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## Liquid Crystals

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I. Chirtoc<sup>ab</sup>; M. Chirtoc<sup>ab</sup>; C. Glorieux Corresponding author<sup>a</sup>; J. Thoen<sup>a</sup>

<sup>a</sup> Katholieke Universiteit Leuven, Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, B-3001 Leuven, Belgium <sup>b</sup> National R&D Institute for Isotopic and Molecular Technology, 3400 Cluj-Napoca 5, Romania

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# Determination of the order parameter and its critical exponent for $n$ CB ( $n=5-8$ ) liquid crystals from refractive index data

I. CHIRTOC†‡, M. CHIRTOC†‡, C. GLORIEUX†\* and J. THOEN†

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

‡National R&D Institute for Isotopic and Molecular Technology, POB 700, 3400 Cluj-Napoca 5, Romania

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We describe the order parameter  $S(T)$  of liquid crystals in the nematic state by a four-parameter expression which is consistent with mean-field theory. A two-step fitting method is applied to high resolution refractive index data for the  $n$ CB ( $n=5-8$ ) liquid crystals, processed according to Vuks and Neugebauer models. We find quasi-universal parameter values. The average critical exponent is  $\beta=0.241\pm 0.012$ , in agreement with the mean-field prediction for a tricritical point. Thus the temperature dependence of the nematic order parameter is quasi-tricritical in all cases. The order parameter at the effective transition point  $T^{**}$  is  $S^{**}=0.143\pm 0.05$  and the relative polarizability anisotropy  $\Delta\alpha/\langle\alpha\rangle=0.69\pm 0.03$ . We show that earlier results using the Haller approximation were too low ( $\beta=0.16-0.19$ ) because of the assumption  $S^{**}=0$  and  $T^{**}=T_{\text{NI}}$ . The chosen fitting function provides the best description of  $S(T)$  both close and far from  $T^{**}$ . For all parameters, the alternating odd-even effect with the number of C atoms in the alkyl chain is about  $\pm 5\%$  except for  $S^{**}$  for which it is  $\pm 30\%$ . 6CB is singled out by a somewhat different set of fitting parameters. 8CB shows a pretransitional smectic behaviour starting from 4K above the smectic-nematic transition point.

## 1. Introduction

There is a wide spread of data in the literature concerning the temperature dependence of the order parameter  $S(T)$  of uniaxial liquid crystals (LCs). It has been pointed out that this is because the results are dependent on the physical quantity whose anisotropy is being measured and on the type of experiment [1]. Nevertheless, for some of the results presented in [1] the scaling condition  $S(T=0)=1$  has not been used.

The motivation for this work was to find out whether the temperature dependence of  $S(T)$  in the nematic (N) phase of a homologous LC series has a universal behaviour. In particular, it was expected that its critical exponent  $\beta$  should indicate membership of one of the possible universality classes of LC critical behaviour [2]. In the expression for  $S(T)$ ,  $\beta$  values of 1/2 or 1/4 are consistent with mean-field results for a critical point [3] or tricritical point [4, 5], respectively, while  $\beta=0.325$  corresponds to an Ising system with short range interactions. Limiting values are incompatible with

existing theoretical insight, although intermediate effective critical exponent values might be obtained at finite distances from the transition in cross-over ranges.

Previous experiments (assuming a simple relationship between a microscopic and macroscopic order parameter [3]) seem to confirm  $\beta=0.25$  for anisotropic quantities such as the dielectric constant [6], the thermal conductivity [7] and the magnetic susceptibility [8]. It is surprising that, while in the field of calorimetric investigations of phase transition it has been common practice to fit the specific heat capacity  $C_p$  to expressions with an appropriate set of adjustable parameters, the analysis of the order parameter  $S(T)$  from refractive index data is still nowadays performed using the Haller approximation [9], which is incompatible with the weakly first order nature of this transition [10]. The critical exponents  $\beta$  obtained in this way have values ranging between 0.16 and 0.19 that do not match any of the predicted theoretical values.

In this work we present a series of new experimental data on the temperature dependence of the refractive index of 5–8CB liquid crystals and we revisit the methodology for the systematic determination of  $S(T)$

\*Author for correspondence;  
e-mail: christ.glorieux@fys.kuleuven.ac.be

in the N phase based on a four-parameter analytical expression. A new combination of two fitting procedures yields not only the optimum values of the parameters, but also allows an overview of the  $\chi_r^2$  hypersurface around the minimum. A strong degeneracy between some parameters is found. For the analysis we needed accurate experimental data, preferably from a homologous series of well known materials. The compounds investigated in this study are members of the 4-*n*-alkyl-4'-cyanobiphenyl homologous series (*n*CB with *n*=5 to 8). These materials with uniaxial molecular symmetry exhibit N phases near room temperature, have high positive optical anisotropy and good (photo)chemical stability. Therefore they have served in the past to test the validity of theoretical models attempting to describe the macroscopic properties of LCs. Numerous reports on refractive index measurements of the *n*CB series are known. However, few of them contain experimental data in tabular form [11–14]. On the other hand, in most cases the accuracy and resolution of refractive index and temperature, especially in the region close to the nematic–isotropic transition temperature  $T_{NI}$ , were unsatisfactory for an approach based on four-parameter fits, as we use here.

## 2. Theoretical background

The *n*CB compounds in the N phase are good candidates for testing molecular theories because these molecules can be considered as rigid rods having cylindrical symmetry about the axis of maximum polarizability. According to Maier and Saupe theory [15], the extent to which they are aligned is described by a (microscopic) order parameter  $S=(1/2)\langle 3\cos^2\theta-1\rangle$ , depending on an average over all molecules (the angled brackets). The orientation of individual molecules is accounted for by the angle  $\theta$  between the molecular axis and the optical axis and it depends strongly on temperature  $T$ .

In the case of optical measurements, the square of the refractive index is equivalent to the high frequency permittivity. A crucial role in modelling optical and electrical properties of a LC is played by the correct estimation of the local field  $E_i$  surrounding the molecule. Two models have been extensively applied to uniaxial materials. The first one of Vuks–Chandrasekhar–Madhusudana (VCM) [16, 17] assumes that  $E_i$  is isotropic even in the anisotropic N phase, and it leads to the result:

$$v = \frac{\Delta n^2}{\langle n^2 \rangle - 1} = \frac{\Delta\alpha}{\langle \alpha \rangle} S(T) \quad (1)$$

where,  $\Delta n^2 = n_e^2 - n_o^2$  is the anisotropy of the square of the refractive index, and the tensorial average  $\langle n^2 \rangle$  is

given by:

$$\langle n^2 \rangle = (1/3)(n_e^2 + 2n_o^2). \quad (2)$$

Here  $n_o$  and  $n_e$  are the ordinary and extraordinary refractive indices, respectively. The polarizability anisotropy is denoted by  $\Delta\alpha = \alpha_l - \alpha_t$ . The mean polarizability is defined similarly to equation (2),  $\langle \alpha \rangle = (\alpha_l + 2\alpha_t)/3$ , with  $\alpha_l$  and  $\alpha_t$  the longitudinal and transverse polarizabilities relative to the molecular axis, respectively.

The second model proposed by Neugebauer–Maier–Saupe (NMS) [18–20] allows for an anisotropic distribution of neighbours around each molecule, giving:

$$K_N = \frac{9}{4B} \left[ \left( B^2 - \frac{10}{3}B + 1 \right)^{1/2} + \frac{B}{3} - 1 \right] = \frac{\Delta\alpha}{\langle \alpha \rangle} S(T) \quad (3)$$

where  $B$  is given by:

$$B = \frac{\langle n^2 \rangle - 1}{\langle n^2 \rangle + 2} \left( \frac{n_e^2 + 2}{n_e^2 - 1} + 2 \frac{n_o^2 + 2}{n_o^2 - 1} \right). \quad (4)$$

Later this model was improved by replacing the representation of the molecule as a point polarizability by an anisotropic polarizable spheroid [21].

The polarizability being a molecular property, it is temperature-independent. The temperature dependence of the order parameter in the nematic phase can be approximated by the following four-parameter expression that is consistent with mean field theory for a critical as well as a tricritical point for a weakly first order transition (non-zero cubic invariant) [2, 10, 22, 23]:

$$S(T) = S^{**} + A\tau^\beta \quad (5)$$

with  $\beta$  the critical exponent and  $\tau = 1 - T/T^{**}$  the reduced temperature.  $T^{**}$  is the effective second order (quasi-critical or quasi-tricritical) phase transition point seen from below  $T_{NI}$  and is slightly higher than the observed transition temperature  $T_{NI}$ . At  $T = T^{**}$ ,  $S(T^{**}) = S^{**}$ , which is a positive quantity. A reasonable scaling condition for the order parameter is  $S(0) = 1$  at  $T = 0$ , which implies  $S^{**} + A = 1$ . We used for the fits the following expression derived from equations (1), (3) and (5):

$$K_{V,N} = (\Delta\alpha/\langle \alpha \rangle) \left[ S^{**} + (1 - S^{**})(1 - T/T^{**})^\beta \right]. \quad (6)$$

Equation (6) contains four parameters:  $\Delta\alpha/\langle \alpha \rangle$ ,  $S^{**}$ ,  $T^{**}$  and  $\beta$ . The temperatures are expressed in K.

Suppose the scaling condition is not fulfilled by a sample having the order parameter  $S'(T)$ . Then  $S'(0)$  can be written as  $S'(0) = cS(0) \neq 1$ . The constant  $c$  would appear in equation (6) as a factor multiplying the first parameter,  $c(\Delta\alpha/\langle \alpha \rangle)$ , and therefore it cannot be determined independently from the latter. This means that in the absence of additional information on

polarizabilities, the validity of the scaling condition ( $c=1$ ) cannot be derived from the fit.

