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R. Stannarius^a; H. Schmiedel^a

^a Sektion Physik, Karl-Marx-Universität, Leipzig, G.D.R.

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Diffusion measurements in chiral liquid crystals

by R. STANNARIUS and H. SCHMIEDEL

Sektion Physik der Karl-Marx-Universität, Leipzig DDR-7010 Leipzig,
Linnestraße 5, G.D.R.

We present results of diffusion investigations in twisted nematics (nematic-cholesteric mixtures). The dependence of the diffusion coefficient along the helix on the concentration of the cholesteric compound, the sample temperature and the diffusion time are measured by a new nuclear magnetic resonance method. The diffusion coefficient was found to decrease with diffusion time in the studied range of about 0.5-50 ms. The results are consistent with data from ^{13}C -N.M.R. experiments, and with field gradient measurements by other authors.

1. Introduction

Diffusion processes in cholesteric liquid crystals still lack a comprehensive theoretical description. The diffusion coefficient in the cholesteric mesophase is a second rank tensor \mathbf{D} . Previous investigations revealed that diffusion depends on the pitch length p_0 of the sample [1-4] and on the diffusion time [5, 6]. In the work reported here we studied the interesting phenomenon of time dependence of the diffusion coefficient. Similar behaviour is known for systems with spatially restricted diffusion and for hindered diffusion in a potential field.

The most successful approach for diffusion studies in liquid-crystalline systems is nuclear magnetic resonance. N.M.R. results have been reported with deuterium and carbon-13 spectroscopy, where the diffusion coefficient is calculated by line shape fitting [2-4, 7], and by field gradient N.M.R. (see, for example [5]).

We have used an alternative approach, a ^1H -N.M.R. line shape fitting method, which is sensitive to the rotation of the molecules caused by the diffusion along the cholesteric helix. Its principles are described in detail in [6]. The molecules at a certain position in the helix are labelled by their nuclear magnetization. After a certain diffusion time the N.M.R. signal is recorded and the distribution of these molecules can be computed from the N.M.R. signal shape. From the distribution width we draw conclusions on the component of the diffusion coefficient along the helix. This diffusion coefficient was determined at several temperatures and for two different pitch lengths. The diffusion time could be varied in the experiment by two orders of magnitude (from about 0.5 to 50 ms).

2. Theory

The magnetic field of the spectrometer is chosen such that it is strong enough to orient the helical axes of the cholesteric liquid crystal in the sample tube. The anisotropy of the diamagnetic susceptibility of the investigated materials is positive (χ is larger in the direction of the local director \mathbf{n} than perpendicular to \mathbf{n}). Hence the helical axes of the bulk sample arrange perpendicular to \mathbf{B}_0 as shown in figure 1 (with macroscopic cylindrical symmetry about \mathbf{B}_0). For the usual diameters of the

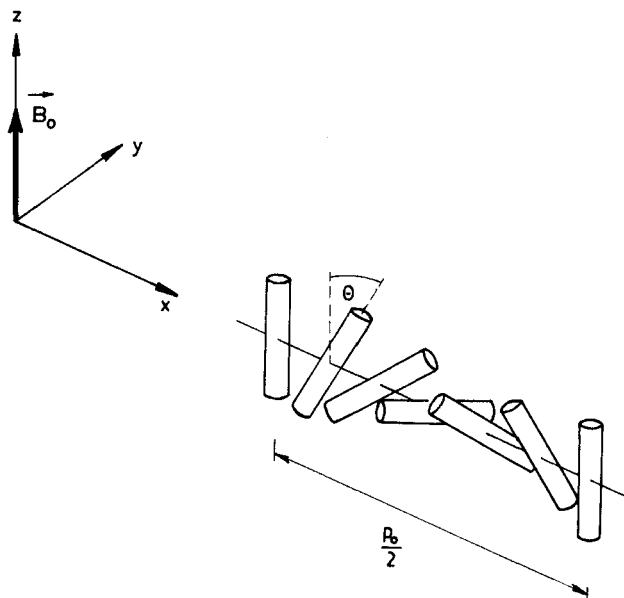


Figure 1. Sample orientation in the spectrometer field \mathbf{B}_0 .

samples of about 5 mm, we can neglect surface effects. On the other hand, the field is chosen sufficiently weak not to distort the helical structure. With this geometry we can describe the variation of the angle θ between the director \mathbf{n} and \mathbf{B}_0 along the helical axis e_x by

$$\theta(x) = 2\pi x/p_0, \quad (1)$$

where p_0 is the pitch length.

