

Weakly first-order character of the nematic-isotropic phase transition in liquid crystals

B. Van Roie,* J. Leys, K. Denolf, C. Glorieux, G. Pitsi, and J. Thoen

Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

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The classification of phase transitions in first-order and second-order (or continuous) ones is widely used. The nematic-to-isotropic (NI) transition in liquid crystals is a weakly first-order transition, with only small discontinuities in enthalpy and specific volume at the transition which are not always easy to measure. On the other hand, fluctuation effects near the transition, typical for a continuous transition, are present because of the only weakly first-order character. In a recent paper [Phys. Rev. E **69**, 022701 (2004)], it was concluded from the static dielectric permittivity in the isotropic phase near the NI transition that less polar mesogens (with little or no pretransitional effects) are characteristic for a first-order NI phase transition, whereas in the case of strongly polar ones (with large pretransitional effects) the NI transition is close to second order. In this paper, we address the question whether it is, indeed, possible to use these fluctuation effects in the isotropic phase to quantify the “strength” of a weakly first-order transition, i.e., how far it is from second order. Therefore, we measured the temperature dependence of the enthalpy near the NI transition of seven liquid crystals with adiabatic scanning calorimetry and compared the measured values of the latent heat with pretransitional effects in the dielectric constant and the specific heat capacity. The compounds used in the comparison are MBBA, 5CB, 8CB, 5NCS, 5CN, 8CHBT, and D7AB. From our analysis we find, contrary to the assertion in the above reference, no correlation between the strength of the NI transition of a given compound and the pretransitional effects observed, neither dielectrically, nor thermally.

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I. INTRODUCTION

Phase transitions are usually classified into first-order transitions and so-called second-order or continuous ones. First-order phase transitions are thermodynamically characterized by finite discontinuities in one or more first derivatives of the relevant thermodynamic potential. For the Gibbs free energy $G(p, T)$ (appropriate for fluids) as a function of pressure p and temperature T , this means that the entropy $S = -(\partial G / \partial T)_p$ and/or the specific volume $V = (\partial G / \partial p)_T$ are discontinuous [1,2]. At second-order (or continuous) phase transitions S and V are continuous. Thus, in order to assess whether a transition is first order or continuous, one has to verify the presence or absence, at the transition, of a discontinuity in the specific volume ΔV or in the entropy ΔS , or more conveniently in the enthalpy, or determine the latent heat given by $\Delta H_L = T_i \Delta S$, with T_i the transition temperature. Experimentally, this is often not a simple task for first-order phase transitions with (very) small discontinuities, and requires very high resolution density or enthalpy measurements. However, contrary to strongly first-order transitions (typically melting transitions), continuous transitions and (very) weakly first-order transitions quite often show pretransitional or so-called critical fluctuation effects (for either of the phases) in several physical parameters on approaching the transition. Although these fluctuation effects are system and physical parameter dependent, it is tempting to use these fluctuation effects in an effort to distinguish between first-order and second-order phase transitions, or to quantify the

“weakness” (or strength) of (very) weakly first-order transitions. This could be potentially applicable for the nematic-isotropic (NI) transition in liquid crystals, which is, indeed, a (very) weakly first-order transition, as theoretically expected [3] and as shown from high-resolution enthalpy measurements [4,5] and high-resolution density measurements [6] for several compounds.

For several liquid crystals one observes in the isotropic phase for the temperature dependence of the (static) dielectric constant a substantial pretransitional anomaly [7,8]. On the other hand in other compounds no such anomaly is detected. In two recent papers by Jadzyn *et al.* [9] and Gionovska *et al.* [10] dielectric results in the isotropic phase were used in an effort to classify NI transitions of different compounds as being first order or “close to first order” (the compounds without dielectric anomaly in the isotropic phase) or as weakly first order or “close to second order” (the compounds with a pronounced dielectric anomaly in the isotropic phase). If this approach holds it is, indeed, a very useful one since dielectric measurements can be readily performed in the isotropic phase.

