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Anomalous rotational diffusion in the vicinity of the isotropic to nematic phase transition

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Abstract

Dielectric relaxation measurements are performed with very high accuracy on a liquid crystalline compound *n*-octylcyanobiphenyl (8CB) in the isotropic (I), nematic (N) and smectic A (S_A) phases. The data obtained display an essential difference in the rotational diffusion process in the vicinity of the I–N phase transition in comparison to that taking place in the vicinity of the N–S_A phase transition. Thus, for the I–N transition, anomalously slow diffusion (subdiffusion), characterized by an anomalous coefficient $\alpha < 1$, is observed, while normal Brownian rotational diffusion with $\alpha \approx 1$ is found for the N–S_A transition. It is also shown how the fractal parameter α is temperature dependent with an extremely sharp variation at the I–N transition point in the form of a lambda-like profile.

1. Introduction

The relaxational behaviour of a system returning to its equilibrium state is strongly affected by the type of diffusion occurring in it. In the case of normal Brownian diffusion, which is well modelled by the Einstein–Smoluchowski theory [1], the relaxation process follows, in the time domain, a simple exponential decay:

$$f(t) = \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

where $f(t)$ is the normalized relaxation function and τ is the relaxation time. This type of decay concerns any physical property of relaxing systems such as the dielectric polarization, the viscoelastic modulus and the shear compliance.

The Einstein–Smoluchowski theory, applied by Debye [2] to the rotational Brownian motion of an assembly of non-interacting dipolar molecules placed in external ac electric field leads, in the frequency domain, to the well-known equation for the complex dielectric permittivity.

However, in many cases of complex liquids, one observes the failure of the Debye theory to adequately describe the experimental relaxation spectra. Indeed, the dielectric absorption plots are broadened in comparison to those predicted by the Debye equation. If the broadening is symmetric with respect to the maximum of the absorption band, the following modification of the Debye equation allows one to correctly reproduce the experimental relaxation spectrum:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{A}{1 + (i\omega\tau)^\alpha}, \quad 0 < \alpha < 1 \quad (2)$$

where ω is the angular frequency of the probing electric field, $A (= \varepsilon_s - \varepsilon_\infty)$ is the dielectric strength, ε_s and ε_∞ are the permittivities measured in the static and high frequency electric fields, respectively.

This equation was first proposed by Cole and Cole in 1941 [3]. For $\alpha = 1$, the above equation is identical to the Debye equation.

The Cole–Cole equation (2) was widely used as an empirical one [4] and only in the last few years have the molecular basis of the equation and the physical meaning of the exponent α been given. It was shown in numerous theoretical papers [5–12], that the Cole–Cole relaxational behaviour is a direct consequence of the anomalously slow rotational processes in a system under investigation. Then, the relaxational processes in the system could be accounted for not by the traditional Brownian description of the random walks with an exponential decay, but by the continuous-time random walk theory for a power-law distribution of the waiting times between the consecutive jumps of rotations of the molecules. In the case of the fractional dynamics [13–22] the exponential way of performing equilibration of time-dependent quantities must be replaced by the Mittag-Leffler pattern [23] that interpolates between an initial stretched exponential and a terminal inverse power-law pattern, both of index α :

$$E_\alpha(-t/\tau)^\alpha \propto \begin{cases} \exp\left[-\frac{(t/\tau)^\alpha}{\Gamma(1+\alpha)}\right], & t \ll \tau, \\ [\Gamma(1-\alpha)(t/\tau)^\alpha]^{-1}, & t \gg \tau. \end{cases} \quad (3)$$

The Mittag-Leffler function is the exact relaxation function for an underlying fractal time random walk process and that function directly leads to the Cole–Cole equation (2). In the limit of $\alpha = 1$, the Mittag-Leffler function reduces to the exponential one. Therefore, the dielectric relaxation spectroscopy can offer a quite simple and reliable way for determining the value of the parameter α , a fundamental quantity measuring the extension of the anomalously slow rotational diffusion in a particular polar liquid.

In this paper, we present the results of dielectric relaxation studies performed on a mesogenic compound *n*-octylcyanobiphenyl (8CB) in the isotropic (I), nematic (N) and smectic A (S_A) phases. The experimental spectra were analysed by using the Cole–Cole equation (2) over the whole temperature range used, which includes the three liquid crystalline phases of 8CB. Special care was, in particular, taken in the vicinity of I–N and N– S_A phase transitions. The care was concerned mainly the accuracy of the measurements since the rotational subdiffusion effects were expected to be not too pronounced in the liquid crystalline materials. That prediction is from the numerous papers devoted to the dielectric relaxation in 8CB and in other compounds from *n*-alkylcyanobiphenyl series [24–28], where subdiffusive effects were not noticed.