Any molecule located at the position x in the helix has the average orientation θ with respect to \mathbf{B}_0 . The fluctuations around this average orientation are fast compared with the N.M.R. time scale. They contribute to the order parameter S . We neglect the change of S in the nematic compound after the addition of a few per cent of cholesteric. This can be justified by comparison of the nematic and cholesteric N.M.R. spectra (cf. §3).

Diffusion leads to a migration of the molecules in the sample. For diffusion coefficients of about $10^{-12} \text{ m}^2 \text{ s}^{-1}$ and pitch lengths of several micrometres, the mean square displacement of a molecule during a time interval of about 10^{-2} s is of the order of $0.1p_0$. Following equation (1), the translational diffusions should be coupled to a rotation of the average molecular orientation. If we assume a markovian diffusion process, the probability for a molecule to be at a position x at time t after starting from x_0 to $t_0 = 0$ is described by the gaussian function

$$P(x, x_0, t) = [1/(4\pi Dt)^{1/2}] \exp [-(x - x_0)^2/4Dt], \quad (2a)$$

and consequently

$$p(\theta, \theta_0, t) = (\tau/\pi t)^{1/2} \exp [-(\theta - \theta_0)^2 \tau/t], \quad (2b)$$

with $\tau = p_0^2/16\pi^2 D$, D being the xx component of the diffusion tensor \mathbf{D} . Obviously, with a time dependent D the distribution function should differ from that of equations (2) and $D(t)$ represents an average taken over the diffusion time, a measure for the mean square displacement $\langle (x - x_0)^2 \rangle$ of the molecules after time t .

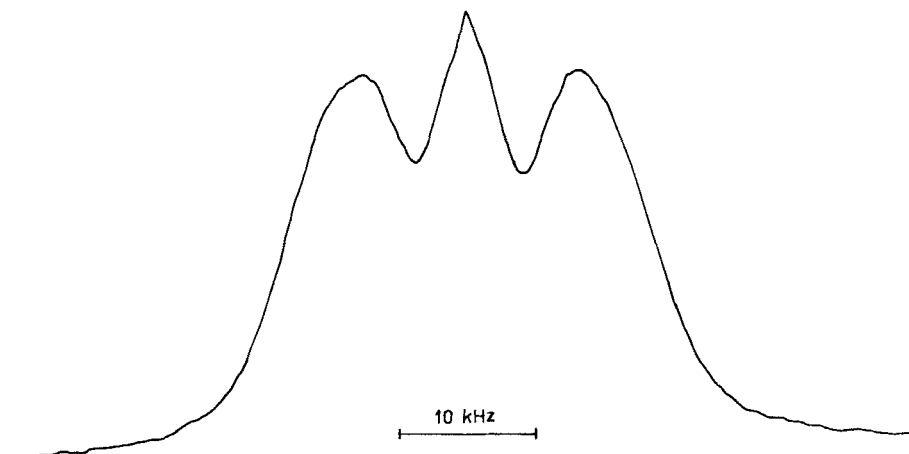


Figure 2. $^1\text{H-N.M.R.}$ line shape $F_0(\omega)$ of 6COO7 in the nematic phase at 335 K, the order parameter S is 0.62.

If we label the molecules at a certain position x_0 or at an angle θ_0 at the time $t_0 = 0$, and the distribution function p is determined at a subsequent moment t , then the diffusion coefficient D can be calculated. For both purposes we use the magnetization of the nuclear spins in the molecules.

