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Influence of director fluctuations on the electric-field phase diagrams of nematic liquid crystals

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Abstract. – We report the first experimental high–electric-field phase diagram of a nematic liquid crystal with *negative* dielectric anisotropy. The variation of the paranematic-nematic transition temperature ($T_{\rm PN}$) is essentially *linear* with $|E|$, whereas the Landau-de Gennes theory predicts a quadratic variation. It is argued that the quenching of director fluctuations by the field contributes significantly to the thermodynamics of the transition.

Introduction. – Nematic liquid crystals have a long-range orientational order of molecules with shape anisotropy. Confining our attention to rod-like molecules, the local average orientation direction of the long axes is denoted by a dimensionless unit vector $\hat{n}$ called the director. It is *apolar* in nature which requires that the orientational order parameter of a nematic is a second-rank tensor given by $Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta})/2$, where $S = \langle 3\cos^2\theta - 1\rangle/2$ is the magnitude of the order parameter, θ being the angle made by the long axis of the molecule with $\hat{n}$. The Landau-de Gennes free-energy expression describing the nematic-isotropic (NI) phase transition will then have a nonzero cubic term (see eq. (1) below), implying that the transition is thermodynamically *first* ordered in nature with S jumping from a finite value ($\simeq 0.3$) to 0 [1]. The dielectric anisotropy $\Delta\epsilon$ ($= \epsilon_\parallel - \epsilon_\perp$, the subscripts referring to directions in relation to $\hat{n}$) is proportional to S. As the orientational part of the dielectric energy density under an external electric field E is $f_{\rm e} = -\frac{\Delta\epsilon\epsilon_0}{2}(\hat{n}\cdot\vec{E})^2$, where ϵ_0 is the vacuum dielectric constant, E^2 is conjugate to S. If E is large, S is increased and further a weak orientational order is induced even above the NI transition temperature ($T_{\rm NI}$), giving rise to a *paranematic* (P) phase. The PN transition temperature increases with field. If $\Delta\epsilon > 0$, N and P phases have the same symmetry and beyond a critical field ($E_{\rm c}$) there is a continuous evolution of S between N and P phases in analogy with the liquid-gas transition under varying pressures [2]. Typically $E_{\rm c} \simeq 2\times 10^7$ V/m and the electric-field phase diagrams of a couple of nematogens with positive $\Delta\epsilon$ have been studied experimentally [3–6].

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The nematic order also gives rise to a curvature elastic response to director-distortions in the medium which can be decomposed into three basic deformations *viz* splay, twist and bend [1]. The relevant energy density in the one-constant approximation is $f_{\rm d} = \frac{K}{2}(\nabla n)^2$, where K, the elastic constant, is rather small, $\sim 10^{-12}$ newtons. Consequently, there are large director fluctuations in the medium, giving rise to a strong scattering of light. The external electric field E quenches the director fluctuations as well, thus increasing the measured value of the order parameter S, as pointed out by de Gennes [1]. The relevant increase in the order parameter, *viz* $(S(E) - S(0))$, is $\propto |E|$, varying linearly with the modulus of the field. At low fields this director fluctuation-quenching effect dominates, as was found experimentally using both electric [4, 6] and magnetic [7] fields. Many compounds exhibit a transition from the N phase to the layered smectic-A (SmA) phase as the temperature is lowered. The SmA-N transition can be second-ordered in nature and, as de Gennes pointed out [8], there is a formal analogy between the SmA-N and superconductor-normal metal transitions. There are two types of smectics *viz* type-I and type-II just as in superconductors. Interestingly Halperin, Lubensky and Ma (HLM) [9] pointed out that in type-I materials of both systems, gauge fluctuations (which are the director fluctuations in the nematic) couple to the (smectic) order parameter, making the relevant transition weakly first-ordered in nature. The HLM effect has been clearly demonstrated in the liquid-crystal case [10–13]. In particular, the quenching of the director fluctuations due to a strong electric field has been shown to restore the second-order character of the SmA-N transition [13].