2. Experimental section

The compound studied: *n*-octylcyanobiphenyl (C_8H_{17} -Ph-Ph-CN, 8CB) with the following sequence of phase transitions: (Cr) 19.5 °C (S_A) 33.6 °C (N) 40.9 °C (I), 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 dielectric relaxation measurements were performed with an HP 4194 A impedance/gain phase analyser in the frequency range lying from 100 kHz up to 100 MHz. The measuring capacitor consisted of three plane electrodes: one central electrode and two grounded electrodes on each side. The electrical heating of high performance, using a Unipan 650H controller, ensured a temperature stabilization better than 10^{-3} K and a possibility of changing the temperature very finely, in steps of 10^{-2} K.

3. Results and discussion

Figure 1 presents the 3D plots of the experimental dielectric relaxation spectra recorded for I, N and S_A phases of 8CB. For the N and S_A phases, an external biasing dc electric field was applied for ordering the sample ($\mathbf{E} \parallel \mathbf{n}$), so the data represent the dielectric spectrum $\epsilon_{\parallel}^*(\omega, T)$.

Figure 2 shows an example of the dielectric absorption spectra recorded at given temperatures for the three phases of 8CB. The spectra were resolved into two Cole–Cole-type (2) elementary contributions (see the dashed curves in figure 2), which correspond to the molecular rotations around the short and long axes. For a rod-like molecule having the dipole moment directed along the long symmetry axis, as is the case of 8CB, the absorption band due to molecular rotation around the short axis is strongly prevailing in the dielectric spectrum. The contribution from the molecular rotation around the long axis is very small, especially in the oriented N and S_A phases, and only weakly depends on the temperature and the type of mesophase [24, 25], so we will not discuss it here.

The temperature dependences of the three relaxation parameters A , τ and α of the band corresponding to the molecular rotation around the short axis, obtained from the fit of the Cole–Cole equation (2) to the experimental spectra, are presented in figures 3–5.

The dependence for the relaxation time (figure 4) is presented in the form of an Arrhenius plot. The derivative of the logarithm of τ with respect to T^{-1} , namely:

$$R \frac{d \ln \tau}{d(1/T)} = E_A(T), \quad (4)$$

yields directly the temperature dependence of the activation energy E_A for the rotation of 8CB molecules in the different phases.

As can be seen in figure 6, only in a relatively narrow temperature range (20–30 °C) in the smectic phase of 8CB is the activation energy temperature independent, which usually means that the Arrhenius dependence ($\ln \tau \sim T^{-1}$) is fulfilled. In the remaining temperature range studied, the activation energy for the molecule rotation around their short axis is temperature dependent and the transition between the nematic and isotropic phases is particularly significant on that score. The problem was discussed in our recent paper [29].

Figure 5 presents temperature dependence of the exponent α as an indicator of the evolution of the anomalous rotational diffusion in the system studied. It is clearly seen that in the vicinity of the isotropic to nematic phase transition we are dealing with a subdiffusion process. The effect is rather moderate in its intensity: the relative deviation of α from unity at the I–N transition point does not exceed 5% at the most, indicating a small broadness of the distribution of the relaxation times [30]. However, the results illustrated in figure 5 undoubtedly show an

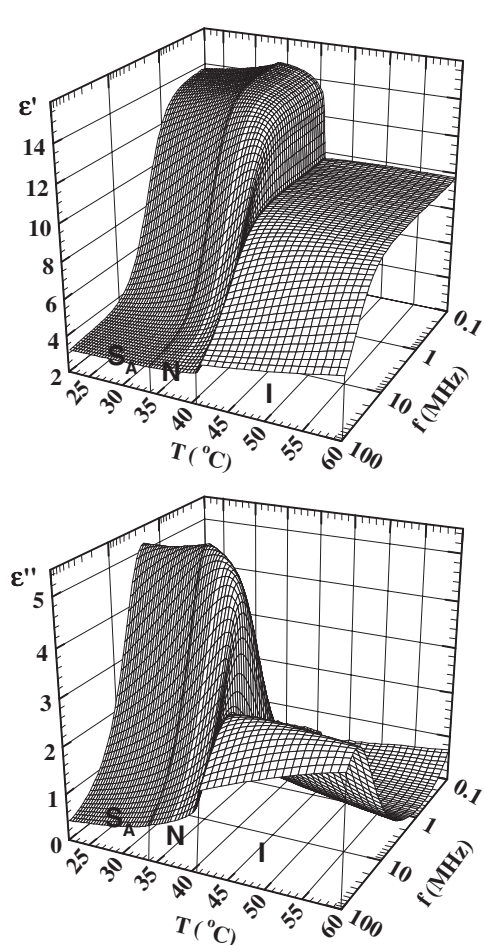


Figure 1. The real (ϵ') and imaginary (ϵ'') parts of the electric permittivity measured in the isotropic (I), nematic (N) and smectic A (S_A) phases of 8CB as a function of the frequency and temperature. In the nematic and smectic A phases, it is the permittivity $\epsilon_{\parallel}^*(\omega, T)$ which is measured.

