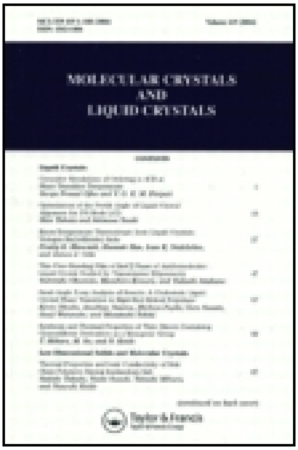

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Influence of Flexoelectricity on the Smectic-Nematic Transition: Can "Bend Grain Boundary Phases" Appear?

Heinz-Siegfried Kitzerow [a]
[a] University of Paderborn, Paderborn, Germany

Version of record first published: 18 Oct 2010

To cite this article: Heinz-Siegfried Kitzerow (2004): Influence of Flexoelectricity on the Smectic-Nematic Transition: Can "Bend Grain Boundary Phases" Appear?, Molecular Crystals and Liquid Crystals, 412:1, 103-110

To link to this article: http://dx.doi.org/10.1080/15421400490431822

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 103/[1713]–110/[1720], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431822

INFLUENCE OF FLEXOELECTRICITY ON THE SMECTIC-NEMATIC TRANSITION: CAN "BEND GRAIN BOUNDARY PHASES" APPEAR?

Heinz-Siegfried Kitzerow
Faculty of Science, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

The possible appearance of an intermediate state between the smectic and the nematic mesophase under the influence of an electric field, due to the flexoelectric effect, is dicussed in this paper. In analogy to the Abrikosov flux lattice in superconductors and twist grain boundary phases in liquid crystals, this state is characterized by a lattice of defects. Here, however, an electric field leading to a bend deformation of the director field is expected to support the formation of edge dislocations. A critical field strength below 10 V/μm may be sufficient to induce these dislocations.

Keywords: flexoelectricity; liquid crystals; phase transitions

INTRODUCTION

Systems which are quite different can neverertheless show a universal behaviour close to a phase transition. A famous example is the analogy between superconductors and liquid crystals [1]. Since the Landau expansion of the free energy for these two types of systems is formally very similar, de Gennes [1] predicted that intermediate states characterized by a lattice of screw dislocations or edge dislocations (Fig. 1) can appear between the smectic and the nematic phase if the liquid crystal is exposed to a twisting or bending force, respectively. These intermediate states are the liquid crystal analogues of the Abrikosov flux lattice in a type-II superconductor. The consideration by de Gennes was confirmed by the theoretical prediction [2] and experimental discovery [3] of twist grain boundary

The authour is very grateful to A. Petrov for sending a reprint of his review article about the flexoelectric effect in nematics [6] and to P. P. Crooker, T. Lubensky, and R. B. Meyer for illuminating discussions about TGB phases and lattices of dislocations.

