

Electric-field-dependent dielectric response in the de Vries–type smectic- A^* phase possessing local orientational order with nanoscale correlation length

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The dielectric strength is shown to increase and the relaxation frequency to decrease for a large temperature range up to a certain value of the electric field in the smectic- A^* phase. This behavior contrasts to that observed in a conventional smectic- A^* , but can be explained in terms of de Vries scenario. On assuming the reorientation of the molecular dipoles with electric field to be of the Langevin type in the de Vries smectic- A^* , we find that around 1300 molecules, corresponding to a minimum correlation length of $\xi_{\perp} \approx 45$ nm in a single layer cooperatively respond to the applied field.

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I. INTRODUCTION

At the transition from smectic- A^* (SmA^*) to smectic- C^* (SmC^*) or smectic- C_A^* (SmC_A^*) phase, the layer shrinkage along with the surface anchoring of the molecules lead to the formation of chevrons. The chevrons of opposite fold directions separated by zigzag defects degrade the quality of electro-optic devices based on ferroelectric liquid crystals (FLCs) and antiferroelectric liquid crystals (AFLCs) [1–4]. Application of the electric field in the SmA^* phase parallel to the smectic layers induces stripes arising from a reduction in the smectic layer spacing due to molecular tilting and the consequent smectic layer buckling [5,6]. This has a detrimental effect on the contrast ratio of electro-optic devices [7,8]. As a result, the materials having zero or low layer shrinkage with decreasing temperature or increasing electric field have drawn significant scientific interests due to their potential for applications in display and photonic devices [9]. In de Vries’ “diffuse cone model” of these materials, the molecular long axis and presumably the local director is tilted through a finite angle, but azimuthally randomized with a uniform distribution $f(\varphi) = 1/2\pi$ on a cone from layer to layer as well as in a single layer [10–13], with the macroscopic director along the layer normal. Landau theory of smectic phases was developed to show that de Vries behavior occurs in materials with unusually small orientational order [14], which has been experimentally demonstrated [12,15–19]. It was also shown that a decrease in the layer shrinkage increases the soft mode strength and decreases the Landau coefficient at the de Vries SmA^* - SmC^* transition [20,21]. Application of an electric field parallel to the smectic layers orders the azimuthal orientation, such that an average director is tilted away from the layer normal. But it has been an issue of discussion in recent years as to how this azimuthal ordering is achieved in these materials with the application of electric field. It has been suggested that the de Vries materials with sufficiently high polarization density exhibit large analog optical axis rotation ($>30^\circ$) accompanied by increased birefringence, as found by the electro-optic

measurements. These can be modeled by Langevin theory of field-induced director orientation on assuming the molecules in the SmA^* phase are confined to a tilt cone [22]. Another theoretical model predicts the dependence of the optical birefringence and tilt angle on electric field and temperature assuming the local order is slightly biaxial [23]. It has also been suggested that perhaps there is some type of modulation or spatial periodicity in the azimuthal angles associated with the tilt directions [24].

Here, we report that on application of an increasing field in the SmA^* phase, the dielectric strength ($\Delta\epsilon$) increases and the relaxation frequency (f_{\max}) decreases up to a certain value of the field over a large temperature range ($\approx 12^\circ\text{C}$). This behavior cannot be explained by the tilt angle fluctuations of conventional SmA^* phase undergoing first- or second-order transition to SmC^* phase, but can be explained in terms of de Vries scenario by assuming the reorientation of the molecules by rotation around the smectic cone with the electric field as suggested in the previous models [22,23]. On assuming that the reorientation of the molecular dipoles with the electric field is of the Langevin type, we show that the tilted molecules in the de Vries–type SmA^* phase possess a local orientational order even without the electric field, and a maximum of around 1300 molecules cooperatively respond to the applied field corresponding to an effective dipole moment, $\mu_{\text{eff}} \approx 2000$ D. This value corresponds to a correlation length, $(\xi_{\perp}) \approx 45$ nm if the local ordering occurs along a single layer and to $(\xi_{\parallel}) \approx 22$ nm if the local ordering occurs along the layer normal as well as within a single layer.