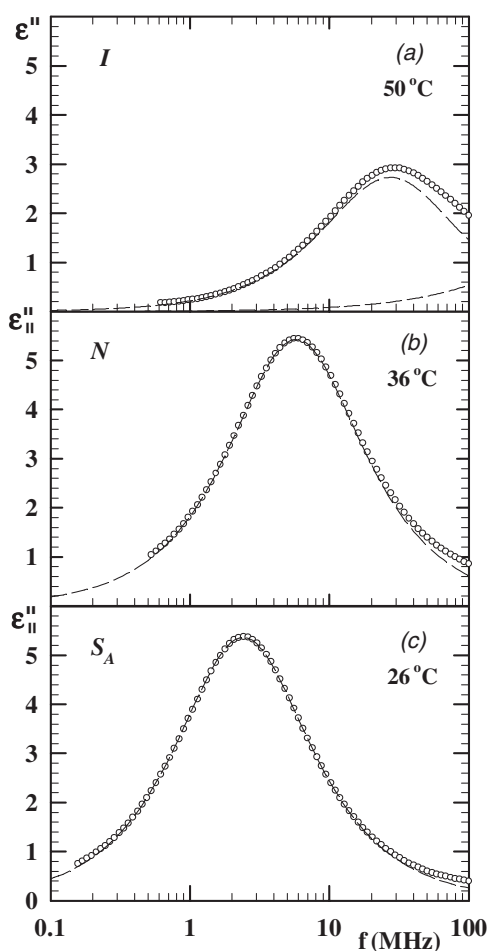


Figure 2. An example of the dielectric absorption spectra recorded in the isotropic (I), nematic (N) and smectic A (S_A) phases of 8CB. Dashed lines are the elementary contributions corresponding to the molecular rotations around the principal molecular axes. The band due to the rotation around the short axes is strongly dominant.

essential difference in the diffusion processes occurring in the vicinity of the I–N and N– S_A transitions.

A strong asymmetry (inverted shape of a lambda-like curve) in the temperature dependence of α in the vicinity of the I–N phase transition gives us 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 the pseudo-nematic domains, the mean size of which increases as one approaches the nematic phase transition. In our recent papers [31–33] we have considered the reorientational dynamics of the pseudo-nematic domains, studied by nonlinear dielectric spectroscopy. It is worthwhile noting that the first detectable signal in the nonlinear dielectric studies was observed in the isotropic phase of mesogenic liquids as far as about 15° from the phase transition to the nematic phase. Figure 5 shows that just about 15° from the transition, α starts to increase, indicating the beginning

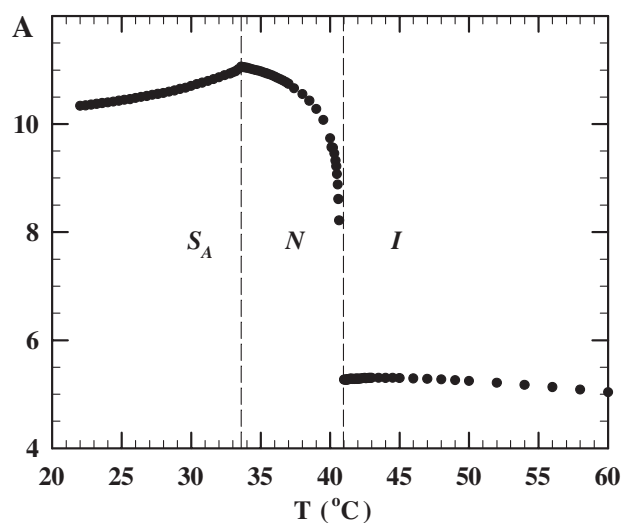


Figure 3. A plot of the temperature dependence of the dielectric strength A for rotation of 8CB molecules around their short axis.

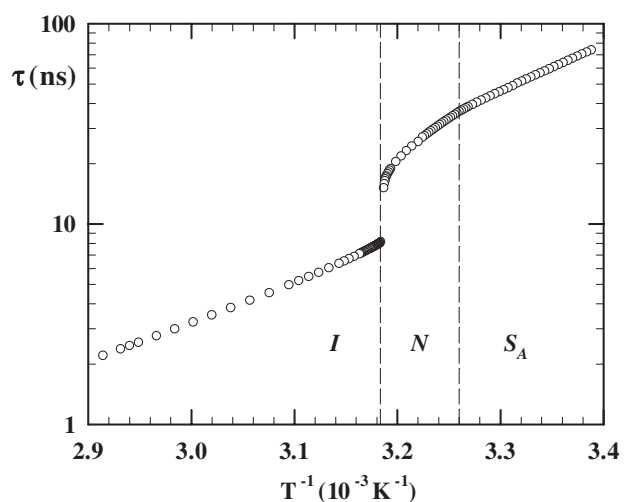


Figure 4. An Arrhenius plot of the longitudinal dielectric relaxation time of 8CB molecules (rotation around the short axis) in various phases.

of a detectable contribution of the anomalous diffusion to the whole diffusion process. So, this anomalous diffusion is undoubtedly due to the microscopic heterogeneity arising from the formation of the pseudo-nematic domains in the isotropic phase of 8CB.

