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New evidence for a liquid–liquid transition in a one-component liquid

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Abstract

Based on specific heat, x-ray diffraction and nonlinear dielectric effect (NDE) measurements the evidence for a liquid–liquid (L–L) transition in *trans*-1,2-dichloroethylene at $T_{L-L} \approx T_m + 23.6 \text{ K} \approx 247 \text{ K}$ is shown. The strong pre-transitional anomaly of NDE, similar to the one observed in the isotropic phase of nematic liquid crystals, makes it possible to estimate the weakly discontinuous character of the transition. Based on NDE measurements, the pressure evolution of the L–L transition up to almost 500 MPa was also obtained. Parameterization by the modified Simon–Glatzel-type equation made possible an insight into the negative pressure domain.

1. Introduction

The existence of a single-component liquid in several liquid mesophases is a well known phenomenon in liquid crystalline (LC) compounds [1]. In such materials the weakly discontinuous phase transition from an isotropic liquid to nematic and eventually smectic mesophases on cooling can occur [1, 2]. The nematic phase is associated with the dominant orientational ordering whereas centers of mass of molecules remain disordered. For smectic mesophases the orientational ordering is accomplished by progressive translational arrangement, beginning from the one-dimensional case of the smectic A phase [1]. However, in the last decade growing evidence has appeared that liquid–liquid (L–L) polymorphism in a single-component and non-mesogenic (non-LC) liquid is also possible. In this case the change of ordering when passing the L–L transition is clearly local and associated with the transition from a low-density liquid (LDL) to a high-density ‘ordinary liquid’ [3–15]. Evidence for such a phenomenon in triphenyl phosphite (TPP) [3, 4], phosphorus [5], carbon [6, 7], silicone [8, 9], aluminate melts [10, 11], polystyrene [12] and nitrogen [13] has been reported in the last decade. Existence of a L–L transition seems to be one of key hypotheses for explaining the puzzling properties of water [14].

Several models have been developed to explain the appearance of this unusual phenomenon in ‘simple’ liquids. They are based on two-liquid models [15, 16], the two order

parameter model of liquids [17], anisotropic potential based models [18] or models based on the isotropic interaction potential with an attractive part and with *two* characteristic short-range repulsive distances [19]. It is noteworthy that the link between the L–L transition and the glass transition is considered as a possible artifact underlying vitrification [17–21]. In fact, the L–L transition is most often located near the glass transition [3–13]. It is also worth recalling the recent evidence for a hypothetical continuous or semi-continuous phase transition hidden slightly below the glass temperature in glass formers where vitrification is dominated by a single, selected element of symmetry [22].

In this paper we present the novel, preliminary evidence for a L–L transition in *trans*-1,2-dichloroethylene. This is a simple, non-mesogenic liquid with enormous applications in the plastics industry, dry cleaning and many other modern material engineering related issues [23–26]. Consequently, it is included in the group of pollutants which can have a hazardous influence on the environment and human health [26]. It also belongs to a group of model materials in molecular physics [27–29].

The first evidence for a novel liquid state (L_2) in *trans*-1,2-dichloroethylene was reported in 1981 by Kawanishi *et al* [30] based on pulsed NMR and density studies. The latter showed a density increase of up to 0.06% when passing the hypothetical L–L phase transition. In the following year Kawanishi *et al* [31] showed the linear pressure dependence of $T_{L-L}(P)$ in studies carried out up to $P \approx 200 \text{ MPa}$.

It was speculatively concluded in [30] that ‘The L_2 phase is a mesomorphic state which lacks freedom of the molecular rotation and is similar to a nematic phase of liquid crystals in this point. A large molecular quadrupole moment in *trans*-1,2-dichloroethylene plays an important role in the ordered state’. The possible existence of a third (L_3) liquid phase was also indicated, although it was found only in pressure-related investigations [31]. We did not note any other reports giving clear evidence for the L–L transition in this compound.

2. Experimental details

2.1. Calorimetric measurements

Specific heat measurements at ordinary pressure were performed on cooling from room temperature and on heating after the crystallization process (223.4 K) through the modulated differential scanning calorimetry (MDSC) technique by means of a commercial Q100 TA Instruments DSC equipped with a RCS cooler. All measurements were done at 0.25 K min^{-1} with a modulation temperature amplitude of $\pm 0.25 \text{ K}$ and a period of 60 s. A conventional heat flow DSC signal was also simultaneously obtained during the same runs.

