB 1H sol5) and a laboratory-made probe, especially designed for electric field NMR experiments, were used. The latter enables one to change the angle between the fields during the experiments. The resonance frequency of 100 MHz is a compromise regarding the NMR sensitivity and the balance between the magnetic torque
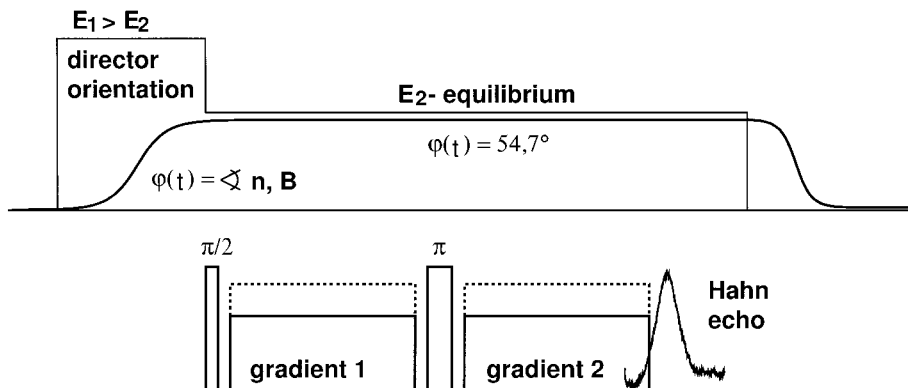
FIG. 1. Design of the electric field experiment in combination with the Hahn-echo PFG NMR sequence. The pretrigger starts the orientation 20–50 ms before the first $\pi/2$-pulse in order to avoid a permanent application of the voltage. During the PFG NMR experiment and data acquisition a lower voltage is used in order to achieve a static orientation. The $\varphi(t)$ curve indicates schematically the change of the angle between the director of the liquid crystal and the magnetic field.

($\propto \mathbf{B}_0^2$) and the electric torque ($\propto \mathbf{E}^2$) (6, 8). The rising influence of the chemical shift at higher magnetic fields can also complicate the interpretation of the spectra. Additionally, magnetically caused reorientations could hamper the observation of electrically induced effects at higher fields. However, mainly for the reason of sensitivity, the PFG NMR diffusion experiments have been performed on a spectrometer operating at 400-MHz proton frequency (9). The electric excitation of the samples has been realized by means of laboratory-made equipment for a special high-voltage design. We achieved an approximately rectangular-shape 1-kV output in the range of 100 μs to 50 ms with rise times of 20 μs. A schematic illustration of the combination of the PFG NMR sequence with the electrical orientation timing is given in Fig. 1.
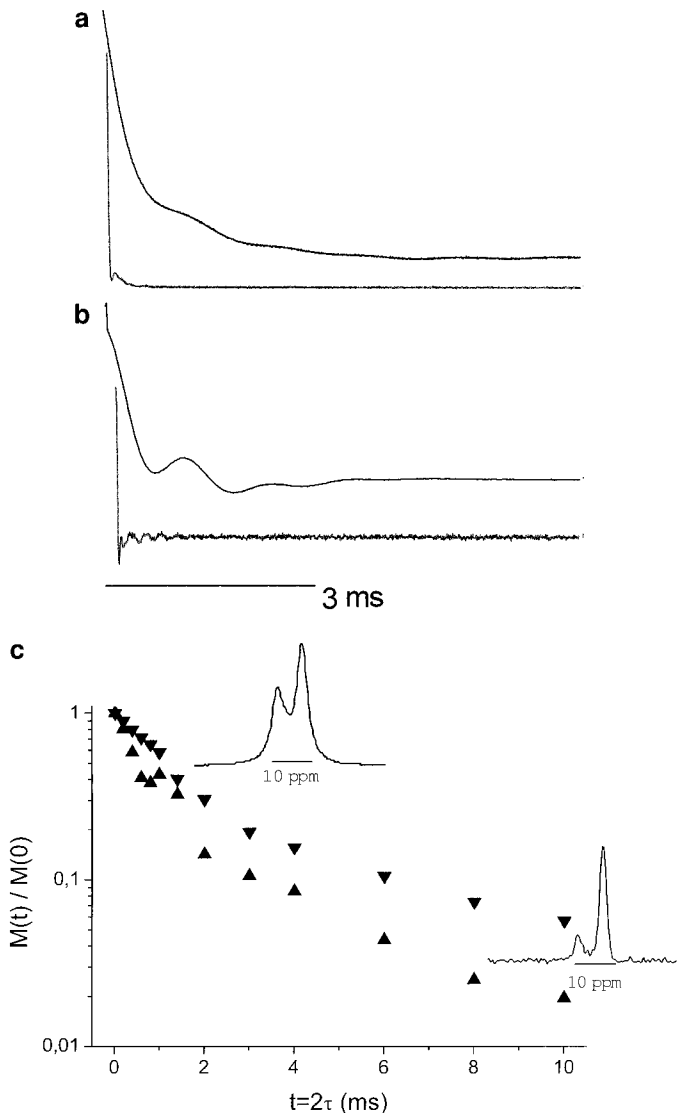
Because relatively high voltages are required to provide the necessary field strength, the investigations must be carried out on thin capacitor samples with a thickness in the order of 100 μm. Deterioration of the signal-to-noise ratio caused by the electrical connections of the sample must be taken into account. The sensitivity gets worse because of the drastically reduced filling factor. Turbulences due to electric currents are avoided by (i) the high ohmic resistance of the material in the cells being in the order of some MΩ and (ii) by the short-time application of the voltage. For test purposes, the nematic liquid crystal p-pentyl-p'-cyanobiphenyl (5CB/E. Merck, Darmstadt, Germany) has been filled in a capacitor cell. This substance is nematic between 22.5 and 35°C. The magnetic and dielectric anisotropies are positive ($\Delta\epsilon \approx 12$ at 1 kHz, $\Delta\chi(10^{-6}) \approx 4.0$ at 20°C) which enables one to produce a uniform director orientation even in the presence of two fields. For comparison, the liquid crystal ZLI 3654 (also obtained from Merck) has been used which has a smectic A phase between 60 and 76°C.

