Gaussian tricritical behavior of heat capacity at the smectic-*A*–smectic-*C* liquid crystal transition in a racemic mixture of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate

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High resolution ac calorimetric measurements have been carried out near the smectic-*A*–smectic-*C* phase transition in a racemic mixture of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate. The heat capacity data show a distinct pretransitional excess above the transition temperature as well as below it. The data have been analyzed in detail with the renormalization-group expression with correction-to-scaling terms. It was found that the data show Gaussian tricritical behavior. It was also found that the present data support the first-order correction exponent Δ_1 to have a value 0.5. The value of nonuniversal amplitude ratio A^-/A^+, and the possibility of the existence of the logarithmic corrections have also been discussed. [S1063-651X(97)11801-3]

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I. INTRODUCTION

The liquid crystalline smectic-*A*–smectic-*C* (Sm-*A*–Sm-*C*) transition and the smectic-*A*–chiral-smectic-*C* (Sm-*C**) transition are theoretically classified into the three-dimensional (3D) *XY* universality class [1]. Therefore, the study of critical behavior at the Sm-*A*–Sm-*C* (or *C**) transitions is an active area of research. Early experimental studies revealed that these transitions exhibit classic mean-field behavior and are well described by the extended Landau theory, which includes up to a sixth-order term in the tilt order parameter (see Refs. [2–5], and also references cited therein).

On the other hand, we recently found that the heat capacity of 4-(1-methylheptyloxycarbonyl)phenyl 4′-octyloxybiphenyl-4-carboxylate (MHPOBC) [6] and some related materials [7,8] show a clear deviation from the Landau behavior at Sm-*A*–Sm-C^*_α transition. Here, the Sm-C^*_α phase is an antiferroelectric version of the Sm-*C** phase. It was also found that the observed heat capacity anomalies are described by the 3D *XY* renormalization expression near T_c, and show a crossover to tricritical behavior. Reed *et al.* [9] reported that the heat capacity near the Sm-*A*–Sm-*C* transition of 5-*n*-decyl-2-[4-*n*-(perfluoropentyl-metheleneoxy) phenyl] pyrimidine (H10F5MOPP) shows a non-Landau, almost tricritical behavior. These examples show that the Sm-*A*–Sm-*C* (or *C**) transition can really exhibit theoretically expected non-Landau critical behavior, and therefore it is of special interest to search for further similar examples.

Optically pure MHPOBC shows the following sequence of phase transitions [10]:

$$\text{Sm-}C^*_A \overset{391.6\ \text{K}}{\leftrightarrow} \text{Sm-}C^*_\gamma \overset{392.4\ \text{K}}{\leftrightarrow} \text{Sm-}C^* \overset{394.1\ \text{K}}{\leftrightarrow} \text{Sm-}C^*_\alpha \overset{395.2\ \text{K}}{\leftrightarrow} \text{Sm-}A \overset{421\ \text{K}}{\leftrightarrow} I.$$

Here Sm-*A* is a paraelectric phase, Sm-*C** is a ferroelectric phase, Sm-C^*_α and Sm-C^*_A are antiferroelectric phases, Sm-C^*_γ is a ferrielectric phase, and *I* stands for the isotropic phase. On the other hand, a racemic mixture of MHPOBC shows a different phase transition sequence [11]:

$$\text{Sm-}C_A \overset{386\ \text{K}}{\leftrightarrow} \text{Sm-}C \overset{394\ \text{K}}{\leftrightarrow} \text{Sm-}A \overset{420\ \text{K}}{\leftrightarrow} I.$$

A racemic mixture does not have chirality as a whole, and each smectic layer does not exhibit net polarization. Because of this, the above Sm-*C* phase is not a ferroelectric but a ferrodistortive phase, and similarly the Sm-C_A phase is an antiferrodistortive phase. It was found that the Sm-C^*_α phase and the Sm-C^*_γ phase diminish in optically impure systems [11], which indicates that the dipolar interactions play an important role in this system.

In this paper we report the results of ac calorimetric measurements on a racemic mixture of MHPOBC [12]. The results described below reveal that the heat capacity shows significant critical behavior at the Sm-*A*–Sm-*C* transition. Moreover, the present system is a clear example of a Sm-*A*–Sm-*C* transition which exhibits Gaussian tricritical behavior. The data have been analyzed in detail with the renormalization-group expression with correction-to-scaling terms. It was found that the present data support the first-order correction exponent Δ_1 to have a value 0.5. The value of nonuniversal amplitude ratio A^-/A^+ and the possibility of the existence of the logarithmic corrections have also been discussed.

