

## Pressure behaviour of dielectric permittivity on approaching the near-critical consolute point

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**Abstract.** – Results are presented of studies on dielectric permittivity ( $\varepsilon$ ) for the isothermal pressure ( $P$ ) path of approaching the near-critical consolute point in 1-nitropropane–hexadecane solution. The pretransitional anomaly is well portrayed by the relation isomorphic to that applied in temperature ( $T$ ) studies under atmospheric pressure. However, the  $\varepsilon(P)$  anomaly is much larger, with almost negligible influence of correction-to-scaling terms and the low-frequency Maxwell-Wagner dispersion (even for  $f = 1$  kHz), than it was observed in temperature studies at atmospheric pressure. This makes possible a reliable estimation of a critical exponent  $\phi = 1 - \alpha \approx 0.88$  which accounts for the critical anomaly. Discrepancies between the  $\varepsilon(P)$  and the  $\varepsilon(T)$  behaviour may be associated with different positions of isothermal pressure and isobaric temperature paths of approaching the critical consolute point.

*Introduction.* – The behaviour of dielectric permittivity ( $\varepsilon$ ) when approaching the critical consolute point in binary solutions has been the subject of studies already for nearly 6 decades [1-15]. The reason for such a long-standing interest was probably the lack of congruence both among experimental results and between theory and experiment (see [1-9] and references therein). This was undoubtedly associated with the weakness of the  $\varepsilon(T)$  critical anomaly, comparable to that of the specific heat ( $c_p \propto (T - T_C)^{1-\alpha}$ ), the diameter of the coexistence curve ( $d \propto (T - T_C)^{1-\alpha}$ ) or the density ( $\rho \propto (T - T_C)^{1-\alpha}$ ), where  $T_C$  denotes the critical temperature and  $\alpha \approx 0.11$  is the critical exponent of specific heat (see [16, 17] and references therein). It is noteworthy that for  $\varepsilon(T)$  and  $\rho(T)$  the critical effect in the homogeneous phase manifests itself in “bending down” from the almost linear behaviour far from the upper critical consolute temperature  $T_C$ . In 1989 Thoen *et al.* [9] found that for lower frequencies ( $f$ ) a strong, “parasitic” contribution due to the Maxwell-Wagner (MW) effect may antidote. It caused that for lower frequencies  $\varepsilon(T)$  “bends up” from the almost linear behaviour far from  $T_C$ . This implies that the critical anomaly predicted by theoretical models [5, 6],

$$\varepsilon(T) = \varepsilon_c + Ct + C_1 t^{1-\alpha} + C_2 t^{1-\alpha+\Delta_1} + \dots, \quad T > T_C, \quad (1)$$

where  $\varepsilon_c$  is the dielectric permittivity at the critical point,  $C$ ,  $C_1$ ,  $C_2$  are amplitudes:  $C_1$  is the critical amplitude and  $C_2$  is the amplitude of the first correction-to-scaling term [16] with

$\Delta_1 \approx 0.5$  is observed only for  $f \gg f_r$ . The “dielectric regime” in which relation (1) may be valid typically starts from  $f = 1$  MHz whereas  $f = 1$  kHz is often chosen as the low-frequency MW reference [9-15].

It is noteworthy that until recently disagreement between theory and experiment in critical solutions was reported also for the critical anomaly of non-linear changes of the dielectric permittivity in a strong electric field (non-linear dielectric effect,  $NDE = \Delta\epsilon^E/E^2 = (\epsilon^E - \epsilon)/E^2$ , where  $\epsilon^E$  is the dielectric permittivity in a strong electric field) [18-20]. When discussing  $\epsilon(T)$  and  $\Delta\epsilon^E/E^2(T)$  pretransitional effects it should be noted that relations describing their critical effects in the homogeneous phase of critical solutions may be also applied for portraying their pretransitional effects in the isotropic phase of liquid crystalline materials on approaching the nematic phase [21].