In this paper we want to verify whether this is, indeed, a reliable approach in the light of the thermodynamic definition and classification of phase transitions. For this purpose we compare high-resolution enthalpy results (including latent heats) near the NI transitions with dielectric data in the isotropic phase. A comparison is made for seven different compounds. Recent enthalpy data from adiabatic scanning calorimetry (ASC) are presented for five compounds, and for the other compounds already published data are used [4,5]. For the dielectric data we use for three compounds the data of Ref. [9,10], and for the other compounds we use (our own) unpublished data or recently measured ones. As far as

*Electronic address: Bert.VanRoie@fys.kuleuven.be

available from literature we also involve data for the specific volume in the analysis.

The compounds considered in the analysis are 4-methoxybenzylidene-4-*n*-butylaniline (MBBA), 4-*n*-pentyl-4'-cyanobiphenyl (5CB), 4-*n*-octyl-4'-cyanobiphenyl (8CB), 1-(4-*trans*-pentyl cyclohexyl)-2-(4-isothiocyanatophenyl)ethane (5NCS), 1-(4-*trans*-pentylcyclohexyl)-2-(4-cyanophenyl)ethane (5CN), 1-(*trans*-4-octylcyclohexyl)-4-isothiocyanatobenzene (8CHBT), and 4,4'-diheptylazobenzene (D7AB).

II. THEORETICAL BACKGROUND

A. Classification of phase transitions

First-order phase transitions are characterized by finite discontinuities in one or more first derivatives of the relevant thermodynamic potentials as a function of their variables. The Gibbs free energy G as a function of pressure p and temperature T is for fluids appropriate. At a first-order phase transition the entropy $S = -(\partial G / \partial T)_p$ and the specific volume $V = (\partial G / \partial p)_T$ are discontinuous. According to the classical Ehrenfest scheme [11] second-order transitions are characterized by finite discontinuities in the second derivatives of the Gibbs free energy. Thus, associated with second-order transitions, finite discontinuities are expected for the specific heat capacity $C_p = T(\partial S / \partial T)_p$, the isobaric thermal expansion coefficient $\alpha_p = V^{-1}(\partial V / \partial T)_p$, and the isothermal compressibility $\kappa_T = -V^{-1}(\partial V / \partial p)_T$. This well-known scheme also makes it possible to predict the change in the equilibrium transition temperature with pressure. For first-order transitions this follows from the Clapeyron equation

$$\left(\frac{dp}{dT}\right)_\sigma = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}, \quad (1)$$

where the index σ indicates the derivative along the transition line. For second-order transitions one can derive the so-called Ehrenfest equations

$$\left(\frac{dp}{dT}\right)_\sigma = \frac{\Delta C_p}{TV\Delta\alpha_p}, \quad (2a)$$

$$\left(\frac{dp}{dT}\right)_\sigma = \frac{\Delta\alpha_p}{\Delta\kappa_T}. \quad (2b)$$

The Ehrenfest scheme may be extended indefinitely to even higher-order transitions; however, these have never been observed. Moreover, even for so-called second-order transitions, where the first derivatives of the thermodynamic potentials remain continuous, the scheme is not useful in practice. Rather than observing discontinuities in the second derivatives of the Gibbs free energy, equal values or simultaneous divergencies from both sides of the transition are observed. In this perspective it would probably be more appropriate to use the term “continuous” transitions rather than second order [12]. For continuous transitions quite often one also uses the term “critical point,” which is only appropriate if one considers the variation of only a single thermodynamic parameter. A dominant characteristic of continuous transi-

tions is the large increase in the microscopic fluctuations in its vicinity which heralds the approaching transition.

Although the Ehrenfest equations can not be used at continuous transitions, it is still possible to obtain an expression for the slope of the transition line [13–15]. These so-called Pippard equations are

$$\frac{C_p}{T} = \left(\frac{dp}{dT}\right)_\sigma V\alpha_p + \left(\frac{\partial S}{\partial T}\right)_t, \quad (3a)$$

$$\alpha_p = \left(\frac{dp}{dT}\right)_\sigma \kappa_T + \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_t, \quad (3b)$$

where $(\partial S / \partial T)_t$ and $(1/V)(\partial V / \partial T)_t$ are quantities to be evaluated at a distance $(T - T_c)$ away from the critical temperature T_c . These quantities are slowly varying ones which can be considered as constants. From Eqs. (3a) and (3b) it should be obvious that, for finite slope $(dp/dT)_\sigma$ of the (continuous) transition line, in a power law description the singularities of C_p , α_p , and κ_T should have the same critical exponent.