II. RESULTS AND DISCUSSIONS

The liquid crystalline compound TSiKN65 (4-{3'-nitro-4'-[(R)-1-methylhexyloxy]phenyl}-phenyl 4-(6-heptylmethyltrisiloxyhexyloxy), chemical structure and phase diagram are shown in Fig. 1), used mainly for our experiment is a recently reported prototype de Vries material having small layer contraction with temperature and electric field, large electroclinic effect, and small orientational order parameter [16,23,25]. For planar alignment, the conducting inner surfaces of the liquid crystalline cell were spin coated with a polyimide RN 1175 (Nissan Chemicals, Japan) align-

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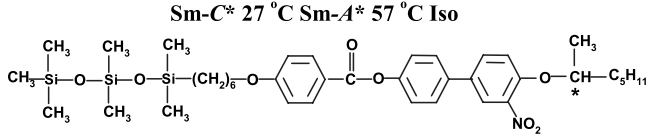


FIG. 1. Phase sequence and chemical structure of TSiKN65.

ment layer and rubbed parallel. Dielectric measurements in the frequency range from 1 Hz to 10 MHz were carried out by using the Novocontrol Alpha High Resolution Dielectric Analyzer. During measurements, the system allowed us to superimpose dc bias voltages up to 40 V on a rms ac voltage of 0.03 V. The results of the high resolution dielectric measurements on cooling a 7 μm cell from the isotropic phase with and without the external electric field in TSiKN65 and Felix-18 (SmC* 67 °C SmA*, Hoechst, Germany) are shown in Fig. 2. Figure 2(a) shows the dependence of $\Delta\epsilon$ and f_{max} on temperature without any electric field for TSiKN65. These are found by fitting the dielectric spectra to the Havriliak-Negami equation. We find that $\Delta\epsilon$ and f_{max} start to diverge as the system approaches transition towards SmC* phase. Figure 2(b) shows the dependence of $\Delta\epsilon$ and f_{max} on electric field in the SmA* phase for Felix-18. The $\Delta\epsilon$ decreases and f_{max} increases with increasing electric field, which are dependent on the electroclinic coupling and the nonlinear field dependence of the induced tilt, and are described by two sets of equations [26,27].

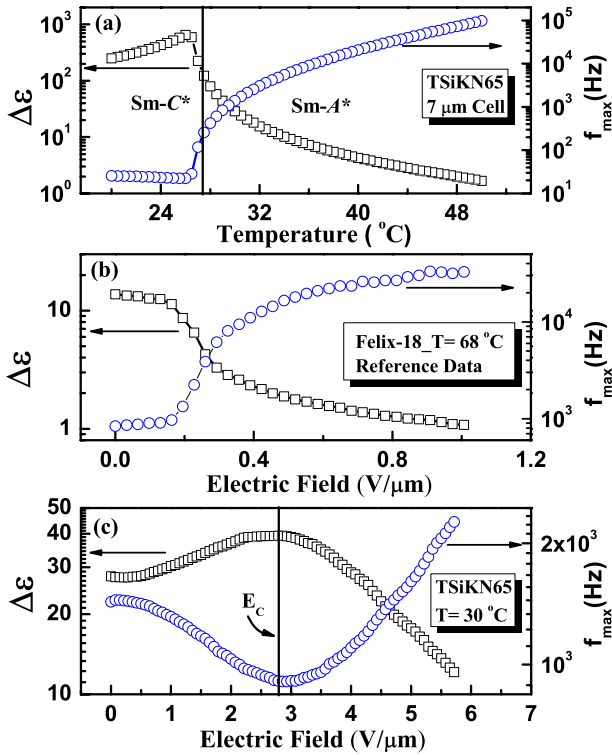


FIG. 2. (Color online) (a) Dependence of the dielectric strength ($\Delta\epsilon$) and relaxation frequency (f_{max}) on temperature in the absence of electric field for TSiKN65. (b) Dependence of $\Delta\epsilon$ and f_{max} on applied electric field for the SmA* phase of Felix-18 (reference data). (c) Dependence of $\Delta\epsilon$ and f_{max} on applied electric field in the SmA* phase for 30 °C temperature of TSiKN65.

