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Static and dynamic dielectric effects in the vicinity of the isotropic to nematic phase transition in 7CB

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Static and dynamic dielectric measurements were performed with very high accuracy on a mesogenic compound *n*-heptylcyanobiphenyl (7CB) in the isotropic (I) and nematic (N) phases. The critical-like temperature behaviour of the static permittivity of isotropic 7CB in the vicinity of the I–N phase transition can be described with the critical exponent close to 0.5, indicating the tricritical nature of the transition. Anomalously slow rotational diffusion (subdiffusion), characterized by a fractal value of the diffusion exponent α, is observed in the vicinity of the I–N transition with a lambda-like profile of the exponent temperature dependence.

1. Introduction

Studies of the physical properties of mesogenic liquids in the vicinity of the isotropic (I) to nematic (N) phase transition are numerous [1–13]. The I–N transition, which is first order in nature, is classified as weakly first order or close to second order because of pretransitional phenomena which show a critical-like temperature dependence, characteristic of continuous, second order phase transitions. The pretransitional phenomena are due to the existence of a short range orientational order of the mesogenic molecules in isotropic liquids, which leads to the formation of pseudonematic domains. The size of the domains increases as the temperature of the liquid approaches the transition to the nematic phase. The phenomenon can be quantitatively described in terms of the intermolecular correlation length ξ. The Landau theory of the second order phase transition, applied by de Gennes to the isotropic to nematic phase transition, leads to the following temperature dependence of the correlation length [14]:

$$\xi(T)=\xi_0\left[\frac{T^*}{T-T^*}\right]^{1/2} \tag{1}$$

where the constant ξ_0 is of the order of the molecular length and T^* denotes the temperature of the virtual second order transition, i.e. the temperature limit of the thermodynamic stability of a supercooled isotropic phase. Usually, the value of T^* is about 1 K below the nematic to isotropic phase transition temperature (T_{NI}), and, as results from equation (1), at that temperature the correlation length reaches its infinitive value.

The peculiarity of the I–N phase transition is that the region closest to the critical point (T^*) is inaccessible to experimental study: the first order transition occurs at the temperature T_{NI}, i.e. somewhat higher than T^*. As a consequence, the determination of the critical exponent must be performed using some extrapolations, which, as a rule, lead to different values of the exponent depending on the different procedures used. This is one of the reasons that, despite the numerous papers devoted to the isotropic to nematic phase transition, the nature of the critical behaviour in the vicinity of the I–N transition is not properly understood.

The pretransitional effects in the vicinity of the I–N transition are revealed, in principle, in nonlinear studies, i.e. when an external stimulus is sufficiently strong. The experimental data are numerous and are concerned with the static measurements of magnetic [15] and electric [16] birefringence, light scattering [17] and nonlinear dielectric effects [7, 18] as well as dynamic studies of molecular spin–lattice relaxation [19, 20], dynamic light scattering [21], the transient grating optical Kerr effect [22, 23] and nonlinear dielectric relaxation [24–26].

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The Landau–de Gennes theory was successfully used for the interpretation of the experimental data obtained with nonlinear techniques.

The prenematic effects that appear in the linear dielectric properties as a peculiar temperature behaviour of the static permittivity [27–30] and the activation energy for molecular rotation derived from the dielectric relaxation time [29, 30] or as the anomalous slowing of rotational diffusion [31], are most apparent for strongly polar mesogenic liquids and still await theoretical description.

This paper presents experimental results on the linear static and dynamic dielectric behaviour of strongly polar *n*-heptylcyanobiphenyl in the vicinity of the isotropic to nematic phase transition.

2. Experimental

The measurements were performed in the isotropic and nematic phases of *n*-heptylcyanobiphenyl, $C_7H_{15}PhPhCN$, 7CB, which was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compound, checked by chromatography, was better than 99.5%. The temperature of the isotropic to nematic phase transition (T_{NI}) was 316.4 K. Dielectric characteristics of the compound were measured with a HP 4194A impedance/gain phase analyser in the frequency region 50 kHz–100 MHz. The static values of the dielectric permittivity were taken as a low frequency plateau of the real part of the permittivity. The accuracy of the permittivity determination was better than 0.5%. The measuring capacitor consisted of three plane electrodes: one central and two grounded on each side. High performance electrical heating of the capacitor, with the use of a Unipan 650H controller, assured a temperature stabilization better than 10^{-3} K and the possibility of a temperature change of 10^{-2} K.

