Heat capacity near the nematic–smectic-A transition of a weakly polar, very wide nematic range liquid crystal

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We report high-resolution ac-mirocalorimetry and birefringence measurements near the nematic–smectic-A (N–Sm-A) transition in a weakly polar very wide nematic range ($T_{N\text{-Sm-}A}/T_{N\text{-}I}=0.768$) liquid-crystal compound 4-n-pentyl-cyclohexyl-4-n-butyl-cyclohexyl benzoate (Merck S-1223). The data show a very weak anomaly at the transition with $\alpha=\alpha_{\text{eff}}\sim 0.2$. The very wide nematic range notwithstanding, birefringence data show coupling between the nematic and sematic-A order parameters, which can explain $\alpha_{\text{eff}}>0$. However, the presence of an underlying discontinuity in C_p at T_c suggests that $\alpha_{\text{eff}}>0$ may alternatively be due to evolution from classical mean-field behavior with Gaussian fluctuation corrections to asymptotic critical behavior, a scenario that is shown to be consistent with the Ginzburg criterion.

I. INTRODUCTION

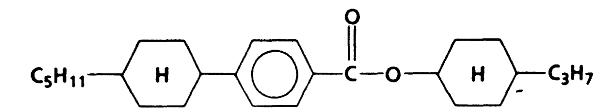
The nematic–smectic-A (N–Sm-A) phase transition has remained an unsolved problem in critical phenomena for fifteen years. Interest was first sparked by mean-field theories of the smectic-A liquid crystal due to Kobayashi[1] and McMillan[2] (KM) and increased dramatically when de Gennes[3] introduced a Ginzburg-Landau (DGL) theory which revealed striking analogies between the smectic-A and the superfluid ^{4}He and superconductor problems. As anticipated by de Gennes, the analogies are imperfect due to a Landau-Peierls[4] instability of the smectic density wave, subsequently predicted[5] and observed by X-ray line-shape experiments.[6]

X-ray,[7] light scattering[8–10] and magnetic deformation[10] measurements of critical exponents are in strong disagreement with all theoretical predictions that have been put forward on the basis of various treatments of the DGL theory, including defect loop unbinding[11–17] models. These predictions include isotropic inverted three-dimensional (3D) XY behavior ($\nu_\parallel=\nu_\perp\sim\frac{2}{3}$) (Refs. 12 and 15–17), isotropic superconductor critical behavior, which may be inverted 3D XY-like for type-II superconductors,[11] and highly anisotropic critical behavior ($2\nu_\perp=\nu_\parallel$) (Refs. 11 and 13). $\nu_\parallel$ and $\nu_\perp$ are the correlation length exponents for smectic correlations parallel and perpendicular to the symmetry axis, respectively. All experiments to date (see Refs. 7–10, and references therein) have found weakly anisotropic exponents ($\nu_\parallel-\nu_\perp\sim 0.1-0.2$), in clear disagreement with theory.

Curiously, heat-capacity experiments are in quite good agreement[18,19] with the usual (noninverted) 3D XY prediction[20] except when tricritical fluctuations are believed to be present[18,21] (as in all but the widest nematic range materials) or where the potential for other forms of multicriticality exist.[22]

The central empirical point about N–Sm-A tricriticality is that in a wide variety of materials wide nematic ranges imply continuous N–Sm-A transition and weak nematic order parameter anomalies (e.g., birefringence anomalies[18]), whereas narrow nematic ranges imply discontinuous (first order in the Ehrenfest sense) N–Sm-A transitions and strong, discontinuous nematic order parameter anomalies. These observations establish the qualitative validity of KM mean-field theories.[1,2] The mean-field theories of KM are quite successful in predicting this phenomenology at least for the nonpolar smectics. Therefore the nematic range as measured by $t_{I\text{-Sm-}A}\equiv(T_{N\text{-}I}-T_{N\text{-Sm-}A})/T_{N\text{-}I}$ where $T_{N\text{-}I}(T_{N\text{-Sm-}A})$ is the nematic-isotropic (nematic-smectic-A) transition temperature, is a good qualitative measure of "distance" from tricriticality; however, the tricritical value of $t_{I\text{-Sm-}A}$ and range of $t_{I\text{-Sm-}A}$ over which tricritical-critical crossover phenomena (such as effective exponents) occur cannot be expected to be universal but rather to depend on details of molecular structure.

