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INVITED ARTICLE

Critical behaviour in liquid-crystalline phase transitions: a comparative study of 9OCB in bulk and Anopore membranes

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As a humble contribution to this special commemorative issue to Professor Alfred Saupe, we present an experimental study on the critical behaviour of the nematic-to-isotropic (N–I) and smectic A-to-nematic (SmA–N) phase transitions of the liquid crystal 4-nonyloxy-4′-cyanobiphenyl (9OCB). Measurements of the specific heat and the dielectric permittivity were performed for bulk 9OCB as well as for 9OCB confined to Anopore membranes, and the influence of the slight-restrictive confinement was analysed. The possibility of driving the weakly first-order SmA–N phase transition to second-order in nature by means of the confinement was confirmed.

Keywords: Alfred Saupe; liquid crystals; phase transitions; confinement; modulated differential scanning calorimetry; dielectric spectroscopy

1. Introduction

Studies of the nature of phase transitions are among the most interesting and intriguing phenomena that have been, and are still being, investigated both theoretically and experimentally, particularly in the field of material science.

Often employed theoretically is the mean-field approach, which replaces all the interactions in a many-body system by an effective potential [1–3]. Despite its relative simplicity, this model is able to predict many of the results of the physics of materials. Unfortunately the approach is not reliable in the vicinity of phase transitions, since in this case the correlation length diverges and fluctuations become increasingly more important. Both correlations and fluctuations are neglected in the mean-field theory, where at best they are treated as small corrections in the free energy expression. Such an analysis is performed by means of the so-called critical exponents. These exponents define the analytical evolution of different physical quantities around the transition temperature in terms of a power law in reduced temperature. In addition, the critical exponents are related through some scaling functions, arising from a renormalisation group theory [4]. From this approach it can be stated that critical exponents are universal, depending on the dimensionality, d, of the system and on the number of components, n, of the order parameter. However, they do not depend on the details of the system itself and hence their universal behaviour – phase transitions in systems with similar d and n should belong to the same universality class. On the other hand, a physical system can be driven from a universality class when a coupling exists between order parameters with a different number of components. In such a case, a so-called multicritical point appears, close to which the character of anomalies changes radically. The simplest example is that of the tricritical point (TCP), at which a first-order and a second-order phase transition meet. Some of the first experimental evidence for the existence of a TCP was found in studies of the superfluid-to-normal liquid phase transition in mixtures of helium isotopes, ^{3}He–^{4}He.

Liquid crystals are among the richest systems by far for performing such studies, due to the exceptional variety of phase transitions they exhibit. These transitions are usually second-order or weakly first-order (the enthalpy, entropy and volume changes are small at the transition temperature), and so they are characterised by critical phenomena behaviour. One of the first theoretical approaches applied to liquid crystals was to the credit of the person commemorated in this special issue, Professor Alfred Saupe. In conjunction with Professor Wilhelm Maier he developed the so-called Maier–Saupe theory [5–7]. The Maier–Saupe molecular-field approach includes contributions from an attractive potential from an induced dipole moment between adjacent liquid crystal molecules, and predicts the order of the nematic–isotropic (N–I) phase transition.

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According to the Maier–Saupe theory the N–I phase transition results from competition between thermally excited forces which tend to destroy the orientational order, and molecular-field forces tending to align the molecular axes. In a molecular-field approach the order parameter is spatially constant and fluctuations are not important. The free energy density expansion in powers of the order parameter is considered up to the sixth power and, due to the cubic term, the N–I phase transition must be first-order in nature. Due to fluctuations of the nematic order parameter this cubic term may become very small, and consequently the N–I transition could become second-order in nature. The fluid-like model [8–10] establishes a hypothetical critical region around the N–I transition temperature (T_{NI}) at which the molecular-field approach is not applicable. The temperature limits of such a region are denoted as T^* and T^{**}, corresponding to the metastable limits of the I and N phases, respectively. It is evident that a second-order transition implies that the cubic term should identically be zero and $T^* = T^{**} = T_{NI}$, but this has not been confirmed experimentally. Small values of the cubic term can also be caused by molecular biaxiality [11, 12], in fact Professor Saupe has been one of the pioneers in studying experimentally this phenomenon by analysing the critical behaviour of the nematic biaxial to nematic uniaxial phase transition in mixtures of lyotropic nematics [13–16].