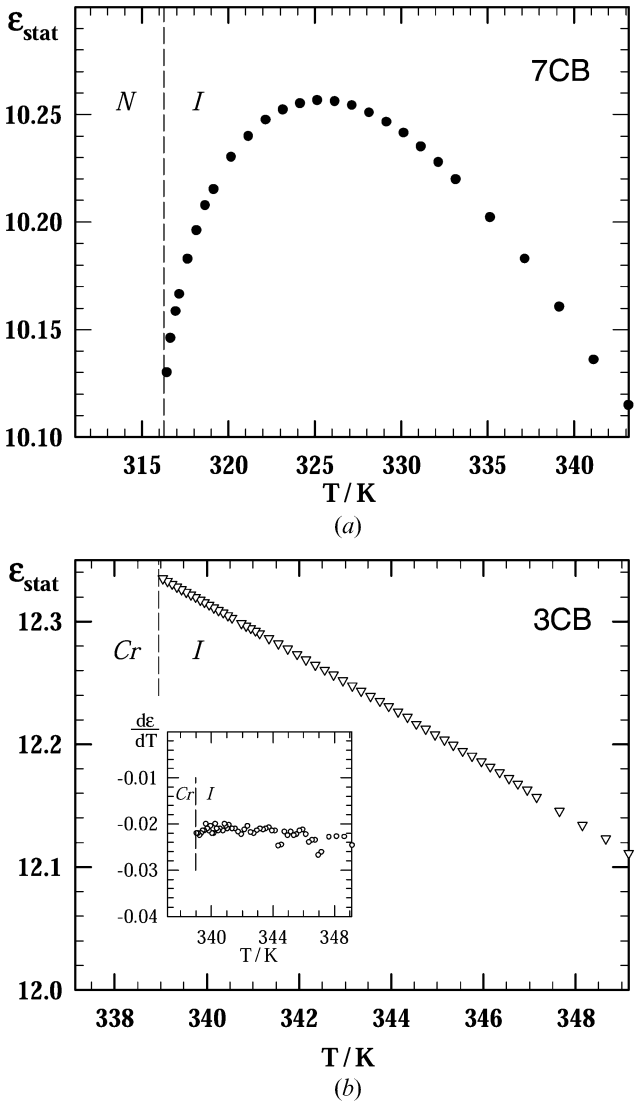

Figure 1. Temperature behaviour of the static dielectric permittivity in the vicinity of (*a*) weakly first order (7CB) and (*b*) first order (3CB) phase transitions. Inset in (*b*) shows temperature dependence of the permittivity derivative of 3CB in the vicinity of the isotropic liquid (I) to crystal (Cr) phase transition.

3. Results and discussion

Figure 1 (*a*) shows the temperature dependence of the static dielectric permittivity of isotropic 7CB. The dependence exhibits a maximum at about 10 K before the transition to the nematic phase, the effect being undoubtedly pretransitional, observed for strongly polar mesogenic liquids [27–30]. As shown in figure 1 (*b*), in the case of a non-mesogenic compound of the same polarity as 7CB — *n*-propylcyanobiphenyl, $C_3H_7PhPhCN$, 3CB — no maximum on approaching the first order transition from the isotropic to crystalline phase is seen [29]. Thus the permittivity dependence on temperature is very close to linear, i.e. the permittivity derivative is only slightly temperature dependent, see the inset in figure 1 (*b*).

As shown in figure 2, in case of the mesogenic 7CB, the permittivity derivative shows a critical-like behaviour as the temperature approaches the I–N phase transition. If one assumes that for mesogenic 7CB the 'normal', non-critical $d\varepsilon/dT$ on T dependence corresponds to that obtained for non-mesogenic 3CB, a critical part of the permittivity derivative of 7CB (taken as a difference between the experimental permittivity