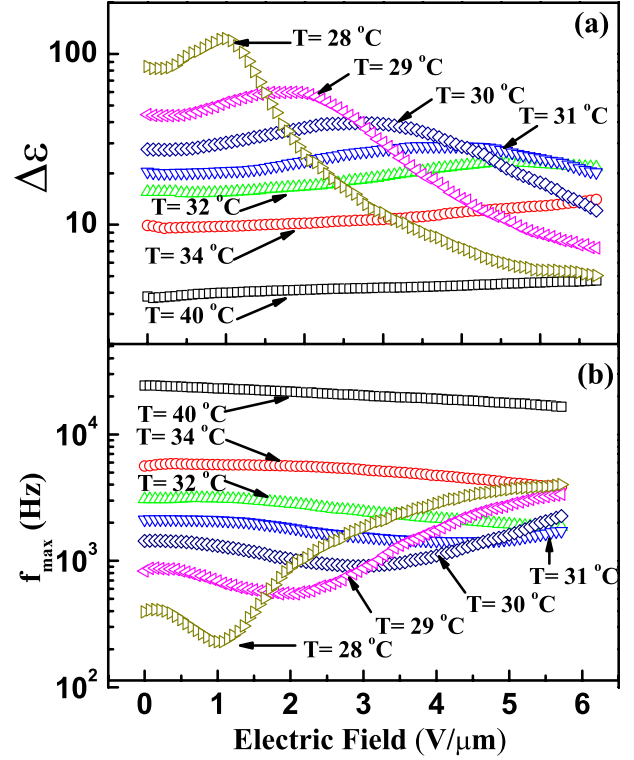


FIG. 3. (Color online) Dependence of the (a) $\Delta\epsilon$ and (b) f_{max} on applied electric field for different temperatures in the SmA* phase of TSiKN65.

For low fields

$$\Delta\epsilon \cong \Delta\epsilon^0 - 4\pi C_1 E^2, \quad (1)$$

$$f_{\text{max}} \cong f_{\text{max}}^0 + \gamma_S (A/2\pi c \chi)^2 C_1 E^2. \quad (2)$$

And for higher fields,

$$\Delta\epsilon \cong C_3 E^{-2/3}, \quad (3)$$

$$f_{\text{max}} \cong (C_2/2\pi) E^{2/3}, \quad (4)$$

where $\Delta\epsilon^0 = 4\pi(\chi c)^2/A$ and $f_{\text{max}}^0 = A/2\pi\gamma_S$ are the dielectric strength and the relaxation frequency in the absence of the field, respectively. A , C_1 , C_2 , and C_3 are constants. χ is a generalized susceptibility, c is the electroclinic coupling constant and γ_S is rotational viscosity associated with the rotation of the director. Equations (1)–(4) suggest that by increasing the electric field E , $\Delta\epsilon$ decreases and f_{max} increases in the SmA* phase as shown in Fig. 2(b) for Felix-18. Whereas, Fig. 2(c) shows that on increasing the electric field, $\Delta\epsilon$ increases and f_{max} decreases up to a certain value of the electric field ($E_c \approx 2.8 \text{ V}/\mu\text{m}$ at 30 °C) in the SmA* phase of TSiKN65. On further increasing the electric field, $\Delta\epsilon$ starts to decrease and f_{max} starts to increase. Figures 3(a) and 3(b) show the dependence of $\Delta\epsilon$ and f_{max} on the applied electric field at various temperatures in the SmA* phase of TSiKN65. We find that for all these temperatures, $\Delta\epsilon$ initially increases and then decreases, and f_{max} initially decreases and then increases. The maximum value of $\Delta\epsilon$ and the minimum value of f_{max} depend on the temperature. For

