

Small quartz silica spheres induced disorder in octylcyanobiphenyl (8CB) liquid crystals: A thermal study

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A photopyroelectric technique has been applied to the study of specific heat and thermal conductivity of homeotropically aligned mixtures of small quartz spheres (aerosil) and octylcyanobiphenyl (8CB) with concentration $0 \leq \rho_s \leq 0.04 \text{ g/cm}^3$. Thermal conductivity data show that, even at these very low concentrations, an annealing of the disorder introduced by the aerosil takes place on cooling at the smectic-*A*-nematic (Sm-*A*-*N*) phase transition and not only at the nematic-isotropic (*N*-*I*) one. This means that there is some elastic strain in the nematic phase of the sample which is not quenched. Accordingly the suppression of the *N*-*I* transition temperature as a function of ρ_s does not fit a random field with a random dilution model that accounts for random quenched disorder only. High resolution specific heat measurements at the *A*-*N* and *N*-*I* transition show the effect of the aerosil is not the same. While in the first case its peak is suppressed with increasing concentration, in the second case there are some indications that outside the two-phase coexistence region it is enhanced. The effect of surface-induced alignment is also discussed to explain some discrepancies between our data and the ones reported in literature. It is concluded that the amount of disorder in the sample does not depend on ρ_s only, but also on other variables such as external fields. Finally, a relaxation phenomenon in the aerosil network that partially compensates the disordering effect of the particles is suggested to explain the concentration dependence of the transition temperatures.

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I. INTRODUCTION

Considerable attention has been paid in recent years to the study of random disorder in liquid crystals (LC) [1]. A variety of techniques have been used to study the physical properties of LC confined in randomly interconnected porous media such as aerogel [2,3] or noninterconnected anisotropic Millipore membranes [4]. More recently [5–9] it has been shown that confinement can be also achieved via a dispersion of small silica spheres (aerosil) in LC which produces a gel if their concentration, $\rho_s = (m_s/m_{LC})\rho_{LC} \sim (m_s/m_{LC})1 \text{ g/cm}^3$, where the suffixes *s* refer to silica, is larger than 0.01 g/cm^3 . This is due to the hydroxyl groups on the particle surface that induce hydrogen bonding among particles. Moreover, the hydrophilic coating produces a strong homeotropic anchoring of polar LC molecules at the surface that, in the ordered phases, can be regarded as a distortion of the local orientation and therefore as induced random disorder. With increasing ρ_s ($< 0.1 \text{ g/cm}^3$) the gel becomes stiffer and stiffer and, being the induced disorder more fully quenched, it resembles the rigid aerogel structure. It must be pointed out, however, that an aerogel+LC sample of a given ρ_s is more rigid than a mixture of LC+aerosil with the same ρ_s and it therefore contains more quenched elastic strain (ES), which affects its properties, as shown in Ref. [9].

The situation is completely different at low ρ_s ($< 0.1 \text{ g/cm}^3$) where the gel is soft and the aerosil particles can rearrange themselves to reduce the ES in the system. It has been proposed [9] that in this regime the ES is partially annealed.

According to this hypothesis a random field (RF) model with random dilution (RD) has been considered a viable approximation for these mixtures [9]. Some recent results [10]

on a mixture with $\rho_s = 0.005 \text{ g/cm}^3$ have shown that, even at this very low concentration, some not quenched ES is present in the nematic phase of octylcyanobiphenyl (8CB) after cooling from the *I* phase and an annealing takes place at the smectic-*A*-nematic (Sm-*A*-*N*) transition also. Doubts have therefore been raised on the applicability of the RF (RD) model to these mixtures with low ρ_s .

It turns out from what was stated before, that the physical mechanisms associated with the generation and the evolution of the disorder in mixtures of aerosil and LC at low ρ_s are far from being fully understood. A deeper understanding of the dynamics of ES can have very important consequences in the study of LC physics as recently suggested [11] by some theoretical and experimental results, showing that even a very low amount of quenched disorder destroys long-range order and that the residual order is short ranged. This can open new scenarios in many fields and in particular in LC phase transition studies.

In this paper we report on photopyroelectric measurements of homeotropically aligned aerosil dispersions in 8CB LC with ρ_s ranging from 0.005 to 0.04 g/cm^3 . It is shown that the decrease of the transition temperatures at the Sm-*A*-*N* (T_{A-N}) and *N*-*I* (T_{N-I}) transitions with increasing ρ_s disagrees with the RF (RD) model predictions. The specific heat (*c*) and the thermal conductivity (*k*) have been derived from the experimental results. The *c* data at the *A*-*N* transition are in a very good agreement with the data reported in Ref. [9] and show a suppression of the specific heat peak and a decrease of the critical exponent α as ρ_s is increased. On the contrary, there are some indications in our data suggesting that the specific heat values close to the *N*-*I* transition, but outside the two-phase coexistence region, increase for increasing ρ_s . Some contradictory results are re-

ported in the literature [5,9] on this issue and this is probably due to the difficulties in obtaining reliable specific heat values in the temperature region where the N and I phases coexist. Our data seem to suggest that the coexistence region in our samples is narrower than the one found in Ref. [9] and this is probably due to the presence in our samples of surface-induced alignment. The thermal conductivity data show, for all mixtures, a hysteresis similar to the one reported in Ref. [10] for the mixture with $\rho_s = 0.005 \text{ g/cm}^3$ and therefore confirm that the ES present in the sample is not completely annealed at the N - I transition if the sample is cooled down from the I phase. It is also shown that the increase of orientational order with decreasing temperatures has approximately the same temperature dependence for all mixtures on heating from the smectic- A phase, though it is affected by the not annealed ES on cooling from the I phase. Finally the mechanisms associated with the disorder introduced by the aerosil particles are discussed and a tentative explanation of the observed behavior of the transition temperatures and thermal conductivities as a function of ρ_s is given.

