

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/6153051>

Contribution to Understanding of the Molecular Dynamics in Liquids

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · SEPTEMBER 2007

Impact Factor: 2.69 · DOI: 10.1021/jp0728252 · Source: PubMed

CITATIONS

23

READS

19

4 AUTHORS, INCLUDING:



Jan Jadżyn

Institute of Molecular Physics, Polish Acade...

215 PUBLICATIONS **1,554** CITATIONS

SEE PROFILE



Margarita Ginovska

Ss. Cyril and Methodius University

9 PUBLICATIONS **95** CITATIONS

SEE PROFILE

Contribution to Understanding of the Molecular Dynamics in Liquids

Jan Jadżyn* and Grzegorz Czechowski

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

Jean-Louis Déjardin

Groupe de Physique Statistique et Moléculaire, MEPS, Université de Perpignan, 52 Avenue Paul Alduy, 66860 Perpignan Cedex, France

Margarita Ginovska

Faculty of Electrical Engineering, University of Saints Cyril and Methodius, P. O. Box 574, 91000 Skopje, Macedonia

Received: April 11, 2007; In Final Form: June 19, 2007

The dielectric relaxation spectroscopy is used for studying the orientational molecular dynamics in the isotropic (I) and nematic (N) phases of two mesogenic liquids composed of the molecules of similar structure and length, but of an essentially different polarity: *n*-heptylcyanobiphenyl, C₇H₁₅PhPhCN, 7CB (molecular dipole moment $\mu \approx 5\text{D}$) and 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene, C₆H₁₃CyHxPhNCS, 6CHBT ($\mu \approx 2.5\text{D}$); advantageously, the temperatures of the I–N phase transition for the two compounds are very close to each other ($T_{\text{NI}} = 316.6 \pm 0.2\text{ K}$). It is shown that regardless of the differences in polarity of 7CB and 6CHBT molecules and their abilities in dipolar aggregation, the values and temperature dependences of the relaxation time (corresponding to the rotational diffusion of the molecules around their short axis) are very close to each other, in both the isotropic and nematic phases of the liquids studied. Therefore, the data show that the dielectric relaxation processes occurring in dipolar liquids in the isotropic and nematic states lead through the rotational diffusion of individual molecules and the diffusion seems to be not influenced by the intermolecular interactions.

Introduction

The interpretation of the dielectric relaxation spectra of dipolar liquids always touches a delicate problem regarding the influence of intermolecular interactions, mainly the dipole–dipole coupling, on the dynamics of molecular reorientational processes which appear in the spectra as an electromagnetic energy absorption.¹ Intuition suggests to us that, in the liquid state, the dipolar molecular aggregation should influence the molecular dynamics and one should expect to observe the strongest effect for molecules having the highest dipole moments. From the experimental point of view, a solution for the problem is, in principle, quite simple. One has to perform the relaxational experiment on two liquids composed of molecules having, as much as possible, different dipole moment values, but, simultaneously, the other properties of the liquids studied, both microscopic (such as the molecular length, the moment of inertia, etc.) and macroscopic (mainly the viscosity), should be as much as possible close to each other. Because compliance with those requirements is rather difficult, the experimental data on that matter are more than modest. Of course, we exclude from our considerations the liquids where the strong and directional intermolecular interactions, such as the hydrogen bonds, occur.

In a recent paper,² we presented the experimental data on two mesogenic liquids composed of molecules of a quite similar

