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Critical behavior of three organosiloxane de Vries-type liquid crystals observed via the dielectric response

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Abstract
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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Smectic A (SmA) and smectic C (SmC) liquid crystals are layered phases possessing quasi-long-range positional order in one dimension represented by a mass-density wave, whose wavevector is either along the director (SmA) or tilted (SmC). Owing to the two-component order parameter describing the tilted structure, the SmA–SmC transition is expected to belong to the XY universality class [1]. Experimentally, however, the classical behavior which can be described with an extended mean-field (EMF) model [2], is generally observed, with exceptions especially found in systems with an antiferroelectric tilted phase [3].

The de Vries SmA (SmA_{dv}) phase has certain features of both the SmA and SmC structures (see figure 1), with the molecules substantially tilted like in an SmC, but having only short-range azimuthal coherence with an averaged uniaxial order as in an SmA [4]. The chiral version of this phase has particularly attracted a great deal of attention [5–7] owing to the absence of certain defects as a direct consequence of the associated minimal layer shrinkage across the SmA–SmC (rather chiral SmC or SmC*) phase transition. Recently, we reported a novel finding of an antiferroelectric-like switching in this phase which could be explained based on different terminal chain interactions [8]. Subsequent to our report, Ghosh et al [9] found a similar behavior in a fluorinated material. Early calorimetric measurements carried out on materials exhibiting the SmA_{dv} phase suggested the behavior associated with the transition to the tilted phase to be compatible with the 3D XY model [10]. On the other hand, birefringence studies [6] showed that the susceptibility critical exponent γ is in the range 1.5–1.75, which is certainly much higher than the 3D XY theoretical expectation of γ = 1.316. Such a disagreement is also seen in
Figure 1. Schematic representation of the molecular arrangement in (a) SmA, (b) one type of SmAdV and (c) SmC* phases. The molecules are along the layer normal in the SmA, while being tilted in the SmAdV and SmC* phases. To be noted is the fact that the tilt is azimuthally correlated in the SmC* but not in the SmAdV phase.

electro-optic measurements [11]. More recently Takekoshi et al [7] described calorimetric and dielectric measurements on a siloxane derivative and claimed the results to be in accordance with the features expected for a quasi-2D Ising-like critical behavior.

An important feature, from a molecular structure point of view, is that systems which have exhibited the antiferroelectric characteristics in the SmA phase have a significantly bent central portion. This feature can help in gaining a substantial orientational (tilt-azimuthal) correlation within the layer. The end groups on the molecule are different and also have a dislike towards each other, a character that weakens the interlayer correlation. The combination of these two factors increases the tendency towards the formation of the de Vries phase having either azimuthal tilt correlated within the layer, but not between layers, a structure labeled as the sliding phase [12], or with short-range tilt correlation within as well as between the layers. Creating a nanophase segregation [13, 14] between layers by having chemically different regions within and between the layers may promote the de Vries phase. From these points of view, the molecules employed here have the desirable properties.

Here we report the soft mode characteristics on three structurally similar siloxane compounds, one of which is the same as that in [7]. We find that the critical exponent describing the growth of tilt susceptibility is strongly dependent on the temperature range considered for evaluation, suggesting that the system may always be in the catchment area of another fixed point. More importantly, we observe that the limiting value of the exponent is 2D Ising-like for these systems, unlike the mean-field values seen for conventional electroclinic materials.

2. Experimental details

The general molecular formula and the transition temperatures of the employed compounds [15], referred to in the literature as EtSiKN65, DSiKN65 and TSiKN65, but labeled simply as EtSi, DSi and TSi in this paper, are given in figure 2. Note that the main difference among the three compounds is the number of siloxane groups; while for EtSi, there is only one siloxane group, DSi and TSi compounds have, respectively, two and three such groups. Also important is the fact that, while one side has pure hydrocarbon termination, the other side has the bulky siloxane group(s). The x-ray measurements were carried out using an apparatus described in [8]. Samples filled in a Lindemann capillary tube and oriented using a magnetic field were employed. The electrical and electro-optic measurements were carried out using a standard apparatus [16]. Dielectric measurements were done with the help of an impedance analyzer (HP4194A).