The strength of the proton dipole-dipole interactions which dominate in the $^1\text{H-N.M.R.}$ spectrum depends on the angle θ by the second Legendre polynomial $P_2(\cos \theta)$. In the oriented nematic sample with $\theta = 0$, we observe the $^1\text{H-N.M.R.}$ spectrum $F_0(\omega)$. A typical spectrum is shown in figure 2. Due to the angular dependence of the dipolar interactions between the proton spins, the line shape F_θ for molecules at an average orientation θ is

$$F_\theta(\omega) = \frac{1}{P_2} F_0\left(\frac{\omega}{P_2}\right), \quad (3)$$

where we drop the argument $\cos \theta$ of P_2 . If the sample consists of a nematic compound mixed with a small amount of cholesteric substance, with an orientation of the helices as illustrated in figure 1, the cholesteric spectrum is calculated by integrating over all orientations of the pitch

$$f_c(\omega) = \int_0^{\pi/2} d\theta I(\theta) F_\theta(\omega), \quad (4)$$

where the intensity $I(\theta)$ is a constant. The free induction decay (F.I.D.) corresponding to equation (3) is

$$G_\theta(t) = G_0(P_2 t), \quad (5)$$

with G_0 being the F.I.D. of the nematic sample. The smaller the value of P_2 , the longer is the F.I.D. The longest decay time is found for molecules at an orientation θ near $\theta_m = 54.7^\circ$, the magic angle (with $P_2(\cos \theta_m) = 0$), where only field inhomogeneity and chemical shift influence the F.I.D.

We apply a $\pi/2, t_1, -\pi/2, t_2, \pi/2$ pulse sequence to the sample. The time t_1 is of the order of T_2 , and t_2 can be varied from T_2 to about 100 ms. At a time t_1 after application of the first $\pi/2$ pulse, the transverse magnetization is damped by dipole-dipole relaxation in all molecules except for those at orientations θ near θ_m . This

magnetization M_s is rotated into the direction z of the B_0 field by the second $\pi/2$ pulse and is stored there for the period t_2 . The nuclear magnetization is exchanged within the molecule by intramolecular interactions, whereas a transfer to other molecules by intermolecular interactions can be excluded. During t_2 the diffusion process will change the average molecular positions and orientations. At time $t_1 + t_2$ we record the F.I.D. after the third $\pi/2$ pulse and perform the Fourier transform. Now, the line shape can be calculated from equation (4), with

$$I(\theta) = \int p(\theta, \theta_0, t_2) * G_{\theta_0}(t_1) d\theta_0$$

being the total magnetization in molecules at orientation θ at the time $t_1 + t_2$. G_{θ_0} is the magnetization remaining after the second $\pi/2$ pulse, and p is the probability of diffusion from θ_0 to θ during t_2 according to equation (2b).

The resultant N.M.R. line shape is

$$f(t_1, t_2, \omega) = 2/\pi \int_0^{\pi/2} d\theta \int_{-\infty}^{\infty} d\theta_0 [\tau/(\pi t)]^{1/2} \exp [-(\theta - \theta_0)^2 \tau/t] * G_0(P_2(\cos \theta_0) t_1) * P_2(\cos \theta)^{-1} F_0(\omega/P_2(\cos \theta)). \quad (6)$$

In equation (6) we did not consider effects of spectrometer field inhomogeneity and chemical shift. Figure 3 displays the high resolution proton spectrum in the isotropic phase. The chemical shift of the protons is less than 10 p.p.m. The field inhomogeneity was of the same order. Thus, the calculated line shape $f(t_1, t_2, \omega)$ was finally convoluted with a spectrometer function that includes both effects. An exact and thorough derivation of equation (6) is given in [6].