Later McMillan [17] and Kobayashi [18], working independently on the basis of the Maier–Saupe theory, developed a molecular-field theory according to which the smectic A-to-nematic (SmA–N) phase transition could be either first- or second-order in nature, depending on the nematic range, namely, the temperature width of the nematic phase. Almost at the same time, de Gennes [19] suggested that the SmA–N transition should belong to the 3D–XY universality class ($d = 3$ is the dimensionality of the system and $n = 2$, or XY is the symmetry of the smectic order parameter, involving the amplitude and the phase of a density wave). The MKG theory (after McMillan, Kobayashi and de Gennes) predicts a crossover behaviour between the 3D–XY universality class, identical to that of the superfluid-to-normal liquid transition in helium and also to the conductor–superconductor transition in certain systems. The coupling of the nematic and smectic order parameters in the SmA–N transition can be parametrised by the nematic range, in terms of the McMillan ratio (T_{NI}/T_{SmAN}), where T_{SmAN} is the SmA–N transition temperature. In contrast, Halperin, Lubensky and Ma [20, 21] suggested that this transition is always weakly first-order in nature; this is known as the HLM theory.

If the crossover behaviour of phase transitions near multicritical points is to be analysed in liquid crystalline systems, it is necessary to control the coupling of the order parameters involved. Essentially, this could be achieved by two alternative approaches: (a) by means of mixtures of compounds [22–28], or (b) by means of an external field which couples with and perturbs the liquid crystalline system.

With respect to the first method the phase diagram, and therefore the temperature ranges of the mesophases, are composition-dependent. Regarding (b), the change of the coupling by the application of some perturbing field, possibilities widely explored [29–55] include either the confinement of the liquid crystal in a restrictive porous structure, or through the dispersion of nanoparticles in the liquid crystal, which induces a decoupling mechanism among the order parameters capable of changing the critical behaviour of the bulk material.

In the summer of 1990 one of the present authors, Daniel Finotello, had dinner with his neighbour Alfred Saupe at Peter Palffy-Muhoray's home. At that time we had begun studies of confined liquid crystals, specifically NMR studies of 4-pentyl-4′-cyanobiphenyl (5CB) in Nuclepore membranes. Nuclepore membranes, and later Anopore membranes, were introduced by Finotello to the liquid crystal community based on his prior work on the helium superfluid transition. The NMR studies [29] involved Crawford, then a graduate student, Yang, a post-doctoral researcher, Zumer, a visiting scientist, Doane, Director of the Liquid Crystal Institute at Kent State, and Finotello himself. In these studies, reductions in the nematic-to-isotropic transition temperature in comparison with the bulk material were attributed to the different liquid crystal alignment exhibited within the porous media, dependent on the surface-to-liquid crystal interaction. Different liquid crystal alignments were obtained by means of surface coating with surfactants such as lecithin or aliphatic acids prior to imbedding the liquid crystal material in the porous media.

Saupe considered this situation, and then asked: ‘How do you know, since your NMR studies are not sensitive to the surfactant, that some of it is not detaching from the surface, thus contaminating the liquid crystal? It is well-known that impurities decrease the transition temperature.’ The immediate reply was that the amount of surfactant used was quite small and therefore unlikely to cause temperature shifts approaching one degree. Saupe appreciated the answer but was not entirely convinced, and felt that a more stringent test was needed. Following a lengthy and illuminating discussion, Finotello decided that proof could be established simply by adding different doses of surfactant to the bulk material and measuring the transition shift. This was carried out, and Iannacchione and Finotello presented a poster at the 4th International Topical Meeting on the Optics of Liquid Crystals (OLC91) in Cocoa Beach [31]: huge amounts of lecithin were needed to reproduce the transition shifts detected in the confined systems.

In the present paper, rather than summarising the results of other confined liquid crystal studies, it has been decided to present more recent work. This testifies to the vitality of the field even two decades later. The current studies indicate that new effects may still be uncovered, and that to obtain a complete and fundamental understanding of these phenomena further studies are still required. In particular, it has been reported recently [56] that the liquid crystal 4-nonyloxy-4′-cyanobiphenyl (9OCB) exhibits both SmA and N mesophases, and thus the corresponding SmA–N and N–I phase transitions, where $T_{SmAN} = 351.08$ K and $T_{NI} = 353.2$ K, yielding a nematic range of just 2.14 K. In that study it was shown not only that the N–I phase transition was first-order in nature, but also that the SmA–N transition was very weakly first-order. Consequently, a further question could be posed: would a slightly restrictive confinement drive these phase transitions to second-order? The answer to the previous question was addressed through an exhaustive experimental investigation which included dielectric as well as thermal measurements, the details of which have been published elsewhere [55, 56]. As a humble tribute to the outstanding scientific career of Professor Alfred Saupe we are honoured to summarise this recent work in the present review.