2.2. X-ray diffraction

A preliminary set of structure factors $S(Q)$ were measured as a function of temperature with a high-resolution x-ray diffractometer (INEL CPS-120 cylindrical position-sensitive detector) using Debye–Scherrer geometry (angular step approximately $0.029^\circ\text{-}2\theta$). Monochromatic $\text{Cu K}\alpha_1$ ($\lambda = 1.54059 \text{ \AA}$) radiation was selected. The generator power was set to 35 kV and 35 mA. Low-temperature measurements were achieved with a liquid nitrogen 700 series Cryostream Cooler from Oxford Cryosystems. The liquid sample was placed into 0.3 mm diameter Lindemann capillaries. External calibration using the $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_4$ cubic phase was performed by means of cubic spline fittings. Details have been previously given in [32].

X-ray profiles were acquired from 283 K down to 223 K every 5 K with acquisition times of 60 min and a stabilization time at each temperature of 10 min.

2.3. Nonlinear dielectric effect

The nonlinear dielectric effect (NDE) describes changes in dielectric permittivity due to the application of a strong electric field, namely [33–35]:

$$\begin{aligned} \varepsilon^E &= \varepsilon_1 + \varepsilon_3 E^2 + \dots \quad \text{and} \\ \varepsilon_{\text{NDE}} &= \varepsilon_3 = \frac{\varepsilon^E - \varepsilon}{E^2} = \frac{\Delta\varepsilon^E}{E^2} \end{aligned} \quad (1)$$

where $\varepsilon_1, \varepsilon^E$ are the dielectric permittivities for a weak, radio-frequency (measuring field) and strong electric field, respectively and ε_{NDE} is the experimental measure of NDE.

In this paper a dual-field modulation domain apparatus was used, the design of which is given in [34, 35]. The

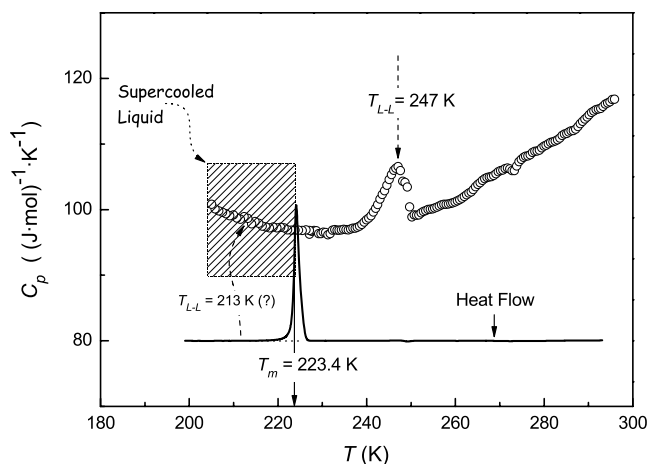


Figure 1. Specific heat data (open circles) as a function of temperature on cooling around the L–L transition (the dashed area delimits the supercooled region of the low-temperature liquid phase). The solid line corresponds to the heat flow recorded on heating.

sample was placed in a flat-parallel capacitor made from Invar, with a gap $d = 0.2 \text{ mm}$ [34]. The total capacitance of the sample was about 40 pF. A strong electric field up to $V_{\text{p-p}}^{\text{strong}} \approx 1 \text{ V}$ 1500 V, in the form of DC pulses lasting 1 ms was used. It induced changes of capacitance $\Delta C(E) \sim 0.1 \text{ fF}$, which were registered with a resolution of two to three digits. For the weak measuring field $f \approx 5 \text{ MHz}$ and $V_{\text{p-p}}^{\text{weak}} \approx 1 \text{ V}$. This method can register a response directly coupled to multimolecular structures, contrary to ‘linear’ dielectric spectroscopy [33, 34]. In fact NDE, or more generally nonlinear dielectric spectroscopy (NDS), is considered to be the successor of broad band dielectric spectroscopy (BDS). It was stated in [36]: ‘while BDS is linked to the 2-point correlation function, NDS can directly probe 4-point correlation function and then it can be an optimal tool for sampling multimolecular ‘heterogeneities’, for instance in glass-forming supercooled liquids’.