For example, in the class of the so-called polar smectic materials (especially those with three benzene rings), many of which show reentrant phases and variations on the classical smectic-A phase (called Sm-A_1) such as Sm-$\tilde{A}$, Sm-A_2, and Sm-A_d, the possibilities for multicriticality are extensive (Ema, Nounesis, and Garland[22]), making a choice of a single parameter, such as $t_{I\text{-Sm-}A}$, as the measure of distance from multicriticality questionable. In extremely wide nematic range polar smectics ($t_{I\text{-Sm-}A}\sim 0.3$) Evans-Lutterodt *et al.*[23] find the heat-capacity exponent α to be comparable with values found in much narrower nematic range materials ($t_{I\text{-Sm-}A}\lesssim 0.07$) composed of nonpolar compounds which have no tendency toward reentrancy. We know of no measurements of nematic-smectic order parameter coupling (e.g., the strength of the birefringence anomaly at



S-1223—4-n-Pentyl-Cyclohexyl-4-n-Butyl-Cyclohexyl Benzoate

Sm-A $\xrightarrow{56.1^\circ C}$ N $\xrightarrow{155.5^\circ C}$ I

$$\frac{T_{N-Sm-A}}{T_{N-I}} = 0.77$$

FIG. 1. Structural formula and mesophase transition temperatures of Merck S-1223.

$T_{N\text{-Sm-}A}$) that would allow us to know whether tricritical phenomenology of the sort found in nonpolar materials[19] is important near $T_{N\text{-Sm-}A}$ in these materials.

In this paper we present heat-capacity data near the N-Sm-A transition of the widest nematic range ($t_{I\text{-Sm-}A}=0.23$) *nonpolar* material studied to date. This work shows that $t_{I\text{-Sm-}A}$ is not a good "distance" parameter even for this restricted class of materials. Furthermore, it is shown that the heat-capacity anomaly is consistent with that expected in a regime where classical mean-field, Gaussian, and critical contributions are present, and that such an interpretation is consistent with the Ginzburg criterion. Alternatively, it is shown that the data are consistent with the form of tricritical behavior found in other nonpolar materials[21] but with the caveat that corrections to scaling are abnormally large.

II. EXPERIMENT

The compound studied is S-1233 (Merck), which has the structural formula and mesophase transition temperatures shown in Fig. 1. Liquid chromatography studies of the as received material indicate that its purity is approximately 99.97%. Our ac calorimetry studies were performed on as received material using a calorimeter described elsewhere,[24] and temperature oscillations of ± 1 mK. The transition temperature, $T_{N\text{-Sm-}A}$ was found to drift slowly (<3 mK/day); the data were corrected for this drift before analysis. Birefringence measurements were made on an Abbe refractometer using homeotropically aligned samples and analyzing the refracted light through a linear polarizer oriented parallel or perpendicular to the director, thus allowing measurements of n_e and n_0, respectively.

III. DATA ANALYSIS AND DISCUSSION

Three features set S-1223 apart from previously studied materials. First it contains two cyclohexane rings and one benzene ring and it contains no strong dipoles (Fig. 1); thus the core is much less aromatic and more weakly interacting than materials studied previously by high-resolution techniques. Second, the nematic range as measured by $t_{I\text{-Sm-}A}$ (0.23) is much wider than for previously studied nonpolar materials, for which $t_{I\text{-Sm-}A} \lesssim 0.07$. Third, in spite of its very wide nematic range, S-1223 exhibits a substantial birefringence anomaly (Fig. 2) suggesting that the nematic order parameter still responds to the smectic field 100 °C below the clearing point ($T_{N\text{-}I}$). The strength of the birefringence anomaly is particularly interesting considering that S-1223 has a weakly interacting central part compared with two or three benzene ring materials, which may explain the failure of the nematic order to saturate far below $T_{N\text{-}I}$. However, weak interactions also reduce nematic-smectic order parameter coupling; thus there are competing effects. Presumably the former is more important; however, the steric interaction may also be quite different in this cyclohexane containing material from that in pure benzene ring materials.