B. Critical fluctuations

As already indicated, continuous transitions are characterized by large fluctuations, which for a properly defined order-parameter diverge in size to infinity, as expressed by a correlation length following a power law

$$\xi(T) = \xi_0 t^{-\nu}, \quad (4)$$

with $t = |T - T_c| / T_c$, ν a positive universal critical exponent for the relevant universality class, and ξ_0 a system-dependent nonuniversal amplitude. Although critical amplitudes (in power law expressions) for different quantities are system dependent, there exist universal relations for a given system between the amplitudes of different physical parameters, the so-called universal amplitude ratios [16]. Moreover, the amplitude for different static physical parameters can be linked to the amplitude of the correlation length ξ_0 [Eq. (4)] by the concept of two-scale factor universality [16,17]. Of particular interest is the relationship between ξ_0 and the critical amplitude A_0 of the specific heat capacity power law

$$C_p(T) = A_0 t^{-\alpha} + B, \quad (5)$$

with α a critical exponent (depending on the universality class) and B a background contribution. Two-scale factor universality results in a universal amplitude ratio R between A_0 and ξ_0 given by

$$R^\pm = \left(\frac{A_0^\pm \rho_c}{k_B}\right)^{1/3} \xi_0^\pm, \quad (6)$$

with k_B Boltzmann's constant and ρ_c the critical density. The actual value of the universal amplitude ratio depends on the universality class, and is different for $T < T_c$ (minus sign superscript) and for $T > T_c$ (plus sign superscript). From Eq. (6) it should be immediately obvious that a large value of ξ_0 (large size fluctuations, resulting in, e.g., large pretransitional effects in light scattering) will correspond with (very) small pretransitional effects in the specific heat capacity. Two-scale

factor universality is consistent with experimental results and has been tested for many systems, in particular for binary liquid mixtures near consolute points. Typical values of ξ_0 are around 0.2 nm, but a value as large as 0.44 nm has been obtained for the homogeneous phase of butoxyethanol-water (BW) [18]. On the other hand, a small value of 0.11 nm was measured for triethylamine-water (TW) [19,20]. Based on Eq. (6) the factor of 4 between the ξ_0 's of these two systems should result in a specific heat capacity anomaly which is about 60 times smaller for BW than for TW. This prediction of two-scale factor universality is consistent with high-resolution ASC results for these systems [19–21]. Thus, depending on the system and the particular physical quantity looked at, the effect of order parameter fluctuations observed might be (very) large or (very) small.

C. The isotropic-to-nematic phase transition

The thermodynamic behavior in the vicinity of the nematic-to-isotropic (NI) transition is usually described in terms of the mean-field Landau–de Gennes theory [3]. For the uniaxial nematic phase one obtains an expansion of the free energy F in terms of the modulus of an order parameter Q

$$F - F_0 = \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \frac{1}{6}DQ^6 + \dots \quad (7)$$

In the isotropic phase $Q=0$ and in the nematic phase $Q \neq 0$. In Eq. (7) one has $A=a(T-T^*)/T_{NI}$ (with $a>0$) and $B>0$ for uniaxial phases with positive anisotropy. The presence of the cubic term, which does not disappear at T_{NI} , leads to a first-order transition with a finite discontinuity in the order parameter [$Q_{NI}=2B/(3C)$]. T^* is the stability limit of the isotropic phase. For $B=0$, a normal second-order transition at $T_{NI}=T^*$ is expected. The excess specific heat capacity in the nematic phase is given by [22]

$$C_p = \frac{a^2}{CT_{NI}} \left[1 + \frac{B}{2(aC)^{1/2}} \left(\frac{T^{**} - T}{T_{NI}} \right)^{-1/2} \right], \quad (8)$$

with T^{**} the stability limit of the nematic phase. One, thus, has a singular contribution with an exponent $\alpha=1/2$ in the nematic phase, resulting in a jump in C_p at T_{NI} equal to $2a/(CT_{NI})$. In the case of a mean-field second-order ($B=0$ and $C>0$) transition, the singular contribution is absent and only a jump $\Delta C_p = a^2/(2CT_{NI})$ is present. Because of the (small) cubic term in Eq. (7) one derives for the enthalpy discontinuity (the latent heat) at T_{NI}

$$\Delta H_L = H_I - H_N = \frac{2aB^2}{9C^2}. \quad (9)$$

a and C being positive and different from zero, it follows that the latent heat is a consequence of the nonzero cubic term in Eq. (7).