structure and essentially different polarities and the conclusion concerning the dielectric relaxation was somewhat unexpected: in the isotropic phase of both compounds, at the same temperature, the dielectric absorption maximum was found to be at the same frequency of the probing electric field. This means that the relaxational processes due to the dipolar rotational diffusion are running in the same way independently of the strength of the dipolar interactions. Moreover, since the liquids studied were different with respect to their mesogeneity (one liquid is nematogenic while the other is smectogenic) and the temperatures of the phase transitions were quite different in the two compounds, the term “at the same temperature” may lead to some misunderstanding, because, in the physics of liquid crystals, it is generally a relative temperature which is used for comparing a given property of different compounds, either the reduced one $T^* = T/T_{\text{NI}}$ (where subscript “NI” refers to the nematic–isotropic phases) or simply the difference $\Delta T = T - T_{\text{NI}}$.³ The main argument for the first way of the temperature expression comes from the Maier and Saupe theory,⁴ which predicts a universal function of the nematic orientational order parameter on the reduced temperature T^* . However, the case of the order parameter is rather particular, and if one has to compare the temperature dependences of other physical quantities, such as the dielectric permittivity, the relaxation time, or the viscosity of different nematogenic compounds, the situation is not so clear.

A uniqueness of the experimental results presented in this paper lies in the fact that the two mesogenic compounds studied

* To whom correspondence should be addressed. E-mail: jadzyn@ifmpan.poznan.pl.

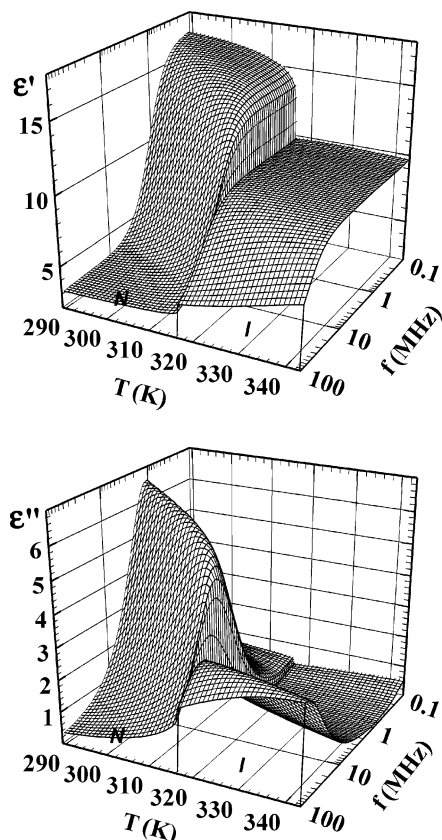


Figure 1. Dielectric relaxation spectra of 7CB in the isotropic (I) and nematic (N) phases.

fulfill not only the requirements concerning the similarity in the molecular structure and the dissimilarity in the polarity of the molecules, but also the phase transitions from the isotropic liquid to the liquid crystalline nematic phase occur practically at the same temperature. It is really an exceptional case which allows us to confront directly all the results obtained for different mesogenic compounds without any hesitation on an appropriate way of temperature expression.

Experimental Section

The compounds that we have considered belong to two well-known homologous series: *n*-alkylcyanobiphenyls, C_nH_{2n+1} -PhPhCN, *n*CB (studied here $n = 7$), composed of the strongly polar molecules (the dipole moment $\mu \approx 5$ D), and 4-(*trans*-4'-*n*-alkylcyclohexyl)isothiocyanatobenzenes, C_nH_{2n+1} CyHxPhNCS, *n*CHBT (studied here $n = 6$), with the molecular dipole moment of about 2.5 D. As mentioned above, the two mesogenic compounds exhibit the transition from the isotropic to the nematic phase practically at the same temperature 316.6 ± 0.2 K. The compounds were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw, and their purities, checked by chromatography, were better than 99.5%.

The dielectric characteristics of the compounds were measured with an HP 4194A impedance/gain phase analyzer in the frequency range of 50 kHz to 100 MHz. The static values of the permittivity were determined from the low-frequency plateau of the real part of the complex dielectric permittivity. The measuring capacitor consisted of three plane electrodes, one central and two grounded on each side, with a distance between the electrodes of about 0.5 mm. In the nematic phase, a dc biasing electric field was applied to the capacitor, so the parallel component of the permittivity ϵ_{\parallel}^* ($\mathbf{n} \parallel \mathbf{E}$) was measured. The