3. Results and discussion

3.1. Translational order

Owing to the nanophase segregation, which is a hallmark of the de Vries phase, and which gets further substantiated in the scenario of the block picture outlined above, the smectic translation order \( \Sigma \) should be higher than usual in the SmAdV phase [4]. In contrast to a very involved method proposed by Leadbetter [17] for calculating the \( \Sigma \) value, Kapernaum and Giesselmann [18] have proposed a very simple technique. They define \( \Sigma^2 \) as \( I/I_o \), where \( I \) is the temperature-dependent integrated area under the fundamental smectic layer peak obtained in the x-ray measurements and \( I_o \), the value of \( I \) at absolute zero temperature. \( I_o \), the intensity of the hypothetical perfectly ordered state, is obtained by assuming that \( I \) would increase in a power-law fashion, with an exponent \( m \), on moving away from \( T_{iso} \), the transition temperature of the disordered state (isotropic phase for the

Figure 2. Molecular structures and transition temperatures of the three compounds studied here.
Figure 3. Variation of the smectic translation order parameter $\Sigma$ extracted from the x-ray integrated intensity measurements as a function of reduced temperature in the SmAdV phase for the compound TSi. Note that $\Sigma$ rises sharply near the transition from the isotropic phase and that the value well into the SmAdV phase is very high.

The extracted temperature dependence of $\Sigma$ thus extracted in the SmAdV phase for a representative compound, TSi, is shown in figure 3. The main feature to be noted is that $\Sigma$ increases rapidly and well inside the SmAdV phase reaches high (~0.9) values, a feature expected for the de Vries phase.

3.2. Electrical and electro-optic switching

To emphasize the special nature of the SmAdV phase investigated here, we present in figure 4, the current and electro-optic profiles obtained upon application of a triangular wavefield to a sample of EtSi, contained in a glass cell (~10 $\mu$m thick) with ITO electrodes and having a unidirectionally rubbed polyimide coating to facilitate uniform orientation of the molecules. The SmAdV phase shows a double-peak profile typical of an antiferroelectric type of switching (figure 4(a)), unlike the single-peak characteristic of the electroclinic response of a normal SmA phase, or the ferroelectric-like response of the SmC* phase (see the inset of figure 4(a)). It may be noted that the strength of the double-peak profile decreases and the separation between the peaks increases with increasing temperature. The electro-optic response, collected simultaneously using a microscope lamp as the light source, also displays a two-step response (figure 4(b)) expected for an antiferroelectric type of switching. These features are supported by the observation of textural changes seen under cross-polarizers, with nearly identical patterns for the two signs of the field which are drastically different from that obtained without the field. Similar features were seen for TSi as well as DSi compounds. These characteristics, as well as the dielectric behavior to be described in detail below, prompted us [8] to propose a molecular model in which the neighboring smectic layers have an antiferroelectric-like arrangement but, as expected for a de Vries phase, the system has no global tilt correlation. It was further argued that this feature could arise owing to a combination of structurally incompatible terminal ends, the bulkiness of one of the terminal groups (siloxane in that case) and the de Vries character of the SmA phase. More recently, Ghosh et al [9] reported such aspects in another compound having different and incompatible terminal ends, with the bulky end being due to fluorine atoms.

3.3. Fixed-frequency dielectric constant

The fixed-frequency dielectric constant $\varepsilon_{\perp}$ data (here the probing electric field is in the plane of the layer) for the three compounds as a function of dc bias shows features similar to the current response discussed above. Figure 5 shows a representative dataset for EtSi. Again, the peaking of the dielectric constant for a finite value of the bias voltage is not typical of the electroclinic SmA phase. Note that in the ferroelectric phase there is only one peak. Considering the antiferroelectric-block picture mentioned above, $V_p$, the bias voltage value corresponding to the peak in this data,
can be associated with the switching from the anticlinic to the synclinic (electroclinic) structure. Figure 6 displays for EtSi and TSi, the temperature dependence of $V_p$, taken as the average of the peak value in the negative and positive bias sweeps (a small difference is found in the two sweeps, which can be attributed to anchoring effects). In all the cases $V_p$ has essentially a linear dependence on temperature, with the slope being higher ($11.1 \pm 0.2$ V °C$^{-1}$) for the ETSi compound than for the TSi sample ($6.7 \pm 0.2$ V °C$^{-1}$). Thus, the larger the number of siloxanes in the molecule, the less is the influence of thermal fluctuations in reducing the antiferroelectric character of the neighboring layers in a block.