Up to now, studies on dielectric permittivity in critical solutions were carried out only as a function of temperature, under atmospheric pressure (see [1-15]) and references therein). In this report we present preliminary experimental studies applying the isothermal, pressure path of approaching the critical consolute point. Temperature and pressure are generally equivalent thermodynamic parameters, nevertheless they affect a system differently: temperature influences mainly processes related to the activation energy whereas pressure changes intermolecular distances. Studies presented in this paper have been conducted in the homogeneous phase of 1-nitropropane–hexadecane near-critical solution for which both  $\epsilon(T)$  behaviour under atmospheric pressure [22] and  $T_C(P)$  dependence have recently been determined [23].

*Experiment.* – Measurements were performed applying a pressure system with a specially designed flat-parallel capacitor (gap  $d = 0.4$  mm and  $C_0 \approx 4.1$  pF) given in ref. [23]. Temperature stabilisation was about 0.02 K/24 hours. It was measured by means of a platinum resistor placed in the jacket of the pressure chamber (A1 class, DIN 43 260) with resolution  $\pm 0.002$  K and accuracy  $\pm 0.1$  using Keithley 195A multimeter and a thermocouple placed inside the chamber. The pressure was measured by a Nova Swiss tensometric pressure meter, with resolution  $\pm 0.1$  MPa and accuracy  $\pm 0.4$  MPa. Measurements of the electric capacitance were carried using SOLARTRON 1260A impedance analyser. The averaging over 1000 periods made it possible to receive 5 digit resolution in the tested range of frequencies: 1 kHz–1 MHz. All errors are given as three standard deviations. The co-ordinates of the critical point of the examined 1-nitropropane–hexadecane solution were determined earlier by means of a visual method [23]:  $x_C = 0.66$  of mole fraction of 1-nitropropane and  $T_C \approx 34.95$  °C. Experimental studies up to 140 MPa gave an almost linear, within the limit of experimental error, dependence  $T_C(p)$  with  $dT_C/dp = 0.11 \pm 0.1$  K  $\times$  MPa $^{-1}$  for a series of 1-nitropropane–*n*-alkane critical solutions [23]. A still open question is the shift of the critical concentration ( $\Delta x_C$ ) caused by the hydrostatic pressure (see [24, 25] and references therein). Studies in a similar critical solution, also composed of a dipolar component and *n*-alkane, gave  $\Delta x_C$  less than 0.02 mole fraction for  $P \approx 100$  MPa [25]. One may expect that the possible weak discontinuity of the transition should not have significant influence on the results presented. Studies in non-critical binary solutions of limited miscibility applying the pseudospinodal hypothesis [26] showed that the discontinuity does not influence the functional form of the critical anomaly and the values of the universal critical exponents [26-28]. The temperature studies of the dielectric permittivity in the tested solution showed the validity of relation (1) and gave  $f = 1$  MHz as frequency high enough to reach the “dielectric regime” (relation (1)) [22]. All compounds were purchased from Fluka: hexadecane (HPLC class) was used without further purification and 1-nitropropane was four times distilled and dried over molecular sieves. The last distillation was conducted just before preparing the solution. The analysis was conducted by means of the non-linear fitting routine in the ORIGIN 3.5 software (Microcal Inc.). Experimental data are collected in table I.

TABLE I. – Isothermal ( $\Delta T \approx 14$  K) pressure data of dielectric permittivity measurements in the tested near-critical solution.