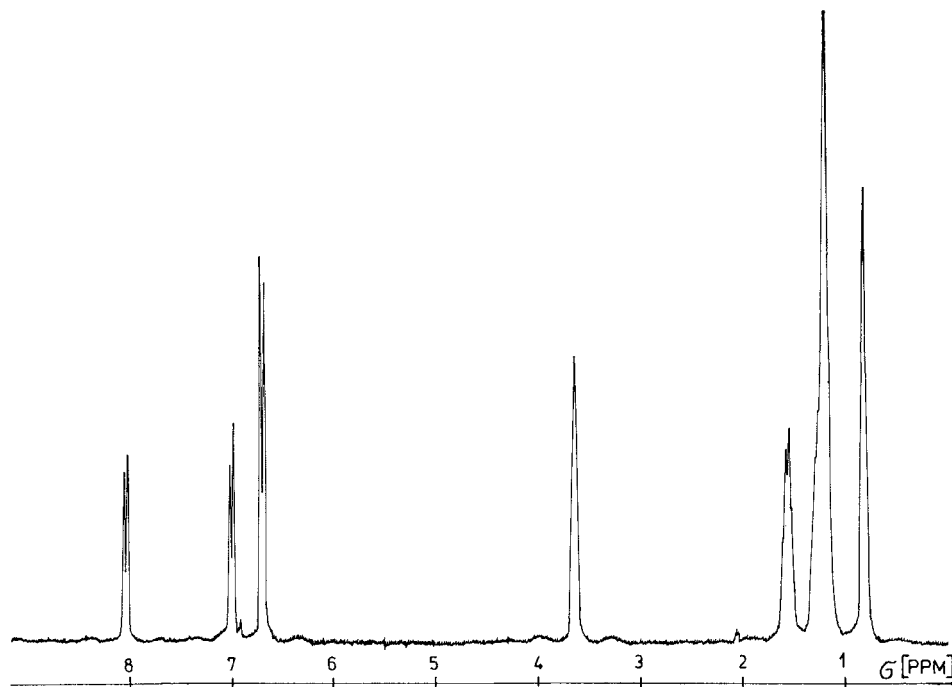


Figure 3. High resolution ^1H -N.M.R. spectrum of 6COO7 in the isotropic phase, reflecting the proton chemical shift.

The parameter τ is used to determine the contribution of diffusion. By fitting $f(\omega)$ to experimental spectra, we obtain the diffusion constant depending on the diffusion time t_2 .

3. Experimental

The measurements were performed with a Bruker ^1H N.M.R. pulse spectrometer at 32 MHz proton resonance frequency. The corresponding B_0 field strength of about 0.7 T met the conditions outlined at the beginning of §2. The magnetic coherence length was much greater than the pitch length and much smaller than the sample diameter.

For the investigations we used the nematogenic compound 4-*n*-heptyloxyphenyl-4'-*n*-hexyloxybenzoate (6COO7) and the cholesteric compound cholesteryl undecyl carbonate (ChUC). Two mixtures with different pitch lengths p_0 were prepared, with 2.68 and 6.34 wt % of ChUC. The corresponding p_0 are 4.30 and 1.85 μm . The cholesteric phase of the mixtures ranges from 326 to 360°C, the transition into the crystalline phase can be supercooled. The sample temperature during the N.M.R. experiments was controlled by an air flow. Temperature stability and homogeneity were < 1 K.

The nematic line shape F_0 at different temperatures as well as the corresponding F.I.D. G_0 were determined in the nematic phase of 6COO7 on the same spectrometer. We have also recorded the spectra in the cholesteric phase with a simple $\pi/2$ pulse experiment. The spectrum of the twisted sample, measured at the same temperature as the nematic one of figure 2, is shown in figure 4. Its line shape is equivalent to that computed with equation (4). This justifies our assumptions on the order parameter S and the orientation of the cholesteric sample.