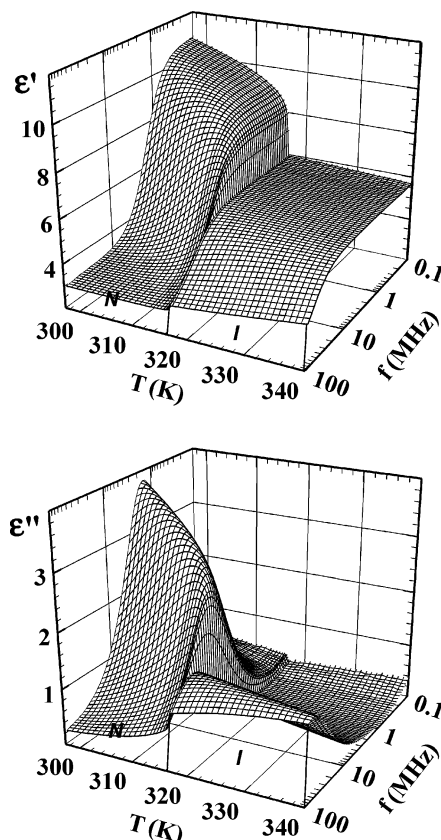


Figure 2. Dielectric relaxation spectra of 6CHBT in the isotropic (I) and nematic (N) phases.

electrical heating of high performance by using a Scientific Instruments temperature controller, model 9700, assured a quite good stabilization of the temperature (at the millikelvin level) with the possibility of varying the temperature by steps of 10^{-2} K. Such equipment allows us to determine the permittivity with a relative accuracy better than 0.5%.

The viscosity was determined with a Haake viscometer RV 20 with the measuring system CV 100, consisting of a rotary beaker filled with the compound studied and a cylindrical sensor of Mooney-Ewart type (M 15) placed in the center of the beaker. The liquid gap was 0.5 mm. The accuracy of the viscosity measurements was 0.5%. The temperature of the sample was controlled with an accuracy of ± 0.1 °C.

Results and Discussion

In Figures 1 and 2 are presented the temperature and the frequency dependences of the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric permittivity ($\epsilon^* = \epsilon' - i\epsilon''$) measured in the isotropic and nematic phases of 7CB and 6CHBT, respectively. As it was mentioned, in the nematic phase, it is the component of the permittivity ϵ_{\parallel}^* parallel to the macroscopic nematic orientation (the director \vec{n}) forced by the biasing electric field, which was measured. For the probing electric field of low frequency, the real part of the permittivity is frequency-independent (the static dielectric constant, ϵ_s) and its value reflects, at a given number of dipolar molecules per unit volume, the collective molecular contribution to the dielectric polarization of the sample studied. As we have shown in a recent paper,⁵ the temperature dependences of the static permittivity and its derivative, measured in the isotropic phase of mesogenic liquids, are very important indicators of the molecular self-organization in the pretransitional region, thus allowing one to correlate the

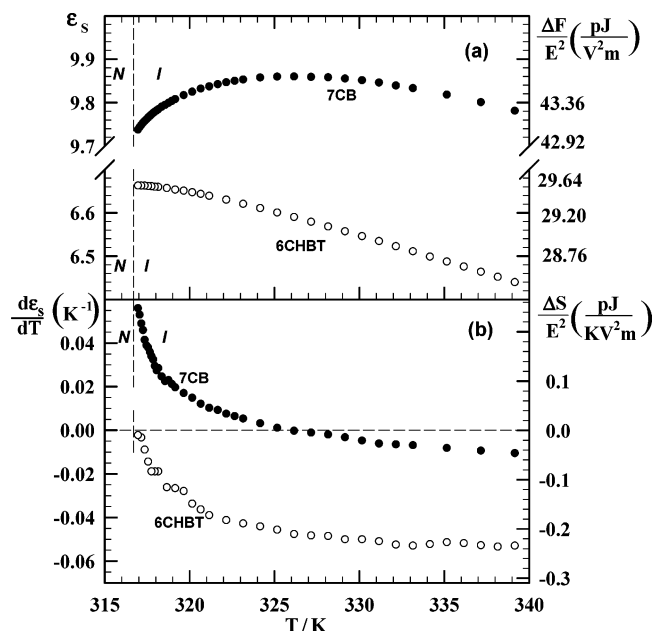


Figure 3. Temperature dependences of the static dielectric permittivity and the Helmholtz free energy (a) and the permittivity derivative and the entropy (b).

