Critical linear thermal expansion in the smectic-A phase near the nematic-smectic phase transition

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Recent high-resolution x-ray investigations of the smectic-A (SmA) phase near the nematic-to-SmA transition provide information about the critical behavior of the linear thermal expansion coefficient \( \alpha \) parallel to the director. Combining such data with available volume thermal expansion \( \alpha_v \) data yields the in-plane linear expansion coefficient \( \alpha_i \). The critical behaviors of \( \alpha_i \) and \( \alpha_v \) are the same as those for \( \alpha_v \) and the heat capacity \( C_p \). However, for any given liquid crystal, \( \alpha_i(\text{crit}) \) and \( \alpha_v(\text{crit}) \) differ in sign. Furthermore, the quantity \( \alpha_i(\text{crit}) \) is positive for SmA\(_{\parallel} \) partial bilayer smectics, while it is negative for nonpolar SmA\(_{\perp} \) monomeric smectics. This feature is discussed in terms of the molecular structural aspects of these smectic phases.

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I. INTRODUCTION

The character of the liquid-crystal nematic (N)-smectic-A (SmA) phase transition is one of the more challenging problems in condensed-matter theory [1,2]. Detailed studies of the critical behavior show a crossover from Gaussian tricritical to \( XY \)-like second order as the width of the nematic range increases (i.e., the McMillan parameter \( R_M = T_{NA}/T_{IN} \) decreases) [2,3]. Due to Landau-Peierls instabilities, the SmA phase has a lower critical dimensionality of 3, and thus algebraic decay of smectic correlations is observed in the SmA phase [4] rather than true long-range order. Nevertheless, on length scales important for many properties, the N-SmA transition in a liquid crystal (LC) with a small \( R_M \) value behaves very much like a three-dimensional (3D) \( XY \) system. Detailed analyses have been made of the N-SmA critical behavior for systems in the tricritical (small N-range [5]) and 3D \( XY \) (large-N range [6]) limits.

The most extensive studies of the N-SmA critical behavior have been carried out in the N phase, and those measurements made in the SmA phase are mostly thermal. Heat capacity [2,3] and volume thermal expansion [7,8] data exist in both the N and SmA phases, and both of these properties show that scaling holds with \( \alpha^* = \alpha^- = \alpha \) for the critical exponent above \( T_{NA} \) and below. The layer compressional elastic constant \( B(T) \) has also been studied in the SmA phase, but its critical behavior is still imperfectly understood [2,9].

Quite recently, detailed x-ray studies of the SmA region have been carried out in connection with randomly perturbed liquid crystal-aerosil dispersions; see Ref. [10] for an overall analysis of one such LC+aerosil system. X-ray studies of some pure bulk LC’s and several LC-aerosil dispersions provide detailed data on the temperature dependence of the smectic layer thickness \( d(T) \). Thus, such x-ray data yield the critical behavior in the SmA phase of the \textit{linear} thermal expansion coefficient \( \alpha_i(T) \) normal to the layer (i.e., parallel to the director). Combining x-ray \( \alpha_i \) values with dilatometric data for the volume thermal expansion coefficient \( \alpha_v(T) \) allows one to determine also \( \alpha_v(T) \), the in-plane linear thermal expansion coefficient.

It will be shown in this paper that both the linear expansion coefficients \( \alpha_i \) and \( \alpha_v \) exhibit the same critical behavior as \( \alpha_v \) and \( C_p \). However, \( \alpha_i(\text{crit}) \) and \( \alpha_v(\text{crit}) \) are observed to differ in sign. Thus consideration of the behavior of the linear coefficients sheds new light on a “structural” aspect of SmA formation. The LC systems analyzed here include two partial bilayer smectics SmA\(_{\parallel} \) (8CB=octyloxycyanobiphenyl and 8OCB=octyloxycyanobiphenyl) and three nonpolar “monomeric” smectics [11] SmA\(_{\parallel} \) (8BS=pentylphenylthiol octyloxybenzoate, 10S5 = the decyl homolog of 8S5, and 4O.8=butoxybenzylidene octylamine). Table I lists the value of the critical heat capacity exponent \( \alpha \) and the phase sequence with transition temperatures for these five LC’s. The structural formulas for these molecules are shown in Fig. 1.