The paper is organised as follows. In Section 2 the experimental details are summarised, and in Section 3 the calorimetric and dielectric results are presented for both bulk and axially confined 9OCB through the N–I and SmA–N phase transitions. Finally, in Section 4 the main conclusions of the work are discussed.

2. Experimental

2.1 *Liquid crystal material*

The pure compound 9OCB was synthesised and purified by Professor Dabrowsky at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. Its purity was stated to be above 99.9% and no further purification was conducted. The liquid crystal was confined to Anopore membranes which consisted of a high purity Al_2O_3 matrix with 200 nm diameter cylindrical pores, these being more or less parallel through the 60 μm thickness of the membrane.

2.2 *Confined sample preparation*

As described in previous investigations [52–54], Anopore membranes were cut into discs about 5 mm in diameter and subjected to a thorough cleaning process [52]. The discs were immersed without surface treatment in an isotropic bath of 9OCB for about 2 h. The membranes filled with liquid crystal were carefully dried and the excess removed from the outer surface. Each disc contained 0.8–0.9 mg of 9OCB, giving an average filling factor of about 85%, similar to that obtained in previous studies [52–54]. As found in similar confined systems, the molecular configuration of confined 9OCB without surface treatment was axial, in other words the molecules tended to be aligned parallel to the pore axis.

2.3 *Specific heat measurements*

Static specific heat data at constant pressure were obtained through the modulated differential scanning calorimetry (MDSC) technique using commercial TA Instruments DSC 2920, of which extensive details are given elsewhere [55–57]. Similar to an AC calorimeter, the MDSC technique, in addition to the specific heat data, simultaneously provides phase shift data (δ) which allow the determination of the coexistence region at weakly first-order transitions. The experimental conditions were adjusted so that the phase delay ($\delta = (\pi/2) - \Phi$) between the heat flow rate (the response to the perturbation) and the induced temperature oscillations (perturbation) was almost zero away from the phase transition, and the imaginary part of the complex specific heat data vanished; essentially, one is sensitive to the real element of the specific heat. Similarly, by means of a special calibration procedure in which very precise latent heat data measured for other homologous compounds using adiabatic calorimetry, the MDSC technique allows quantitative measurements of the latent heat of first-order transitions, even when the values are very small.

Typically, measurements were performed on cooling from the isotropic phase down to the Smetic A mesophase and then on heating; the rate of temperature change in both cases was 0.01 K min^{-1}, with a modulation temperature amplitude (temperature oscillations) of ±0.035 K and a period of 25 s.

2.4 *Dielectric measurements*

Measurements of the dielectric permittivity, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, in the range 10^2 to 1.8×10^9 Hz, were performed using two impedance analysers, HP 4192A and HP 4291A. The cell consisted of two gold-plated brass electrodes (diameter 5 mm) separated by silica spacers (in the bulk system) or by the

Anopore membrane (in the confined system), making a plane capacitor of about either 50 or 60 μm thick, respectively. A modified HP 16091A coaxial test fixture was used as the sample holder. It was held in a cryostat made by Novocontrol, both temperature and dielectric measurements being computer controlled. Two different alignments of the sample in the plane capacitor were considered for bulk 9OCB: parallel (director parallel to the probing electric field) and perpendicular (director perpendicular to the probing electric field). For the parallel alignment, no treatment of the electrodes was necessary, even if a DC bias voltage was not present. To obtain perpendicular alignment, both metal electrodes were originally spin-coated with PI2555 polyamide (HD Microsystems) following the procedure described by the manufacturer; they were later rubbed uniaxially to obtain the required perpendicular alignment of the director. Although polyamide layers are very thin, they contribute to the measured capacity in such a way that a correction procedure is necessary. To determine the dielectric permittivities in the bulk and in the confined geometries, the residual high frequency permittivities in the isotropic phase can be compared by means of a rescaling factor R, defined as the ratio between $\varepsilon_{\infty,\mathrm{bulk}}$ and $\varepsilon_{\infty,\mathrm{app}}$. Additional details of the technique are given elsewhere [52–54].

Finally, dielectric measurements were performed on heating and on cooling, with stabilisation at different temperature steps and a temperature control of the order of 20 mK.