$P$ (MPa)	$\varepsilon$ $f = 1$ MHz	$\varepsilon$ $f = 100$ kHz	$\varepsilon$ $f = 10$ kHz	$\varepsilon$ $f = 1$ kHz	$P$ (MPa)	$\varepsilon$ $f = 1$ MHz	$\varepsilon$ $f = 100$ kHz	$\varepsilon$ $f = 10$ kHz	$\varepsilon$ $f = 1$ kHz
0.1	8.960	8.998	9.056 <sub>7</sub>	9.130	95.5	9.419 <sub>6</sub>	9.466 <sub>5</sub>	9.619 <sub>7</sub>	9.584 <sub>7</sub>
4.5	9.9894	9.028 <sub>8</sub>	9.089 <sub>2</sub>	9.162 <sub>1</sub>	96.6	9.422 <sub>4</sub>	9.468 <sub>5</sub>	9.522 <sub>8</sub>	9.586
9.6	9.019 <sub>7</sub>	9.063 <sub>3</sub>	9.121	9.200	97.5	9.424 <sub>3</sub>	9.471 <sub>2</sub>	9.524 <sub>4</sub>	9.589
14.7	9.051 <sub>6</sub>	9.093 <sub>5</sub>	9.150 <sub>7</sub>	9.219 <sub>2</sub>	98.6	9.426	9.473 <sub>6</sub>	9.528	9.589 <sub>6</sub>
19.7	9.0812	9.1235	9.179	9.2475	99.6	9.427 <sub>8</sub>	9.475 <sub>4</sub>	9.529 <sub>7</sub>	9.592 <sub>7</sub>
24.5	9.110	9.150 <sub>2</sub>	9.206 <sub>4</sub>	9.273 <sub>5</sub>	100.6	9.429 <sub>6</sub>	9.476 <sub>2</sub>	9.531 <sub>4</sub>	9.595
29.8	9.139 <sub>5</sub>	9.179 <sub>8</sub>	9.235 <sub>2</sub>	9.304 <sub>3</sub>	101.5	9.431 <sub>1</sub>	9.478 <sub>2</sub>	9.533 <sub>4</sub>	9.597 <sub>1</sub>
34.5	9.165 <sub>5</sub>	9.207	9.262 <sub>3</sub>	9.328 <sub>9</sub>	102.5	9.4331	9.480	9.5357	9.5978
39.4	9.190	9.233 <sub>7</sub>	9.285	9.353 <sub>3</sub>	103.5	9.434 <sub>2</sub>	9.480 <sub>6</sub>	9.538	9.597 <sub>8</sub>
44.7	9.217 <sub>3</sub>	9.262 <sub>4</sub>	9.314 <sub>2</sub>	9.380 <sub>7</sub>	104.5	9.435 <sub>4</sub>	9.480 <sub>4</sub>	9.540 <sub>3</sub>	9.600
49.5	9.239 <sub>7</sub>	9.285 <sub>4</sub>	9.337 <sub>6</sub>	9.405 <sub>9</sub>	105.5	9.436 <sub>5</sub>	9.480 <sub>5</sub>	9.538 <sub>4</sub>	9.600 <sub>8</sub>
54.4	9.264 <sub>1</sub>	9.311	9.363 <sub>6</sub>	9.427 <sub>5</sub>	106.6	9.437	9.483 <sub>6</sub>	9.538 <sub>4</sub>	9.603
59.6	9.287 <sub>8</sub>	9.334	9.386	9.450 <sub>6</sub>	107.5	9.437	9.4836	9.5384	9.603
64.6	9.311 <sub>2</sub>	9.355 <sub>5</sub>	9.407 <sub>3</sub>	9.472 <sub>6</sub>	108.5	9.436 <sub>8</sub>	9.482	9.540	9.603 <sub>5</sub>
69.5	9.330 <sub>8</sub>	9.380 <sub>1</sub>	9.427 <sub>7</sub>	9.492 <sub>4</sub>	109.5	9.437	9.481	9.541 <sub>6</sub>	9.603 <sub>7</sub>
74.4	9.350 <sub>4</sub>	9.398	9.447 <sub>2</sub>	9.512	110.4	9.436 <sub>2</sub>	9.480 <sub>7</sub>	9.540	9.603 <sub>7</sub>
79.5	9.369	9.417 <sub>7</sub>	9.466 <sub>8</sub>	9.532 <sub>4</sub>	111.4	9.435 <sub>4</sub>	9.480	9.538	9.603 <sub>5</sub>
82.5	9.380 <sub>5</sub>	9.427 <sub>9</sub>	9.479 <sub>8</sub>	9.541 <sub>6</sub>	112.5	9.433 <sub>9</sub>	9.478	9.537	9.602
85.6	9.391 <sub>2</sub>	9.437 <sub>4</sub>	9.491	9.555	113.4	9.432	9.475 <sub>8</sub>	9.536 <sub>2</sub>	9.600
88.6	9.400 <sub>5</sub>	9.448 <sub>4</sub>	9.500	9.565 <sub>8</sub>	114.2	9.430	9.473 <sub>3</sub>	9.535 <sub>3</sub>	9.599 <sub>5</sub>
91.6	9.409	9.456 <sub>6</sub>	9.509 <sub>7</sub>	9.574	115.1	9.427 <sub>2</sub>	9.470	9.534 <sub>4</sub>	9.597 <sub>8</sub>
93.5	9.414 <sub>8</sub>	9.461 <sub>5</sub>	9.514 <sub>5</sub>	9.579	116	9.420	9.464	9.530	9.596 <sub>5</sub>