3.4. Dielectric relaxation

Apart from the molecular modes, the collective dielectric behavior of the SmC* phase is dominated by two relaxation modes. In situations where the helical structure of the SmC* phase is present, the azimuthal angle fluctuations, also connected with the pitch of the helix, give rise to, at quite low frequencies, a symmetry-recovering mode, referred to as the Goldstone mode (GM). The second mode associated with the softening of the polar part of the tilt fluctuations, and seen only close to the transition to the SmA phase, is called the soft mode (SM). In the SmA phase, these modes become degenerate and only the SM is seen. These modes can be conveniently investigated by measuring the frequency dependence of the dielectric constant $\varepsilon_\perp$. In addition to the probing ac field, if a dc bias field is also applied the helix in the SmC* phase can be unwound, thereby reducing the contribution of the GM. Figure 7 shows the exemplary raw absorption profiles ($\varepsilon'''$ versus $f$, $\varepsilon''$ and $f$ being the imaginary part of the dielectric constant and the measuring frequency, respectively) for a representative compound, EtSi, at a few temperatures in the SmA$_{dV}$ phase. To extract the two parameters of interest, namely the dielectric relaxation strength $\varepsilon_R$ and the relaxation frequency $f_R$, the dielectric spectra were fitted to the Havriliak–Negami (HN) equation using commercially available software (WinFit, Novocontrol). The HN equation is given by

$$
\varepsilon(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_R}{1 + (\omega \tau)^\alpha}.
$$

(2)

Here $\varepsilon_\infty$ is the permittivity at $f (= 1/2\pi \omega) \gg f_R$ and $\tau$, the relaxation time. $\alpha$ and $\beta$ are fitting parameters describing the shape of the curve. For all the spectra obtained in this study, the values of $\alpha$ and $\beta$ remained close to one, indicating the relaxation to be of Debye type. Figures 8–10 show the temperature dependence of the $\varepsilon_R$ and $f_R$ for the three compounds, in the absence of, and for, a bias voltage of 10 V. Two common features for all the three materials are (1) a strong variation of the relaxation parameters: decrease in $f_R$ and increase in $\varepsilon_R$ on approaching the transition temperature, and (2) application of bias, yielding a clear minimum in $f_R$ and a concomitant maximum in $\varepsilon_R$ at the transition point. These features clearly suggest the presence of the SM in the SmA$_{dV}$ phase and the GM in the SmC*. To look at a structure–property correlation we compare the relaxation parameters obtained at a fixed reduced temperature $T - T_c$ (where $T_c$ is the SmC*–SmA$_{dV}$ transition temperature) in the SmA$_{dV}$ phase. At $T - T_c = 2.5$ °C, the relaxation parameter values for EtSi, DSi and TSi compounds are, respectively, $f_R = 3.84, 1.8$ and 0.4 kHz, and $\varepsilon_R = 18, 46$ and 51. Bearing in mind that the rest of the molecular structure remains intact for the three different compounds, these data suggest that the number of siloxane groups in the structure has a definitive influence on the value of the relaxation parameters: the frequency decreases and the strength goes up with increasing siloxane entities. Considering the fact that the siloxane group is quite bulky, compared to the hydrocarbon, such a feature indicates that the increased bulkiness of the molecule slows down the dynamics of the relaxation.

3.5. Quantitative analysis: mean-field model

In the following, we analyze the critical behavior of the SM susceptibility, employing expressions developed [19] for the
Figure 7. Dielectric absorption peaks at several temperatures in the SmAdV phase of the compound EtSi. The temperature for the topmost profile is 39°C and increases in steps of 0.5°C for the lower curves.

Figure 8. Thermal variation of the relaxation frequency ((a), (c)) and strength ((b), (d)) without (filled) and with (open) a bias voltage of 10 V for the sample EtSi.

Figure 9. Thermal variation of the relaxation frequency ((a), (c)) and strength ((b), (d)) without (filled) and with (open) a bias voltage of 10 V for the sample DSi.

Figure 10. Thermal variation of the relaxation frequency ((a), (c)) and strength ((b), (d)) without (filled) and with (open) a bias voltage of 10 V for the sample TSi.

Here $K$ is an elastic term, related to the bend elastic constant, $q_0$ is the wavevector corresponding to the helical pitch of the low temperature tilted smectic phase, $\eta$ is the viscosity associated with the mode, $\varepsilon$ is the strength of the high frequency modes. $C$ is a coefficient representing the linear coupling between polarization and tilt angle and $a$ is the usual Landau coefficient associated with the square of the order parameter. In the mean-field limit the critical exponent $\gamma$ has a value of 1. In a simple-minded analysis, $Kq_0^2$ and $\eta$ can be assumed to be weakly dependent on temperature (as is often done in the literature), and therefore both $f_R$ and $1/\varepsilon_R$ can be taken to decrease linearly with temperature, a feature referred to as the Curie–Weiss law. However, it is obvious from the data shown in figures 8–10 that the behavior is not strictly linear. Notice that in equations (2) and (3) $\gamma$ being equal to 1, is in the mean-field limit. This condition can be relaxed by treating the growth of the dielectric strength (or the susceptibility) as a (non-mean-field) critical parameter and thus its temperature dependence is essentially dictated by a critical exponent whose value depends on the universality class to which the phase transition belongs. By symmetry considerations, the SmA–SmC* transition belongs to the XY universality class [1]. In a majority of the cases, experiments have shown mean-field behavior [2, 20], which in some materials...
is associated with a crossover to tricritical behavior [21], a feature well described by the Landau theory. However, exceptions do exist: in compounds having an antiferroelectric state (although not immediately below the SmA phase), the critical exponents associated with the heat capacity variation suggest 3D XY class behavior [3]. As already mentioned, the qualitative change across the transition from the SmA$_{LV}$ to the SmC* involves build-up of the long-range azimuthal correlation (the appearance of the helix in the SmC* phase is not a parameter driving the transition) and not that of the polar tilt. Therefore it has been argued that the critical behavior across this phase transition should be described, not by the XY class but by a quasi-2D Ising explanation [7]. In fact, Takekoshi et al. analyzed dielectric dispersion data limited only to the SmA phase of one of the materials (TSi) studied here and found the behavior to be described by a $\gamma$ value which is in agreement with the expectations of the 2D Ising model, and thus supportive of the analysis of the birefringence data [6].

