# Reorientational dynamics of the pseudonematic domains studied with nonlinear dielectric spectroscopy

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Nonlinear dielectric spectroscopy was used for studies of the reorientational dynamics of the pseudonematic domains in the isotropic phase of the mesogenic substance in the vicinity of the isotropic to nematic phase transition. The results were interpreted in the frame of the Landau–de Gennes theory.

## I. INTRODUCTION

Critical-like behavior of many physical properties of isotropic mesogenic liquids in the vicinity of the nematic phase transition shows that the transition is not a typical first order. As the transition is associated with a small volume change and the latent heat, the most often is classified as a weakly first order or close to second order. The pretransitional phenomena are due to the existence of a short range orientational order of the mesogenic molecules, which leads to the formation of pseudonematic domains in the isotropic phase. The size of the domains increases as the temperature of the liquid comes up to the nematic phase transition. The phenomenon can be quantitatively described in terms of the intermolecular correlation length $\xi$. 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 [1]

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

where $\xi_0$ is on the order of the molecular length and $T^*$ denotes the temperature of virtual transition of the second order. Usually the value of $T^*$ is a few degrees below the nematic to isotropic phase transition temperature ($T_{NI}$). According to Eq. (1), the correlation length becomes infinite at $T^*$.

The peculiarity of the isotropic to nematic phase transition consists in the fact, that an access to the region closest to the critical point ($T^*$) is not possible in the experiment: the transition of the first order in nature occurs at the temperature $T_{NI}$, a few degrees higher that $T^*$. As a consequence, the determination of the critical exponents must be performed with the use of some extrapolations, which, as a rule, lead to the diversity in final results obtained by different authors. It is probably one of the reasons that, despite of the numerous papers both theoretical [2–4] and experimental [5–8] de-

voted to the isotropic to nematic phase transition, the nature of the critical behavior in the vicinity of the transition, is not properly understood [9].

The validity of the Landau–de Gennes theory has been experimentally confirmed in the static measurements of magnetic [10] and electric [11] birefringence, light scattering [12], nonlinear dielectric effect [7], as well as in the dynamic studies such as molecular spin-lattice relaxation [13,14], dynamic light scattering [15], and optical Kerr effect [16–20]. However, the measurements of magnetic and electric birefringence [16,21] and transient grating optical Kerr effect [18,19] performed in a large temperature range reveal the deviations from the Landau–de Gennes theory for temperatures sufficiently higher (about 20 K) than $T_{NI}$.

In this paper we present the results of the studies of the dynamics of pretransitional effects in the vicinity of the isotropic to nematic phase transition performed for the first time with the nonlinear dielectric spectroscopy. A nonlinearity in the dielectric spectroscopy is caused by applying to the studied liquid an additional static electric field of a very high strength.

## II. A BACKGROUND OF THE NONLINEAR DIELECTRIC SPECTROSCOPY

The dielectric polarization (**P**) of isotropic liquids placed in a weak electric field is proportional to the field strength (**E**):

$$\mathbf{P} = \varepsilon_0 (\varepsilon - 1) \mathbf{E}, \tag{2}$$

where $\varepsilon_0 = 8.85 \times 10^{-12} F/m$ and $\varepsilon$ is the (relative) electric permittivity of the liquid. This linear relation shows that the permittivity $\varepsilon$ of isotropic liquid, determined as

$$\frac{\partial P}{\partial E} = \varepsilon_0 (\varepsilon - 1), \tag{3}$$

does not depend on the electric field strength (Fig. 1). For the frequency-dependent fields, the polarization shows a relaxation in the frequency region depending on molecular dynamics of the system studied. The linear dielectric spectroscopy is one of the principal methods for investigation of the
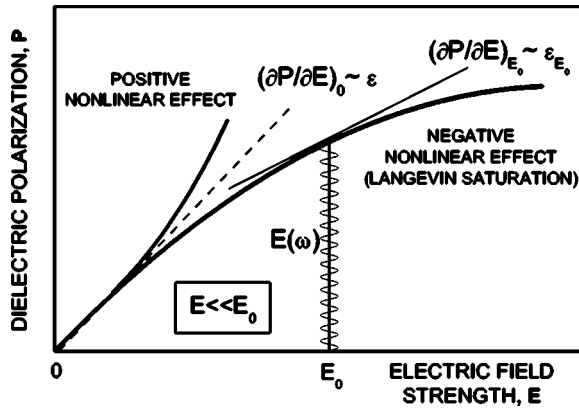
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FIG. 1. Strong electric field $E_0$ causes a nonlinearity in the dielectric polarization vs field strength dependence. The nonlinearity can lead to an increase (positive effect) or to a decrease (negative effect) of the permittivity measured by ac field $E(\omega)$ of low intensity.

molecular dynamics in liquids and liquid crystals. The molecular interpretation of the experimental results is based on the Smoluchowski-Debye model of rotational diffusion of the dipoles in liquids [22,23].