The orientation of permanent dipole moments linked to molecules may be considered as the basic molecular contribution to NDE. This method can also register the appearance of intermolecular coupling, multimolecular associations, intramolecular rotations or statistical fluctuations of polarization or density [33–35]. The latter is considered as the smallest contribution to NDE, of the order of $10^{-19} \text{ m}^2 \text{ V}^{-2}$ [33]. For comparison, pre-transitional fluctuations in critical mixtures and liquid crystals can yield effects of the order of up to $10^{-14} \text{ m}^2 \text{ V}^{-2}$ [33–35, 37].

Measurements were carried out for *trans*-1,2-dichloroethylene purchased from Fluka. The pressure set-up used for NDE measurement was the same as in [2].

3. Results and discussion

Specific heat related measurements are commonly considered to be the basic experimental tool for indicating the existence of a phase transition or the transformation to the glassy state. As shown in figure 1, specific heat measurements for

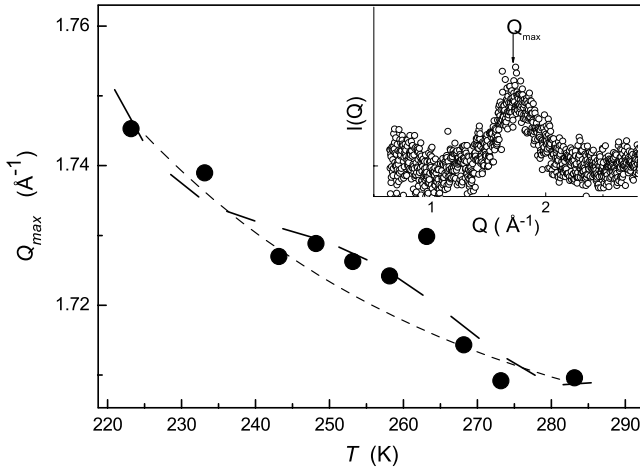


Figure 2. The temperature evolution of the location of the maximum (Q_{\max}) of the structure factor $S(Q)$ as a function of the temperature. Inset: structure factor at 233 K.

trans-1,2-dichloroethylene reveal a clear L–L phase transition related to the maximum at 247.0 K. Upon heating from the supercooled state the sample crystallized at $T_m = 223.4$ K on the conventional DSC heat flow signal (lower curve on figure 1). It is noteworthy that in the supercooled domain one may infer the existence of the hallmark of a possible second L–L transition. It also seems to be visible in NDE tests, shown in figure 3 below.

Figure 2 shows results focusing on the emergence of hypothetical changes in structure when passing the L–L transient. Due to the reduced Q -range measured, we obtained only qualitative information from the position of the maximum of the first broad diffraction peak (Q_{\max}) characteristic of long-range disordered systems. The variation of the peak position as the function of temperature, to which we restrict the discussion in this paper, clearly displays an anomaly around the transition.

To achieve the final goal concerning the possible change of the short-range order at the transition further studies should be performed with a shorter wavelength in order to increase the momentum transfer range, Q , and to derive the radial distribution function from $S(Q)$. In addition such a study should be performed with synchrotron radiation or neutron scattering due to the high absorption of the sample.

The nonlinear dielectric effect is a fluctuation-sensitive method, like the Kerr effect or light scattering [33, 34]. However, for NDE the sampling is associated with radio-frequencies and then with much longer time-scales than for methods employing light. NDE exhibits a strong pre-transitional anomaly on approaching the critical consolute point in critical binary mixtures (CM) of limited miscibility or the isotropic–nematic (I–N) transition in rod-like liquid crystalline (LC) compounds. For the latter, in the static case [38]:

$$\epsilon_{\text{NDE}} \propto \langle \Delta M^2 \rangle_V \chi \propto \chi_0 \frac{(\Delta M)^2}{T - T^*} \quad (2)$$

where $T^* = T_{\text{I–N}} - \Delta T$ is for the extrapolated, hypothetical continuous phase transition, $T > T_{\text{I–N}}$, $\langle \Delta M \rangle_V$ is for the mean of the order parameter and $\chi = \chi_0(T - T^*)^{-1}$ is for the order parameter related susceptibility (compressibility).

