Proton magnetic relaxation study of pretransitional phenomena in the isotropic phase of a nematic liquid crystal I. Dynamics of local order fluctuations

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Proton magnetic relaxation study of pretransitional phenomena in the isotropic phase of a nematic liquid crystal
I. Dynamics of local order fluctuations

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Nuclear magnetic relaxation was investigated in a broad temperature region above the clearing point (T_c) of a nematic liquid crystal. Dependence of spin–spin relaxation time on the pulse interval observed in the Curr–Purcell–Meiboom–Gill (CPMG) experiment indicates an exchange of nuclei between the states differing in local magnetic fields. By fitting of the Luz–Meiboom equation to the CPMG results, the mean lifetime of sites and modulation frequency $\delta\omega$ were determined. The rather slow exchange (lifetimes changing with temperature in the range 20–90 ms) is suggested as manifesting the local order fluctuations in the pretransitional zone of the LC. A simple two-site model of a pretransitional zone was considered (cluster ⇔ isotropic surrounding). Dipole–dipole interactions in clusters are unaveraged due to the local ordering, whereas in the isotropic subphase local magnetic fields are motionally averaged. Therefore, local order fluctuations are accompanied by the exchange observed in the CPMG sequence. Correspondence of the temperature dependence of $\delta\omega$ to the Curie–Weiss law was established: $\delta\omega^{-2} \propto T - T^*$, ($T^* = T_c - 1$), thus providing proof of our interpretation.

1. Introduction

It is well known [1–3] that although the long range order vanishes above the clearing point (T_c) of a liquid crystal (LC), the short range order still remains within the correlation length. At a first approximation, a pretransitional region can be considered as being biphasic, consisting of locally ordered clusters of a finite lifetime dispersed in an isotropic surrounding [1]. According to Landau's mean field theory, the correlation length ξ (or, in other words, the cluster radius) decreases with temperature as

$$\xi^2 \propto 1/(T - T^*) \tag{1}$$

where $T^* = T_c - \Delta T (\Delta T \approx 1\,\text{K})$ is a temperature limit at which the cluster size is infinite. Equation (1), in fact, governs temperature dependences of various static properties in the pretransitional region [4]. For example, the temperature dependence of the magnetic susceptibility χ is known to obey the Curie–Weiss law at $T > T_c$:

$$\chi^{-1} \propto T - T^*. \tag{2}$$

In the pretransitional region, clusters reveal themselves in anomalous high birefringence in the presence of external electric and magnetic fields (Kerr and Cotton–Muton effects, respectively), and in the anomalously high light scattering. As to NMR in relation to pretransitional phenomena, dispersion of nuclear spin-lattice relaxation, self-diffusion, and NMR spectra of ^{14}N resonance have been studied [5–8]. It should be noted that optical methods are able to detect pretransitional effects several degrees above T_c, whereas NMR, being a technique sensitive to local interactions, shows the existence of pretransitional effects well above T_c. Most work has concerned the pretransitional effects in nematic LC, and the influence of pretransitional effects on the spin–spin relaxation remains almost unstudied. In the present articles we report the results of proton magnetic relaxation investigations above T_c for a nematic LC. We shall prove that the isotropic phase of the LC is magnetically inhomogeneous due to the presence of locally ordered clusters. The dynamics of local order fluctuations in the nematic LC will be examined by the Curr–Purcell–Meiboom–Gill (CPMG) pulse sequence $90^\circ_x - t - 180^\circ_y - t_{cp} - 180^\circ_y - t_{cp} - 180^\circ_y - t_{cp} - 180^\circ_y - \dots$ ($t_{cp} = 2t$ being the time interval between pulses). This technique was initially developed to study the so-called 'chemical exchange' of molecules undergoing exchange reactions (for instance, proton exchange) or conformational jumps accompanied by large changes of the local magnetic

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field (for example, the internal rotation about the N–C bond in *N,N*-dimethylamides $(CH_3)_2N$–COR) [9–12]. The manifestation of exchange between sites differing in local magnetic field is the dependences of spin–spin relaxation times T_2 on t_{cp}. At low values of t_{cp} the CPMG sequence is known to eliminate the influence of exchange on spin–spin relaxation, i.e. at $t_{cp} \to 0$, $T_2 \to T_2^0$, where T_2^0 is the true relaxation time not 'spoiled' by the exchange. At large pulse separations, spin–spin relaxation is completely governed by exchange ($T_2 < T_2^0$). By fitting of the Luz–Meiboom equation describing exchange [9] to experimental dependences of $T_2(t_{cp})$ between these two extremes, the life times of exchanging sites τ_λ can be obtained.