Returning to the PN transition, for materials with *negative* $\Delta\epsilon$, the phase diagrams can be expected to have a different character from those for positive $\Delta\epsilon$ materials [2]. The long axes of the molecules in the field-induced paranematic (P) phase tend to orient orthogonal to E but without any preference in azimuthal angles. Thus the P phase is uniaxial with a negative sign ($N_{\rm U-}$) with $S < 0$. In the N phase the medium becomes weakly biaxial under E, which has a contribution from the differential suppression of the fluctuations of $\hat{n}$ in the plane containing E and $\hat{n}$ compared to that in the orthogonal plane [14]. The first-ordered biaxial nematic $N_{\rm B}$ to $N_{\rm U-}$ transition is expected to go over to a second-ordered one above a tricritical field $E_{\rm tc}$ [2,15]. In the following we describe the first experimental electric-field phase diagram of a nematic with *negative* $\Delta\epsilon$. Our main result is to show that the quenching of thermal fluctuations of the director significantly contributes to the field-dependent shift of the PN transition temperature.

Experimental results. – Application of a large electric field to a nematic heats the sample both due to ionic currents and dielectric relaxation. Durand *et al.* [3, 4] used short high-frequency electric pulses with long time intervals between the pulses to overcome this problem. Basappa *et al.* [5] developed a technique of measuring the *local* temperature using a patterned nickel thermometer. We adopted the latter technique which allows us to measure both $\epsilon_\perp$ and the birefringence $\Delta\mu(= \mu_\parallel - \mu_\perp)$ using a light beam travelling along the field direction of a planar aligned sample taken between an indium tin oxide-coated top plate and an aluminium (Al)-coated bottom plate. The Al coating is separated from the nickel thermometer by a thin insulating layer. The experiment was controlled by a computer and the details will be published elsewhere [16]. The optical measurement is made in the reflection mode of a polarising microscope (Leitz; Orthoplan). The laser beam which is polarised at an angle of 45° to the director is reflected from the bottom aluminium electrode after passing through the sample, and the intensity transmitted through a crossed polariser is measured using a photodiode. The sample is 4′ butyl-4 heptyl-bicyclohexyl-4-carbonitrile (CCN-47) obtained from Merck. It has the highly polar cyano group making a large angle with the long axis of the molecule and two fully saturated cyclohexane rings. Thus the medium has very low birefringence ($\Delta\mu$). The phase sequence of the compound is Cr 28 °C SmA 30.6 °C N 59.7 °C I.

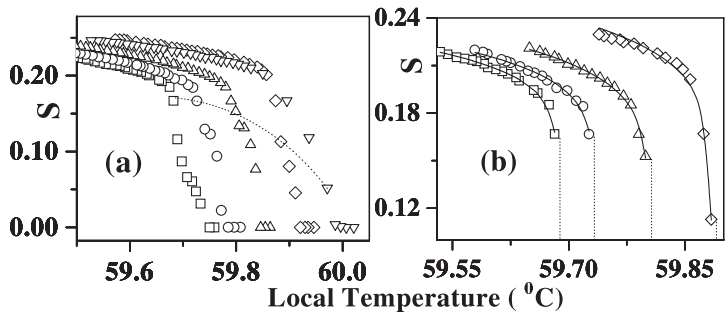

Fig. 1 – (a) Variation of order parameter (calculated using $S = \Delta\mu/\Delta\mu_0$) at 15×10^4 V/m (open squares), 3.3×10^6 V/m (open circles), 6.5×10^6 V/m (upward triangles), 9.8×10^6 V/m (diamonds), 1.3×10^7 V/m (downward triangles). (b) Variation of order parameter in the nematic phase within 0.15 °C of the transition point. Data points are those below the temperatures limited by the dashed line shown in (a). Continuous lines are the theoretical fits to $S = S_0 + \alpha(1 - T/T^{**})^\beta$. Vertical dotted lines indicate the temperatures corresponding to the calculated values of T^{**}.