extent of that self-organization to the properties of the individual mesogenic molecules. The importance of this problem was first realized by Fröhlich in 1958,⁶ who showed that the electric field induced increments of two basic thermodynamic quantities, namely, the Helmholtz free energy ΔF and the entropy ΔS , are directly related, respectively, to the static permittivity and its derivative:

$$\frac{\Delta F}{E^2} \equiv \frac{F(T, E) - F_0(T)}{E^2} = \frac{\epsilon_0}{2} \epsilon_s \quad (1)$$

$$\frac{\Delta S}{E^2} \equiv \frac{S(T, E) - S_0(T)}{E^2} = \frac{\epsilon_0}{2} \frac{\partial \epsilon_s}{\partial T} \quad (2)$$

where F_0 and S_0 denote the values of the thermodynamic quantities in the absence of the electric field, E is the amplitude of the probing field, T is the absolute temperature, and $\epsilon_0 = 8.85 \text{ pF/m}$ is the permittivity of free space.

The above equations give us a simple thermodynamic interpretation of the static dielectric properties of the material under consideration.^{7–9} The static permittivity itself corresponds to the Helmholtz free energy, i.e., represents a maximum of the energy which can be yielded during the isothermal discharge of the capacitor filled with the dielectric material. The temperature derivative of the permittivity, in turn, is related directly to the entropy change due to an application of the probing electric field to the system. Of particular importance is the sign of the entropy increment $\Delta S = S(T, E) - S_0(T)$ which depends directly on the sign of the permittivity derivative. A negative value of $d\epsilon_s/dT$, i.e., $\Delta S < 0$, means that, due to an application of the electric field to the dielectrics, the entropy decreases (the molecular order in the system increases). This is the normal behavior of dipolar liquids.

Figure 3 presents the temperature dependences of the static permittivity (a) and its derivative (b) together with the increments of the free energy and the entropy (per unit volume and unit field strength, and the entropy, per kelvin) calculated from eqs 1 and 2, for 7CB and 6CHBT. The different polarities of the two compounds are manifested clearly by the different values

of the permittivity and its temperature dependences. In the case of strongly polar 7CB, the static permittivity exhibits a maximum in the prenematic region and, as a consequence, the permittivity derivative and the entropy increment change their sign to the positive in that region. The static permittivity of a less polar 6CHBT also shows the pretransitional anomalous temperature behavior, but of a greatly reduced extent: the permittivity attains a maximum just at the temperature of the I–N phase transition, and the entropy increment attains the value close to zero at the transition.

As illustrated in Figure 3b, in the isotropic phase of the liquids studied, at a temperature very close to the I–N transition—in the case of 6CHBT—and at a temperature of about 8 degrees before the transition—in case of 7CB—the entropy increment $\Delta S = 0$; i.e., the *resulting field-induced ordering effect* on the dipolar molecules disappears. In the case of strongly polar 7CB molecules, as the temperature decreases, the increment of the entropy increases, changes its sign, and becomes positive ($\Delta S > 0$). So, here, the electric field applied to the isotropic dipolar liquid acts as a *decreasing factor of the resulting order* on the molecular level. The observed effects certainly result from the competition between the normal field ordering of the molecular dipoles in the liquids and the field interference in the intermolecular entities spontaneously formed as the precursors of the nematic state (prenematic domains). The problem was discussed in detail in ref 5.

The presented data clearly show that a large difference in the polarity of 7CB and 6CHBT molecules reflects itself very strongly on the static dielectric properties and related thermodynamic quantities measured in the isotropic phase of the two compounds.