*Results and discussion.* – Measurements of dielectric permittivity were conducted for the isotherm far from the critical temperature under atmospheric pressure by  $\Delta T \approx 14$  K. The results, for frequencies  $f = 1$  MHz, 100 kHz, 10 kHz and 1 kHz are shown in the main part of fig. 1. The figure also contains the pressure scale transformed to the temperature one, which makes the comparison with isobaric temperature studies easier. The visible systematic shift of the dielectric permittivity with decreasing frequency was also observed in studies under atmospheric pressure and is associated with the polarisation of capacitor plates due to ionic contaminations [8-15]. The isothermal pressure behaviour of  $\varepsilon$  may be portrayed by the pressure analogue of relation (1):

$$\varepsilon(P) = \varepsilon_c + C^p \tilde{P} + C_1^p \tilde{P}^{1+\alpha} + \dots, \quad T = \text{const}, \quad (2)$$

where  $\tilde{P} = P_C - P$  is the pressure distance from the phase transition point and  $P_C$  denotes critical consolute pressure.

For each frequency the same values, within the limit of the experimental error, of the fitted parameters in relation (2) were found (table II). For comparison, results of temperature

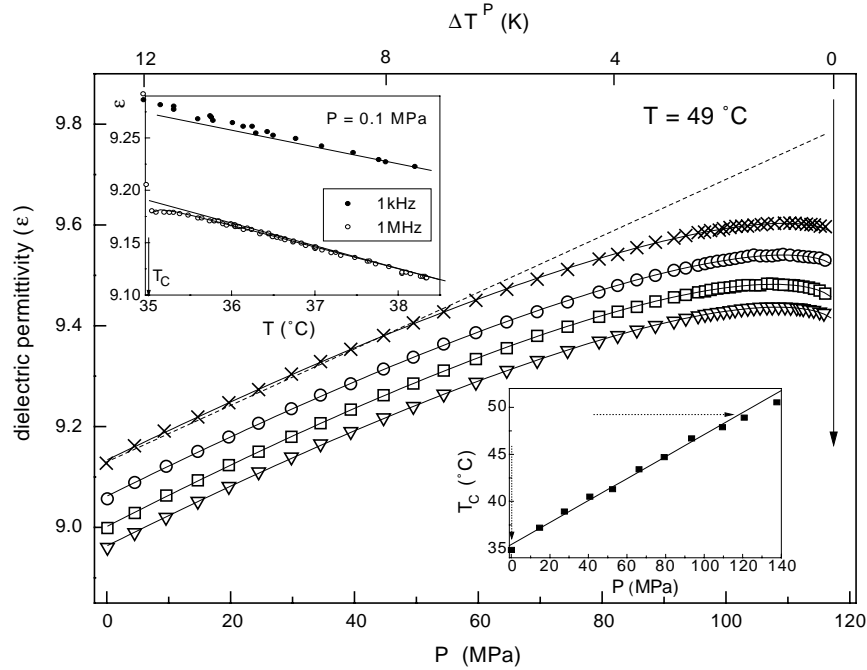


Fig. 1. – Pressure dependence of the dielectric permittivity in a near-critical 1-nitropropane-hexadecane solution for the isotherm far from the critical temperature under atmospheric pressure by  $\Delta T \approx 14$  K. Parameters of the critical consolute point:  $T_C = 49.0$  °C and  $P_C = 117.5$  MPa. Results are for 1 kHz (crosses), 10 kHz (circles), 100 kHz (squares) and 1 MHz (triangles). Solid lines present results of fitting of these data by means of relation (2), with parameters given in table II. The inset in the top-left corner shows the  $\varepsilon(T)$  dependence under atmospheric pressure in the immediate vicinity of  $T_C$  for  $f = 1$  MHz and 1 kHz [29]. The inset in the bottom-right corner shows the  $T_C(P)$  behaviour in the tested solution (ref. [24] with few additional data points obtained in these studies). Dotted arrows indicate the applied paths of approaching the near-critical consolute point and solid arrows show the position of this point. The dashed line shows the extrapolated behaviour of  $\varepsilon(P)$  far from  $T_C$ . The upper scale represents the pressure experimental scale transformed into the temperature one:  $\Delta T^P = dT_C/dP \times (P_C - P)$ , which makes the comparison with temperature studies under atmospheric pressure easier.

measurements under atmospheric pressure, which are presented in the inset on the top left-hand corner of fig. 1 [22] for  $f = 1$  MHz, can be approximated by the relation:

$$\varepsilon(T) = 9.2 - 0.039 \times \tilde{T} + 0.02 \times \tilde{T}^{1+\alpha} + 0.001 \times \tilde{T}^{1-\alpha+0.5} + \dots, P = \text{const}, \quad (3)$$

where  $\tilde{T} = T - T_C$  and  $\phi = 1 - \alpha = 0.88 \pm 0.06$ .