II. EXPERIMENT

The hydrophilic aerosil particles we have used have a diameter of approximately 7 nm [12]. They have been mixed with a solvent-diluted 8CB and the mixture was put in an ultrasound bath for one night. During this period the solvent was allowed to evaporate and, to complete this process, the mixture was heated to about 50 °C for 12 h in vacuum.

A standard back detection photopyroelectric (PPE) setup [13] has been used for the measurements, with the sample, 30 μm thick, sandwiched between the pyroelectric transducer and a glass plate. A temperature oscillation ($\sim 1 \text{ mK}$) was produced on one side of the LC and detected by the transducer on the opposite one. Measurements were performed in the optically opaque and thermally thick regime in which the amplitude and the phase of the photopyroelectric (PPE) signal are given for a homogeneous sample by [14]

$$|V| \propto \frac{1}{\sqrt{1 + (2\pi f \tau_e)^2}} \frac{e^{-\sqrt{\pi f/D} l_s}}{(e_s/e_p + 1)}, \quad (1)$$

$$\varphi = -\arctan(2\pi f \tau_e) - \sqrt{\pi f/D} l_s, \quad (2)$$

where f is the frequency of the temperature oscillation, l_s is the sample thickness, $1/2\pi\tau_e$ is the transducer plus detection electronic cutoff frequency, $D = k/\rho c$ is the sample thermal diffusivity, and $e_{s,p} = \sqrt{\rho c k}_{s,p}$ are the thermal effusivities of the sample and transducer, respectively.

The two surfaces in contact with the LC have been treated with a trimethylcetylammmonium bromide solution in chloroform which induces homeotropic alignment. The sample cell was put in an oven with a temperature rate change that was approximately 10 mK/min for measurements on a wide temperature range and 1 mK/min for high resolution runs close to the phase transitions.

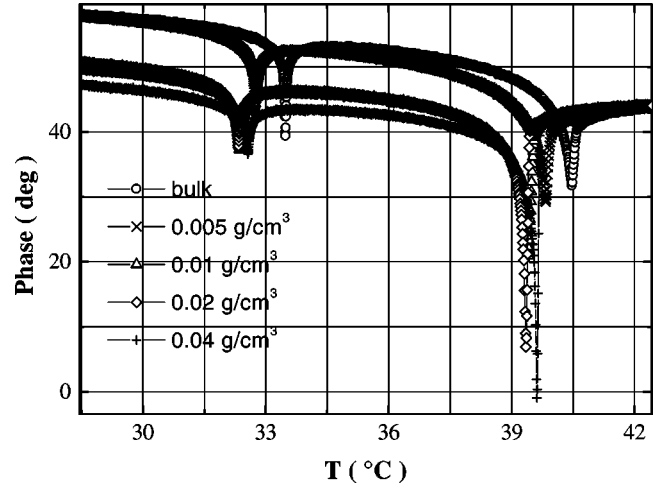


FIG. 1. PPE phase for bulk 8CB and mixtures as a function of temperature.

III. RESULTS

A. Transition temperatures

Figure 1 shows the PPE signal phase as a function of temperature for bulk 8CB and four mixtures with ρ_s ranging from 0.005 to 0.04 g/cm^3 for $f \gg 1/2\pi\tau_e$. The PPE phase, in our measurements, is proportional to the sample thermal diffusivity [Eq. (2)], but this is not true close to T_{N-I} . This is due to the fact that the N - I is well known to be a weakly first-order phase transition and there is, therefore, a temperature region close to T_{N-I} in which the nematic and the isotropic phases coexist. The sample is not homogeneous in this region and the above described model, which allows the determination of the thermal parameters from the PPE signal amplitude and phase, cannot be applied.

The two dips present in each curve represent the A - N and the N - I transitions and assuming that the two minima correspond to T_{N-I} and T_{A-N} respectively, it turns out, as expected, that the two transition temperatures are lower in the mixtures than in the bulk.

In Fig. 2 the transition temperatures vs ρ_s are reported. Both T_{A-N} and T_{N-I} rapidly decrease for $0 \leq \rho_s$

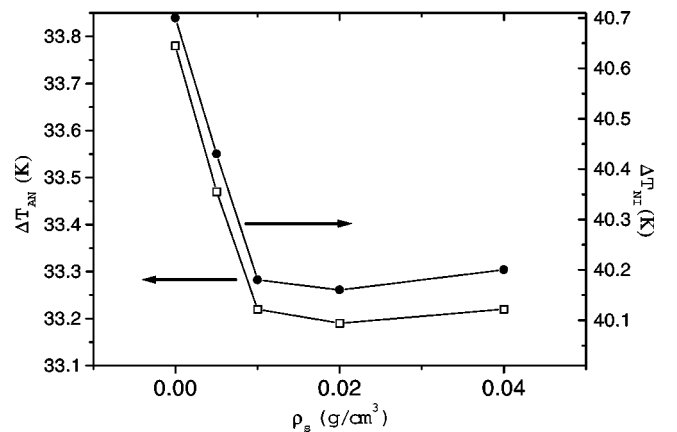


FIG. 2. A - N and N - I transition temperatures as a function of aerosil concentration.