The microcalorimetry data are graphed in Fig. 3 on two expansions of the temperature axis. Two gross features of the data are that the anomaly is quite weak and there appears to be a step $[C_p^+(T_{NA}) < C_p^-(T_{N\text{-Sm-}A})]$ or a continuous but rapid decrease in C_p on warming through $T_{N\text{-Sm-}A}$. Initial fits of the data were made to the simple power-law forms

$$C_p^{\pm} = A^{\pm}|t_{\pm}|^{-\alpha^{\pm}} + B^{\pm} \,, \qquad t_{\pm} = (T - T^{\pm}_{N\text{-Sm-}A})/T^{\pm}_{N\text{-Sm-}A} \tag{1}$$

with no parameter constraints. The resulting fit parameters were $T^{+}_{N\text{-Sm-}A} = 56.3857 \pm 0.0014$ °C, $T^{-}_{N\text{-Sm-}A} = 56.3837 + 0.0002$ °C, $\alpha^+ = 0.172 \pm 0.028$, $\alpha^- = 0.184 \pm 0.020$, $B^+ = 44.4 \pm 1.5 R_0$, $B^- = 49.5 \pm 0.9 R_0$, $A^+ = 2.71 \pm 0.99$ R_0, $A^- = 2.09 \pm 0.55$ R_0, and $\chi^2 = 1.79$. The fit was excellent. This fit illustrates that although the constraints $\alpha^+ = \alpha^-$ and $T^{+}_{N\text{-Sm-}A} = T^{-}_{N\text{-Sm-}A}$ may be allowed by the data, $B^+ = B^-$ clearly is not. $B^- - B^+ = 5.1$ R_0 is the magnitude of the apparent step in the data at $T_{N\text{-Sm-}A}$ (Fig. 3).

Introduction of the above constraints on $\alpha^{\pm}$ and $T^{\pm}_{N\text{-Sm-}A}$ does indeed lead to good fit ($\chi^2 = 1.79$) with pa-

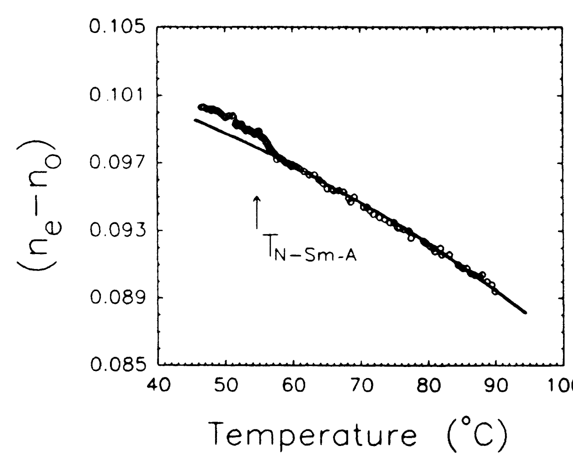


FIG. 2. Birefringence vs temperature near the N-Sm-A transition of S-1223.

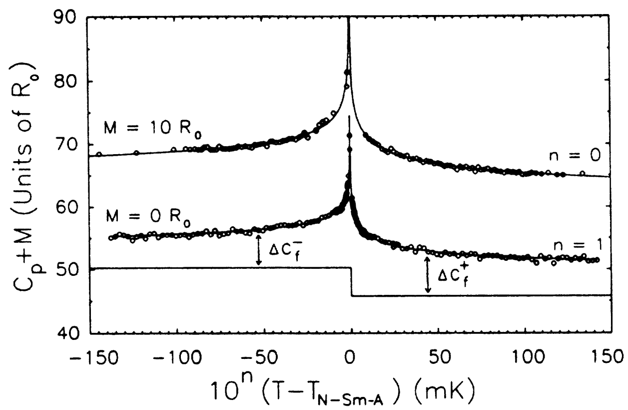


FIG. 3. Specific heat (C_p) vs relative temperature ($T-T_{N\text{-Sm-}A}$) of S-1223 on two expansions of the ($T-T_{N\text{-Sm-}A}$) axis (-150 to 150 mK and -1.5 to 1.5 K). See text for discussion of solid lines.