Previously we observed the CPMG manifestation of the intermolecular exchange in the solutions of main chain liquid crystalline polymers (LCPs) [13–16]. Obviously, this exchange could not be attributed to the two reasons described above. We proposed that this exchange takes place between locally ordered clusters and the isotropic surroundings, the local field in a cluster being different from that in the isotropic phase (a full description of the model is given below). However, since main chain LCPs do not exhibit lyotropic mesomorphism, the existence of pretransitional phenomena in their solutions has been doubted. In other words, our results indicated pretransitional phenomena in systems where the real transition to a lyotropic LC state is thermodynamically and/or kinetically forbidden [17].

Therefore, in continuation of our previous work on solutions of main chain LCP, we present here the study of spin-echo decay (SED) in a model classical system where the presence of pretransitional phenomena is not doubted, i.e. in a low molecular mass nematic LC.

2. Experimental

The 4-*n*-hexylphenyl ester of 4-*n*-oxybenzoic acid (HEOB) exhibiting nematic mesomorphism (Cr 29°C N 49°C I) was studied. Its structural formula is:

$$CH_3(CH_2)_3{-}O{-}\bigcirc{-}\overset{\displaystyle O}{\underset{\displaystyle O}{C}}{-}O{-}\bigcirc{-}(CH_2)_5CH_3$$
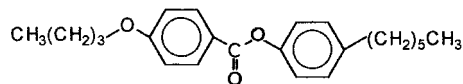
The chemical structure of HEOB was confirmed by PMR spectroscopy. PMR spectra of the chloroform-d solution and of the melt at 100°C of HEOB were recorded using a Bruker AC-200 spectrometer at the resonance frequency of 200 MHz.

Measurements of proton magnetic relaxation were carried out at 16 MHz. A pulsed relaxometer (made in the Institute Neftechimavtomatica, St-Petersburg) equipped with a variable temperature unit was used. The dead time is 10 μs, and duration of the 90° pulse is 2.7 μs. Spin-lattice relaxation was measured using

the 90° − *t* − 90° pulse sequence. Spin-lattice relaxation times were obtained from the slope of the dependence $\ln[1 - A(t)/A_0] = -t/T_1$, where A_0 is the initial amplitude of magnetization measured after the 90° pulse, $A(t)$ is the current magnetization, and T_1 is the spin-lattice relaxation time. Spin–spin relaxation was measured with the help of the CPMG pulse sequence: $90_x^\circ - t - 180_y^\circ - t_{cp} - 180_y^\circ - t_{cp} - 180_y^\circ \dots$. In order to study the exchange, CPMG pulse sequences were applied at different t_{cp}. The upper limit of variation of t_{cp} depends on T_2, since several echoes should be observed during the spin-echo decay. Therefore, the condition $t_{cp} < T_2/4$ arises. To avoid the overlap of echoes, t_{cp} should not be less than 2 ms. In our experiments t_{cp} was varied in the range 2–40 ms.

3. Results

Dependences of T_2 on t_{cp}, of HEOB are shown in figure 1 for different temperatures above T_c. These dependences indicate an exchange between some sites differing in local magnetic fields.

Before discussing the origin of the exchange observed by the CPMG-sequence, let us first obtain its parameters using the well developed NMR formalism. For this purpose the dependences T_2 vs. t_{cp} were fitted using the Luz–Meiboom equation [9], derived for the simplest case of fast two-site exchange between states with equal spin–spin relaxation times ($T_{2a} = T_{2b}$) and different local
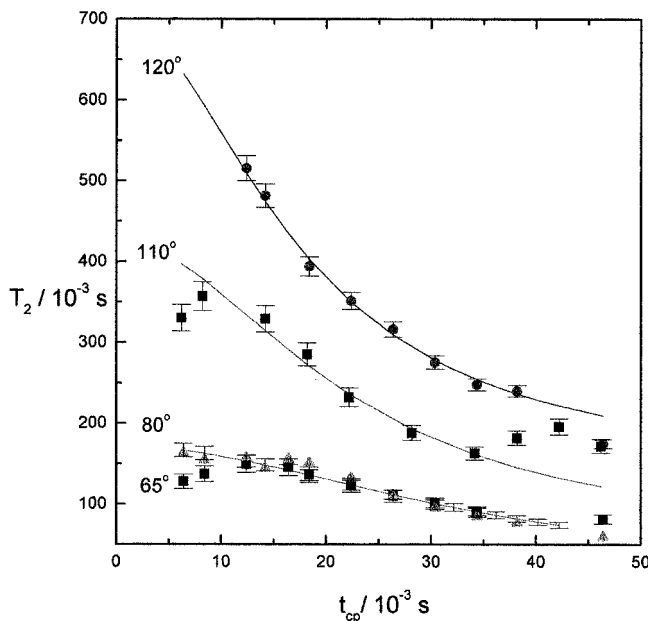