II. METHOD AND RESULTS

The heat capacity was measured using an ac calorimeter with basically the same setup as described elsewhere [6,13,14]. Hermetically sealed gold cells that contained 30–50 mg of liquid crystal sample were used. Temperature scan rate was about 0.03 K/h in the transition region. Measurements were made on two sample cells, including several heating and cooling runs for each of them, which gave an

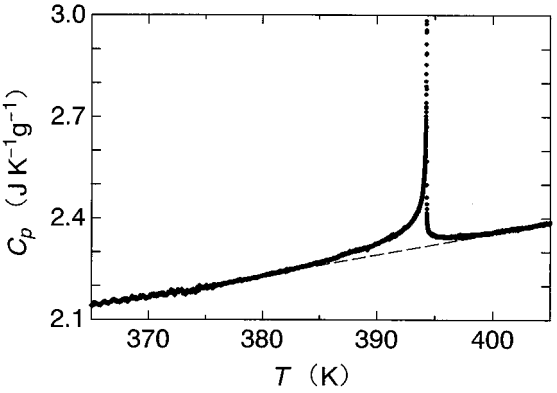

FIG. 1. Overall temperature dependence of the heat capacity C_p for a racemic mixture of MHPOBC. The dashed line shows the background heat capacity.

excellent reproducibility. A very slow drift rate in the transition temperature of about -0.004 K/d ensured the high quality of the sample.

Figure 1 shows the overall temperature dependence of the heat capacity C_p. A large anomaly is seen at the Sm-A–Sm-C transition located at 394.2 K. The dashed line in Fig. 1 shows the normal background part of the heat capacity determined as a linear function of the temperature, which smoothly joins the observed data at temperatures far away from the transition on the both sides. After subtracting the normal part, the excess heat capacity ΔC_p has been plotted in the vicinity of the Sm-A–Sm-C transition in Fig. 2. It is seen that the heat capacity shows significant divergent character on *both* sides of the transition temperature. In particular, the existence of such divergent excess above the transition temperature clearly indicates that this transition is not of the mean-field type.

Since we will discuss below the tricritical nature of the present transition, whether any indication of first-order character exists or not should be checked carefully. Generally, the most typical manifestation of the first-order transition is the thermal hysteresis, where the heating and cooling data do

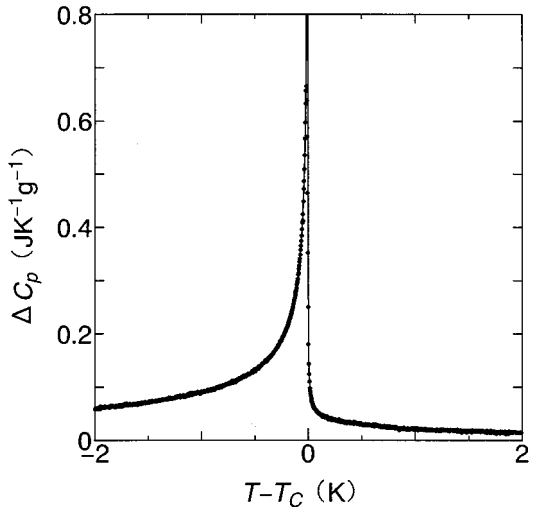

FIG. 2. Detailed view of the excess heat capacity ΔC_p near the Sm-A–Sm-C phase transition for a racemic mixture of MHPOBC. Solid line shows the theoretical tricritical fit with Eq. (3).

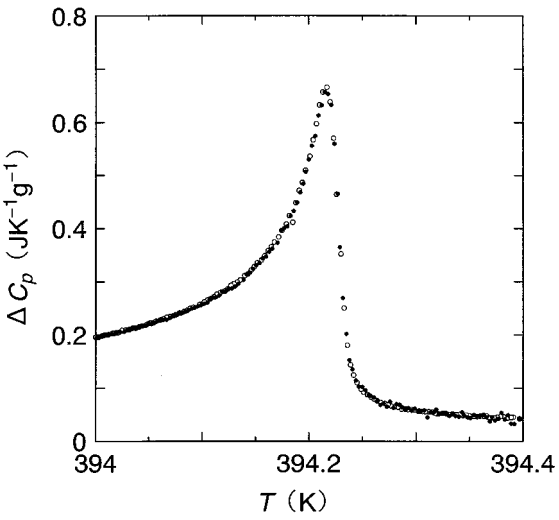

FIG. 3. A comparison of heating (closed circles) and cooling (open circles) data near the Sm-A–Sm-C transition temperature.