Electric fields of high intensity ($10^6$ V/m, or higher) applied to polar liquids cause a deviation from the linear dependence (1), as sketched in Fig. 1. In the experiment one determines the nonlinear dielectric increment $\Delta\varepsilon$, which is defined as a difference between the permittivity measured by an a.c. electric field of small amplitude $E(\omega)$ in the presence ($\varepsilon_{E_0}$) and in the absence ($\varepsilon$) of a biasing field $E_0$ of high strength:

$$\Delta\varepsilon = \varepsilon_{E_0} - \varepsilon. \qquad (4)$$

The dielectric nonlinearity can be caused, in general, by two molecular phenomena occurring in isotropic liquids. First of all, it is the Langevin ($L$) saturation of the orientation of the dipoles forced by the strong electric field. The effect leads to a decrease of the permittivity of polar liquid, i.e., the increment $\Delta\varepsilon_L$ is negative. The value of $\Delta\varepsilon_L$ is proportional to the square of $E_0$. The increment shows the relaxation (nonlinear orientational dielectric relaxation) in the same frequency region as for the linear dielectric relaxation [at least for small values of the dipolar energy ($\mu E_0$) to the thermal energy ($kT$) ratio [24]], and can be presented in the complex form

$$\Delta\varepsilon_L^*(\omega) = \Delta\varepsilon_L'(\omega) - i\Delta\varepsilon_L''(\omega), \qquad (5)$$

where $\Delta\varepsilon_L'$ and $\Delta\varepsilon_L''$ stand for the real and imaginary parts of the nonlinear dielectric increment, respectively.

The Langevin dielectric saturation occurs always when a dipolar liquid is placed in a strong electric field. However, the studies of the effect or even its recording in a neat-state is hard to perform because of the second molecular phenomenon causing a nonlinearity of the dielectric properties of dipolar liquids. The phenomenon concerns the liquids in which the intermolecular interactions (e.g., dipole-dipole or
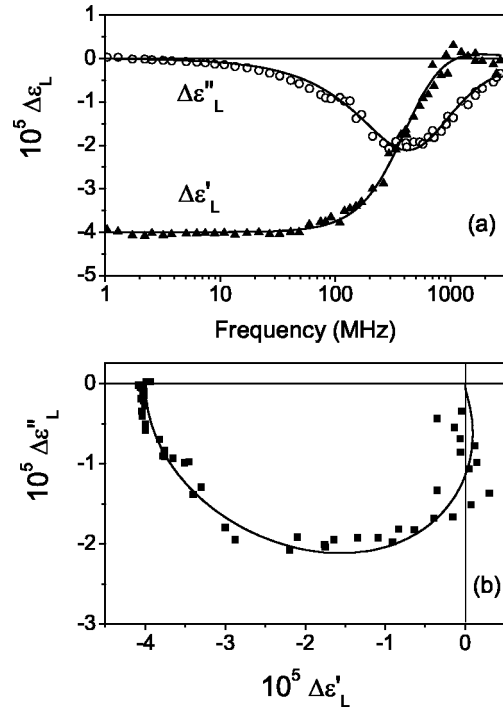


FIG. 2. Nonlinear dielectric relaxation spectrum (a) and nonlinear Cole-Cole plot (b) for the Langevin dipolar saturation effect in strong electric field ($E_0 = 1.1 \times 10^7$ V/m) recorded for a diluted solution of 6CHBT in benzene (1% mol. fr.) at 25°C [29]. Solid lines represent the Coffey-Kielich theory [31,32].