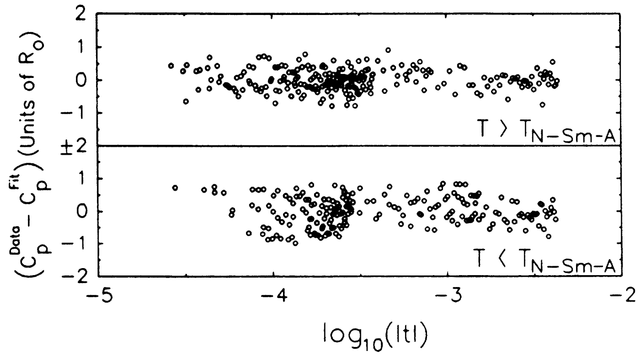


FIG. 4. Deviation ($C_p^{\text{data}}-C_p^{\text{fit}}$) vs logarithm of reduced temperature ($\log_{10}t$) for first fit in Table I [Eq. (1)].

rameters shown in Table I for three ranges of reduced temperature. The range of reduced temperature spanned by the entire data set is $-4.58(-5.5)\leq\log_{10}|t_+|$ $(\log_{10}|t_-|)\leq -2.37(-2.38)$. This range was shrunk toward the asymptotic limit by removing ten points at a time from the data furthest from $T_{N\text{-Sm-}A}$. Results for three values of $|t|_{\max}$ are given in the first three lines of Table I. Due to the weakness of the anomaly and the strong correlation among the parameters $A^{\pm}$, α, and $B^{\pm}$, the variations in $A^{\pm}$ on range shrinking are quite large ($\gtrsim 50\%$); nevertheless the exponent is reasonably stable. The solid line through the data in Fig. 3 is the first fit listed in Table I; the underlying mean-field-like step function is also shown. Deviations of the data from this fit are shown in Fig. 4. Fixing the base-line term at the values found for the $\log_{10}|t|_{\max}=-2.88$ gave reasonably stable parameters on range shrinking and reasonable quality fits as the last three lines of Table I show. The addition of a regular slope term (Et) to the fit equation and imposition of the constraints $B^+=B^-$ led to poor fits ($\chi^2=2.4$) and to a large negative slope term ($E<0$) which is unphysical.

We conclude from the above fits that if $B^->B^+$ is physically allowed then $\alpha\sim 0.24\pm0.04$ describes the data very well over the approximately two and half decades of reduced temperature spanned by the experiment. Except for the special case $\alpha=0(\log_{10})$, however, $B^+\neq B^-$ is inconsistent with simple scaling arguments. It is possible, nonetheless, that $B^--B^+>0$ is a remnant of underlying mean-field behavior upon which is superposed a fluctuation contribution to C_p, ΔC_f, that can be described by a singular term with an effective exponent ($\alpha\sim 0.24$) that lies between the Gaussian value of 0.5 and the N-Sm-A critical value which is empirically close to the 3D XY value ($\alpha\sim -0.01$) (Refs. 18 and 19). In such a case the apparent step in the data would presumably be describable by a large number of correction to scaling terms which produce a very sharp but in fact continuous variation in C_p. The physics of the N-Sm-A transition in S-1223 would then be intermediate between mean field with Gaussian corrections where two lengths are defined,[25]

TABLE I. Fit parameters for fits of data to Eq. (1) under the constraints $\alpha^+=\alpha^-$, $T^+_{N\text{-Sm-}A}=T^-_{N\text{-Sm-}A}$. Three ranges of data were fit in which $\log_{10}|t_\pm|'_{\max}$ is reduced by one decade to show results of range shrinking toward the asymptotic limit. $B^{\pm}$ given in square brackets are fixed at the values given in parentheses.

$\log_{10}\lvert t\rvert_{\max}$	A^+/R (A^-/R_0^0)	α	B^+/R_0 (B^-/R_0)	$T_{N\text{-Sm-}A}$ (°C)	χ^2
−2.37	1.864±0.21 (1.658±0.18)	0.2026±0.01	45.77±0.41 (50.29±0.34)	56.3839±0.0002	1.79
−2.88	0.7749±0.17 (0.7068±0.14)	0.2679±0.02	48.61±0.55 (52.67±0.40)	56.3843±0.0002	1.88
−3.38	0.9138±0.38 (0.8153±0.32)	0.2562±0.03	48.08±0.12 (52.36±0.96)	56.3842±0.003	1.98
−2.37	0.6699±0.01 (0.6137±0.01)	0.2838±0.002	[48.61] ([52.67])	56.3844±0.0001	1.99
−2.88	0.7749±0.02 (0.7068±0.02)	0.2679±0.002	[48.61] ([52.67])	56.3843±0.0001	1.87
−3.38	0.7640±0.021 (0.6981±0.019)	0.2693±0.003	[48.61] ([52.67])	56.3843±0.0001	1.96

and asymptotic criticality where only one length is defined.