≤ 0.01 g/cm³, slightly decrease for $0.01 \leq \rho_s \leq 0.02$ g/cm³ but then increase for $\rho_s > 0.02$ g/cm³. A similar behavior has been observed in Ref. [9] where, however, the increase after the initial decrease of T_{A-N} and T_{N-I} was observed for $\rho_s > 0.052$ g/cm³ and was followed by a monotonous decrease for $\rho_s > 0.092$ g/cm³. The measurements in Ref. [9] have been performed in mixtures with $0.022 \leq \rho_s \leq 0.436$ g/cm³, while in our case, due to the characteristics of our technique that have been in Ref. [10], we have focused our attention on mixtures with low ρ_s . Nevertheless, a comparison between the transition temperature shifts we have obtained for samples with $\rho_s = 0.02$ and 0.04 g/cm³ and the ones obtained in Ref. [9] for samples with $\rho_s = 0.022$ and 0.052 g/cm³ can be attempted. In our case we have obtained a downshift for T_{N-I} and T_{A-N} that are 0.54 and 0.59 K for $\rho_s = 0.02$ g/cm³ and 0.50 and 0.54 K for $\rho_s = 0.04$ g/cm³. These values are in all cases smaller than the ones reported in Ref. [9] which are 0.79 and 0.75 K for $\rho_s = 0.022$ g/cm³ and 0.94 and 0.85 K for $\rho_s = 0.052$ g/cm³, respectively. Such a disagreement cannot be due, in our opinion, to the difference in the concentrations in the two cases. A possible explanation for the different results we have obtained could be due, as discussed later on, to the fact that our samples are aligned, while the ones in Ref. [9] are not.

It has been suggested [9] that the temperature shifts for low ρ_s mixtures appear to be described in a random field (RF) with a random dilution (RD) model, even though this can be regarded as an approximation and more realistic theories are needed. The basic idea of this model is the following. Because of the hydrophilic layer covering the aerosil, LC molecules are aligned perpendicular to the almost spherical particle surface. Since this is a strong anchoring, those molecules having a different orientation with respect to the director can be considered as the sources of quenched random disorder in the sample. Using a mean field approach, it has been obtained [9] that the depression of T_{N-I} is given by

$$T_{N-I}(p) = T_{N-I}(0)(1-p), \quad (3)$$

where $T_{N-I}(0)$ is the transition temperature of the bulk material while p represents the fraction of quenched LC that has been estimated by assuming around each aerosil particle there is a spherical shell of the thickness of one molecular length l and that in the case of 8CB three is approximately 20 Å of quenched disorder. Considering that the specific area covered by hydroxyl groups has been found to be $a = 0.3$ cm²/g [9], and taking into account the density of the aerosil particles, it turns out that $p = la\rho_s = p'\rho_s \sim 0.6\rho_s$.

Some doubts have been raised, however, on the description of aerosil+LC mixtures in terms of the RF (RD) model [10]. It has been experimentally shown, even for a very low concentration ($\rho_s = 0.005$ g/cm³) that the T_{N-I} depression is much smaller than the one predicted by the model [10]. Moreover, it has been found that, at the same concentration, there is some disorder in the nematic phase which is not quenched as shown by the annealing process found at T_{A-N} .

The data reported in Fig. 2 allow an experimental verification of Eq. (3) and also a more accurate determination of the p' ($=p/\rho_s$) value. An approximately linear dependence

between $T_{N-I}(p)$ and ρ_s has been found, as shown in Fig. 2, in the range $0 \leq \rho_s \leq 0.01$ g/cm³ and this seems to agree with what is predicted by Eq. (3). If we calculate the slope $p'T_{N-I}(0) = -\Delta T_{N-I}/\Delta\rho_s$ of the curve, however, in the same range, we get $p' \sim 0.17$, which means that the T_{N-I} suppression with increasing ρ_s is less steep than the one suggested in Ref. [9].

A possible reason for such a small value could be due to the clustering of aerosil particles that at this concentration, are known to form strands that for $\rho_s > 0.01$ g/cm³ are interconnected to give rise to a soft gel. The $p \sim 0.6\rho_s$ relation has been obtained considering that the surface area which induces quenched disorder in the LC is approximately the sum of the surface area of all the aerosil particles present in the sample. Due to the above-mentioned clustering, the aerosil area available for quenching the LC molecules could be smaller and therefore the amount of quenched material is reduced. This essentially means that the specific area a could be smaller than 0.3 cm²/g. We do not believe, however, that such an effect can account for the p' value we have found.

We should also consider the possibility that the surface-induced alignment induces some ordering of the aerosil strands or network. If, for the sake of simplicity, we consider the case of mixtures below the gelation threshold, then, under the effect of the aligning field, they tend to align perpendicular to the director. With respect to the zero field case in which the strands are randomly oriented, the fraction of molecules in the spherical shell around each silica particle that has a different orientation with respect to the direction of the aligning field and gives rise to quenched disorder could be smaller. This should cause a reduction of the p' value that, again, can hardly justify the obtained results.

We have restricted the analysis reported above to T_{N-I} only because the proposed RF (RD) model uses a mean field approach, which is known to be not applicable to the $A-N$ transition. On the other hand, the similarity between the T_{N-I} and T_{A-N} behavior as a function of ρ_s seems to envisage some common physical aspects in the two cases that the theoretical description should consider.