Figure 1. Results of the CPMG experiment above the clearing point of the LC: dependences of spin–spin relaxation times vs. the pulse spacing at different temperatures. Curves are the results of fitting of equation (4); the corresponding fitting parameters are listed in the table.

magnetic fields $H_a \neq H_b$:

$$1/T_2 = 1/T_2^0 + p_a p_b \delta\omega^2\tau[1 - (2\tau/t_{cp})\text{th}\,(t_{cp}/2\tau)]$$
$$= 1/T_2^0 + BF \qquad (3)$$

where $B = p_a p_b \delta\omega_2\tau$, $F = [1 - (2\tau/t_{cp})\text{th}\,(t_{cp}/2\tau)]$; 2τ is the mean life time in the Luz–Meiboom notation (in our notation it is τ_λ); p_a and p_b $(p_a + p_b = 1)$ are the populations of states a and b, $\delta\omega = \gamma\delta H = \gamma(H_a - H_b)$ is the modulation frequency. The populations of states are determined by their life times:

$$p_a = \tau_a/(\tau_a + \tau_b). \qquad (4)$$

The life times of states are:

$$\tau_a = \tau_\lambda/p_b, \quad \tau_b = \tau_\lambda/p_a. \qquad (5)$$

The mean lifetime τ_λ is determined as:

$$1/\tau_\lambda = 1/\tau_a + 1/\tau_b. \qquad (6)$$

Following the fitting procedure described in [10], equation (3) was represented as a straight line $1/T_2$ vs. F with slope B and intercept $1/T_2^0$. At the correctly chosen parameter τ the mean square deviation (MSD) of experimental points from this straight line is minimal. However, while trying to fit equation (3) to all the range of t_{cp} studied, the minimum of MSD vs. τ was not obtained. This could be a manifestation of a slower exchange than that described by equation (3). As shown in [10], even in this situation equation (3) describes the initial variation of T_2 with t_{cp}. If high t_{cp} values were not considered, the desired minimum of SD vs. τ was achieved, and the parameters τ and B were obtained. Using the parameter B determined, the values of $\delta\omega$ were calculated as:

$$\delta\omega = (B/\tau/p_a/p_b)^{1/2} \qquad (7)$$

for the equal population of states $(p_a = p_b = 0.5)$ and for predominance of one of the states $(p_a = 0.05, p_b = 0.95)$.

The results of fitting are shown in figure 1, and the corresponding exchange parameters are listed in the table for a wide temperature range above T_c. Spin-lattice

Table. Parameters of exchange obtained by fitting of the Luz–Meiboom equation to the CPMG results in the pretransitional zone of a low molecular mass nematic LC.

$T/°C$	T_2^0/s	τ/s	$\delta\omega/\text{rad s}^{-1}$	
			$p_a = 0.5$	$p_a = 0.05$
65	0.200	0.045	115	265
70	0.286	0.022	90	206
80	0.295	0.020	75	170
90	0.289	0.018	61	139
110	0.425	0.012	63	143
120	0.735	0.011	48	109

relaxation was found to be exponential. In figure 2 the temperature dependence of the spin-lattice relaxation time T_1 and of the initial amplitude of magnetization A_0 are shown in Arrhenius coordinates. We have also plotted the temperature dependence of T_2^0 obtained above. Figure 2 shows, that $T_2^0 < T_1$, thus indicating that the values of T_2^0 obtained in the fitting procedure are quite reasonable.

