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Ferroelectric Liquid Crystals

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FERROELECTRIC LIQUID CRYSTALS

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A review of the ferroelectricity in liquid crystals is given, beginning with a discussion of the symmetry properties allowing a macroscopic polarization in some of the more ordered liquid crystal phases. The fundamental mechanisms behind the dipolar ordering are discussed in some detail. The two linear electric effects, ferro- and flexoelectricity, give rise to completely different phenomena. In the smectic C phase there is one ferroelectric coefficient and nine flexoelectric ones, giving independent contributions to the polarization of the medium. We further discuss helical and non-helical structures, doped and intrinsic infinite-pitch ferroelectrics and, finally, the rich potential of liquid crystal ferroelectrics aligned in the »book-shelf geometry» for fast electro-optic devices.

Whether a material can be ferroelectric or not is decided by symmetry considerations. The electric polarization must be invariant under symmetry operations of the medium, and this requires the polar axis to be along a unique rotation axis (only one may exist) to which no perpendicular plane of reflection symmetry belongs. Most crystal classes (22 out of 32) then contain too many symmetry elements to allow for ferroelectricity.

A look at the symmetry of liquid crystals at first does not give any promise of ferroelectric properties. The generally very high symmetry of the common phases, nematics ($D_{\infty h}$, uniaxially birefringent) and smectics (smectic-A: D_{∞}; smectic C: C_{2h}, biaxially birefringent) is not compatible with a spontaneous macroscopic polarization vector **P**. The least symmetric of these phases, the smectic C, has the same symmetry group as the letters N, S or Z, which cannot be associated with vectors due to their mirror reflection plane of the paper.

However, a smectic C phase composed of chiral molecules (C^*) has the symmetry allowing it to be ferroelectric, because now the symmetry plane has vanished. This was realized in 1974 by R.B. Meyer, then at Harvard, whereupon the synthesis of the DOBAMBC series was performed by the chemists L. Liébert, L. Strzelecki and P.

Keller, at the University of Paris. Their joint paper, which for the first time demonstrated the existence of ferroelectricity in liquid crystals, was rejected by The Physical Review, illustrating that it may sometimes be hard to publish really original work. It was subsequently published by Journal de Physique[1].

Before giving a simple demonstration of the prerequisite symmetry condition for ferroelectricity, which we will do in the next section, we want to draw attention to one point that illustrates a peculiarity with liquid crystal ferroelectrics, leading also to properties that are very different from those characteristic of solid state ferroelectrics. As is well known, the local axis of symmetry in liquid crystals is given by a unit vector $\hat{n}$, the director, which plays a very important role in the general description of the liquid crystalline state. At first one might think that, as in solids, any descriptive vector would fit well into the definition of a polarization of the medium. However, in liquid crystals, it is likewise fundamental that in the formulation of all properties the medium is invariant against sign reversal in the director,

$$\hat{n} \rightarrow -\hat{n}\ , \quad \text{symmetry operation.} \qquad (1)$$

In fact, if this invariance were not required, the ferroelectricity would have been found already long ago in the common nematic liquid crystals. (The earliest theory of the nematic liquid crystalline state, given by Max Born[2], fails on this point.) Thus, $\hat{n}$ is not a variable that lends itself as a direction for introducing polarization symmetry, except in the very opposite sense: if the medium has a macroscopic polarization $\mathbf{P}$, any component of it along $\hat{n}$ clearly violates the condition (1). Therefore, in a ferroelectric liquid crystal, as long as the invariance condition (1) is valid, *the polarization vector is always locally perpendicular to the director,*

$$\mathbf{P} \perp \hat{n} \qquad (2)$$

1. Symmetry considerations

In order to illustrate which liquid crystal phases can and which cannot be ferroelectric we want to use a famous and fundamental principle, enunciated by F.E. Neumann in the last century. Neumann's principle can be stated in several ways, e.g.[3]

The symmetry elements of any physical property of a medium must include the symmetry elements of the point group of the medium.

The principle specifically allows the physical property to have more symmetry (which is very often the case) than the point group, never less. Adopted to our case, it means that a polarization vector **P**, which is an intrinsic property of the liquid crystal, must remain invariant by all symmetry operations that leave the medium invariant. In order to avoid a slight complication for the pertinent case of smectic C^*, we shall here with »medium» understand a portion of, say, ten smectic layers, and then afterwards

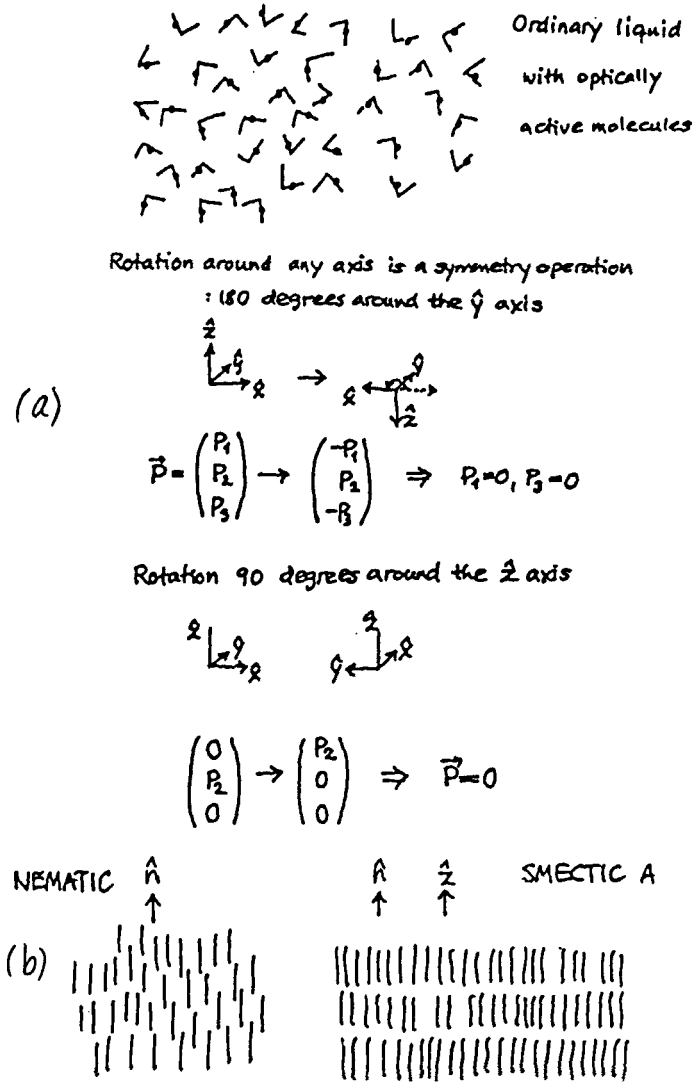

Figure 1. Application of Neumann's principle to the cases of isotropic (a), nematic and smectic A liquids (b), illustrating that none of these can possess an intrinsic macroscopic polarization. The filled and unfilled rings in (a) indicate a dipole moment that together with the perpendicular parts of the molecule make a, say, right-handed system. The symmetry elements in (b) are $C_{2x}, C_{2y}, C_{\infty z}, \sigma_{xy}, \sigma_{xz}, \sigma_{yz}$.

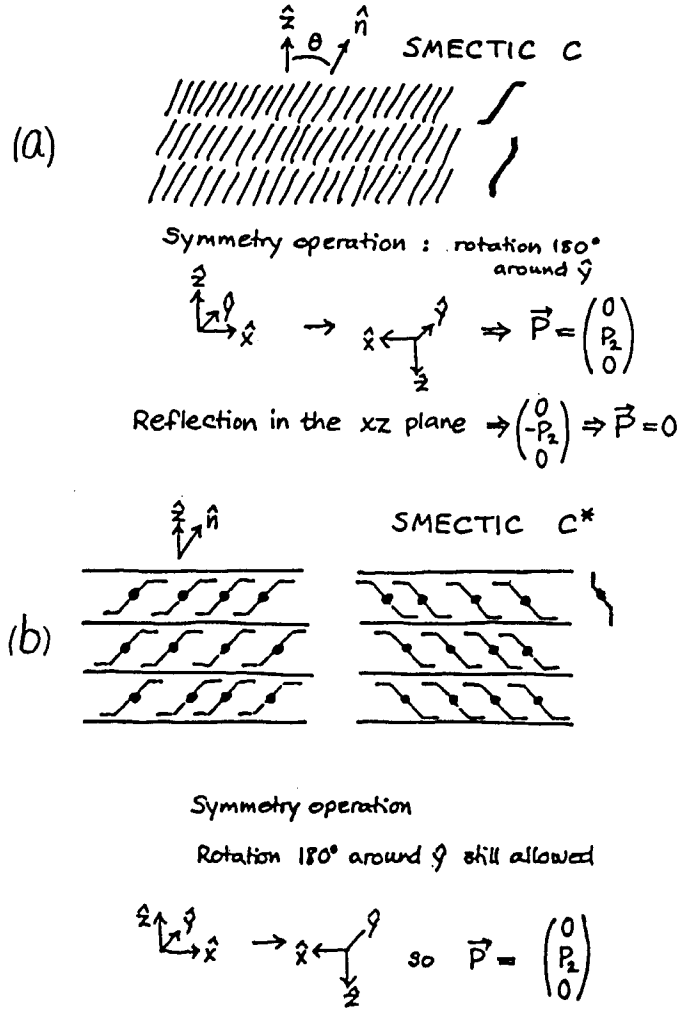

Figure 2. The same consideration applied to the phases smectic C (a) and smectic C(b), where the symmetry elements have been reduced to C_{2y}, σ_{xz} and C_{2y}, respectively. Only the latter may possess a macroscopic polarization, along the C_2 axis. Θ is the tilt angle.*

discuss the effects of a long range precession of the director. This precession is at a two orders of magnitude larger scale and only changes the symmetry globally, not locally.