We believe that this small value of p' , despite the linear dependence found between T_{N-I} and ρ_s for $0 \leq \rho_s \leq 0.01$ g/cm³, gives an additional indication that the proposed RF (RD) model could not be appropriate to describe the behavior of the mixtures. A more accurate theoretical description, which considers not only quenched disorder but, as we shall see later on, also some residual ES in the ordered phases of low ρ_s mixtures, is therefore needed. Some indications in this direction can be found in the theoretical and experimental results obtained in nematic elastomers [15], where elastic effects have been included in the RF model or in the theory of Bragg glasses [16].

Apart from the above-mentioned downshift of the phase transition temperatures, it is clearly evident from Fig. 1 that the effect of the aerosil particles is not the same at the $A-N$ and $N-I$ transitions. An increase of ρ_s produces a suppression of the dip in the PPE phase at T_{A-N} , while the one at T_{N-I} becomes more pronounced. This last feature is somewhat surprising and seems to indicate that the effect of the disorder introduced in the sample by the aerosil is not the usual

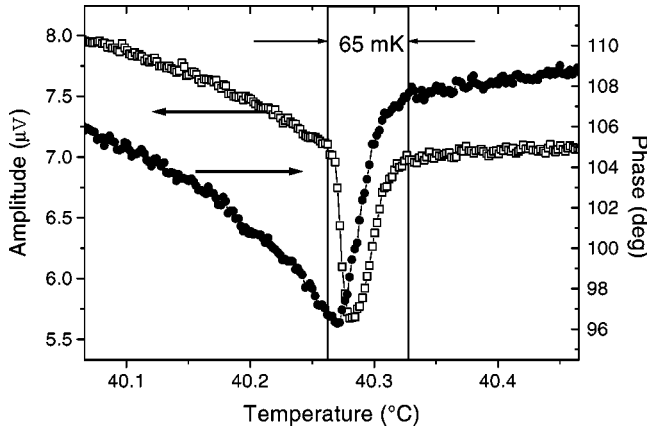


FIG. 3. PPE amplitude and phase for bulk 8CB as a function of temperature at the $N-I$ transition.

one that normally produces a suppression of the anomalies at the transition temperatures as in the case of the $A-N$ one, but it induces some other physical effects. Before any attempt to clarify these aspects, it could be interesting to understand if the temperature region in which the dip increases at T_{N-I} is contained or not in the two-phase coexistence region. If this is the case, in fact, the explanation of the above-mentioned behavior at T_{N-I} could be very complicated and not easily compared to the one at T_{A-N} , where no coexistence region is present. It is well known that ac calorimetry does not allow any direct measurement of the width of this region and in the following we shall try to overcome, at least qualitatively, this limitation.

Figure 3 shows high resolution PPE signal amplitude and phase, measured simultaneously, of pure 8CB close to T_{N-I} . The phase minimum is at approximately 10 mK below the amplitude one. A similar effect has been detected at the $N-I$ transitions of all the investigated mixtures, but also at first-order phase transitions of other liquid crystals. At the $A-N$ transition, on the other hand, the two minima almost coincide and the above-mentioned effect can be therefore possibly related to the presence of latent heat. At present no quantitative explanation for the above-mentioned results is available and an attempt of theoretical modeling is presently underway.

A change in the slope in the amplitude of the PPE signal below T_{N-I} at $T=313.412$ K and above $T=313.477$ K is clearly evident. If we assume that this drastic change in the temperature dependence is due to the presence of the two-phase coexistence region, then it turns out that this region has a width of 65 mK (vertical lines in Fig. 3), which is in very good agreement with the value of approximately 60 mK found in the literature for 8CB [17].

Applying the same criteria to high resolution measurements of the mixture with $\rho_s=0.02$ g/cm³, we found that $\Delta T(\text{coex})\approx 100$ mK. This value and the values we have found for the other mixtures are systematically smaller than the ones reported in Ref. [9]. As discussed in more details later on, this could be due to the fact that our samples are aligned.

Extending this argument to all the mixtures that have been investigated, it turns out that the temperature region in which

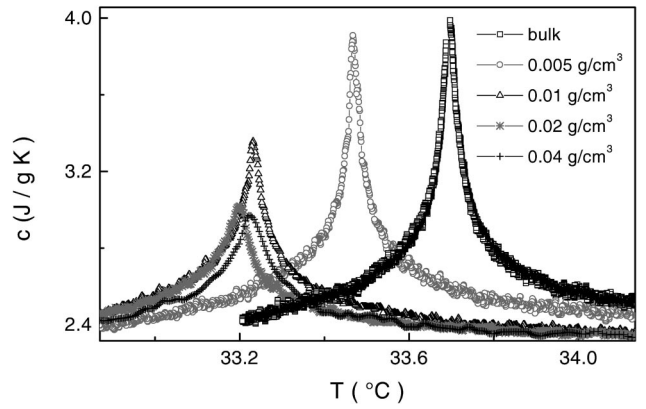


FIG. 4. Specific heat as a function of temperature for bulk 8CB and mixtures.

increases of the dip at T_{N-I} with increasing aerosil concentration have been observed is not completely contained in the coexistence region.

If the analysis reported above is correct, then the coincidence of the PPE signal amplitude and phase at T_{A-N} seems to suggest that the $A-N$ transition is a second-order one. It has been recently proposed [18], however, that it has, in bulk 8CB, a first-order character, but our results cannot rule out this hypothesis due to the very small latent heat that should be involved in the transition. It could well be, in fact, that the resolution of our measurements is too small.