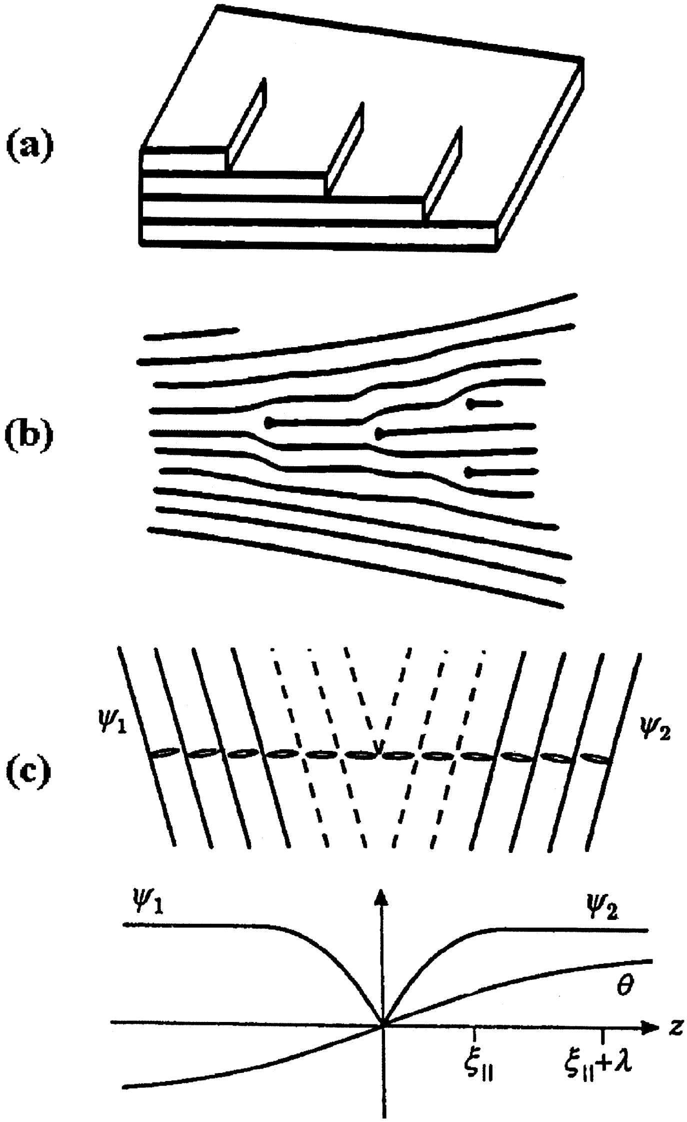

FIGURE 1 (a) Grain boundary made of screw dislocations between two twisted smectic slabs in a TGB phase. (b) Edge dislocations forming a domain wall (according to Pershan [8]). (c) Melted grain boundary [according to Dozov and Duran [9]): Instead of isolated edge dislocations, the smectic order parameter vanishes on a plane. The lower curves show the amplitude of the smectic order parameter ψ and the director tilt θ, respectively.

TABLE 1 Analogy Between Superconductors in Magnetic Fields and Liquid Crystals Exposed to a Chiral-Induced Twist or Electric Field-Induced Bend Deformation

Superconductors	Liquid crystals
Wave function of the Cooper pairs ψ	Complex amplitude of the density wave ψ
Vector potential A	Director **n**
Meissner phase	Smectic-A phase (SmA)
Normal metal	Uniform Nematic phase (N)
Inverse mass of the Cooper pairs $(\hbar^2/2\,m_e)$	Smectic elastic contant $C_\perp$
Charge of the Cooper pairs $(2\,e/\hbar)$	Wave vector $Q_0 = 2\pi/d$
Coherence length $\xi = \hbar/(2\,m_e\lvert\alpha\rvert)^{1/2}$	Smectic correlation length $\xi = (C_\perp/\lvert\alpha\rvert)^{1/2}$
Coupling between magnetic field and momentum (Lorentz force)	Coupling between director and smectic layer displacement
Magnetic energy	Frank-Oseen elastic energy
Magnetic flux quantum $\Phi_0 = h/2\,e$	Layer spacing d

External Magnetic Field	**Chirality**	**Bend Deformation**
Magnetic Field H	Chirality 'field' $h_{twist}\colon = K_{22}k_0 = K_{22}\,\mathbf{n}_0(\nabla\times\mathbf{n}_0)$	Bending field $h_{bend}\colon = K_{33}/R_0 = K_{33}\mathbf{n}_0\times(\nabla\times\mathbf{n}_0) = e_3E$
Magnetic induction $\mathbf{B} = V^{-1}\int d^3\times(\nabla\times\mathbf{A})$	Average twist $k_0 = V^{-1}\int d^3\times\mathbf{n}(\nabla\times\mathbf{n})$	Average bend ${R_0}^{-1} = V^{-1}\int d^3\times\mathbf{n}\times(\nabla\times\mathbf{n})$
Normal metal in a magnetic field	Cholesteric phase (N*)	Polar nematic phase
Inverse magnetic permeability $(\mu)^{-1}$	Elastic coefficient for twist of the director field K_{22}	Elastic coefficient for bending K_{33}
Meissner effect	Twist expulsion	Expulsion of bend deformation
London penetration depth $\lambda = (m_e\beta/\mu\lvert\alpha\rvert)^{1/2}(2e)^{-1}$	Twist penetration depth $\lambda_{2,t} = (K_{22}\beta/2C_\perp\lvert\alpha\rvert)^{1/2}{Q_0}^{-1}$	Bend penetration depth $\lambda_{2,b} = (K_{33}\beta/2C_\perp\lvert\alpha\rvert)^{1/2}{Q_0}^{-1}$
Ginzburg parameter $\kappa = (\beta/2\mu)^{1/2}\,m_e\hbar^{-1}e^{-1}$	Twist Ginzburg parameter $\kappa = (K_{22}\beta/2)^{1/2}{C_\perp}^{-1}{Q_0}^{-1}$	Bend Ginzburg parameter $\kappa = (K_{33}\beta/2)^{1/2}{C_\perp}^{-1}{Q_0}^{-1}$
Magnetic flux tube (Vortex)	Screw dislocation	Edge dislocation
Shubnikov phase/ Abrikosov vortex lattice	Twist grain boundary (TGB) phase	Bend grain boundary (BGB) phase

(TGB) phases. Not only one, but many TGB phases have been found since then (for a recent review, see [4]).

