Dynamic critical behavior of thermal parameters at the smectic-A –nematic phase transition of octyloxythiolbenzoate

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The dynamic as well as the static critical behavior associated with the thermal parameters was investigated over the smectic-A– nematic phase transiton of octyloxythiolbenzoate ($\bar{8}$S5) through the simultaneous determination of the specific heat, thermal conductivity, and thermal diffusivity obtained by the photopyroelectric technique. The critical exponent of the specific heat is close to the one predicted for three-dimensional XY like ($n = 2, d = 3$) transitions, such as the superfluid transition in helium. A dip in the diffusivity was observed and the critical exponent results were consistent with a dynamic model, also with $n = 2$ and $d = 3$, which considered dissipative couplings between the order parameter and the conserved energy density in the free energy functional. A smooth thermal conductivity has been obtained over the transition temperature.

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INTRODUCTION

The study of the critical behavior of dynamic thermal parameters such as the thermal diffusivity (D) and thermal conductivity (k) over a liquid crystal phase transition is a matter of controversy. The few experimental results which are available in the literature for different transitions could not be interpreted in terms of existing theoretical models. Data showing a dip in D and a peak in k have been reported over the hexatic-B –smectic-A (BA) transition in n-hexyl-4'-n-pentyloxybiphenyl-4-carboxilate (65OBC) [1], but no theoretical explanation for the obtained critical exponents was possible. Data are also available over the smectic-A –smectic-C (AC) transition in several compounds where progressively stronger divergence in D was found as the tricritical point was approached [2]. Also, in this case, the existing models could not explain the theoretical results, which, moreover, violated the dynamic scaling assumption [3]. In the case of the smectic-A –nematic (AN) phase transition, which is the subject of this paper, D and k behaviors have been reported for cyanobiphenyl mixtures [4] with increasing nematic range, but the studied compounds had critical behaviors dominated by crossover effects, and again no conclusive interpretation of the results was possible.

Most of the theoretical work on the AN transition originates from the description given by de Gennes [5] of the static critical behavior that places the transition itself in the three-dimensional (3D) XY universality class. It is based on the so-called "helium analogy" which predicts the same behavior for the present transition, the superfluid-normal fluid and the superconductor-normal metal ones. The analogy is, however, not complete for several reasons. Due to the Landau-Peierls theorem, it is not possible to have true long range order in smectics and, moreover, the Frank-Oseen elastic energy must be

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considered in the free energy functional, thus making it different from the normal superconductor one. The experimental results reflect these uncertainties since specific heat data [6] are in quantitative agreement with the predictions of the 3D XY model, while x-ray measurements lead to different critical exponents for the correlation length measured parallel and perpendicular to the molecule long axis ($v_{\parallel} \neq v_{\perp}$) [7], which is not expected from the helium analogy. These difficulties have recently been partially overcome [8] on the basis of theoretical developments [9,10], but not fully resolved.

The question may arise whether the helium analogy can be extended to critical dynamics, and this is the issue we want to address in the present paper. It is well known that mode-mode couplings are responsible for the anomalies observed at T_c for the transport and kinetic coefficients [11] that cannot be explained by the conventional theory [12]. In the case of superfluid He, to explain the experimentally observed divergence [13] of the thermal conductivity above T_c, a model with a *nondissipative* coupling of the nonconserved energy density and the order parameter in the free energy functional has been proposed (model F [11]). In liquid crystals, the thermal diffusion mode and the order parameter mode are coupled, since the order parameter fluctuations are strong thermal modes of the system. Following the hydrodynamic analysis of smectics [14], it has been suggested [2] that their dynamics should be described by the so-called model C [11], which is based on a free energy functional in which an isotropic *dissipative* coupling of the order parameter with the conserved energy density has been included. It should be noted that the two models predict the same static critical behavior, but that they differ significantly when critical dynamics is considered. In the case of model C it is expected that a dynamic quantity such as the thermal diffusivity goes to zero at T_c, while k remains constant all over the transition temperature region. All the existing results are not consistent with these predictions.

