

XY behavior for the heat capacity at nematic–smectic- A_1 liquid-crystal transitions

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(Received 29 August 1988)

High-resolution ac calorimetric data are reported for three polar liquid-crystal systems: octyloxyphenylcyanobenzoxybenzoate (8OPCBOB), a mixture of pentylphenylcyanobenzoxybenzoate (DB₅CN)+cyanobenzoyloxy-pentylstilbene (C₅ stilbene), and a mixture of DB₆CN+C₅ stilbene. All three exhibit nematic–smectic- A_1 liquid-crystal transition heat-capacity peaks well described by the XY critical exponent $\alpha_{XY} = -0.007$. The critical amplitude ratio A^-/A^+ ($=0.99$) agrees fairly well with the XY value and is inconsistent with the theoretically expected inverted-XY value. Correction terms also play an important role.

The three-dimensional XY model (the $d=3, n=2$ vector model) represents an important universality class in the theory of phase transitions. However, detailed predictions^{1,2} for the XY critical behavior of the heat capacity C_p have been tested only on helium near its normal superfluid transition.³ The nematic (N) to smectic- A (Sm- A) liquid-crystal transition is also expected to be in the XY universality class, albeit with an inverted C_p amplitude ratio.⁴ Critical N–Sm- A liquid-crystal exponents reported previously⁵ for nonpolar systems that exhibit the monomeric Sm- A_m phase and polar systems that exhibit the partial bilayer Sm- A_d phase do not conform completely with theoretical XY values.⁶ In this Rapid Communication, we report heat-capacity data on three polar-liquid-crystal systems that exhibit a monolayer Sm- A_1 phase. The analysis presented below will show that these $C_p(N\text{--}Sm\text{--}A_1)$ data agree well with the theoretically expected XY exponent α , amplitude ratio A^-/A^+ , and dimensionless ratio $R_{B_c}^+$.

The investigated N–Sm- A_1 systems are more stable than those studied previously^{7,8} and thus permit high-resolution calorimetric measurements unaffected by drifts in the critical temperature due to thermally generated impurities. Measurements were made with a computer-controlled ac calorimeter described in detail elsewhere.⁹ The systems investigated are pure octyloxyphenylcyanobenzoxybenzoate (8OPCBOB)¹⁰ and two mixtures of alkylphenylcyanobenzoxybenzoate (DB_{*n*}CN)+cyanobenzoyloxy-pentylstilbene (C₅ stilbene).¹¹ One mixture contained the pentyl compound DB₅CN and had a C₅ stilbene mole fraction $X=0.492$; the other mixture contained the hexyl homolog DB₆CN and had $X=0.505$. The heat-capacity variation associated with the N–Sm- A_1 transition is shown for these systems in Figs. 1–3. The critical behavior is in good agreement with the XY model for all three systems. In particular, these $C_p(N\text{--}Sm\text{--}A_1)$ data yield critical amplitude ratios A^-/A^+ that agree with XY behavior rather than the predicted inverted-XY behavior.⁴

The heat-capacity data have been analyzed using the renormalization-group expression

$$C_p^\pm = A^\pm |t|^{-\alpha} (1 + D_1^\pm |t|^{\Delta_1} + D_2^\pm |t|^{2\Delta_1}) + B + E\Delta T, \tag{1}$$

where $t \equiv (T - T_c)/T_c$ and \pm indicates above and below the transition. The corrections-to-scaling exponent Δ_1 is taken to be 0.5, and both first- and second-order correction terms are taken into account.^{12,13} The temperature-independent quantity B consists of a regular (background) contribution B_{reg} and a critical contribution B_c .¹ The value of E in the regular term $E\Delta T$ has been set equal to zero for all the present fits since C_p^+ data in the nematic phase far from T_c do not indicate any significant variation with temperature.^{10,11} It has been demonstrated that any physically plausible value for E ($0\text{--}0.007 \text{ JK}^{-2} \text{ g}^{-1}$) has no effect on the important parameters α and A^-/A^+ .