The significant influence of the MW effect for  $f = 1$  kHz was clearly visible [22].

Particularly noteworthy is the agreement of the basic parameters in relations (2) and (1), (3):  $\phi = 1 - \alpha \approx 0.88$ ,  $C, C^P > 0$  and  $C_1, C_1^P < 0$ . This may be considered as the appearance of the postulate of isomorphism of critical phenomena [16, 27, 30] tested so far in liquids mainly for thermodynamic properties (see [16, 27] and references therein). The postulate predicts the same values of the universal critical parameters for approaching the critical point along an arbitrary field-type variable (for instance,  $T$  or  $P$ ). However, there are also major differences between the isothermal and isobaric behaviour of dielectric permittivity. The first difference is that for the pressure path the pretransitional anomaly is much more significant. The strength

TABLE II. – Fitted parameters (relation (2)) of the pressure critical anomaly of dielectric permittivity for data presented in fig. 1.

Frequency	$\varepsilon_c$	$C^p$ (MPa $^{-1}$ )	$C^p$ (MPa) $^{\alpha-1}$	$\phi = 1 - \alpha$
1 MHz	9.408 $\pm$ 0.0004	-0.0235 $\pm$ 0.001	0.0345 $\pm$ 0.003	0.883 $\pm$ 0.02
100 kHz	9.449 $\pm$ 0.0006	-0.0245 $\pm$ 0.001	0.0365 $\pm$ 0.003	0.881 $\pm$ 0.03
10 kHz	9.516 $\pm$ 0.0006	-0.025 $\pm$ 0.001	0.0033 $\pm$ 0.006	0.885 $\pm$ 0.04
1 kHz	9.58 $\pm$ 0.01	-0.025 $\pm$ 0.005	0.033 $\pm$ 0.007	0.89 $\pm$ 0.05

( $\Delta\varepsilon$ ) of the anomaly defined as the difference between the  $\varepsilon(T)$  or  $\varepsilon(P)$  dependences far away from  $T_C$ ,  $P_C$  extrapolated linearly up to this point and the experimental values of  $\varepsilon(T_C)$  and  $\varepsilon(P_C)$  equals  $\Delta\varepsilon \approx 0.02$  for the temperature path under atmospheric pressure (see [22] and the upper inset in fig. 1) but can be as high as  $\Delta\varepsilon \approx 0.2$  for the pressure path (these studies, fig. 1). The second difference is that for the pressure path the satisfactory description of the anomaly can be obtained without introducing correction to scaling terms which significantly reduces the number of fitted parameters. The validity of the fitting of experimental data by means of relation (2) with such approximation is emphasised by the fact that the average deviation from fitted functions (solid line in fig. 1) does not exceed  $\pm 0.001$   $\chi_v^2 \approx 1.3$ . The facts that the pretransitional anomaly of  $\varepsilon(P)$  is so strong that even omitting the experimental data in the immediate vicinity of the transition point ( $P_C - P < 20$  MPa) does not influence significantly the values of fitted parameters and that the correction to scaling terms does not appear in relation (2) enabled a reliable estimation of the critical exponent  $\phi = 1 - \alpha$ . The third specific feature of the tested  $\varepsilon(P)$  critical anomaly is the negligible influence of the Maxwell-Wagner effect even for  $f = 1$  kHz.