III. EXPERIMENT

A. Adiabatic scanning calorimetry

In order to thermally characterize the NI transition of different compounds, and in particular to determine the latent

heat ΔH_L , we used adiabatic scanning calorimetry, a high-resolution technique, capable of measuring both specific heat capacity and enthalpy as a function of temperature. In ASC, a known power P is continuously applied to (or extracted from) a sample, and the resulting temperature change $T(t)$ as a function of time is measured. The total heat capacity C , being the sum of the sample contribution C_s and the holder contribution C_h , is then given by

$$C = C_h + C_s = \frac{P}{\dot{T}}. \quad (10)$$

$\dot{T}=dT/dt$ is calculated by numerically differentiating the $T(t)$ data. The specific heat capacity of the sample is easily obtained by subtracting the holder contribution C_h , which can be measured in a calibration experiment, and dividing by the sample mass. Contrary to other calorimetric techniques, ASC allows one to measure directly the enthalpy change of the sample $H(T)$ as a function of temperature, by inverting the $T(t)$ data to

$$H(T) - H(T_s) = P[t(T) - t(T_s)], \quad (11)$$

with T_s the starting temperature of a given run. This makes it possible to distinguish clearly between continuous phase transitions and first-order transitions and determine the latent heat ΔH_L for the latter. Moreover, it is possible to apply very slow scanning rates (typically 1 mK per minute) to ensure thermodynamic equilibrium of the sample. While measuring, the sample can be continuously stirred by tilting the calorimeter periodically, which makes a ball inside the sample cell roll from one side of the cell to the other. More information about the technique can be found in the literature [23,24].

In this paper we present recent ASC results near the NI transition of five compounds (MBBA, 5NCS, 5CN, 8CHBT, and D7AB). For the compounds 5CB and 8CB we used previously obtained ASC results [4,5,25] for the analysis.

B. Dielectric measurements

The dielectric data for 5CB, 8CB, and D7AB were taken from previous work [8,26–28]. The measurements on 5CB and 8CB have been carried out in the frequency range between 10 Hz and 100 kHz by means of General Radio 1615A and 1616A ratio transformer capacitance bridges. In the indicated frequency range, no frequency dependence was observed. The capacitors in the measuring cells were constructed as three-terminal capacitors, which allowed for accurate cancelations of the lead capacitances by the ratio transformer bridges. More details of the two types of measuring cells and the temperature controlling and measuring system can be found elsewhere [8]. D7AB has been measured using a HP4285A Precision LCR Meter, with a frequency range from 75 kHz to 30 MHz. The sample was placed in a homemade parallel plate capacitor with a thickness of about 200 μm . The alignment of the sample, to identify the phase transition, was induced by permanent magnets, delivering a field of 0.4 T to the sample. Temperature control was assured by a homemade oven. Details can be found in [28].

For MBBA we report recent data obtained by a Novocontrol Alpha High Resolution Dielectric Analyzer in the frequency range between 100 Hz and 3 MHz. The sample was contained in the Novocontrol BDS1308 Liquid Sample Cell, which is a closed parallel plate capacitor. The electrodes were coated with a polyimide, SE1211 from Nissan Chemicals, which induces homeotropic alignment in the nematic phase and as such makes the phase transition clearly visible. The temperature of the cell was controlled by the Novocontrol Quatro Cryosystem. For all measurements, temperature control was better than 0.1 K; in most cases better than 0.05 K. For the other compounds (5CN, 5NCS, and 8CHBT) we used the data from Refs. [9,10] in the analysis.

The dielectric response of a liquid crystal sample typically contains two types of contributions. At low frequencies, the signal is dominated by conduction phenomena, such as electrode polarization and Ohmic conduction, respectively attributed to charge buildup at the electrodes and the movement of ionic impurities in the samples. At higher frequencies, orientation relaxations of the liquid crystal molecules can be seen as downward steps in the value of the real part of the permittivity. In between those two regions, a plateau is present. The value of the permittivity in this plateau is considered the static value. Typically, this plateau ranges from 10 or 100 Hz to 1 MHz. Historically 1 kHz has been taken as a standard frequency to determine ϵ_{st} . Modern methods can easily provide spectra over this frequency range. So a more careful choice of frequency has become possible. This way, data for 5CB and 8CB were taken at 1 kHz, data for D7AB at 100 kHz, and data for MBBA at 34 kHz. For the data on 5CN, 5NCS, and 8CHBT, no indication was given in Ref. [10], but the lower-frequency limit of the equipment used was 50 kHz.