In the present paper we shall report on the simultaneous measurement of c and D, with k calculated from the equation $D = k/\rho c$, ρ being the sample density, at the AN transition of octylaxythiolbenzate ($\overline{8}$S5). This compound has a wide nematic range (~ 23 K), and is therefore far away from the AN tricritical point. As expected, we have found a specific heat critical exponent close to the one predicted for the 3D XY universality class. We have also found a dip in the thermal diffusivity and a smooth behavior of the thermal conductivity over the transition. The value of the critical exponent for the diffusivity we have obtained, fitting the data well within the critical region, is also in good agreement with the prediction of a dynamic model with $n = 2$ and $d = 3$, which assumes dissipative coupling between the conserved energy density and the order parameter (model C) and the dynamic scaling hypothesis [3].

EXPERIMENT

Measurements have been performed using a photopyroelectric technique which was previously described [15]. The sample was sandwiched between a 300-μm-thick LiTaO$_3$ pyroelectric transducer and a glass cover whose surface in contact with the liquid crystal was coated with a 500-nm, optically opaque, metallic film. The sample thickness was 30 μm. Light from a He-Ne laser, modulated at 21 Hz, was absorbed by the metallic coating, thus inducing thermal waves propagating through the sample. The amplitude and delay, with respect to a given reference, of the temperature oscillation at the sample back surface were obtained from the transducer signal analyzed by a two phase lock-in amplifier. It has been shown [16] that if the sample is optically opaque and thermally thick (with the wavelength of the thermal wave much smaller than the sample thickness), c and D can be simultaneously measured and k therefore calculated [15]. A calibration of the technique requires a knowledge of c, k, and D at a given temperature away from T_c. The diffusivity has been measured, using the same setup, from a frequency scan [15] at 62 °C, while the specific heat at the same temperature was taken from Ref. [15]. The density was moreover considered constant all over the temperature of the measurements [17]. The sample plus transducer assembly was contained in an oven, and the temperature rate change was 3 mK/min. To reduce the influence of thermal gradients that could be introduced by too fast a heating rate or too large a light power density, these two quantities have been reduced to values where a further decrease did not produce any substantial change in the signal behavior in the vicinity of T_c. Data were collected every 0.3 mK.

RESULTS

Figure 1(a) shows the data that have been obtained for the specific heat. They have been fitted with a nonlinear least squares fitting routine with an equation of the form

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

(1)

where $\pm$ indicates, respectively, values relative to data above and below T_c, B, E, A^+, α, A^-/A^+, T_c, D^+, and D^- were the adjustable parameters. We choose a fitting expression with $|T - T_c|$ instead of the standard one with $|(T - T_c)/T_c|$ to reduce the statistical correlation among the parameters. Provided we consider $|T - T_c|$ as $|(T - T_c)/[1 \, (\mathrm{K})]|$ the parameters in the two cases have the same units, even if the statistical errors cannot be compared easily. The solid line in Fig. 1(a) presents the best fit with the parameter values reported in Table I. The α value and the amplitude ratio are close to the ones expected for the 3D XY model ($\alpha = -0.007$ and $A^-/A^+ = 0.9714 \pm 0.0216$, respectively [18]). The correction to scaling terms resulting from the best fit are rather small with quite large uncertainties in the $D^{\pm}$ parameters. We have tried to fit the data fixing $D^+ = D^- = 0$ and, as expected, a very good fit with $\alpha = -0.021 \pm 0.005$ and $A^-/A^+ 0.98 \pm 0.02$ has been obtained. The $\chi_\nu^2 = 1.09$ value obtained in this case confirms a fit quality comparable to the best fit reported in Fig. 1 ($\chi_\nu^2 = 0.98$). It should be noted, however, that even though the D values obtained in the best fit are opposite in sign, within uncertainties they are shown to be approximately equal, as expected. Figure 1(b) shows the devia-
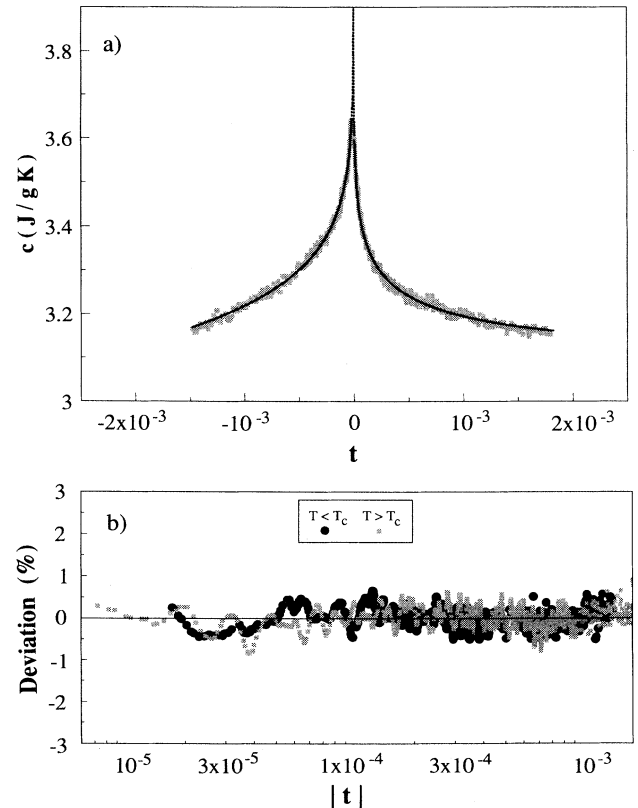