Table I lists the values of the critical exponent α , the amplitude ratio A^-/A^+ , and the other adjustable parameters when data over three t_{max} ranges are least-squares fit with Eq. (1) holding D_2^\pm fixed at zero, as is the usual practice. Some data points just below T_c have been excluded from the fit, and the t_{min} values are given for each system in the caption of Table I. A discussion of this issue will be given elsewhere.¹⁰ For comparison, analogous fits are also reported for previously published data on butyloxybenzylideneheptylaniline (abbreviated as 40.7),⁵ which is the only well-characterized nonpolar material

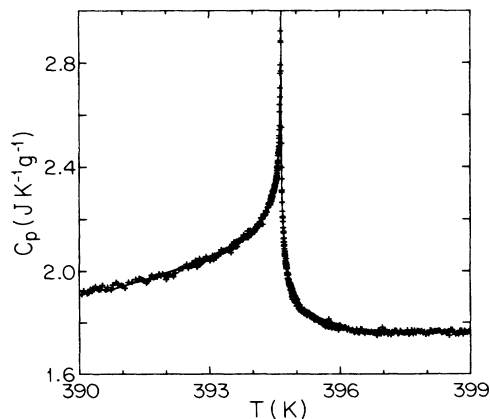


FIG. 1. Heat capacity near the N–Sm- A_1 transition in 8OPCBOB. The reduced temperature range of the fit is $\pm 10^{-2}$, and the line represents fit 1* in Table II.

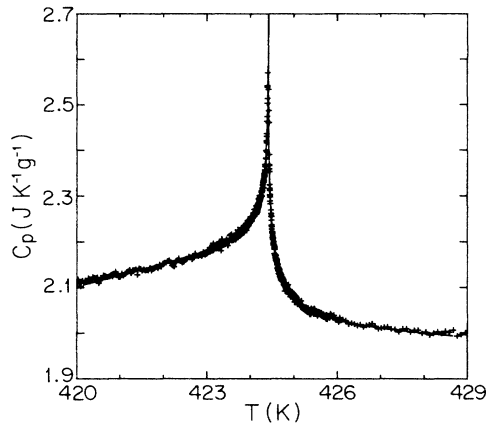


FIG. 2. Heat capacity near the N -Sm- A_1 transition in a DB_5CN+C_5 stilbene mixture. The reduced temperature range of the fit is $\pm 10^{-2}$, and the line represents fit 2* in Table II.

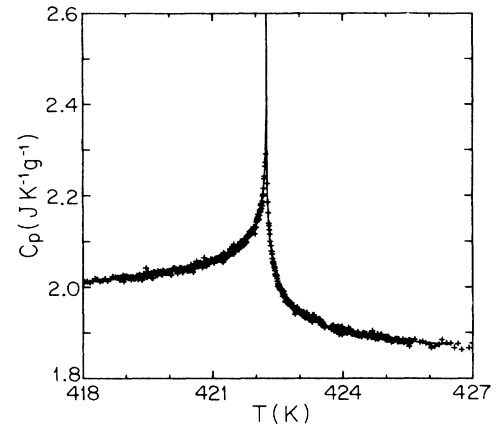


FIG. 3. Heat capacity near the N -Sm- A_1 transition in a DB_6CN+C_5 stilbene mixture. The reduced temperature range of the fit is $\pm 10^{-2}$, and the line represents fit 3* in Table II.

with XY behavior for the heat capacity at a N -Sm- A_m transition. It is clear from Table I that each of these four systems yields an α value in good agreement with the 3D XY value of -0.007 .⁶ Since the standard deviations in the least-squares α values are moderately large (± 0.009 for the three polar systems and ± 0.019 for the 40.7 system), these data do not provide a stringent test of the theoretical α_{XY} value. However, the important conclusion is that the C_p (N -Sm- A_1) data are fully consistent with the α_{XY} exponent value.

It is clear from Table I that χ^2_ν for the polar systems increases as the value of $|t|_{\max}$ is increased. This is due to systematic deviations that occur for $|t| > 3 \times 10^{-3}$. Furthermore, the adjustable parameters A^+ , A^-/A^+ , D_1^+ , D_1^-/D_1^+ , and B exhibit small but systematic trends as $|t|_{\max}$ is increased from 10^{-3} to 10^{-2} . Allowing E to be nonzero does not help appreciably, but allowing nonzero values for the coefficients D_2^\pm produces sig-

nificant improvements.

The least-squares parameter values and the χ^2_ν values for fits with Eq. (1) including the D_2^\pm terms are shown in Table II. For these fits, the critical exponent has been fixed at the theoretical 3D XY value. The parameters in Table II were obtained by fitting data over range C, the widest range. Values of χ^2_ν are given for that range and also for ranges A and B. As shown in Table II and Figs. 1-3, very good fits are achieved in all three ranges with no further adjustment of parameters as the range is narrowed.