Previous attempts to determine the temperature dependence of the order parameter assumed a smaller number of unknown parameters. Haller's approximation [9] consists of determining  $\Delta\alpha/\langle\alpha\rangle$  and  $\beta$  from an expression similar to equation (5) in which  $S^{**}=0$  and  $T^{**}=T_{\text{NI}}$ . Only points situated far from  $T_{\text{NI}}$  were considered in the fit. As will be shown later, this procedure leads to systematically lower values for the critical exponent,  $\beta < 0.20$ .

Despite its rather simple assumptions, the Maier–Saupe theory [15] yields good results for many LCs. It can be approximated analytically to within 1% by the following expression [24]:

$$S(T) = [1 - 0.98 TV^2 / (T_{\text{NI}} V_{\text{NI}}^2)]^{0.22} \quad (7)$$

where  $V$  is the molar volume. Starting from the Maier–Saupe theory, Picken improved equation (7) mainly by adding a term of 0.1. The semi-empirical equation (8) was found to describe  $S(T)$  well for several classes of LC [25]:

$$S(T) = 0.1 + 0.9[1 - 0.99(T/T_{\text{NI}})^\varepsilon]^{0.25}. \quad (8)$$

For the  $n\text{CB}$  series,  $\varepsilon$  is close to 1.

In other reports  $S(T)$  was taken as a mean-field function of temperature and was fitted to birefringence data [26]. Higher order parameters have also been determined [27].

### 3. Experimental

We measured the refractive indices of 5–8CB LC with two refractometers based on the same principle: determination of the critical angle by back reflection (the light beam does not have to pass through the sample). The prisms of the instruments were treated in order to induce the orientation of LC in the N phase. The deposition on one of the prisms of a film of polyvinylalcohol, that was subsequently rubbed with velvet tissue, induced the planar orientation (yielding  $n_o$ ). For homeotropic orientation (yielding  $n_e$ ) the other prism was treated with cetyl-trimethylammonium bromide. The sample layer between the main prism and the secondary prism was 0.2 mm thick. The cell was loaded with LC sample at  $T > T_{\text{NI}}$  to avoid flow orientation. Subsequently, measurements were performed whilst decreasing the temperature.

The ordinary refractive index  $n_o$  was measured on an Atago–Abbe type 1130 refractometer, calibrated for the D-line ( $\lambda = 589.3$  nm) of Na lamp emission. The distance between two divisions marked on the instrument's scale are equal to  $\Delta n = 2 \times 10^{-4}$ . By visual interpolation of the position of the boundary line between the dark and light fields, one may reach an

ultimate resolution of  $5 \times 10^{-5}$ . An automatic instrument model GPR 11–37 manufactured by 'Index Instruments' was used to measure the extraordinary refractive index  $n_e$  with a resolution of  $10^{-4}$ . The light source was a Na lamp emitting at  $\lambda = 589.3$  nm.

The temperature of the two instruments was controlled by the same thermostat, assuring a temperature stability of 0.04 K. The instruments were connected in series by silicon rubber tubes insulated by larger rubber foam tubes. This allowed for simultaneous measurements of  $n_o$  and  $n_e$  in one run, and for samples from the same batch (obtained from Merck). Measurements were carried out between 20 and 50°C in steps of 0.1 K. A quartz crystal thermometer (based on temperature–frequency conversion) with a resolution of 0.01 K was positioned in the circulating water close to the prism of the Atago instrument. The absolute temperature of  $n_e$  measured by the GPR instrument was shifted when necessary such as to bring into coincidence the N–I transition on both  $n_o$  and  $n_e$  branches. We considered the transition temperature  $T_{\text{NI}}$  to be the lowest temperature of a measured point in the I phase. The observed  $T_{\text{NI}}$  temperatures ( $\pm 0.03$  K) are: 308.47 K, 301.27 K, 315.50 K and 313.64 K for 5–8CB, respectively.

Because of high  $n_e$  values of the LC (comparable to that of the glass prism,  $n_p = 1.73976$ ), the accessible temperature interval in the N state was smaller than 9 K ( $< 4$  K for 5CB). This problem can be circumvented by deriving  $n_e$  from  $n_o$  and  $\Delta n$  determined by the wedge method [11, 24], but then the attainable resolution is only 1–2%. Absolute  $n$  values found in the literature [11–14] are spread in an interval of  $\pm 0.003$  about our results.

### 4. Results and discussion

The experimental values of  $n_o(T)$  and  $n_e(T)$  in the N phase and of  $n(T)$  in the I phase, are listed in tables 1 and 2. In the N state the refractive index values were averaged over results obtained in three runs. To allow averaging, measured data were interpolated at the same temperature intervals. Data for 8CB below the smectic–nematic transition at 33.6°C ( $T - T_{\text{NI}} = -6.9$  K) are not shown here, and will be discussed elsewhere.

The refractive indices as a function of the shifted temperature  $T - T_{\text{NI}}$  are shown in figure 1. The figure contains only the data of tables 1 and 2 that are situated in the interval  $-10 \text{ K} < T - T_{\text{NI}} < 2 \text{ K}$ . In the N phase, typical noise levels per point (as a function of temperature) are  $\sigma = 0.16 \times 10^{-4}$  and  $0.48 \times 10^{-4}$  for  $n_o$  and  $n_e$ , respectively, leading to  $\sigma = 1.3 \times 10^{-4}$  of  $K_V$  function. For comparison, the corresponding noise levels of data available in the literature [11, 12] are  $\sigma = 0.4 \times 10^{-4}$ ,  $1.0 \times 10^{-4}$  and  $3.5 \times 10^{-4}$ . Our gain of a

Table 1. Refractive indices  $n_o$  and  $n_e$  for 5–8CB in the nematic phase as a function of temperature. The values represent averages over three runs.

| 5CB                |         |         | 6CB                |         |         |
|--------------------|---------|---------|--------------------|---------|---------|
| $T/^\circ\text{C}$ | $n_o$   | $n_e$   | $T/^\circ\text{C}$ | $n_o$   | $n_e$   |
| 35.198             | 1.55205 | 1.66160 | 27.934             | 1.55370 | 1.64525 |
| 35.101             | 1.55112 | 1.66370 | 27.849             | 1.55277 | 1.64737 |
| 35.063             | 1.55081 | 1.66440 | 27.733             | 1.55170 | 1.64980 |
| 34.967             | 1.55003 | 1.66610 | 27.723             | 1.55160 | 1.65000 |
| 34.880             | 1.54940 | 1.66760 | 27.646             | 1.55095 | 1.65140 |
| 34.812             | 1.54899 | 1.66860 | 27.598             | 1.55059 | 1.65230 |
| 34.678             | 1.54820 | 1.67045 | 27.540             | 1.55018 | 1.65320 |
| 34.601             | 1.54780 | 1.67140 | 27.477             | 1.54979 | 1.65410 |
| 34.523             | 1.54744 | 1.67230 | 27.385             | 1.54927 | 1.65530 |
| 34.408             | 1.54692 | 1.67352 | 27.346             | 1.54904 | 1.65580 |
| 34.321             | 1.54654 | 1.67442 | 27.279             | 1.54870 | 1.65660 |
| 34.235             | 1.54620 | 1.67526 | 27.211             | 1.54837 | 1.65750 |
| 34.061             | 1.54552 | 1.67699 | 27.129             | 1.54799 | 1.65835 |
| 33.930             | 1.54505 | 1.67817 | 27.091             | 1.54784 | 1.65875 |
| 33.843             | 1.54478 | 1.67898 | 26.989             | 1.54742 | 1.65980 |
| 33.757             | 1.54449 | 1.67968 | 26.960             | 1.54728 | 1.66010 |
| 33.660             | 1.54422 | 1.68049 | 26.902             | 1.54706 | 1.66070 |
| 33.564             | 1.54393 | 1.68122 | 26.787             | 1.54661 | 1.66180 |
| 33.487             | 1.54372 | 1.68177 | 26.709             | 1.54636 | 1.66250 |
| 33.362             | 1.54341 | 1.68261 | 26.584             | 1.54594 | 1.66360 |
| 33.275             | 1.54321 | 1.68321 | 26.536             | 1.54577 | 1.66400 |
| 33.179             | 1.54298 | 1.68385 | 26.410             | 1.54539 | 1.66500 |
| 33.082             | 1.54276 | 1.68445 | 26.304             | 1.54505 | 1.66580 |
| 32.996             | 1.54259 | 1.68500 | 26.246             | 1.54488 | 1.66630 |
| 32.890             | 1.54236 | 1.68566 | 26.033             | 1.54429 | 1.66785 |
| 32.784             | 1.54214 | 1.68631 | 25.860             | 1.54388 | 1.66905 |
| 32.668             | 1.54193 | 1.68699 | 25.589             | 1.54327 | 1.67077 |
| 32.591             | 1.54178 | 1.68743 | 25.425             | 1.54294 | 1.67173 |
| 32.485             | 1.54159 | 1.68800 | 25.300             | 1.54269 | 1.67245 |
| 32.408             | 1.54146 | 1.68844 | 24.759             | 1.54172 | 1.67535 |
| 32.302             | 1.54125 | 1.68904 | 24.315             | 1.54093 | 1.67755 |
| 32.196             | 1.54107 | 1.68959 | 23.784             | 1.54021 | 1.67990 |
| 32.119             | 1.54092 | 1.69000 | 23.301             | 1.53961 | 1.68190 |
| 32.013             | 1.54071 | 1.69057 | 22.867             | 1.53912 | 1.68360 |
| 31.936             | 1.54058 | 1.69096 | 22.413             | 1.53866 | 1.68530 |
| 31.820             | 1.54041 | 1.69153 | 21.950             | 1.53821 | 1.68690 |
| 31.733             | 1.54024 | 1.69198 | 21.409             | 1.53772 | 1.68870 |
| 31.647             | 1.54010 | 1.69241 | 20.926             | 1.53733 | 1.69027 |
|                    |         |         | 20.434             | 1.53699 | 1.69180 |
| 7CB                |         |         | 8CB                |         |         |
| $T/^\circ\text{C}$ | $n_o$   | $n_e$   | $T/^\circ\text{C}$ | $n_o$   | $n_e$   |
| 42.262             | 1.53760 | 1.63970 | 40.371             | 1.53420 | 1.62980 |
| 42.125             | 1.53661 | 1.64250 | 40.314             | 1.53359 | 1.63120 |
| 42.039             | 1.53601 | 1.64410 | 40.208             | 1.53267 | 1.63340 |
| 41.913             | 1.53520 | 1.64610 | 40.102             | 1.53180 | 1.63530 |
| 41.846             | 1.53478 | 1.64710 | 40.025             | 1.53126 | 1.63660 |
| 41.750             | 1.53425 | 1.64850 | 39.919             | 1.53063 | 1.63820 |
| 41.673             | 1.53386 | 1.64950 | 39.822             | 1.53008 | 1.63950 |
| 41.557             | 1.53332 | 1.65080 | 39.726             | 1.52960 | 1.64060 |
| 41.461             | 1.53290 | 1.65190 | 39.626             | 1.52910 | 1.64180 |
| 41.355             | 1.53247 | 1.65300 | 39.539             | 1.52875 | 1.64270 |
| 41.249             | 1.53206 | 1.65400 | 39.500             | 1.52859 | 1.64320 |
| 41.153             | 1.53169 | 1.65490 | 39.443             | 1.52838 | 1.64375 |
| 41.066             | 1.53137 | 1.65580 | 39.375             | 1.52810 | 1.64450 |