We test our symmetry argument first on the case of an ordinary liquid with optically active molecules, in figure 1. The medium has the full rotational symmetry of the SO(3) group (no reflections allowed). Under a 180° rotation around the $\hat{y}$ axis any assumed polarization vector is forced to change sign in its x and z components, which therefore must be zero for **P** to remain invariant. The remaining P_y is transformed into P_x at a subsequent 90° rotation around the $\hat{z}$ axis, and so likewise has to vanish. Thus, an isotropic liquid can be optically active but not ferroelectric. We note the fundamental difference between optical acitivity and polarization: the first is a pseudoscalar (that also changes sign on reflection) but is independent of the direction of the molecule and, therefore, never averages out spatially in contrast to the polarization vector. The argument is identical for the nematic phase and for the smectic A phase. In the smectic C phase, however, we see (figure 2) that the 90° rotation around the $\hat{z}$ axis is not a symmetry operation. To get $P_y = 0$ we must then use the mirror symmetry that this phase exhibits in the xz plane (the plane of the tilt). The conclusion is that even a smectic C phase (with a point group C_{2h}) cannot have a spontaneous electric polarization among its physical properties. The reflection symmetry could be broken by an external field **E** along the $\hat{y}$ axis, and in such a case the molecular dipoles perpendicular to the long axis would try to orient along the field. But the symmetry could also be spontaneously broken: the reflection operation that we just applied requires that our medium consists either of molecules with mirror symmetry or of a racemic mixture of asymmetric (chiral) molecules. If it were built up by a molecule with one single handedness (or a mixture of different molecules with the same or of one dominant handedness), we reduce the point group symmetry to C_2, and the remaining symmetry operation (the two-fold rotation around $\hat{y}$) cannot cancel out a polarization along this axis. A chiral smectic C phase (C^*) may thus have a spontaneous macroscopic polarization going perpendicularly out of the tilt plane. As expected, **P** is perpendicular to $\hat{n}$, lying along the $|\hat{z} \times \hat{n}|$ direction. In order to make the molecules chiral one asymmetric carbon atom or any other chiral center may be sufficient. One can imagine this as attaching a small »propeller» (of a certain handedness) somewhere to the molecule, as illustrated in figure 2. The symmetry argument then amounts to saying that any molecular dipole component perpendicular to the molecular axis will contribute to a non-vanishing macroscopic polarization characterizing the medium.

Nevertheless, the symmetry argument has to be pursued a little further, and »contribute» does not simply mean »add up». In reality one measures a polarization in the C^* phase of about two orders of magnitude smaller than would be expected if the dipoles added to full strength. This is due to inner rotations of parts of the molecule and the rotation of the molecule itself around its long axis, both of which are relatively free and rapid. Although the molecule itself will normally have C_1 symmetry (no symmetry element) the usefulness of their »zeroeth order description» as rigid rods of axial symmetry is due to this rotation. Actually, the rotation is never free but somewhat hindered in the smectic, nematic, and even in the isotropic phase. But

whereas it is unbiased in the N and A phases - the time-averaged distribution of the molecule as seen around its long axis is circularly symmetric - it is biased in all tilted smectic phases. For instance, in the C phase, apart from becoming more hindered the larger the tilt, the time-averaged rotation is now only symmetric around the tilt plane. In figure 2 both the rotational hindrance and bias are symbolized by a rigid model (to the right in (a); all molecules in (b)) whose shape would give these properties. In the C^* case the distribution can never even be symmetric with respect to the tilt plane as long as the chirality lifts out this symmetry element, and, if the dipole is at all coupled to the rotation, the deviation from rotational symmetry around the tilt plane, however slight, leads by necessity to a non-zero polarization **P**, i.e. to ferroelectricity. We see that, except for the strength of the lateral dipole itself, the interesting factors are (i) the strength of the rotational bias of the chiral part of the molecule and (ii) the strength of the rigid steric coupling between the dipole and this chiral part. The second of these factors seems rather easy to control, e.g. by attaching the dipole as one of the substituents directly to an asymmetric carbon atom. This has been done in molecules of type HOBACPC[4], shown in figure 3, which, among the so far fairly few reported liquid crystal ferroelectrics, seem to have the highest polarization.

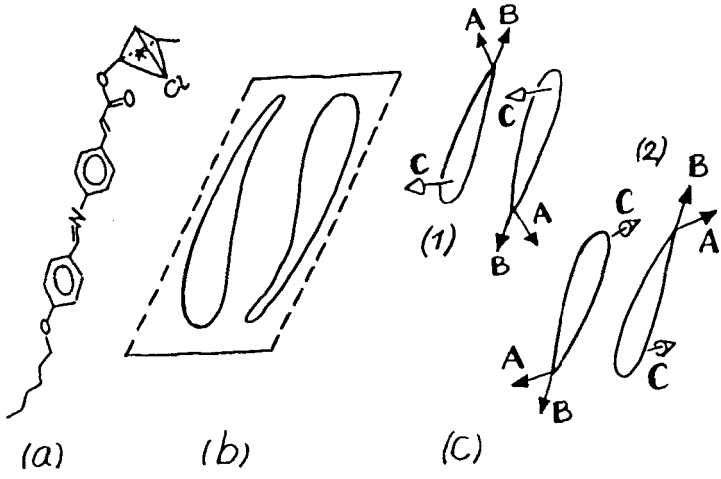

Figure 3. Different representations of molecules in the smectic C/C phase. In (a) HOBACPC is taken as an example. The chiral group at the upper end is represented by a distorted tetrahedron with the asymmetric carbon in the middle and the polar chlorine as one of the apexes. In (b) and (c) molecules with and without reflextion symmetry are represented.*

It is seen that the fundamental interaction leading to ferroelectricity in liquid crystals takes place wholly on the molecular level. The symmetry argument actually refers to a dissymmetry in the time-averaged position of the chiral part. The rest of the molecule is included in the overall function of all neighbouring molecules to arrange in a tilted fashion into smectic layers thus providing the monoclinic structure necessary to render the chirality significant.

Finally, in our discussion of molecular symmetry, figure 3 illustrates the difficulties with a pictorial representation of the properties referred to. The static steric formula (a) of the molecule is certainly inadequate for the symmetry reasoning but suitable for a judgement of distribution of dipoles and rotational degrees of freedom. A rigid body illustration of the dynamic situation also has its shortcomings (b) (The two equivalent up and down positions in the monoclinic »unit cell» only illustrate the required invariance under sign reversal of the director, trivially fullfilled in figures 1 and 2). The rotation around the $\hat{n}$ axis is supposed to be biased but reflection-symmetric for the non-chiral molecules. If the molecules are chiral their sterical feature allows a definition of a vectorial triad, **A, B, C** with reference to the body. In the figure this has been chosen as left-handed and the vectors separated to illustrate the importance of the coupling within the molecule. **A, B** and **C** should really be thought of as steric features that do influence the rotational position in the unit cell. It is then intuitively clear that positions (1) and (2) should not be of exactly the same energy, and one of them is going to be preferred, on the average, giving the net polarization. De Gennes has given a vivid illustration that comprises many aspects of the symmetry argument by representing the molecule by a fish, whose right eye (or left, but not both) is connected with a lateral dipole[5]. This has been used in our figure 4, which is an adaption of an original illustration used by the Orsay group[6] summarizing and comparing the symmetries of the N, A, C and C^* phases. Unfortunately, in spite of some NMR[7] and neutron scattering[8] studies, still very little is known about the relevant rotation or flipping motion of various parts of liquid crystal molecules.

To conclude, the symmetry arguments tell that *all chiral tilted smectics can be expected to be ferroelectric.* Thus, ferroelectricity is expected not only in the C^* phase but in all chiral versions of tilted smectics of still lower symmetry such as F, G, H, I, J, K (now by their denominations more similar to spectroscopy terms or to stellar objects than liquid crystals - there is a strong need for a rational classification based on symmetry groups) and the recently described O phase[6]. The chiral tilted columnar (discotic) phases also have C_2 symmetry and should be ferroelectric, as pointed out by Prost[10].

2. A »nematic» description

The ground state of the chiral tilted smectic in the bulk is not likely to be homogeneous regarding the director configuration in space, i.e. it will not correspond to the simple picture in figure 2. One way to appreciate this is to look, for a moment, at the

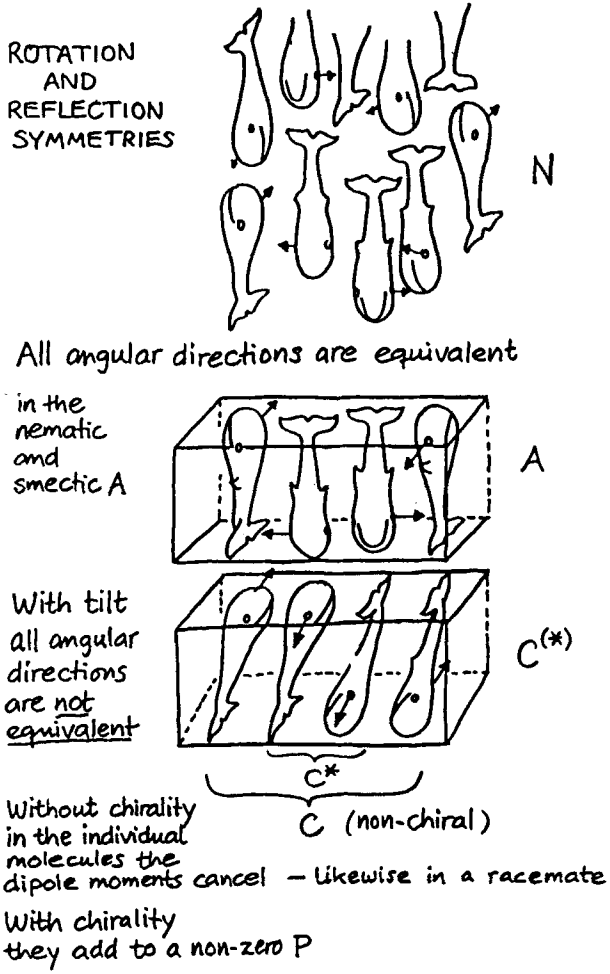

Figure 4. A comparison of the symmetries characteristic of liquid crystals in their nematic (N), smectic A, smectic C and smectic C states. (Adapted from reference 6.) On the average there are, in all phases, as many fishes head up as head down, illustrating the invariance condition (1).*