Note that the magnitudes of the first correction coefficients D_1^\pm are large for the polar liquid crystals compared to those for the 40.7 system or those for the normal superfluid transition in helium ($D_1^+ \approx D_1^- = -0.020$).¹² Thus, it is not surprising that the D_2^\pm terms also play an important role in fitting the polar N -Sm- A_1 data.^{13,14} Furthermore, it should be noted that

TABLE I. Least-squares parameter values obtained on fitting $C_p(N$ -Sm- $A_1)$ data over three ranges: $|t|_{\max} = 10^{-3}$ (range A), $|t|_{\max} = 3 \times 10^{-3}$ (range B), and $|t|_{\max} = 10^{-2}$ (range C). The values of $10^5 t_{\min}$ are +1 and -9 for 8OPCBOB, +2 and -8 for DB_5CN+C_5 stilbene, +3 and -7 for DB_6CN+C_5 stilbene, and +2 and -4 for the 40.7 system. The coefficients D_2^\pm and E in Eq. (1) were held fixed at zero for these fits. The units of A^+ and B are $JK^{-1}g^{-1}$. Fits to N -Sm- A_m data for the nonpolar 40.7 system (Ref. 5) are shown for comparison.

Fit	System	Range	α	A^+	A^-/A^+	D_1^+	D_1^-/D_1^+	B	T_c (K)	χ^2_ν
1A	8OPCBOB	A	-0.0093	-23.48	0.984	-0.326	1.062	23.65	394.661	1.20
1B		B	-0.0082	-22.91	0.983	-0.225	0.763	23.36	394.662	1.36
1C		C	-0.0075	-21.69	0.980	-0.172	0.423	22.36	394.664	2.25
	DB_5CN									
2A	$+C_5$ stilbene	A	-0.0078	-16.98	0.993	-0.258	1.269	18.06	424.422	0.99
2B		B	-0.0064	-16.87	0.991	-0.142	1.128	18.17	424.426	1.12
2C		C	-0.0054	-16.79	0.990	-0.090	0.808	18.23	424.429	1.85
	DB_6CN									
3A	$+C_5$ stilbene	A	-0.0070	-14.16	0.995	-0.114	2.249	15.42	422.241	0.98
3B		B	-0.0070	-13.09	0.991	-0.123	1.358	14.40	422.245	1.06
3C		C	-0.0067	-12.06	0.989	-0.093	1.126	13.46	422.250	1.10
	40.7									
4A		A	-0.0070	-10.16	0.991	-0.026	-1.413	12.82	329.752	1.10
4B		B	-0.0069	-10.15	0.989	-0.038	-1.988	12.82	329.753	1.02
4C		C	-0.0070	-10.16	0.988	-0.053	-1.611	12.81	329.753	0.92

TABLE II. Least-squares values of the adjustable parameters (with their standard deviations) obtained on fitting $C_p(N\text{-Sm-}A_1)$ data with Eq. (1). The slope $E=0$ for all fits, and the critical exponent α is fixed at the 3D XY value (-0.007). Data were fit over range C ($|t|_{\max}=10^{-2}$). The units for A^+ and B are $\text{JK}^{-1}\text{g}^{-1}$. A fit to the $N\text{-Sm-}A_m$ data for the nonpolar 40.7 system is shown for comparison. In each case, a χ^2 value is given for range A ($|t|_{\max}=10^{-3}$) and range B ($|t|_{\max}=3\times 10^{-3}$) as well as range C.

Fit	System	A^+	A^-/A^+	D_1^+	D_1^-/D_1^+	D_2^+	D_2^-/D_2^+	B	$T_c(\text{K})$	$\chi^2(\text{A})$	$\chi^2(\text{B})$	$\chi^2(\text{C})$
1*	8OPCBOB	-28.54 ± 0.32	0.987 ± 0.002	-0.241 ± 0.007	1.03 ± 0.02	0.50 ± 0.05	2.55 ± 0.28	28.87 ± 0.30	394.662 ± 0.002	1.60	1.39	1.21
2*	DB ₅ CN +C ₅ stilbene	-17.26 ± 0.23	0.992 ± 0.002	-0.236 ± 0.008	1.31 ± 0.03	0.72 ± 0.06	2.11 ± 0.15	18.43 ± 0.21	424.425 ± 0.0002	1.09	1.02	1.04
3*	DB ₆ CN +C ₅ stilbene	-13.58 ± 0.33	0.992 ± 0.003	-0.147 ± 0.013	1.57 ± 0.09	0.23 ± 0.09	3.6 ± 1.2	14.86 ± 0.31	422.245 ± 0.0003	1.07	0.99	0.94
4*	40.7	-10.16 ± 0.38	0.989 ± 0.006	-0.045 ± 0.040	-1.45 ± 2.0	-0.08 ± 0.29	-2.7 ± 12	12.82 ± 0.40	329.753 ± 0.0004	1.16	1.06	0.91

the ratio D_1^-/D_1^+ in Table II is close to +1 for the three polar systems, as expected theoretically.¹²