not agree with each other near the transition temperature. Such examples are seen in Fig. 1 of Ref. [15], and Fig. 6 of Ref. [16]. Figure 3 shows a comparison of typical heating and cooling data near the heat capacity peak obtained in the present study. It is seen that the heating and cooling data agree quite well. In the ac calorimetry, the existence of the two-phase coexistence region at the first-order transition is often detected as an abrupt change in the phase shift of the ac temperature response (see Fig. 5 of Ref. [17]). However, the phase shift in the present measurement remained unchanged within 0.005 rad near the transition. After all, we conclude that the present data show no first-order nature within the experimental resolution.

III. DATA ANALYSIS

Firstly, the ΔC_p data have been analyzed with the following renormalization-group expression including the correction-to-scaling terms [18]:

$$\Delta C_p = A^{\pm}|t|^{-\alpha}(1+D_1^{\pm}|t|^{\Delta_1}) + B_c, \tag{1}$$

where $t \equiv (T-T_c)/T_c$ is the reduced temperature, and the superscripts $\pm$ denote above and below T_c. The exponent α was adjusted freely in the least-squares fitting procedure. The correction-to-scaling exponent Δ_1 is actually dependent on the universality class, but has a theoretically predicted value quite close to 0.5 (0.524 for 3D XY, and 0.496 for 3D Ising model [18]). Therefore, we fixed its value at 0.5 in this fitting procedure. There is usually a narrow region very close to T_c where data are artificially rounded due to impurities or instrumental effects. The extent of this region was carefully determined in the way described elsewhere [19], and data inside this region were excluded in the fitting. Typically, the rounding region thus determined is $-4\times10^{-5} < t < +1\times10^{-5}$. Fits were made for the data over three ranges, $|t|_{\max} = 0.001$, 0.003, and 0.01, where $|t|_{\max}$ is the maximum value of $|t|$ used in the fit. The first three lines in Table I show the values of the critical exponent α, the critical amplitude ratio A^-/A^+, and other adjustable parameters thus obtained. It is seen that the fits yield α values very close

TABLE I. Least-squares values of the adjustable parameters for fitting ΔC_p with Eqs. (1) and (2). Here $\Delta B = B^+ - B^-$. For the fits with Eq. (1), B_c is shown in place of B^+. The number of data points used N was 209, 550, and 1481 for $|t|_{\max} = 0.001$, 0.003, and 0.01, respectively. The number of degrees of freedom ν is given as $\nu = N - p$, where p is the number of free parameters. Quantities in brackets were held fixed at the given values. The units for A^+, B^+, and ΔB are J K^{-1} g^{-1}.

Eq.	$\lvert t\rvert_{\max}$	T_c (K)	α	$10^4 A^+$	A^-/A^+	Δ_1	D_1^+	D_1^-	B^+	ΔB	χ_ν^2
1	0.001	394.232	0.494	5.52	9.16	[0.5]	−221.0	−28.5	0.134	[0]	0.98
1	0.003	394.233	0.528	2.45	14.20	[0.5]	837.5	57.2	−0.226	[0]	1.14
1	0.010	394.233	0.516	2.91	13.46	[0.5]	1337	96.9	−0.413	[0]	0.97
1	0.001	394.232	[0.5]	4.85	9.80	0.48	150.1	11.7	−0.065	[0]	0.98
1	0.003	394.232	[0.5]	4.18	11.13	0.45	163.6	12.2	−0.078	[0]	1.29
1	0.010	394.232	[0.5]	4.45	10.25	0.54	−379.5	−40.6	0.146	[0]	1.02
2	0.001	394.232	[0.5]	5.29	9.03	[0.5]			0.018	0.019	1.06
2	0.003	394.232	[0.5]	5.86	8.16	[0.5]			0.013	0.016	2.88
2	0.010	394.232	[0.5]	6.46	7.60	[0.5]			0.007	0.016	5.65

to the tricritical value 0.5. Thus we see that the present data show nonclassical (Gaussian) tricritical behavior in contrast with the Landau tricritical behavior reported so far on some Sm-A–Sm-C transitions [4,15]. We also note that the inclusion of the correction-to-scaling term is crucial in describing the present data. In fact, neglecting the $D_1^\pm$ term in Eq. (1) resulted in very poor fits, $\chi_\nu^2 = 5.8$, 14.5, and 33.3 for $|t|_{\max} = 0.001$, 0.003, and 0.01, respectively.

