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The pretransitional anomaly of dielectric permittivity in the isotropic phase of nematogens and in the homogeneous phase of critical solutions

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Abstract. The pretransitional behaviour of static dielectric permittivity in the isotropic phase of nematogens and in the homogeneous phase of a weakly off-critical binary solution is compared. The pretransitional anomalies are described by analogous relations, with critical exponents $\phi = 1 - \alpha \approx 0.50$ and $\phi = 1 - \alpha \approx 0.89$, respectively. Tests were conducted for pressure paths approaching the virtual critical point. The specific-heat-like dependences of derivatives of dielectric permittivities in both systems have been shown. This result agrees with the dependence suggested for critical mixtures by Mistura (1973 *J. Chem. Phys.* **59** 4563). Results obtained point to the validity of the recently formulated hypothesis on the fluid-like critical behaviour of the isotropic–nematic transition (Mukherjee P K *et al* 1995 *Phys. Rev.* E **51** 4570, Mukherjee P K 1998 *J. Phys.: Condens. Matter* **10** 9191).

1. Introduction

Recent studies showed a striking similarity in the pretransitional behaviour of dielectric permittivity in systems as different as the homogeneous phase of the critical solution and the isotropic phase of liquid crystalline compounds (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1999, Drozd-Rzoska and Rzoska 2000). In critical solutions (Sengers *et al* 1980, Orzechowski 1994, Thoen *et al* 1989, Hamelin *et al* 1995):

$$\varepsilon = \varepsilon_C + a(T - T_C) + B(T - T_C)^{1-\alpha}\lfloor 1 + b_1(T - T_C)^{\Delta_1}\rfloor \qquad (1)$$

where T_C is the critical consolute temperature, $\alpha \approx 0.11$ is the critical exponent of the isobaric heat capacity (C_p) for the $d = 3$, $n = 1$ universality class; d is the thermodynamic dimensionality, n is a dimension of the order parameter. The bracket contains the first correction-to-scaling term with $\Delta_1 \approx 0.5$. Its influence is significant for $T - T_C > 3$ K (Habdas *et al* 1999).

Relation (1) can be derived applying the droplet model (Goulon *et al* 1979) or using the thermodynamic analysis of a critical mixture in an electric field (Sengers *et al* 1980). Its form is in agreement with an earlier prediction of Mistura (1973): $\mathrm{d}\varepsilon/\mathrm{d}T \propto C_p \propto (T - T_C)^{-\alpha}$, where C_p is the isobaric heat capacity. Probably due to the weakness of the $\varepsilon(T)$ anomaly the experimental verification of the Mistura dependence in critical mixtures is still lacking.

It has been shown by (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1999) that in the isotropic phase of nematogens a similar equation portrays the temperature behaviour of the static

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dielectric permittivity:

$$\varepsilon = \varepsilon^* + a' \times (T - T^*) + B' \times (T - T^*)^{1-\alpha} \qquad T > T_{I-N} = T^* + \Delta T$$
$$\alpha = 0.50 \pm 0.02 \tag{2}$$

where T^* and ε^* denote coordinates of a virtual continuous phase transition, T_{I-N} is the isotropic–nematic (I–N) transition temperature (clearing temperature) and ΔT denotes the discontinuity of the transition.

In both systems asymptotic pretransitional (critical) effects are manifested in bending down from the almost linear behaviour remote from the continuous phase transition point. Quite similar behaviour can be found for the isobaric heat capacity mentioned above (Anisimov 1993) and density ($\rho(T) = \rho^* + d(T - T^*) + D(T - T^*)^{1-\alpha} + \ldots$) (Gulari and Chu 1975). However, these anomalies are weak and are usually limited in a range to a few degrees above the phase transition point, particularly in nematogens. The discontinuity of the I–N transition causes that measurement are only above the nematic clearing point i.e. one cannot approach closer than 1–2 K from the virtual critical point. Moreover, at least for $C_p(T)$ anomaly the influence of correction-to-scaling terms seems to be important. These features significantly restricts the quantitative analysis of $C_p(T)$ and $\rho(T)$ pretransitional anomalies in the isotropic phase of nematogens.