3. Results and discussion

3.1 *Specific heat measurements*

Specific heat data for the N–I and SmA–N phase transitions in bulk 9OCB were published a few years ago by some of the authors of the present review [57] and were later analysed quantitatively [56]. Subsequently, calorimetric studies of the 9OCB confined to untreated Anopore membranes were conducted and analysed [55]. The results of these studies are presented in Figures 1 and 2, which show the specific heat together with the δ phase shift data in a region of ±2 K around both the N–I and the SmA–N phase transitions, respectively. The phase shift was used to identify (and thus exclude points) both coexistence regions for first-order phase transitions; the coexistence regions are represented by the shaded areas in both figures.

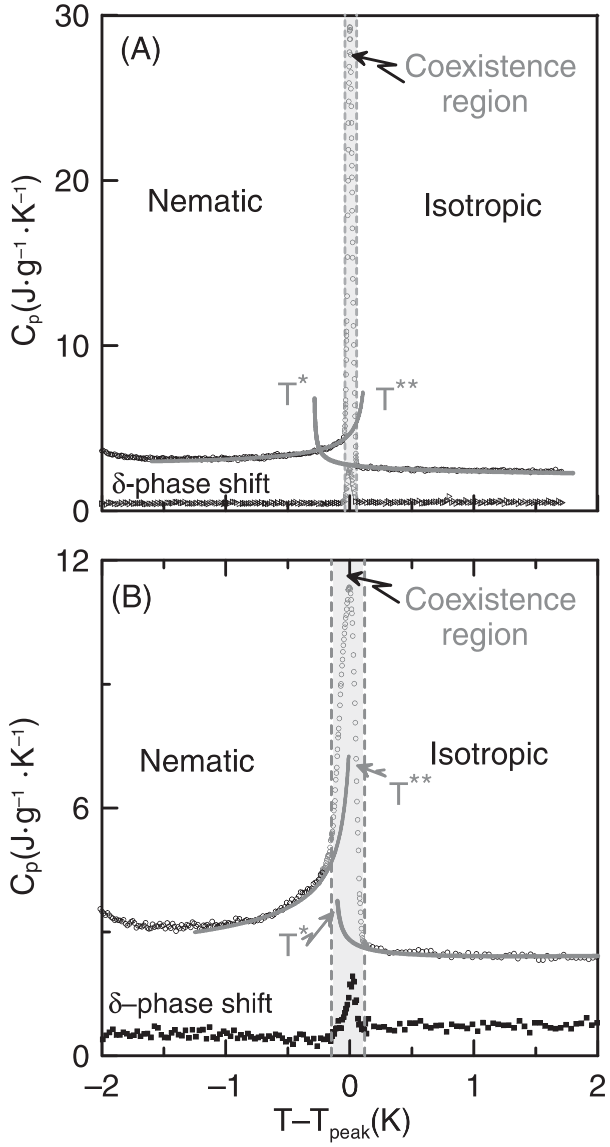

Figure 1. Specific heat data in the vicinity of the N–I phase transition for bulk 9OCB (A) and axially confined 9OCB (B) versus (T – T_{peak}). δ phase shift data are included to delimit the coexistence region (shaded area). Grey-solid lines are fits using Equations (1a) and (1b).

In each of these figures, the behaviour of the bulk and axially confined samples through the transitions are compared. Figure 1 clearly reveals how the temperature width of the coexistence region around the N–I phase transition increases with Anopore confinement. In addition, from the δ phase shift data also shown, and as confirmed by the peak at the transition, it can be concluded that the N–I is a first-order phase transition.

A quantitative analysis of the N–I phase transition for the bulk and the confined system is also presented in Figure 1. The specific heat data for these first-order phase transitions were analysed in a region about ±3 K within the transition temperatures and after excluding data in the coexistence region. We have used the standard expressions [11, 33, 52, 55–56]:

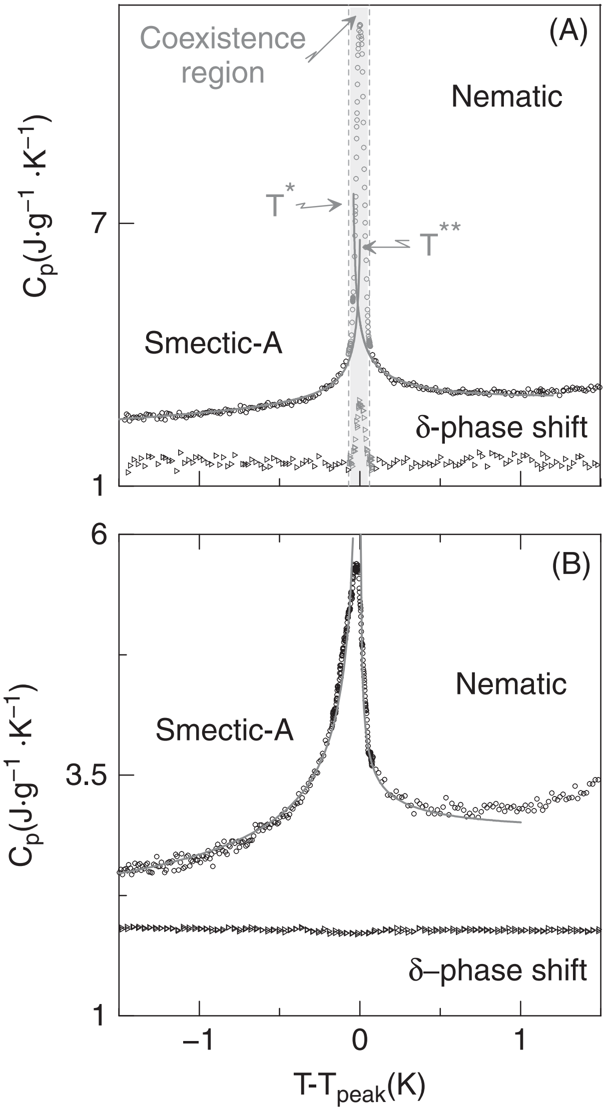

Figure 2. Specific heat data bracketing the SmA–N phase transition for bulk 9OCB (A) and axially confined 9OCB (B) versus ($T - T_{\text{peak}}$). δ phase shift data for the bulk are included to delimit the coexistence region (shaded area). Grey-solid lines are fits according to Equations (1a) and (1b) (A), and Equations (2a) and (2b) (B).

$$C_{p,H} = B_C + D_C\left[\frac{T}{T^*} - 1\right] + A_{C,H}\left|\frac{T}{T^*} - 1\right|^{-\alpha} \quad (1a)$$

$$C_{p,L} = B_C + D_C\left[\frac{T}{T^{**}} - 1\right] + A_{C,L}\left|\frac{T}{T^{**}} - 1\right|^{-\alpha} \quad (1b)$$

where the subscripts H and L refer to the phases above and below the transition, respectively.

As noted earlier, the temperatures T^* and T^{**} define the limits of the metastability of the phases above and below the transition, respectively; α is the specific heat critical exponent, which should be about 0.5 according to the tricritical hypothesis. $A_{C,H}$ and $A_{C,L}$ are the amplitudes above and below the transition, respectively, and B_C and D_C account for the specific heat non-singular background. Common parameters in both phases (B_C, D_C and α) were simultaneously refined after a previous independent fit.

The fitted value for the critical exponent of both bulk and axially confined samples at the N–I transition is that corresponding to the tricritical value, $\alpha = 0.50$, within experimental error. Evidently, under axial confinement the first-order character of the N–I phase transition is unaltered; however, parameters such as (T^{**}–T^*) or the amplitude ratio ($A_{C,L}/A_{C,H}$) are affected.

Firstly, there is a downward shift in the specific heat transition temperature: T_{NI} shifts from 353.22 K in the bulk system to 352.33 K in the confined system. This downward temperature shift at the transition may be the result of two different effects, one due to surface-induced order which tends to increase the transition temperature, and a much stronger disordering effect from the elastic forces which tend to decrease the transition temperature. Secondly, the magnitude of the specific heat peak decreases in apparent height (the peak maximum is about 38% that of the bulk) and is also somewhat broadened under the confinement. The broadening of the specific heat peak is due to the formation of an induced nematic layer growing at the surface of the confining pores. Finally, the overall critical behaviour is also somehow perturbed, as is observed from an increase in the width of the coexistence region as well as by a smaller region of metastability, T^{**}–T^*, which decreases from 0.43 K in the bulk to 0.21 K in the confined system.

Experimental results and the quantitative analysis for the SmA–N phase transitions are shown in Figure 2. For the bulk system, the analysis was performed by the use of both Equations (1a) and (1b). The specific heat and δ phase shift data, together with the fitting results, are shown in Figure 2A. This phase transition is shown to be first-order, as there is a coexistence region and the critical exponent, α, is again found to be 0.50, within experimental error. Comparing with the N–I phase transition, both in bulk and in the confined 9OCB, this SmA–N transition appears to be more weakly first-order in nature, as the latent heat and the volume jump indicate [56]. The specific heat and δ phase shift data for the axially confined 9OCB are shown in Figure 2B.