Tricritical fits. We next fitted the data fixing α at the tricritical value 0.5, while Δ_1 was adjusted freely. The obtained parameters are shown in the fourth to sixth lines in Table I. It is seen that the obtained Δ_1 value lies close to 0.5. A slight increase in the Δ_1 value for larger $|t|_{\max}$ may be ascribed to the effect from the second-order correction term, which has the exponent of around 1 [20,21]. If we assume that Δ_1 is exactly equal to 0.5, still having $\alpha = 0.5$, the correction-to-scaling term in Eq. (1) merges with the constant term B_c. As a result, we can rewrite Eq. (1) as

$$\Delta C_p = A^\pm |t|^{-1/2} + B^\pm, \tag{2}$$

where $B^\pm = B_c + A^\pm D_1^\pm$ and $\Delta B \equiv B^+ - B^- \neq 0$. The seventh through ninth lines in Table I show the results of fits with Eq. (2). The fit is quite good for $|t|_{\max} = 0.001$ but becomes clearly worse for $|t|_{\max} = 0.003$ and 0.01.

Fits were also tried with an equation including both first- and second-order correction terms [16,18,20]. Adding the second-order term to Eq. (2), we have

$$\Delta C_p = A^\pm |t|^{-1/2}(1 + D_2^\pm |t|) + B^\pm. \tag{3}$$

Table II shows the obtained parameter values. Because higher-order correction terms are expected to have significant influence away from T_c, only the result for $|t|_{\max} = 0.01$ is shown. In Fig. 2, the solid curve shows the theoretical fit with Eq. (3). The agreement between the observed data and the theoretically calculated smooth curve is satisfactory. The present $D_2^\pm$ values are in a qualitative agreement with those obtained for the tricritical nematic–Sm-A_1 transition [16,22] in the sense that $D_2^\pm < 0$. However, $D_2^-/D_2^+ \cong 0.1$ for the present results is further away from the theoretical expectation $D_2^+ = D_2^-$ and in the opposite direction in comparison with the nematic–Sm-A_1 transition, where $D_2^-/D_2^+ \cong 2.6$–5.0.

Fits with logarithmic corrections. Logarithmic corrections are theoretically expected at tricritical points since the upper marginal dimension d_u is 3. We tried fits with the following asymptotic heat capacity variation as predicted by Lawrie and Sarbach [16,23]:

$$\Delta C_p = A^\pm |t|^{-1/2}(1 + L^\pm \ln|t|)^q + B_c, \tag{4}$$

where $q = -6(n+4)/(3n+22) = -9/7$ for an XY model $(n=2)$. This fitting should be done carefully for the following reasons: (A) Because of its weak temperature dependence, the temperature range of the used data should be as wide as possible. (B) On the other hand, if the data relatively far away from T_c are used, the correction-to-scaling terms should be added, which makes accurate estimate of the logarithmic terms difficult. From point (B), it is better to limit $|t|_{\max}$ within 0.001 or so. Even in these cases, however, the results described above show that at least the first-order correction-to-scaling term should be included. In a similar manner of obtaining Eq. (2), we thus allow the constant term B_c to be independent for above and below T_c, which we denote as B^+ and B^-. We further assumed $L^+ = L^-$. As a result, we obtained $L = -0.008$ for $|t|_{\max} = 0.001$ with $\chi_\nu^2 = 0.99$. Other parameters are $A^+ = 5.929 \times 10^{-4}$, $A^- = 5.298 \times 10^{-3}$, $B^+ = 0.017$, and $B^- = -0.007$ (in J/g K). Since the improvement of the fit is only slight compared with the case without the logarithmic correction, $\chi_\nu^2 = 1.06$, we

TABLE II. Least-squares values of the adjustable parameters for fitting ΔC_p with Eq. (3). Here, $\Delta B \equiv B^+ - B^-$. The units for A^+, $B^\pm$, and ΔB are J K^{-1} g^{-1}.