RESULTS

The reduction of the dipolar interaction could be demonstrated for the smectic A liquid crystal, achieved by a mechan-

ical rotation of the sample in the magic angle and for a nematic liquid crystal in a capacitor cell as well. The narrowing factor is for 5CB in the order of 150 (30 kHz to 200 Hz). This enables the observation of the chemical shift in the spectrum. The resonances of the aliphatic and phenyl parts of the molecules are clearly resolved even at 100 MHz. Anisotropy effects of the chemical shift are in the order of 2 ppm (7) and do not influence the PFG NMR experiments. Similarly, the prolongation of relaxation which is necessary in order to carry out a PFG NMR experiment has been proved in a Hahn-echo experiment (Fig. 2) in the order of 40 μs for parallel orientation. The reduced dipolar interaction in the optimized magic angle situation gives a $T_{2\mathrm{Hahn}}$ which is long enough to involve gradient pulses. Small changes in the director orientation yield a drastically reduced $T_{2\mathrm{Hahn}}$. Originally, the electric field approach has been developed in order to observe fast reorientation processes in liquid crystals (6). Regarding the fact that the reorientation phenomena are influenced by collective molecular properties some domain properties could influence diffusion data. A possible spatial displacement by electrically or magnetically induced rotation (the externally induced reorientation) would be in a similar order as it can be accessed in diffusion measurements. Therefore, the stabilization of the adjustment in the Hahn-echo experiment for long τ-values has been taken as an indication of the quality of the stability of the orientation. An unstable orientation during the Hahn-echo decay affects the first term in Eq. [2]. This would provide an additional attenuation in the Hahn-echo envelope which appears only at signal magnitudes below 1‰ ($2\tau \approx 50$ ms). The attenuation in the PFG NMR experiment based on the Hahn-echo sequence is given by

