

● *Short Communication***MOLECULAR DYNAMICS AND ORDER OF MICROCONFINED LIQUID CRYSTALS**

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A new technique based on the dipolar-correlation effect was applied in combination with field-cycling-relaxometry to study ordering effects and slow director fluctuations in a nematic liquid crystal confined in porous glasses. Both methods demonstrate a strong influence of geometrical confinements on the distribution of director fluctuation modes. The mean-squared fluctuation estimated from the dipolar-correlation effect decreases exponentially with decreasing pore diameter. The critical mean pore size for the onset of bulk behaviour was found to be of the order of 120 nm. Frequency dependences of spin-lattice relaxation times exhibit sudden sharp deviations from the square root law at frequencies below the MHz-range. These changes are assumed to reflect the lack of long wavelength fluctuations in the spectrum of director fluctuation modes due to finite pore sizes.

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INTRODUCTION

Confinements by pores produce strong effects on order and dynamics of collective molecular motions in liquid crystals. Field-cycling nuclear magnetic resonance (NMR) relaxometry¹ has been used to probe orientational director fluctuations (ODF), which represent a significant mechanism of spin-lattice relaxation of liquid crystals² at frequencies below 10^5 – 10^6 Hz. The low-frequency scale accessible for this method is however limited at about a few KHz. Promising perspectives in studies of slow molecular motions were recently recognized in view of favourable combination of field-cycling relaxometry with a new experiment based on the dipolar-correlation effect^{1,3} (DCE) which is extremely sensitive to the order and ODF. The DCE permits one to monitor dipolar correlations in the time scale from $\approx 10^{-4}$ s up to the order of spin-lattice relaxation times. This extends the low frequency range of the field-cycling relaxometry by an additional three orders. In this work, we report the application of the DCE and field-cycling NMR-relaxometry to studies of ordering effects and slow director fluctuations in a

nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl (5CB) confined in porous glasses.

RESULTS AND DISCUSSION

Figure 1 shows frequency (ν) dependences of spin-lattice relaxation times (T_1) of 5CB in bulk and confined in Bioran glasses with pore diameters 30, 70 and 200 nm. The data refer to 303 K and 316 K. Above the isotropization temperature ($T_c = 308.5$ K) only slight dispersions are observed both in bulk and confined samples. Below T_c , a square-root term⁴ characteristic for three-dimensional ODF dominates the spin-lattice relaxation of bulk 5CB in the low-frequency range.⁵ Dispersion curves of confined samples exhibit sudden sharp changes from $\nu^{1/2}$ toward ν^2 -law at frequencies below the MHz-range. These changes cannot be ascribed to local field effects, which under certain circumstances may mask contributions of dynamical processes in spin-lattice relaxation at low frequencies. This conclusion is based on spectral linewidths of the confined samples increasing with pore diameters from 5000 Hz at 30 nm to 7000 Hz at 200 nm. Local field effects, thus, would be stronger (or at least not weaker) at higher frequencies for bigger

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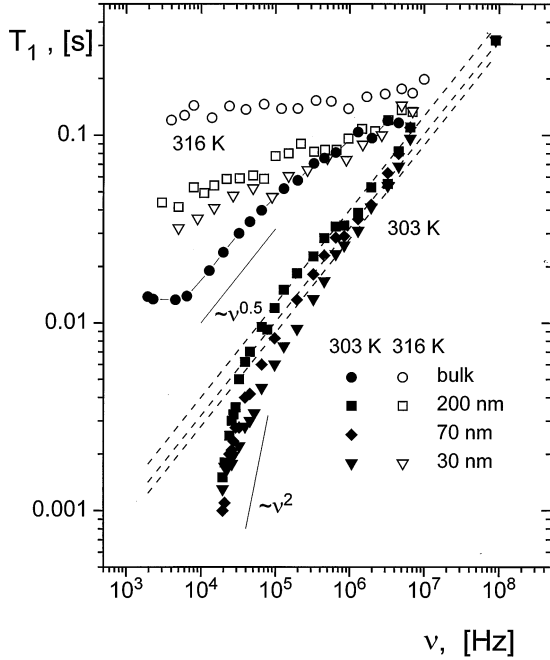