Regarding the nematic phase of 8CB, the heterogeneity due to the pseudo-isotropic domains disappears very rapidly, within about 1° . Next, throughout the whole nematic and smectic A phases of 8CB, the dielectric spectra are described by the Debye equation with a very good approximation ($\alpha \geq 0.995$). Hence, one can conclude that in the two oriented liquid crystalline phases of 8CB, the rotational diffusion processes are of Brownian type, and the relaxation processes evolve according to the exponential pattern. This is also verified

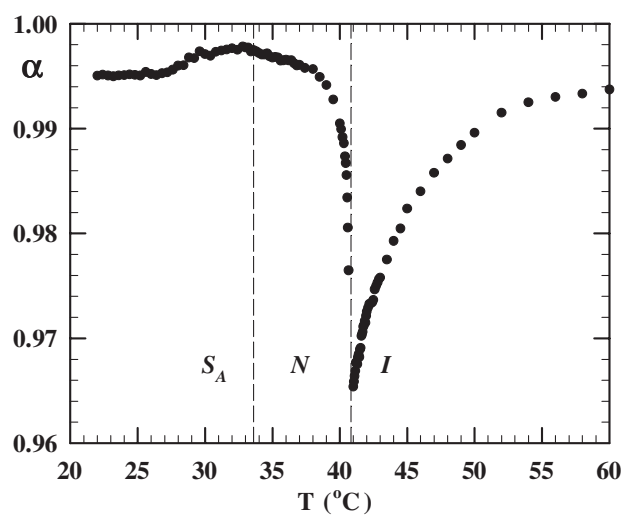


Figure 5. A plot of the temperature dependence of the anomalous rotational diffusion exponent, calculated from the best fit of the Cole–Cole equation (2) to the experimental data for the dielectric spectra of 8CB.

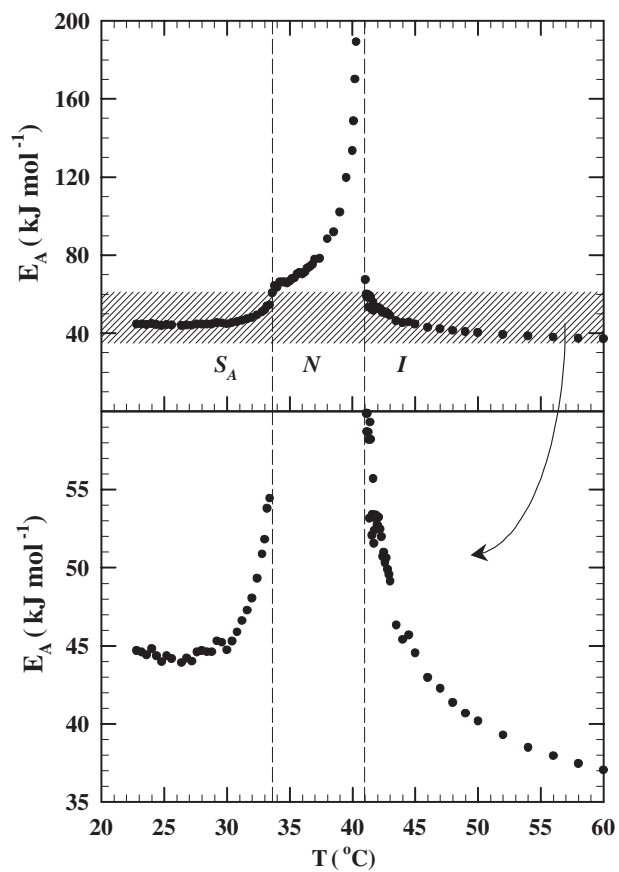


Figure 6. The activation energy of 8CB molecules in rotation around their short axis as a function of the temperature in the isotropic, nematic and smectic A phases.

in the vicinity of the N–S_A transition. The pre-smectic effects due to the formation of the pseudo-smectic layers in the nematic phase, which manifest themselves as an anomalous behaviour of the shear viscosity [34, 35] or elastic constants [36, 37], have no influence on the diffusional rotation of the molecules. The reorientational motions of the molecules conserve their Brownian character both in the situation when the precursors of the smectic layers are formed in the nematic phase and when stable layers comprise the whole sample of the liquid crystalline smectic A phase.

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