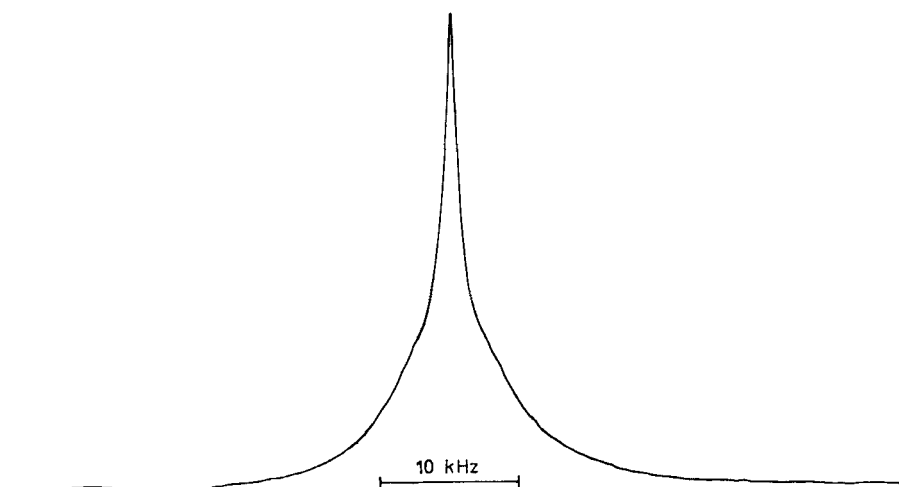


Figure 4. ^1H N.M.R. spectrum $f_c(\omega)$ of the twisted nematic in the cholesteric phase at 335 K.

In the multipulse experiment the phases of the second and the third $\pi/2$ pulse were alternated during signal accumulation, in order to average disturbing contributions of T_1 relaxation during the time period t_2 (T_1 is of the order of 130 ms, cf. [6]).

The pulse spacing t_1 was chosen to be 200 μs , t_2 was varied from 1 to 40 ms. Figure 5 illustrates several experimental N.M.R. signals recorded at different diffusion

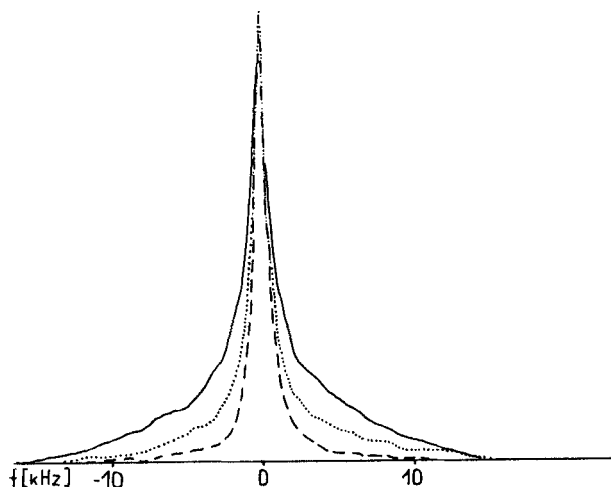


Figure 5. Experimental ^1H N.M.R. lines for $t_1 = 200 \mu\text{s}$ and different t_2 . (---) $t_2 = 0.8 \text{ ms}$, (\cdots) $t_2 = 5.0 \text{ ms}$, (—) $t_2 = 40 \text{ ms}$.

times. At small t_2 a very narrow line shape is obtained. The signal comes mainly from regions near the magic angle θ_m , where the dipole-dipole interactions are small. With increasing t_2 , as the molecules are distributed by diffusion, the predicted line broadening is observed.

4. Results and discussion

The line shape changes depicted in figure 5 are solely diffusion effects, they are a measure of the component D of the diffusion coefficient along the helical axis. Perhaps, a similar effect could be found as in cholesterics in chiral S_C , and in smectic A powder samples as the result of diffusion across domain walls.