C. Compounds

The 5CB and 8CB compounds were obtained from BDH Chemicals Ltd. MBBA was purchased from Acros Organics. For the ASC measurements on 5CN, 5NCS, 8CHBT, and D7AB we used compounds synthesized at the laboratory of Professor Dabrowski (Military University of Technology, Poland). The samples used for the dielectric measurements of Refs. [9,10,28] were also synthesized in the same laboratory.

IV. EXPERIMENTAL RESULTS

A. Latent heats

All enthalpy data were obtained from ASC heating runs with scanning rates of approximately 1.5 mK/min in the region far away from the transition. In the two-phase region, the scanning rate was even substantially lower since the added heat is used to accomplish the phase transition and the temperature remains nearly constant. Apart from these low heating rates, thermal equilibrium inside the samples was even more increased by continuously stirring the samples during the measurements.

An overview of the enthalpy as a function of temperature for the investigated compounds is given in Fig. 1. For each curve, a (different) linear background term is subtracted, corresponding to the regular increase of the enthalpy (which is

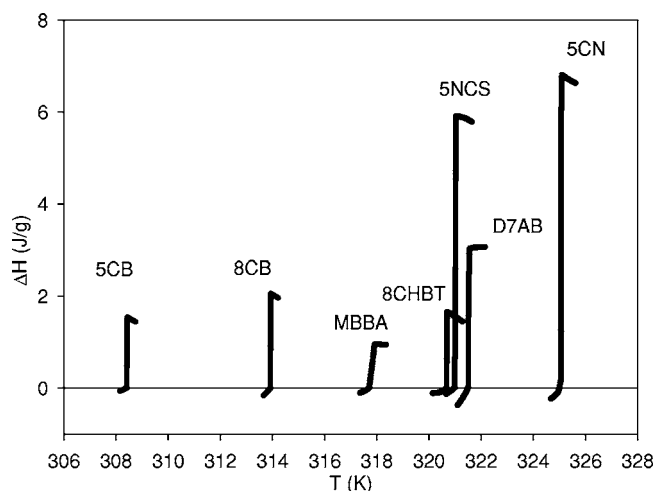


FIG. 1. Overview of the enthalpy jump at the NI transition for the investigated compounds.

the integral of the constant background specific heat capacity) away from the transition. The linear enthalpy background was shifted such that $\Delta H(T_{NI}^-) = 0$ with T_{NI}^- the lower boundary of the two-phase region. The latent heat ΔH_L can be determined from the jump in these curves by compensating for the width of the two-phase region, since part of the enthalpy change in this region is due to the temperature increase.

For MBBA the two-phase region is substantially wider (≈ 0.2 K) than for the other compounds, as can be seen in Fig. 1. This might be caused by impurities resulting from hydrolysis of MBBA molecules [29] which broaden the transition and lower its temperature [30]. The latent heat on the other hand is much less influenced by the impurities, since the only effect on this parameter is that only the intact MBBA molecules contribute to its value, while the nonmesogenic substances do not. Based on the shift of T_{NI} and the width of the two-phase region, we estimate that the effect on the value of ΔH_L is only a few percent.

Table I gives the obtained values for the latent heats for the different compounds, together with an overview of the other relevant physical parameters for our analysis.

B. Pretransitional specific heat capacity

For the seven compounds, we also analyzed the pretransitional increase in the specific heat capacity in the isotropic phase. All data for this analysis were obtained from fast (typically 30 mK/min) cooling runs to be able to cover a large temperature region above the transition. The previously measured 5CB and 8CB runs were heating runs. In all cases the samples were stirred during the measurements.

Figure 2 shows the pretransitional specific heat capacity in the isotropic phase for the investigated compounds. The data were shifted to make the higher-temperature limit of the two-phase region for each liquid crystal coincide with the origin. For clarity, the figure is split into two parts. Qualitatively, large differences in the pretransition are already visible. Since some of the curves clearly show a linear contri-

TABLE I. Overview of the measured values and literature data available for the liquid crystals used in our analysis.