However a regular lattice of edge dislocations, a kind of 'bend grain boundary' (BGB) phase has not observed, so far. Here, it is speculated that an electric field may induce an intermediate state due to the flexoelectric effect [5]. In the following section, the basic ideas of the Landau-de Gennes theory are reviewed. In the subsequent paragraph, the influence of the flexoelectric effect is considered.

Let us first review the basic ideas of the Landau-de Gennes theory. Calamitic liquid crystals are anisotropic fluids which are characterized by a local parallel orientation of rod-like molecules. The locally preferred orientation is described by the director field $\mathbf{n}(\mathbf{r})$. In the nematic (N) phase, there is only orientation order, whereas smectic (Sm) phases show additionally a layer structure, i.e. a spatially periodic deviation of the density ρ from the average value ρ_0 which may be written [2] as $\rho(\mathbf{r}) - \rho_0 =: \psi(\mathbf{r}) + \psi^*(\mathbf{r})$. The complex quantity $\psi(\mathbf{r})$ can serve as an order parameter to describe the Sm–N phase transition, and the Landau-de Gennes free energy density reads

$$\begin{aligned} g_L = {} & 1/2\{\alpha|\psi|^2 + 1/2\beta|\psi|^4 + 1/3\gamma|\psi|^6 \\ & + [(C_\parallel - C_\perp)n_i n_j + C_\perp \delta_{ij}][(\nabla - iQ_0 n)_i \psi (\nabla + iQ_0 n)_j \psi^*]\} \\ & + 1/2K_{11}(\nabla\cdot\mathbf{n})^2 + 1/2K_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 \\ & + 1/2K_{33}[\mathbf{n}\times(\nabla\times\mathbf{n})]^2 + h(\mathbf{n}\cdot\nabla\times\mathbf{n}), \end{aligned} \tag{1}$$

where $\alpha = a\ (T - T_{SmA\text{–}N})$, and $a > 0$. A second order transition can be described by $\beta > 0$ and $\gamma = 0$. The gradient term $\nabla\psi$ with the coefficients $C_\parallel$ and $C_\perp$ appears due to the stiffness of the layers. Its coupling to the director field $\mathbf{n}(\mathbf{r})$ corresponds to the well defined orientation of the director with respect to the layer normal. The terms with coefficients K_{11}, K_{22}, and K_{33} describe the elastic behaviour of the director field for a splay, twist and bend deformation, respectively. Finally, the linear term with the coefficient h appears only for systems containing chiral molecules. If this 'chiral field' h is non-zero, the (chiral) nematic phase shows a twisted structure with a helical pitch of $p_0 = 2\pi/|q_0| = 2\pi\ K_{22}/h$. The striking similarity of the above expression with the free energy of a superconductor leads to the analogy summarized in the left part of Table 1.

INFLUENCE OF THE FLEXOELECTRIC EFFECT

In liquid crystals with a polar (e.g. cone-like or bow-like) molecular shape, a curved director field can lead to a preferred orientation of the molecular dipoles (flexoelectric effect [5]). The coupling of the flexoelectric polarization to an external field corresponds to the free energy density

$$g_{\mathbf{fl}} = -\mathbf{E} \cdot \mathbf{P}_{\mathbf{fl}} = -\mathbf{E} \cdot \{e_1[\mathbf{n}(\nabla \cdot \mathbf{n})] + e_3[\mathbf{n} \times (\nabla \times \mathbf{n})]\} \tag{2}$$

