Fluidlike behavior of dielectric permittivity in a wide range of temperature above and below the nematic-isotropic transition

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Singular behavior of the static dielectric permittivity of *n*-alkyloxycyanobiphenyls (C_nH_{2n+1}O-Ph-Ph-C$\equiv N$, $n=6$, 7) was studied above and below the nematic clearing point ($T_{I\text{-}N}$). On approaching the clearing point, the evolution of principal components of the nematic permittivity tensor, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, is described by the order parameter exponent $\beta\approx 0.25$. The mean value of the nematic permittivity $\varepsilon_{\text{mean}}=(\varepsilon_{\parallel}+2\varepsilon_{\perp})/3$ exhibits a singular behavior similar to that observed in the isotropic phase and that for the diameter of the coexistence curve in binary mixtures. The derivative of experimental data $d\varepsilon_{\text{iso}}(T)/dT$ and $d\varepsilon_{\text{mean}}(T)/dT$ shows the specific-heat-like behavior with universal exponents $\alpha=\alpha'\approx 0.5$. Results obtained confirm the hypothesis of the *fluidlike, pseudospinodal*, and *tricritical* behavior of the isotropic to nematic phase transition. [A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999)].

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INTRODUCTION

In 1970, Widom and Rowlinson [1] described a model for the liquid-vapor transition showing the singularity of the diameter of the coexistence curve if the system has a specific heat critical anomaly. The first unambiguous experiment confirming this hypothesis was made by Jüngst, Knuth, and Hensel [2] for liquid-metal–gas transition. This result concluded the long-standing discussion on the possible validity of the Caillet-Matthies law of rectilinear diameter [3–5]. Similar singularity of the binodal diameter was also found in binary mixtures of limited miscibility, belonging to the same universality class ($d=3$, $n=1$) [4,5]. If we compare experimental results of various physical properties, as, for instance, density, refractive index, concentration, dielectric permittivity [3–8], the diameter anomaly seems to be particularly pronounced for the latter [6–8]. Noteworthy here is the similarity of the permittivity behavior above and below the critical consolute temperature (T_C) [6–13],

$$\varepsilon=\varepsilon_C+a|T-T_C|+A|T-T_C|^{1-\alpha}+\cdots$$

and

$$\frac{d\varepsilon}{dT}\propto C_v\propto|T-T_C|^{-\alpha}, \tag{1}$$

where $\varepsilon=\varepsilon_{\text{homogeneous}}$ for $T>T_C$ and $\varepsilon=\varepsilon_{\text{diameter}}=(\varepsilon_L+\varepsilon_U)/2$ for $T<T_C$. ε_U and ε_L are static dielectric permittivities in the upper and lower coexistence phase, respectively. In the homogeneous phase the relationship between the anomalies of dielectric permittivity and the specific heat was first suggested in the theory of Mistura in 1974 [14]. When discussing the two-phase region below T_C, the order parameter is the next significant quantity [4,5]. It can be related to dielectric permittivity as [7,8]

$$S=\varepsilon_U-\varepsilon_L\propto(T_C-T)^{\beta}, \tag{2}$$

where the critical exponent $\beta\approx 0.325$.

Recently, the *fluidlike* behavior hypothesis was proposed for describing properties of the isotropic-nematic (*I-N*) transition in liquid crystalline materials. It assumes that the nematic-clearing temperature ($T_{I\text{-}N}$) lies on the branch of the hypothetical binodal curve [15–19]. Recent studies based on linear and nonlinear dielectric permittivity tests showed a very good agreement with the *fluidlike* model when considering the pretransitional behavior in the isotropic phase. The obtained set of experimental results could not be explained within the simple mean-field description dominating in the last few decades [17–19]. Hence, the question arises whether the *fluidlike* description may also be valid for the low temperature phase (nematic). In the opinion of the authors, experimental results in the isotropic phase are puzzling [5,20–30]. The quantitative analysis is restricted to the behavior of the order parameter. To parametrize experimental data, the empirical Haller dependence is often used [20,22,23,26–28],

$$S=\varepsilon_{\parallel}-\varepsilon_{\perp}\propto|T-T_{I\text{-}N}|^{b},\quad T<T_{I\text{-}N}, \tag{3}$$

where $b=0.15$–0.2 is an empirical material dependent parameter. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric permittivities of the ordered sample in the direction parallel and perpendicular to the director *n*.