To conclude, the results discussed above show the isomorphism of the dielectric permittivity behaviour when approaching the critical consolute point along the pressure and temperature paths. In studies conducted up to now under atmospheric pressure a critical anomaly much weaker than that presented in this paper, additionally disturbed by the MW effect, was fitted by relation (1) containing two non-linear terms. In the presented pressure studies the critical anomaly is relatively strong, the MW effect seems to be negligible and the number of fitted parameters is reduced. The distinguished features of  $\varepsilon(T)$  and  $\varepsilon(P)$  critical anomalies may be due to the fact that the shift of temperature mainly influences the excitation energy of rotational and vibrational states, while the shift of pressure is associated with density changes, particularly efficient in liquids. These essential differences in the insight into the properties of a system are strongly manifested, for instance, in the pressure studies of phase transition phenomena [32, 33] and in the dielectric properties in supercooled liquids [34] or in liquid crystalline materials [35]. Significant influence on the specific behaviour of  $\varepsilon(P)$  may have the position of the isothermal pressure path of approaching the line of near-critical consolute points (bottom inset in fig. 1). The small value of  $dT_C/dP$  implies that for this path the region of the strong influence of critical fluctuations is much broader than for the temperature path. The possible importance of this factor is shown by the measurements of relaxation times ( $\tau$ ) of critical fluctuations in near-critical solutions after switching off the strong electric field. For temperature studies under atmospheric pressure the experimental values of  $\tau$  did not exceed 10–20 ms (for  $T - T_C \approx 0.01$  K) [32]. When the critical consolute point along the pressure path was approached a value as large as  $\tau \approx 0.2$  s (for  $P_C - P \approx 1$  MPa and

$P_C \approx 60$  MPa) [33] was obtained. In pressure studies even at 50 MPa from  $P_C$  the relaxation time is still as large as  $\tau \approx 1$  ms [33]. In the opinion of the authors such a behaviour of relaxation times and a pressure-induced increase of viscosity may be responsible for the negligible influence of the Maxwell-Wagner effect at low frequencies in pressure studies. The authors hope that further pressure studies will make it possible to understand the molecular origins of the critical anomaly of the dielectric permittivity. This is now possible only in the isotropic phase of nematogens where a fluid-like pretransitional behavior in the isotropic phase is observed (see [21] and references therein). In critical solutions even the theoretically predicted dependence of the critical amplitude  $C_1$  on phenomenological coefficients  $dT_C/dE^2$  and  $dT_C/dP$  is still controversial [29,31].