Fig. 1. Frequency dependences of spin-lattice relaxation times of 5CB in bulk and when confined in Bioran glasses with pore diameters 200 nm, 70 nm and 30 nm. Closed symbols refer to a nematic state at 303 K, open symbols refer to an isotropic state at 316 K. Straight lines serve as guides for the eye.

pores. On the contrary, the deviations from a square-root law appear at lower frequencies for bigger pores. The observed behaviour of T_1 -dispersion curves in confined samples must rather originate from the lack of long wavelength fluctuations in the spectrum of ODF due to finite pore size. However, abrupt cut-offs imposed by pores, i.e., the absence of any fluctuation modes with wavelengths bigger than the pore size, would result in low-frequency plateaus⁶ of the dispersion curves. In the investigated samples, instead, a clear tendency towards the ν^2 -law typical for single-correlation-time processes was observed. This indicates that one or a few fluctuation modes survive at the low-frequency end of the spectrum of director fluctuation modes. The modes below 10^4 Hz are then subject to the DCE.

In nematic liquid crystals, the DCE reveals itself via the quotient of the stimulated, A_{st} , and the primary, A_{pr} , echoes according to:³

$$\frac{A_{st}}{A_{pr}} = \exp \left\{ -\frac{1}{4} \langle \Omega_d^2 \rangle C_1 \right\} \left(1 + \cos(\langle \Omega_d \rangle \tau_1) \exp \left\{ -\frac{1}{2} (\delta \Omega_d^2) C_2 \right\} \right), \quad (1)$$

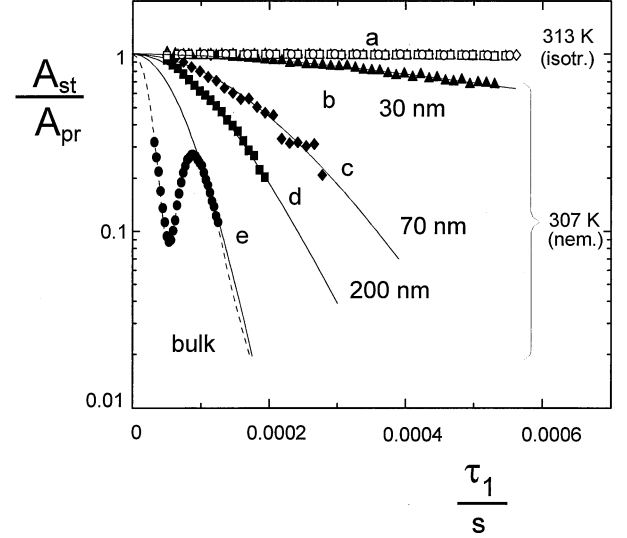


Fig. 2. The quotient of the stimulated and the primary echo amplitudes of bulk 5CB (a, e) and 5CB confined in Bioran glasses with pore diameters 200 nm (a, d), 70 nm (a, c) and 30 nm (a, b) in dependence on τ_1 . Closed symbols represent data measured in a nematic state at 307 K. Open symbols refer to a temperature above T_c . The solid lines (curves b-d) represent a fit to the experimental data of Eqs. (1-3) with $\cos(\langle \Omega_d \rangle \tau_1) = 0$.

where $\langle \Omega_d \rangle$ is the mean dipolar coupling constant, $\delta \Omega_d$ is the fluctuating part of the coupling constant. That is, $\delta \Omega_d(t) = \Omega_d(t) - \langle \Omega_d \rangle$. Coefficients C_1 and C_2 are functions of the time intervals between the first two (τ_1) and between the second and the third pulses (τ_2) of the standard three 90° -pulse sequence. In the case of an exponential correlation function, for instance, they turn out to be:³

$$C_1 = \tau_c^2 (e^{-\tau_1/\tau_c} - 1)^2 (1 - e^{-\tau_2/\tau_c}) \quad (2)$$

$$C_2 = \tau_c^2 (e^{-\tau_1/\tau_c} - 1)^2 e^{-\tau_2/\tau_c}, \quad (3)$$

where τ_c is the correlation time.