hydrogen bonds) lead to the formation of aggregates susceptible to the electric field. The susceptibility may denote here many effects, but the most important for nonmesogenic, isotropic liquids is the shift of the equilibrium between the aggregates and the free molecules. Of course, the shift can be induced by an electric field in case of the different polarity of the both side partners of the equilibrium. A classical example of such a kind of equilibrium is the cyclic dimerization of the carboxylic acids or lactams leading to practically nonpolar dimers. Then a strong electric field shifts the equilibrium between monomers and dimers ($2A_1 \rightleftharpoons A_2$), in favor of more polar species (monomers). It gives an increase of the permittivity, i.e., the field induced increment (4) is positive. The increment measured with an ac electric field $E(\omega)$ of low strength shows the relaxation in the frequency region corresponding to the kinetics of the "chemical reactions" occurring in the system studied. Up to now, the nonlinear dielectric spectroscopy was mainly used for studies of the kinetics of the reactions of type of dimerization [25,26] or the multimolecular aggregations [27,28] due to the hydrogen bonds formation.

The Langevin saturation phenomenon can be investigated for the noninteracting dipolar systems. Only one efficient way for the reduction of dipole-dipole interactions in liquids is known: it is the dilution of a dipolar substance in nonpolar medium. Unfortunately, a decrease of the dipole number in the unit volume leads simultaneously to a decrease of the measured signal amplitude.

Figure 2 presents the nonlinear dielectric relaxation spectrum obtained for diluted solution (1% in molar fraction)

of 4-(*trans*-4′-*n*-hexylcyclohexyl) isothiocyanatobenzene (6CHBT) in benzene [29]. It is a mesogenic compound which is the subject of our studies in a pure (isotropic) state presented in the next parts of the paper. The concentration of dipoles in the experiment presented in Fig. 2 was the compromise between the effectiveness of the dipole-dipole interaction reduction and the limit of the measuring apparatus sensitivity. The results presented in Fig. 2 and those presented in our papers [29,30] have shown that the nonlinear dielectric spectra recorded for sufficiently diluted dipolar solutions are well reproduced by the theory of Coffey *et al.* [31], Kielich *et al.* [32], and Dejardin and Kalmykov [33–35], which were formulated for noninteracting dipolar systems.

As a number of dipolar molecules in the unit volume increases, the intermolecular interactions in a larger and larger extent determine the structure and dynamic properties of liquids. In pure mesogenic liquids the interactions are so effective that even in the isotropic phase can lead to a high degree of local order, which persists for an extended time period. The effect manifests itself most of all in the vicinity of the transition to the nematic phase in the form of the pseudonematic domains. The dynamics of these entities is the subject of the present paper.

## III. EXPERIMENT

4 -(*trans*-4′ - *n* - hexylcyclohexyl)isothiocyanatobenzene, $C_6H_{13}$ CyHx Ph NCS, 6CHBT (melting point=285.6 K, the transition from the nematic to isotropic phase at $T_{NI}$ =316.2$K$) was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compound, checked by the chromatography, was 99.5%.

The measurements of the nonlinear dielectric effect in the frequency domain were performed with the precise equipment designed at the University of Leuven, Belgium [25].

In the method used the electric field of high strength $E_0$ and low frequency (85 Hz) perturbs periodically the system and the permittivity is measured with a weak field $E(\omega)$ of high frequency. The nonlinear dielectric data are obtained by monitoring the modulation of the parameters of a resonant circuit induced by the application of a high field to the capacitor of the circuit, filled with the liquid studied. An LC resonance circuit with exchangeable coils covers the frequency range from 1 to 100 MHz. The details of the method and the set up used are described in Ref. [25].

The viscosity was measured with a Haake RV20 rotational viscometer. The details were described in Ref. [36].

## IV. RESULTS AND DISCUSSION

Figure 3 presents the nonlinear dielectric spectra recorded in the isotropic phase of 6CHBT within the temperature range of about 15 K from the transition to the nematic phase. Two features of the spectra seem to be important. First of all, the field-induced dielectric increment (4) is positive and it relaxes in the frequency range essentially lower than that corresponding to the reorientational motions of 6CHBT mol-
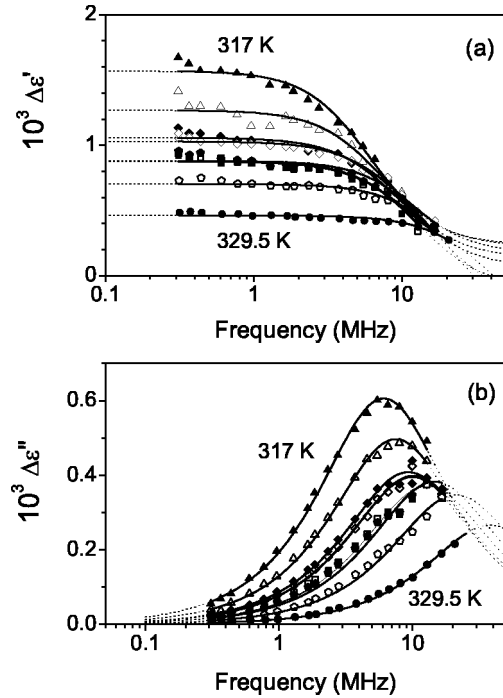