Table 1. (Cont.)

|        |         |         |        |         |         |
|--------|---------|---------|--------|---------|---------|
| 40.960 | 1.53101 | 1.65670 | 39.269 | 1.52774 | 1.64540 |
| 40.864 | 1.53071 | 1.65755 | 39.163 | 1.52743 | 1.64630 |
| 40.748 | 1.53038 | 1.65840 | 39.086 | 1.52717 | 1.64690 |
| 40.690 | 1.53023 | 1.65880 | 38.961 | 1.52683 | 1.64790 |
| 40.584 | 1.52997 | 1.65960 | 38.874 | 1.52657 | 1.64860 |
| 40.478 | 1.52972 | 1.66030 | 38.749 | 1.52623 | 1.64950 |
| 40.401 | 1.52954 | 1.66080 | 38.696 | 1.52614 | 1.64990 |
| 40.315 | 1.52935 | 1.66140 | 38.580 | 1.52587 | 1.65060 |
| 40.209 | 1.52914 | 1.66210 | 38.484 | 1.52563 | 1.65125 |
| 40.112 | 1.52897 | 1.66270 | 38.388 | 1.52544 | 1.65190 |
| 40.035 | 1.52881 | 1.66310 | 38.311 | 1.52527 | 1.65240 |
| 39.929 | 1.52860 | 1.66380 | 38.195 | 1.52504 | 1.65315 |
| 39.843 | 1.52845 | 1.66420 | 38.099 | 1.52486 | 1.65365 |
| 39.746 | 1.52828 | 1.66470 | 38.022 | 1.52469 | 1.65410 |
| 39.650 | 1.52810 | 1.66510 | 37.925 | 1.52450 | 1.65460 |
| 39.573 | 1.52798 | 1.66550 | 37.800 | 1.52428 | 1.65530 |
| 39.467 | 1.52782 | 1.66610 | 37.714 | 1.52413 | 1.65575 |
| 39.371 | 1.52769 | 1.66660 | 37.608 | 1.52397 | 1.65630 |
| 39.265 | 1.52753 | 1.66720 | 37.531 | 1.52385 | 1.65680 |
| 39.159 | 1.52738 | 1.66770 | 37.434 | 1.52371 | 1.65720 |
| 39.072 | 1.52727 | 1.66810 | 37.338 | 1.52355 | 1.65780 |
| 38.966 | 1.52712 | 1.66860 | 37.242 | 1.52342 | 1.65820 |
| 38.889 | 1.52702 | 1.66900 | 37.145 | 1.52329 | 1.65870 |
| 38.783 | 1.52685 | 1.66950 | 37.068 | 1.52317 | 1.65910 |
| 38.687 | 1.52676 | 1.67000 | 36.953 | 1.52300 | 1.65960 |
| 38.590 | 1.52660 | 1.67040 | 36.876 | 1.52289 | 1.66000 |
| 38.494 | 1.52649 | 1.67085 | 36.798 | 1.52278 | 1.66040 |
| 38.398 | 1.52639 | 1.67120 | 36.683 | 1.52262 | 1.66090 |
| 38.311 | 1.52628 | 1.67160 | 36.596 | 1.52251 | 1.66125 |
| 38.205 | 1.52615 | 1.67210 | 36.500 | 1.52238 | 1.66175 |
| 38.109 | 1.52601 | 1.67260 | 36.394 | 1.52224 | 1.66225 |
| 38.022 | 1.52589 | 1.67300 | 36.288 | 1.52207 | 1.66275 |
| 37.916 | 1.52577 | 1.67340 | 36.182 | 1.52192 | 1.66315 |
| 37.839 | 1.52570 | 1.67360 | 36.081 | 1.52178 | 1.66360 |
| 37.724 | 1.52559 | 1.67410 | 35.975 | 1.52164 | 1.66405 |
| 37.646 | 1.52550 | 1.67450 | 35.869 | 1.52151 | 1.66455 |
| 37.541 | 1.52539 | 1.67480 | 35.811 | 1.52144 | 1.66480 |
| 37.425 | 1.52527 | 1.67525 | 35.715 | 1.52130 | 1.66520 |
| 37.309 | 1.52514 | 1.67565 | 35.609 | 1.52115 | 1.66570 |
| 37.252 | 1.52508 | 1.67585 | 35.512 | 1.52100 | 1.66610 |
| 37.155 | 1.52499 | 1.67620 | 35.406 | 1.52087 | 1.66650 |
| 37.069 | 1.52491 | 1.67655 | 35.329 | 1.52078 | 1.66690 |
| 36.953 | 1.52480 | 1.67700 | 35.223 | 1.52061 | 1.66730 |
| 36.866 | 1.52473 | 1.67730 | 35.127 | 1.52048 | 1.66760 |
| 36.770 | 1.52464 | 1.67765 | 35.026 | 1.52037 | 1.66810 |
| 36.674 | 1.52457 | 1.67800 | 34.920 | 1.52019 | 1.66850 |
| 36.577 | 1.52450 | 1.67830 | 34.824 | 1.52006 | 1.66900 |
| 36.491 | 1.52440 | 1.67860 | 34.756 | 1.51998 | 1.66930 |
| 36.385 | 1.52431 | 1.67900 | 34.669 | 1.51987 | 1.66950 |
| 36.279 | 1.52421 | 1.67930 | 34.554 | 1.51971 | 1.66990 |
| 36.192 | 1.52415 | 1.67960 | 34.448 | 1.51957 | 1.67020 |
| 36.086 | 1.52408 | 1.67990 | 34.352 | 1.51945 | 1.67050 |
| 35.903 | 1.52395 | 1.68050 | 34.275 | 1.51935 | 1.67080 |
| 35.710 | 1.52381 | 1.68120 | 34.178 | 1.51923 | 1.67120 |
| 35.537 | 1.52370 | 1.68170 |        |         |         |
| 35.335 | 1.52358 | 1.68230 |        |         |         |
| 34.872 | 1.52329 | 1.68360 |        |         |         |
| 34.391 | 1.52302 | 1.68486 |        |         |         |
| 33.928 | 1.52278 | 1.68616 |        |         |         |
| 32.936 | 1.52230 | 1.68880 |        |         |         |
| 31.992 | 1.52188 | 1.69111 |        |         |         |

Table 2. Refractive index  $n$  for 5–8CB in the isotropic phase as a function of temperature.