II. DATA ANALYSIS

In recent years, high-resolution dilatometry has yielded excellent \( V(T) \) data and thus volume thermal expansion coefficients \( \alpha_v(T) \) in both the N and SmA phases of several LC’s [7,8,13,14]. These results, which provide much better \( V(T) \) data than that obtained with Paar-type vibrating tube instruments [15], are especially good for 8CB, 8OCB, 8S5, and 10S5 [7,8]. For all four of these LC’s, the analysis of the critical behavior of \( \alpha_v(T) \) yields critical exponents \( \alpha \) in excellent agreement with those obtained from \( C_p \) studies. The available \( \alpha_v(T) \) data for 4O.8 [13] are somewhat less detailed but still of considerable value.

Detailed x-ray data have been obtained for smectic scattering in the SmA phase of a few LC’s. A by-product of such...
high-resolution x-ray studies is good Bragg wave vector $q_0(T)$ data from the $S(q)$ scattering profiles for five LC’s: 8CB [16–18], 8OCB [18–20], S5 [20–22], T0S5 [23], and 4O.8 [24]. Some of this x-ray work has been associated with recent studies of LC+aerosil systems. In the case of such LC+aerosil studies, it has been shown that $q_0(T)$ for a LC with a low density of dispersed aerosil particles is essentially the same as $q_0(T)$ for the pure bulk LC [17,19,20]. Although the critical behavior of $C_p$ for LC+aerosil systems evolves with aerosil density [10], the apparent change in $d(T)$ is subtle and only visible close to $T_c$, where the available data are too sparse to allow a determination of a trend. Thus, utilizing data from both pure LCs and dilute LC+aerosils, the smectic layer thickness $d=2\pi/q_0$, with an average uncertainty of ±0.014 Å, is well known for these five LC’s as a function of temperature, yielding the linear thermal expansion coefficient $\alpha(T)$ normal to the layer.

Figure 2 shows the $d(T)$ data in the SmA$_d$ phase of 8CB and 8OCB as a plot of $\Delta d=d(T)-d_c$ versus $\Delta T=T-T_c$, where $d_c$ is the layer thickness at the N-SmA critical temperature $T_c$. Comparable plots in the SmA$_m$ phase of S5 and T0S5 are shown in Fig. 3. The linear coefficients $\alpha(T)=\partial^2d/\partial T^2$ are obtained by differentiation of smooth-curve fits to such $d(T)$ data. The fitting form used is

$$d - d_c = \Delta d = A|\Delta T|^{1-\alpha}(1 + D|\Delta T|^{0.5}) + B(T - T_c), \quad (1)$$

from which one obtains, for $T < T_c$, \(\alpha = \alpha_{\text{reg}} + \alpha_{\text{crit}}\) where the regular (noncritical) background contribution is a temperature-independent constant:

$$\alpha_{\text{reg}} = B/d_c. \quad (3)$$

The critical term $\alpha_{\text{crit}}$ has a power-law form with corrections to scaling:

$$\alpha_{\text{crit}} = \frac{1}{\delta_c} \frac{\partial d}{\partial T} = \frac{A(1 - \alpha)}{d_c} |\Delta T|^{1-\alpha} \left[ 1 + D \left( \frac{1.5 - \alpha}{1 - \alpha} \right) |\Delta T|^{0.5} \right]$$