4. Discussion

What is the origin of the observed exchange? It could not be an intramolecular exchange as, for example, in N,N-dimethylamides [10–12], because the molecule studied does not have the C–N bond, the conformational jumps around which are accompanied by large variations of local magnetic fields. Exchange of protons which could also be detected by the CPMG technique in hydrogen bonded molecules is also impossible in our case. We think that it is a peculiar 'physical' exchange that takes place in pretransitional zones of LCs. As we have already mentioned, we propose local order fluctuations to be the origin of the observed exchange phenomenon (figure 3). In this case the pretransitional zone of the LC should be magnetically inhomogeneous, the local magnetic field in clusters being different from that of the isotropic surrounding. In fact, from NMR theory it is known that the magnetic field H is the sum of
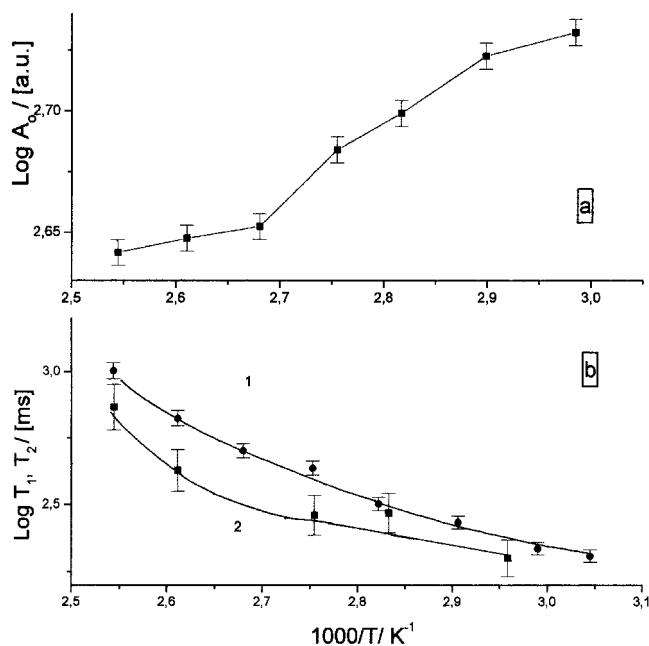

Figure 2. (a) Semi-log dependence of the initial magnetization vs. the reciprocal temperature; (b) semi-log dependences of the spin-lattice relaxation time (1) and 'true' spin–spin relaxation time T_2^0 (2) vs. the reciprocal temperature.
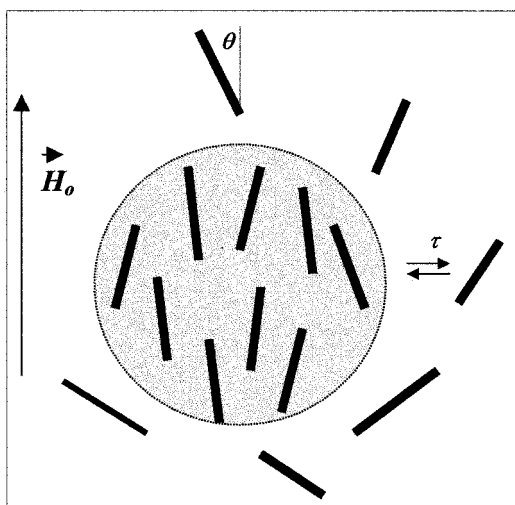
Figure 3. Schematic representation of the bicomponent model: local order fluctuations as the origin of the observed exchange.

$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_L$, where $\mathbf{H}_0$ is the external magnetic field and $\mathbf{H}_L$ is the local field arising from the interactions of neighbouring nuclei. For the dipole–dipole interactions of two nuclei $\mathbf{H}_L \sim \langle 3\cos^2\theta - 1\rangle / r_{ij}^3$, where r_{ij} is the distance between the nuclei, θ is the angle between the nuclei–nuclei radius vector and $\mathbf{H}_0$. For the protons of the benzene ring $\mathbf{H}_L \approx 3$ G. The brackets $\langle\,\rangle$ mean averaging over time, the term in brackets being proportional to the local order parameter within the clusters (S).

Therefore, in the isotropic phase $\mathbf{H}_L = 0$ due to the motional averaging; in the clusters $\mathbf{H}_L \neq 0$ due to the motional anisotropy of molecules. Clusters could be oriented in the external magnetic field, even as low as 3800 G, because of the low viscosity of the isotropic surroundings and the limited size of the cluster (in the LC state only super-strong magnetic fields give orientation). Therefore, the magnetic field of every cluster can be characterized by the mean value $\mathbf{H}_L$. While departing from clusters during the local order fluctuations, the molecules experience the change in the local field $\delta\mathbf{H} = \mathbf{H}_L$, and in the resonance frequency $\delta\omega = \gamma\mathbf{H}_L$, $\delta\omega$ being the modulation frequency obtained by the Luz–Meiboom procedure.