B. Critical behavior of the specific heat

1. $A-N$ transition

Figure 4 shows high resolution specific heat data at the $A-N$ transition for bulk 8CB and for the mixtures. It is clearly evident that by increasing ρ_s , a decrease of the peak value of c and an increase of the rounding close to T_{A-N} takes place. The data have been fitted with the expression

$$c = B + E(T - T_c) + A^\pm |T - T_c|^{-\alpha} (1 + D^\pm |T - T_c|^{0.5}) \quad (4)$$

and the results are reported in Table I. The α values we have obtained are consistent with the ones of Ref. [9] and we show that the critical exponent decreases with increasing aerosil concentration. This behavior is quite similar to the one observed in bulk materials with increasing nematic range [19]. In this case the decrease of the ratio T_{A-N}/T_{N-I} produces a weakening of the coupling of the smectic and nematic order parameter and a crossover to a three-dimensional (3D) XY critical behavior has been observed. Therefore, it has been suggested that the same mechanisms take place in the mixtures where the aerosil particles and the disorder associated with their presence is responsible for the above-mentioned decoupling.

The variation of the A^-/A^+ ratio with increasing concentration is within the statistical uncertainties and its value is in all cases consistent with the bulk one. The same is also true for the D^-/D^+ ratio where T_{A-N}/T_{N-I} does not considerably

TABLE I. Best-fit results obtained fitting the data with Eq. (4).

ρ_s	α	A^-/A^+	D^-/D^+	B	E	T_c	χ_ν
0	0.32 ± 0.01	0.97 ± 0.05	0 ± 1	2.00 ± 0.02	0.20 ± 0.03	306.80 ± 0.01	1.02
0.005	0.31 ± 0.01	1.0 ± 0.2	-0.2 ± 1.1	1.99 ± 0.08	0.096 ± 0.002	306.50 ± 0.04	1.03
0.01	0.27 ± 0.02	1.05 ± 0.29	0.5 ± 0.6	2.05 ± 0.10	0.080 ± 0.001	306.25 ± 0.01	1.03
0.02	0.24 ± 0.01	1.24 ± 0.26	1.19 ± 0.082	2.08 ± 0.06	0.045 ± 0.002	306.23 ± 0.01	1.01
0.04	0.12 ± 0.03	1.16 ± 0.85	-0.58 ± 0.43	1.28 ± 0.41	0.013 ± 0.012	306.26 ± 0.01	1.1

change but the obtained values are, considering the uncertainties, consistent with the value of approximately 1 which is expected for the bulk [20].

The variation of the B and E coefficients are quite small for $0 \leq \rho_s \leq 0.02 \text{ g/cm}^3$, while a significant decrease of both values have been obtained for $\rho_s = 0.04 \text{ g/cm}^3$. These coefficients are connected with the nonsingular background term in the specific heat. We think that this background could be affected by the presence of the aerosil, especially for large concentrations, and this could be the reason for the observed behavior. If we assume, however, as in Ref. [9], that the variation in the background term from mixture to mixture is negligible, then the variation of B is entirely due to its critical part B_C . This leads to the conclusion that B_C decreases with increasing ρ_s as was also found in Ref. [9].

It must be noted that the analysis of the critical behavior of the specific heat becomes more and more difficult with increasing ρ_s as the uncertainties found in the fit of the mixture with $\rho_s = 0.04 \text{ g/cm}^3$ clearly demonstrate. This is essentially due to the suppression of the specific heat peak and also to the rounding. For small concentrations, on the other hand, the differences found in the critical exponent and in the A^-/A^+ ratio could be too small, thus giving a clear indication of the limitation of such measurements for the study of the disorder introduced by the aerosil.

2. $N-I$ transition

Though the results shown in Fig. 1 are in qualitative agreement with the results reported in Ref. [9], there are, however, some discrepancies. The specific heat reported in that paper shows a double peak structure for $\rho_s > 0.022 \text{ g/cm}^3$ that has been attributed to annealed ES (peak at higher temperature) and to ES coarsening with increasing concentration (rounded peak at lower temperature). No double peak structure has been found in our samples and this, as discussed in Ref. [10], could be due to the fact that they are aligned. The surface-induced order can help in reducing the amount of strain in the sample, as was also shown by the smaller depression of the transition temperatures we found with respect to the Ref. [9] temperatures and this could be the reason why we do not find the peak at low temperature.

Using the criteria described above for the evaluation of the width of the two-phase coexistence region, we have calculated the specific heat of the mixture with $\rho_s = 0.04 \text{ g/cm}^3$ outside this region but close to T_{N-I} . We have tried to compare our data for this mixture with the data corresponding to the mixture with $\rho_s \cong 0.052 \text{ g/cm}^3$ reported in

Ref. [9]. We have found that the two data sets almost overlap, apart from the temperature region of the low temperature peak in Ref. [9]. It could be, therefore, that the increase of the coexistence region found in Ref. [9] is mainly due to the presence of some ES which is larger than the one present in our samples.

It is interesting to note that while this conclusion is supported by this last result and also by the smaller downshift of the transition temperatures and the smaller coexistence region close to T_{N-I} , the α critical exponents obtained from the fit of our specific heat data at the $A-N$ phase transition and the critical exponents obtained in Ref. [9] almost coincide. These results clearly indicate that the specific heat critical behavior has a limited sensitivity to the presence of disorder in the sample.

Calculating the specific heat for all the mixtures as for the one with $\rho_s = 0.04 \text{ g/cm}^3$, it turns out that the peak value of c out of the coexistence region increases with increasing ρ_s . This result seems to be consistent with the one reported in Ref. [5], but in contradiction with the one in Ref. [9]. We do not think at this point that, mainly due to the qualitative determination of the coexistence region, any definite conclusion can be drawn on the critical behavior of c close to the $N-I$ transition and more measurements are therefore needed.