Let us now consider the critical amplitude ratio A^-/A^+ . The best available calculation of A^-/A^+ for the 3D XY universality class is 0.9714 ± 0.0126 .² Thus the inverted-XY ratio is $A^-/A^+ = 1.0294 \pm 0.0134$. The experimental A^-/A^+ ratio, which lies in the range 0.987–0.992, is close to the XY value and is inconsistent with the inverted-XY value. It should be stressed that there is a large *qualitative* difference in the C_p curve when $A^- < A^+$, $A^- = A^+$, and $A^- > A^+$. Since the theoretical fitting function represents a finite cusp where B is the value of C_p at T_c , the (negative) critical amplitudes A^- and A^+ indicate how large a quantity is to be subtracted from B as $|t|$ grows. The difference $C_p^- - C_p^+$ at any given $|t|$ value is well approximated by $-A^+[1 - (A^-/A^+)]|t|^{-\alpha}$. Since the experimental value of $C_p^- - C_p^+$ is always positive, it follows that $A^-/A^+ < 1$. Indeed, the quality of the fits is very sensitive to A^-/A^+ . If range-A data for 8OPCBOB are fit with $\alpha = -0.007$ and fixed A^-/A^+ ratios, we obtain $\chi^2 = 4.1$ for $A^-/A^+ = 0.971$, $\chi^2 = 1.2$ for $A^-/A^+ = 0.988$, $\chi^2 = 10.4$ for $A^-/A^+ = 1.0$ (a symmetrical form), and $\chi^2 = 30.3$ for $A^-/A^+ = 1.029$ (inverted-XY form). This conclusion about the A^-/A^+ ratio in $N\text{-Sm-}A_1$ systems is also supported by the $N\text{-Sm-}A_m$ heat-capacity data on the 40.7 system. It is, of course, possible that C_p will cross over to inverted-XY behavior very close to T_c ($|t| < 2 \times 10^{-5}$), but the deviations observed in the region $2 \times 10^{-5} < |t| < |t_{\min}|$ do not support such a trend.¹⁰ The predicted crossover from XY to inverted-XY behavior depends on fluctuations in the nematic director having a significant influence on the smectic-liquid-crystal order parameter asymptotically close to T_c . It appears that data in the currently available experimental range

$|t| > 2 \times 10^{-5}$ do not show inverted-XY behavior (unless one wishes to consider $A^-/A^+ = 0.99$ as an effective ratio reflecting the early stages of a very broad crossover from 0.97 to 1.03). This conclusion is independent of the fitting range and the inclusion or exclusion of corrections-to-scaling terms. In summary, $N\text{-Sm-}A$ -liquid-crystal heat-capacity peaks that are well described by the XY critical exponent do not show inverted-XY amplitude ratios.

The character of the fits reported in Table II can be further tested by considering the correlations between A^+ , D_1^+ , and $B_c = B - B_{\text{reg}}$. The dimensionless ratio $R_{B_c}^+ \equiv A^+ |D_1^+|^{\alpha/\Delta_1} / B_c$ is a universal quantity¹⁵ and the 3D XY value is estimated to be -1.057 ± 0.022 .^{1,15} Choosing B_{reg} from the noncritical C_p behavior far from T_c , we obtain $B_c = 27.11$ (8OPCBOB), 16.44 (DB₅CN+C₅ stilbene), 13.00 (DB₆CN+C₅ stilbene), and 10.52 (the 40.7 system), all in units of $\text{JK}^{-1}\text{g}^{-1}$. The resulting values of $R_{B_c}^+$ with their standard deviations are -1.074 ± 0.025 (8OPCBOB), -1.071 ± 0.029 (DB₅CN+C₅ stilbene), -1.073 ± 0.054 (DB₆CN+C₅ stilbene), and -1.008 ± 0.085 (the 40.7 system). The agreement between experimental and theoretical $R_{B_c}^+$ values is excellent for all three polar systems and satisfactory for the 40.7 system.

The observation of XY behavior for the heat capacity does not, of course, guarantee that all aspects of $N\text{-Sm-}A_1$ critical behavior will conform to the XY model, as the global $N\text{-Sm-}A_m$ results on the 40.7 system show.⁵ It would be of great interest to carry out high-resolution x-ray studies of these polar $N\text{-Sm-}A_1$ systems.

We wish to acknowledge stimulating discussions with A. Aharony, B. Halperin, and T. Lubensky. This work was supported by National Science Foundation Grants No. DMR-87-02052 and No. DMR 87-19217.

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