The measured optical phase difference is $2\Delta\phi = \frac{4\pi}{\lambda}(\Delta\mu)d$, where d is the sample thickness ($\simeq 16.0\,\mu$m, measured using an interferometric technique), and the factor 2 comes from the double passage of the light beam through the sample in the reflection mode. The medium exhibits a wide nematic range and the measured temperature variation of $\Delta\mu$ [16] is used to estimate $\Delta\mu_0$, the value for perfect orientational order ($S = 1$) by using the Haller extrapolation procedure [17]. As $\Delta\mu$ is very small, the order parameter is given to a very good approximation by $S = \Delta\mu/\Delta\mu_0$. Under an electric field, the medium becomes biaxial and $\Delta\mu$ is a measure of $S - P$, where P is the biaxial order parameter which is two orders of magnitude lower than S [14] and is ignored in further discussion. The data collected at different sinusoidally varying fields at a frequency of 4111 Hz over narrow temperature ranges around the PN transition temperatures are shown in fig. 1(a) as functions of the local temperature measured by the nickel thermometer to an accuracy of ~ 8 mK. In the paranematic phase (N_{U-}), with the orientational order induced by the electric field, the optic axis is defined by the field, and no birefringence is measured as the light beam travels along the optic axis. A simultaneous measurement of the dielectric constant shows an enhancement ($\propto E^2$) reflecting the induced order in the paranematic phase [16]. The obliquely coated SiO on the electrodes induces a *surface* order above T_{NI} even in the absence of the field. This gives rise to a measurable birefringence below some temperature. As seen in the data at the lowest field (fig. 1(a)), the thickness-averaged value of S tends to diverge as the temperature approaches the transition point to the bulk nematic phase, as predicted by theory [18]. Below the bulk transition temperature (T_{PN}), the order parameter variation has the opposite curvature, tending to saturate as the temperature is lowered (fig. 1(a)). The dotted line in fig. 1(a) connects the temperatures up to which the smooth bulk-like variation of S is seen in different voltage runs. In order to get a quantitative measure of T_{PN}, we fitted the data within a range of 0.15 °C below the temperature lying on the dotted line to the functional form $S = S_0 + \alpha(1 - T/T^{**})^\beta$ in which S_0 is the value at T^{**}, the superheating temperature of the nematic, and α and β are constants. This form is predicted by the Landau-de Gennes theory with $\beta = 0.5$, but, as is well known [1], experimentally β is found to be much smaller. Our data can be fitted reasonably well up to a field of 10^7 V/m to the above form with $\beta \simeq 0.17$ (fig. 1(b)). T^{**} is very close to the bulk transition temperature T_{PN} and can be taken as a measure of the latter. We plot both $\Delta T^{**} (= T^{**}(E) - T^{**}(0))$ and ΔT corresponding to the temperature at which

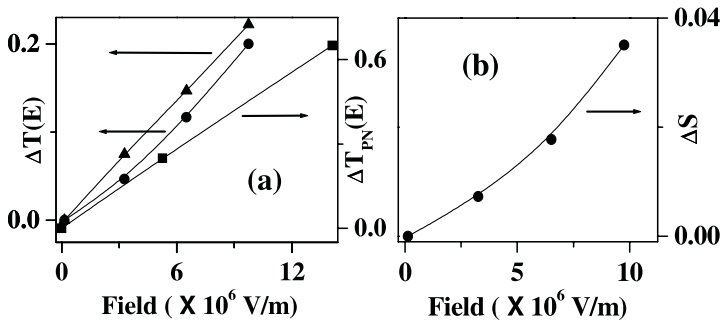

Fig. 2 – (a) Dependence on electric field of $\Delta T = T(E) - T(0)$ (filled triangles), the temperatures at which the birefringence starts to rise from zero (see fig. 1(a)), and of $\Delta T^{**} = T^{**}(E) - T^{**}(0)$ (filled circles, see fig. 1(b)). Variation of $\Delta T_{\rm PN}$ (filled squares) of 5CB obtained from fig. 3 of ref. [3] is also shown. (b) Variation of the measured enhancement of order parameter $\Delta S = S(E) - S(0)$ at a temperature of 59.6 °C in CCN-47. The lines are guides to the eye.