However, this equation cannot be satisfied close to $T_{I\text{-}N}$ at which the discontinuous transition occurs. From the Landau–de Gennes (LdG) model one may conclude [5,30,31] that

$$S=S^{**}+B|T-T^{**}|^{\beta},\quad T<T_{I\text{-}N}=T^{**}+\Delta T', \tag{4}$$

where T^{**} is the extrapolated temperature of the supercooled nematic phase and S^{**} is a function of constant amplitudes in the LdG series. In the simple LdG model, $\beta=\frac{1}{2}$ [5] (mean field value) [5,30]. For the LdG expansion considered up to sixth order, the tricritical behavior appears and then $\beta=\frac{1}{4}$ [5,31,32].

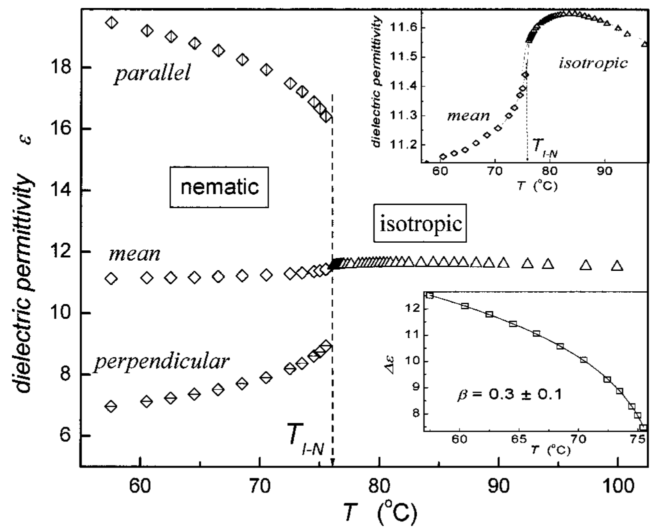

FIG. 1. Static dielectric permittivity behavior in the isotropic and in the nematic phases of 6OCB. The upper inset shows the behavior of the dielectric permittivity in the isotropic phase and the behavior of the mean permittivity in the nematic phase. The lower inset presents the behavior of dielectric strength—order parameter. Solid lines in insets are fitted by Eqs. (4)–(6). Arrows denote the clearing point.

No conclusive experimental support for the mean field or tricritical description has been obtained yet [20–30]. Only last year Marinelli and Mercuri [33] reported results of precise photopyroelectric measurements of the anisotropy in the thermal conductivity, strongly supporting the tricritical point hypothesis.

In the present paper studies of dielectric permittivity in the isotropic and nematic phase of *n*-hexyloxycyanobiphenyl (6OCB) and *n*-heptyloxycyanobiphenyl (7OCB) are reported. Tests were conducted in a wide range of temperatures: up to $T-T_{I\text{-}N}\approx 30\,\mathrm{K}$ in the nematic phase and $T-T_{I\text{-}N}\approx 80\,\mathrm{K}$ in the isotropic liquid. It was shown that data obtained can be exceptionally well parametrized by the equations analogous to those applied in the case of critical binary mixtures. Particularly, there is a clear evidence of the pretransitional behavior for the ''*diameter*'': $\varepsilon_{\mathrm{mean}}(T)=\frac{1}{3}\varepsilon_{\parallel}+\frac{2}{3}\varepsilon_{\perp}$.