C. Thermal conductivity

Figure 5 shows the thermal conductivity vs temperature for a homeotropic and planar bulk samples and for homeotropic mixtures obtained on heating (gray symbols) and on cooling (black symbols). While in the isotropic phase there is

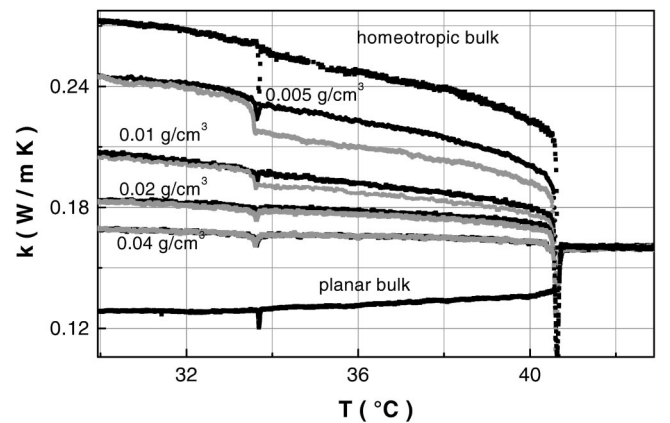


FIG. 5. Thermal conductivity for bulk 8CB (homeotropic and planar) and mixtures (homeotropic).

no significant difference among the various samples, in the nematic and smectic phases the k values of the mixtures are smaller than the homeotropic bulk and larger than the planar one.

It is well known [21] that, due to the anisotropy of the thermal conductivity, which in the case of 8CB results in a larger value of k along the long axis of the molecule (k_{\parallel}) than the one perpendicular to it (k_{\perp}), the better the homeotropic (planar) alignment, the larger (the smaller) the k_{\parallel} (k_{\perp}) value is in the ordered phases. The k temperature dependence can therefore be easily understood in terms of sample alignment. For homeotropic bulk samples it remains approximately constant in the isotropic phase and increases with the sample ordering when the temperature decreases, while for planar bulk samples it decreases below the isotropic value when the sample enters the nematic phase and continues to decrease slightly with the increase of planar ordering with decreasing temperature. The introduction of aerosil induces some disorder in the sample which degrades the alignment and therefore reduces the k_{\parallel} values and increase the k_{\perp} ones below T_{N-I} . In the following, since we are considering only homeotropic mixtures, we shall omit the \parallel suffix in the thermal conductivity.

It is interesting to note that for $\rho_s = 0.04 \text{ g/cm}^3$, there is only a very small increase of k in the ordered phases with respect to the value in the isotropic phase. The k temperature dependence is approximately a straight line; this means that the amount of disorder in this case is so high that, from the thermal transport point of view, the sample is almost isotropic at all temperatures. This gives an indication on the sensitivity of the above-reported measurements to the presence of disorder. No useful information on the amount of disorder can be obtained for $\rho_s > 0.04 \text{ g/cm}^3$ but, on the other hand, the sensitivity is quite large for very low ρ_s .

It must be pointed out at this point that in a sample where the alignment is induced by the surface treatment of the cell walls, there are essentially two mechanisms associated with the introduction of the aerosil particles responsible for the degradation of the sample alignment. The first one is the already-mentioned mechanism associated with the distortion of the local orientation produced by the homeotropic anchoring of the molecules at the particle surface. This distortion, moreover, produces a ‘‘screening’’ of the orientational order induced by the treated surfaces, thus introducing a second effect which results in a reduction of the strength of the aligning field that the molecules away from the surface feels once the aerosil concentration is increased. This could produce an inhomogeneity of the alignment of the LC across the cell that becomes more and more important with increasing ρ_s , thus decreasing the thermal conductivity values obtained as average values over the sample thickness. This also means that if the alignment of the sample is obtained via other methods, such as electric or magnetic fields acting homogeneously over the whole sample volume, then the amount of disorder present in the sample could be different.

A different behavior of the thermal conductivity in the nematic phase on heating from the smectic phase and on cooling from the isotropic one is evident in Fig. 5 for mixtures $0.005 \leq \rho_s \leq 0.02 \text{ g/cm}^2$. This effect has been already

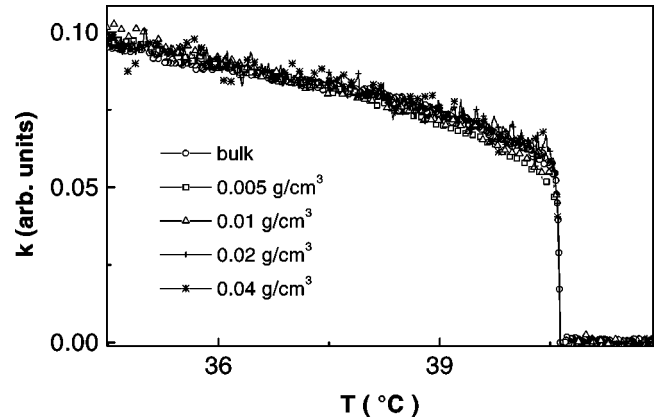


FIG. 6. Rescaled thermal conductivity for bulk 8CB and mixtures as a function of temperature.

described for the lowest concentration only in a previous paper [10] and it has been attributed to the annealing of the disorder that takes place not only at the $N-I$ transition but also at the $A-N$ one and in the nematic phase. The suggested scenario is the following. A rearrangement of the aerosil takes place at the $N-I$ transition and reduces the ES present in the sample. The annealing is not complete, as shown by the increase of k at the $A-N$ transition on cooling, this increase being much larger than the one due to the smectic layering contribution to the orientational order that is evident in the homeotropic bulk [19]. This increase means that the sample alignment has improved and this can only be due to a further reduction of the disorder following an annealing process. If the sample is heated from the smectic phase back into the nematic one, the amount of ES is now lower, and the k values are therefore larger than the one present in the sample cooled from the isotropic phase, as can be easily seen in the figure.