$$M(t = 2\tau) = M_0\left[\exp\left(-\frac{t}{T_{2\mathrm{Hahn}}}\right)\exp\left(-\frac{1}{2}\,\gamma^2\delta^2 g^2\langle z^2\rangle\right)\right],$$
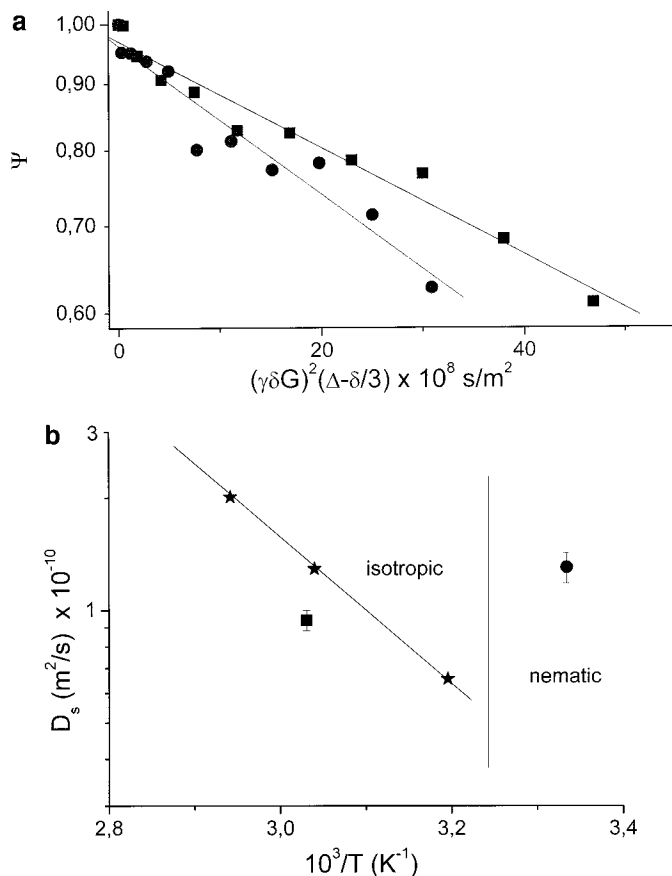
[2]

The prolongation of the relaxation in the Hahn-echo experiment and of the FID enables the use of the PEG NMR technique on electrically oriented nematic liquid crystals even in the case of weak NMR signals. Due to the technical specifications of the diffusion NMR probes (longer ring-down delays) there is only an echo signal available for the adjusted magic angle situation. The PFG NMR experiment with simultaneously applied electrical field is shown in Fig. 3.

For the adjustment of the magic angle in the magnetic field of 9.4 T, 240 V must be applied on the 200-μm sample. The angle between the normal of the electrode and $\mathbf{B}_0$ was 84°. This voltage was kept constant during the PFG NMR experiment and switched off immediately after the data acquisition. A higher voltage has been used in order to rotate the director (20 ms pretrigger, 300 V). The detection of the signal at larger gradients is complicated by the worse signal-to-noise ratio due to the use of the electrically contacted capacitor cell, but it should be emphasized that no specific

FIG. 2. The prolongation of the FID and the echo decay by changing the orientation relative to the magnetic field (100 MHz). (a) FIDs of the liquid crystal *ZLI 3654* at 65°C at $\theta = 0°$ and $\theta = 54.7°$. (b) FIDs of 5CB at 25°C without and with voltage on 200 μm, which is adjusted for the longest decay. (c) Envelope of the Hahn-echo decay measured at the "magic angle" adjustment of 54.7° (5CB, 200 μm). Insets are the spectra at $2\tau \rightarrow 0$ ms and $\tau = 5$ ms (▼, aliphatic protons; ▲, phenylene protons).

with M_0 denoting the signal intensity following the $\pi/2$ pulse (free induction decay). δ describes the duration of the gradient pulses with amplitude g. The second factor in Eq. [2] $\Psi(t) = \exp(-\frac{1}{2}\gamma^2\delta^2g^2\langle z^2\rangle)$ is the additional attenuation due to diffusion in the presence of the gradient.

The self-diffusion coefficient is related to the average square of the displacement $\langle z^2 \rangle$ by Einstein's equation ($\langle z^2 \rangle = 2D_s\Delta$) where $\Delta = \tau$ is the observation time. D_s can be estimated from the semi-logarithmic plot of Ψ vs $(\gamma\delta g)^2\Delta$.