FIG. 3. Frequency dependence of the real (a) and imaginary (b) parts of the nonlinear dielectric increment measured in the isotropic phase of 6CHBT in the vicinity of the isotropic to nematic phase transition. The solid lines correspond to the Debye-type function (6) with a single relaxation time.

ecules. Secondly, the frequency dependence of the increment can be perfectly described by a simple Debye-type function with a single relaxation time ($\tau$):

$$\Delta\varepsilon^* = \Delta\varepsilon' - i\Delta\varepsilon'' = \frac{\Delta\varepsilon^0}{1 + i\omega\tau}, \tag{6}$$

where $\Delta\varepsilon^0$ is the strength of the nonlinear dielectric effect and $\omega$ is the angular frequency of the probing field $E(\omega)$. Consequently, the Cole-Cole plot of the imaginary part of the increment ($\Delta\varepsilon''$) vs the real part ($\Delta\varepsilon'$) has a form of the semicircle with the center placed on the $\Delta\varepsilon''=0$ axis. Figure 4 presents the plots for two temperatures: close to the tran-
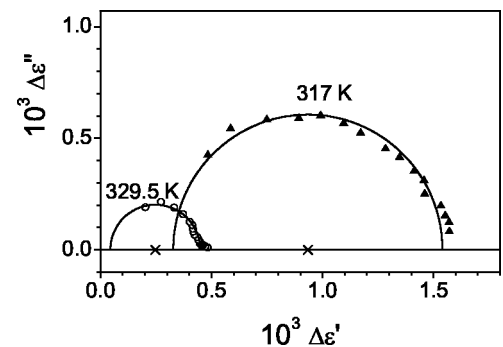


FIG. 4. Cole-Cole plots for the complex nonlinear dielectric increment recorded in the isotropic phase of 6CHBT at the temperature close (317 K) and far (329.5 K) from the transition to the nematic phase.
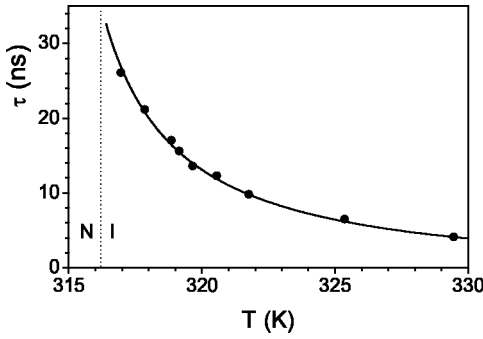
FIG. 5. Temperature dependence of the relaxation time corresponding to the best fitting of Eq. (6) to the experimental nonlinear dielectric spectra.

sition to the nematic phase of 6CHBT and far from the transition.

The values of the relaxation time resulting from the best fitting of Eq. (6) to the experimental nonlinear dielectric spectra are depicted in Fig. 5 as a function of temperature. Both the values of the relaxation time (tens of nanoseconds) and the temperature dependence suggest that the nonlinear dielectric spectra recorded in the mesogenic 6CHBT reflect the dynamics of the pseudonematic domains as a whole. The suggestion is based on the results obtained up to now with the different experimental methods used for studies of the dynamics of the prenematic effects in isotropic liquids [16,11,18].

The local order in the isotropic phase of mesogenic liquids is a consequence of the substantial anisotropy in the intermolecular interactions leading to the molecular self-organization in the nematic phase and still existing in the isotropic phase. The molecular ordering within the pseudonematic domains can be expressed by the local order parameter $S_l = \langle 3\cos^2\Theta - 1 \rangle/2$, where $\Theta$ is the angle between the long molecular axis and the local director. However, due to a random distribution of the domains directors, the resultant macroscopic order parameter $S$ in the isotropic phase is equal to zero. The static electric field of a high intensity $E_0$ moves the macroscopic system away from the state $S=0$, what gives a positive change in the electric permittivity. The return of the system to the random state, measured with a weak electric field of high frequency $E(\omega)$, provides the data on the dynamics of the phenomenon.