It has been shown in 7CB [10] that a rearrangement of the aerosil, and therefore a reduction of the ES, can also take place away from the transition temperature in the nematic phase as a consequence of the increase of the order with decreasing temperature. These effects can be seen in our samples because of the surface-induced alignment. The increase of the amount of disorder with increasing ρ_s degrades the alignment and makes the effect of the annealing on the orientational order, and therefore on k , less and less evident. This effect also produces the reduction in the average slope that the k curves have in the ordered phases with increasing concentration. The increase of the disorder produces, in other words, a reduction of the absolute variation of k and therefore also a reduction in the sensitivity of the thermal conductivity to variations produced by the increase of the order.

Figure 6 shows the thermal conductivity of the homeotropic bulk and of the mixtures in the isotropic and nematic phase. The data are the same obtained on heating from the smectic phase and have been already shown in Fig. 5 but they have been rescaled in the following way: a constant background [$k_0 = 0.0016 \text{ W/(m K)}$], extrapolated from the k temperature dependence in the isotropic phase, has been subtracted from the data in the nematic phase and they have been subsequently normalized so to have the same value at

$T=310.15$ K. The normalization factor was 1.34 ($\rho_s = 0.005$ g/cm³), 2.60 ($\rho_s = 0.01$ g/cm³), 4.75 ($\rho_s = 0.02$ g/cm³), and 13.10 ($\rho_s = 0.04$ g/cm³). This procedure has been adopted to try to highlight a relative variation in the thermal conductivity due to the temperature evolution of the orientational order. It turns out that all the samples have almost the same temperature dependence and lead to the conclusion that the temperature dependence of the macroscopic orientational order parameter is not affected by the presence of aerosil, at least at these low concentrations and in samples where the disorder has been drastically reduced by the annealings in the ordered phases. On the other hand, it is evident from Fig. 5 that samples cooled from the isotropic phase have a less rapid increase of the orientational order in the nematic phase with decreasing temperature to those that have been heated from the smectic phase. This is particularly evident for samples with $\rho_s = 0.005$ g/cm³, becomes less evident with increasing ρ_s , and almost disappears for $\rho_s = 0.04$ g/cm³. Therefore, it can be that the temperature dependence of the orientational order is affected, at least in samples with low aerosil concentration, by the presence of ES in the nematic phase, while nothing can be said for larger concentrations due to the limitations of our technique.

We have performed measurements on mixtures with planar alignment (not shown). From these measurements the thermal conductivity perpendicular to the molecular long axis can be calculated, thus leading to the determination of the orientational order parameter $S \propto k_{\parallel} - k_{\perp}$. We faced many problems during these measurements and we did not get any useful result. The main reason for this was that the surface-induced planar alignment (grazing angle deposition of quartz) in the mixtures is less efficient than the one used for homeotropic alignment and it is very difficult to have monodomain samples. Nevertheless, we have found, as expected, an increase of the k_{\perp} values with increasing concentrations in the ordered phase that is obviously due to the disorder (remember that the poorer the quality of the planar alignment, the larger the k_{\perp} value, while the opposite is true for k_{\parallel} in homeotropic samples).

IV. DISCUSSION

The results we have shown, and particularly the thermal conductivity ones shown in Fig. 5, suggest that, even at very low ρ_s , there is some ES that is not annealed at the $N-I$ transition on cooling. This is probably the reason why the RF (RD) model, which considers only quenched disorder at the aerosil surface due to the anchoring of the LC molecules, does not succeed in explaining the experimental data. We believe that distortions of the local orientation in the ordered phases away from the particle surfaces play a role and must be properly accounted for in the theoretical description of the system. If this is true, then it immediately comes out that the amount of disorder present in the ordered phases depends not only on ρ_s but also on other variables, such as, for example, applied fields that can be responsible for the reduction of the disorder present in the sample at a given aerosil concentration and a given temperature. Differences in the strength of these fields can produce differences, in terms of the amount

of disorder, in samples with the same ρ_s and be the origin of the discrepancies between our results and the ones reported in literature for the transition temperature suppression, the width of the coexistence region, and the shape of c close to the $N-I$ transition.

In the case of the coexistence region, for example, at low values of ρ_s we expect that it increases due essentially to the disordering effect of the particles that act as impurities. At concentrations much larger than the ones used in this work, on the other hand, due to the strong confinement, a suppression of the first-order character of the transition is expected and therefore the coexistence region must decrease [22]. The narrower coexistence region we got for $\rho_s = 0.02$ g/cm⁻³ with respect to the ones reported in Ref. [9] is therefore consistent with the fact that our samples are less disordered.

Regarding the behavior of the transition temperatures and particularly the slight increase observed for $\rho_s > 0.02$ g/cm³, we think that it can be explained in the following way. If we assume, as we have done before, that the depression in the transition temperatures is due to the disordering effect of the aerosil, then an increase of T_{A-N} and T_{N-I} can be associated with the fact that in the sample with $\rho_s = 0.04$ g/cm³ this effect is weaker than in the one with $\rho_s = 0.02$ g/cm³.