The most widely recognized theoretical description of the I–N transition is based on the Landau–de Gennes (LdG) phenomenological model (de Gennes 1974). Its application made it possible to parametrize strong, susceptibility-related, pretransitional anomalies in the isotropic phase of the Kerr effect (KE), the Cotton–Mouton effect (CME), the light scattering (I_L) and the nonlinear dielectric effect (NDE) (Anisimov 1993, de Gennes and Prost 1994, Drozd-Rzoska 1999). However, the mean-field (MF) based models failed to explain the small value of ΔT obtained from KE, CME, I and NDE measurements (Mukherjee 1998). It also does not predict anomalies of physical properties associated with the exponent α (c_p, ρ, ε) in the high temperature phase (Pfeuty and Toulouse 1978). A very good agreement between the experiment and theory offers hypothesis of the fluidlike, critical behaviour in the isotropic phase proposed recently (Mukherjee and Saha 1995, Mukherjee and Mukherjee 1995, Mukherjee *et al* 1995, Mukherjee 1998). According to this model the properties in the isotropic phase are described by a fluidlike equation of state where the clearing temperature is located at a branch of a hypothetical coexistence curve. It gave reasonable small value of ΔT and $\alpha = 0.5$ in the isotropic phase.

The relatively strong pretransitional anomaly of dielectric permittivity in the isotropic phase of nematogens originates in the cancellation of antiparallel oriented permanent dipole moments contained in prenematic fluctuations. For a critical mixture only the proportionality of the critical amplitude (A) for such thermodynamic coefficients as the electric field (E) and pressure (P) induced by a shift of T_C has been established (Sengers *et al* 1980). The latter dependence causes the critical amplitude for the isothermal pressure approaching the critical consolute point to be 30–40 times larger than the amplitude of the critical effect in temperature studies at constant pressure. Recently, this feature facilitated an unequivocal estimation of the exponent ϕ in pressure studies (Rzoska *et al* 1999). Such a difference between the 'temperature' and the 'pressure' amplitude is not observed for the I–N transition (Drozd-Rzoska 1999). Both in critical solutions (Rzoska *et al* 1999, Habdas *et al* 1999) and in nematogens (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1999) the value of the critical exponent does not depend on whether the continuous phase transition point is approached isothermally, as a function of pressure or along a temperature path. This may be treated as a clear confirmation of the isomorphism postulate of critical phenomena (Chu *et al* 1969, Anisimov 1993).

The aim of this paper is to compare the pretransitional behaviour of dielectric permittivity in the isotropic phase of nematogens and in the homogeneous phase of critical solutions. Owing to the weakly discontinuous character of the I–N transition a slightly non-critical binary solution was tested for which a weakly discontinuous phase transition might have been expected. Studies were carried out for the isothermal pressure path. This made it possible to avoid the problem of the weakness of the $\varepsilon(T)$ anomaly in a binary solution, which might strongly inhibit a quantitative analysis for a discontinuous transition. Noteworthy is also the absence of a parasitic low-frequency Maxwell–Wegner (MW) dispersion (Thoen *et al* 1989) in pressure studies (Habdas *et al* 1999), even for $f = 100$ Hz. Presented tests were conducted in 1-nitropropane–hexadecane (1-np–hxd) near critical mixture. The critical parameters under atmospheric pressure: $x_c = 0.72_5$ mole fraction of 1-np, $T_c = 307.3$ K. They were determined by means of a visual cathetometric method (Rzoska 1990). The components were purchased from Fluka; 1-np was distilled twice, the last time immediately prior to measurements. Pentylcyanobiphenyl (5CB) as the liquid crystalline compound was chosen. Its clearing temperature under atmospheric pressure: $T^C = 308.6$ K. The sample was obtained by courtesy of Krzysztof Czupryński (Technical Military Academy, Warsaw, Poland). The experimental set-up applied in the present research was described in our previous papers (Drozd-Rzoska 1999). Measurements of the static dielectric permittivity were performed using a Solartron 1260 impedance analyser with 1000 period averaging. This enabled a permanent five-digit resolution in electric capacitance measurements.

2. Results and discussion

Figure 1 shows the behaviour of dielectric permittivity for a tested 1-nitropropane–hexadecane binary solution of concentration $x = x_c - 0.05$. It may be is clearly seen that the pressure