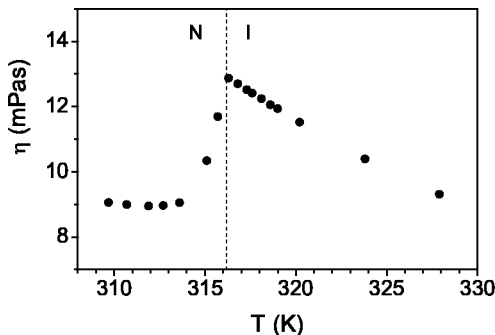The results obtained in our experiment can be quantita-

tively interpreted in the frame of the Landau–de Gennes theory, which predicts the following temperature dependence of the relaxation time for the reorientation of the pseudonematic domains in the medium of the viscosity $\eta$:

$$\tau(T) = \frac{V_{\text{eff}}^* \eta(T)}{k(T-T^*)^\gamma}, \qquad (7)$$

where $V_{\text{eff}}^*$ denotes the constant connected with the effective volume of the rotating entity [37,38] and $k$ is the Boltzmann constant. The mean field theory [1] predicts for the exponent $\gamma$ the value close to the unity.

Figure 6 present the temperature dependence of the shear viscosity measured in the isotropic and nematic phase of 6CHBT. A sharp decrease of the viscosity observed at the isotropic to nematic phase transition is due to the flow alignment effect occurring in a flow of the nematic liquid crystals without external ordering forces [36].

According to Eq. (7), at the virtual temperature $T^*$, the viscosity to the relaxation time ratio is equal to zero, irrespective of the value of the exponent $\gamma$. As shown in Fig. 7, $T^*$ found in this way is equal to 313.5 K. The difference $T_{NI} - T^*$ is equal to 2.7 K for 6CHBT, which is a typical value obtained for other mesogenic compounds with the use of different experimental methods [16,11,18].

Finally, with the known value of $T^*$ one can determine the exponent $\gamma$ in Eq. (7). Figure 8 shows that predicted in the Landau–de Gennes theory linear relation of $\ln(\eta/\tau)$ vs



FIG. 7. An extrapolation procedure for the determination of the virtual temperature $T^*$ for mesogenic 6CHBT.



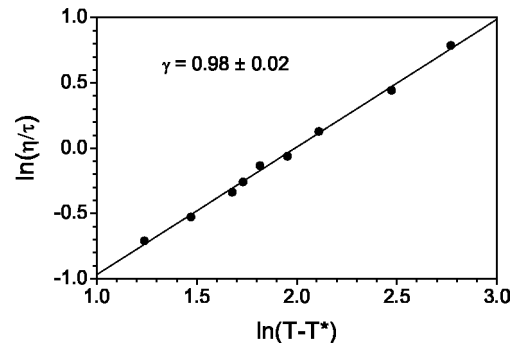FIG. 6. Shear viscosity of 6CHBT as a function of temperature.



FIG. 8. According to Eq. (7) the $\ln(\eta/\tau)$ vs $\ln(T-T^*)$ dependence should be linear; the slope of the line is equal to the critical exponent $\gamma$ value.

$\ln(T-T^*)$ is very good fulfilled in our nonlinear dielectric experiment. The slope of the line gives for the exponent $\gamma$ the value $0.98\pm0.02$, which, as mentioned above, is predicted by the mean field theory.

In conclusion, it should be stressed that the picture of the dynamics of the orientational randomization of the pseudo-onematic domains in the isotropic liquids, which results from the analysis of the nonlinear dielectric spectra of 6CHBT, is in a good agreement with that resulting from the experiment of the light scattering [15], the optical Kerr effect [10,16], as well as the transient grating optical Kerr effect [18–20] performed for other isotropic mesogens. It concerns, in particu-lar, the critical exponent $\gamma$, the value of which is very close to the unity, independently on the experimental method used.

[1] P.G. de Gennes, *Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974).

[2] P.K. Mukherjee, T.R. Bose, D. Ghose and M. Saha, Phys. Rev. E **51**, 4570 (1995).

[3] A. Sengupta and M.D. Fayer, J. Chem. Phys. **102**, 4193 (1995).