Thus, $\alpha_{\text{crit}} = \alpha_{\text{reg}} + \alpha_{\text{reg}}$. The following table shows the N-SmA critical exponent $\alpha$ for the smectic-A liquid crystals studied in this work. SmA$_d$ denotes a partial bilayer, and SmA$_m$ denotes a nonpolar monomeric smectic. The $\alpha$ values characterize both the heat capacity and the volume thermal expansion critical behavior and show that these systems lie in an $XY$ to tricritical crossover regime. Also given are the stable phases (K=rigid crystal, CrB=plastic crystal B, SmC=smectic-C, SmA, N, I=isotropic) and transition temperatures. In the case of K, the melting point on heating is given. Note that the SmC phase is $8S5$ and $10S5$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Smectic type</th>
<th>$\alpha$ [2,7,8,12]</th>
<th>Phases and transition temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8CB</td>
<td>SmA$_d$</td>
<td>0.31±0.02</td>
<td>K 294.4 SmA 307.0 N 314.0 I</td>
</tr>
<tr>
<td>8OCB</td>
<td>SmA$_d$</td>
<td>0.20±0.03</td>
<td>K 327.6 SmA 340.0 N 353.4 I</td>
</tr>
<tr>
<td>S5</td>
<td>SmA$_m$</td>
<td>$-0.02±0.02$</td>
<td>K 331 SmC 329.2 SmA 336.7 N 359.3 I</td>
</tr>
<tr>
<td>T0S5</td>
<td>SmA$_m$</td>
<td>0.45±0.05</td>
<td>K 339 SmC 337.3 SmA 354.4 N 359.6 I</td>
</tr>
<tr>
<td>4O.8</td>
<td>SmA$_m$</td>
<td>0.13±0.02</td>
<td>K 311.5 CrB 322.3 SmA 336.9 N 352.1 I</td>
</tr>
</tbody>
</table>

FIG. 1. Structural formulas for liquid crystals referred to in this work.

FIG. 2. Dependence of the SmA$_d$ layer thickness $d$ on $T-T_c$, where $T_c$ is the critical $T_{\text{NA}}$ transition temperature, for 8CB (LC +sil values: $\triangle$ from [16] and $\bullet$ from [17]) and 8OCB ($\circ$ pure LC, $\bigcirc$ and LC+sil values [20]). $\Delta d=d-d_c$, where $d_c$ is the value of $d$ at $T_c$ ($d_c=31.634$ Å for 8CB and $d_c=31.720$ Å for 8OCB). The solid lines are fits with Eq. (1).
Combining the x-ray smooth curves given in Figs. 2 and 3 are listed in Table II. The solid lines are fits with Eq. (1). The \( T_{AC} \) arrow marks the position of the SmA-SmC transition for \( \overline{8}S5 \). The values of the in-plane linear coefficient \( \alpha_\parallel \) can be obtained from the fact that in the SmA phase

\[
\alpha_{\parallel}(T) = \alpha_{\parallel} + 2\alpha_\perp.
\]

Thus, combining the x-ray \( \alpha_i(T) \) values with literature \( \alpha_i(T) \) data yields \( \alpha_{\parallel}(T) \). The resulting \( \alpha_i(T) \) and \( \alpha_{\parallel}(T) \) behaviors, along with \( \alpha_{\parallel}(T) \), are shown in Figs. 4–7 for two

\[
\alpha_{\parallel}(\text{reg}) = \alpha_{\parallel}(\text{reg}) - \alpha_{\parallel}(\text{reg}) \text{ since } \alpha_{\parallel}(\text{reg}) \text{ is known from the } V(T) \text{ data [7,8]. Note the dramatic differences in the magnitude and sign of } \alpha_{\parallel}(\text{crit}) \text{ and } \alpha_{\parallel}(\text{crit}) = \alpha_\parallel - \alpha_\perp. \text{ For both SmA, LC’s } 8CB \text{ and } 8OCB, \alpha_{\parallel}(\text{crit}) \text{ is positive while } \alpha_{\parallel}(\text{crit}) \text{ is negative. The signs of these two terms are reversed for the SmA, LC’s } \overline{8}S5 \text{ and } \overline{10}S5.
\]

### III. CRITICAL BEHAVIOR

The temperature dependences of \( \alpha_i \) and \( \alpha_\parallel \) exhibit obvious critical behavior, as shown by Figs. 4–7. Indeed, differentiation of the least-squares fit to \( \Delta d(T) \) data points yields the form expected for \( \alpha_i \) near a second-order critical point.