EXPERIMENT

The static electric permittivity was measured with a Wayne Kerr 6425 precision analyzer at 10 kHz with a 5-digit resolution. The samples were placed in a flat-parallel copper capacitor with gold-covered electrodes with a gap $d=0.5\,\mathrm{mm}$. Components $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of dielectric permittivity were measured in the sample ordered by the magnetic field ($B=0.8\,\mathrm{T}$). The temperature was controlled with an accuracy of $\pm 0.01\,°\mathrm{C}$. Tested samples of rodlike nematogens (6OCB, $T_{I\text{-}N}=75.8\pm 0.2\,°\mathrm{C}$ and 7OCB, $T_{I\text{-}N}\approx 73.50\pm 0.05\,°\mathrm{C}$) were prepared at the Military University of Technology, Warsaw, Poland. The purity of the compounds was better than 99.9%. The analysis of data was conducted using a nonlinear fitting procedure and the derivative calculus procedures in ORIGIN 6.1 software. Errors are given as three standard deviations.

RESULTS AND DISCUSSION

Figure 1 shows results of measurements of dielectric permittivity in 6OCB. In agreement with Refs. [16,18,19] the behavior in the isotropic phase is well portrayed by the *fluidlike* relation

$$\varepsilon_{\mathrm{isot}}(T)=\varepsilon^{*}+a_I|T-T^{*}|+A_I|T-T^{*}|^{1-\alpha}$$
$$\text{for}\ \ T>T_{I\text{-}N}=T^{*}+\Delta T. \tag{5}$$

The anomalous behavior associated with the almost-continuous character of the *I-N* transition is also clearly visible for the diameter in the nematic phase (the inset in Fig. 1),

$$\varepsilon_{\mathrm{mean}}(T)=\varepsilon^{**}+a_N|T-T^{**}|+A_N|T-T^{**}|^{1-\alpha}$$
$$\text{for} T<T_{I\text{-}N}=T^{**}-\Delta T'. \tag{6}$$

Parameters for relations (5) and (6) are collected in Table I. In both cases the same value of the exponent $\alpha\approx 0.5$ was obtained within limits of experimental errors. The lower inset in Fig. 1 shows the behavior of the order parameter. Assuming $S^{**}=0$ one gets the value $\beta\approx 0.2$ for $T^{**}=77\,\mathrm{K}$. For $S^{**}\neq 0$ the value of β ranging from 0.24 to 0.5 is capable of parametrizing data. For $\beta\approx 0.29$ the obtained value of the singular temperature T^{**} is the same as that obtained in Eq. (6) from the *diameter* analysis.

Figure 2 shows results of similar measurements in 7OCB but with much higher ''experimental point density'' applied than usual. The singular behavior of $\varepsilon_{\mathrm{iso}}(T)$ and $\varepsilon_{\mathrm{mean}}(T)$ is shown in detail in Fig. 3. Obtained dependencies are almost perfectly portrayed by relations (5) and (6) (solid lines), with parameters given in Table I. Within the limit of experimental error data are described by the same values of critical exponents $\alpha'=\alpha=0.5$ and critical amplitudes $A/A'=-1$. This is

TABLE I. Results of fitting in the isotropic and in the nematic phases of 6OCB and 7OCB using Eqs. (5) and (6).

Mesogen (phase)	$\varepsilon^{*}(I)$, $\varepsilon^{**}(N)$	a_I, a_N (K^{-1})	A_I, A_N ($\mathrm{K}^{-\varphi}$)	$\varphi=1-\alpha$	T^{*}, T^{**} (°C)
6OCB (*I*)	11.41 ± 0.1	-0.028 ± 0.005	0.164 ± 0.02	0.51 ± 0.04	74.88 ± 0.1
6OCB (*N*)	11.48 ± 0.1	0.009 ± 0.003	-0.12 ± 0.02	0.51 ± 0.06	75.6 ± 0.3
7OCB (*I*)	9.902 ± 0.002	-0.023 ± 0.001	0.163 ± 0.003	0.506 ± 0.01	72.36 ± 0.05
7OCB (*N*)	9.996 ± 0.05	0.005 ± 0.002	-0.161 ± 0.006	0.49 ± 0.04	73.41 ± 0.15