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#### REFERENCES

- [1] PIEKARA A., *Phys. Rev.*, **42** (1932) 1342.
- [2] SEMENCHENKO V. V. and AZIMOV M., *Ž. Fiz. Khim.*, **29** (1955) 1342.
- [3] GIVON M., PELAH I. and EFROH U., *Phys. Lett. A*, **48** (1974) 1.
- [4] THOEN J., KINDT R. and v. DAEL W., *Phys. Lett. A*, **76** (1980) 445.
- [5] GOULON J., GREFFE J.-L. and OXTOBY D. W., *J. Chem. Phys.*, **70** (1979) 4742.
- [6] SENGERS J. V., BEDEAUX D., MAZUR P. and GREER S. C., *Physica A*, **104** (1980) 573.
- [7] TVEEKREM J. L., GREER S. C. and JACOBS D. T., *Macromolecules*, **21** (1988) 147.
- [8] KINDT R., THOEN J. and v. DAEL W., *Int. J. Thermophys.*, **9** (1988) 749.
- [9] THOEN J., KINDT R., v. DAEL W., MERABET M. and BOSE T. K., *Physica A*, **156** (1989) 92.
- [10] HAMELIN J., BOSE T. K. and THOEN J., *Phys. Rev. A*, **42** (1990) 4735.
- [11] EARLY M. D., *J. Chem. Phys.*, **96** (1992) 641.
- [12] ORZECOWSKI K., *J. Chem. Soc. Faraday Trans.*, **90** (1994) 1757.
- [13] HAMELIN J., GOPAL B. R., BOSE T. K. and THOEN J., *Phys. Rev. Lett.*, **74** (1995) 2733.
- [14] HAMELIN J., BOSE T. K. and THOEN J., *Phys. Rev. E*, **53** (1996) 779.
- [15] ORZECOWSKI K., MARCZAK W. and ERNST S., *J. Mol. Struct.*, **415** (1997) 45.
- [16] ANISIMOV M. A., *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach Sci. Pub., Reading) 1992.
- [17] STANLEY H. E., *The Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford) 1971.
- [18] RZOSKA S. J., *Phys. Rev. E*, **48** (1993) 1136.
- [19] RZOSKA S. J., DEGIORGIO V. and GIARDINI M., *Phys. Rev. E*, **49** (1994) 5234.
- [20] RZOSKA S. J., DROZD-RZOSKA A., GÓRNY M. and ZIOŁO J., *Phys. Rev. E*, **52** (1995) 6325.
- [21] DROZD-RZOSKA A., RZOSKA S. J. and ZIOŁO J., *Phys. Rev. E*, **54** (1996) 6452.
- [22] PALUCH M., HABDAS P., RZOSKA S. J. and SCHIMPEL T., *Chem. Phys.*, **213** (1996) 483.
- [23] URBANOWICZ P., RZOSKA S. J., PALUCH M., SAWICKI B., SZULAC A. and ZIOŁO J., *Chem. Phys.*, **201** (1995) 575.
- [24] ROWLINSON J. S. and SWINTON F. L., *Liquids and Liquid Mixtures* (Buttenworth Sci. Pub., London) 1982.
- [25] URBANOWICZ P. and RZOSKA S. J., *Phase Trans.*, **56** (1996) 239.
- [26] CHU B., SHOENES F. J. and FISHER M. E., *Phys. Rev.*, **195** (1969) 219.

- [27] KUMAR A., KRISHNAMURTHY H. R. and GOPAL E. S. R., *Phys. Rep.*, **98** (1983) 59.
- [28] ABDULAGATOV J. M. and ALIBEKOV B. G., *Tepl. Vys. Temp.*, **23** (1985) 472.
- [29] Note that in different critical solutions  $dT_C/dp$  can be positive or negative (see ref. [23]) whereas  $\varepsilon(T)$  always bends down on approaching the upper critical consolute point.
- [30] GRIFFITHS, R. B. and WHEELER J. C., *Phys. Rev. A*, **4** (1971) 253.
- [31] ONUKI A., *Europhys. Lett.*, **29** (1995) 611. The paper indicated a significant discrepancy between experimental and theoretical values of  $dT_C/dE^2$ .
- [32] RZOSKA S. J., DEGIORGIO V., BELLINI T. and PIAZZA R., *Phys. Rev. E*, **49** (1994) 3093.
- [33] RZOSKA S. J., ZIOŁO J. and DROZD-RZOSKA A., *Phys. Rev. E*, **56** (1997) 2587.
- [34] PALUCH M., RZOSKA S. J., HABDAS P. and ZIOŁO J., *J. Phys. Condens. Matter*, **10** (1998) 4131.
- [35] URBAN S. and WUERFLINGER A., *Dielectric properties of liquid crystals under high pressure*, in *Adv. Chem. Phys. XCVIII*, edited by I. PRIGOINE and S. A. RICE (John Wiley & Sons Inc., New York) 1997, p. 143.