From the determined values of the modulation frequency, the local order parameter is obtained as described below. In locally ordered orientated liquid crystalline clusters, as in a nematic, the doublet should arise due to the nematic ordering. The resonance frequencies of a doublet are:

$$\omega^c = \gamma\left(\mathbf{H}_0 \pm \frac{3}{2}S\mathbf{H}_L\right). \tag{8}$$

Therefore, during the exchange from the disordered phase to a cluster phase the frequency change should be:

$$\delta\omega = \omega^c - \omega_0 = \pm\frac{3}{2}\gamma S\mathbf{H}_L. \tag{9}$$

This frequency $\delta\omega$ is, in fact, the modulation frequency, as determined in our experiment. From equation (9) the local order parameter within clusters can be estimated: for $\delta\omega = 100$–200 rad s^{-1} (see the table), $S \approx 0.001$.

What temperature dependence of $\delta\omega$ should be expected in the case of local order fluctuations? According to the fluctuation-dissipation theorem [18], the local order fluctuations $\delta S^2 = \langle \overline{S^2} - (\overline{S})^2\rangle$ are proportional to the magnetic susceptibility χ, the temperature dependence of which in the pretransitional region is known to obey the Curie–Weiss law, see equation (2). Local order fluctuations $\delta S^2 \propto \delta\omega^2$, and therefore $\delta\omega^{-2} \propto T - T^*$. To check our assumptions, the temperature dependence of the modulation frequency was plotted in the Curie–Weiss co-ordinates, i.e. $\delta\omega^{-2}$ vs. T. Results are shown in figure 4. Linear fits for equal and different populations of states give $T^* \approx T_c - 1°$, as expected for the Curie–Weiss law. Therefore, our data are in accord with the Curie–Weiss law, and so the observed modulation of dipole–dipole interactions is due to the local order fluctuations. Correspondingly, the value 2τ as determined from the Luz–Meiboom approach is the cluster lifetime. Its temperature dependence is shown in figure 5.
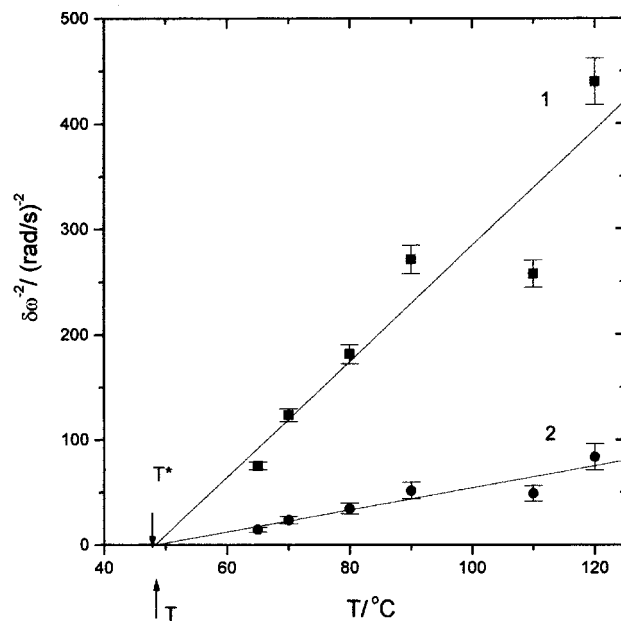

Figure 4. Temperature dependence of two modulation frequencies of the exchange determined by fitting of the Luz–Meiboom equation at $p_a = 0.5$ (curve 1) and $p_a = 0.05$ (curve 2) in Curie–Weiss coordinates. Straight lines are the results of the least-square fits.
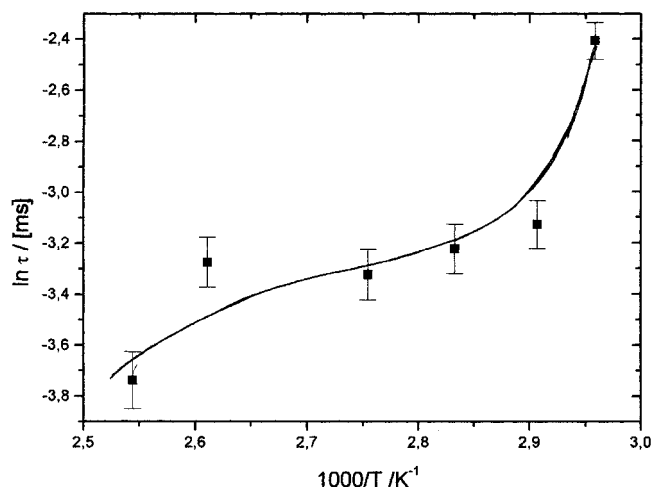
Figure 5. Temperature dependences of the mean life time 2τ in Arrhenius coordinates.