FIG. 1. (a) Specific heat data vs reduced temperature $t = (T - T_c)/T_c$. The solid curve corresponds to the best fit. The dotted line corresponds to the reduced temperature region which has not been considered in the fit. (b) Deviation plot corresponding to the best fit.

TABLE I. Values of the adjustable fitting parameters for the specific heat c as derived from Eq. (1) and for the thermal diffusivity D as derived from Eq. (2) and Eq. (3) respectively.

	α	A^-/A^+	T_c (K)	B (J/gK)	E (J/gK)	A^+ (J/gK)	D^-	D^+	χ_v^2
c (J/gK)	-0.022 ±0.008	0.968 ±0.020	336.200 ±0.004	7.8 ±0.1	-0.01 ±0.23	-4.78 ±0.11	0.02 ±0.06	-0.03 ±0.05	0.98
	b	U^-/U^+	T_c (K)	$10^{-6}\,V$ (cm²/s)	$10^{-6}W$ (cm²/s)	$10^{-4}U^+$ (cm²/s)	F^-	F^+	χ_v^2
D (cm²/s)	-0.027 ±0.005	0.97 ±0.03	336.200 ±0.003	2 ± 8	-0.5 ±1.3	2.83 ±0.06	0.01 ±0.06	-0.02 ±0.05	1.1
	b'	$\bar{U}^-/\bar{U}^+$	T_c (K)	$10^{-4}D_0$ (cm²/s)	$10^{-3}\bar{W}$	$\bar{U}^+$	$\bar{F}^-$	$\bar{F}^+$	χ_v^2
D (cm²/s)	-0.023 ±0.006	0.97 ±0.03	336.200 ±0.003	1.1 ± 0.1	-4 ± 9	-0.60 ±0.06	0.01 ±0.07	-0.03 ±0.06	1.1

tion plot that gives an idea of the fit quality. Although the conclusion concerning the universality class of the transition is the same as the one of Ref. [19], the results of the fit are different. It should be noted that while the width and maximum value of the peak in the specific heat we have measured are quite comparable with the ones reported in Ref. [19], in the latter case the temperature resolution and therefore the number of data points used in the fit is considerably lower (by about a factor of 15). Moreover data in Ref. [19] could not be fitted satisfying the condition $E^+=E^-$, and the author concluded that the E term could not represent a regular background term. In the present case, on the contrary, the data can be easily fitted with $E^+=E^-$ as shown by the deviation plot. As already stated, a 3D XY behavior has been demonstrated for the specific heat at the AN transition [6]. Even though the α value we have obtained is somewhat larger in absolute value than -0.007, the amplitude ratio $A^-/A^+=0.97\pm0.02$ seems to confirm the 3D XY-like behavior. We have tried to fix $\alpha=-0.007$, but the fit we obtained showed small but systematic deviations in the deviation plot (not shown) and $\chi_v^2=1.92$. This means that a reasonably small influence of the crossover to tricritical behavior is still present in $\bar{8}S5$.