| 5CB                |         | 6CB                |         | 7CB                |         | 8CB                |         |
|--------------------|---------|--------------------|---------|--------------------|---------|--------------------|---------|
| $T/^\circ\text{C}$ | $n$     | $T/^\circ\text{C}$ | $n$     | $T/^\circ\text{C}$ | $n$     | $T/^\circ\text{C}$ | $n$     |
| 49.806             | 1.5809  | 28.763             | 1.58325 | 54.294             | 1.5656  | 54.350             | 1.5596  |
| 48.469             | 1.5814  | 28.688             | 1.58315 | 52.381             | 1.5664  | 52.315             | 1.56025 |
| 47.046             | 1.5820  | 28.603             | 1.5832  | 51.373             | 1.5668  | 50.507             | 1.56105 |
| 45.736             | 1.5826  | 28.603             | 1.58325 | 50.516             | 1.5672  | 48.594             | 1.56185 |
| 44.389             | 1.5832  | 28.509             | 1.58315 | 49.442             | 1.5676  | 48.142             | 1.56205 |
| 42.882             | 1.5839  | 28.405             | 1.5832  | 48.952             | 1.5678  | 47.737             | 1.5623  |
| 41.977             | 1.5843  | 28.339             | 1.5833  | 48.490             | 1.5680  | 47.530             | 1.5624  |
| 41.045             | 1.5847  | 28.198             | 1.58335 | 48.283             | 1.5681  | 47.332             | 1.56245 |
| 40.574             | 1.5850  | 28.113             | 1.5835  | 48.142             | 1.5682  | 47.124             | 1.5625  |
| 40.074             | 1.5852  |                    |         | 47.972             | 1.5683  | 46.992             | 1.5626  |
| 39.914             | 1.5852  |                    |         | 47.784             | 1.5684  | 46.917             | 1.5626  |
| 39.773             | 1.5853  |                    |         | 47.586             | 1.5685  | 46.832             | 1.5627  |
| 39.650             | 1.5853  |                    |         | 47.501             | 1.5685  | 46.738             | 1.5627  |
| 39.547             | 1.5854  |                    |         | 47.407             | 1.5685  | 46.682             | 1.56275 |
| 39.443             | 1.5854  |                    |         | 47.294             | 1.5686  | 46.559             | 1.5628  |
| 39.349             | 1.58545 |                    |         | 47.190             | 1.5686  | 46.465             | 1.5628  |
| 39.236             | 1.5855  |                    |         | 47.115             | 1.5687  | 46.380             | 1.56285 |
| 39.179             | 1.5855  |                    |         | 47.040             | 1.5687  | 46.267             | 1.56285 |
| 39.076             | 1.5856  |                    |         | 46.898             | 1.5687  | 46.201             | 1.5629  |
| 38.972             | 1.5856  |                    |         | 46.861             | 1.5687  | 46.107             | 1.5629  |
| 38.878             | 1.5856  |                    |         | 46.766             | 1.56875 | 46.003             | 1.5630  |
| 38.793             | 1.5857  |                    |         | 46.653             | 1.5688  | 45.881             | 1.5630  |
| 38.718             | 1.5857  |                    |         | 46.569             | 1.5688  | 45.815             | 1.5631  |
| 38.605             | 1.5857  |                    |         | 46.465             | 1.56885 | 45.721             | 1.5631  |
| 38.548             | 1.5858  |                    |         | 46.371             | 1.5689  | 45.608             | 1.5632  |
| 38.492             | 1.5859  |                    |         | 46.286             | 1.5690  | 45.523             | 1.5632  |
| 38.360             | 1.5859  |                    |         | 46.192             | 1.5690  | 45.419             | 1.5632  |
| 38.350             | 1.5859  |                    |         | 46.079             | 1.5690  | 45.334             | 1.56325 |
| 38.237             | 1.5859  |                    |         | 46.003             | 1.5691  | 45.240             | 1.5633  |
| 38.153             | 1.5860  |                    |         | 45.900             | 1.5691  | 45.155             | 1.5634  |
| 38.058             | 1.5860  |                    |         | 45.805             | 1.56915 | 45.052             | 1.5634  |
| 37.983             | 1.58605 |                    |         | 45.721             | 1.5692  | 44.948             | 1.56345 |
| 37.879             | 1.5861  |                    |         | 45.626             | 1.5693  | 44.854             | 1.5635  |
| 37.776             | 1.5861  |                    |         | 45.523             | 1.56935 | 44.769             | 1.5635  |
| 37.691             | 1.58615 |                    |         | 45.429             | 1.5694  | 44.675             | 1.56355 |
| 37.587             | 1.5862  |                    |         | 45.334             | 1.5694  | 44.600             | 1.5636  |
| 37.493             | 1.5862  |                    |         | 45.240             | 1.5695  | 44.534             | 1.56365 |
| 37.408             | 1.5863  |                    |         | 45.137             | 1.5695  | 44.449             | 1.5637  |
| 37.305             | 1.5864  |                    |         | 45.024             | 1.5696  | 44.355             | 1.56375 |
| 37.192             | 1.58645 |                    |         | 44.948             | 1.5696  | 44.232             | 1.5638  |
| 37.088             | 1.58645 |                    |         | 44.845             | 1.56965 | 44.119             | 1.5638  |
| 37.003             | 1.5865  |                    |         | 44.750             | 1.5697  | 44.025             | 1.5639  |
| 36.909             | 1.5865  |                    |         | 44.666             | 1.5697  | 43.950             | 1.5639  |
| 36.843             | 1.5866  |                    |         | 44.562             | 1.56975 | 43.855             | 1.56395 |
| 36.758             | 1.5866  |                    |         | 44.468             | 1.5698  | 43.742             | 1.5640  |
| 36.636             | 1.5867  |                    |         | 44.392             | 1.5698  | 43.667             | 1.5640  |
| 36.560             | 1.5867  |                    |         | 44.289             | 1.5699  | 43.563             | 1.5641  |
| 36.466             | 1.5867  |                    |         | 44.194             | 1.56995 | 43.478             | 1.5641  |
| 36.363             | 1.5868  |                    |         | 44.110             | 1.5700  | 43.403             | 1.56415 |
| 36.268             | 1.5868  |                    |         | 44.015             | 1.5700  | 43.309             | 1.5642  |
| 36.184             | 1.5869  |                    |         | 43.931             | 1.57005 | 43.186             | 1.5642  |
| 36.080             | 1.5869  |                    |         | 43.827             | 1.5701  | 43.092             | 1.5643  |
| 35.986             | 1.5870  |                    |         | 43.723             | 1.5702  | 42.998             | 1.56435 |
| 35.882             | 1.5870  |                    |         | 43.639             | 1.5702  | 42.913             | 1.5644  |
| 35.778             | 1.5871  |                    |         | 43.535             | 1.57025 | 42.828             | 1.5644  |
| 35.694             | 1.5871  |                    |         | 43.460             | 1.5703  | 42.725             | 1.5644  |
| 35.599             | 1.58715 |                    |         | 43.375             | 1.5703  | 42.659             | 1.5645  |
| 35.533             | 1.5872  |                    |         | 43.281             | 1.5704  | 42.536             | 1.5645  |

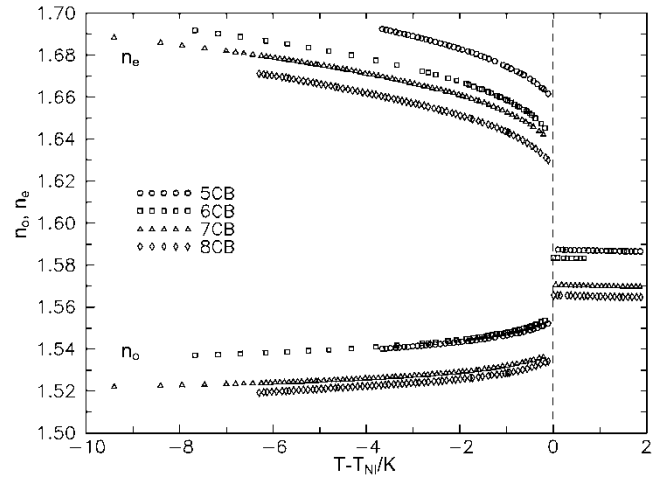


Figure 1. Experimental values of refractive indices  $n_o$  and  $n_e$  in the nematic phase of 5–8CB liquid crystals, as a function of shifted temperature  $T-T_{NI}$ . For scaling reasons, in the isotropic phase only values within two degrees of the transition are plotted.

factor 2.7 in  $K_v$  noise is materialized by a significant decrease (factor  $(2.7)^2=7.25$ ) of the noise level. Higher noise level would lead to an unacceptably large uncertainty of  $\beta$ . It emerges that repetition of the measurements and averaging of data is a necessary approach for successful fits using equation (6). The data of table 2 and figure 1 referring to the I phase were obtained with the Atago instrument. Typical noise level

Table 2. (Cont.)

| 5CB                |        | 6CB                |     | 7CB                |         | 8CB                |         |
|--------------------|--------|--------------------|-----|--------------------|---------|--------------------|---------|
| $T/^\circ\text{C}$ | $n$    | $T/^\circ\text{C}$ | $n$ | $T/^\circ\text{C}$ | $n$     | $T/^\circ\text{C}$ | $n$     |
| 35.430             | 1.5873 |                    |     | 43.177             | 1.5704  | 42.452             | 1.5645  |
|                    |        |                    |     | 43.083             | 1.57045 | 42.357             | 1.5646  |
|                    |        |                    |     | 42.989             | 1.5705  | 42.263             | 1.5646  |
|                    |        |                    |     | 42.894             | 1.5705  | 42.169             | 1.5647  |
|                    |        |                    |     | 42.810             | 1.5706  | 42.075             | 1.5647  |
|                    |        |                    |     | 42.715             | 1.57065 | 41.971             | 1.56475 |
|                    |        |                    |     | 42.612             | 1.5707  | 41.896             | 1.5648  |
|                    |        |                    |     | 42.518             | 1.5708  | 41.792             | 1.5649  |
|                    |        |                    |     | 42.395             | 1.5708  | 41.698             | 1.5649  |
|                    |        |                    |     |                    |         | 41.594             | 1.56495 |
|                    |        |                    |     |                    |         | 41.491             | 1.5650  |
|                    |        |                    |     |                    |         | 41.415             | 1.5650  |
|                    |        |                    |     |                    |         | 41.321             | 1.5651  |
|                    |        |                    |     |                    |         | 41.217             | 1.5652  |
|                    |        |                    |     |                    |         | 41.142             | 1.5652  |
|                    |        |                    |     |                    |         | 41.048             | 1.56525 |
|                    |        |                    |     |                    |         | 40.954             | 1.5653  |
|                    |        |                    |     |                    |         | 40.850             | 1.5654  |
|                    |        |                    |     |                    |         | 40.775             | 1.5654  |
|                    |        |                    |     |                    |         | 40.633             | 1.56545 |
|                    |        |                    |     |                    |         | 40.567             | 1.5655  |
|                    |        |                    |     |                    |         | 40.483             | 1.56555 |

per point is  $\sigma=0.3 \times 10^{-4}$ , achieved without data averaging.

We have performed fits of equation (6) on our data and on data selected from the literature. The quantities  $K_{V,N}$  were calculated from the experimental curves  $n_{o,e}(T)$  in the N phase. We took the following starting values for the parameters:  $\Delta\alpha/\langle\alpha\rangle=0.7$ ,  $S^{**}=0.15$ ,  $T^{**}=T_{NI}+0.2$ ,  $\beta=0.25$ . The results (with  $K_V$ ) are summarized in table 3.