A quantitative analysis of these results using Equations (1a) and (1b) does not yield reliable results.

Specifically, a major difference in the confined transition as compared to that of the bulk is the absence of any signature in the δ phase shift evolution through the phase transition, making it impossible to determine whether a coexistence region exists. This fact could be an indication of a confinement-induced change in the order of the transition.

Towards this end, the confined specific heat data are now re-analysed according to the renormalisation-group expressions:

$$C_{p,N} = B_C + D_C\left[\frac{T}{T_C} - 1\right] + A_{C,N}\left|\frac{T}{T_C} - 1\right|^{-\alpha}\left[1 + E_{C,N}\left|\frac{T}{T_C} - 1\right|^{-0.5}\right] \quad (2a)$$

and

$$C_{p,S} = B_C + D_C\left[\frac{T}{T_C} - 1\right] + A_{C,S}\left|\frac{T}{T_C} - 1\right|^{-\alpha}\left[1 + E_{C,S}\left|\frac{T}{T_C} - 1\right|^{-0.5}\right]. \quad (2b)$$

In Equations (2a) and (2b), a correction term depending on the parameters $E_{C,N}$ and $E_{C,I}$, has been added and T^* and T^{**}, which must coincide, have been substituted by the critical temperature, T_C. Ranges of data spanning about 2 K in the SmA phase and about 0.7 K in the N phase have been used in Equations (2a) and (2b) to fit the SmA and N sides, respectively. As performed for the other phase transitions, common parameters in both phases (B_C, D_C, T_C and α) were adjusted simultaneously after a previous independent fitting. Through such a fitting procedure, a critical exponent of 0.45 (±0.02), which may be interpreted as that the SmA–N phase transition of the confined system is becoming second-order in nature, and beginning to show a crossover behaviour from tricritical ($\alpha = 0.5$) to the 3D–XY universality class, where $\alpha = -0.007$. While such a crossover has been observed under an interconnected type of confinement, this would be the first time, to the present authors' knowledge, that the well-defined restrictive cylindrical Anopore axial confinement is able to drive a very weak first-order transition to second-order. Finally, it should also be noted that, as for the N–I transition, there is a downward shift in transition temperature (from 351.08 K to 350.28 K) and that the specific heat peak is broadened by the confinement.

3.2 *Dielectric permittivity study*

A thorough and systematic analysis of the static dielectric permittivity and its critical behaviour in bulk [56] and confined 9OCB [55] has recently been published; the emphasis will here focus on the critical behaviour. Figure 3A shows the dependence of the mean static dielectric permittivity, ε, on temperature, referred to the SmA–N transition temperature, T_{SmAN}. Figure 3B shows, on the same scale, the dependence of the derivative of the dielectric permittivity with temperature, calculated by distortion sensitive analysis (smoothed point-by-point derivative) of the original data of the dielectric permittivity.

The critical behaviour analysis procedure has assumed a valid scaling relationship between the specific heat and the recently demonstrated dependence of ε on temperature [56]. Accordingly, the following