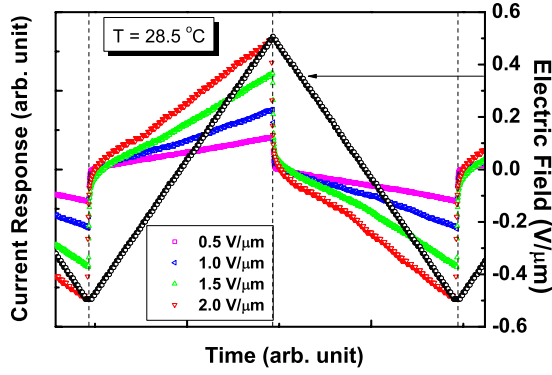


FIG. 4. (Color online) The current response to an applied triangular wave of the sample kept at the conditions for maximally unusual dielectric response, $T=28.5\text{ }^\circ\text{C}$ and 0.5 to $2.0\text{ V}/\mu\text{m}$ field strength.

lower temperatures, the maximum value of $\Delta\epsilon$ is higher, whereas the minimum value of f_{max} is lower. E_C also depends on temperature, which is lower for lower temperatures. For temperatures of $34\text{ }^\circ\text{C}$ and $40\text{ }^\circ\text{C}$ the value of the applied field was not high enough to obtain E_C . A similar behavior was observed for a very narrow range of temperatures ($\approx 0.8\text{ }^\circ\text{C}$) in the SmA^* phase of C-7, undergoing a first-order transition to SmC^* phase due to a shift in SmA^* - SmC^* transition temperature [28]. Such a possibility is excluded by measuring the current response to an applied triangular wave in TSiKN65 kept at temperature of $28.5\text{ }^\circ\text{C}$ ($1.5\text{ }^\circ\text{C}$ above the transition temperature). This is a temperature where the maximum unusual dielectric response is observed. We note no polarization peaks are visible as in Fig. 4. Moreover, the electric-field-induced tilt angle and polarization curves always show a continuous increase in contrast to discontinuous increase in C-7. However, this unusual field-dependent dielectric response can well be explained by the de Vries scenario on assuming the reorientation of the molecules by azimuthal angle fluctuations with the application of electric field as discussed below.

With the application of E in the de Vries SmA^* , and on assuming a uniform molecular distribution $f(\varphi)=1/2\pi$ on a cone in a single layer, the local polarization \mathbf{P}_l couples φ to the applied field with an energy $U_P=-\pi d(\xi_\perp/2)^2\mathbf{P}_l\cdot\mathbf{E}=-\mu_{\text{eff}}E\cos\varphi$, where ξ_\perp is the temperature-dependent molecular correlation length in a single layer and

$$\mu_{\text{eff}} = \pi d(\xi_\perp/2)^2 P_l, \quad (5)$$

is the effective dipole moment. P_l is the magnitude of \mathbf{P}_l , and E is the magnitude of \mathbf{E} . This equation is introduced to calculate the temperature dependence of the correlation length. With the application of E , the apparent optic axis orientation increases from zero (with $\langle\cos\varphi\rangle=0$, $\langle\cos^2\varphi\rangle=1/2$) to θ_A (with $\langle\cos\varphi\rangle\approx 1$, $\langle\cos^2\varphi\rangle\approx 1$, where θ_A is the smectic cone angle. The averages $\langle\cos\varphi\rangle$ and $\langle\cos^2\varphi\rangle$ can be evaluated using the Langevin equation for the azimuthal probability distribution described by the ratio of an electric aligning energy $\mu_{\text{eff}}E$ to thermal energy $k_B T$ given by