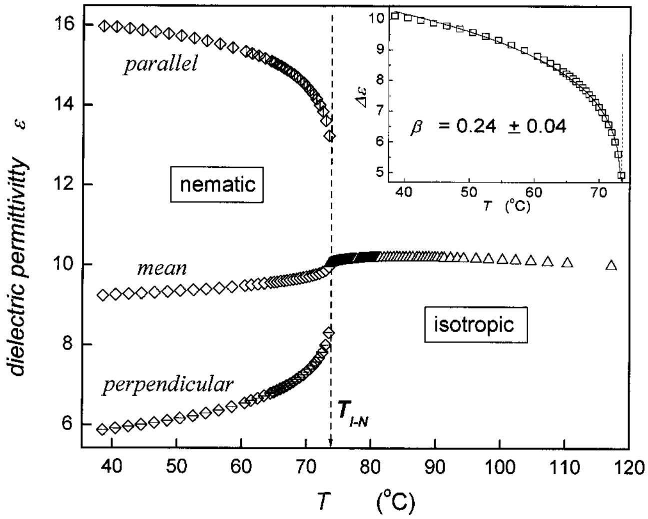

FIG. 2. Static dielectric permittivity behavior in the isotropic and in the nematic phases of 7OCB. The inset shows the behavior of dielectric strength. Solid line is fitted by Eq. (4).

additionally confirmed by distortion-sensitive derivative analysis of experimental data presented in Fig. 4. On both sides of the nematic clearing temperature the specific-heat-like anomaly is clearly visible,

$$\frac{d\varepsilon_{\mathrm{iso}}}{dT}, \frac{d\varepsilon_{\mathrm{mean}}}{dT} = \mathrm{const} + (T - T_{\mathrm{sing}})^{-\alpha}, \quad \alpha \approx 0.5, \tag{7}$$

where $T_{\mathrm{sing}} = T^*$ for $T > T_{I\text{-}N}$ and $T_{\mathrm{sing}} = T^{**}$ for $T < T_{I\text{-}N}$.

Noteworthy is the large range of the validity of the pretransitional description in comparison with the specific-heat and density experimental results. It is worth mentioning here

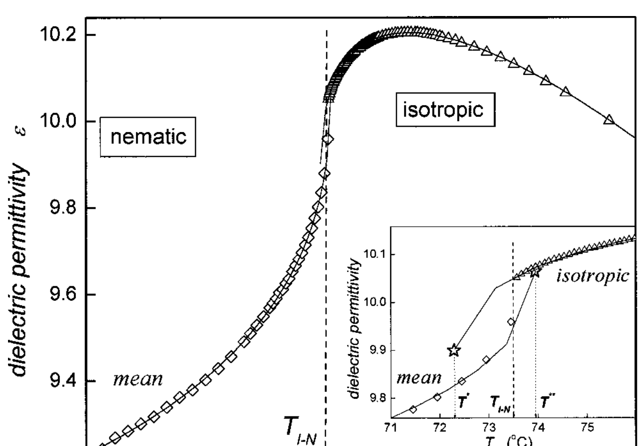

FIG. 3. The behavior of the dielectric permittivity in the isotropic phase and the behavior of the mean permittivity in the nematic phase of 7OCB. Solid lines in insets are fitted by Eqs. (5) and (6). The inset shows the behavior in the immediate vicinity of the clearing point. Stars and dotted arrows denote positions of extrapolated virtual critical (tricritical) points. The solid line in the inset represent a smooth curve. The ''discontinuity'' is caused by the ORIGIN GRAPH software.