Compound	T_{NI} (K)	μ (D)	ΔH_L (J g ⁻¹)	$10^3 \Delta V$ (cm ³ g ⁻¹)	$(dp/dT)_{NI}$ (bar K ⁻¹)	A_0 (J kg ⁻¹ K ⁻¹)	$T_{NI}-T^*$ (K)
MBBA	318	3	0.92 ^a	1.10 [31]	26.4 [31]	1.6	0.09
				1.05 [32]	25.6 [32]		
				1.47 [33]	28.8 [34]		
5CB	308.4	5	1.56	1.98 [35]	25.8 [36]	11	0.5
8CB	313.9	5	2.10	2.35 [6]	29 [37]	13	0.26
					27.8 [38]		
					31 [39]		
5NCS	321.1	2.5	5.90			0.5	0.23
5CN	325.1	5	6.70			1.3–4.8 ^b	
8CHBT	320.7	2.5	1.66			1.0	0.05
D7AB	321.6	0	2.98			9.0	0.40

^aValue corrected for the presence of nonmesogenic impurities.

^bValues obtained for $T_{NI}-T^*$ fixed at 0.05 and 0.5 K (see text).

tribution to the background specific heat capacity, we performed fits with a power-law-like behavior to separate this linear behavior from the real pretransitional increase, using the formula

$$C_p(T) = A_0 \left(\frac{T - T^*}{T^*} \right)^{-0.5} + B + E \left(\frac{T - T^*}{T^*} \right). \quad (12)$$

In this expression, A_0 is the amplitude of the fluctuation induced pretransitional effect, T^* is the lower limit of stability of the isotropic phase where, according to Eq. (12), the specific heat capacity would diverge, and B and E represent a constant and linear background term, respectively. All four parameters were fitted simultaneously. Fit values for A_0 and $T_{NI}-T^*$ are shown in Table I. Values of T^* for the different samples are between 0.05 and 0.5 K lower than the measured values for T_{NI} . For 5CN, the fit yielded a value which was 2 K lower. Since this looks unrealistically low, we fixed two values for T^* for this system: one 0.05 K below T_{NI} and one 0.5 K below. The large difference in the corresponding amplitudes illustrates how much the parameters in Eq. (12) are correlated and how much precaution must be taken to find correct results.

C. Dielectric pretransitional effect

According to the theory of Onsager [40], one expects that ϵ_{st} increases as the temperature decreases toward the NI transition, as $\epsilon_{st} \sim \mu^2/kT$. As can be seen in Fig. 3, this is the case for all compounds deep in the isotropic phase, far away from the transition. On approaching the transition, three types of behavior are observed: (i) a decrease in ϵ_{st} , (ii) a curvature, without decrease, and (iii) a straight line behavior. This difference is caused by the dipole moments of the molecules.

According to Bradshaw and Raynes [7] the decrease in ϵ_{st} is caused by a decrease of the effective dipole moment $g\mu^2$ because of an increase of the antiparallel correlation between the molecules: the molecules lie with their dipoles next to each other but in opposite direction, forming dynamically dimers with reduced effective dipole moment. The Kirkwood correlation factor g quantifies this behavior, g being <1 for antiparallel correlation, $=1$ for no correlation and >1 for parallel correlation [40]. Depending on the magnitude of the