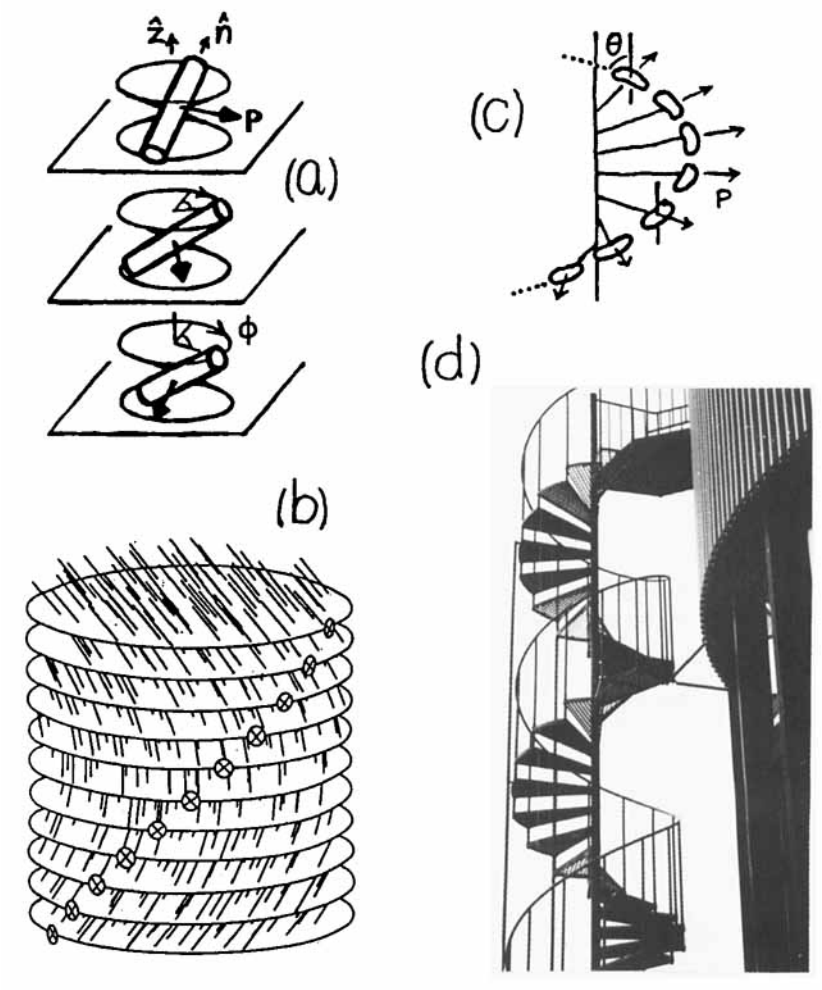

Figure 5. Director twist-bend deformation in the ground state of smectic C^* The director field is twisting in a helical fashion in space, at constant tilt angle Θ to the helix axis (a). The bend component is not as easy to distinguish, especially if the pitch is short, but can be seen from the model in (b) where the director is pointing away from the observer, changing its azimuthal direction Φ (as indicated on each disc) in a right-handed fashion between successive layers. The bend is also seen well extracted in (c) which is an adaption from reference 18. In a common spiral staircase the two components are well separated spatially (d): the constant »cholesteric» twist is represented by the steps, whereas the constant bend can be found in the hand-rail. In (a) and (c) the bulk cancellation of P is also illustrated.

smectic as if it were a nematic. For our purpose, we can forget about the layers, after having noticed that the layers permit us to define a second vector (in addition to $\hat{n}$) which we cannot do in a nematic. The second vector represents the layers and is $\hat{z}$, the layer normal, which differs from the $\hat{n}$ direction by the tilt angle. The implicit understanding that $\hat{z}$ is constant in space represents the condition of undeformed smectic layers.

We use the Oseen-Frank elastic energy expression for a nematic medium as a starting point,

$$G = \tfrac{1}{2}K_1(\nabla\cdot\hat{n})^2 + \tfrac{1}{2}K_2[\hat{n}\cdot(\nabla\times\hat{n})]^2 + \tfrac{1}{2}K_3[\hat{n}\times(\nabla\times\hat{n})]^2, \qquad (3)$$

representing the independent splay, twist and bend deformations. Now according to our assumption the medium is chiral, and an ever so slight chiral addition to a nematic, by symmetry transforms the twist term according to[11]

$$[\hat{n}\cdot(\nabla\times\hat{n})]^2 \rightarrow [\hat{n}\cdot(\nabla\times\hat{n}) - q]^2 \qquad (4)$$

The ground-state now corresponds to a twisted structure with non-zero value of $\hat{n}\cdot(\nabla\times\hat{n})$ given by a wave vector q, the sign of which indicates the handedness. Note that the reflection symmetry is lost but the invariance condition (1) is still obeyed.

Chirality thus introduces a new *scalar* quantity, a length characteristic of the medium. If the medium is also conjectured to be polar, one might ask if it is possible, in a similar way, to introduce a true *vector*. ($\hat{n}$ and $\hat{z}$ are not true vectors, since there is one symmetry operation that changes the sign of both.) A look at the first term of the expression (3) clearly shows that this would not admit such a thing. In fact, it is not possible to add or subtract any true scalar or vector in the splay term without violating the invariance of $(\nabla\cdot\hat{n})^2$ under the operation $\hat{n} \rightarrow -\hat{n}$ Thus, no ground-state can exist with a spontaneous splay. Is there a way to introduce a vector in the bend term? There is. The bend transforms, obeying (1), as follows:

$$[\hat{n}\times(\nabla\times\hat{n})]^2 \rightarrow [\hat{n}\times(\nabla\times\hat{n}) - \mathbf{v}]^2 \qquad (5)$$

where $\mathbf{v}$ is a vector. Only a vector $\mathbf{v}$ parallel to $\hat{n}\times(\nabla\times\hat{n})$ can be introduced in the bend term. For undeformed smectic layers, $\hat{n}\times(\nabla\times\hat{n})$ lies in the $|\hat{z}\times\hat{n}|$ direction, and $\mathbf{v}$ can be written

$$\mathbf{v} = \alpha\hat{z}\times\hat{n} \qquad (6)$$

where α is a scalar, that must be zero in the non-chiral case. If α is non-zero, the medium is characterized by the local vector $\mathbf{v}$ and the reflection symmetry is lost. The tilted smectic can be ferroelectric if the spontaneous polarization is identified with $\mathbf{v}$ or is chosen collinear to $\mathbf{v}$. The form of the bend expression in presence of a local polarization then corresponds to a *constant spontaneous bend* in the local frame of the director. The converse to this is the flexoelectric effect.

From the above reasoning we see two things. First, that this description also permits the smectic C^* to be polar and requires the polarization vector to be perpendicular to the tilt plane, a result that we achieved before. Second, that the chiral and polar medium will be characterized by both a spontaneous twist and by a spontaneous bend. The smectic C^* is, in fact, such a medium where we have a space-filling director structure with uniform twist and bend[19]. This can also be directly seen from the different illustrations in figures 5 and 6 showing both features: the obvious director helix and the constant radius of curvature of the perhaps less obvious bend.

It is important to notice that, although chirality is the only reason for the helix, in the sense that without chirality there can be no helix, its influence is nevertheless more complex: we first have a »cholesteric-like» contribution represented by q. Second, there is a contribution from the spontaneous bend coupled to $\mathbf{P}$, with a strength represented by α. Both contributions are independent and sufficient to induce a helix by themselves in the C^* state. They may also counteract each other because the sign of the helicity depends on the sign of q and α, respectively. This could even give a helix-free ferroelectric smectic C^* state, in spite of the chirality of the medium. A discussion of their importance might therefore be useful even if, at this point, no experimental data are available except for cholesterics.

The parameters α and q represent two different aspects of the chiral properties at the molecular level. We know that q solely determines the cholesteric pitch. We might ask the question: Is the chirality in the smectic C^* phase closely related to the chirality in the cholesteric phase, in the sense that we can expect some relation between the helical pitches in the two phases? To investigate this we start from the Orsay group expression[34,36] of the elastic energy for the smectic C state, in the reformulation by Dahl and Lagerwall[36]. For the case of constant layer normal this simplifies to

$$G = \tfrac{1}{2}B_1[\hat{z}\cdot(\nabla\times\hat{c})]^2 + \tfrac{1}{2}B_2(\nabla\cdot\hat{c})^2 + \tfrac{1}{2}B_3[\hat{c}\cdot(\nabla\times\hat{c})]^2 -$$

$$B_{13}[\hat{z}\cdot(\nabla\times\hat{c})][\hat{c}\cdot(\nabla\times\hat{c})] + D_1\hat{z}\cdot(\nabla\times\hat{c}) - D\hat{c}\cdot(\nabla\times\hat{c}) \qquad (7)$$

The vector $\hat{c}$ is a unit vector along the projection of $\hat{n}$ in the plane of the smectic layer (cf figure 10) and B_1 through D are elastic constants (cf ref. 5, p. 316). Using the relation

$$\hat{n} = \hat{z}\cos\Theta + \hat{c}\sin\Theta \qquad (8)$$

we might identify (7) with our »nematic» expression,

$$G = \tfrac{1}{2}K_1(\nabla\cdot\hat{n})^2 + \tfrac{1}{2}K_2[\hat{n}\cdot(\nabla\times\hat{n}) - q]^2 + \tfrac{1}{2}K_3[\hat{n}\times(\nabla\times\hat{n}) - \mathbf{v}]^2 \qquad (9)$$

with $\mathbf{v} = \alpha\hat{z}\times\hat{n}$,

which gives the following relations between the elastic constants in the two descriptions

$$\begin{aligned} B_1 &= K_2\sin^2\Theta\cos^2\Theta + K_3\sin^4\Theta \\ B_2 &= K_1\sin^2\Theta \\ B_3 &= K_2\sin^4\Theta + K_3\sin^2\Theta\cos^2\Theta \\ B_{13} &= (K_3 - K_2)\sin^3\Theta\cos\Theta \\ D_1 &= -K_2 q\sin\Theta\cos\Theta + K_3\alpha\sin^3\Theta \\ D &= (K_2 q + K_3\alpha\cos\Theta)\sin^2\Theta \end{aligned} \qquad (10)$$

The helical pitch of the medium is $2\pi B_3/D$, which tends to infinity for $\alpha/q = -K_2/K_3\cos\Theta$. In the one-constant approximation this gives $\alpha = -q$ in the small tilt angle limit. Primarily, we see that α and q give comparable contributions to the pitch, and that the smectic pitch in no way can be taken to be similar to the cholesteric one. In principle, the expressions (10) give the temperature dependence, through Θ, of the smectic pitch, but have to be used with caution, due to our »nematic» description. There also is only one case (PACMB) for which the helix has been observed to cancel for a certain temperature[12], with different signs of helicity above and below this temperature, but this should rather be taken as an evidence for the conflicting effects of the *two* chiral centers in this molecule.