Eq.	$\lvert t\rvert_{\max}$	T_c (K)	$10^4 A^+$	A^-/A^+	D_2^+	D_2^-	B^+	ΔB	χ_ν^2
(3)	0.01	394.232	5.27	8.96	−338.3	−30.8	0.021	0.004	1.02

see that the logarithmic correction is still not significant in the present temperature range. It was found that the L value is relatively stable against data-range shrinking, $L=-0.012$ for $|t|_{\max}=0.002$, and $L=-0.011$ for $|t|_{\max}=0.0005$. These results indicate that the present data are consistent with the existence of small but nonzero logarithmic correction.

Classical and quasiclassical fits. The existence of distinct excess heat capacity above T_c in the present case automatically prevents one from fitting the data with the extended Landau theory, which predicts no excess above T_c. Nevertheless, we describe here briefly the results of the extended Landau fits for a quantitative comparison with the scaling fits. The expression used is

$$\Delta C_p = A^- \frac{T}{T_c}\left(|t|+\frac{t_0}{3}\right)^{-1/2}+B_c \tag{5}$$

for $T \leqslant T_c$, and

$$\Delta C_p = B_c \tag{6}$$

for $T>T_c$. The definition of t_0 here is consistent with that by Reed *et al.*. [9], and $t_0>0$. When the same rounding region as above is assumed, the fits turned out to be very poor, $\chi_\nu^2=110$ with $|t|_{\max}=0.003$, for example. We also tried fits assuming wider rounding region. Even when the data in a range $T_m-0.05\ \mathrm{K}<T<T_m+0.3\ \mathrm{K}$ (T_m is the temperature of ΔC_p maximum) have been excluded in the fitting, the fit was still not good, $\chi_\nu^2=18.7$ for $|t|_{\max}=0.003$. Thus we clearly see that the present heat anomaly is incompatible with the extended Landau theory [24].

We also tried quasiclassical fits used by Reed *et al.*. for analyzing the data on H10F5MOPP for the cases of finite and infinite sample thickness [9]. The heat anomaly consists of a Landau part and a correction term of the Gaussian type. For the infinite thickness sample it becomes

$$\Delta C_p = A_L \frac{T}{T_c}\left(|t|+\frac{t_0}{3}\right)^{-1/2}+A^-\left(\frac{T}{T_c}\right)^2|t|^{-1/2}+B_c \tag{7}$$

for $T<T_c$, and

$$\Delta C_p = A^+\left(\frac{T}{T_c}\right)^2|t|^{-1/2}+B_c \tag{8}$$

for $T>T_c$. We used the same assumption made by Reed *et al.* [9] that $A^-=2^{1/2}A^+$. The fits were still rather poor, $\chi_\nu^2=5.5$ for $|t|_{\max}=0.001$, with $A_L=3.60\times10^{-3}$ J/g K, $A^+=6.42\times10^{-4}$ J/g K, $B_c=0.0108$ J/g K, and t_0 was practically zero ($|t_0|<10^{-8}$). This result indicates that in the present data the fluctuation effect is so significant that it cannot be viewed as a small correction to the classical behavior as in Eq. (7).

IV. DISCUSSION

Theoretically, the critical exponents are expected to have classical values for the tricritical transition. While the exponent values of the leading singularities have been studied by many experiments on various tricritical transitions, the experimental examination of the correction-to-scaling terms has been made in only limited cases. As for liquid crystal systems, Stine and Garland [16] reported that choosing Δ_1 to be around 1 resulted in inferior fits than those with $\Delta_1=0.5$ in their analyses on tricritical nematic–Sm-A systems. Our present result gives another direct evidence that Δ_1 for the tricritical transition has a classical value 0.5 [25].

It is known that the tricritical amplitude ratio A^-/A^+ is not universal over experimentally accessible $|t|$ ranges. Fisher and Sarbach [26] showed that the tricritical amplitude ratios in an exactly solvable spherical ($n=\infty$) model are functions of the single variable $z=(a/R_0)^3$, where a is the lattice spacing and R_0 is the range of interaction. Their results yield $A^-/A^+=(1-z^2)^{1/2}/z$, so that as the interaction range becomes infinitely large, z goes to zero and therefore A^-/A^+ goes to infinity, recovering the Landau behavior. The value of A^-/A^+ obtained in the present work shown in Table II yields $z=0.11$. For tricritical nematic–Sm-A transitions, it was found that $z=0.530$ in nonpolar mixtures, and $z=0.707$ in polar cyanobiphenyls [16]. Other examples where z values are reported are $z=0.12$ for ^{3}He-^{4}He, and $z=0.21$ for the metamagnet $Dy_3Al_5O_{12}$ [dysprosium aluminum garnet (DAG)] [26]. The present system is less removed from the classical Landau tricriticality than nematic–Sm-A systems, and almost the same as ^{3}He-^{4}He and DAG. In particular, we now have three different tricriticalities in liquid crystals, the one in nematic–Sm-A systems is most different from the classical Landau behavior, the traditional Sm-A–Sm-C (or C^*) systems shows purely classical behavior, and the present case of racemic MHPOBC lies in between. We also note that the smallness of the logarithmic correction amplitude L can be explained by the prediction $L\propto z^2$ expected in the multicomponent limit [26].