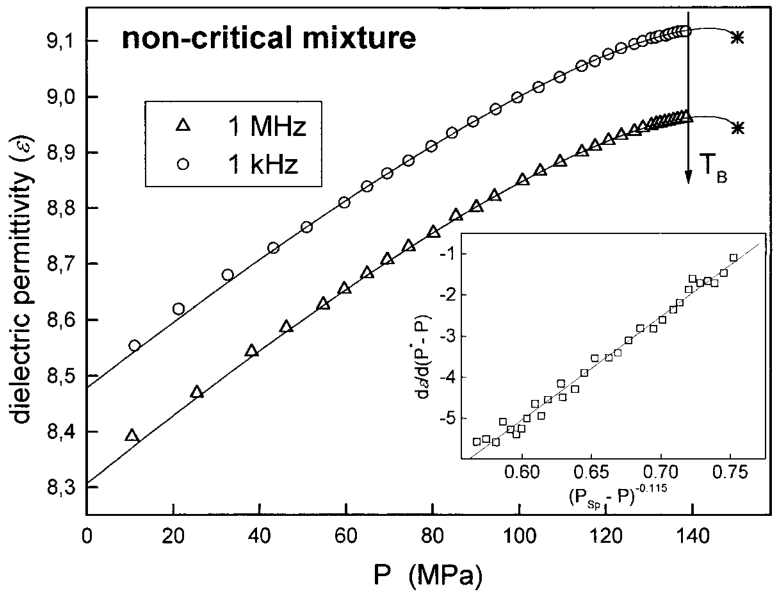

Figure 1. The pressure dependence of static dielectric permittivity in the homogeneous phase of a tested non-critical 1-nitropropane–hexadecane mixture. The inset shows results of the differential analysis of experimental data from the main part of the figure.

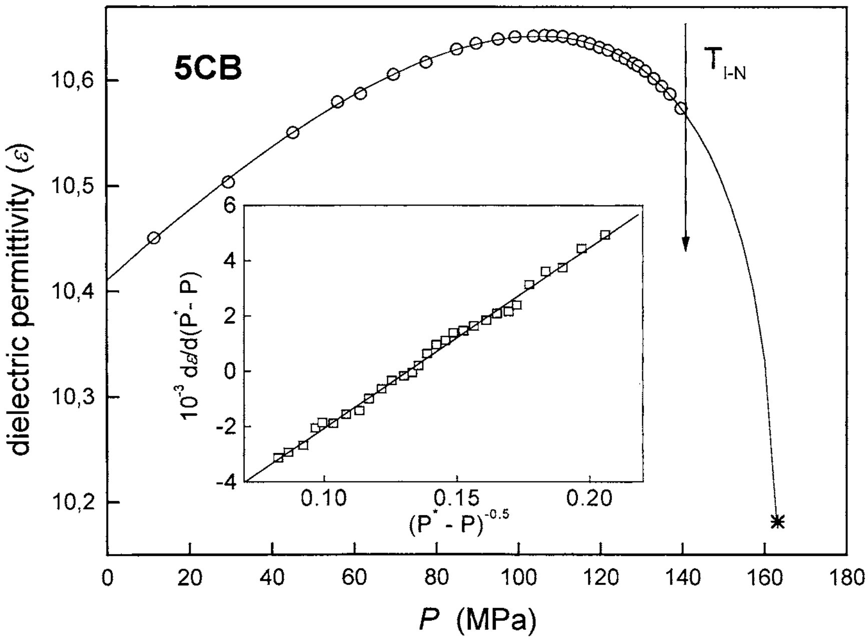

Figure 2. The pressure dependence of dielectric permittivity in the isotropic phase of 5CB. The inset presents results of the differential analysis of experimental data from the main part of the figure.

analogue of equation (1) parametrizes experimental data (solid line):

$$\varepsilon = \varepsilon_{Sp} + A_p(P_{Sp} - P) + B_p(P_{Sp} - P)^{1-\alpha} \qquad P < P_B = P_{Sp} + \Delta P \qquad T = \text{const.}$$

$$\varepsilon(P) = 9.10 - 0.0204(P_{Sp} - P) + 0.028(P_{Sp} - P)^{0.89} \qquad \text{for } f = 1\text{ kHz}$$

$$\varepsilon(P) = 8.954 - 0.019(P_{Sp} - P) + 0.030(P_{Sp} - P)^{0.89} \qquad \text{for } f = 1\text{ MHz.} \tag{3}$$

where P_B and P_{Sp} stand for the binodal pressure, and for extrapolated pressure of the extrapolated virtual critical (pseudospinodal) point, respectively. ΔP is the measure of the discontinuity of the transition in the non-critical mixture of limited miscibility.

The estimated value of the critical exponent $\phi = 1 - \alpha = 0.88 \pm 0.06$ (i.e. $\alpha \approx 0.12$) is the same as the one obtained in the studies of mixtures of critical concentrations where $P_{Sp} = P_c$ and consequently $\Delta P = 0$. The presented result agrees with predictions of the pseudospinodal postulate originally formulated in light scattering studies as a method of determining the position of the spinodal curve from measurements in the stable region of the homogeneous phase (Chu *et al* 1969, Chrapeć *et al* 1987).