$\Delta\mu$ becomes nonzero, as functions of the RMS values of the applied field in fig. 2(a). The most important observation, which has also been confirmed on an independent sample [16], is that the variations have finite slopes at zero field, and increase essentially *linearly* with $|E|$. The electric-field phase diagrams of nematogens with positive dielectric anisotropy have been analysed [3] by using the standard Landau-de Gennes model (see eq. (1) below). However, $T_{\rm PN}$ has not been plotted as a function of $|E|$ in these studies. We use the data given in fig. 3 of ref. [3] and plot the shift $\Delta T_{\rm PN}(= T_{\rm PN}(E) - T_{\rm NI})$ of pentyl cyanobiphenyl (5CB) also in fig. 2(a). It is clear that $T_{\rm PN}$ shifts *linearly* with $|E|$ in this case as well. The Landau-de Gennes free energy density of a nematic with $\Delta\epsilon > 0$ subjected to an electric field is given by

$$F_{\rm LdG} = F_0 - hSE^2 + \frac{a(T - T^*)}{2}S^2 - \frac{B}{3}S^3 + \frac{C}{4}S^4, \tag{1}$$

where a, B, C are the Landau coefficients, T^* is the maximum supercooling temperature of the isotropic phase, and $h = \epsilon_0\Delta\epsilon_0/3$, where $\Delta\epsilon_0$ is the value of $\Delta\epsilon$ for $S = 1$. As eq. (1) contains a term *quadratic* in the field, it can only predict that $\Delta T_{\rm PN} \propto E^2$ [19]. The *linear* dependence on $|E|$ clearly shows the importance of the director fluctuations even in the thermodynamics of the PN transition under electric fields.

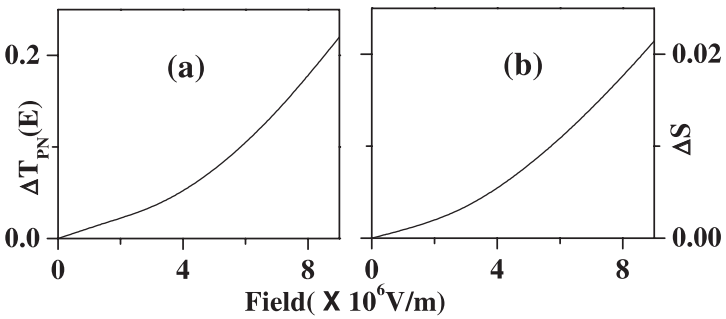

Fig. 3 – (a) Calculated variation of $\Delta T_{\rm PN}$ as a function of electric field. (b) Calculated variation of ΔS in the nematic phase at $T_{\rm NI} - 0.1^\circ$ as a function of field.

Indeed, as we mentioned earlier, the quenching of director fluctuations in the nematic phase gives rise to an enhancement in the measured value of S, *viz* $S(E) - S(0)$, which is $\propto |E|$. We show in fig. 2(b) the order parameter of CCN-47 at the fixed local temperature of 59.6 °C as a function of field. The variation is linear with $|E|$ at low fields and the quadratic contribution becomes more visible at high fields.