FIG. 3. PFG NMR experiments. (a) ^{1}H PFG NMR spin echo attenuation Ψ in the isotropic phase (■, 330 K) of the liquid crystal 5CB and in the nematic phase under electric field orientation (●, 300 K). The observation time Δ (*x*-axis) is replaced by Δ-$\delta/3$ in order to correct the influence of the finite duration of the gradient pulses. (b) The temperature dependence of the self-diffusion coefficient of a bulky sample (★) is compared with an anisotropic value of D_s of the capacitor sample (●) and a D_s of the same sample in the isotropic phase (■) as follows from the attenuation plots of (a).

modifications for E-field PFG NMR experiments have been done (as was the case for preparing the experiments). The diffusion coefficients measured on the capacitor sample are $(1.30 \pm 0.12) \times 10^{-10}$ m^{2}s^{-1} in the nematic phase (at 300 K) and $(0.94 \pm 0.06) \times 10^{-10}$ m^{2}s^{-1} in the isotropic phase. For comparison, some self-diffusion coefficients of 5CB in the isotropic phase have been measured by means of a bulk sample which demonstrates that the obtained values for the capacitor are in the correct order. In the experiment there was only access to one value of the self-diffusion tensor. It is known that the diffusion tensor of nematic liquid crystals is axially symmetric, which can be described by the two principal values $D_\parallel$ and $D_\perp$ (*10–12*),

$$\tilde{\mathbf{D}} = \begin{bmatrix} D_\perp & 0 & 0 \\ 0 & D_\perp & 0 \\ 0 & 0 & D_\parallel \end{bmatrix}. \tag{3}$$

Because of the parallel orientation of the direction into the field direction, only a projection of the displacement is effective:

$$\langle z^2 \rangle = 2\Delta(D_\parallel \cos^2\theta + D_\perp \sin^2\theta), \tag{4}$$

where θ (54.7° in our case) is the angle between the director orientation (also the parallel axis of the diffusion tensor) and the magnetic field gradient direction (in our spectrometer the z-direction) and Δ is the spacing of the gradient pulses (diffusion time).

In nematics, the diffusion parallel to the director is faster than that perpendicular to it. It would be necessary to measure the complete orientational dependence of the diffusion tensor. However, as mentioned above, a change of the gradient direction would be needed.

Preliminary experiments have been performed with fluorine containing nematic liquid crystals where the dipolar interaction is dominated by the internuclear proton–fluorine contribution. However, in order to achieve a suitable angular independent narrowing, additional proton decoupling must be applied. In that case the electric field could be used to change the orientation relative to a fixed gradient orientation. Access to the complete tensor information would be possible.

CONCLUSIONS

The experiments have shown that the reduction of the linewidth in nematic liquid crystals by means of the *in situ* electric field orientation enables the application of pulsed field gradient NMR techniques for the measurement of diffusion coefficients. The experiments can be carried out with a small amount of material in capacitor cells. The experiment does not need special geometric modifications of the probe and can be done with horizontal and perpendicular coils as well. Further options would be possible if the gradient direction could be changed. In systems with a sufficient long transverse relaxation time the electrical field could be used to change the relative orientation between the director and the field gradient.

REFERENCES

1. J. Krüger, *Phys. Rep.* (Review Section of Physics Letters) **4**, 229–269 (1982).
2. R. Blinc, J. R. Pirš, and I. Zupančič, *Phys. Rev. Lett.* **30**, 546–549 (1973).
3. R. Blinc, M. Burgar, M. Luzar, J. Pirš, I. Zupančič, and S. Žumer, *Phys. Rev. Lett.* **33**, 1192–1195 (1974).
4. J. Stepišnik, *Physica* **104B**, 350–364 (1980).
5. M. S. Crawford, B. C. Gerstein, A. L. Kuo, and C. G. Wade, *J. Am. Chem. Soc.* **102**, 3728–3732 (1980).
6. P. Holstein, A. C. D. Lopes, J. Rauchfuß, and D. Geschke, *Magn. Res. Chem.* **35**, 420–423 (1997).
7. P. Holstein, J. Rauchfuß, M. Winkler, G. Klotzsche, and D. Geschke, *Solid-State NMR* **10**, 225–234 (1998).
8. P. Holstein, M. Bender, M. Winkler, and D. Geschke, *Polym. Adv. Technol.* **9**, 659–664 (1999).
9. J. Kärger, N.-K. Bär, W. Heink, and H. Pfeifer, *Z. Naturforschung* **50A**, 186–190 (1995).
10. R. Y. Dong, "NMR of Liquid Crystals," Springer Verlag, NY (1994).
11. G. Lindblom and G. Orädd, Liquid crystalline samples, *in* "Encyclopedia of NMR" (D. M. Grant and R. K. Harris, Eds.), pp. 2760–2766. Wiley, NY (1996).
12. P. T. Callaghan, Section 6.3.3, Anisotropic self-diffusion, *in* "The Principles of NMR Microscopy," Clarendon Press, Oxford (1991).