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_c ) ((^\degree)C)</th>
<th>( \alpha )</th>
<th>( A )</th>
<th>( D )</th>
<th>( B )</th>
<th>( 10^3A_1 )</th>
<th>( D_1 )</th>
<th>( 10^3\alpha_{\parallel}(\text{reg}) )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8CB</td>
<td>306.17</td>
<td>0.30±0.05</td>
<td>-0.060±0.008</td>
<td>-0.143±0.015</td>
<td>[0.0067]</td>
<td>1.319</td>
<td>-0.245</td>
<td>0.212</td>
<td>1.055</td>
</tr>
<tr>
<td>8OCB</td>
<td>340.09</td>
<td>0.20±0.06</td>
<td>-0.037±0.007</td>
<td>-0.138±0.014</td>
<td>[0.0060]</td>
<td>0.928</td>
<td>-0.224</td>
<td>0.189</td>
<td>1.135</td>
</tr>
<tr>
<td>( \overline{8}S5 )</td>
<td>336.71</td>
<td>0.05±0.10</td>
<td>0.040±0.015</td>
<td>-0.208±0.028</td>
<td>[-0.003]</td>
<td>-1.356</td>
<td>-0.318</td>
<td>-0.108</td>
<td>1.095</td>
</tr>
<tr>
<td>( \overline{10}S5 )</td>
<td>353.82</td>
<td>0.42±0.04</td>
<td>0.079±0.006</td>
<td>-0.083±0.013</td>
<td>[-0.006]</td>
<td>-1.526</td>
<td>-0.154</td>
<td>-0.199</td>
<td>1.056</td>
</tr>
</tbody>
</table>
The success of Eq. (1) in fitting $d(T)$ implies through Eqs. (2)–(4) that $\alpha_i$ consists of a regular background contribution, which is independent of $T$, and a power-law critical contribution. The structure of Eq. (4) is exactly the same as that for the critical heat capacity $C_p - C_p^{\text{reg}}$ [2,10,19] and the critical volume thermal expansion coefficient [7,8]. Furthermore, the critical exponents $\alpha$ given in Table II and those given in Table I, which were obtained from $C_p^{\text{crit}}$ and $\alpha_i^{\text{crit}}$, are in excellent agreement. This agreement between the independently determined exponents $\alpha$ that characterize the critical behavior of $\alpha_i$ and $\alpha_i$, is essentially required if a power-law form is valid for either quantity. Equation (5) is a completely general expression, and it could not be satisfied if $\alpha_i$, $\alpha_i$, and $\alpha_i$ had different critical singularities.

It should be noted that we have fixed the fit parameter $B$ in order to prevent strong coupling between the terms $B(T - T_c)$ and $AD|\Delta T|^{(1.5 - \alpha)}$ in Eq. (1) from causing unstable least-squares minimization. However, this does not have a great influence on the least-squares value of the critical exponent $\alpha$. Stepping $B$ values through a series of physically plausible values changes $\alpha$ by about $\pm 0.05$ (95% confidence limit) except for 8S5 where it is $\pm 0.1$. Furthermore, $\alpha_i^{\text{reg}}$ must have a physically reasonable value. This consideration puts another constraint on possible choices for the value of $B$.