It should be mentioned that only the rotational mobility of clusters has been examined until recently [19]. However, cluster life time is a very important characteristic of the isotropic phase, since the results of the relaxation experiment mainly depend on the ratio $\delta = t_{obs}/\tau_\lambda$, where t_{obs} is the observation time, i.e. on Deborah's number. The importance of accounting for the Dedorah numbers has already been illustrated in our studies of solutions of main chain LC polyesters [13–16]. The observation time depends on the kind of experiment. In relaxation methods, the measure of the observation time is the relaxation time (in fact, during the relaxation we 'observe' the system, and if during that time exchange takes place, the results will be 'spoiled' by the exchange). If exchange is slow or intermediate, i.e. at $\delta \leqslant 1$, clusters reveal themselves as particles of a new LC phase. In the case of fast exchange, at $\delta > 1$, the system behaves as a homogeneous medium, its parameters being an average of the parameters of the isotropic and locally ordered states. In the studies of spin–spin relaxation $t_{obs} = T_2^0$, then from the table it follows that $\delta = T_2^0/2\tau > 1$, i.e. the exchange is fast. Therefore, the spin-echo decays of clusters and of their isotropic surroundings are not observed separately. The same holds for the spin-lattice relaxation, which is found to be exponential. Hence, both relaxation times, T_2^0 and T_1 are in fact an average over locally ordered and disordered regions. T_1 increases monotonically with temperature (figure 2(b)) indicating that there is an increase of mobility. Temperature dependences of τ (figure 5), T_2^0 (figure 2(b)) and A_0 (figure 2(a)) are apparently non-linear. After the initial decrease of τ, A_0 and $1/T_2^0$ the intermediate plateau region appears, thus demonstrating complex (at least bicomponent) dynamic behaviour in the pretransitional zone. The high temperature decrease

of τ and $1/T_2^0$ is probably due to the onset of cluster mobility taking place at $T > 100°C$, i.e. 50° higher than T_c. Let us consider the temperature dependence of A_0, figure 2(a). It is known, that the temperature dependence of initial magnetization is governed by the term $\exp(-\mu\mathbf{H}/kT)$, where μ is the magnetic moment of the nuclei and k is the Boltzman constant. Therefore, the initial magnetization should decrease linearly in Arrhenius coordinates. However, A_0 is less than the initial magnetization, because it can be measured only after the dead time during which relaxation occurs. In motionally inhomogeneous systems, the 'melting' of an immobile component can slow the natural decrease of A_0 with temperature. In fact, figure 2 shows that the dependence is markedly non-linear, and above 100°C it is slowed down. This can be due to the 'melting' of clusters, which start to contribute to A_0 due to the increase of their relaxation time with temperature. This means that exchange between sites with $T_{2a} \neq T_{2b}$ takes place. The Luz–Meiboom equation does not account for this difference. It should also be mentioned that in the over-simplified treatment of the data we did not consider the influence of spin–spin couplings on SED in the CPMG experiment Luz–Meiboom equations also do not account for the spin-coupling. In fact, spin-couplings can produce modulations of SED, but in our case SED were exponential. On the other hand, spin-coupling does not depend on temperature, and we have studied the temperature dependences of SED.

5. Conclusions

The sensitivity of spin–spin nuclear magnetic relaxation to the dynamics of local order fluctuations above the clearing point is demonstrated. To a first approximation, the isotropic phase of the LC is considered to be biphasic in the NMR sense, the local magnetic field in clusters being different from that of the isotropic surroundings due to the local ordering within clusters. The kinetics of the exchange of nuclei between the sites differing in magnetic fields were studied with the help of the CPMG sequence. The correspondence of the dependences of the modulation frequency obtained to the Curie–Weiss law was shown, thus proving our idea of the influence of pretransitional effects on the nuclear magnetic relaxation.

As we have already mentioned in the Introduction, the dependences $T_2(t_{cp})$ were also observed previously for solutions of LCPs [13–16]. The similarity of the observed anomalies of spin–spin relaxation suggests a similarity of the phenomena studied in the pretransitional zone of the nematic LC and in the solutions of thermotropic main chain LCP, though the latter are not forming a lyotropic phase. It will be interesting to discuss these differences in the future, but the global

similarity of the results is more important, drawing attention to this similarity of phenomena never considered before.

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