It should be noted that in the event that the N–Sm-A transition in S-1223 is in some sense close to a Gaussian mean-field transition one may *not* assume that the underlying mean-field contribution is represented by a simple step function. Adding a sixth power term to an even power Landau expansion leads to specific heat of the form ($T < T_{N\text{-Sm-}A}$)

$$C_p^- = aT(1-bt)^{-1/2} , \tag{2}$$

where the b term ($b > 0$) comes in as a result of the sixth power term. With this in mind we also fit the data to a function of the form

$$C_p^\pm = A^\pm t^{-1/2} + aT(1-bt)^{-1/2} + B \tag{3}$$

to learn whether the additional mean-field temperature dependence below $T_{N\text{-Sm-}A}$ could relieve the need for the smaller than Gaussian exponent. Such was not the case as the fits to Eq. (3) were poor ($\chi^2 \sim 3.5$). Thus in the mean-field–Gaussian–asymptotic critical behavior scenario the asymptotic critical contribution to C_p is evidently substantial. In this regard we note that fitting only the data above $T_{N\text{-Sm-}A}$ gave $\alpha \sim 0.18$ which is certainly far from the Gaussian value; suggesting that Eq. (3) was in any case unlikely to yield a good fit of the data. We return to the question of evolution between mean-field and asymptotic critical behavior below.

The fact that S-1223 exhibits a relatively strong birefringence anomaly at $T_{N\text{-Sm-}A}$ (Fig. 2) suggest that its N–Sm-A transition may not be far from tricriticality. Therefore we have tried fitting the data to forms that have been found successful (in the empirical sense) in materials known to exhibit N–Sm-A tricriticality. We are constrained to this approach because there is no clear theoretical guidance concerning tricriticality generally[26] or N–Sm-A tricriticality specifically. Empirically it is quite clear that the leading singularity near the N–Sm-A tricritical point is close to the classical value, $\alpha = 0.5$; this value also has theoretical support[26] and empirical support in other systems.[27] Clearly, however, the fits described above rule out $\alpha = 0.5$ unless some appropriate correction to scaling terms may be added. Unfortunately, although theory predicts logarithmic corrections to the amplitude of the leading singularity, it provides no help with correction to scaling terms (see discussion in Ref. 21).

We have used the form

$$C_P = A^\pm |t|^{-\alpha}(1 + D^\pm t^{1/2}) + B \tag{4}$$

without theoretical justification, but it appears to work well empirically in a case where N–Sm-A tricriticality is known to exist.[21]

Fits to this form gave good χ^2 values (~ 1.8) but the parameters were very unstable on range shrinking. Furthermore, the magnitude of the correction to scaling terms was 4 to 40 times larger than the leading singularity ($\alpha \sim 0.46$) in the range of the experiment. The baseline term for the fit of the entire data set was $\sim 79\ R_0$, which is larger than the largest measured value of the heat capacity. Note that fixing $\alpha = \frac{1}{2}$ in Eq. (4) is equivalent to allowing $B^+ \neq B^-$ which, for $\alpha^+ = \alpha^-$ and $T^+_{N\text{-Sm-}A} = T^-_{N\text{-Sm-}A}$, brings us back to Eq. (1) except for having fixed α. But as we saw above, letting α adjust in this case gives $\alpha \sim 0.24$, which is far from $\alpha = 0.5$. Indeed fixing $\alpha = 0.5$ in Eq. (4) gave very ppor fits ($\chi^2 \sim 3.4$). So the difference between $\alpha = 0.46$ and 0.5 in Eq. (4) is very important. This is due to the very large values of $D^\pm$. We conclude that Eq. (4) is probably inappropriate for our data.