[4] P.K. Mukherjee, Liq. Cryst. **22**, 239 (1997).

[5] I. Lelidis, M. Nobili, and G. Durand, Phys. Rev. E **48**, 3818 (1993).

[6] E.I. Rjumtsev, M.A. Osipov, T.A. Rotinyan, and N.P. Yevlampieva, Liq. Cryst. **18**, 87 (1995).

[7] A. Drozd-Rzoska, S.J. Rzoska, and J. Ziolo, Phys. Rev. E **54**, 6452 (1996).

[8] A. Drozd-Rzoska, S.J. Rzoska, and J. Ziolo, Phys. Rev. E **55**, 2888 (1997).

[9] P.K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).

[10] J.D. Litster and T.W. Stinson III, J. Appl. Phys. **41**, 996 (1970).

[11] J.C. Filippini and Y. Poggi, Phys. Lett. **65A**, 30 (1978).

[12] T.D. Gierke and W.H. Flygare, J. Chem. Phys. **61**, 2231 (1974).

[13] B. Cabane and G. Clarke, Phys. Rev. Lett. **25**, 91 (1970).

[14] S. Gosh, E. Tettamanti, and E. Indovina, Phys. Rev. Lett. **29**, 638 (1973).

[15] T.W. Stinson III and J.D. Litster, Phys. Rev. Lett. **25**, 503 (1970).

[16] G.K.L. Wong and Y.R. Shen, Phys. Rev. Lett. **30**, 895 (1973).

[17] F.W. Deeg and M.D. Fayer, J. Chem. Phys. **91**, 2269 (1989).

[18] F.W. Deeg, S.R. Greenfield, J.J. Stankus, V.J. Newell, and M.D. Fayer, J. Chem. Phys. **93**, 3503 1990.

[19] J.J. Stankus, R. Torre, C.D. Marshall, S.R. Greenfield, A. Sengupta, A. Tokmakoff, and M.D. Fayer, Chem. Phys. Lett. **194**, 213 (1992).

[20] J.J. Stankus, R. Torre, and M.D. Fayer, J. Phys. Chem. **97**, 9478 (1993).

[21] H.J. Coles, J. Mol. Cryst. Liq. Cryst. **49**, 67 (1978).

[22] B.K.P. Scaife, *Principles of Dielectrics* (Oxford University Press, Oxford, 1989).

[23] W.T. Coffey, *Dynamical Processes in Condensed Matter,* edited by M. W. Evans (Wiley, New York, 1985).

[24] W.T. Coffey, Y.P. Kalmykov, and K.P. Quinn, J. Chem. Phys. **96**, 5471 (1992).

[25] L. Hellemans and L. De Maeyer, J. Chem. Phys. **63**, 3490 (1975).

[26] K. De Smet, P. Kędziora, J. Jadżyn, and L. Hellemans, J. Phys. Chem. **100**, 7662 (1996).

[27] J. Jadżyn and L. Hellemans, Acta Phys. Pol. A **67**, 1093 (1985).

[28] J. Jadyn and L. Hellemans, Ber. Bunsenges. Phys. Chem. **97**, 205 (1993).

[29] P. Kędziora, J. Jadżyn, K. De Smet, and L. Hellemans, Chem. Phys. Lett. **289**, 541 (1998).

[30] J. Jadżyn, P. Kędziora, L. Hellemans, and K. De Smet, Chem. Phys. Lett. **302**, 337 (1999).

[31] W.T. Coffey and B.V. Paranjape, Proc. R. Ir. Acad. Sect. A, Math. Astron. Phys. Sci. **78**, 17 (1978).

[32] B. Kasprowicz-Kielich and S. Kielich, Adv. Mol. Relax. Processes **7**, 275 (1975).

[33] J.L. Dejardin and Y.P. Kalmykov, J. Chem. Phys. **112**, 2916 (2000).

[34] J.L. Dejardin, Y.P. Kalmykov, and P.M. Dejardin, Adv. Chem. Phys. **117**, 275 (2001).

[35] Y.P. Kalmykov, Phys. Rev. E **65**, 021101 (2001).

[36] J. Jadzyn and G. Czechowski, Phys. Rev. E **64**, 052702 (2001).

[37] F. Perrin, J. Phys. Radium **5**, 497 (1934).

[38] C. Hu and R. Zwanzig, J. Chem. Phys. **60**, 4354 (1974).