There is another way to show that the critical behavior of $\alpha_i$ is the same as that for $\alpha_V$, which does not depend on using power-law fits to either quantity. The generalized Pippard equations [25,26] are thermodynamic expressions that have been shown to hold for the thermal and elastic properties near second-order phase transitions. The significant equations for the present purposes are

$$\alpha_V = s_V \left( \frac{C_p}{VT} \right) - g_V. \quad (6)$$
The important conclusion from the existence of a linear region where $\alpha_{\parallel}$ is large. In this region, any variation in $u$ is small compared to the critical contributions to $\alpha_{\parallel}$ and $\alpha_{\perp}$ are due to differences in the variation of $T_c$ with uniaxial pressure normal to the smectic layer ($p_i$) and in the plane of the layer ($p_\perp$). Since the pattern of signs is the same for 8CB and 8OCB and opposite signs hold for 8S5 and T0S5, one might be tempted to think that all SmA$_x$ LC’s are like 8CB and all SmA$_m$ LC’s are like S5. This speculation may be true with regard to signs, but consideration of data for 4O.8, another SmA$_m$ material, shows a dramatic difference in the magnitude of $dT_c/dp_\parallel$ for S5 and nO.m LC’s.

<table>
<thead>
<tr>
<th>Material</th>
<th>$dT_c/dp_{\parallel}$</th>
<th>$dT_c/dp_{\parallel}$</th>
<th>$dT_c/dp_{\perp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8CB</td>
<td>22.85 [28,29]</td>
<td>131.7</td>
<td>−54.4</td>
</tr>
<tr>
<td>8OCB</td>
<td>17.36 [30,31]</td>
<td>103.5</td>
<td>−43.1</td>
</tr>
<tr>
<td>8S5</td>
<td>20.20 [32]</td>
<td>−60.38</td>
<td>40.29</td>
</tr>
<tr>
<td>T0S5</td>
<td>18.35</td>
<td>−18.94</td>
<td>18.64</td>
</tr>
<tr>
<td>4O.8</td>
<td>20.40 [13]</td>
<td>0</td>
<td>10.2</td>
</tr>
</tbody>
</table>
X-ray data obtained in the SmA phase of 4O.8 [24] show that the layer thickness $d$ is independent of $T$ over the entire 15-K-wide SmA range. Thus, $\alpha_0=0$ and $\alpha_\perp=\alpha_\parallel/2$ for 4O.8. This striking result $\alpha_\parallel=0$ in the SmA phase is not some accidental value for 4O.8 but holds for many nO.m LC’s such as 4O.7 [34], 5O.6 and 5O.7 [35], and 50.8 and 50.10 [36]. Note that the critical behavior of $C_p$ and $\alpha_\parallel$ for 4O.8 [5,13,37] and other nO.m compounds [38,39] fits into the same pattern as the $\pi S$5 compounds; see Ref. [2]. Since $C_p$ exhibits a critical singularity for 4O.8 but $\alpha_\parallel$ does not, Eq. (7) requires that $dT_c/dp_{\perp}=0$. Further support for the idea that nO.m materials differ from other SmA materials is provided by the fact that $\alpha_\parallel(\Delta T)$ near the $T_c(p)$ critical line for the N-SmA transition is independent of hydrostatic pressure for 4O.8 [13] and 80.m with $m=5, 6, 7, 9$ [39]. Equation (6) then implies that $C_p(\text{crit})$ must be a function of $(T-T_s)$ only and independent of $p$ at least over a moderate pressure range from 1 to 1000 bars. This differs greatly from the strong pressure dependence of $C_p(\text{crit})$ observed in other LC’s such as 8CB and 8OCB [40,41].

![Graph showing integrated N-SmA enthalpy vs. pressure](image)

**IV. DISCUSSION**

Determination of $\alpha_0(\text{crit})$ and $\alpha_\perp(\text{crit})$ provides some insight into the stability of the SmA phase to stresses and is thus linked to the tendency for SmA on cooling to form SmC, Crb, or even reentrant nematic $N_s$. We shall address here the plausible reasons that $\alpha_0(\text{crit})$ is positive for 8CB and 8OCB (SmA$_m$ materials with biphenyl cores) but negative for $\pi S$5 and $\pi 0 S$5 (SmA$_m$ materials with a flexible -C(O)-S-link between the core phenyl rings).