The chirality does not only give helicity to the medium. The elastic constant D_1 gives a tendency for spontaneous bend in the $\hat{c}$ director, corresponding to a tendency for a spontaneous splay in the polarization **P**. This, again, is equivalent to a tendency for **P** to point inwards at the edges of the smectic layers, or outwards, depending on the sign of D_1. This tendency should at least for small tilt angles be closely connected to the cholesteric pitch, and only weakly influenced by α.

We can also try to find those properties at the molecular level that determine the spontaneous twist and bend of the director. One way is to study the »cage» for one molecule, as it is defined by the surrounding molecules. In the case of an undeformed nematic, we can for simplicity assume that this space is rod-shaped with a square or hexagonal section. In the presence of cholesteric twist, two of the sides of the rod must be slightly twisted with respect to each other (see figure 6). If the molecule fits better in such a deformed rod than in the undeformed, we could expect a spontaneous twist. In the case of smectic C^*, the rod will be tilted with respect to the layers, and will be subject to both twist and bend if the medium forms a helix. The bend will force the rod into a banana shape, and we can in reverse draw the conclusion that such a shape of the molecules might induce spontaneous bend, and this in turn may contribute to the tendency to form a helix. The important point to understand in this case is that the radius of curvature must be parallel to the spontaneous polarization, so that the rod bends out of the plane defined by $\hat{n}$ and $\hat{z}$ (cf figure 5). To get a spontaneous bending of this kind, there must of course as primary source be chiral centers in the molecule.

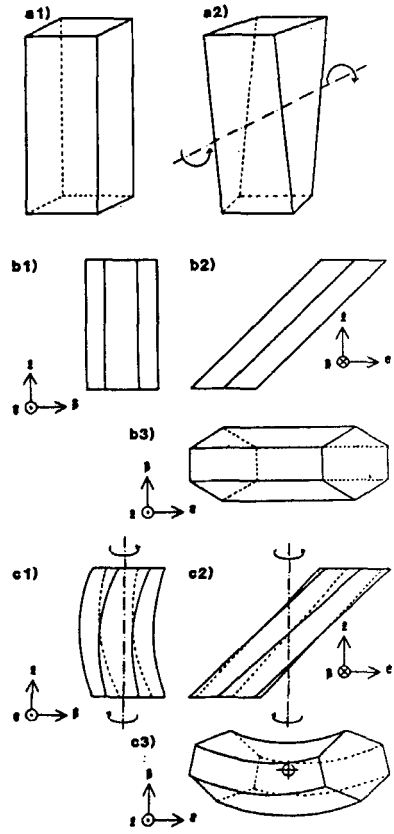

Figure 6. In a1) we let the volume available to one molecule in a nematic liquid crystal be represented by a rod with, for simplicity, quadratic cross-section. In a cholesteric environment, with finite pitch, two of the rod's sides will be slightly twisted with respect to each other, as in a2). In b) a tilted hexagonal rod, representing the corresponding volume in a smectic C liquid crystal, is shown. For clarity, it is displayed from the three viewing directions $\hat{p}$, $\hat{c}$ and $\hat{z}$. In c) the rod is distorted as by a chiral smectic helix. The cholesteric twisting of the sides is most easily seen in c2), the banana-like bending of the molecule out of the xz-plane in c1) and c3). Some finite value of bending of the molecules will thus be most favourable energetically in the presence of the helix.

3. The ferroelectric polarization

According to our previous discussion we may now represent the molecule by a rigid body, non-free to rotate around its long axis, to which we attach an effective dipole of about 1/100 of the strength it has in the molecule and in a manner so as to make the object chiral. In figure 7 the tilt angle Θ is constant in size corresponding to a constant temperature.

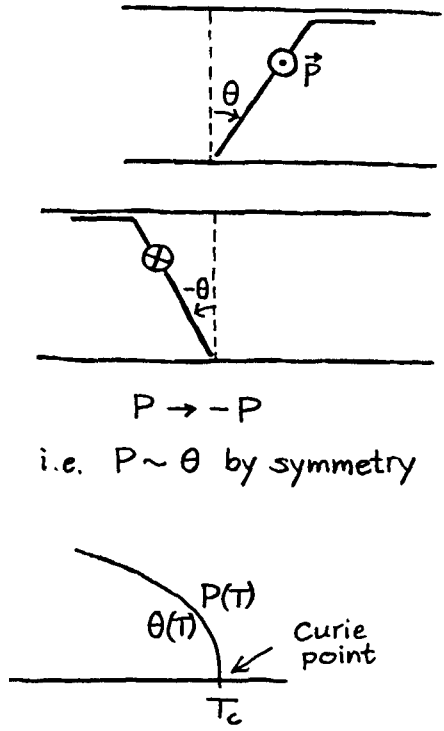

Figure 7. Inverting the sign of the tilt angle inverts the direction of polarization of the smectic layer. The ice-hockey stick representation of the molecule illustrates the hindered rotation along the director axis. The change of sign involves a conical collective motion around the layer normal. The linear relation between Θ and P gives a Curie point at the C^*-to-A transition, illustrated below. If the chiral smectic phase instead is adjacent to a (chiral) nematic phase, P(T) will instead correspond to a first order transition.

To change sign in the order parameter (whose full representation is complex, $\Psi = \Theta e^{i\Phi}$, where Φ is the azimuthal space angle) from $+\Theta$ to $-\Theta$, the molecule has to swing around the outside of a cone thereby inverting the sign of P. Thus, by symmetry, P will be a linear function of the tilt angle Θ. If the liquid crystal undergoes a phase change from smectic A to smectic C at lowering the temperature through a transition point T_c where a non-vanishing Θ starts out from zero according to the 2nd order characteristic, then P will behave in a very similar way and T_c will represent a kind of Curie point. The transition characteristic is that of smectic A-smectic C with a two-component order parameter (similar to the superfluid helium case) where a continuous rotational symmetry (in the gauge variable Φ) is broken. In addition to that, for the case A-C*, a reflexion symmetry is broken, leading to a non-vanishing P. The polarization is, however, only an indirect order parameter that does not drive the transition. P is only a secondary result of a very special ordering on a molecular scale, brought about by the short-range van der Waals interactions responsible for liquid crystal ordering (in this instance specifically the tilt at T_c), and not by long-range dipole-dipole interactions.

Whereas thus the temperature dependence of P shows the typical behaviour of common ferroelectrics, confirmed experimentally in all cases so far[11,12,13] and typical hysteresis loops have been observed[14,15] by field reversal, there are a number of important differences between liquid crystal and solid state ferroelectrics. The polarization typically is 100 to 1000 times lower for the liquid crystals and the dielectric constant only of order 10, non-diverging and obeying the Curie-Weiss law in a very narrow range of about 1K from T_c[13] as had been predicted by Blinc[16]. The most striking - and useful - difference lies in the fact that the »coercive force», that for differently ordered smectics may vary in order of magnitude and have different cause, is always still very small leading to the large optic effects at low fields typical of liquid crystals.

Strictly speaking, one may refer the liquid crystal ferroelectrics to the class of improper ferroelectrics, although the distinction in this case is not as important as it is in solids (For an account of improper ferroelectrics, see ref. 17, cf also the discussion in ref. 16). Due to the helix, one could also use the name helielectric, but this distinction is fairly semantic, and several authors[18,10] bringing up this point return to the designation ferroelectrics just as the general physics community uses the term ferromagnets for rare earths like holmium, erbium and others, even if a diversity of helicoidal spin arrangements can be found in these. The helix, of course, has interesting consequences. It is a long-range perturbation in the $\hat{n}$ field that introduces another periodicity in addition to the smectic layer periodicity; C* is thus an incommensurate phase. The helix also restores the symmetry broken at the A-C transition: it gives C* the global D_∞ symmetry instead of the local C_2 symmetry,just as in the A phase. Although the C phase is biaxial, the C* phase in bulk is therefore uniaxial and the macroscopic polarization zero by symmetry. On a molecular scale we see how this is brought about by $\mathbf{P}$, rigidly fixed to $\hat{n}$ in each layer, spiralling together with $\hat{n}$ to cancel all dipolar contributions in a sufficiently thick sample. The overall effect certainly is that the ferroelectricity is »hidden», as it were, in the medium. The first attempts of determining P were, therefore, rather indirect. Meyer himself watched

conoscopically along the helix axis how a perpendicular electric field first distorted and shifted the uniaxial image, unwinding the helix just as in the cholesteric case, and finally transforming it into the biaxial conoscopic image characteristic of the unwound C phase at a certain critical field E_c[1,19]. He convincingly showed both the linearity of the effect and estimated the polarization P from the measured E_c (this method will give P if the elastic constants are known). A second very illuminating way[20] of demonstrating the existence of a polarization in the medium is to apply a shear along a certain direction parallel to the layers as shown in figure 8. The shear will distort the helix towards a limiting unwound state (the one shown in the figure) at very high shear rates where all molecules are tilted in the same direction.

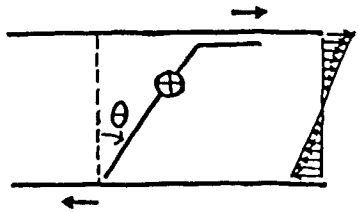

Figure 8. If subjected to a shear along the layers the bulk C structure will be distorted and a finite polarization will appear at a right angle to the shear. In the figure a »plus» substance is chosen, giving a P vector directed into the paper (cf the discussion to figure 9). The experiment corresponds to the unwinding of the helix in an electric field (the symmetry is broken, P appears, uniaxiality is changing to biaxilality) and the figure, for simplicity, corresponds to the completely unwound state. In reality this state is unobtainable: because the medium is a liquid the shear cannot be static, and only a slight structural distorsion can be achieved in a dynamic experiment.*

When an alternating shear is applied alternating polarization charges, growing linearly with shear, will appear at lateral electrodes in the cell. As pointed out by Prost[10], it is illustrative to analyze this situation according to symmetry principles. For this case, an alternative common formulation of Neumann's principle is convenient: *The symmetry elements of the medium in the presence of a cause cannot be less than those held in common by the medium in absence of the cause and the cause in absence of the medium.* The medium in absence of the cause (the undistorted smectic C^*) has D_∞ symmetry. The cause (the shear) has C_{2h} symmetry. Their only common symmetry element is C_2, which is the symmetry of the polarized smectic (and a subgroup, as it has to be, of the symmetry group C_∞ of P itself).