As a final attempt to fit the data to an empirical form known to give good fits in the tricritical regime we have applied Eq. (7) of Stine and Garland (SG) (Ref. 21)

$$C_p^\pm = A^\pm t^{-1/2}(1 + D^\pm |t| + E^\pm |t|^{3/2}) + B^\pm . \tag{5}$$

Although this form also has no theoretical basis it does give good fits to their data on a near tricritical mixture. It is a form that makes sense if the correction to scaling exponent is $\frac{1}{2}$, as then the exponent of the leading singularity cancels the exponent in the leading correction to scaling term allowing for a step in the base line (which we apparently have). The $D^\pm$ and $E^\pm$ terms are higher-order correction to scaling terms.

We found that this form gave only marginally better fits than the form omitting the $E^\pm$ terms, and that the parameters were unstable on range shrinking for both cases, although the quality of the fits was quite good ($\chi^2 \sim 1.8-1.9$). The result of fitting the entire data set omitting the $E^\pm$ terms is given in the first row of Table II. Also shown are the results of range shrinking while holding $B^\pm$ fixed at the values obtained in fitting the entire data set. It is important to note that the correction to scaling terms $D^\pm |t|$ range from 0.03 to 3 over the range of the data. Thus they are comparable with or exceed the leading singularity over a considerable fraction of the experimental range (see Fig. 5). Although this may be unexpected it cannot be *a priori* ruled out as unphysical. Deviations of the data from the first fit listed in Table II are shown in Fig. 6. Finally we note that the sign of $B^- - B^+$ is opposite to that found by SG and consistent with a mean-field discontinuity. We conclude that our data give results consistent with the results of SG on their nearly tricritical mixture but with substantially larger correction to scaling contributions and an inverted step discontinuity.

Several other attempts were made at fitting the data to tricritical ($\alpha = \frac{1}{2}$) forms including lgoarithmic amplitude correction and various assumed correction to scaling forms. Based on the results it would appear that any form with $\alpha \sim 0.5$ and $C_p^+(T_{N\text{-Sm-}A}) = C_p^-(T_{N\text{-Sm-}A})$ (no step at $T_{N\text{-Sm-}A}$) either gives poor fits or results in anomalously large correction to scaling terms. The SG form, however, is consistent with our data but gives large correction terms. If, in fact, the N–Sm-A transition $S-1223$ is near tricriticality, as fits to the SG form could suggest, this may explain the birefringence anomaly and would indicate that the tricritical values of $t_{I\text{-Sm-}A}$ may be a strong function of molecular structure even within the class of nonpolar (or weakly polar) materials.

Central features of the data appear to be that

TABLE II. Fit parameters for fits of data to Eq. (5) with $E^{\pm}=0$. Three ranges of data were fit in which $\log_{10}|t_{\pm}|_{max}$ is sequentially reduced to show the results of range shrinking toward the asymptotic limit. $B^{\pm}$ values shown in square brackets were fixed at the values given in parentheses.

$\log_{10}\|t\|_{max}$	A^+/R_0 (A^-/R_0)	D^+ (D^-)	B^+/R_0 (B^-/R_0)	$T_{N\text{-Sm-}A}$ (°C)	χ^2
−2.38	0.04085±0.0032 (0.04235±0.0041)	−1329.3±17.3 (−1061.6±16.2)	54.00±0.10 (57.24±0.15)	56.3854±0.0002	1.86
−2.88	0.4114±0.0004 (0.4214±0.0005)	−1353.8±38.9 (−1042.7±30.8)	[54.00] [(57.24)]	56.3853±0.0002	1.94
−3.38	0.04095±0.0005 (0.04195±0.0008)	−1323.1±64.9 (−1010.2±78.4)	[54.00] [(57.240)]	56.3853±0.0002	2.06

$0.2 \lesssim \alpha_{eff} \lesssim 0.5$ and that there exists a steplike change in C_p at $T_{N\text{-Sm-}A}$ consistent in sign with mean-field theory and comparable with the fluctuation contribution to C_p in the experimental range. Both of these features are consistent with the hypothesis that the transition is in the evolutionary regime between mean field with Gaussian fluctuation corrections ($\alpha_G \cong 0.5$) and asymptotic N–Sm-A criticality ($\alpha_{N\text{-Sm-}A} \lesssim 0$). To further test this hypothesis one can apply the Ginzburg criterion (GC) to the data.[25] The solid line in Fig. 3 is a fit of the data to Eq. (1) (line 1 in Table I). The step function below the data would by hypothesis approximate the underlying classical mean-field contribution. Thus the fluctuation contribution $\Delta C_f^{\pm}$ is as shown in the figure.