where $P_{\mathbf{fl}}$ is the flexoelectric polarization, and $e_1$and e_3 are flexoelectric coefficients corresponding to splay and bend, respectively. The size of these coefficients for a rather usual liquid crystal like MBBA or 8OCB is of the order 10^{-11} As/m [6]. For molecules with a more polar shape, these coefficients are expected to be higher. Note that the linear term e_3E $[\mathbf{n} \times (\nabla \times \mathbf{n})]$ has a similar effect on the bending energy as the linear term $h(\mathbf{n} \cdot \nabla \times \mathbf{n})$ on the twist energy. Thus, a bend deformation is induced in the nematic phase if $E \neq 0$. In the smectic phase, a bend deformation cannot easily be induced because this would require a dilation of the layer spacing. Instead, the formation of edge dislocations is supported. Extending the analogy between superconductors and liquid crystals to bent structures (Table 1), it can be seen that the Landau-Ginzburg parameters in the twist and bend case are very similar, except that K_{22} is replaced by K_{33}. The condition for an intermediate state, $\kappa > 1/\sqrt{2}$, is likely to be fulfilled for materials similar to TBG compounds, because typically $K_{33} > K_{22}$. In particular, BGB structures are expected close to a N-SmA-SmC triple point, where $C_\perp$becomes small [7]. Turning to the critical field which is necessary to induce an intermediate state, note that the product (e_3E) replaces the chiral field h. Typical values for a chiral liquid crystal are $p_0 = 0.3\,\mu m$, $K_{22} = 5\ 10^{-12}$ N, and thus $h \approx 10^{-4}\,J/m^2$. For $e_3 = 10^{-11}$ As/m and a reasonable field strength of $E = 10\,V/\mu m$, the effective 'flexoelectric field' $e_3E = 10^{-4}\,J/m^2$ is of the same order of magnitude as the chiral field h in the TGB case. One could conclude that even in a smectic phase, a bend deformation appears gradually through edge dislocations if the smectic phase is exposed to a d. c. field close to the smectic-nematic transition temperature. In principle, edge dislocations tend to form domain walls [8] (Fig. 1b). Instead of an array of edge dislocations, one might also expect the appearance of melted grain boundaries [9,10] where the smectic order parameter vanishes on an entire plane along the grain boundary (Fig. 1c).

Of course, the application of a d. c. field for long periods can result in decomposition of the sample. In addition, there is also a quadratic coupling to the external electric field due to the dielectric anisotropy $\Delta\varepsilon$. The corresponding free energy per volume is of the order $-\varepsilon_0\Delta\varepsilon\, E^2$, and tends to align the director either uniformly along the electric field or perpendicular to the electric field, depending on the sign of $\Delta\varepsilon$. In order to avoid this uniform alignment, either the flexoelectric coefficient e_3 must be larger (and the field smaller) than the values given above, or the dielectric anisotropy has to be very small ($|\Delta\varepsilon| < 1.0$). However, it should be emphasized that molecules exhibiting a more polar shape than MBBA or 8OCB, may have much larger flexoelectric coefficients. Bow- or banana-shaped molecules [11] are good candidates and may even show a tendency towards spontaneous bending.

Finally, one may speculate whether not only some edge dislocations or defect walls of edge dislocations, but even a very regular structure of grain boundaries can appear, a structure which deserves the name bend grain

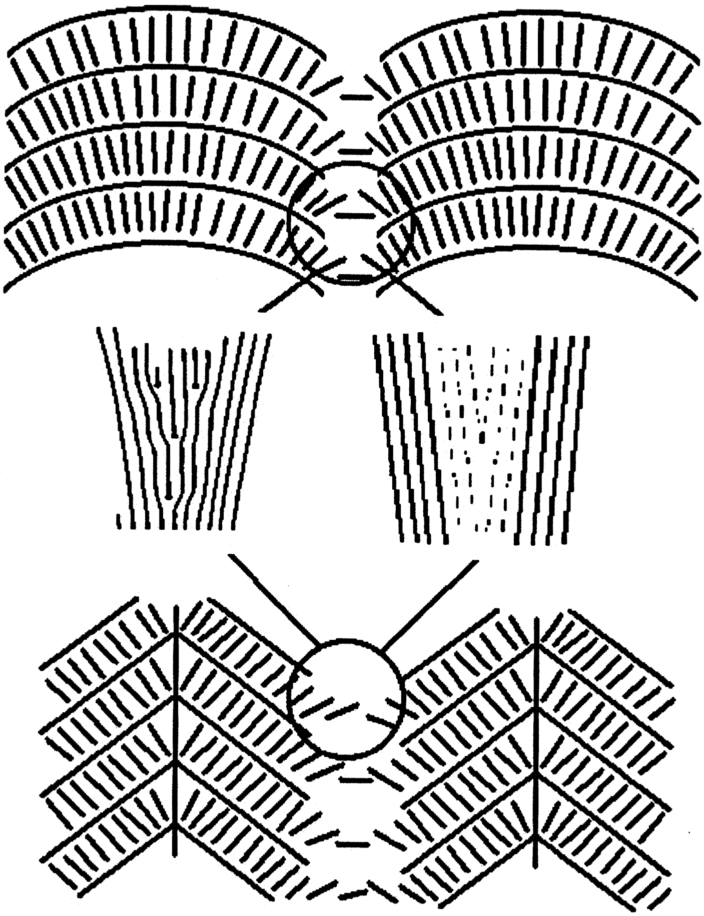

FIGURE 2 Top: Periodic structure of a frustrated smectic structure showing alternating areas with bend and splay deformation of the director field, respectively. Bottom: Periodic structure showing chevrons instead of the continuous splay deformation. The circled areas in both structures contain either edge dislocations or melted grain boundaries.