Discussion. – For modest fields, such that the PN transition has a first-order character, the fluctuations in the *magnitude* of the order parameter S can be expected to be relatively small. The long-wavelength director fluctuations are partially quenched by the electric field, thus decreasing the entropy of the medium. The resulting increase in the free energy has not been taken into account in eq. (1). We may point out an analogous problem of the undulation interaction, which arises in lamellar systems. In this case, the layer fluctuations are restricted due to the presence of the neighboring layers and the corresponding increase in the free energy was calculated by Helfrich [20]. In the case of nematic liquid crystals, the amplitudes of the director fluctuations are reduced in the presence of the field. We can use a dimensional analysis to estimate the corresponding increase in the free energy density. There are two length scales in this problem. One is the electric coherence length $\xi(E) = (\frac{K}{\epsilon_0 \Delta\epsilon})^{\frac{1}{2}} \frac{1}{|E|}$, which is a length such that the director fluctuations with wavelengths longer than ξ are essentially suppressed by the field [1]. The other length gives rise to the cut-off wave vector $q_c = 2\pi/l$, for the applicability of the elasticity theory, where l is a typical molecular dimension. As the additional contribution arises from an entropic origin, we write the additional free energy *density* with the following combinations of the thermal energy and the above two lengths: $\Delta F = k_B T \frac{q_c^2}{\xi} + k_B T \frac{q_c}{\xi^2}$. In the mean-field model $K = K_0 S^2$ and $\Delta\epsilon = \Delta\epsilon_0 S$, and we can write $\xi(E) = C\sqrt{S}/|E|$, where the constant $C = (K_0/\epsilon_0 \Delta\epsilon_0)^{\frac{1}{2}}$. Thus,

$$\Delta F = \frac{\alpha T}{\sqrt{S}}|E| + \frac{\beta T}{S}E^2, \tag{2}$$

where $\alpha = k_B q_c^2/C$, and $\beta = k_B q_c/C^2$ are constants and $\beta \ll \alpha$. The contribution of the above unconventional expression to ΔF is zero when $E = 0$. In order to justify eq. (2), we first consider a material with positive $\Delta\epsilon$ for the sake of simplicity. Treating the director fluctuation as a random variable [1], the fluctuation amplitude $n_\perp$ in a plane perpendicular to the director can be assumed to have a Gaussian distribution:

$$W(n_\perp) = \frac{1}{C'\sqrt{2\pi\langle n_\perp^2\rangle}} \exp\left[-\frac{n_\perp^2}{2\langle n_\perp^2\rangle}\right], \tag{3}$$

where C' is a normalising constant which can be found by setting $\int_0^1 W(n_\perp)\mathrm{d}n_\perp = 1$. It should be pointed out that the limit of the integration is taken from 0 to 1 instead of 0 to ∞ as for a usual Gaussian distribution. In the absence of the field, the fluctuation amplitude is given by $\langle n_\perp^2\rangle_0 = (k_B T/2\pi^2 K) q_c$ [1]. We estimate $\langle n_\perp^2\rangle_0 \simeq 0.14$ in the nematic phase at 50 °C, assuming $l \simeq 10$ Å, and the elastic constant $K \simeq 5 \times 10^{-12}$ newtons. For this value of $\langle n_\perp^2\rangle_0$, 95% of the area of the variation of $W(n_\perp)$ is covered within $n_\perp \simeq 0.8$ and hence the upper limit of integration can be taken to be infinity and the normalising constant is then $C' \simeq 1$. With increasing field, $\langle n_\perp^2\rangle_E$ decreases and hence the approximation is more justifiable. The entropy due to this distribution is given by $\zeta = -k_B \int_0^1 W(n_\perp)\ln(W(n_\perp))\mathrm{d}n_\perp$. This can be simplified to get

$$\Delta\zeta = \zeta_E - \zeta_0 = k_B\left[\ln\left(\sqrt{\langle n_\perp^2\rangle_E}\right) - \ln\left(\sqrt{\langle n_\perp^2\rangle_0}\right)\right], \tag{4}$$

where ζ_E and ζ_0 are the entropies and $\langle n_\perp^2\rangle_E$ and $\langle n_\perp^2\rangle_0$ are the mean-square fluctuation amplitudes in the presence and in the absence of electric field, respectively. The sum of the distortion and electric free energy densities f_d and f_e for each Fourier mode can be equated with the thermal energy $1/2k_\mathrm{B}T$ (equipartition theorem). The mean-square fluctuation amplitude is then given by [1]

$$\left\langle n_\perp^2(q)\right\rangle_E = \frac{k_\mathrm{B}T}{V}\,\frac{1}{K(q^2+\xi^{-2})}\,, \tag{5}$$

where V is the volume of the sample and ξ the electric coherence length defined earlier. In real space the fluctuation amplitude is given by

$$\left\langle n_\perp^2\right\rangle_E = \frac{k_\mathrm{B}T}{2\pi^2K}\left(q_\mathrm{c} - \frac{1}{\xi}\left(\frac{\pi}{2} - \frac{1}{q_\mathrm{c}\xi}\right)\right). \tag{6}$$