According to the GC the asymptotic critical regime should occur when the fluctuation contribution to the heat capacity, ΔC_f, is much larger than the mean-field contribution

$$\Delta C_f^{\pm} \gg \Delta C_{MF} = B^- - B^+ \qquad (6)$$

and conversely for the classical mean-field regime. Now

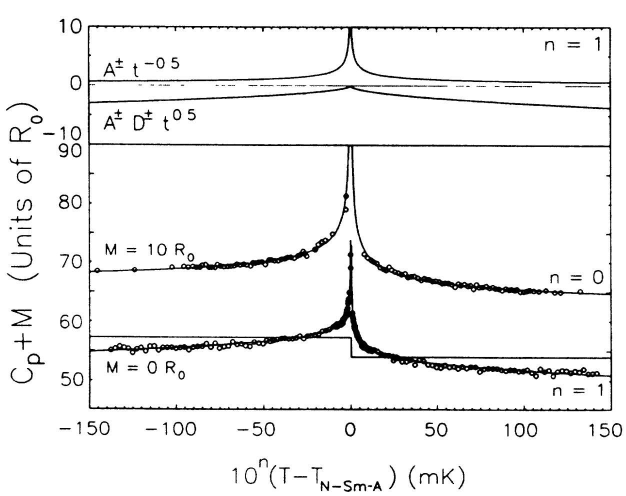


FIG. 5. Specific heat (C_p) vs relative temperature ($T-T_{N\text{-Sm-}A}$) of S-1223 on two expansions of the ($T-T_{N\text{-Sm-}A}$) axis (−150 to 150 mK and −1.5 to 1.5 K). See text for discussion of solid lines.

$$\Delta C_f^{\pm} = A^{\pm}|t_{\pm}|^{-\alpha} \qquad (7)$$

with $A^{\pm}$ and α given in the first row of Table I. $\Delta C_f^{\pm}$ is clearly comparable with but somewhat greater than ΔC_{MF} throughout the range of data (see Fig. 3), thus the data lie intermediate between the Gaussian mean-field and the asymptotic critical regime according to the GC, in agreement with $\alpha_{N\text{-Sm-}A} \sim -0.01 < \alpha_{eff} \sim 0.24 < 0.5 = \alpha_G$.

The reduced temperatures $t_G^{\pm}$ that separate the two regimes are given by the conditions

$$\Delta C_{MF} = B^- - B^+ = \Delta C_f^{\pm} = A^{\pm}|t_G|^{-\alpha} . \qquad (8)$$

Using the parameters in line 1 of Table I this gives t_G^+ (t_G^-)$=1.27\times10^{-2}$ (7.15×10^{-3}); to be compared with $|t_{\pm}|^{max} \sim 4\times10^{-3}$. If one chooses the second or third fit in Table I one gets t_G^+ (t_G^-)$=3\times10^{-3}$ (2×10^{-3}). Clearly the $t_G^{\pm}$ are comparable with $|t_{\pm}|^{max}$; therefore neither the GC [Eq. (6)] nor its converse is valid. It would appear that the data are too close to the asymptotic critical regime to be described by Gaussian fluctuations ($\alpha_G=0.5$), because $|t^{\pm}|_{max} \sim |t_G^{\pm}|$, and too far from asymptotic criticality to be described by empirically observed N–Sm-A critical behavior ($\alpha \lesssim 0$) (Refs. 18, 19, and 24), even with lowest-order corrections to scaling [Eq. (4)] included, because $|t_{max}^{\pm}| \ll |t_G^{\pm}|$ is not true. Finally we note that the measured value of $B^- - B^+$ ($\sim 4.5\ R_0$) may be somewhat