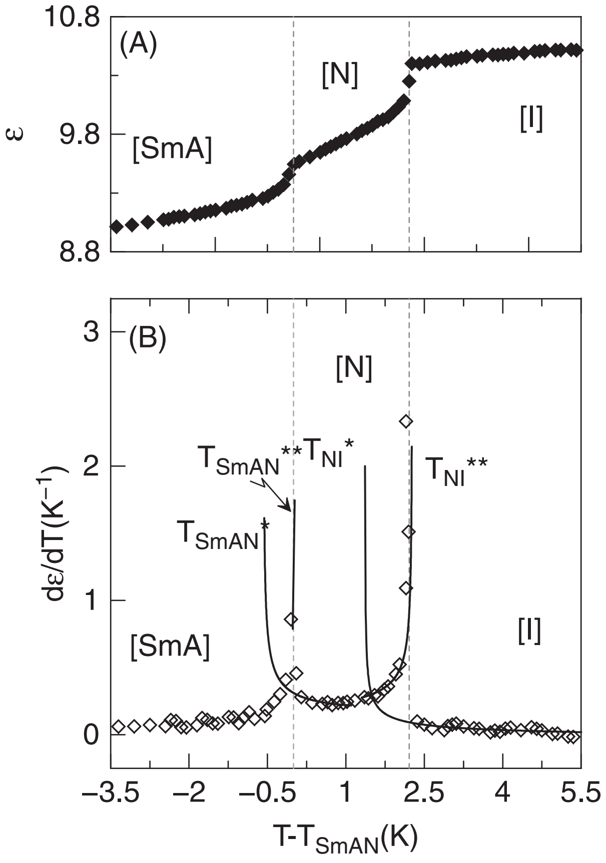

Figure 3. Mean static dielectric permittivity (A) and derivative of the static dielectric permittivity (B) as a function of the shifted temperature (T – T_{SmAN}) for bulk 9OCB. Solid lines are fits to Equations (3a) and (3b).

expressions have been adopted for this relationship for a first-order phase transition:

$$\left(\frac{d\varepsilon}{dT}\right)_H = B_E + D_E\left[\frac{T}{T^*} - 1\right] + A_{E,H}\left|\frac{T}{T^*} - 1\right|^{-\alpha} \quad (3a)$$

and

$$\left(\frac{d\varepsilon}{dT}\right)_L = B_E + D_E\left[\frac{T}{T^{**}} - 1\right] + A_{E,L}\left|\frac{T}{T^{**}} - 1\right|^{-\alpha}. \quad (3b)$$

The parameters in Equations (3a) and (3b) have a similar meaning to those in Equations (1a) and (1b).

Fits according to Equations (3a) and (3b) for bulk at both phase transitions are displayed in Figure 3. It should be stressed that despite the fact that the data showed some scattering inherent in the derivative procedure, the fits are good enough for information to be extracted about the critical behaviour at both phase transitions. As reported from the specific heat results, both N–I and SmA–N phase transitions were first-order in nature, with a critical exponent α of 0.50. With respect to the metastability regions, T^{**}–T^*, the values were 0.91 K for the N–I transition and 0.61 K for the SmA–N transition. These values are larger than those in the specific heat measurements, which may be attributed to the presence of the external electric field as well as to the difference in experimental procedure.

The dielectric study of the critical behaviour on axially confined 9OCB was also based on a scaling relationship between the specific heat data and the absolute value of the derivative of the apparent dielectric permittivity with temperature. Such a scaling relationship has yet to be confirmed experimentally, but its validity may be assumed by comparison with the bulk data. With this in mind, Figure 4 for the confined sample was analogous to Figure 3 for the bulk, and the critical behaviour of the first-order N–I phase transition could be studied by means of Equations (3a) and (3b).

Fits to the data at the N–I phase transition for confined 9OCB yielded a critical exponent 0.50 of α, and a metastability region (T^{**}–T^*) of 1.1 K. Further, under confinement the transition temperature was not shifted with respect to the value for the bulk. The differences in regard to the specific heat measurements may be explained by noting that a stronger ordering was possible here due to the presence of the external electric field; of course, the different experimental procedure between calorimetric and dielectric measurements cannot be neglected.

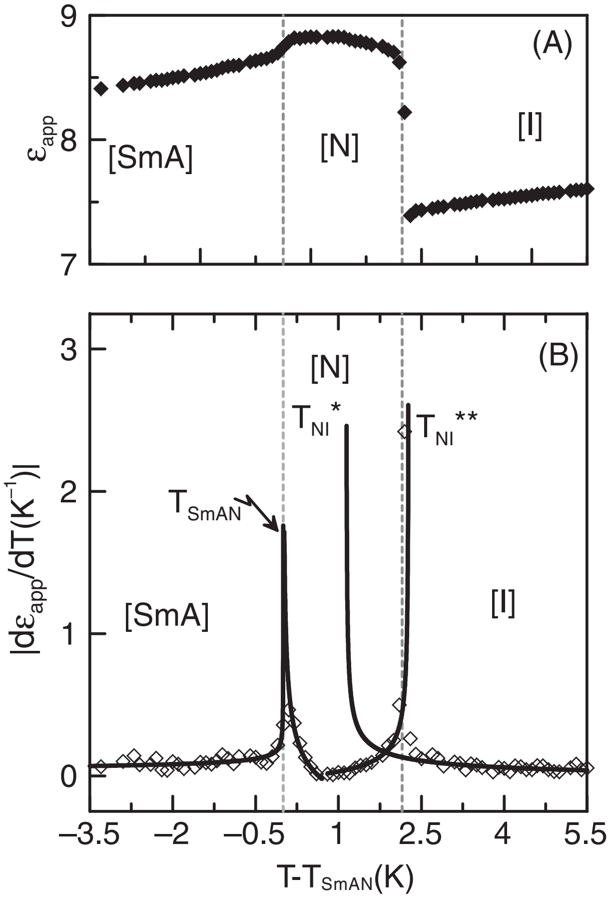

Figure 4. Apparent static dielectric permittivity (A) and absolute value of the derivative of the apparent static dielectric permittivity (B) as a function of the shifted temperature ($T - T_{SmAN}$) for confined 9OCB. Solid lines are fits to Equations (3a) and (3b) for the N–I transition and to Equations (4a) and (4b) for the SmA–N transition.