In [34, 38, 39] the possibility of the common description of NDE and the electrooptic Kerr effect in the isotropic phase of LC and in the homogeneous CM was shown. Recently, the validity of a similar relation for nitrobenzene, a simple non-mesogenic molecular liquid, was reported, namely: $\epsilon_{\text{NDE}} \propto 1/T - T^+$, where the singular temperature T^+ is hidden in the weakly supercooled domain [35]. This behavior was linked to the appearance of quasi-nematic structures—filaments in the isotropic surroundings. However, in nitrobenzene the crystallization occurred before reaching T^+ [35].

Figure 3 shows the temperature evolution of NDE in *trans*-1,2-dichloroethylene. The results presented show clear

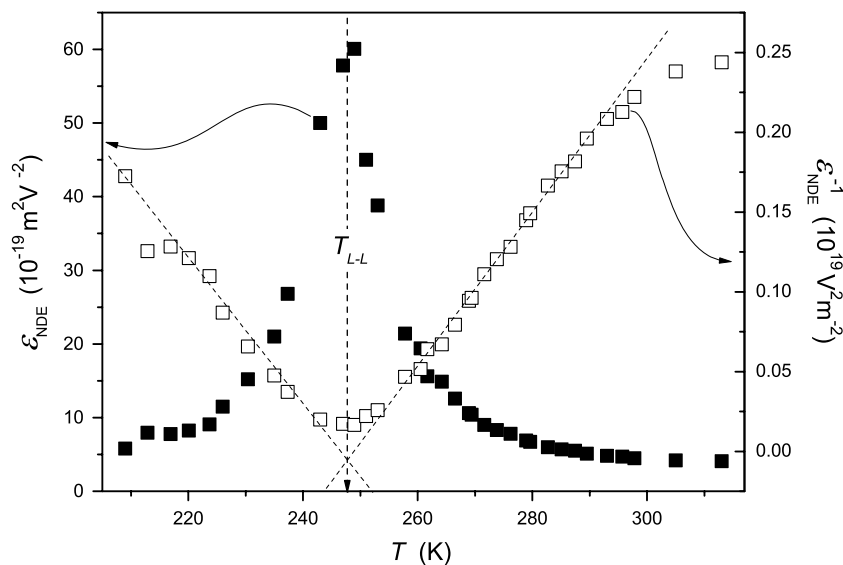


Figure 3. Temperature dependence of NDE in *trans*-1,2-dichloroethylene. Solid squares and the left-hand scale are for the measured NDE. Open squares and the right-hand scale are for the reciprocal of the measured NDE values. The dotted lines indicate the possibility of parameterization via equation (3).

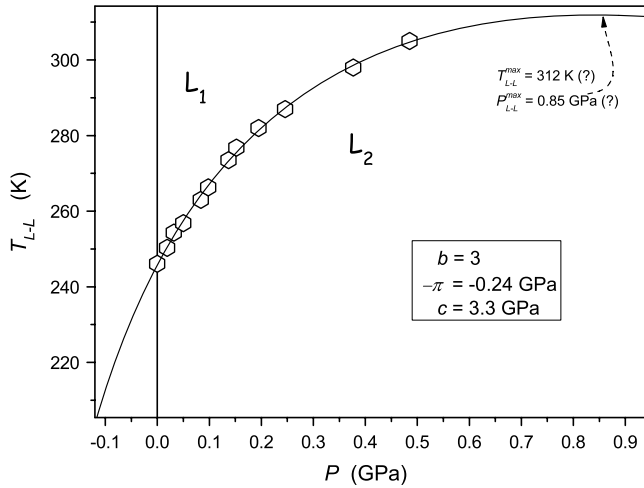


Figure 4. The pressure dependence of the L–L transition temperature in *trans*-1,2-dichloroethylene, estimated from NDE measurements. The solid curve is for the Simon–Glatzel-type equation (4), with pressure invariant parameters given in the plot.