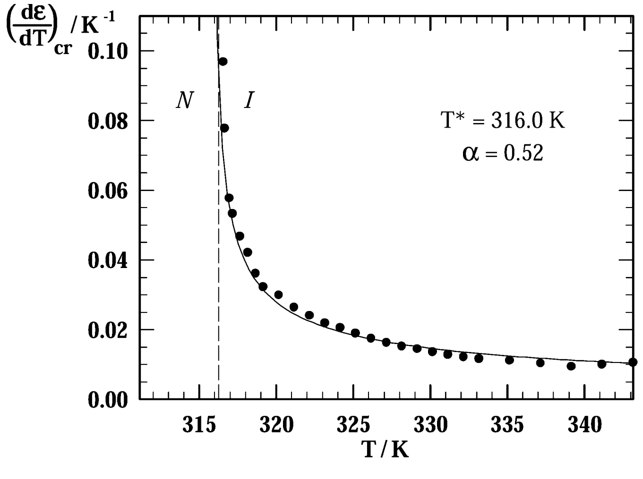

Figure 2. The critical part of the derivative of the static permittivity of 7CB as a function of temperature. The solid line represents the best fit of equation (2) to the experimental data (points).

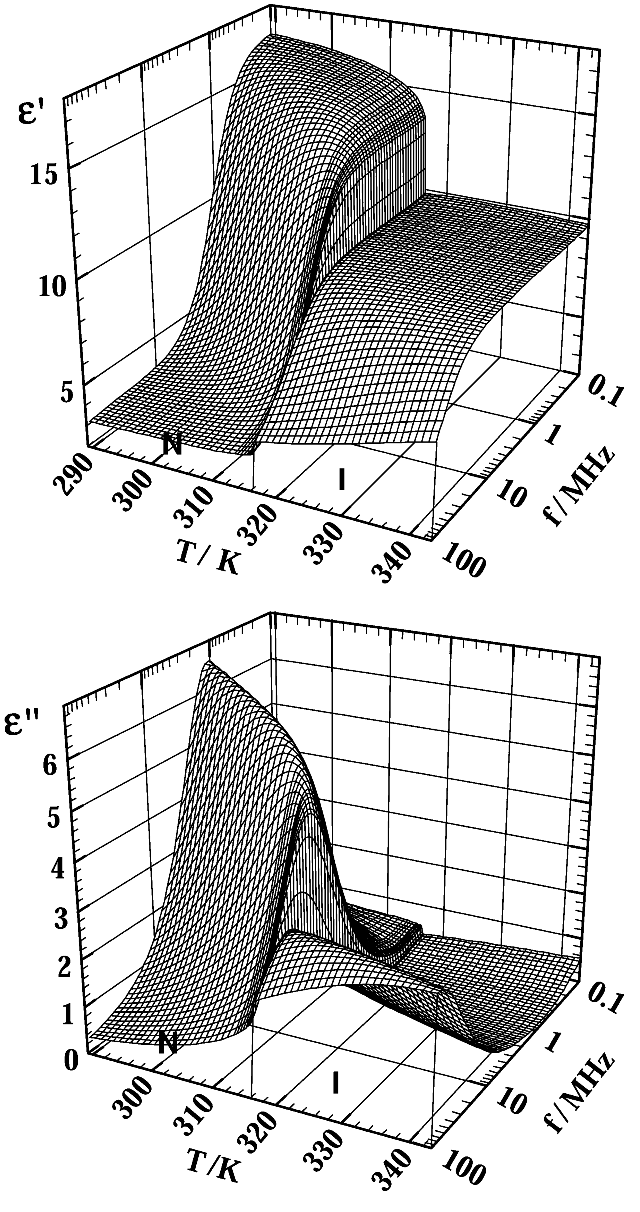

Figure 3. Dielectric relaxation spectra of 7CB in the isotropic and nematic phases.

derivatives for 7CB and 3CB), can be well reproduced by the equation [29]:

$$\left(\frac{d\varepsilon}{dT}\right)_{cr} \propto A(T-T^*)^{-\sigma} \tag{2}$$

where A is a constant and σ is the critical exponent. The best fit of equation (2) (shown in figure 2 as the solid line) to the experimental data, gives the following values of the parameters: $T^*=316.0\,\mathrm{K}$ and $\sigma=0.52$. The difference $T_{NI}-T^*=0.4\,\mathrm{K}$ obtained lies in the low limit of the values reported in the literature [7, 8, 32–36], and the value of the critical exponent corresponds to the tricritical hypothesis [37–39]. Recently, reasonably convincing support of this view was reported by Żywociński [8] based on very precise measurements of the molar volume changes close to the isotropic to nematic transition in 8CB.