Let us consider mixtures with ρ_s below the gelation threshold ρ_g : almost isolated aggregates of aerosil float in the LC and they are responsible for the induced disorder. If ρ_s increases, still remaining below ρ_g , the disorder simply increases. Now, if we have a mixture with $\rho_s > \rho_g$ in the I phase and cool it down in the N phase, another effect comes into play. The anisotropic properties of the LC produce a relaxation of the aerosil network that lowers the elastic energy of the system through particles rearrangement. This relaxation reduces the disorder of the system and we therefore expect that it partially compensates the increase of disorder due to the increase of ρ_s . It is obvious that the larger the ES, the more evident the relaxation and therefore the compensation. This can explain the slower decrease of the transition temperatures observed just above $\rho_g = 0.01$ g/cm³ with respect to the one for $\rho_s < \rho_g$ and also the slight increase of the T_{A-N} and T_{N-I} for larger $\rho_s = 0.02$ g/cm³. In this last case, it could be that the compensation due to the relaxation is larger than the increase of the disorder when ρ_s is increased from 0.02 to 0.04 g/cm³. A further increase of ρ_s (> 0.092 g/cm³) makes the gel stiff, no relaxation can take place, and the transition temperatures decrease again in a monotonous way.

The results we have obtained on the behavior of transition temperatures as a function of concentration seem to indicate that an overall decrease of the disorder due to the mechanisms described above takes place only in the sample with $\rho_s = 0.04$ g/cm³.

A similar increase in the transition temperatures after an initial decrease as a function of ρ_s has been also reported in Ref. [9]. The concentration value at which the increase occurs, however, is 0.052 g/cm³, approximately a factor 2 larger than the one we have observed. We think that this is due to the presence in our samples of the surface-induced alignment which enhances the anisotropy of the LC and

therefore the relaxation of the gel, thus making this effect detectable at lower aerosil concentrations.

It must be pointed out that this “ordering effect” and the reduction of the disorder that takes place for $\rho_s > 0.02 \text{ g/cm}^3$ is very small. The increase of T_{N-I} is, in fact, much smaller than the reduction of T_{N-I} that we found in the pure sample with respect to the mixture with $\rho_s > 0.005 \text{ g/cm}^3$. The amount of the disorder that could be removed by the ordering effect must be, therefore, much smaller than the one introduced in the mixture at the lowest concentration.

Following what was stated before on the importance of the strength of a possible external field on the determination of the disorder present in samples with the same ρ_s , it must be pointed out that the same fields can affect the hysteresis found in the thermal conductivity in the nematic range. Recent DNMR [23] measurements performed in mixtures with $\rho_s = 0.005 \text{ g/cm}^3$, in fact, do not show such hysteresis. These measurements require strong magnetic fields and it could well be that such fields anneal the disorder responsible for the above-mentioned hysteresis.

A question may be raised at this point: why is the above-mentioned ordering effect not detected in the thermal conductivity, where a monotonous decrease of the k values in the nematic range with increasing ρ_s has been found? It must be pointed out that while the transition temperatures depend on the intermolecular interaction potentials which are also affected by the disorder of the system, the thermal conductivity mainly senses the macroscopic orientational order [21]. It could be, in other words, that the reduction of the disorder in the system following the relaxation of the aerosil network does not imply in all cases a detectable improvement in the homeotropic alignment of the molecules. This improvement has been, however, observed in our samples, apart from the mixture with $\rho_s = 0.04 \text{ g/cm}^3$, as a consequence of the $A-N$ transition as shown by the hysteresis in Fig. 5. It is particularly evident for very low ρ_s and decreases with increasing ρ_s . This can be easily understood if we consider that in the sample with the $\rho_s = 0.005 \text{ g/cm}^3$, only isolated strands of aerosil are probably present in the LC. A reduction of ES, in this particular case, can take place only if the strands align perpendicular to the direction of the aligning field. This rearrangement means an improvement of the homeotropic

alignment and therefore an increase of k . If ρ_s increases, the strands start to interact and form a gel and they are therefore less free to move even though the gel is soft. Their ability to align perpendicular to the director is reduced and so is the improvement of the orientational order after the annealing of the ES. This means that when the above-mentioned relaxation occurs, because of the constraint in the network, its effect on the orientational order is less evident than the one on the transition temperatures. We can therefore conclude that the relaxation is stronger in the mixture with $\rho_s = 0.04 \text{ g/cm}^3$ than in any other mixture, as suggested by the transition temperature dependence on ρ_s , but the orientational part of this relaxation decreases with increasing ρ_s , both for the increased screening of the surface-induced order and also the rigidity of the gel.

V. CONCLUSIONS

The results and the discussion reported above allow us to draw the following conclusions: (i) the RF (RD) model that follows from the assumption that all the strain in the sample is annealed in ordered phases and that quenched disorder is only present very close to the aerosil particle surface does not seem applicable to low ρ_s mixtures; (ii) it is not sufficient to consider only ρ_s as the variable that describes the amount of disorder present in the mixture, but applied (ordering) fields must be taken into account due to their influence in the strain annealing; (iii) the behavior of the transition temperatures as a function of ρ_s seems to suggest that a relaxation of the aerosil network takes place for $\rho_g < \rho_s < 0.04 \text{ g/cm}^3$ that partially compensates the depression of T_{A-N} and T_{N-I} induced by the disorder.

It has been also shown that the effect of the aerosil is not the same at the $A-N$ and $N-I$ transition. While in the first case the usual suppression of the anomalies with increasing ρ_s has been observed, the situation is completely different at the $N-I$ transition where the peak of the specific heat, in the concentration range we have investigated, increases.

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