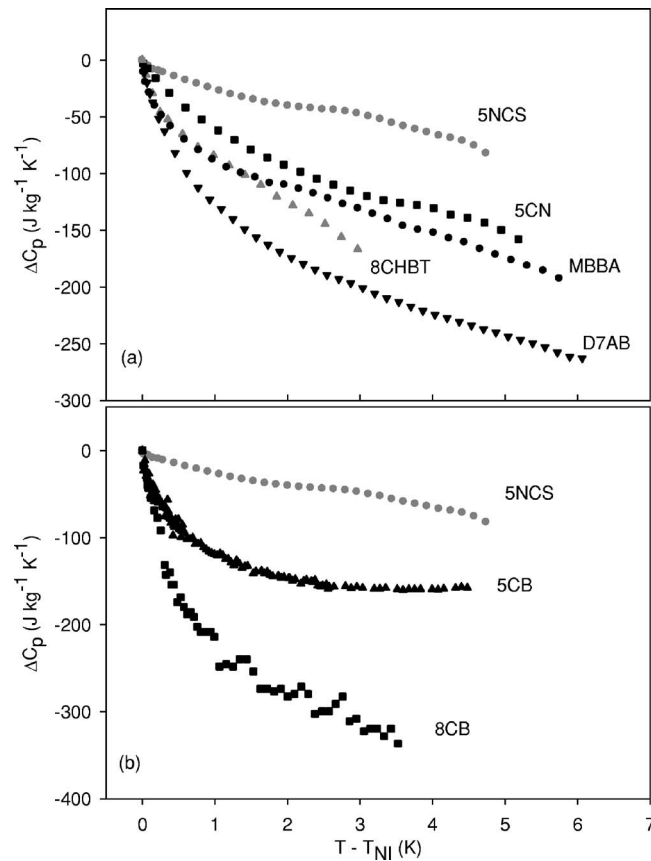


FIG. 2. Pretransitional specific heat capacity of the investigated compounds.

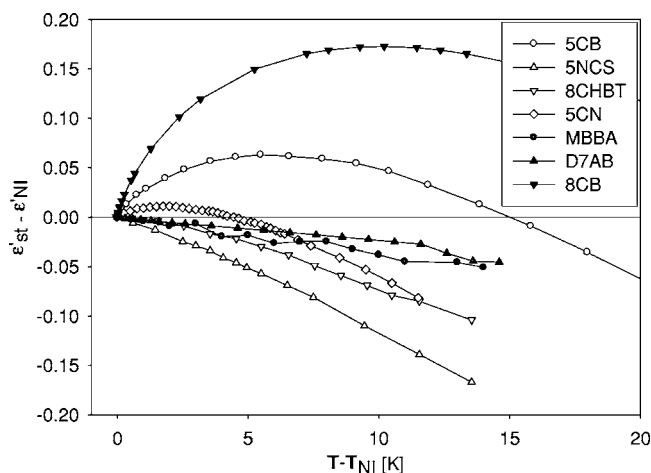


FIG. 3. Pretransition in the static dielectric constant in the isotropic phase.

dipoles, ϵ_{st} will decrease or only show a small curvature.

Although the existence of dimers has been shown for the entire isotropic phase (see, e.g., [27]), the occurrence of dimers is limited by the isotropic character of the fluid. However, on approaching the NI transition, nematic fluctuations occur [29,41], resulting in local orientational ordering, thus making it more easy to form dimers and to decrease the static dielectric permittivity.

For compounds without permanent dipole moment no pretransitional effect is expected. Even for compounds with a rather large central μ , it can be absent if dimerization is geometrically not very likely.

V. DISCUSSION

For three of the investigated compounds (MBBA, 5CB, and 8CB), experimental data are available from literature and from our measurements to test consistency with the Clapeyron equation (1). Using the values of Table I, we can calculate the value $\Delta H/(T\Delta V)$ and compare this with the measured value of $(dp/dT)_{NI}$. This yields for MBBA calculated values of 26.3, 27.6, and 19.8 bar/K (using the different literature values of ΔV). The first two values agree well with the measured ones (25.6–28.8 bar/K); the last is lower due to the rather high value of ΔV . The same calculation for 5CB gives 25.5 bar/K (25.8 bar/K experimentally) and for 8CB 28.5 bar/K (29, 27.8, and 31 bar/K experimentally). It thus can be said that these data are fairly well consistent with the Clapeyron equation.

Three of the investigated liquid crystals in our analysis show a large pretransitional effect in the dielectric constant on approaching the NI transition in the isotropic phase: 5CB, 8CB, and 5CN. Each of them has a dipole moment μ of approximately 5 D (see Table I). There is, however, a clear difference in the size of this effect despite the comparable dipole moment. Even for 5CB and 8CB, two compounds from the same homologue series, there is a large difference in pretransitional effect. This is probably caused by fluctuation effects from the nearby smectic-A phase in 8CB and the increased antiparallel coupling of the molecules. For the

compounds with $\mu < 5$ D, the pretransitional effect is much smaller: while there is still a small bending for 5NCS and 8CHBT (both with $\mu \approx 2.5$ D), the curves for MBBA ($\mu = 3$ D) and D7AB ($\mu = 0$ D) are straight lines within the experimental accuracy. For MBBA, with its nonzero dipole moment, this is due to the fact that the central dipole moment is at an angle close to 55° with the long molecular axis, which makes antiparallel coupling geometrically difficult.