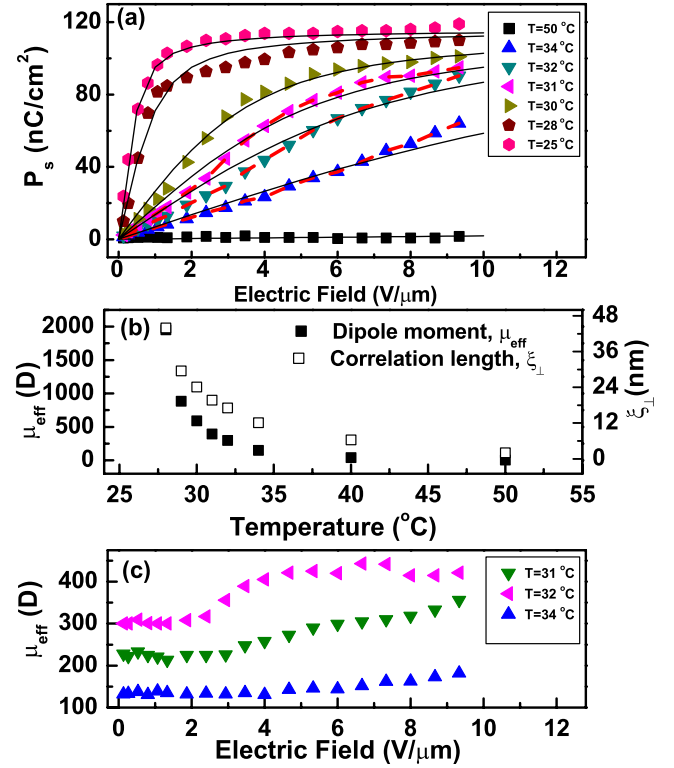


FIG. 5. (Color online) (a) The electric-field-induced polarization (P_s) for different values of temperatures in TSiKN65 . The solid black lines are the best fits of the data to the Langevin process described in Eq. (6). (b) The variation of effective dipole moment (μ_{eff}) and correlation length (ξ_\perp) with temperature in the de Vries-type SmA^* phase. (c) Values of the electric-field-dependent μ_{eff} determined by fitting the electric-field-dependent P_s as shown by red dashed lines in (a) to the Langevin process considering the increase of μ_{eff} with field.

$$P_s = P_l \langle \cos \varphi \rangle = \frac{\int_0^\pi \exp\left(\frac{\mu_{\text{eff}} E \cos \varphi}{k_B T}\right) (P_l \cos \varphi) d\varphi}{\int_0^\pi \exp\left(\frac{\mu_{\text{eff}} E \cos \varphi}{k_B T}\right) d\varphi}, \quad (6)$$

where k_B is the Boltzmann constant and P_s is the field-induced macroscopic polarization. The electric-field-induced Langevin-like alignment of the local in-plane dipoles against thermal fluctuations and constraints imposed by surface interfaces, induces the net polarization gradually. Note that the Langevin process described above assumes μ_{eff} as constant for different values of E . Figure 5(a) shows the electric-field-dependent P_s for different temperatures. The black solid lines in Fig. 5(a) are the best fits of the Langevin theory described by Eq. (6) to the experimental results. The observed results are well simulated for the values of μ_{eff} varying from approximately 4 to 2000 D depending on the temperature in the de Vries-type SmA^* phase as shown in Fig. 5(b). The magnitude of typical dipole moment of a single molecule is in the order of $1-2\text{ D}$ [29]. On assuming the dipole moment of a single molecule as 1.5 D , we find μ_{eff} corresponds to a