Now, we will see how the difference in the polarity reflects itself on the dynamics of 7CB and 6CHBT molecules, as recorded by dielectric relaxation spectroscopy. The dielectric spectra presented in Figures 1 and 2 were resolved into two elementary contributions of the Cole–Cole type:¹⁰

$$\epsilon^*(\omega, T) = \epsilon'(\omega, T) - i\epsilon''(\omega, T) = \epsilon_\infty(T) + \sum_{k=1}^2 \frac{A_k(T)}{1 + [i\omega\tau_k(T)]^\alpha}, \quad 0 < \alpha \leq 1 \quad (3)$$

corresponding to molecular rotations around their two principal axes. In eq 3 ω denotes the angular frequency, ϵ_∞ is the permittivity measured at a sufficiently high frequency to prevent dipolar reorientation, A_k is the dielectric strength, and τ_k is the relaxation time of the k th relaxation process. The exponent α refers to the symmetric broadening of the dielectric absorption band with respect to the Debye-type band ($\alpha = 1$).¹¹ For a rodlike molecule with the dipole moment directed along the long symmetry axis (it is the case of molecules studied), 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 relatively small and only weakly depends on the temperature and the type of phase, so we will not discuss it here.

The temperature dependences of the two principal relaxation parameters, namely, the dielectric strength A and the relaxation time τ , corresponding to the molecular rotation around the short axis, obtained from the best fit of the Cole–Cole eq 3 to the experimental spectra of 7CB and 6CHBT, are presented in Figures 4 and 5, respectively. The obtained values of the third fitting parameter—the exponent α —show that the dielectric absorption bands of compounds studied are very close to the Debye-type bands with an exception of the pretransitional region

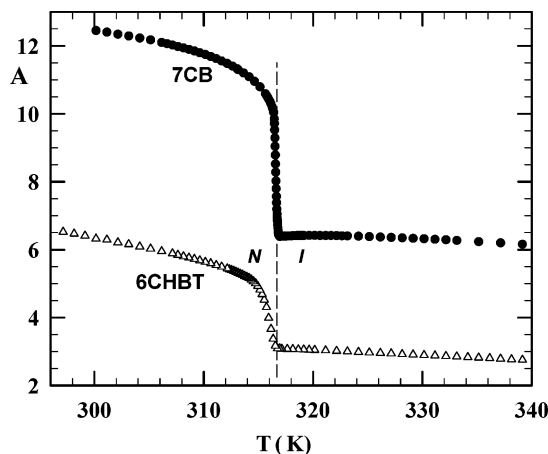


Figure 4. Temperature dependences of the dielectric strength of the band corresponding to the rotational diffusion of 7CB and 6CHBT molecules around their short axis.

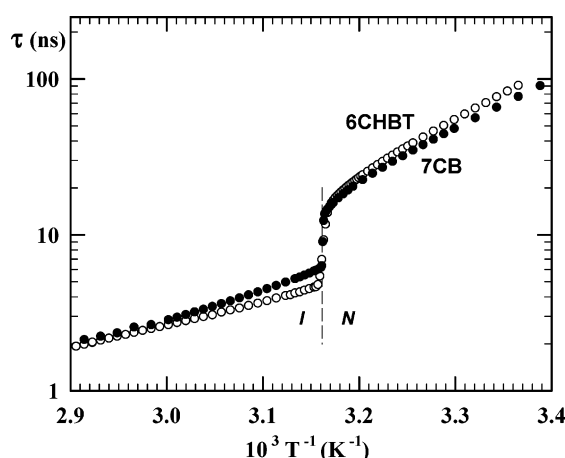


Figure 5. Arrhenius plots for the relaxation time corresponding to the rotational diffusion of 7CB and 6CHBT molecules around their short axis.

where, both from the isotropic and the nematic side, one observes a rather small broadening (about 5%) of the bands with a maximum at the I–N transition. The effect was discussed in refs 12–14 and is not essential for the problem treated in this paper.