Figure 2 shows the thermal diffusivity data we obtained. In analogy with our previous works [20], the data have been initially fitted with an equation of the form

$$D=V+W(T-T_c)+U^\pm|T-T_c|^{-b}(1+F^\pm|T-T_c|^{0.5})$$

$$\text{(with } b<0)\,, \quad (2)$$

where V, W, T_c, $U^\pm$, b, and F were the adjustable parameters. A very good fit was obtained, as shown by the deviation plot in Fig. 2(b), with the parameters reported in Table I. The critical exponent $b=-0.027\pm0.008$ is very similar to the one of the specific heat. The sign of $U^\pm$ is, of course, opposite with respect to $A^\pm$, but $U^-/U^+\sim A^-/A^+$. The corrections to scaling terms are also small in this case, and we have therefore tried to fit the data with the constraint $F^-=F^+=0$. The quality of the fit was again comparable with the best fit reported in Fig. 2(a), since the χ_v^2 values were 1.3 and 1.1, respectively. In spite of the excellent fits for both c and D with the previous expressions, however, the results seem to

contradict the hypothesis of a constant k value all over the critical region, as suggested by both our experimental data shown in Fig. 3 and by the theoretical prediction of model C. In fact, the k value starts decreasing in a critical region extremely close to T_c ($|t|<10^{-7}$) and reaches a minimum value at T_c, where $k=\rho BV$ ($\rho=0.98$ g/cm³), yielding, with the above best fit data, a value of about 0.15×10^{-4} W/cm K, considerably smaller than the experimental values in the rest of the critical region (about
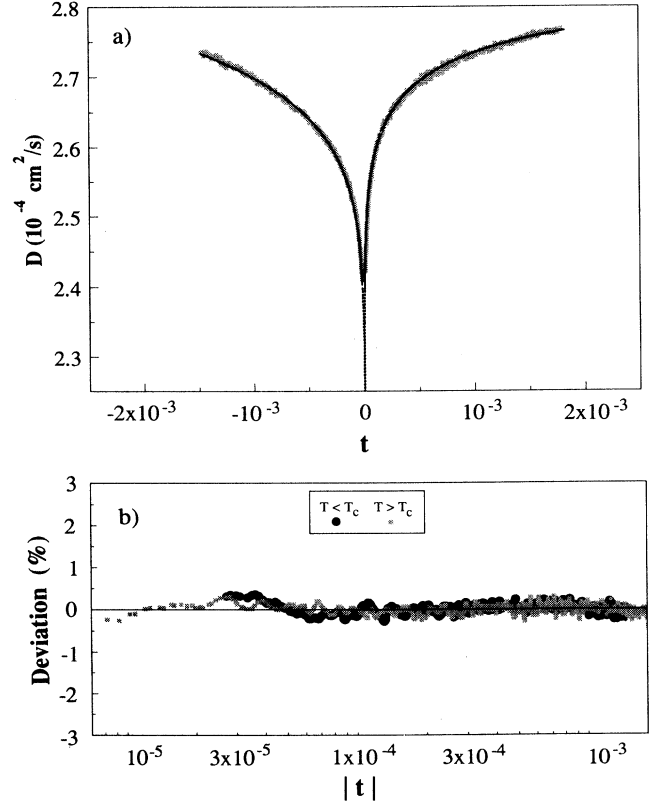