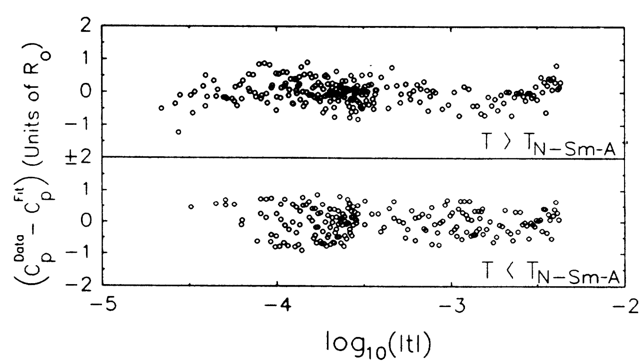


FIG. 6. Deviation ($C_p^{data}-C_p^{fit}$) vs logarithm of reduced temperature ($\log_{10}t$) for first fit in Table II [Eq. (5)].

low since we are nearer to asymptotic criticality ($\alpha_{\rm eff} < 0.5$) than the GC calculation assumes and, of course, $B^- = B^+$ is required in the asymptotic regime. Thus our estimates of $|t_G^\pm|$ may be upper limits which would make GC estimates of the bare correlation lengths (see below) lower limits.

With the above estimates of $t_G^\pm$ one may estimate the bare correlation lengths from the theoretical form of the GC that follows from Eq. (6) when $\Delta C_{\rm MF}$ is calculated from fourth-order Landau theory and $\Delta C_f^\pm$ are calculated in the Gaussian approximation from Ginzburg-Landau theory. This gives

$$t_G^\pm = \frac{1}{64\pi^2(\xi_0^\pm)^6 \Delta C_{\rm MF}^2} . \tag{9}$$

Here $\Delta C_{\rm MF}$ is measured in units of Boltzmann's constant per volume. In doing this it is necessary to recall that for the anisotropic N–Sm-A transition one has[11]

$$\xi_0 = (\xi_{0\perp}^2 \xi_{0\parallel})^{1/3} \tag{10}$$

with $\xi_{0\parallel} \sim 6\xi_{0\perp}$ (Refs. 6–8). Using $t_G^+ = 1.27\times10^{-2}$ and $\Delta C_{\rm MF} = 4.52\ R_0$ one gets $\xi_0^+ = 3.8$ Å; therefore

$$\xi_{0\perp}^+ = 2.1, \quad \xi_{0\parallel}^+ = 12.6 \tag{11}$$

(in Å) are lower limits on the bare lengths. They are comparable with measured bare lengths in other systems[6–8] (which, however, are certaintly measured in the critical regime) and approximately two times smaller than the molecular dimensions. Using other estimates of t_G and $\Delta C_{\rm MF}$ obtained from Table I fits does not substantially alter these results because of the sixth power dependency of t_G and ξ_0. Clearly the interpretation of S-1223 data in terms of the GC is internally consistent. One significance of this is that the N–Sm-A transition in S-1223 may be the first example of an N–Sm-A transition that is *not* dominated by critical fluctuations.

IV. CONCLUSIONS

The specific-heat exponent is in the range $0.2 < \alpha_{\rm eff} < 0.5$ and the data are consistent with evolution from mean field to Gaussian to asymptotic critical behavior and, alternatively, with near tricriticality of the N–Sm-A transition. The former hypothesis gives slightly better fits of the data with one less parameter and results in extensive consistency with Ginzburg criterion ideas. There are no other known examples of such N–Sm-A transition behavior. The latter has the advantage that it can explain the birefringence anomaly in a straightforward way but at the cost of introducing large correction to scaling terms. If the latter explanation is correct S-1223 would have the widest nematic range ($t_{I\text{-Sm-}A} \cong 0.23$) of any nonpolar material exhibiting a nearly tricritical N–Sm-A transition. In any case the birefringence anomaly is unexpected both theoretically (KM) and by comparison with other materials, given the large value of $t_{I\text{-Sm-}A}$. Given either of the above scenarios S-1223 represents a very interesting class of materials from the point of view of N–Sm-A transition phenomenology.

The molecular structure of S-1223 is, of course, very different from that of all materials whose N–Sm-A transitions have been previously studied. Therefore it will be important to complement this study with x-ray and elastic constant studies of S-1223 and to extend experimental characterization to its homologs and other cyclohexane based materials.

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