maximum of around 1300 molecules at 28 °C. Thus, the interaction of a molecular dipole and the applied electric field does not involve one molecule, but a maximum of around 1300 molecules cooperatively respond to the applied electric field. Hence, we note that the molecules in the de Vries-type SmA* phase possess a local order even without the application of electric field. A similar type of behavior has been observed in a nontilted smectic phase of an asymmetric bent-core liquid crystalline compound [30]. The number of molecules possessing the local order depends upon the temperature. Normally, we need a large electric field to orient randomly distributed dipoles under the action of thermal energy. But, in the case of de Vries-type SmA*, because of the existing local order of the molecules, a relatively low electric field is sufficient to induce a large polarization. For lower temperatures, the number of molecules possessing the local order is higher, as a result, less electric field is needed to induce a large polarization. As a result, we observe higher $\Delta\epsilon$ and lower f_{\max} for lower temperatures. By inserting the measured saturated value of $P_s = 119 \text{ nC/cm}^2$ ($\approx P_l$ at high field) and by assuming a perfect ordering of dipoles, the minimum value of the correlation length, ξ_{\perp} for different values of μ_{eff} and d for different temperatures are calculated from Eq. (5) as shown in Fig. 5(b). Note that if the dipolar ordering decreases, ξ_{\perp} increases. The variation of d with temperature of TSiKN65 is taken from Ref. [25]. We note that the correlation length, ξ_{\perp} is of the order of 45 nm for 1300 molecules at 28 °C. If we consider the local ordering of the molecules is along the layer normal as well as a single layer, the expression for the effective dipole moment becomes $\mu_{\text{eff}} = (4\pi/3)(\xi_{\parallel}/2)^3 P_s$, and ξ_{\parallel} becomes 22 nm, the correlation length along the layer normal for the measured value of the P_s .

By applying the Langevin model, in the de Vries SmA*, we find that a maximum of around 1300 molecules cooperatively act as a single entity and respond to the electric field. Since the Langevin model describes the field-induced molecular reorientation by azimuthal angle fluctuations, we must conclude the Langevin-type concentration of $f(\varphi)$ on the smectic cone with application of electric field is accompanied by the field-dependent dielectric response in the de Vries SmA*. Thus the field-dependent dielectric response corresponds to the azimuthal angle (φ) fluctuations. Moreover, the relaxation frequencies for the lower temperatures in the de Vries SmA* are much closer to that of typical values of azimuthal angle fluctuations ($\approx 20\text{--}5000 \text{ Hz}$) rather than

the tilt angle fluctuations ($\approx 1\text{--}10^4 \text{ kHz}$) [31,32]. The Langevin process described by Eq. (6) does not consider the increase of μ_{eff} with electric field, which is supposed to be the case in the de Vries SmA* since application of field tends to align the transverse dipole of these molecules. This is confirmed by achieving a better fitting of the field-dependent P_s to the Langevin process as shown for temperatures of 34 °C, 32 °C, and 31 °C by red dashed lines in Fig. 5(a) considering the increase of μ_{eff} with field. The values of the field-dependent μ_{eff} for which the P_s are simulated are plotted in Fig. 5(c) for these temperatures. We note that with increasing field, μ_{eff} increases, hence the number of molecules cooperatively responding to the field also increases, and so does the correlation length. As a result, $\Delta\epsilon$ increases and f_{\max} decreases with the application of an increasing field. At $E = E_C$, the de Vries SmA* assumes the same symmetry as SmC* through an azimuthal ordering of the already tilted molecules and on further increasing the field, the azimuthal angle fluctuations are suppressed, as a result, $\Delta\epsilon$ starts to decrease and f_{\max} starts to increase.

III. CONCLUSIONS

In conclusion, we find that (i) the molecules in the de Vries SmA* possess a local orientational order even without the application of the electric field, i.e., the molecules are not randomly oriented but orient with a finite correlation length which is of the order of a few tens of nm, and these molecules cooperatively respond to the applied electric field, (ii) application of an electric field produces a bias in the distribution of the tilt direction, forcing the molecules to reorientate by rotation around their cone angle, (iii) with increasing field, the number of molecules cooperatively responding to the electric field increases, hence the correlation length, and as a result, $\Delta\epsilon$ also increases and f_{\max} decreases with increasing applied field in de Vries SmA*.

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