An important difference in the dielectric strength of the two compounds (Figure 5) reflects directly the difference in the polarity of the molecules from which are formed the compounds. In that context, the results presented in Figure 5 are certainly unusual. The *dielectric relaxation times* corresponding to the rotational motion around the short axis of 7CB and 6CHBT molecules of so different polarity are *practically equal to each other both in the isotropic and the nematic phases*. This experimental fact seems to be a solid base for confirming an apparent single-molecular mechanism of the relaxation processes in liquids, as seen in the conventional dielectric spectroscopy.

Because the viscosity of a liquid is an essential factor determining the value of the dielectric relaxation time, one can suppose that in the case of the compounds studied here we can deal with some exceptional viscosity dependences leading to some compensations in the relaxation times. It is rather difficult to imagine such a situation especially since it should concern at the same time two quite different phases of the compounds. Figure 6 shows the temperature behavior of the shear viscosity measured in the isotropic and nematic phases of 7CB and

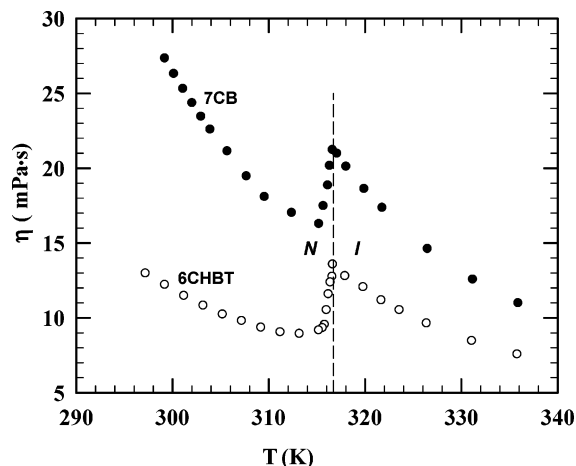


Figure 6. Shear viscosity of freely flowing 7CB and 6CHBT in the isotropic and nematic phases.

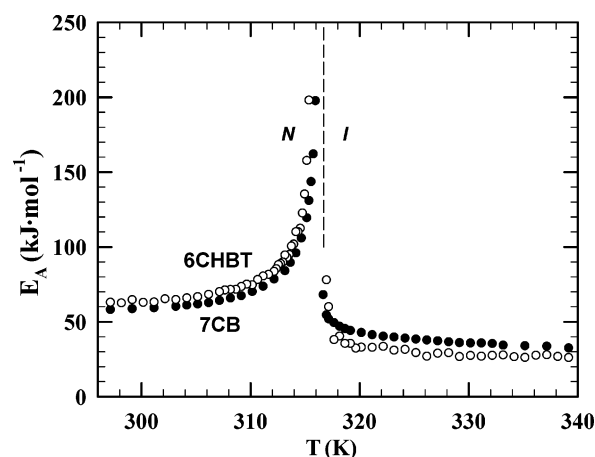


Figure 7. Activation energy for 7CB and 6CHBT molecules rotation around their short axis as a function of temperature.

6CHBT in their free flow. Both compounds belong to the low-viscosity group of the mesogenic liquids, and their viscosities are enough close to each other for eliminating its unexpected role in the relaxation processes. The details on the viscous behavior of freely flowing mesogenic liquids are described in refs 15 and 16.

In Figure 5, the temperature dependences of the relaxation time are presented in the form of Arrhenius plots. According to the Arrhenius equation

$$\tau(T) = C \exp\left(\frac{E_A}{RT}\right) \quad (4)$$

the value of the relaxation time is determined by the ratio of the activation energy (E_A), which is, in general, assumed to be temperature-independent, and the thermal energy (RT). C is a constant. However, since the meaning of the “activation energy” for the rotational Brownian motion is not too clear, the postulate of a constant E_A value as a function of the temperature seems to have no solid physical basis. It is why we have proposed¹⁷ a procedure for determination of E_A by the differentiation of eq 4: the derivative of the logarithm of τ with respect to T^{-1} yields directly the temperature dependence of the activation energy E_A for the rotational diffusion of molecules under study. Of course, the procedure does not exclude the temperature independence of the activation energy. Figure 7 presents the results obtained in that way. The temperature behavior of the activation