FIG. 2. (a) Thermal diffusivity data vs reduced temperature $t=(T-T_c)/T_c$. The solid curve corresponds to the best fit. The dotted line corresponds to the reduced temperature region which has not been considered in the fit. (b) Deviation plot corresponding to the best fit obtained employing Eq. (2).
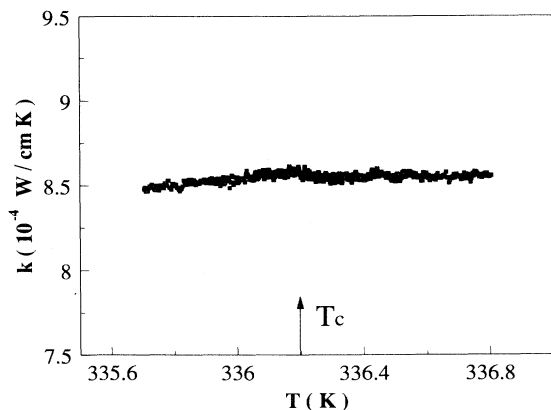
FIG. 3. Thermal conductivity data vs temperature over the transition temperature T_c.

8.5×10^{-4} W/cm K). Therefore, assuming no anomaly in k, and in analogy with what was previously reported in Ref. [20], we have next fitted our D data with the expression

$$D = \frac{D_0}{1 + \overline{W}(T - T_c) + \overline{U}^{\pm}|T - T_c|^{-b'}(1 + \overline{F}^{\pm}|T - T_c|^{0.5})},$$

(3)

which indicates that the anomaly in D is related only to the one in c. The fitting parameters are reported in Table I, and the deviation plot is shown in Fig. 4. The best fit quality is comparable with the one obtained from Eq. (2). The exponent value b' is very close to the one obtained previously. The D_0 value, combined with the B one, ensures in this case a k value of $(8.4 \pm 0.8) \times 10^{-4}$ W/cm K, in agreement with the k values reported in Fig. 3. The important issue is, however, that with both fitting functions, the critical behavior of D is governed, within uncertainty, by the same critical exponent similar to the one of the specific heat.

Thermal diffusivity data close to the AN transition have been already reported for nCB mixtures [4]. It was shown that moving away from the tricritical point, the exponent decreased with increasing nematic range. In
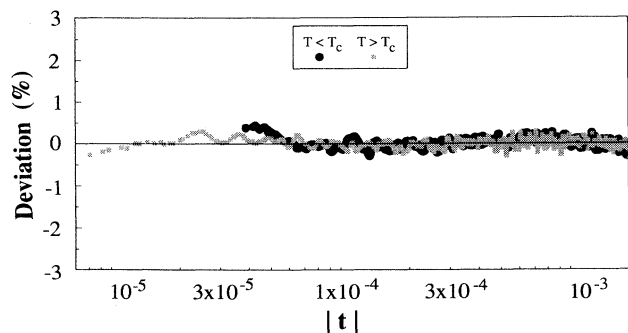

FIG. 4. Deviation plot corresponding to the best fit obtained employing Eq. (3).

particular for $T_{AN}/T_{NI} = 0.994$, $b = -0.08 \pm 0.04$, while for $T_{AN}/T_{NI} = 0.962$, $b = -0.01 \pm 0.03$. The sample we have used in the present work was $T_{AN}/T_{NI} = 0.936$, and it is farther away from the tricritical point than in previous cases. This aspect is very important since, as already stated, it has been suggested [2] that tricriticality may influence the D critical behavior. It should be noted, moreover, that the apparent contradiction between the b value in Ref. [4] and the one obtained in the present case can be explained taking into account the uncertainties. The smaller uncertainty values reported in this work give a hint about improved resolution of the photopyroelectric technique with respect to the one used in Ref. [4], as suggested in Ref. [15].