After these conclusive but indirect experiments, P has been measured directly in the C^* phase, first by Martinot-Lagarde[13], by field reversal methods, by bridge methods[14,15] and by measuring the pyroelectric response to laser heat pulses[22]. Recently Wahl and Jain[21] extended the measurements to some of the other chiral smectic phases (I^*, J^*) and, as expected, found higher values of P the more ordered the smectic. The pertaining pyroelectric[22] and piezoelectric[23] effects were first reported in 1976 and 1977. Since then dielectric properties, tilt and helical pitch and, increasingly, electro-optical properties have been fairly extensively studied by American[23], Yugo-

slavian[24], French[25,26,31], Russian[27,28] and Japanese[29,30] groups, all using the same or nearly the same material within a very narrow spectrum of chemical substances that has been available. Except for the more recent work on electro-optics, a good part of this work has been discussed in the two previous review articles, the one by Meyer[19] from 1977, the other by Durand and Martinot-Lagarde[18] from 1980. We, therefore, only conclude this section by a comment on a property that, in our opinion,has been largely neglected so far. It refers to the *sign* of the polarization, or its absolute direction in space. The symmetry arguments in sections 2 and 3 only told us that **P** has to be perpendicular to the tilt plane, but not in which direction it is going to point. Nature thus allows for two classes of ferroelectric liquid crystals, symbolized by the reference systems of figure 9, and the question is whether both possibilities are actually realized in concrete substances.

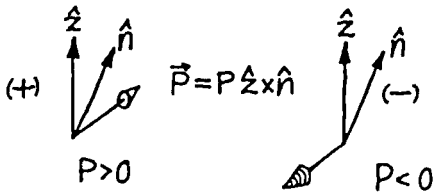

Figure 9. Spatial relation between layer normal, director and local polarization for the two possible classes (+/-) of chiral smectic ferroelectrics.

The direction of **P** can be determined in the shear flow or field reversal method if, by a simultaneous optical observation the director motion is correlated with the direction of the applied field or shear, respectively (this is very clearly seen from figure 8). The only case where attention was payed to this problem is in the Orsay work[31], and Martinot-Lagarde, Duke and Durand[31] list their results on this point with the aid of a steric drawing (their figure 14) representing two situations which are mirror images of each other. Unfortunately, their drawing brings confusion into the problem by seemingly indicating, that the handedness of the $\hat{z}$, $\hat{n}$, **P** reference system bears a relation to the handedness of the helix. It is important to note that these two things are completely independent of each other. A convention which is simple and natural is being proposed[32] in order to distinguish the two possible classes of substances. If $\hat{z}$, $\hat{n}$ and **P** make a right-handed system, we will call the polarization P positive, in the left-handed case negative, corresponding to the sign of P in the vector product $\mathbf{P} = P\hat{z} \times \hat{n}$.

The convention can alternatively be stated : *when the director is tilted out from the layer normal, as happens at the transition A-C, then a polarization* **P** *appears, with* $P = P_0\Theta$. *If* **P** *is directed in the positive direction of rotation, it is defined as positive.*

A sign convention is preferable to a handedness convention in order to avoid confusion with the handedness of the helix. The sign of P is a substance-specific property, just as is the handedness of the helix, and both properties ought to be determined for any given substance. Assume, for instance, that we know that X is a minus substance ($P<0$), whereas Y is a plus substance. Both have a right-handed helix. Then by mixing

X with the optical antipode of Y (or the converse) we can cancel the helix keeping the polarization reinforced. Obviously, for any specified molecular species (the R,S designation of the optical stereoisomer has to be known), the sign of P and the sense of the helix are two technologically important parameters, and the very fact that they do not depend on each other is the starting point for making electro-optically useful infinite-pitch cocktails. Unfortunately, published data are scarce: the Orsay findings on HOBACPC and DOBAMBC (in their »natural» forms R and S, respectively) both to be minus substances have been confirmed in Göteborg and several classes of new materials have been found to belong to the same category. Only in one case (two cyano-substituted DOBAMBC homologs), P>0 was reported, though in this case we likewise found the minus sign. Thus for some reason the »naturally» occurring substances reported so far seem to be minus substances, whence their optical antipodes ought to be plus. In order for »molecular engineering» to progress, three pieces of information are at least required for each molecule: 1) R/S , 2) P, +/- , and 3) helix, right/left. This information is hardly available today, except for a handful of molecules, showing the virgin state of knowledge regarding this (for the applications important) aspect of liquid crystal ferroelectrics.

4. The flexoelectric polarization

In contrast to the chiral nematic helix, the chiral smectic helix contains a bend. This bend leads to a local flexoelectric polarization[33]. The question then may arise: is the ferroelectric polarization in the C^* phase a flexoelectric effect? Or, if it is related, then in what sense? The similarity is also underlined by the fact that ferro- and flexoelectricity both are linear effects in the electric field, and the only ones having this property.

The difference is, however, fundamental and could be illustrated by the following example: if starting with a homogeneously aligned smectic C you twist the layers mechanically (this could be done just as preparing a twisted nematic) so as to produce a helical director structure identical with that in a smectic C^*, you can never produce a ferroelectric polarization. What you do achieve is a flexoelectric polarization of a certain strength and sign, that is everywhere perpendicular to the local tilt plane, just as the ferroelectric polarization would be. But the flexoelectric polarization is strictly fixed to the deformation itself and cannot, unlike the ferroelectric one, be switched around by an external electric field. On the other hand, it is clear from the example that the two effects interfere: the flexoelectric contribution, which is independent of whether the medium is chiral or non-chiral, will partly cancel or reinforce the ferroelectric polarization in all situations where the director configuration is non-homogeneous in space. This is then true in particular for all chiral smectic samples where the helix is not unwound, and this might appreciably influence the electro-optic switching behaviour. The importance of this effect is hard to predict as it depends on the magnitude of the flexoelectric coefficients (which show a tendency to increase in recent estimations). Nevertheless, it necessitates a general consideration of the flexoelectric properties of the smectic C phase.

In the nematic phase there are two independent flexoelectric coefficients corresponding to two different deformations in the director field. Only one of these is retained (for uncompressional and dislocation-free deformations) in the smectic A phase. In the smectic C case the flexoelectric effects were first discussed by Pikin and Indenbom[35]. Because they ignore all in-layer deformations in the director field and all deformations of the layers they only find one flexoelectric coefficient, the one corresponding to the deformation discussed above in our example. A complete analysis of the flexoelectric effects in the C phase have been given only recently by Dahl and Lagerwall[36]. It turns out that there are nine independent coefficients corresponding to the six deformations illustrated in figure 10.

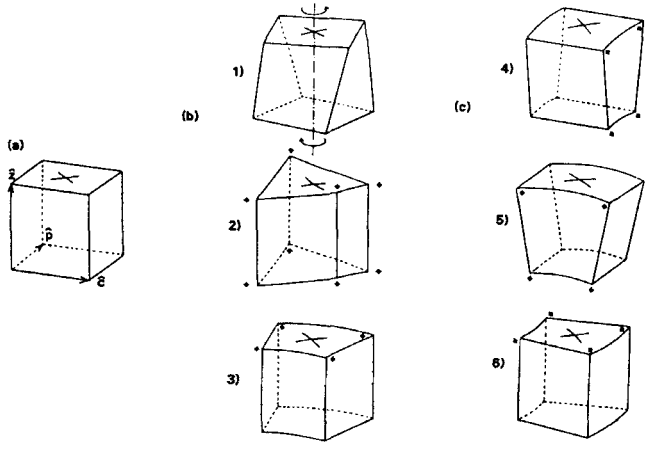

Figure 10. The six basic deformations of the smectic C phase. a) is a cube filled with homogeneous smectic C material. By deforming the walls at the cube while keeping the boundary condition that $\hat{z}$, $\hat{c}$ and $\hat{p}$ are orthogonal to the sides, we can obtain the six basic deformations, illustrated in (b) and (c). The deformations do occur spontaneously in (b). 1) gives the spontaneous helix; 2) gives a tendency for the smectic layers to bend around bending axes 45 degrees from the C-director. This can be seen as »saddle-splay» of the layer normal; 3) gives the spontaneous splay of the polarization mentioned in section 2. The deformations in (c) do not occur spontaneously and represent two different types of splay of the layer normal plus splay of the C director.

The different contributions are conveniently discussed in relation to an undeformed cube spanned by the orthogonal unit vectors $\hat{z}$ (layer normal), $\hat{c}$ (in-layer C director) and $\hat{p}$ (direction of positive ferroelectric polarization). As seen from the figure, the deformations can be divided into two categories. The first three deformations couple to each other and give, in the chiral case, linear terms in the free energy. They all give

contributions to the flexoelectric polarization in the direction along $\hat{p}$. The following three deformations also couple to each other but not to the first ones. They give no linear energy terms and their flexoelectric contributions are along the tilt plane giving three independent coefficients each for polarization along the $\hat{z}$ and $\hat{c}$ directions. For more detail the reader is referred to the discussion in ref. 36; cf also ref. 37.

Flexoelectric effects may be used in meaningful applications for which some hints have appeared in the case of nematics, cf ref. 38. In other cases they are a nuisance. To avoid them in chiral smectics, in measuring P as well as in electro-optic applications, one should preferably work with defect-free samples, where the helix is inherently absent (»infinite pitch» substances) or permanently unwound.