For the LC’s nCB and nOCB, permeation along the director is the dominant mechanism for the growth of SmA$_d$ order below the transition. During this process, there is only a minor change in the lateral alignment of neighboring LC molecules and the ordering primarily involves better interdigitation of rodike molecules to form a “dimerlike” partial bilayer [42]. Thus, one can understand why increasing the uniaxial pressure $p_\parallel$ would push the LC rods into a better layer structure and stabilize the SmA$_d$ phase. This implies that $dT_c/dp_{\parallel}>0$, and the Pippard equation (7) then predicts $\alpha_\parallel(\text{crit})>0$. In the same context, increasing the in-plane pressure $p_{\perp}$ will force the bulky “dimer” cores to shift up or down away from the center of the SmA$_d$ layer in order to allow better in-plane packing. Thus, an increase in $p_{\perp}$ destabilizes the SmA$_d$ phase, which implies that $dT_c/dp_{\perp}<0$ and leads via Eq. (8) to $\alpha_\perp(\text{crit})<0$ (see Fig. 1).

For the liquid crystals $\pi S$5, the flexible -C(O)-S-link in the core means that the molecule is slightly bent near the center [32] and the two aromatic rings are twisted quite a bit relative to each other. As the SmA$_m$ order increases on cooling below the transition, there is an improvement in the lateral alignment of these bent rods, and permeation along the director plays an important but smaller role. For such LC’s, increasing the in-plane pressure $p_{\perp}$ may tend to partially straighten the molecules and will definitely improve the “nesting” of such molecules. This improves the layer structure and stabilizes the SmA$_m$ phase, which implies that $dH_NA$.

![Graph showing the McMillan ratio vs. temperature](image)

FIG. 10. The integrated N-SmA enthalpy $\delta H_{NA}$ versus the McMillan ratio $R_M$ for a variety of smectic liquid crystals. The dashed line gives the empirical trend for these SmA$_d$ LC’s, and the dashed-dot line represents $\delta H_{NA}$ values that are arbitrarily taken to be 7.5 times larger.

$dT_c/dp_{\perp}>0$ and therefore $\alpha_\parallel(\text{crit})>0$. An increase in $p_{\parallel}$ will tend to buckle the molecule (increase the bend at the core link), and this makes these molecules pack less well in the SmA$_m$ layer. Thus, SmA$_m$ is destabilized and $dT_c/dp_{\perp}<0$, leading to $\alpha_\perp(\text{crit})<0$.

Support for the above ideas is provided by Fig. 10, which shows the variation of the integrated enthalpy $\delta H_{NA}$ with the McMillan parameter $R_M$ [43–45]. Note that $\delta H_{NA}$ for the cyanobiphenyl SmA$_d$ compounds is ~7.5 times smaller than that for $\pi S$5 SmA$_m$ compounds with the same $R_M$ value. These low $\delta H_{NA}$ values for SmA$_d$ compounds are due to the fact that most of the N-SmA enthalpy in any LC is due to changes in the van der Waals term related to changes in the lateral alignment of neighboring molecules. In SmA$_d$ compounds, there is not much enthalpy associated with sliding molecular pairs (loose “dimers”) up and down along the director. Another source of support for the above ideas is the variation with $R_M$ of the enhancement $\delta S$ of the nematic orientational order when a LC system goes from the nematic phase into the SmA phase. In general, $\delta S$ decreases as $R_M$ decreases. It is also observed that the magnitude of $\delta S$ is appreciably smaller for SmA$_d$ than for SmA$_m$ compounds for a given $R_M$ [46]. This indicates that the orientational order in the nematic phase just above $T_{NA}$ is better for SmA$_d$ than for SmA$_m$ materials, which means the axis for permeation is “easier,” with less change occurring in the lateral packing on cooling into the SmA$_d$ phase.