Figure 3 presents the experimental dielectric relaxation spectra recorded in the isotropic and nematic phases of 7CB. In the latter phase, an external biasing d.c. electric field was applied for ordering the sample (**E**||**n**), so the dielectric spectrum $\varepsilon^*_{\parallel}(\omega, T)$ was recorded. The spectra were resolved into two elementary contributions of the Cole–Cole type [40]:

$$\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)=\varepsilon_\infty+\sum_{k=1}^{2}\frac{A_k}{1+(i\omega\tau_k)^{\alpha_k}} \tag{3}$$

corresponding to the molecular rotations around the short and long axes. In equation (3), ε_∞ denotes the permittivity measured at a sufficiently high frequency to prevent dipolar reorientation; A_k is the dielectric strength of the k-th relaxational process, ω is the angular frequency, and τ_k is the relaxation time. The dashed lines in figure 4 give, for example, the resolution of the dielectric spectrum recorded in the isotropic and nematic phases of 7CB into the two contributions. For rod-like molecules with the dipole moment directed essentially along the long axis, as in the case of 7CB, the absorption band due to molecular rotation around the short axis dominates the dielectric spectrum. The contribution from the molecular rotation around the long axis has a very low strength, especially in the oriented nematic phase. In addition, the band (situated at about 1 GHz) depends only weakly on temperature and the type of mesophase [41], so it will not be discussed here.

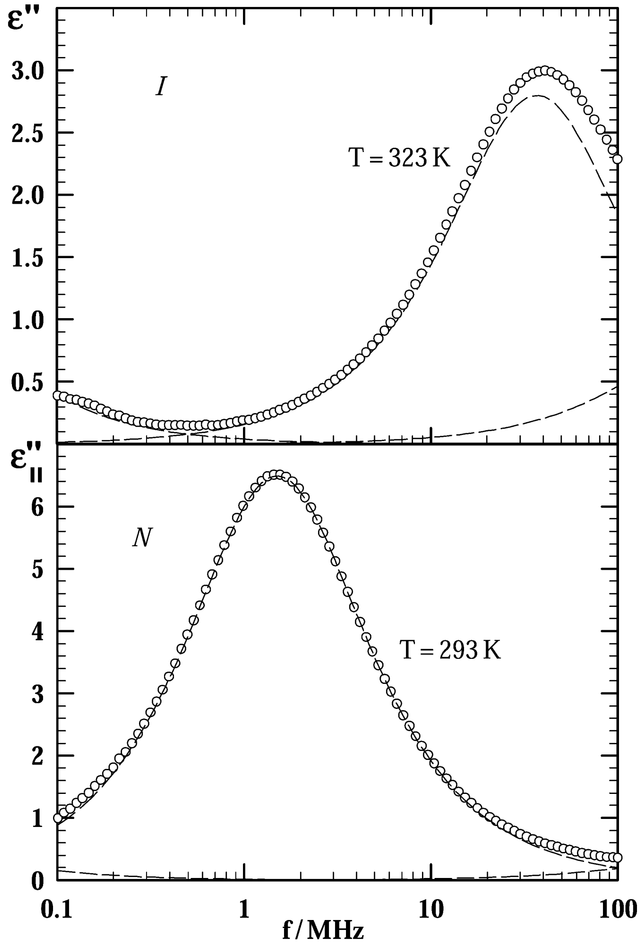

Figure 4. An example of the dielectric absorption spectra recorded in the isotropic (I) and nematic (N) phases of 7CB. Dashed lines are the elementary contributions corresponding to molecular rotations around their principal axes. The band due to rotation around the short axis is strongly dominant.

Figures 5–7 show the temperature dependences of the three spectral parameters (A, τ and α) of the band corresponding to 7CB molecules rotating around the short axis ($k=1$), obtained from the best fit of the Cole–Cole equation to the experimental dielectric spectra. The temperature dependence of the relaxation time (figure 6) is presented in the form of an Arrhenius plot:

$$\ln \tau = C + \frac{E_A}{RT} \tag{4}$$

where E_A is the activation energy, R the gas constant, T the absolute temperature, and C is a constant. Even a cursory analysis of the data from figure 6 shows, that the linear dependence $\ln \tau$ versus T^{-1} is not satisfied here over the whole temperature range studied. It is obvious that in such a situation a reliable value of the activation energy cannot be determined as the slope of the dependence (4). Two issues are in common practice in the literature. Most often the nonlinearity in $\ln \tau$ versus T^{-1} dependence is ignored and the activation energy is determined as a mean slope of the dependence. This is used when the nonlinearity is not too pronounced, as in experiments performed over restricted temperature ranges, for example. The second leads through some modifications of the Arrhenius equation. In both one assumes that the activation energy E_A should be temperature-independent. In fact, the assumption seems to have no physical basis. Because the basic properties of liquids, such as the number of molecules in unit volume, depend on temperature, one may expect an increase of the activation energy for

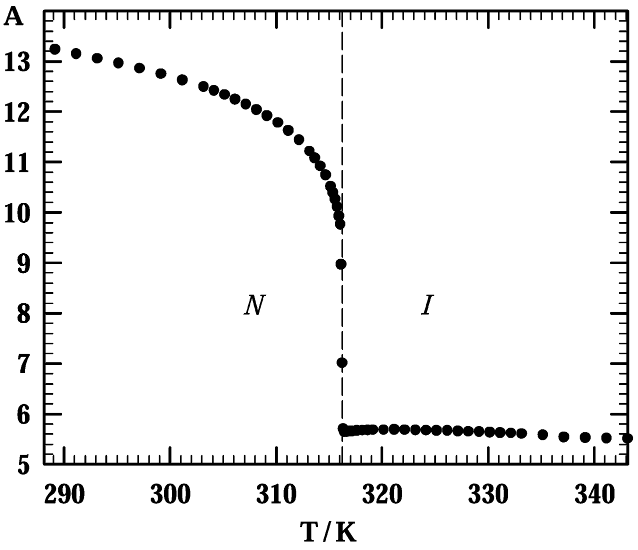

Figure 5. Temperature dependence of the dielectric strength A for the rotation of 7CB molecules around their short axis.

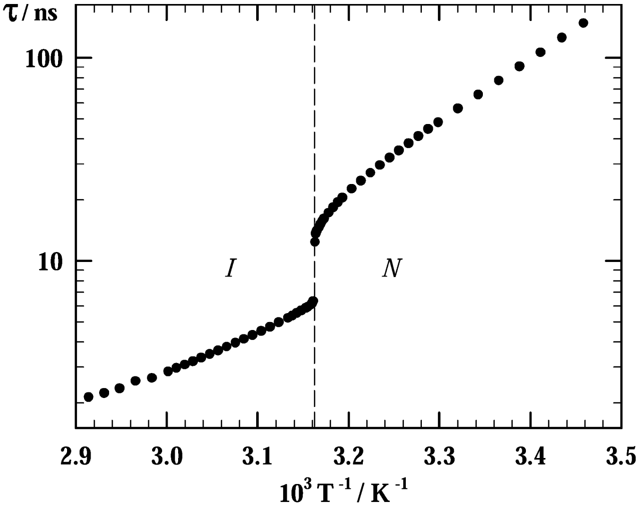

Figure 6. Arrhenius plot of the longitudinal relaxation time of 7CB molecules in the isotropic and nematic phases.

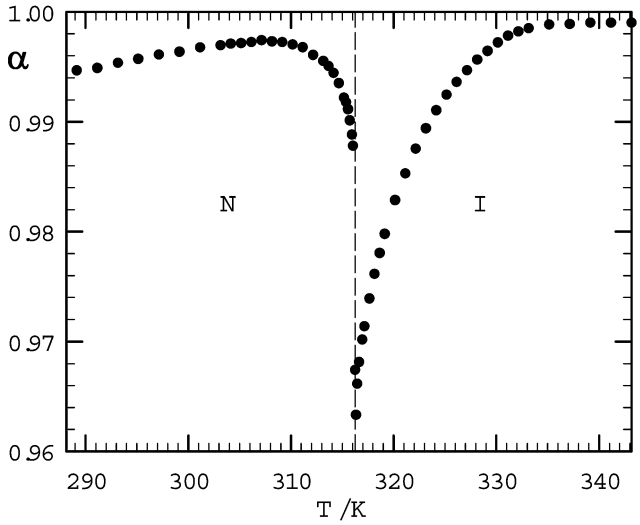

Figure 7. Temperature behaviour of the anomalous rotational diffusion exponent obtained from the best fit of the Cole–Cole equation (3) to the experimental dielectric spectra of 7CB.