5. Helix-free ferroelectric liquid crystals

If we apply a common definition like »Ferroelectrics are materials that display an electric polarization in the absence of an external field, with the additional important requirement that the polarization can be reoriented by an external field», then it should be clear from the foregoing that even with the complication of the helix present in most chiral smectics, the effects that have been the main point of our discussion must be classed as ferroelectric. In his review from 1977 Meyer addresses the principal counterargument by pointing out that it is always possible to obtain helix-free materials by mixing (and this can be done in a number of ways), thus achieving a permanent non-zero polarization that may be homogeneous in space. However, semantics occupy people even in situations where the physics is clear, and therefore it seems important to report at least some of the many cases in which such »truly» ferroelectric liquid crystals have been observed. The first such observation was made[39] in the interesting but special case where the helical wave vector vanishes spontaneously in a pure compound at a certain temperature T_c. This is the substance PACMB referred to earlier. The first study of a substance which, for all practical purposes has the same property (infinite pitch) in the whole temperature range of its smectic C^* phase, was reported in 1980 by Kuczynski and Stegemeyer[40]. Their work is interesting not only for the uniform polarization achieved but even more so because it is the first example of inducing ferroelectricity by doping a non-chiral smectic C with a chiral and polar guest molecule orienting itself preferentially in the monoclinic environment of the host. The corresponding study of helix cancellation by mixing was reported in 1981 by Beresnev, Baikalov, Blinov, Pozhidayev and Purvanetskas[41]. By using the compensating forms of DOBAMBC and HOBACPC they obtained a mixture with strictly vanishing helix and, nevertheless, with a polarization P amounting to about a third of the value for pure HOBACPC in the C^* phase. Note that this, like the foregoing case, is a helix-free chiral smectic phase: it does *not* possess reflection symmetry and its correct denomination is C^*, not C. The same Moscow group also followed up the doping studies initiated by Kuczynski and Stegemeyer, with interesting results[42]. In addition to achieving substantially higher values of polarization they also reported various lower chiral smectic phases to be inherently helix-free. This feature of the more ordered tilted smectics seems to have been discussed first by Helfrich[43] who

pointed out that increasing structural order in the chiral smectics cannot be compatible with a twist. The more solid-like chiral smectics, e.g. the smectic G^*, as mentioned by Helfrich, can therefore be expected to be untwisted and uniformly ferroelectric. The first experimental confirmation of the tilted chiral smectic state in twisted *and* untwisted form was presented slightly later by Doucet, Keller, Levelut and Porquet[44] in their X-ray studies on HOBACPC, and their results have been confirmed since then by several groups, see for instance the recent paper by Jain and Wahl[45]. These studies indicate that, below the C^* phase, in HOBACPC there is first the hexagonal I^* phase (with short in-plane correlation and no layer-layer correlation; Sm III in Doucet et al.) which is twisted, and then the likewise hexagonal J^* phase (with strong correlation between layers; Sm IV in Doucet et al.) in which the helix has been suppressed. Both are ferroelectric[45]. Similar observations have been made in a number of other compounds. The J^* and G^* phases (the tilted versions of smectic B, i.e. liquid crystals with three-dimensional ordering) generally are found to be untwisted, whereas the corresponding I^* and F^* phases (the tilted versions of hexatic-B, with two-dimensional ordering) seem to possess a helix. In the I^* and F^* phases observations of the twist are, however, sometimes difficult to make due to very pronounced hysteresis phenomena: once the helix is unwound by an electric field it may take many hours to have it return, even in relatively thick samples. The helix-free phase found recently by Brand and Cladis[46] in the new compound 8SI* is probably a J^* or a G^* phase. Whether these phases should be classed as liquid crystals, soft crystals or crystals should not be of much concern to us; in any case their ferroelectric properties are those of liquid crystals and not of solids.

The suppression of the helix due to structural order has been discussed in 1981 by Prost, in the framework of the Landau description[10]. Prost develops the free energy including both a Lifshitz invariant to account for the helical structure and a Ψ^6 term to account for the hexagonal symmetry that he chooses as an example. He finds that, as a function of the tilt angle, the substance may be characterized by a helical twist, a partial lock-in and a complete lock-in, leading thus to a transition in stages from a helielectric to a uniformly ferroelectric state at a certain temperature. The richness of such possible structures is striking and, as more chiral smectic compounds are synthesized by the chemists and made available for experimentation, the pattern of observed structures and transitions will certainly gain in complexity.

For two of the structures reported to be helix-free the Moscow group proposed a model where the tilt is alternating in sign from layer to layer thus representing a kind of antiferroelectric ordering. A chiral smectic could, in principle, have this kind of ordering, but no direct evidence has been found so far. It might be interesting to note that a racemate, in contrast, could not be built up by a similar ordering principle; not even in a bilayer structure. Optical antipodes of opposite tilt in alternating layers would violate the reflection symmetry and give a macroscopic polarization. Alternating regions of opposite twist would also fail to satisfy the symmetry requirement. The racematic compensation thus has to take place within each layer.

Over the last five years, work on the existence of antiferroelectric ordering in liquid crystals has developed into one of the specialities of the Bordeaux group, in the frame

of their studies, both theoretical[47] and experimental[48], of monolayer-bilayer smectics and incommensurate phases. Antiferroelectric phases have been found, of a different kind than that proposed in ref. 41. A new type of ferroelectric liquid crystal has been predicted[10] but not yet found experimentally. Both areas are too extensive and, as yet, too much in the state of development to be within the scope of this review. We, therefore, refer to the articles already cited above and, for the longitudinal ferroelectricity in modulated smectics, to the recent discussion by Barois and Prost[49].

The possibilities of producing helix-free chiral smectics by using chiralizing, dechiralizing dopants and multicomponent systems are still just beginning to be explored. There is nothing magic with a pure substance liquid crystal; on the contrary, a vast variety of multicomponent phase diagrams will have to be studied in order to develop the necessary systems to be used in all devices, where they play exactly the same role as alloys in metallurgy or materials science in general. There is, however, another method of producing uniform electric polarization, which is fundamentally different in nature (but could very well be used in combination) and which leads to some additional features, long sought for in device applications: bistability and very high speed. This was demonstrated in 1980 by Clark and Lagerwall[50] who showed that both the C^* and I^* phases of HOBACPC could be rendered helix-free and bistable in a surface-stabilized structure.

6. The surface-stabilized structure

In the surface-stabilized structure the helix is inherently absent, unwound as it were by the elastic interaction with the surrounding surfaces. The surface interaction is equivalent to a permanently applied external field, of a different nature and non-interacting with the electric field that is to be applied. In terms of unwinding there is, of course, no principal difference between a cholesteric helix and a chiral smectic helix. Their deformation in external electric and magnetic fields is just a question of the balance between electric or magnetic field energy on the one hand and energy of elastic deformation in the liquid crystal on the other, contributions which are essentially equivalent in the two cases. The same is true for their surface interactions. That cholesteric phases are dechiralized by surface action in thin samples is a well-known experience since the classic studies on wedges by Grandjean[51], and the corresponding phenomena in smectics were convincingly demonstrated by Brunet and Williams in their studies of defects and dechiralization lines in the C^* phase[52]. If an entire sample can be made helix-free it has the C^* structure represented in figure 2 with a uniform polarization, and clearly must be of special electro-optic interest. As Clark and Lagerwall showed, by an appropriate combination of essentially three factors, a surface-stabilized ferroelectric liquid crystal (SSFLC) structure can be made, in which the uniform polarization can point in either of two ways, giving the device some unusual properties, illustrated in figure 11.

The main features distinguishing it from other liquid crystal devices are the following: (i) a change of sign in the electric field applied across the sample switches the optic

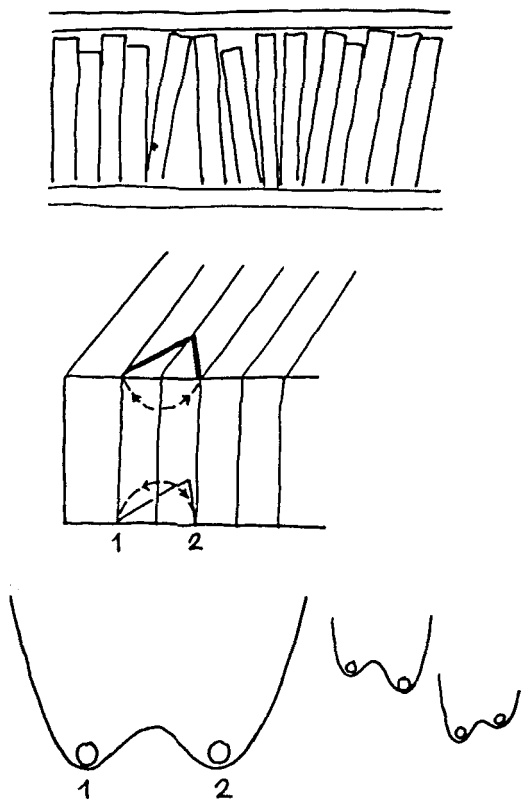

Figure 11. The basic geometry of the SSFLC device. The layers are standing upright, perpendicular (or slightly inclined) to the glass plates, like books in a bookshelf (»bookshelf geometry«). The sample is thin enough to ensure a twist-free uniform director from top to bottom, conditioned by the requirement that the director has to be horizontal at the boundaries. The ensuing bistability is essentially a geometric consequence of the combined arrangement.

axis of the molecule symmetrically between two equivalent »off» and »on» states. This makes a switching by pulses feasible. After the application of the short pulse the optic axis stays in its position until a pulse of opposite sign might switch it back to the other position. This means that the device is (symmetrically) *bistable*. Moreover, this switching has (ii) a speed that goes far beyond what was previously possible with liquid crystals. Switching times in previous devices typically lie between 0.1 and 0.01 second and can be pushed (but only one way, not back) to the millisecond regime. The SSFLC device, apart from being symmetric on-off, extends the regime from milliseconds to below microseconds, at present performing down to 100 nanoseconds. Design of better materials will probably lower this limit further by a factor of ten. Finally (iii) in contrast to other liquid crystal electro-optic mechanisms, this one implies that the optic axis (that is switched by 2Θ, twice the tilt angle) is essentially perpendicular to and switched around an axis parallel to the transmitted/reflected light. This gives a large optic effect with an excellent viewing angle.