To extract information about the critical behavior, the $1/\varepsilon_R$ data in the SmA$_{LV}$ phase is described by a power law, $\varepsilon_R^{-1} = A t^\gamma + B$, where $t = (T - T_c)/T_c$. To achieve a stable fitting without fixing $T_c$, the following power-law expression was employed by including the data on either side of the transition:

$$\frac{1}{\varepsilon_R} = A^\pm |t^\gamma|^\pm + B.$$  \hspace{1cm} (5)

The fitting was carried out by floating all the parameters: the constant $B$, the amplitudes $A^\pm$ (± indicating the high and low temperature sides), the transition temperature $T_c$ and the power $\gamma^\pm$. Note that our main interest is in the parameters on the SmA$_{LV}$ side and that the parameters on the SmC* side are merely for obtaining a proper fitting. Anticipating a temperature-range-dependent $\gamma$ value, a range-shrinking analysis was performed by varying the range of the data considered for fitting to equation (5). In each case, $t_{\min}$ was fixed at a value corresponding to 1°C in the SmC* phase, and varying $t_{\max}$, the maximum value of the reduced temperature that described the highest temperature point in the SmA$_{LV}$ phase. Figure 11 shows the variation of $\gamma^+$ with $t_{\max}$ for the three compounds, displaying a strong dependence on the temperature range used for the fitting. The attractive feature seen is that in all the cases the limiting values of the exponent obtained (at the lowest $t_{\max}$) are in the vicinity of the value of 1.75, expected for the 2D Ising model [22]. But even considering the error bars, the values (1.7–1.94) are slightly larger than the theoretical expectation. A possible reason for this deviation could be the following. The analogy with the 2D Ising model implies that the order parameter has a single degree of freedom and that its fluctuations are strictly limited to the plane. In the present case, this would mean that, across the transition, while the azimuthal angle $\phi$ gets ordered, the polar angle should remain constant. However, in all the X-ray measurements reported to date, including the ones for the compounds investigated here [8], the layer thickness does diminish in the SmC* phase. Consequently, the polar angle undergoes an increase with respect to its value in the SmA$_{LV}$ phase. Further, as described above, to account for the double-peak profile response, a structure was proposed [8] in which the neighboring layers have a strong anticlinic coupling [8], with such two-layer blocks having a very weak tilt direction coupling on a global scale. Therefore the criterion that the order parameter fluctuations should be entirely 2D may not be strictly valid. It should further be pointed out that, when the entire SmA range is considered for fitting, the exponent obtained is close to 1.3. Since this value is close to that predicted for the XY universality class, we cannot rule out the critical behavior to be governed by that, at least in the region away from the transition. But, given the fact that there is a monotonic increase in the $\gamma$ value with range shrinking, it could definitely be said that the system is in the catchment region of a crossover to the true critical behavior, which could be a modified form of the standard 2D Ising model. These features need to be incorporated into theoretical modeling to find out whether the small discrepancy in the critical exponent seen here can be accounted for.

4. Conclusion

We have investigated the critical dielectric behavior of three organosiloxane derivatives exhibiting the de Vries SmA phase, with the recently discovered antiferroelectric-block structure. With a range-shrinking analysis we find that the exponent describing the growth of the susceptibility increases monotonically from a near-mean-field value far away from the transition to a value slightly higher than that predicted for the 2D Ising model. The latter is suggested to be due to the antiferroelectric nature of the two-layer block structure and to the change of the polar tilt angle across the transition to the smectic C* phase.

References

   For a review see Lagerwall J P F and Giesselmann F 2006 ChemPhysChem 7 20