Figure 6 shows the value of τ depending on the diffusion time. The uncertainty of the fitting procedure is about 10 per cent. In contrast to field gradient measurements, systematic errors are easily avoided, whereas the scattering of individual data points is higher. At low diffusion times $t_2 < 1 \text{ ms}$, two additional error sources are present. First, the intramolecular exchange of the magnetization remaining after t_1 takes approximately the time T_2 . Secondly, we have neglected the diffusion influence during t_1 and during signal recording. This assumption is justified and is made in any ^1H N.M.R. experiment and in the field gradient measurements, too. If, however, t_2 is of the order of t_1 , the diffusion during the preparation time t_1 should be taken into account. An influence of motional averaging on the proton line shape can be neglected as long as the F.I.D. time is much smaller than the time a molecule takes to cover a diffusion path comparable to the pitch length that is $T_2^{-1} \ll 2Dp_0^{-2}$.

The diffusion coefficient increases with temperature. If an Arrhenius type behaviour is assumed, we find an activation energy of 46 kJ mol^{-1} at $t_2 = 1 \text{ ms}$, decreasing to about 15 kJ mol^{-1} at $t_2 = 40 \text{ ms}$.

The increase of τ with increasing t_2 is obvious. It corresponds to a decrease in the diffusion velocity. The time dependence of τ surely violates the validity of equations (2a) and (2b). Strictly, they hold only for markovian diffusion. Thus, the measured diffusion coefficients represent only an average measure of the mean square displacement of the molecules during the diffusion time t_2 . The sample with shorter pitch