The sufficient conditions that in combination give these features bear on the layer geometry in the cell, on the cell thickness and on the boundary conditions at the surface. These have to be chosen so as to facilitate switching by the electric field while being in sharp conflict with the formation of the helix. The helix is unwound (elastic unwinding) by making it incompatible with the $\hat{n}$ directions prescribed by the boundary conditions. How this comes about is explained in figure 12: if, in some way, we have succeeded in arranging the smectic layers homogeneously parallel to each other but perpendicular to the bounding surfaces (this is an unusual geometry difficult to obtain; we call this the »book-shelf geometry», cf fig 11) then, in a thick sample, the helix characteristic of the C^* phase will be well developed in the middle of the sample and the director will spiral around the layer normal, all the time lying on the surface of the tilt cone (cf also fig 5a).
Assume now the boundary condition to imply that the director be *in* the plane of the boundary but without directional preference in that plane. Clearly now the surface state will be in conflict with the bulk state. There are only two directions in space where the molecular orientation would satisfy both the requirements of being parallel to the bounding plane and to lie along any of the directions prescribed by the cone. Those two directions are given as the cut between cone and plane. By the curvature elasticity of the liquid crystal the surface condition propagates to a certain depth into the medium and, if the sample is made sufficiently thin, completely unwinds the helix to the benefit of one of the two common directions. The unwound state thus corresponds to a smectic C medium where the infinite, continuous director degeneration has been lifted to only two-fold by the surface action, with the important difference that the possible tilt states now, due to the chirality, correspond to uniformly polarized **P** states of opposite sign. Thus in the surface-stabilized structure we can expect ferroelectric domains to appear, similar to those known in solid ferroelectrics, and such domains were found[53], cf figure 13.

Although the reason for the helix in the C^* phase is fundamentally different from the reason for the domains in solid ferroelectrics or ferromagnetics, its effect is the same: to cancel the overall macroscopic polarization (magnetization) in the absence of an external field. For instance, iron spheres are unpolarized with domains of a charac-

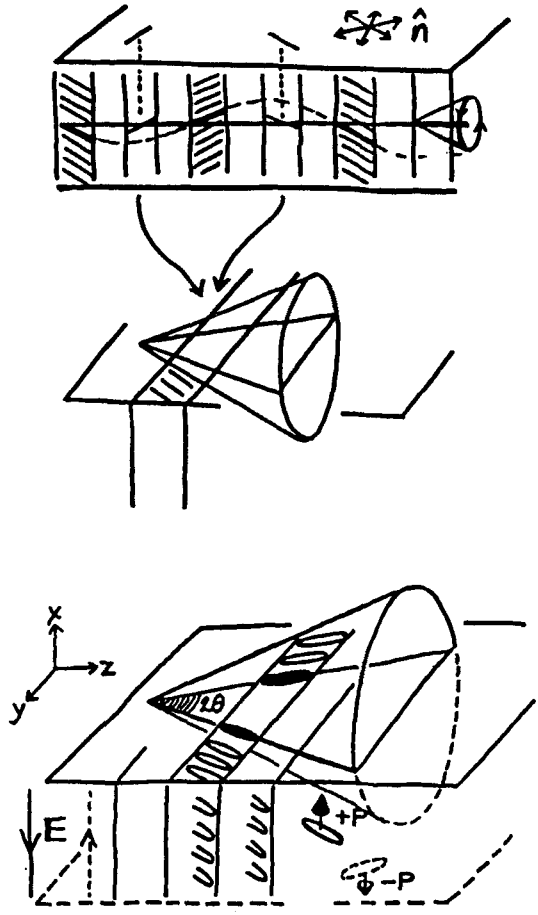

Figure 12. Elastic unwinding. n̂ is allowed any direction in the horizontal plane at the boundaries. In the middle of the sample the spontaneous helix tries to keep n̂ along the conical tilt surface. Two directions of n̂ in space fulfil both requirements. At sufficiently small sample thickness, the helix is uniformly unwound giving two equivalent director states, one corresponding to UP, the other to DOWN polarization. The angular difference between these symmetric states are 2Θ, twice the smectic C tilt angle.

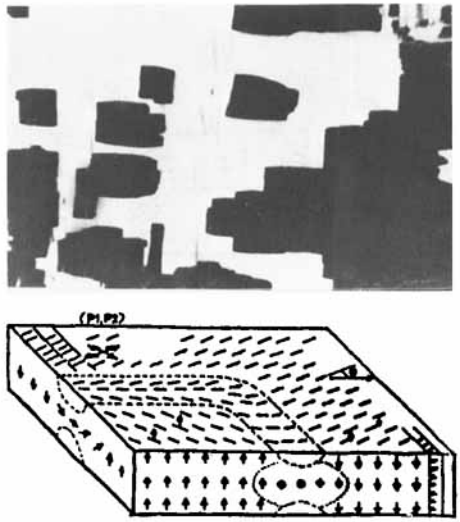

Figure 13. Ferroelectric domains with UP and DOWN polarization state appear when the spontaneous helical director structure is suppressed by surface action in the SSFLC structure. On the horizontal cross section the orientation of the optic axis (n̂ field) is shown, on the vertical side sections the corresponding polarization (**P** *field). Walls (of a mixed Bloch-Neel character in the* **P** *field) separate domains of opposite sign. By changing the polarizer setting the wall itself can be made visible rather than the domains (several examples of this are given in ref.55). The thickness of the wall is most often comparable to the cell thickness.*

teristic width of the order of only 100 Ångströms. As shown by de Gennes and Pincus[57] a medium like the smectic C^*, with continuous »spin» degeneracy, cannot have any domains. Once the helix is suppressed by the surfaces, however, the domains appear. If you get rid of the helix you get domains instead, because the surfaces have simultaneously changed the spin degeneracy. In the solid-like and helix-free phases J^* and G^* the situation is different. These phases have not a continuous but a discrete orientational degeneracy: 6 easy directions, not necessarily equivalent. Their domains observed so far also seem to be surface-stabilized rather than inherent.

In the C^* and I^* phases of HOBACPC the behaviour of the domains under applied fields has been studied[53-55]. If no field has been applied previously to a sample, domains of both signs are normally found. If a DC field is applied, increasing slowly from zero, domains with **P** along the field grow, by motion of the domain walls, at the cost of the non-favorable domains until the whole sample is uniformly polarized. The walls sweep the sample with a velocity which, in the limit of low fields, is directly proportional to the applied voltage. This motion, except for pinning irregularities, is reversible if the field is reversed. Even if it is slow - and thus not the one of prime importance in electro-optic applications (cf next section), it is still of interest in char-

acterizing our medium: »It is this relatively rare capability of being switched between two equally stable states of opposite polarization which causes certain polar crystals to be classified as ferroelectric» (cited from Axe[56]). We see that in the case of the liquid crystal C^* phase the medium had to be forced out of its natural crystallographic state to yield this feature.

7. Fast switching and bistability

The main electro-optic switching characteristics have been described early[53-55] for the C^* as well as for the I^* phase of HOBACPC (in 1981, before the recent code letter recommendation, the I phase was referred to as the F phase) and lately extended to considerable detail and to new phenomena found in other substances[58]. Here, we only pick out two important issues to consider from a principal point of view.

In a thin C^* monocrystal involving neither helix nor topological defects the molecular axes can be switched in unison as a collective molecular rotation with a characteristic time $\tau \approx \eta/P \cdot E$ going below a microsecond. This bulk reorientation taking place at high fields (about 10 to 50 volts applied across a 1μm sample) is the most rapid electro-optic mechanism in the medium. If we write the order parameter as $\Psi = \Theta \cdot e^{i\Phi}$, the ideal bulk switching amounts to controlling the director $\hat{n}$ along the lowest energy path that is available, corresponding to the zero wave vector limit in the continuous spectrum of excitations in the phase variable Φ. Thus, the chosen geometry allows the electro-optic use, in a driven fashion, of the symmetry-restoring Goldstone-mode of the C phase. This corresponds to a spin wave at $q = 0$ in a ferromagnet, the collective mode requiring a minimum of excitation energy.

The bistability, as can easily be seen from figure 11, is a consequence of the broken symmetry in phase variable. The potential curves along this variable, whether symmetric or slightly non-symmetric, illustrate that the bistability is an inherent feature of the chosen geometry. It will be there, as long as there is an energy maximum (activation energy) between the two states 1 and 2 that correspond to the two tilt directions. But this maximum always exists, in principle, because already the slight elastic distorsion involved in turning around all molecular axes inwards amounts to such a thing. The practical question is how large the difference may be between the stable states 1 and 2 and the transition state in between. This will determine the practical bistability. It seems reasonable that the bistability is more pronounced the thinner the sample and that it will bemore pronounced in the I^* phase than in the C^* phase. This is certainly found experimentally; in the C^* phase the activation energy is small and the balance delicate: a very careful surface treatment together with a sophisticated layer alignment procedure is required for good bistability. In the I^* phase the bistability is achieved much easier, without much particular care in the treatment, and disconnected samples have been stored for months in the I^* phase without any visible change. Of course, the higher bistability corresponds to a lower fluidity and switching speed (current state: 5μs).

Finally, we want to mention that the bistability varies with switching mode and substance and that it does not have to be of the nature illustrated in figure 11; several kinds exist, depending on the director profile through the sample and thereby on the sample conditions. Consider, for instance, that the director is not lying along the boundary plane but is pointing inwards as shown in figure 14.

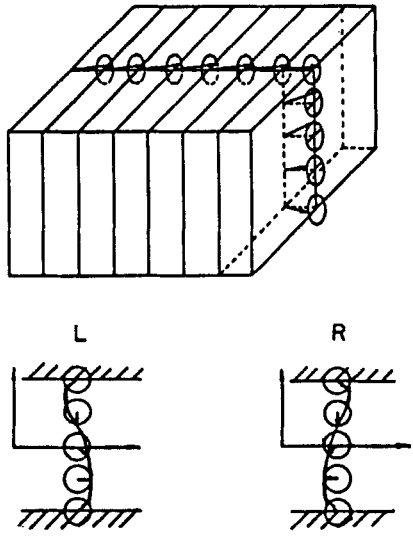

*Figure 14. Director configuration with twist from top to bottom plate (»twisted smectic»), examplified for the case when n̂ makes a 45° angle with the surface normal. If the boundary condition is non-polar the structure would be symmetrically bistable, in principle, but much harder to switch than the SSFLC structure. If the boundary condition is polar, the L(eft) and R(ight) structures will be non-equivalent and the device unsymmetric. (**P** always makes a right angle with the director shown.) For a general discussion of this structure and similar ones, see reference 32.*

The two director configurations L and R may be equivalent in energy and can be switched into each other in a bistable way. As in the previously discussed case, this also presupposes a boundary condition of the composite character »strong-weak». In our example the director, as in the figure, might want to maintain a fixed angle (here 45 degrees) with the surface normal while being otherwize unrestricted as for the direction in space. Similar bistable structures are possible in which the boundary conditions are rather »strong-strong». Some will be interesting for electro-optic purposes (**P** oblique to the surface), others (**P** perpendicular to the surface) will be unsuitable for switching.