It is necessary to comment now on the behavior of 4O.8 and other nO.m compounds, where $\alpha_0(\text{crit})=0$. The reason that this is different from the behavior of $\pi S$5 LC’s can be found in the molecular structure. 4O.8 has a rigid -C(H)_=N-link between the rings in the core. Thus the 4O.8 mol-

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S5 are monomeric smectics [47], but the ̅8S5 compounds with their bent shape exhibit a SmC phase when SmA\textsubscript{m} is cooled. In contrast, 40.8 exhibits a plastic crystal CrB phase [48] when SmA\textsubscript{m} is cooled, and the “layer” spacing in CrB is only 1% greater than the SmA\textsubscript{m} d value. Most nO.m compounds show that same phase sequence [39,49]. Thus increasing p\textsubscript{||} for 40.8 has little or no effect: there is no dominant permeation mechanism, so p\textsubscript{||} will not stabilize the SmA\textsubscript{m} phase; there is no bend or buckling tendency, so p\textsubscript{||} will not destabilize SmA\textsubscript{m}. Thus it is not surprising that dT\textsubscript{c}/dp\textsubscript{||}=0 for 40.8, which is implied by the observed α\textsubscript{||}=0. The application of an in-plane pressure $p_\perp$ to 40.8 should somewhat improve the lining up of molecules in the SmA\textsubscript{m} phase and thus stabilize this phase. Therefore, one would expect dT\textsubscript{c}/dp\textsubscript{\perp}>0, which is consistent with α\textsubscript{\perp}>0. Note, however, that dT\textsubscript{c}/dp\textsubscript{\perp} is small, presumably due to the similar packing in the SmA\textsubscript{m} and CrB phases, which implies that the molecules are already fairly well aligned in the SmA\textsubscript{m} phase at ambient (1-bar) pressure.

Future work on the linear expansion coefficients α\textsubscript{||} and α\textsubscript{\perp} in the SmA phase would be of interest. Such studies would be easy for 9CB (critical exponent α=0.50), where V(T) and dT\textsubscript{c}/dp data are already available [14,50] and only x-ray data are lacking. In the case of 40.7 (critical α=-0.007) and 9S5 (critical α=0.22), good x-ray data on the smectic phase layer spacing d(T) are available [23,34], but data on both V(T) and dT\textsubscript{c}/dp are needed. It would also be especially interesting to study frustrated smectics like DB\textsubscript{8}ONO\textsubscript{2} (octyloxyphenylnitrobenzoxyloxy benzoate) and T7 (heptyloxybenzoyloxy cyanostilbene), where there are rigid three-ring cores and huge N ranges. It is observed in these materials that the critical behavior of all properties near $T_{NA}$ is close to the ideal 3D XY limit [6].

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[46] Values of $\delta S$ at the N-SmA transition have been determined from both birefringence $\Delta n$ and NMR quadrupolar splitting $\delta v$. Unfortunately, high-resolution and precise data for $\delta S$ are sparse, but the difference between SmA$_m$ and SmA$_s$ compounds is qualitatively clear. See N. Boden et al., Mol. Phys. 42, 565 (1981); D. Catalano et al., Liq. Cryst. 2, 345 (1987); B. M. Fung et al., ibid. 4, 1495 (1993); R. Y. Dong, Phys. Rev. E 60, 5631 (1999) for NMR data. See N. R. Chen, S. K. Hark, and J. Ho, Phys. Rev. A 24, 2843 (1981); E. F. Gramsbergen and W. H. de Jeu, J. Chem. Soc., Faraday Trans. 2 84, 1015 (1988); J. Ho (private communication) for birefringence data.

[47] For 8S5 at a temperature in the center of the SmA$_m$ phase, the layer spacing $d=27.97\pm0.2$ Å and a Gaussian quantum-mechanical calculation gives $29.0\pm0.1$ Å for the length $L$ of a single molecule. Thus $d/L=0.965$. For 4O.8, $d=28.2\pm0.2$ Å for all $T$ in the SmA$_m$ range, and the Gaussian-calculated value of $L$ is $27.3\pm0.1$ Å. Thus $d/L=1.033$ for 4O.8.