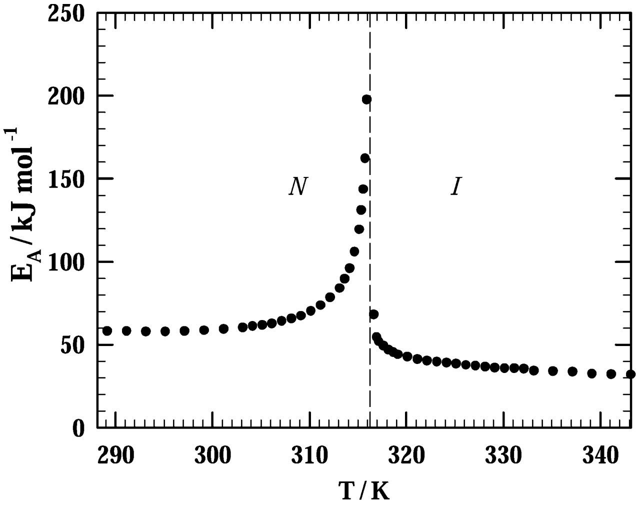

Figure 8. Plot of the activation energy of 7CB molecules in rotation around their short axis in the isotropic and nematic phases as a function of the temperature.

molecular rotation with decreasing temperature. The pretransitional regions are of special interest for this reason.

Recently, we proposed [29] a procedure for the determination of the activation energy E_A, involving the differentiation of the experimental $\ln \tau$ versus T^{-1} dependence. As results from equation (4), the derivative $\partial \ln \tau / \partial (T^{-1})$ gives E_A directly at a given temperature, allowing one to analyse temperature dependence of the activation energy. Of course, the procedure requires very accurate data for the relaxation time determined for an appropriate temperature change step, especially in the vicinity of the phase transition. The experimental results presented in figure 6 satisfy these requirements. In the vicinity of the isotropic to nematic transition the temperature change step was equal to 10^{-2} K.

Figure 8 presents the temperature dependence of the activation energy for the rotation of 7CB molecules around their short axis. As can be seen in the figure, in only a relatively narrow temperature range (290–300 K) in the nematic phase of 7CB, is the activation energy temperature-independent, which customarily means that the Arrhenius dependence ($\ln \tau \sim T^{-1}$) is fulfilled. In the remaining temperature range studied, the activation energy for the molecular rotation around the short axis is temperature-dependent and the dependence is particularly significant in the vicinity of the I–N phase transition. We have discussed this problem in a recent paper [30].

Figure 7 presents the temperature dependence of the Cole–Cole exponent α, the importance of which has recently increased considerably since the molecular basis of the Cole–Cole equation (3) and the physical meaning of the exponent α, have been given. Until now equation (3) was used as empirical [42]. As shown in numerous theoretical papers [43–49], the Cole–Cole relaxational behaviour (3) is a direct consequence of the anomalously slow rotational diffusion processes (the subdiffusion) in a system under investigation.

Subdiffusion occurs in systems in which the transport processes are slower than Brownian diffusion. From the most fundamental point of view, the phenomenon can be expressed in terms of the mean square displacement of particles, which for subdiffusion is described by the power law pattern [50]:

$$\langle x^2(t) \rangle \propto K_\alpha t^\alpha \tag{5}$$

instead of the Brownian linear dependence [51, 52]. K_α denotes the generalized diffusion coefficient and α is the anomalous diffusion exponent. Subdiffusion corresponds to $0<\alpha<1$, while $\alpha>1$ is referred to as superdiffusion or enhanced diffusion. For normal Brownian diffusion the exponent α is equal to unity.

Subdiffusion has been modelled in numerous ways. Mostly, these are generalizations of the equations of normal Brownian diffusion to fractional Brownian motions [53–55]. In particular, the concept of a continuous time random walk [56–58] (i.e. a walk with a long tailed distribution of the waiting times between the elementary jumps of particles) has played an essential role in understanding the physical basis of the anomalous dielectric relaxation in some complex systems [42]. Such waiting times reflect the existence in a medium of some deep traps, which immobilize the diffusing particle for a certain time.