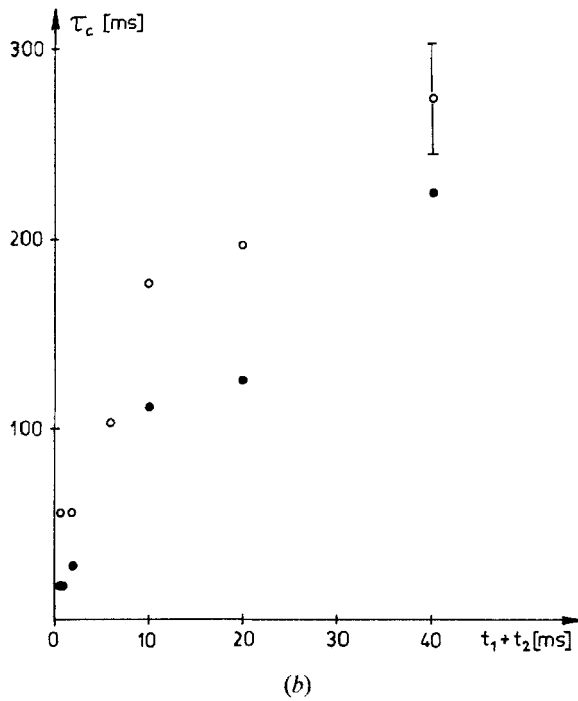
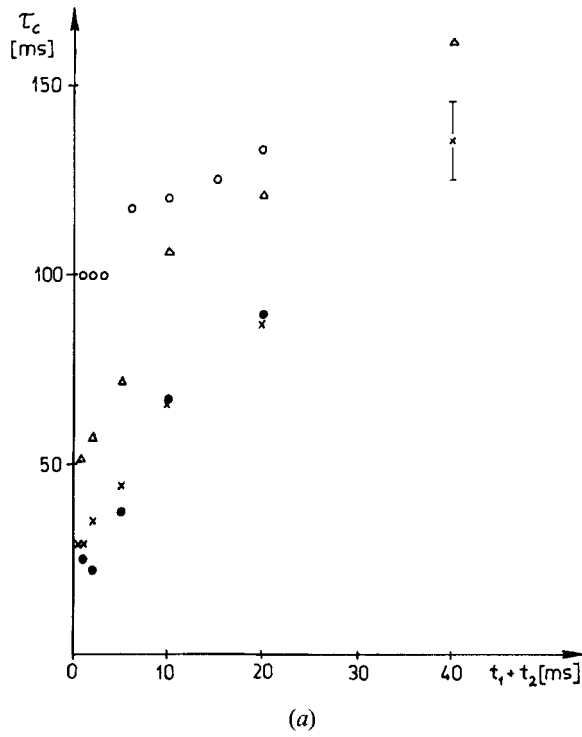
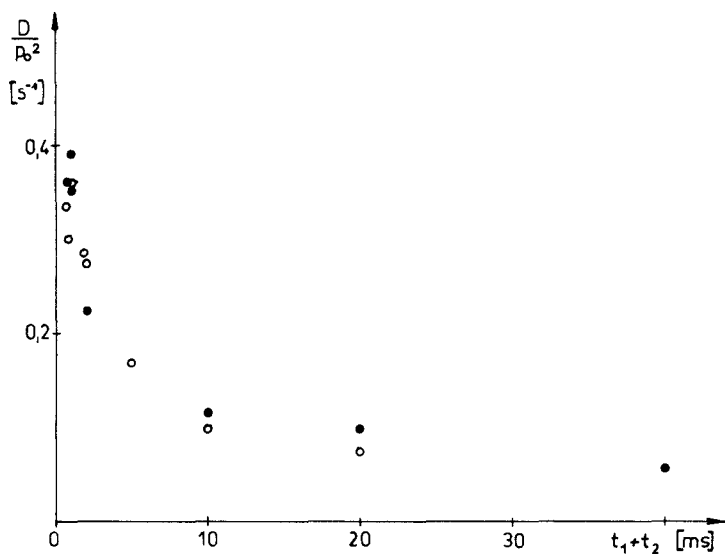
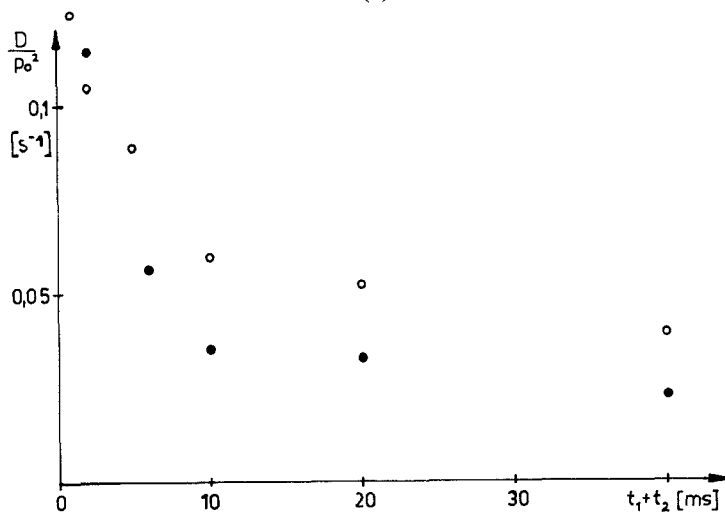


Figure 6. Correlation time τ versus the diffusion interval t_2 . (a) Sample A, pitch length $4.30 \mu\text{m}$, 2.68 per cent ChUC; (b) sample B, pitch length $1.85 \mu\text{m}$, 6.34 percent ChUC. \bullet , 355 K; \times , 345 K; Δ , 335 K; \circ , 325 K.



(a)



(b)

Figure 7. Diffusion coefficient versus diffusion time for two different pitch lengths (●, 1.85 μm, ○, 4.30 μm): (a) $T = 355$ K and (b) $T = 335$ K.

length clearly shows a smaller diffusion coefficient (see figure 7). For all samples at all temperatures, the critical value of t_2/τ is about 0.2–0.3, corresponding to an average $\langle\theta^2\rangle$ of about 25°. This suggests that there is a rotational barrier which hinders the diffusion along the helix. Possibly the long time behaviour is governed by other mechanisms than the short time diffusion in twisted nematics.

A similar time dependence of the diffusion coefficient was already found by Blinc *et al.* [5]. It should be noted that in our experiment the rotational diffusion is measured whereas the field gradient N.M.R. used in [5] is sensitive to translational diffusion. Both experiments should, however, yield equivalent results as long as equation (1) holds.

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