To check whether a strong dielectric pretransition in the isotropic phase really corresponds to a “close to second-order” transition (and thus a very small value for the latent heat), and vice versa, we can compare the dielectric data with our ASC results on the enthalpy at the NI transition. Two of the investigated compounds have a substantially larger latent heat than the others and can therefore be regarded as the strongest first-order: 5CN ($\Delta H_L = 6.70$ J/g) and 5NCS ($\Delta H_L = 5.90$ J/g). Their dielectric behavior is, however, quite different with a clear pretransitional effect for 5CN and only a small deviation from linear behavior for 5NCS. Consequently, in this case the dielectric data do not yield a reliable criterion for determining the strength of the transition. For 5CB and 8CB the pretransitional effect is the most pronounced, suggesting large fluctuations, while they still have moderate latent heats compared to the other liquid crystals used in our comparison and thus cannot be considered as the closest to second-order. D7AB, with absolutely no fluctuation effect in the dielectric constant, has a latent heat of 2.98 J/g which is only moderately high. The smallest latent heat is found for MBBA, and therefore this compound can be regarded as the closest to second order of all the liquid crystals in our analysis. Still, its dielectric constant shows a purely linear behavior.

From the above comparison, it is clear that there is no direct connection between the value of the latent heat and the size of the pretransitional effect observed in the dielectric constant in the isotropic phase at the NI transition. Therefore, the assumption of Jadzyn *et al.* [9,10] that the dielectric pretransition can be used to distinguish between a close to first-order and a close to second-order transition becomes questionable, since it is the presence or absence of latent heat which makes the difference between a first-order and a second-order transition.

We can also compare the latent heat with the size of pretransitional effect in the specific heat capacity in the isotropic phase (via the amplitude A_0) to check if there is a connection between these two thermal properties. This is, however, not the case. The liquid crystals with high latent heat (5CN and 5NCS) have a rather small pretransitional increase in specific heat capacity, suggesting small fluctuations and thus a system farther from second order, but a comparable A_0 value is found for the compound with the smallest latent heat, MBBA. For 5CB and 8CB, high values for A_0 are found, suggesting large fluctuation effects, while their latent heats are comparable to ΔH_L of 8CHBT with a ten times smaller amplitude for the pretransition. It thus appears that the interplay between the latent heat (i.e., how close a weakly first-order transition is to second-order) and the size of the thermal fluctuation effects is far more complicated and a straightforward classification purely on the basis of pretransitional effects is impossible.

The fitting of Eq. (12) to our data provides, next to A_0 , a second parameter which might contain information on how far a weakly first-order transition is from second order: T^* , the lower stability temperature of the isotropic phase. Indeed, at a second-order phase transition one expects a power-law-like divergence at the critical temperature T_c , so if the NI transition was nearly second order, we would expect $T^* \approx T_{NI}$. Once again, however, the connection between this parameter and the latent heat is not clear as can be seen from Table I. If we compare the difference $T_{NI} - T^*$ between the measured transition temperature and the fitted value for T^* with the latent heat, we see, e.g., similar $T_{NI} - T^*$ values for 5NCS and 8CB, despite the difference of a factor of 3 in latent heat.

VI. CONCLUSION

We investigated the nematic-to-isotropic phase transitions in seven liquid crystal compounds: MBBA, 5CB, 8CB,

5NCS, 5CN, 8CHBT, and D7AB. This transition is known to be very weakly first order, and our goal was to clarify the issue whether it is possible to determine how strong this first-order character is on the basis of pretransitional fluctuation effects in the isotropic phase as was stated in the literature [9,10]. Therefore, we measured the latent heat of the NI transition using adiabatic scanning calorimetry and compared this with the pretransitional anomalies (in the isotropic phase) of the static dielectric permittivity and the specific heat capacity.

Our measurements show that it is not possible to decide, purely on the basis of the observed pretransitional effects, whether a weakly first-order transition is very close to second order or more strongly first-order since the size of the pretransitional effects cannot be correlated to the latent heat at the transition. Therefore, we conclude that fluctuation effects are not a reliable tool for determining the strength of a weakly first-order transition.

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