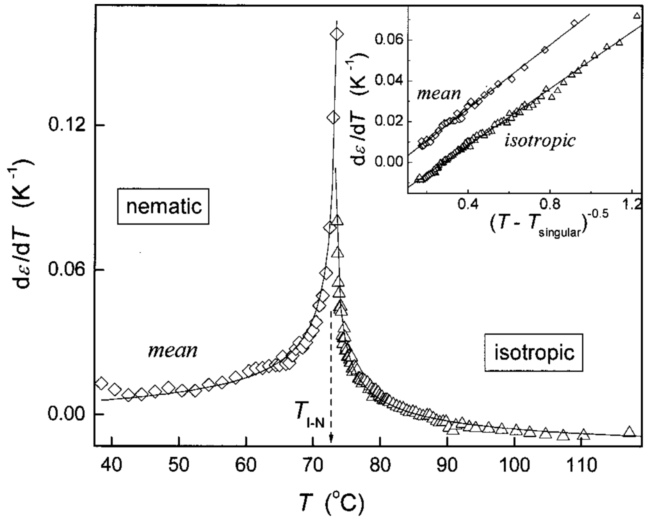

FIG. 4. The derivative analysis of experimental data from Fig. 3. Solid lines are described by relation (7). The inset presents the same data in a way showing the obtained value of exponent $\alpha = 0.5$.

that linear terms in relations (5) and (6) do not describe experimental data at any distance from the phase transition point. Hence, they cannot be considered as the noncritical background effect. The inset in Fig. 2 shows the behavior of the order parameter of 7OCB. In comparison to results discussed for 6OCB the scattering of exponent β has been reduced but the obtained value still remains puzzling.

Figure 5 shows results of derivative analysis of the ''*order parameter data*'' from the inset in Fig. 2. It removed the constant parameter S^{**} in Eq. (4) and consequently simplified the analysis to the linear-regression fit. Results obtained clearly show that up to $T^{**} - T < 7$ K behavior of $\Delta\varepsilon(T)$ is described by the tricritical order parameter exponent $\beta = 0.245 \pm 0.02$. For $7 < T < 37$ K the temperature behavior is essentially different. This may be related to correction-to-scaling terms or to the influence of fluctuations associated

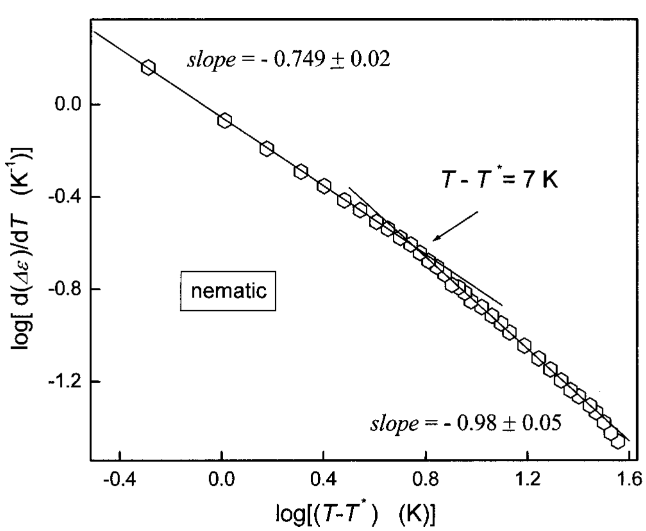

FIG. 5. The derivative analysis of experimental data for dielectric strength (order parameter) in the nematic phase of 7OCB (data taken from the inset in Fig. 2).

with more complex mesophases. The comparison of the analysis of results for 6OCB and 7OCB shows the essential influence of the quality of experimental data on results obtained. The influence of the experimental error is stronger on the order parameter than on $\varepsilon_{\mathrm{mean}}$, which can be related to their definitions. Moreover, in the analysis of critical phenomena, particular attention should be paid to the immediate vicinity of the continuous phase transition: the experimental temperature resolution of data has a fundamental effect on the results obtained. This factor is particularly important for the IN transition because of its discontinuity.