The uncertainties of  $\beta$  fit values (<sup>a</sup> in table 3) are large in the case of 5CB (only 4 K available data range) and of 8CB (only 3 K useable data range determined by range shrinking). For 6CB and 7CB the available data range were 8 K and 9 K, respectively, resulting in smaller uncertainties. Extending the temperature range by just one point (fits <sup>b</sup> in table 3) reduces the uncertainties at the cost of moderate increase of  $\chi_r^2$ . However, the value  $\beta=0.29 \pm 0.02$  for 5CB is probably too high due to incompatibility of our data with the added point, as indicated by the rather poor fit ( $\chi_r^2=2.22$ ). The fits (<sup>c,d</sup> in table 3) on best data found in the literature are consistent with fits of our data. For 5–7CB, in spite of broader temperature ranges, the parameter uncertainties are larger than ours, since experimental errors are also higher. However, the temperature differences  $T^{**}-T_{NI}$  of 5CB, 6CB and 8CB are centred at negative values, which has no

physical significance. The liquid crystal 8CB (<sup>d</sup> in table 3) yielded an unacceptable fit quality ( $\chi_r^2=4.10$ ). Due to insufficient data (only seven points within 4 K below  $T_{NI}$ ), the range could not be reduced enough. This result is left in table 3 only to illustrate the relevance of the discussion in the appendix with relation to figure 9.

Figure 2 shows the profiles of  $\chi_r^2$  error functions corresponding to fits (<sup>a</sup> in table 3) ( $\beta$  free), determined by varying  $\beta$  in steps of 0.02 during the fitting procedure. The solid lines are parabolic fits to the points in the vicinity of the minima. The average  $\langle\beta_{opt}\rangle=0.241 \pm 0.012$  with a smaller standard deviation than the uncertainties of individual fits. The average is close to  $\beta=0.25$  and excludes higher theoretical values, as indicated by the sharp increase of  $\chi_r^2$  above  $\beta=0.30$ , for all compounds. A confirmation of this statement comes from fits (<sup>a</sup>,  $\beta$  fixed) of table 3. The error function is not significantly higher than in the case when  $\beta$  was left free, meaning that a three-parameter fit with  $\beta=0.25$  is also satisfactory. We conclude that within experimental uncertainties, the critical exponent of the order parameter is correctly predicted by the tricritical hypothesis with  $\beta=0.25$  for all the investigated  $n$ CB compounds.

Figure 3 shows the correlation between parameters  $\beta$  and  $S^{**}$  along the degenerate river. The trajectories in

Table 3. Values of fit parameters of equation (6) ( $K_V$ ) and the corresponding  $\chi_r^2$  error function obtained from four-parameters fits (unless differently indicated) applied to experimental data of refractive indices as a function of temperature, for 5–8CB liquid crystals in the nematic phase. The molar mass  $M$  and the order parameter  $S(T)$  (from equation 5) at  $\tau=0.02$  ( $T \approx T^{**}-6$  K) are also given.

| LCM/kg        | $\Delta\alpha/\langle\alpha\rangle$ | $S^{**}$            | $S(\tau=0.02)$ | $T^{**}-T_{NI}/K$ | $\beta$         | $\chi_r^2$ | Remarks                      |
|---------------|-------------------------------------|---------------------|----------------|-------------------|-----------------|------------|------------------------------|
| 5CB<br>249.35 | $0.727 \pm 0.008$                   | $0.157 \pm 0.008$   | 0.474          | $0.29 \pm 0.03$   | (0.25)          | 1.63       | <sup>a</sup> , $\beta$ fixed |
|               | $0.72 \pm 0.11$                     | $0.15 + 0.05/-0.25$ | 0.478          | $0.30 \pm 0.18$   | $0.24 \pm 0.11$ | 1.52       | <sup>a</sup>                 |
|               | $0.78 \pm 0.01$                     | $0.19 + 0.01/-0.02$ | 0.445          | $0.22 \pm 0.06$   | $0.29 \pm 0.02$ | 2.22       | <sup>b</sup>                 |
|               | $0.76 \pm 0.05$                     | $0.16 + 0.10/-0.29$ | 0.451          | $-0.03 \pm 0.95$  | $0.27 \pm 0.11$ | 1.26       | <sup>c</sup>                 |
| 6CB<br>263.38 | $0.690 \pm 0.005$                   | $0.121 \pm 0.005$   | 0.451          | $0.15 \pm 0.03$   | (0.25)          | 1.49       | <sup>a</sup> , $\beta$ fixed |
|               | $0.67 \pm 0.04$                     | $0.09 + 0.06/-0.11$ | 0.463          | $0.20 \pm 0.12$   | $0.23 \pm 0.05$ | 1.29       | <sup>a</sup>                 |
|               | $0.64 \pm 0.03$                     | $0.01 + 0.08/-0.14$ | 0.483          | $0.30 \pm 0.12$   | $0.19 \pm 0.04$ | 1.93       | <sup>b</sup>                 |
|               | $0.70 \pm 0.06$                     | $0.18 + 0.05/-0.15$ | 0.443          | $-0.24 \pm 0.42$  | $0.29 \pm 0.09$ | 1.24       | <sup>d</sup>                 |
| 7CB<br>277.40 | $0.691 \pm 0.008$                   | $0.172 \pm 0.009$   | 0.483          | $0.20 \pm 0.06$   | (0.25)          | 2.00       | <sup>a</sup> , $\beta$ fixed |
|               | $0.70 \pm 0.06$                     | $0.18 + 0.05/-0.13$ | 0.479          | $0.18 \pm 0.22$   | $0.26 \pm 0.08$ | 1.98       | <sup>a</sup>                 |
|               | $0.68 \pm 0.03$                     | $0.16 + 0.05/-0.09$ | 0.489          | $0.22 \pm 0.16$   | $0.24 \pm 0.05$ | 1.98       | <sup>b</sup>                 |
|               | $0.71 \pm 0.22$                     | $0.17 + 0.05/-0.17$ | 0.473          | $0.65 \pm 0.60$   | $0.26 \pm 0.21$ | 1.66       | <sup>d</sup>                 |
| 8CB<br>291.43 | $0.674 \pm 0.007$                   | $0.166 \pm 0.007$   | 0.480          | $0.14 \pm 0.03$   | (0.25)          | 1.91       | <sup>a</sup> , $\beta$ fixed |
|               | $0.65 \pm 0.11$                     | $0.15 + 0.06/-0.29$ | 0.492          | $0.17 \pm 0.16$   | $0.23 \pm 0.11$ | 1.84       | <sup>a</sup>                 |
|               | $0.85 \pm 0.20$                     | $0.20 + 0.01/-0.06$ | 0.388          | $-0.20 \pm 0.23$  | $0.38 \pm 0.13$ | 4.10       | <sup>d</sup>                 |

<sup>a</sup>Fits on our data

<sup>b</sup>Fits on our data with temperature ranges extended by one additional point at  $T_{NI}-T=34.2$  K for 5CB [11], at  $T_{NI}-T=13.8$  K for 6CB [12], and at  $T_{NI}-T=20.0$  K for 7CB [13]. The points from [12, 13] are corrected for the wavelength used (633 nm) to the wavelength of 589 nm according to [28].

<sup>c</sup>Fit on data of [11].

<sup>d</sup>Fit on data of [12]. The  $\Delta\alpha/\langle\alpha\rangle$  values are corrected by +2% for the wavelength used (633 nm) to the wavelength of 589 nm according to [13, 28]. The other fit parameters are wavelength independent.

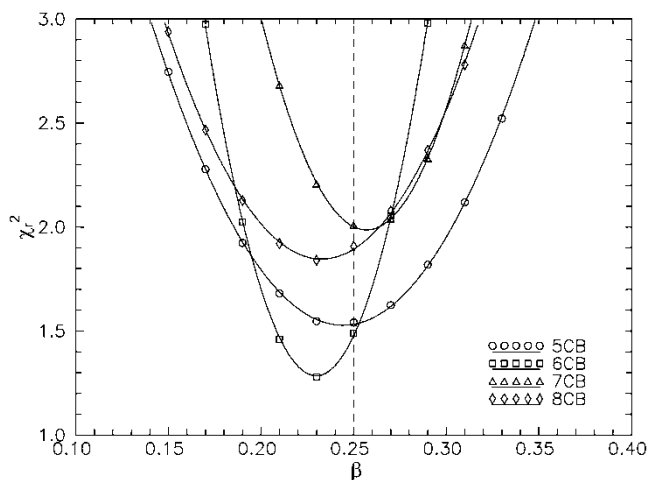


Figure 2. Parabolic profiles of  $\chi_r^2$  error functions obtained from three-parameter fits and stepwise variation of  $\beta$ . The minima correspond to  $\beta_{\text{opt}}$  (see fit results <sup>a</sup> in table 3).

the  $(\beta, S^{**})$  plane are similar except that of 6CB which is singled out by a lower position. This is also true for fits <sup>(c,d)</sup> in table 3) on literature data. The trajectories follow a curved path so that there is an absolute maximum  $S^{**}_{\text{max}}=0.2-0.25$ . This explains the asymmetry of  $S^{**}$  error intervals about  $S_{\text{opt}}$  (table 3). The  $2\chi_r^2_{\text{min}}$  contour plots (shown only for 6CB) are very elongated. The ratios between the long and short axes of the distorted ellipses are about 50, which is an

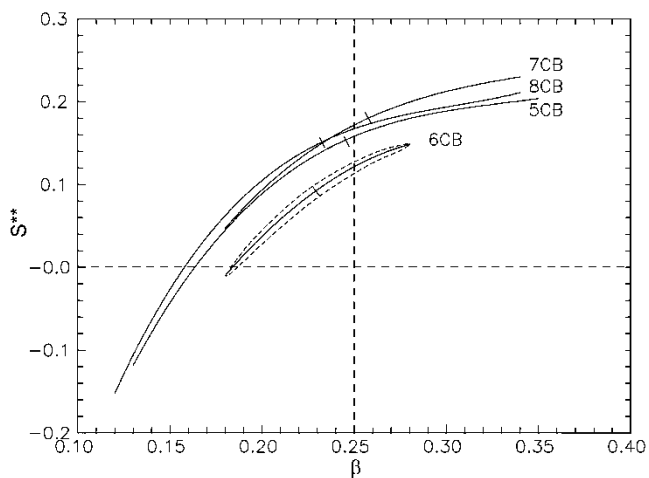


Figure 3. Correlation of four-parameter fit results in the  $(\beta, S^{**})$  plane around the optimal values. For each compound are shown the trajectories *along* the degenerate river (long lines) and *across* it (short lines). The extension of the lines away from the intersection at  $(\beta_{\text{opt}}, S^{**}_{\text{opt}})$  corresponds to the doubling of  $\chi_r^2_{\text{min}}$ . The contour plot representing  $2\chi_r^2_{\text{min}}$  is shown only for 6CB (dashed distorted ellipse). Only positive  $S^{**}$  values have physical significance.

indication of strong degeneracy between the two parameters.