With regard to the SmA–N phase transition, it was fitted by using the renormalisation group expressions for the specific heat:

$$\left|\frac{d\varepsilon_{app}}{dT}\right|_N = B_E + D_E\left[\frac{T}{T_C} - 1\right] + A_{E,N}\left|\frac{T}{T_C} - 1\right|^{-\alpha} \times \left[1 + E_{E,N}\left|\frac{T}{T_C} - 1\right|^{-0.5}\right] \quad (4a)$$

and

$$\left|\frac{d\varepsilon_{app}}{dT}\right|_S = B_E + D_E\left[\frac{T}{T_C} - 1\right] + A_{E,S}\left|\frac{T}{T_C} - 1\right|^{-\alpha} \times \left[1 + E_{E,S}\left|\frac{T}{T_C} - 1\right|^{-0.5}\right]. \quad (4b)$$

The fitting procedure was similar to that for the specific heat data for the similar phase transition using Equations (2a) and (2b). The fitted value for the critical exponent, α, was found to be 0.45 ($\pm$0.04), which is similar to that obtained from the specific heat measurements. Furthermore, there was no change in the experimental transition temperature under confinement; this was probably influenced by the presence of the electric field and its ordering effects, which counteracted those from the porous surfaces.

4. Concluding remarks

The results of the critical behaviour of the N–I and SmA–N phase transitions of the 9OCB liquid crystal have been summarised, both in bulk and under the slight-restrictive confinement of a sub-micron porous Anopore membrane. The membranes were not treated with surfactant, and the molecules were therefore on average aligned parallel to the axes of the cylindrical pores (axial confinement). The critical behaviour was analysed both for calorimetric and dielectric measurements. The N–I and SmA–N phase transitions, which were weakly first-order in nature for the bulk system, underwent some changes when the liquid crystal was confined.

Regarding the specific heat measurements, the transition temperatures shifted downwards, a consequence of the ordering–disordering competition under confinement, disorder being the more significant. This was not the case in the static dielectric measurements, as the presence of an external electric field changes the ordering–disordering competition, the ordering effects becoming more important.

A similar feature of both kinds of measurements was that the N–I phase transition remained first-order under the influence of the restrictive geometry, while the SmA–N transition was driven to second-order by the confinement. This is suggested by the specific heat critical exponent, α, which decreased from 0.50 in the bulk to 0.45 in the confined system, a value corresponding to a crossover behaviour between the tricritical point and the 3D–XY universality class. The presence of such a crossover is confirmed by the fact that the metastability region, (T^{**}–T^{*}), a characteristic of first-order phase transitions and present in the bulk, disappeared for confined 9OCB. These two results are indicative of the second-order nature of the SmA–N phase transition for the confined sample.

We have also carefully analysed the metastability regions of the N–I phase transition in both bulk and confined 9OCB. According to the specific heat results, the confinement yielded a narrower region, which could indicate that the phase transition, although still first–order, was weaker under the influence of the restrictive geometry. In contrast, by means of the dielectric measurements, this metastability region for the N–I phase transition seemed unaffected, probably due to the scattered values of the dependence of the dielectric permittivity on temperature as well as to the presence of the external electric field.

By using the derivative of the dielectric permittivity, we were able to perform this study of the critical behaviour by means of dielectric measurements, despite the extremely narrow nematic range, and from this analysis we can observe how the SmA–N phase transition becomes second-order as a result of the confinement.

Finally, when combining the slight change in critical exponent and the change in the order of the phase transition, it should be noted that this study may be the first in which a well-defined cylindrical confinement changes the critical exponents from a mean-field-like value to an intermediate value, suggesting a possible crossover to 3D–XY type of behaviour. This could be better verified through confined studies in which the cylindrical pore size could be decreased while retaining uniform parallel pores and an axial cylindrical alignment; such porous materials would need to be created.

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