boundary phase (in analogy to the twist grain boundary phases). However, the possible geometry of such a structure is not obvious. A bent director field with given polarity (given sign of $\{\nabla \times \mathbf{n}\}$ and given radius of curvature R_0) cannot infinitely continue in space (in contrast to a helical structure with constant pitch). Thus, the bend deformation in some areas of the sample has to be compensated by splay and/or twist deformation in other areas of the sample (Fig. 2, top), or by additional discontinuities such as chevron-like structures (Fig. 2, below). A periodic splay-bend pattern in the (x,y)-plane (Fig. 2, top) without twist along the z-direction is described by the director field $\mathbf{n}(\mathbf{r}) = (\cos\{\varphi(x)\}, \sin\{\varphi(x)\}, 0)$ where $\varphi(x)$ is either a monotonously increasing or monotonously decreasing function. If the field is applied along the y-axis, $\mathbf{E} = (0, E_y, 0)$, the flexoelectric contribution to the free energy (Eq. 2) becomes

$$g_{\mathbf{fl}} = e_1 E_y (d\varphi/dx) \sin^2\{\varphi(x)\} + e_3 E_y (d\varphi/dx) \cos^2\{\varphi(x)\}. \qquad (3)$$

Since $\varphi(x)$ is a monotonous function, the sign of the derivative $(d\varphi/dx)$ is constant and thus the volume integral of $g_{\mathbf{fl}}$ is non-zero. In order to stabilize such a pattern, the coefficient e_1 should have the same sign as e_3. However, a chevron containing structure (Fig. 2, below) may be even more favourable than an extended region with splay deformation of the director field, since the layer compression or dilation is diminished.

In conclusion, the Ginzburg-Landau criterion and the flexoelectric contribution to the free energy make the appearance of edge dislocations or melted grain boundaries in a smectic phase under the influence of a d. c. field possible, if the flexoelectric coefficients are large enough to overcome the effect of the dielectric anisotropy. In this case, a field induced bend deformation of the director field can gradually enter a smectic liquid crystal close to the smectic-nematic transition temperature. However, the appearance of a bend grain boundary phases with regularly arranged grain boundaries remains speculative.

REFERENCES

[1] de Gennes, P. G. (1972). An analogy between superconductors and smectics A. *Solid State Commun.*, *10*, 753–756.

[2] Renn, S. R. & Lubensky, T. C. (1988). Abrikosov dislocation lattice in a model of the cholesteric-to-smectic-A transition. *Phys. Rev. A*, *38*, 2132–2147.

[3] Goodby, J. W., Waugh, M. A., Stein, S. M., Chin, E., Pindak, R., & Patel J. S. (1989). Characterization of a new helical smectic liquid crystal. *Nature*, *337*, 449–452.

[4] Kitzerow, H.-S. (2001). Twist grain boundary phases. In: *Chirality in Liquid Crystals*, Kitzerow, H.-S. & Bahr, C. (Eds.), Springer: New York, Chapter 10, 296–354.

[5] Meyer, R. B. (1969). Piezoelectric effects in liquid crystals. *Phys. Rev. Lett.*, *22*, 918–921.

[6] Petrov, A. G. (2001). Measurements and interpretation of flexoelectricity. In: *Physical Properties of Liquid Crystals: Nematics.* Dunmur, D. A., Fukuda, A., & Luckhurst, G. R. (Eds.), EMIS Datareviews Series, No. 25. Stevenage: Institution of Electrical Engineers, Chapter 5.5.

[7] Lubensky, T. C. & Renn, S. R. (1990). Twist-grain-boundary phases near the nematic-smectic-A-smectic-C point in liquid crystals. *Phys. Rev. A*, *41*, 4392–4401.

[8] Pershan, P. S. (1974). Dislocation effects in smectic-A liquid crystals. *J. Appl. Phys.*, *45*, 1590–1604.

[9] Dozov, I. & Durand, G. (1994). Quantized grain boundaries in bent smectic-A liquid crystal. *Europhys. Lett.*, *28*, 25–30.

[10] Dozov, I. (1995). Melted-grain-boundary phase in chiral smectic-C liquid crystals near the triple $N^*A^*C^*$ Point. *Phys. Rev. Lett.*, *74*, 4245–4248.

[11] Pelzl, G., Diele, S., & Weissflog, W. (1999). Banana-shaped compounds – A new field of liquid crystals. *Advanced Materials*, *11*, 707–724.