Figure 3 explains why in Haller's approximation ( $S^{**}=0$ , horizontal dashed line) the  $\beta$  values obtained are systematically lower,  $\beta < 0.20$ . Moreover,  $\Delta\alpha/\langle\alpha\rangle$  is also lower by 8–12% and  $\chi_r^2$  is larger by a factor 1.3–1.8 compared with four-parameter fit results. On the other hand, for a fixed value  $\beta=0.25$  (vertical dashed line) the corresponding  $S^{**}$  takes a value between 0.12 and 0.17 (see also table 3). A somewhat broader interval ( $S^{**}=0.09-0.18$ ) results from four-parameter fits <sup>(a)</sup> in table 3). This is in qualitative agreement with the semi-empirical equation (8) with  $S^{**}=0.1$ , as proposed by Picken [25]. Large uncertainties in  $S^{**}$  fit values are due to the low sensitivity of  $S(T)$  to this parameter. The smallest uncertainties ( $< \pm 0.1\%$ ) are obtained for  $T^{**}$  due to highest sensitivity of  $S(T)$  to it, but nevertheless the temperature differences  $T^{**}-T_{\text{NI}}$  have uncertainties of about  $\pm 100\%$ . The average  $\langle T^{**}-T_{\text{NI}} \rangle = 0.21 \pm 0.04$  K and is better defined.

The polarizability cannot be measured directly and therefore reported values depend on models relating the polarizability tensor to optical properties [29]. We found that the quantity  $\langle\alpha\rangle/M$  ( $M$  being the molar mass) is remarkably constant (to within  $\pm 0.3\%$ ) for 5–9CB [30]. Therefore in figure 4 we chose to plot the quantity  $(\Delta\alpha/\langle\alpha\rangle)M$ . In this way the observed

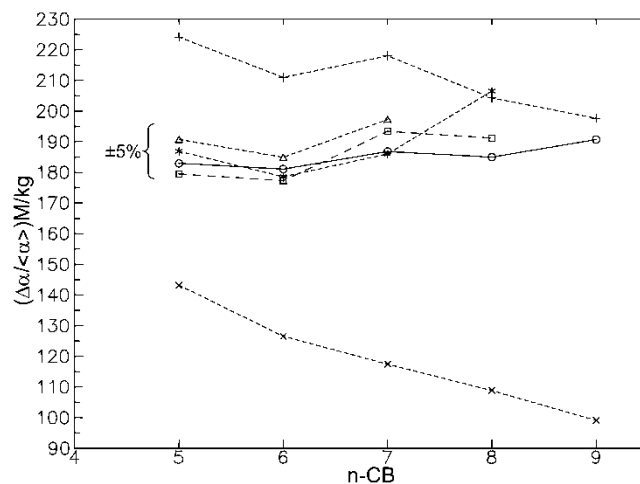


Figure 4. Product of relative polarizability anisotropy  $\Delta\alpha/\langle\alpha\rangle$  and molar mass  $M$  as a function of alkyl chain length of the  $n$ CB homologous series: (squares) results <sup>(a)</sup> from table 3; (triangles) results <sup>(c,d)</sup> from table 3; (stars) results of [13] normalized to Raman depolarization data; (crosses) from [14] where Maier and Meier theory [31] was used to interpret refractive index and dielectric constant data; (x) results from Kerr effect in LC solutions [14]; (solid line) odd-even increments computed by bond additivity [24], starting from the  $\Delta\alpha/\langle\alpha\rangle$  value of 6CB (average of our result and that of [12]).



alternation (odd–even effect) should be due to  $\Delta\alpha$  alone. Fits on our data (squares), on literature data (triangles), results involving Raman depolarization [13] (stars), and theoretical prediction of odd–even increments based on bond additivity [24] (solid line) agree within  $\pm 5\%$  (except 8CB from [13], for the same reason as that shown in figure 3). Nevertheless, consistently higher values [14] (crosses) were obtained by using the Maier and Meier formalism [31] while lower values (x) were obtained from the Kerr effect of LC in solution [14].

When fitting the  $K_N$  quantity, the parameters  $S^{**}$ ,  $T^{**}$ ,  $\beta$  and the error  $\chi_r^2$  remained practically unchanged, but the polarizability anisotropy decreased by a factor 1.24 (1.23 in [32]) to  $(\Delta\alpha/\langle\alpha\rangle)M \approx 140$ . This is in better agreement with curve (x) of isolated molecules as determined from the Kerr effect in solution (figure 4) where the anti-parallel coupling is absent. It turns out that the Vuks assumption of isotropic internal field is more appropriate for pure LC.

All parameters and  $S(T)$  at  $\tau=0.02$  show the known odd–even effect [13] with an amplitude of  $\pm 5\%$ , except  $S^{**}$  which has  $\pm 30\%$ , see figure 5. Based on equation (1), this means that the alternation of the square of the refractive index anisotropy is due to contributions from both the polarizability anisotropy and the order parameter. In figure 6 we show the order parameter of 5–8CB as a function of reduced temperature  $\tau$ . 6CB is situated in the lowest position, as in [13, 14]. The fits with equation (5) are indistinguishable from the points and provide the best description of experimental results both at large and small  $\tau$  values. The other models fail in one or other of the temperature ranges.

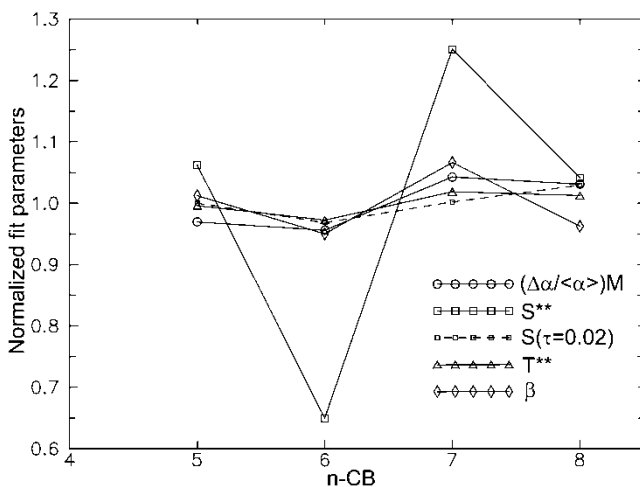


Figure 5. Odd–even effect of normalized fit parameters and of the order parameter  $S(T)$  at  $\tau=0.02$  ( $\approx T^{**}-6$  K), (with values <sup>a</sup> of table 3) as a function of alkyl chain length of the  $n$ CB homologous series.

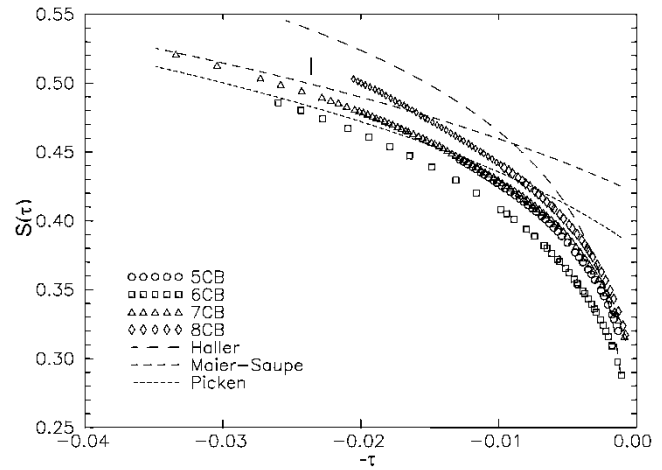


Figure 6. Order parameter vs. reduced temperature, as determined from equation (1) applied to our experimental data of 5–8CB, with fit values <sup>a</sup> of table 3. For 8CB only data points displayed by large rhombi were considered in the fit (corresponding to temperature range  $T^{**}-T=3.05$  K in figure 3). The marker indicates the position of the smectic–nematic (SN) phase transition. Dashed curves represent traditional theoretical models for the order parameter: Haller (equation (5) with  $S^{**}=0$ ,  $T^{**}=T_{NI}$ ), Maier–Saupe equation (7), and Picken equation (8).

## 5. Conclusions

The starting point of this work rests in the earlier disagreement between theoretical and experimental values of the critical exponent  $\beta$  of the order parameter  $S(T)$  obtained from (but not only) refractive index data of liquid crystals. In the past,  $\beta$  was extracted from experimental data of anisotropic physical quantities, by fits with empirical equations containing two or three parameters. We demonstrate that this approach leads systematically to  $\beta$  values too low as compared with predictions of existing theories.

We used in our approach a four-parameter expression that is consistent with mean-field theory. We determined  $S(T)$  in the nematic phase of  $n$ CB LC, from high temperature resolution refractive index data. The fit function can be applied to any anisotropic quantity characterizing the LC. The data were processed according to two models: (i) the Vuks approximation assuming an isotropic internal field, and (ii) the Neugebauer model of anisotropic local field. We find that  $S(T)$  is the same with the two models, but the relative polarizability anisotropy  $\Delta\alpha/\langle\alpha\rangle$  of pure LC is better described by Vuks' model while that of LC in solution (equivalent to isolated LC molecules) is better accounted for by Neugebauer's model.

Despite an advanced two-step fitting procedure, a detailed theoretical study of fit function, and a correction method for the localization of the minimum

of the error function (see appendix), the four-parameter fits proved to be a difficult task. The parameter pairs  $(\beta, S^{**})$  and  $(\beta, \Delta\alpha/\langle\alpha\rangle)$  are strongly correlated. Their separation is facilitated by the availability of data in a wide temperature range (both high and low temperature end). The statistical analysis showed that in order to determine the parameter set with a reasonable uncertainty, it is necessary to average the data over several runs.