It is apparent that the relaxational behaviour of a system returning to the equilibrium state is determined by the type of the diffusion processes occurring in the system. In the case of normal Brownian diffusion, which is well modelled by the Einstein–Smoluchowski theory [52], the relaxation processes show a simple exponential decay in the time domain. That theory, applied by Debye [42] to the rotational Brownian motion of the dipolar molecules placed in an external a.c. electric field, leads to the well known Debye equation for complex permittivity, which is a particular case of the Cole–Cole equation (3) for $\alpha=1$.

According to Debye's approach, for systems in which normal rotational Brownian diffusion occurs, the experimental values of the real (ε') and imaginary (ε'') parts of the permittivity, depicted in the complex plane ε'' vs. ε' (the Cole–Cole plot), represent a semicircle with a centre placed on the ε' axis. The experiment shows that the dielectric relaxation recorded for most simple liquids under normal conditions behaves according to Debye's equation, i.e. as predicted by the model of normal Brownian diffusion.

However, in many cases of complex liquids, the Debye theory becomes inadequate to describe the dielectric relaxation — the experimental spectra are broadened in comparison with the Debye prediction. Then, the relaxational processes in the system cannot be interpreted in the frame work of a traditional Brownian description of random walks with an exponential decay, but by the continuous time random walks theory for a power law distribution of the waiting times between consecutive jumps of the molecules. In such cases of subdiffusive dynamics, the exponential mode of equilibration of time-dependent quantities must be substituted by the Mittag-Leffler pattern [59], which interpolates between an initial stretched exponential and a terminal inverse power law pattern, both of index β:

$$f(t) \propto E_\beta(-t/\tau)^\beta \propto \begin{cases} \exp\left[-\dfrac{(t/\tau)^\beta}{\Gamma(1+\beta)}\right], & t << \tau \\ \Gamma(1-\beta)(t/\tau)^\beta, & t >> \tau. \end{cases} \tag{6}$$

In the limit of $\beta=1$, function (6) reduces to the exponential one. The Mittag-Leffler function is the exact relaxation function leading directly to the Cole–Cole equation (3), i.e. the exponent α in equation (3) is just the exponent β in the Mittag-Leffler pattern (6). Therefore, dielectric relaxation spectroscopy is one of the few experimental methods which offers a method for determining the value of the exponent α — a fundamental quantity describing the extension of the anomalously slow diffusion in liquids.

It is clearly seen in figure 7 that, in the vicinity of the isotropic to nematic phase transition, we are dealing with a subdiffusion process. The anomalous diffusion exponent α increases as the temperature approaches the phase transition from both the isotropic and the nematic sides. The temperature dependence of the exponent in the vicinity of the I–N phase transition shows a strong asymmetry (inverted shape of a lambda-like curve) with an extremely sharp variation at the I–N transition point. The dependence provides important information on the extension of the heterogeneity on the microscopic scale on both sides of the transition. The microscopic heterogeneity in the isotropic phase is due to the formation of pseudo-nematic domains, the mean size of which increases as one approaches the nematic phase transition. In recent papers [24–26], we have investigated the reorientational dynamics of pseudo-nematic domains with the use of nonlinear dielectric spectroscopy. It is worthwhile noting that the nonlinear dielectric effect can be detected in the isotropic phase of mesogenic liquids as far as about 15 K from the phase transition to the nematic phase. The data presented in figure 7 show that this is just the temperature distance from the I–N transition where, in the isotropic phase of 7CB, the exponent α starts to decrease, indicating the beginning of a detectable contribution of the anomalous diffusion to the whole rotational diffusion process. This fact seems strongly to support the view that anomalous rotational diffusion in the isotropic phase of mesogenic compounds is due to microscopic heterogeneity arising from the formation of pseudo-nematic domains.

After the transition of 7CB to the nematic phase, the anomalous diffusion exponent α decreases quite soon — within a few degrees. So, one can conclude that the microscopic heterogeneity due to the existence of pseudo-isotropic domains in the nematic phase disappears much more efficiently than the pseudo-nematic domains in the isotropic phase. Also, in the whole nematic phase of 7CB, the dielectric spectra are described by the Debye equation with a very good approximation ($\alpha \geqslant 0.99$), i.e. the rotational diffusion processes are of Brownian type and the relaxation processes evolve according to the exponential pattern.

Acknowledgments

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