The α value obtained in the fits with Eq. (1) agrees remarkably well with the tricritical value 0.5, especially for small $|t|_{\max}$. Further, the t_0 value obtained in the quasiclassical fits with Eqs. (7) and (8) was very close to 0. We found that $|t_0|<10^{-8}$ for $|t|_{\max}=0.001$. This value is much smaller, for example, than $t_0\cong10^{-5}$ reported for H10F5MOPP [9]. When the transition is not exactly tricritical and the quartic term in the free energy has small but nonzero coefficient u, the crossover from tricritical to normal critical behavior is expected. For small u, the crossover function as discussed by Rudnick and Nelson [27,28] can be expanded, and yields a correction with an exponent $-1/2$. We therefore tried fits adding a correction term $D_u^\pm|t|^{-1/2}$ to Eq. (2),

$$\Delta C_p = A^\pm|t|^{-1/2}(1+D_u^\pm|t|^{-1/2})+B^\pm. \tag{9}$$

As for $|t|_{\max}=0.001$, we obtained $\chi_\nu^2=0.92$, $D_u^+=-8.8\times10^{-4}$, and $D_u^-=6.8\times10^{-4}$. The improvement of the fit is slightly better than the case of including the logarithmic correction. However, this improvement seems artifi-

cial at first because $D_u^-/D_u^+<0$ while it is thoretically expected that $D_u^-/D_u^+>0$. Further, parameter values were found to be unstable against data-range shrinking. For example, D_u^- for $|t|_{\max} = 0.0005$ is about 4.5 times larger than that for $|t|_{\max} = 0.002$. To summarize these facts, we conclude that the transition in the present system is extremely close to the tricritical point.

A racemic mixture represents a very special position in a mixture system of two enantiomers where the chirality of the total system vanishes. Therefore, it seems quite improbable that the tricriticality would fall on the racemic point just by chance. Quite interestingly, one further example is known where a racemic mixture exhibits a tricritical behavior at the Sm-A–Sm-C transition: 4- (3-methyl-2-chlorobutanoyloxy) 4′-heptyloxybiphenyl (A7) [15]. On the contrary, racemic 2-methylbuthyl-4′-n-pentyloxybiphenyl-4-carboxylate (2M45OBC) showed an ordinary second-order transition [29]. Although we do not have any theoretical reasoning, it is conceivable that the transition in a racemic mixture is driven to a tricritical one due to some symmetrical reason when a certain requirement is satisfied. The difference between the above two cases is that the transition is first order in chiral (nonracemic) A7, while it is second-order in case of 2M45OBC. The Sm-A–Sm-C_α^* transition in optically pure MHPOBC is second order [10], but the nature of the transition close to but some way from the racemic point is not clearly known. Anyway, such situations will be clarified by a systematic detailed study of the phase diagram in the present system.

In a few cases it was found that the heat capacity shows Landau behavior while the ultrasonic velocity shows non-Landau behavior [30,31]. Benguigui and Martinoty [30] claim that the critical region for the Sm-A–Sm-C transition is dependent on the observable property studied, and they assert that the heat capacity is less sensitive to fluctuation effects than ultrasonic velocities. It is therefore of interest to study elastic constants of chiral and racemic MHPOBC. In particular, since their argument is based on the difference of the fourth-order coefficient in the free energies expressed as strain and as stress, the tricritical case when the fourth-order coefficient vanishes may provide a special situation.

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to 3D XY critical crossover of the heat capacity (see Ref. [7]). Nevertheless, it gives a correct leading correction due to the crossover. It is also to be noted that the crossover function used by the present authors instead of the Rudnick-Nelson-type function gives the same correction in the first approximation.

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