We found for 5–8CB an average value of  $\langle\beta\rangle = 0.241 \pm 0.012$ , which confirms the tricritical hypothesis predicting  $\beta = 0.25$ . Thus, other possible theoretical values are excluded. There is no evidence for a trend in  $\beta$  values within the homologous series 5–8CB. The free term  $S^{**}$  takes values between 0.09 and 0.18, while  $S^{**} = 0$  (Haller approximation) yields significantly worse fits. On average, the temperature difference  $\langle T^{**} - T_{NI} \rangle = 0.21 \pm 0.04$  K.

All fit parameters and  $S(T)$  exhibit an odd–even effect that parallels the  $T_{NI}$  temperatures. Its amplitude is consistent with theoretical increments computed by bond additivity. However, the polarizability anisotropy is larger than that resulting from bond additivity, due to the conjugation effect along the alkyl chain. The 6CB compound is singled out by lower  $S^{**}$  and  $S(T)$  values in comparison with the other compounds. Care should be taken when processing 8CB data in order to exclude from the fit the temperature range where pretransitional smectic order influences the N phase.

Our fit expression provides the best description of  $S(T)$  when compared with Haller, Maier–Saupe and Picken models. Future work will be devoted to the analysis of other anisotropic quantities characterizing the LC, by using the same fit method.

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### Appendix:

#### *Sensitivity of the fit function to variations of parameters*

The result of a multi-parametric fit is unequivocal only if the parameters are not degenerate. The covariance matrix gives a global view of the degeneracy between them over the whole interval (of the temperature variation, in our case). Similar information can be gained by analysing the sensitivity of the fit function to the variation of parameters, with the advantage that it

reveals possible correlations within restricted regions of the variable  $T$ .

In general, the relative sensitivity of  $S(T, i)$  to parameter  $i$  ( $i = \Delta\alpha/\langle\alpha\rangle, S^{**}, T^{**}, \beta$ ) is defined as:

$$R_i = (dS/S)/(di/i) = d(\ln S)/d(\ln i). \quad (\text{A1})$$

High sensitivity results in low uncertainty on the fit value (good fit). According to equation (9), if  $R_i$  takes a value  $k$  at temperature  $T'$ , then  $S(T')$  is directly proportional to  $i^k$ . For  $k=1$ ,  $S(T') \propto i$ . If two sensitivities are equal over a given interval, the respective parameters are fully correlated (degenerate) and cannot be separated. In the case of partial degeneracy, the variation of one parameter is compensated for by another one, leading to increased uncertainty of the fit result.

An example of computed sensitivities is shown in figure 7. The pairs  $R_\beta, R_{S^{**}}$  and  $R_\beta, R_{\Delta\alpha/\langle\alpha\rangle}$  depend in a similar way on temperature, indicating a certain degree of degeneracy. A wider temperature range for the fit reduces the correlation. From the slopes of the curves it emerges that  $T^{**}$  and  $S^{**}$  are determined mainly by experimental points situated close to  $T_{NI}$  (highest  $R_{T^{**}}$  and  $R_{S^{**}}$  within approx. 1 K). Unlike this,  $R_{\Delta\alpha/\langle\alpha\rangle}$  and  $R_\beta$  are (nearly) constant at any temperature. The increasingly strong dependence (compared with that of other parameters) of  $S(T)$  on  $T^{**}$  upon approaching the transition is illustrated by the following relations based on values from figure 1:

$$S(T^{**} - 6) \propto (S^{**})^{0.14} \beta^{0.75} (T^{**})^{9.6} \quad (\text{A2 a})$$

$$S(T^{**} - 0.2) \propto (S^{**})^{0.34} \beta^{1.07} (T^{**})^{213}. \quad (\text{A2 b})$$

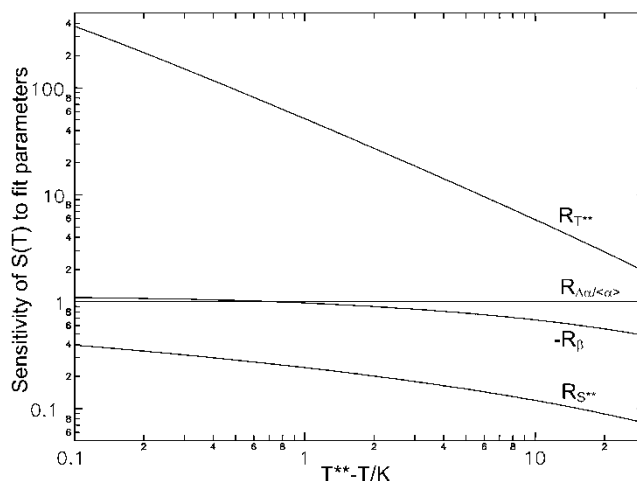


Figure 7. Relative sensitivities equation (9), of the order parameter  $S(T)$  to the variation of parameters, computed from equation (5) for typical values  $S^{**} = 0.1$ ,  $A = 1 - S^{**}$ ,  $T^{**} = 305$  K and  $\beta = 0.25$ . The sensitivity  $R_{\Delta\alpha/\langle\alpha\rangle} = 1$  results from equation (6).

From this discussion one concludes that the quality of the fit depends on the availability of experimental data in a wide temperature range that should approach  $T_{\text{NI}}$  as much as possible. In our case the best fit can be obtained for  $T^{**}$  while the worst one for  $S^{**}$ .

#### Fitting methods

We have developed a non-linear multi-parametric fitting program using a subroutine of Matlab<sup>TM</sup>, based on the conjugated gradient method. The optimization criterion is the minimization of the reduced  $\chi_r^2$  error function that is given by the ratio between the variance of the fit  $s^2$  and the variance of the data  $\sigma^2$  [28]:

$$\chi_r^2 = \frac{s^2}{\sigma^2} = \frac{\frac{1}{N-p} \Sigma(\text{res})^2}{\sigma^2} \quad (\text{A3})$$

where  $\Sigma(\text{res})^2$  represents the sum of squared residues between the fit and  $N$  data points, while  $p$  is the number of adjustable parameters (maximum four in our case). In practice  $\sigma$  is estimated directly on the same data, as the standard deviation (per point) of a parabolic fit in a limited temperature interval (a few degrees) situated far away from  $T_{\text{NI}}$ . For an ideal fit  $\chi_r^2 = 1$ , while a good fit yields  $\chi_r^2 \approx 1.5$ .

The quantity  $\chi_r^2$  can be mapped in the  $p$ -dimensional space by a hypersurface with equal error contours. For independent parameters, the contours around a local minimum are more or less circular, like ‘lakes’. In the case of partial degeneracy, the contours are elongated ellipses, eventually turning into ‘rivers’ with low slopes and shallow minima.

In general, the gradient fit method is a very efficient one but it does not converge rapidly as the search approaches the minimum [28]. In our case, the fitting procedure easily optimizes the parameters starting downwards from the *sides* of the river, but it might not continue the optimization *along* the river if the gradient is too low. Thus, the result may be influenced by the starting values of the parameters. Therefore, we combined two fitting methods. We fixed the value of one parameter (for instance,  $\beta = \beta'$ ) and performed (with the gradient method) a fitting sequence with the remaining three parameters left free. The resulting local minimum is situated at the intersection of the river with the plane  $\beta = \beta'$ . By repeating this procedure in steps of  $\beta$ , one obtains the whole profile of the river in the vicinity of the absolute minimum. This is equivalent to the identification of the path of lowest  $\chi_r^2$ , which is known as the ravine search method [28]. Next, the absolute minimum is precisely located by a parabolic fit of the  $\chi_r^2$  curve on few  $\beta$  points. The four coordinates ( $\beta_{\text{opt}}$  and the respective other three parameter values) represent the best fit. The standard deviation of each

value corresponds to the doubling of minimum  $\chi_r^2$ . This uncertainty is equivalent to performing a one-parameter fit and considering the covariances with the other parameters. Any independent information on one of them (such as theoretical predictions for  $\beta$  or theoretical and experimental polarizability values) will remove the degeneracy along the river resulting in narrower  $\chi_r^2$  parabola.

Compared with the normal procedure of performing a four-parameter fit in one sequence, the application of the combined method has the following advantages:

- (i) It sets a lower demand on the fitting program since the number of free parameters is decreased from four to three; the determination of the absolute minimum along the river is done in a separate step,
- (ii) It reveals the whole trajectory of the  $\chi_r^2$  error function in the parameter hyperspace, rather than yielding a single set of best-fit results.