Figure 2 shows that the analogous relation portrays experimental data in the isotropic phase of 5CB (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1999):

$$\varepsilon = \varepsilon^* + A_P^{LC}(P^* - P) + B_P^{LC}(P^* - P)^{1-\alpha} \qquad P < P_{I-N} = P^* + \Delta P.$$

In our case,

$$\varepsilon(P) = 10.135 - 0.0088(P^* - P) + 0.13(P^* - P)^{0.48\pm0.06} \tag{4}$$

where: $P^* = 162.7$ MPa and $\Delta P = 23$ MPa, $T = 355.6$ K, $f = 10$ kHz.

The estimated value of the critical exponent $\phi = 1 - \alpha = 0.50 \pm 0.04$ is the same as in temperature studies under atmospheric pressure. It is noteworthy that in relations (1) and (2) the correction-to-scaling term could be neglected.

The validity of equations (3) and (4) supports the results of the differential analysis given in the insets in figures 1 and 2. Results obtained clearly show the validity of the dependence suggested by Mistura (1973) for the derivative of dielectric permittivity, originally proposed for critical mixtures. For the binary mixture the differential analysis of experimental data was possible due to the application of the pressure path of measurements where the pretransitional anomaly is much stronger than in isobaric, temperature studies (Habdas *et al* 1999). The applied scale of the insets directly shows the obtained values of the critical exponent α. They agree with results given in relations (3) and (4).

For 5CB a shift of the measurement frequency within the 'static region' from 1 kHz to 100 kHz changes the measured values of ε only within the limit of experimental error. For higher frequencies relaxation processes associated with the relaxation processes of large, rodlike molecules influence the registered values of ε (Vertogen and de Jeu 1988). In critical mixtures tested under atmospheric pressure equation (1) was found to be valid from $f = 100$ kHz to at least $f = 10$ MHz (Hamelin *et al* 1995). For lower frequencies the MW effect predominated over the critical effect (Thoen *et al* 1989, Orzechowski 1994, Hamelin *et al* 1995). This behaviour does not appear in pressure studies where the 'static region' extends even up to $f = 100$ Hz (Habdas *et al* 1999). This is also the case of figure 1 where equation (3) portrays well experimental data for $f = 1$ kHz.

Concluding, it has been shown that isomorphic dependences can be applied for the description of pretransitional anomalies of dielectric permittivity in the isotropic phase of nematogens and in the homogeneous phase of nematogens. This points to the validity of the fluidlike, critical hypothesis for the I–N transition (Mukherjee 1998 and references therein). Results obtained also suggest that the extrapolated, hypothetical point of a continuous phase transition in nematogens may be treated as a pseudospinodal point. However, the value of the exponent $\alpha = 0.5$ in the isotropic phase of 5CB and other nematogens (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1999) indicate that the fluid-like behaviour may be associated with the Gaussian (Pfeuty and Toulouse 1978) or tricritical (Anisimov 1993) pseudospinodal point. It is noteworthy that both for the nematogen and the binary mixture the Josephson scaling relation (Anisimov 1993) is valid with dimensionality $d = 3$. It should be noted there are strongly interacting, 'nonclassical' fluctuations in a near-critical mixture and almost non-interacting, 'classical' prenematic fluctuations in the LC compound. One may speculate that the last factor may be the reason of the lack of correction-to-scaling terms in 5CB.

When discussing the behaviour of 'linear' dielectric permittivity compounds worth recalling are results for 'nonlinear' changes of dielectric permittivity: the nonlinear dielectric effect. In critical mixtures the strong, steady electric field induces a quasi-nematic structure leading to the classical value of the critical exponent $\gamma = 1$ (Rzoska 1993) which is the same as in the isotropic phase nematogens. The fact that such agreement does not take place for the intensity of the scattered light (I) was first noticed by de Gennes in his monograph in 1974. The same disagreement can be noted for the Kerr effect (Rzoska 1993, Rzoska *et al* 1994). Noteworthy are also recent NDE studies of the relaxation time (τ) of critical fluctuation in off-critical mixtures where the dependence $\tau \propto (T - T_{Sp})^{-y}$ with $y \to 1$ was found (Rzoska *et al* 2000). An analogous relation is valid in the isotropic phase of nematogens (Anisimov 1993, Drozd-Rzoska and Rzoska *et al* 1999).

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