The excess free energy density is given by $\Delta F = -T\Delta\zeta$. Using eqs. (4) and (6), the simplified form of the free energy can be recast in the form of eq. (2). Using eqs. (1) and (2), the total free energy density is given by $F = F_\mathrm{LdG} + \Delta F$. Close to the critical point $\langle n_\perp^2\rangle$ can be large and the above approximation is no longer valid, and further the fluctuations of order parameter S should also be taken into account. In the paranematic phase there is no director in the *absence* of field and hence the free energy density in that phase is given by eq. (1). The equilibrium value of S minimises the appropriate free energies. The paranematic-to-nematic transition temperature is found numerically by comparing the two minimised energies (F and F_LdG). For illustration, we use the Landau coefficients which are known for 5CB [3]: $a = 0.13\times10^6\,\mathrm{J/Km^3}$, $B = 1.6\times10^6\,\mathrm{J/m^3}$, $C = 3.9\times10^6\,\mathrm{J/m^3}$, and $h = 6\times10^{-11}$. The parameters α and β are estimated to be 3×10^{-8} and 10^{-15}, respectively. We find that ΔT_PN shows practically a linear variation up to $5\times10^6\,\mathrm{V/m}$, and beyond that the influence of the quadratic component is seen (fig. 3(a)). This reflects the trend seen in fig. 2(a) qualitatively. The calculated variation of order parameter in the nematic phase (fig. 3(b)) also has a trend similar to that of the measured variation shown in fig. 2(b). The experimetnal data reported in this letter pertain to a material with negative $\Delta\epsilon$. In this case, the field is applied orthogonal to $\hat{n}$. The director fluctuations are suppressed only in the $\hat{n}-\vec{E}$ (*i.e.*, $\hat{z},\hat{x}$)-plane, but not in the orthogonal ($\hat{z},\hat{y}$)-plane. Unlike in a material with positive $\Delta\epsilon$, the distribution function is not cylindrically symmetric for $E\neq0$. It can be written as $\mathrm{W}(n_x,n_y) = W_1(n_x)W_2(n_y)$. The width $\langle n_x^2\rangle_E$ is given by eq. (6), while $\langle n_y^2\rangle_E = \langle n_y^2\rangle_0$. The net result is that the change in entropy due to the suppression of director fluctuations is reduced by a factor of 2 compared to that in a material with positive $\Delta\epsilon$. This may partly account for the higher slope seen in fig. 2(a) in the latter case.

Conclusion. – To conclude, our measurements as well as an analysis of the data available in the literature show that under an electric field the paranematic-nematic transition temperature (T_PN) varies lineraly with $|E|$ in both materials with $\Delta\epsilon<0$ and $\Delta\epsilon>0$. It is argued that the quenching of the director fluctuations under strong electric fields significantly contributes to the thermodynamics of the nematic-to-paranematic transition. Using a dimensional argument as well as a simple physical model, we have calculated the entropic contribution to the free energy density. The calculated trends in ΔT_PN as well as $S(E)-S(0)$ reflect the experimental ones. The quenching of the director fluctuation thus plays a significant role in the thermodynamics of both SmA-N and PN transitions. As mentioned earlier, for materials with negative $\Delta\epsilon$ the field-induced N_B to $N_{\mathrm{U}-}$ transition becomes second-ordered above a tricritical field. This has been explored using the 3rd harmonic of the electric current which is a measure of the susceptibility of the sample [6]. This result will be discussed elsewhere [16].

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