#### Correction of fit results

Once the profile of the river is determined, the localization of the true absolute minimum encounters another problem. Figure 8 shows for the 7CB data the variance of the fit  $s^2$  along the river as a function of  $\beta$ . Curve (1) is obtained for an ideal noise-free data set (72 points in the temperature range  $T^{**} - T = 0.5 - 10.5$  K). The data were generated with equation (6), with the optimum values of the four parameters (see further table 1). Obviously, the minimum  $s^2$  tends to zero and it can be easily identified at  $\beta = 0.257$ . Away from the

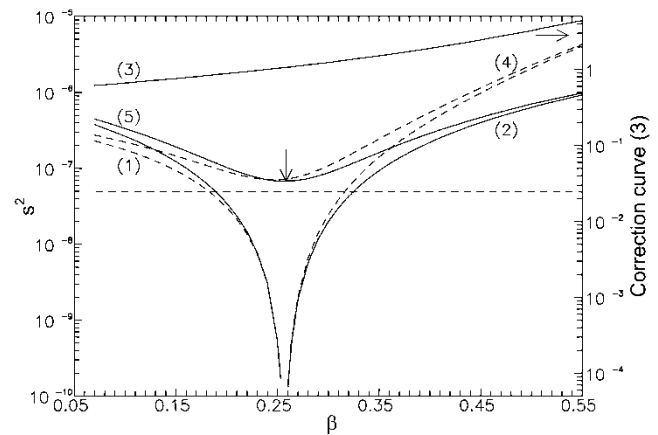


Figure 8. Illustration of two-step fitting method for 7CB. The variance  $s^2$  of three-parameter fits is determined in steps of  $\beta$  values: (1) fit on ideal noise-free data; (2) extrapolation of a narrow region of curve (1) around the minimum; (3) correction function obtained as the ratio of (1) and (2); (4) fit on experimental points; (5) corrected fit obtained as the ratio of (4) and (3). The corrected  $\beta_{\text{opt}}$  value is indicated by the arrow.

minimum, the error increases sharply, but the two wings of the curve are not symmetrical. This is the consequence of the non-linear dependence of  $S(T)$  on  $\beta$ . Curve (2) is a parabolic fit to curve (1) restricted to a narrow interval ( $\beta = 0.253\text{--}0.261$ ) around the minimum, and extrapolated to the whole  $\beta$  range. Curve (3) is the ratio of curve (1) and (2) and expresses the non-linear dependence of the error function on  $\beta$ . This curve should be used as a weighting factor for the representation of  $\chi_r^2$  versus  $\beta$ . Curve (3) is also valid for other  $n$ CB compounds, and does not change significantly for  $\beta=0.2\text{--}0.3$ , nor with the temperature interval of the data points. The relevance of this correction is illustrated by the fit (curve 4) to experimental points of 7CB situated in the same temperature interval. The apparent position of the minimum is shifted to lower  $\beta$  values due to the bias of the baseline (curve 3). The weighted  $\chi_r^2$  error curve (5) is obtained as the ratio of curve (4) to curve (3). Its minimum ( $\beta=0.26\pm 0.08$ ) indicated by the arrow coincides now with that of curve (1). The effect of the correction is more pronounced for broad minima. Similar curves are obtained for the other parameters. All data were corrected according to this procedure.

In the case of a good fit ( $s_{\min}^2 \approx \sigma^2$ ), curve (4) is the sum of curve (1) and of the experimental noise level  $\sigma^2$  (horizontal dashed line). The latter broadens the minimum and limits its depth. The possibility of identifying the minimum depends on the relative position of these two curves. It is desirable to have a curve (1) with high wings and at the same time to have a low noise level. The height of curve (1) depends on the extension of the data temperature range in both directions. Unfortunately, at the high temperature end the experiment cannot go beyond  $T_{\text{NI}}$  (about 0.2 K below  $T^{**}$ ). At the low temperature end, expanding the range for instance from 10.5 to 30 K raises curve (1) by a factor 10, while shrinking the range to  $T^{**}-5$  K lowers curve (1) by the same factor.

#### Effect of range shrinking on fit results

In order to check the consistency of fit results, we applied the double 'range shrinking' technique. It consists of eliminating gradually from the fit the points situated at each end of the data set, while observing the stability of the results. At the high temperature end, the range shrinking showed that occasionally some points too close to  $T_{\text{NI}}$  had to be eliminated. They were probably situated in the narrow region of coexistence of phases. In any case, for these points it is required to have a temperature accuracy better than 0.05 K since we showed before that the whole fit is extremely sensitive to data errors near  $T_{\text{NI}}$ .

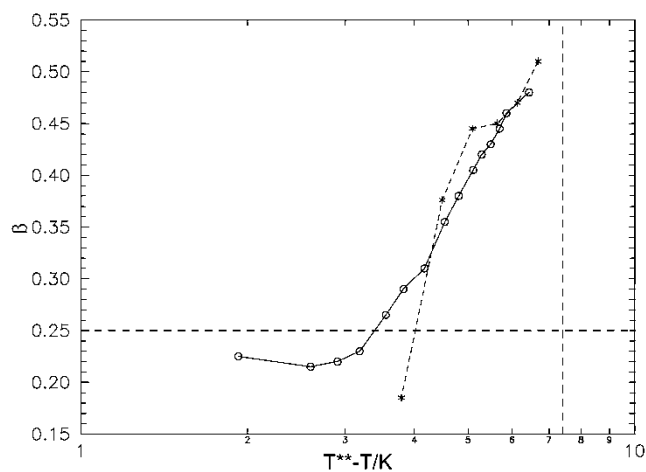


Figure 9. Effect of range shrinking (at the low temperature data end) on the critical exponent  $\beta$  of 8CB: (o) fits on our data; (\*) fits on data from [12]. The vertical dashed line marks the smectic A to nematic (SN) phase transition temperature. The increase of  $\beta$  upon approaching  $T_{\text{SN}}$  is due to the influence of smectic behaviour in the nematic phase.

At the low temperature end, the stability with range shrinking for 5CB, 6CB and 7CB was good. The 8CB compound is a special case because it exhibits a smectic A–nematic (SN) phase transition at  $T_{\text{SN}}=33.6^\circ\text{C}$  and its influence is present in the nematic state [32]. This is clearly seen in figure 9. The  $\beta$  value stabilizes only for a data range  $T^{**}-T < 3.5$  K, meaning that the pretransitional smectic behaviour continues to play a role up to 4 K above  $T_{\text{SN}}$ , well into the nematic state.

#### References

- [1] URBAN, S., WÜFLINGER, A., and GESTBLOM, B., 1999, *Phys. Chem. chem Phys.*, **1**, 2787.
- [2] THOEN, J., and BOSE, T. K., 1999, in *Handbook of Low and High Dielectric Constant Materials and their Applications*, Vol. 1, edited by H. S. Nalwa (London: Academic Press), pp. 501–561.
- [3] DE GENNES, P. G., and PROST, J., 1993, *The Physics of Liquid Crystals*, 2nd Edn (Oxford: Clarendon Press).
- [4] KEYES, P. H., 1978, *Phys. Lett.*, **A 67**, 132.
- [5] ANISIMOV, M. A., GARBER, S. R., ESIPOV, V. S., MAMMITSKII, V. M., OVODOV, G. I., SMOLENKO, L. A., and SORKIN, E. L., 1977, *Sov. Phys. JETP*, **45**, 1042.
- [6] THOEN, J., and MENU, G., 1983, *Mol. Cryst. Liq. Cryst.*, **97**, 163; MENU, G., 1988, PhD., thesis, Catholic Univ. Leuven, Belgium (in Dutch).
- [7] MARINELLI, M., and MERCURI, F., 2000, *Phys. Rev. E*, **61**, 1616.
- [8] BUKA, A., and DE JEU, W. H., 1982, *J. Phys. (Paris)*, **43**, 361.
- [9] HALLER, I., 1975, *Progr. solid State Chem.*, **10**, 103.
- [10] THOEN, J., 1992, in *Phase Transitions in Liquid Crystals*, edited by S. Martellucci and A.N. Chester (New York: Plenum Press), pp. 155–174.
- [11] BARAN, J. W., BOROWSKI, F., KEDZIERSKI, J.,

- RASZEWSKI, Z., ZMIJA, J., and SADOWSKA, K. W., 1978, *Bull. Pol. Acad. Sci.*, **26**, 117.
- [12] COLES, H. J., 1998, in *The Optics of Thermotropic Liquid Crystals*, edited by S. Elston and R. Sambles (London: Taylor and Francis), pp. 57–84.
- [13] KARAT, P. P., and MADHUSUDANA, N. V., 1976, *Mol. Cryst. liq. Cryst.*, **36**, 51.
- [14] DUNMUR, D. A., MANTERFIELD, M. R., MILLER, W. H., and DUNLEAVY, J. K., 1978, *Mol. Cryst. liq. Cryst.*, **45**, 127.
- [15] MAIER, W., and SAUPE, A., 1959, *Z. Naturforsch.*, **14a**, 882.
- [16] VUKS, M. F., 1966, *Opt. Spectrosc.*, **20**, 361.
- [17] CHANDRASEKHAR, S., and MADHUSUDANA, N. V., 1969, *J. Physique Colloq.*, **30**, C4–24.
- [18] NEUGEBAUER, H. E. J., 1954, *Can. J. Phys.*, **32**, 1.
- [19] SAUPE, A., and MAIER, W., 1961, *Z. Naturforsch.*, **16a**, 816.
- [20] SUBRAMHANYAM, H. S., and KRISHNAMURTI, D., 1973, *Mol. Cryst. liq. Cryst.*, **22**, 239.
- [21] DE JEU, W. H., and BORDERWIJK, P., 1978, *J. chem. Phys.*, **68**, 109.
- [22] ANISIMOV, M. A., 1990, *Critical Phenomena in Liquids and Liquid Crystals* (Philadelphia: Gordon and Breach).
- [23] GRAMSBERGEN, E. F., LONGA, L., and DE JEU, W. H., 1986, *Phys. Rep.*, **135**, 195.
- [24] DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (New York: Gordon and Breach).
- [25] PICKEN, S. J., NOIREZ, L., and LUCKHURST, G. R., 1998, *J. Chem. Phys.*, **109**, 7612.
- [26] TOUGH, R. J. A., and BRADSHAW, M. J., 1983, *J. Phys. (Paris)*, **44**, 447.
- [27] DUNMUR, D. A., HITCHEN, D. A., and HONG, X.-J., 1986, *Mol. Cryst. liq. Cryst.*, **140**, 303.
- [28] BEVINGTON, P. R., 1970, *Data Reduction and Error Analysis for the Physical Sciences* (New York: McGraw-Hill).
- [29] CLARK, S., 2001, in *Physical Properties of Liquid Crystals: Nematics*, edited by D. Dunmur, A. Fukuda and G. Luckhurst (London: The Institution of Electrical Engineers), pp. 113–123.
- [30] CHIRTOC, I., CHIRTOC, M., GLORIEUX, C., and THOEN, J., 2001, poster 2-P25 presented at the 6th European Conference on Liquid Crystals, 25–30 March, 2001, Halle (Saale), Germany.
- [31] MAIER, W., and MEIER, G., 1961, *Z. Naturforsch.*, **16a**, 262.
- [32] HORN, R. G., 1978, *J. Physique*, **39**, 105.