energy of both 7CB and 6CHBT is practically identical: in the isotropic phase E_A (≈ 30 kJ/mol) is slightly temperature-dependent (slow increase with decreasing temperature), and only its small prenematic effect is observed. In the nematic phase the situation is quite different: the activation energy shows an increase from the value of about 60 kJ/mol (far from the transition) and in the vicinity of the transition to the isotropic phase the $E_A(T)$ dependence shows a critical-like behavior. The dependences presented in Figure 7 are surprisingly similar to those recorded by Iannacchione and Finotello¹⁸ as the temperature dependence of the specific heat measured for bulk cyanobiphenyls with a use of the high-resolution calorimetry method.

In conclusion, the results presented in this paper clearly show that from the molecular dynamics point of view, as observed by the dielectric relaxation spectroscopy in the isotropic liquids and the nematic liquid crystals, the polarities of the molecules play a secondary role only (if any). The two compounds studied, composed of molecules of essentially different polarity, exhibit the same way of returning to the equilibrium state after perturbation of that equilibrium by the probing electric field. This relaxation process proceeds mainly with an exponential time dependence, i.e., as a normal Brownian rotational diffusion, and the relaxation time value appears to be not influenced by the intermolecular interactions.

References and Notes

- (1) Bagchi, B.; Chandra, A. *Adv. Chem. Phys.* **1991**, *80*, 1.
- (2) Jadżyn, J.; Czechowski, G.; Bauman, D.; Déjardin, J. L.; Kresse, H.; Douali, R.; Legrand, C. *Phys. Rev. E* **2005**, *71*, 052701.
- (3) de Gennes, P. G. *Physics of Liquid Crystals*; Oxford University Press: Oxford, U.K., 1974.
- (4) Maier, W.; Saupe, A. Z. *Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1958**, *13*, 564.
- (5) Jadżyn, J.; Czechowski, G. *J. Phys. Chem. B* **2007**, *111*, 3727.
- (6) Fröhlich, H. *Theory of Dielectrics*, 2nd ed.; Clarendon Press: Oxford, U.K., 1958.
- (7) Becker, R. *Electromagnetic Fields and Interactions*; Blackie and Son: London, 1964.
- (8) Landau, L. D.; Lifshitz, E. M.; Pitaevskii, L. P. *Electrodynamics of Continuous Media*, 2nd ed.; Pergamon Press: Oxford, U.K., 1984.
- (9) Scaife, B. K. P. *Principles of Dielectrics*; Clarendon Press: Oxford, U.K., 1998.
- (10) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.
- (11) Debye, P. *Polar Molecules*; Chemical Catalog: New York, 1929.
- (12) Jadżyn, J.; Czechowski, G.; Déjardin, J. L.; Ginovska, M. *J. Phys.: Condens. Matter* **2005**, *17*, 813.
- (13) Jadżyn, J.; Bauman, D.; Déjardin, J.-L.; Ginovska, M.; Czechowski, G. *Acta Phys. Pol., A* **2005**, *108*, 479.
- (14) Déjardin, J.-L.; Jadżyn, J. *J. Chem. Phys.* **2005**, *123*, 174502.
- (15) Jadżyn, J.; Czechowski, G. *J. Phys.: Condens. Matter* **2001**, *13*, L261.
- (16) Jadżyn, J.; Czechowski, G. *Phys. Rev. E* **2001**, *64*, 052702.
- (17) Jadżyn, J.; Czechowski, G.; Legrand, C.; Douali, R. *Phys. Rev. E* **2003**, *67*, 041705.
- (18) Iannacchione, G. S.; Finotello, D. *Phys. Rev. E* **1994**, *50*, 4780.