DISCUSSION AND CONCLUSIONS

It has been shown [21] for model C that, in the case $n = 2$ and $d = 3$ and with $-c\eta > \alpha/\nu$, where c is a constant and η is the critical exponent for the susceptibility, the singular part of the energy correlation function has a characteristic frequency for the energy that, according to the dynamic scaling hypothesis, is $\omega_E = iDq^2 \propto q^{z_E}$, where q is the mode wave vector and $z_E = 2 + (|\alpha|/\nu)$. If the energy is conserved, the heat conduction mode is purely diffusive, and since $D \propto |T - T_C|^{-b}$ we have $\omega_E = (q\xi)^{b/\nu} q^{2-b/\nu}$, where ξ is the correlation length. We then have $-b = |\alpha|$, which is consistent with our data analysis. In the case of $n = 1$ and $d = 3$, model C predicts $-b = \alpha$ with $\alpha > 0$. We have previously also confirmed such a result with our photopyroelectric measurements on Ising-like systems [20,22]. In the present case the inequality $-c\eta > \alpha/\nu$ seems to be satisfied, since the constant c, which has been calculated to first order in ε, and α are negative, while ν and η are positive $(-c\eta > 0, \alpha/\nu < 0)$. It must also be pointed out that the predictions of model C are in some cases uncertain, but this does not seem to be the case for $n = 2$ and $d = 3$ [21].

Measurements have been performed in nonaligned samples. Nevertheless we observed a tendency, on a time scale of days, to homeotropic alignment, probably due to the sample geometry used in the present experiment. We did not observe any significant change in the measured critical behavior of thermal parameters. Measurements on aligned samples are presently being run, and the results will be reported in a forthcoming paper.

As previously stated, k and D critical behaviors have already been reported for liquid crystal phase transitions. In the case of the BA transition of 65OBC [1], a divergence in k and a dip in D were found. In particular, in contrast to the case of helium, a stronger thermal conductivity divergence with respect to the anomaly in D was reported. The data could not be explained in terms of any existing model. Data are also available for the AC transition [2], where a smooth decrease in D was observed sufficiently far from T_c, but a divergence showed up in the region close to T_c. Such a temperature region was observed to shrink as the ratio of the fourth- to sixth-order terms in the extended mean field free energy expansion decreases. In this case an attempt was made to fit

the D data using the model C predictions, but this was only possible when using an uncoupled free energy functional and a Gaussian approximation, in the temperature regions where D decreases smoothly. Since model C, which seems to be a reasonable approximation to describe the critical dynamics of smectics [2], considers only dissipative couplings the divergence in D and k which must be due to nondissipative couplings cannot be accounted for. The authors suggest which the data close to T_c, which also violate the dynamic scaling hypothesis, could indeed be explained in terms of other anisotropic nondissipative couplings, whose origin is, however, not clear. In the case of nCB, a divergence in k and a dip D, which could not be explained in terms of existing theoretical predictions, have been reported and this point will be addressed below. In all cases, it was therefore not possible to compare the experimental data with the theoretical predictions successfully in a temperature region close to T_c. Conversely, in the present experiment, we have been able to describe the data over the entire investigated temperature region, which extends well within the critical region, according to model C, which is based on isotropic dissipative coupling between the conserved energy density and the order parameter. Our data are, moreover, fully compatible with the dynamic scaling assumption.

The data reported in Fig. 3 show no anomaly in thermal conductivity. In Ref. [4], however, a divergent k has been reported close to the AN transition of nCB. The divergence in that case was present over a very narrow reduced temperature region close to T_c, and the peak height of k decreased moving away from the tricritical point. One possibility is that in a pure XY-like behavior the peak could disappear as in the present case, but we believe that, more likely, the data points relative to the peak are due to thermal gradients. This conclusion is supported by the fact that the anomaly in k occurs over a reduced temperature region very close to T_c, where the c and D data were found to be affected by rounding and were thus not considered in the fit in Ref. [4]. It has been shown, moreover, that the photopyroelectric technique is more sensitive to the thermal parameter variation in the vicinity of a phase transition [15] with respect to the photoacoustic configuration employed in Ref. [4], and for this reason we consider the data very close to T_c reported in the present paper more reliable.

In conclusion, we have demonstrated that the helium analogy cannot be extended to the critical dynamics of thermal parameters at the AN transition. The data, showing a dip in D and a smooth k over the transition region, are in good agreement with the predictions of a dynamic model based on an isotropic dissipative coupling of the conserved energy density and the order parameter.

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