8. Aligning methods for SSFLC samples

The unconventional SSFLC geometry requires a new and unconventional alignment problem to be solved: first of all the smectic layers should be perpendicular to the glass plates, and this, second, has to be achieved without locking the director in a certain direction. This important practical problem has not yet found a satisfying solution, probably due simply to the trivial reason that available ferroelectric substances are not suited for the standard surface treatment methods, that all influence the nematic director. HOBACPC and most of the few other available ferroelectrics do not possess a nematic phase but only smectic ones. In order to align them correctly we may start from a confocal texture in the A phase like the one in figure 4 of reference 55 where the method is discussed, and apply a weak shear on the two glass plates, straigtening out the layers in the shear directions and perpendicular to the glass plates. Having the A-layers ordered homogeneously we then cool down to the C phase. On a clean surface without coating the director will orient rather freely along the surface. The method may give excellent results but is in itself hard to control.

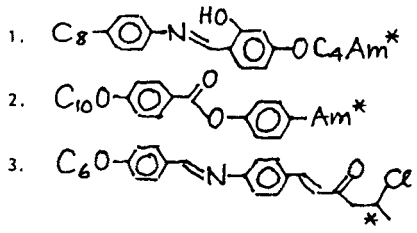

Figure 15. Three molecules with fairly different alignment or/and electro-optic behaviour in their C^* phase: (1) 4-(6-methyl)octyl-resorcylidene-4'-octylaniline (MORA 8), (2) 4-(2-methyl-butoxy)-phenyl-4'-decyloxy-benzoate, and (3) hexyloxy-benzylidene-amino-2-chloro-α-propyl-cinnamate (HOBACPC).

Different substances also show strikingly different behaviour. Of the three compounds shown in figure 15, the first one cannot be aligned this way at all, the third behaves reasonably well and the second very well, resulting in excellent contrast and bistability. The smectic layers may also be oriented in a magnetic field when passing from the isotropic to the A phase. This has been studied particularly by Kondo et al[59]. The results indicate that a reasonably well-aligned A phase can be formed directly in a magnetic field of about 20 kG at sample thicknesses of about 250 μm, far too thick to be of interest for electro-optic effects. If a mixture is used instead of a pure compound, the broader phase transition range permits either working with thinner samples or in fields of lower strength. A field of 10 kG may now have the same effect as one of 100 kG applied to a pure compound[60]. Still, for the very small thickness d, of about 1-2 μm, that is desirable in our case, a magnetic field is probably

impractical. A different method of attractive simplicity is spinning on and then buffing a nylon polymer and is reported to work well[60]. However, it would clearly be satisfying if the other standard methods developed for the surface alignment of nematics could be used here as well. The method of oblique SiO evaporation, for instance, is well suited if the ferroelectric substance has a phase sequence of isotropic-N-A-C. In that case the director could be aligned and locked along certain evaporated stripes whereas in between it grows out »epitaxially» in the same direction, without being locked. Descending down to first the A and then the C phase would, in turn, first lock the layers, then unlock the director in the layers. This method[32] should give as excellent alignment quality as that produced today in normal twisted nematic cells. The basic requirement is, of course, that conventional materials with N-A-C sequence have been synthesized, which they have not, at the time of writing this article . (Note that an N-C sequence is not sufficient, because at the transition N down to C, the layer direction is not unambiguously defined and an inhomogeneous distribution of »layer domains» will result.) Thus, the important practical problem of alignment in SSFLC cells awaits a directed synthetic effort from the part of the organic chemists toward N-A-C substances with the C phase at or near room temperature. Because this is just a technological »transport distance» where a lot of skills but no fundamental problems are involved, one can be fairly sure of success within a time span of the order of a year.

9. The unwinding condition and thick samples

By chosing the sample thickness very small, 1-2 μm, Clark and Lagerwall, in their first experiments, avoided a number of complications which will now be discussed. The main issue is how to obtain a uniform polarization that can be reoriented by an electric field without the appearance and disappearance of topological defects in the sample. For this, a neccessary but perhaps not sufficient condition is that the helix is initially absent. This condition can hardly be stated more precisely than $d \approx \lambda$, where d is the thickness and λ the wavelength (or »pitch») of the helix. One reason is that a critical unwinding thickness must be a function both of the boundary conditions per se and of the surface anchoring strength. Another reason is that, in the chiral smectic case, the boundary condition is likely to be vectorial in character (polar) and this may stabilize a remaining twist in the orientation field even after the helix in bulk has been unwound by the surface action. Such a twist structure is seen in figure 14: the simplest case is obtained if the angle between the director and the surface plane is set equal to zero, corresponding to our earlier discussion. In that case, the polarization **P** is pointing into (or out from) the liquid crystal obeying the same condition at both surfaces, and presenting a splay of 180 degrees from the top to the bottom surface. Even if the cell thickness has been reduced sufficiently to suppress any visible helix in the bulk, we may be left with this twisted structure that is completely unsuitable for electro-optic switching purposes and thus we may have to reduce the thickness further in order to force, by the same elastic interaction, the tilt/polarization to change sign at one of the surfaces. The critical cell thickness, d_c, for uniform polarization throughout the sample, is therefore a more important parameter than the unwinding thick-

ness. Twisted structures of the kind just described were observed by Handschy, Clark and Lagerwall[56] and the problem was independently taken up by Pavel and Glogarová[61]. These latter authors found that the polarization vector **P**, for the substances studied (including DOBAMBC) has the direction from the glass surfaces into the liquid crystal. They also found that, corresponding to the two-step elastic unwinding, there are two different critical values describing the un-twisting in an external electric field, E_{c1}, for which the bulk helix unwinds, and $E_{c2} > E_{c1}$, for which the remaining twist unwinds into a homogeneous director orientation.

The above-mentioned phenomena make the electro-optic behaviour of thick samples quite complex. Certain substances, e.g. of the MORA series[62], also strongly prefer the twisted structure and are hard to bring into the uniform state even in very thin samples. Different smectic phases, as can be expected, behave differently. In a given cell filled with DOBAMBC, the structure may be twisted in the C^* phase ($d > d_c$) but untwists on lowering of the temperature into the I^* phase ($d < d_c'$).

The tendency to twisted structure without visible helix but a splay in the **P** field ($\nabla \cdot \mathbf{P} \neq 0$) is not the only possible complication we will confront when trying to increase the sample thickness, yet maintain a uniform polarization ($\nabla \cdot \mathbf{P} = 0$). In the preparation of monodomain samples we must further take care of the other two types of spontaneous deformation shown in figure 10. It is then convenient to look at all kinds of disturbance from uniformity in the same way. To each of the spontaneous deformations it is possible to associate a characteristic length; the spontaneous deformation is then only important for samples of dimensions of the order of, or larger than, the characteristic length. Symmetry arguments indicate what kind of tilt angle dependence we can expect. For the helix we can choose the pitch as characteristic length: it is of zeroth order in the tilt angle. The tendency of the macroscopic polarization to splay has a characteristic length that is typically proportional to the tilt angle, and this tendency should therefore be most pronounced at small tilt angles. The splay of the polarization is intimately related to polar boundary conditions, which in the same way are dominating at low tilt angles. These boundary conditions, with polarization directed inwards the sample for book-shelf geometry, are unsuitable for bistable switching: we get bistability but switching requires electric fields parallel to the boundary plates. The spontaneous deformation of the smectic layers should on the other hand have a characteristic length inversely proportional to the tilt angle squared, and this kind of deformation should thus dominate for large tilt angles.

At the present state of knowledge it is hard to make a comparative evaluation of all effects discussed above. However, one may guess that the spontaneous splay state due to polar boundary conditions will be the most severe obstacle when trying to increase the thickness of electro-optic cells. These may have to stay thin even when filled with substances characterized by very long or infinite pitch.

A very interesting question is brought up by the G^*, J^* and similar phases where the 3D crystallinity has already untwisted the medium. As pointed out by Prost[10], below the helielectric-ferroelectric transition there are in principle six stable positions of the director which could be controlled by an electric field. For the electro-optic use of

these materials we will essentially encounter the same problem as above: to speed up switching, the sample should not be too thick, the boundary condition should still be strong-weak (the surface must accept some of the discrete states but not dominate, otherwise the cell would tend to be only bistable). There will always be a competition between surface control and lattice control of available states, i.e. the lattice has to be adjusted to the boundary. Preparation of monodomains may not be altogether trivial due to the long range order. At present,[64] this whole area has not been pursued very far, and it is unclear if, and to what extent, the inherent crystalline states can be made stable, and thus whether more states can be achieved in these phases than in their pure SSFLC mode. Moreover, the SSFLC mode may in itself be able to produce more than two stable states in the non-crystalline phases. This might be achieved by slight variations of the basic SSFLC conditions. Those variations (conical boundary conditions and oblique layers) and the new effects permitted, among other things possibilities for fast continuous control of the tunable birefringence type, are treated in reference 32. A number of observational remarks of practical relevance for these generalized conditions can be found in reference 56. However, also this area is too vast and, experimentally,too little has been pursued so far, to motivate a discussion in the present review.

10. Concluding remarks

Ferroelectric liquid crystals present a number of intriguing and challenging problems on a fundamental level. One of them, that we have not been able to stress accordingly in this review is the interplay between chiral properties of the molecules and their manifestations on a macroscopic scale. In this respect liquid crystals are an absolutely unique form of matter, and among the liquid crystals, the chiral smectics exhibit the richest and most diversified aspects. It does not seem unlikely that the coming years of research will here contribute essentially to and change our presently rather diffuse understanding of the physics and chemistry of chirality. Another important problem that we have been forced to leave out refers to phase transitions involving ferroelectric liquid crystals, especially in the presence of external fields (existence of a Lifshitz point etc, cf. reference 63). On the level of technical applications ferroelectric liquid crystals also have shown great promise, in spite of the very embarrassing shortage of convenient substances that have been at the disposal of experimenters. A devoted effort in developing new materials from the part of the organic chemists working in the liquid crystals area, together with a good collaboration on molecular design between chemists and physicists, will be decisive for the potential devices that may extend considerably the useful range of liquid crystals in the area of electro-optics.

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