Figure 2 represents the quotient of the stimulated and primary echoes of 5CB in bulk and confined in Bioran glasses. Above T_c , the quotient of all bulk and confined samples is equal to 1 (curve a) as expected for isotropic liquids, where dipolar interactions are averaged out by fast stochastic motions. Below T_c , the attenuation curves reflect director fluctuations in the time scale of interpulse spacings. This result is consistent with our findings from the field-cycling-relaxometry data.

Confined 5CB does not exhibit the oscillations observed in the bulk (compare curves b-d and e). The oscillations are characteristic for macroscopically ordered systems and indicate, consider the cosine term in

Table 1. The values of $\langle\delta\Omega_d^2\rangle$ obtained by fits of Eqs. (1–3) to experimental data in Fig. 2. The corresponding value of the bulk sample is taken from Ref. 3.

d , nm	30	70	200	bulk
$\langle\delta\Omega_d^2\rangle$, $\text{rad}^2 \text{ s}^{-2}$	$9.0 * 10^6$	$9.6 * 10^7$	$2.3 * 10^8$	$6.0 * 10^8$

Eq. (1), a finite mean dipolar coupling constant which is directly proportional³ to the order parameter. The absence of any modulations in confined 5CB suggests that surface interactions spoil the uniformity of local director orientations so that no macroscopic preferential director orientation exists anymore.

The attenuation rate of the quotient exhibits a strong dependence on the pore size. It is determined by the mean squared fluctuation of the dipolar coupling constant, $\langle\delta\Omega_d^2\rangle$, characterising the distribution of director fluctuation modes.⁷ The values of $\langle\delta\Omega_d^2\rangle$ in confined 5CB were obtained by a fit to the experimental data of Eqs. (1–3) for $\cos(\langle\Omega_d\rangle\tau_1) = 0$ (solid lines b–d in Fig. 2). The mean squared fluctuation decreases with decreasing mean pore diameter (d) as given in Table 1. This reflects the decrease of director fluctuations caused by surface interactions which dictate fixed local orientations of the molecules and thus hinder spontaneous fluctuations. The dependence of $\langle\delta\Omega_d^2\rangle$ on the inverse pore diameter can be approximated using the empiric relation with:

$$\langle\delta\Omega_d^2\rangle = \langle\delta\Omega_d^2\rangle_{d=\infty} \exp\left(-\frac{d_c}{d}\right), \quad (4)$$

where $\langle\delta\Omega_d^2\rangle_{d=\infty} = 4.99 \times 10^8 \text{ rad}^2/\text{s}^2$ and $d_c = 120.5 \text{ nm}$. The relation given by Eq. (4) suggests the existence of a critical pore size of about 120 nm for the crossover to bulk behaviour. Due to its strong pore size dependence, the DCE of nematics may be suitable for the determination of mean pore diameters in porous materials.

REFERENCES

1. Kimmich, R. NMR: Tomography, Diffusometry, Relaxometry. Heidelberg: Springer-Verlag; 1997.
2. Noack, F.; Notter, M.; Weiss, W. Relaxation dispersion and zero-field spectroscopy of thermotropic and lyotropic liquid crystals by fast field-cycling NMR. *Liquid Crystals* 3:907–925; 1988.
3. Grinberg, F.; Kimmich, R. Characterization of order fluctuations in liquid crystals by the dipolar-correlation effect of the stimulated echo. *J. Chem. Phys.* 103:365–370; 1995.
4. Blinc, R. Spin-lattice relaxation in nematic liquid crystals via the modulation of the intramolecular dipolar interactions by order fluctuations. In: P. Diehl, E. Fluck, R. Kosfeld (Eds). *NMR: Basic Principles and Progress*, Vol. 13. Berlin: Springer-Verlag, 1976: pp. 97–111.
5. Köllner, R.; Schweikert, K.H.; Noack, F. NMR field-cycling study of proton and deuteron spin relaxation in the nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl. *Liquid Crystals* 13:483–498; 1993.
6. Ziherl, P.; Vilfan, M.; Žumer, S. Nematic order fluctuations and nuclear magnetic relaxation of a confined liquid crystal. *Phys. Rev. E* 52:690–701; 1995.
7. Grinberg, F.; Kimmich, R. Pore size dependence of the dipolar-correlation effect on the stimulated echo in liquid crystals confined in porous glass. *J. Chem. Phys.* 105: 3301–3306; 1996.