Concluding, the behavior of dielectric permittivity in the nematic and isotropic phases of nematogens can be well portrayed by relations that are analogous to those applied to binary liquid mixtures of limited miscibility. The tricritical values of exponents describing the behavior of the dielectric permittivity exponent have been obtained: $\beta \approx 0.25$, $\alpha \approx \alpha' \approx 0.5$. This agrees with the *fluidlike*, *pseudospinodal*, and *tricritical* nature of the I-N transition deduced from linear and nonlinear dielectric measurements in the isotropic phase [18]. Worth mentioning is also the fluidlike dimensionality [15,17,18] $d=3$ of the tricritical description [5]. In the opinion of the authors, particularly worth stressing is the evidence for the ''*diameter*'' $\varepsilon_{\mathrm{mean}}(T)$ singular dependence. It shows in an unequivocal way that the *fluidlike* behavior is clearly manifested in the nematic phase for $T_{I\text{-}N} < T < T_{I\text{-}N} + 30\,\mathrm{K}$.

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[1] B. Widom and J. S. Rowlinson, J. Chem. Phys. **52**, 1670 (1970).
[2] S. Jüngst, B. Knuth, and F. Hensel, Phys. Rev. Lett. **55**, 2160 (1985).
[3] J. S. Rowlinson, Nature (London) **319**, 362 (1986).
[4] A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 59 (1983).
[5] M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, Philadelphia, 1991).
[6] Z. Ziejewska, J. Piotrowska, and J. Ziolo, Acta Phys. Pol. A **56**, 347 (1979).
[7] R. Kindt, J. Thoen, and W. Van Dael, Int. J. Thermophys. **9**, 749 (1988).
[8] P. Habdas, M. Paluch, S. J. Rzoska, and T. Schimpel, Chem. Phys. **213**, 483 (1996).
[9] J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Green, Physica A **104**, 573 (1980).
[10] J. Hamelin, T. K. Bose, and J. Thoen, Phys. Rev. Lett. **74**, 2733 (1995).
[11] K. Orzechowski, J. Chem. Soc., Faraday Trans. **90**, 2757 (1994).
[12] S. J. Rzoska, M. Paluch, P. Habdas, A. Drozd-Rzoska, and P. Urbanowicz, Europhys. Lett. **45**, 334 (1999).
[13] A. Drozd-Rzoska, S. J. Rzoska, J. Ziolo, and P. Habdas, in *Dielectric and Related Phenomena*, special issue of IEEE Trans. Dielectr. Electr. Insul. Conference, Spala 2000 (Poland).
[14] L. Mistura, J. Chem. Phys. **59**, 4563 (1973).
[15] P. K. Mukherjee and T. B. Mukherjee, Phys. Rev. B **52**, 9964 (1995).
[16] A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, Phys. Rev. E **54**, 6452 (1996).
[17] P. K. Mukherjee, J. Phys.: Condens. Matter **10**, 9191 (1998).
[18] A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).
[19] A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, Acta Phys. Pol. A **98**, 637 (2000).
[20] R. Desai and R. Pratao, Mol. Cryst. Liq. Cryst. **75**, 287 (1981).
[21] J. Thoen and G. Menu, Mol. Cryst. Liq. Cryst. **97**, 163 (1983).
[22] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals*, Springer Series in Chemical Physics Vol. 45 (Springer-Verlag, Berlin, 1986).
[23] T. J. Phillips, J. C. Jones, and D. G. McDonnel, Liq. Cryst. **15**, 203 (1993).
[24] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1994).
[25] E. Wolarz and D. Bauman, Liq. Cryst. **19**, 221 (1995).
[26] S. Urban and A. Wuerflinger, in *Advances in Chemical Physics*, edited by I. Prigoine and A. Rice (Wiley, New York, 1997), Vol. XCVIII, p. 143.
[27] M. L. Magnuson, B. M. Fung, and J. P. Bayle, Liq. Cryst. **19**, 823 (1995).
[28] *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spicess, and V. Vill (Wiley-VCH, Weinheim, 1998), Vol. 1.
[29] S. Urban and A. Wuerflinger, Liq. Cryst. **27**, 8 (2000).
[30] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974); P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
[31] P. J. Keyes, Phys. Lett. **67A**, 132 (1978).
[32] P. K. Mukherjee, Int. J. Mod. Phys. B **12**, 1585 (1998).
[33] M. Marinelli and F. Mercuri, Phys. Rev. E **61**, 1616 (2000).