evidence of the anomalous behavior, with the peak near $T_{L-L} \approx 247$ K. The plot of the reciprocal of NDE, also given in figure 3, shows the validity of the following parameterization of the obtained anomaly:

$$\begin{aligned} \varepsilon_{\text{NDE}} &\propto \frac{1}{T - T^+} && \text{for } T > T_{L-L} + 10 \text{ K} && \text{and} \\ \varepsilon_{\text{NDE}} &\propto \frac{-1}{T - T^{++}} && \text{for } T < T_{L-L} - 10 \text{ K}. \end{aligned} \quad (3)$$

It is also possible to estimate the value of the ‘discontinuity’ of the $L_1 \leftrightarrow L_2$ transition as $\Delta T_{L_1 \rightarrow L_2} = T_{L-L} - T^+ \approx 5$ K and $\Delta T_{L_2 \rightarrow L_1} = T^{++} - T_{L-L} \approx 5$ K from NDE results in figure 3. It is should be recalled that for rod-like LC the value of the discontinuity of the I–N transition is one of basic parameters characterizing this weakly discontinuous transition [1]. We would like to stress that in LC materials, near-critical mixtures or nitrobenzene it is not possible to carry out NDE or similar measurements in the low-temperature phase [1, 2, 38].

The peak of NDE when passing the L–L transition makes it possible to use this feature for estimating the pressure evolution of the temperature of the $L_1 \leftrightarrow L_2$ transition. Such results are presented in figure 4. The solid curve shows the parameterization of $T_{L-L}(P)$ via the Simon–Glatzel-type dependence proposed for describing the pressure evolution of the melting temperature, the glass temperature and the VFT ideal glass temperature [40]. In [37] the possibility of using this function for portraying the pressure dependence of the critical consolute temperature was also shown. For data presented in figure 4 this expression has the form:

$$\begin{aligned} T_{L-L}(P) &= F(P)D(P) = T_{L-L}^0 \left(1 + \frac{\Delta P}{\pi + P_{L-L}^0} \right)^{1/b} \\ &\times \exp \left(-\frac{\Delta P}{c} \right) \end{aligned} \quad (4)$$

where $F(P)$ is the rising function and $D(P)$ the damping function; $\Delta P = P - P_{L-L}^0$; P_{L-L}^0 and T_{L-L}^0 are the

reference pressure and temperature, respectively, from which the $T_{L-L}(P)$ estimation begins; c denotes the damping pressure coefficient; $-\pi$ is the negative pressure asymptote for $T \rightarrow 0$; the coefficients $\Pi = \pi + P_{L-L}^0$.

Relation (4) shows several unique features, namely [40]: (i) it is governed by pressure invariant coefficients $-\pi$, b and c ; (ii) in a natural way it can be extended into the negative pressures domain; (iii) it can portray the system with the inversion (maximum) of the pressure dependence of the transition temperature; (iv) the latter can be predicted even based on data in a moderate range of pressure due to the mentioned pressure invariance of key parameters.

All these features are clearly visible in figure 4, where related values of parameters are also given.

Concluding, a set of novel experimental results showing clear evidence of the L–L transition in *trans*-1,2-dichloroethylene are reported, namely for the specific heat, x-ray structural studies and the nonlinear dielectric spectroscopy (NDE). For the latter a strong pre-transitional anomaly was obtained, similar to the one observed in the isotropic phase of LC compounds or in supercooled nitrobenzene. These results suggest that on approaching the L–L transition multimolecular heterogeneities—fluctuations with dielectric permittivity slightly different from the ‘isotropic’ surrounding—appear. The obtained NDE evolution gives evidence for the weakly discontinuous character of the L–L transition. The peak of NDE at the L–L transition enabled a reliable estimation of the pressure evolution of the L–L transition, as well the estimation of $T_{L-L}(P)$ dependence in the negative pressure domain or for very high pressures. It is also worth recalling that the proximity of a critical point significantly changes the properties of any system [41]. Consequently, the question arises about the influence of this artifact on *trans*-1,2-dichloroethylene, since it can be considered as a supercritical liquid in the range of temperatures and pressure used in fundamental and technological applications.

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