Polar biaxial liquid crystalline phases with fluidity in two and three spatial dimensions

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Abstract

We discuss the macroscopic properties of several classes of polar liquid crystalline phases. We focus on polar biaxial liquid crystalline phases made of achiral molecules with fluidity in two and three spatial dimensions. The classes we examine include polar biaxial nematic phases, orthogonal biaxial smectic phases with anisotropic in-plane fluidity and tilted polar biaxial smectic phases with in-plane fluidity. We show that many of the phases discussed are ferroelectric. In addition, we find that in each of the three classes discussed, there is one phase which has C_1 symmetry thus allowing spontaneous helix formation. Finally we investigate in detail the properties of a tilted phase with C_2 symmetry (C_{B2}), which is probably very important for liquid crystalline phases composed of banana-shaped molecules.

1 Introduction

Over the last few years many compounds composed of achiral [1] and bent or banana-shaped molecules have been synthesized and the investigation of their physical properties has started [1-12]. This increased activity followed after a number of predictions concerning the type of electric properties, for example ferro- and antiferroelectricity, in liquid crystalline materials composed of achiral [13] molecules had been made [14,15]. In Ref.[14], for example, we had predicted that suitably

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[1] Throughout the present paper we use the word 'chiral' according to its meaning in a physics context: 'characteristic of an object that cannot be superposed upon its mirror image'. This use must be distinguished from its common use in chemistry, where it refers to a molecular property: 'the handedness of an asymmetric molecule'.

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bent achiral molecules arranged on smectic layers on average parallel to their bend direction could form a biaxial fluid smectic phase with a macroscopic polarization in the smectic layer planes: smectic C_P. This phase has C_{2v} symmetry, that is a vertical symmetry plane perpendicular to the smectic layers and a two fold symmetry axis lying in the vertical mirror plane.
Stimulated by the experimental results, we have recently addressed theoretically [16] a number of questions. These include, for example: how can one obtain left and right handed helices in fluid smectic phases when the constituents are achiral? We found [16] that there are at least two such phases, namely C_{B2} (which has C_2 symmetry) and C_G (which has C_1 and thus no symmetry), provided there is one polar direction and the triad of unit vectors associated with the orientational order is suitably tilted with respect to the layer normal. We have also given a discussion in Ref.[16] how the smectic C_M phase, which is a fluid biaxial orthogonal smectic phase [17], fits into this picture. This phase is also of practical relevance, since it has been observed experimentally in side-on side chain liquid crystalline polymers [18,19]. Various aspects of physical properties of this phase have been addressed in refs.[14,20,21].
The purpose of this paper is a systematic generalization of the results presented in Ref.[16] in several directions. One of the main motivations for doing this is to help the experimentalist in identifying so far unknown liquid crystalline phases with polar axes (axis). We will present a first discussion of the influence of one or more polar direction(s) on the physical properties of biaxial nematic phases. We will also analyze biaxial orthogonal fluid smectic phases with in-plane fluidity allowing for the presence of one, two and three polar directions. Finally we will give a first discussion of liquid crystalline bulk phases with spontaneous bend.
The present paper is organized as follows. In next section we discuss biaxial nematic phases, which have one or more polar direction(s). Section 3 deals with orthogonal biaxial fluid smectic phases and their physical properties. In Section 4 we investigate tilted fluid smectic phases without or with one polar direction followed in Section 5 by an examination of the stacking possibilities of phases with C_2 symmetry in each smectic layer. In Section 6 we present an overview over the possibility of liquid crystalline phases with spontaneous bend concentrating on polar biaxial nematics and polar orthogonal smectic phases. Section 7 gives the conclusions and a brief outlook.

2 Biaxial nematic phases with polar directions

Nonpolar biaxial nematic phases, that is nematic phases with two (and thus three) preferred directions, which do not distinguish between head and tail, have been studied in detail [17]. They have been discovered experimentally in lyotropic materials two decades ago by Yu and Saupe [22] and later in side-on side chain liquid crystalline polymers [18,19]. All experimentally observed biaxial nematic systems have orthorhombic symmetry, specifically D_{2h}, using for their macroscopic description the triad of orthogonal unit vectors $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$. We emphasize that this type of biaxial nematic phase has $\hat{\mathbf{l}} \to -\hat{\mathbf{l}}$, $\hat{\mathbf{m}} \to -\hat{\mathbf{m}}$ and $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$ symmetry separately.

With the synthesis of many compounds composed of banana-shaped molecules, it seems natural to investigate the options for biaxial nematic phases with polar direction(s). We note, however, that so far all these compounds appear to show an isotropic to smectic phase transition with no intervening nematic phase [1-12]. Thus there appears to be a challenge for the synthetic chemists to suppress the tendency towards the formation of smectic layering. From a symmetry point of view one can imagine to have polar biaxial nematic phases with one, two or even three polar directions.

Table 1

The expected defect structures and the electrical hysteresis properties for the four different classes of biaxial nematic phases[a]

Class of phase	Symmetry	Strength of defects	Electro-optic response	LH and RH helices
N_{bx}	D_{2h}	Half integer	Dielectric	No
N_I	C_{2v}	Integer	Ferroelectric, $\mathbf{P} = (P_x, 0, 0)$	No
N_{II}	C_{1h}	Integer	Ferroelectric, $\mathbf{P} = (P_x, P_y, 0)$	No
N_{III}	C_1	Integer	Ferroelectric, $\mathbf{P} = (P_x, P_y, P_z)$	Yes

[a] Here we focus on the phases that are either dielectric or ferro- (ferri-) electric.

For the case of orthogonal biaxial nematics these possibilities - together with the conventional nonpolar biaxial nematic phase - have been summarized in Table 1 and Fig. 1. Already for one polar direction, phase N_I, the electric properties change drastically from dielectric to ferro- or ferrielectric. The global symmetry of the N_I phase when compared to N_{bx} is reduced from D_{2h} to C_{2v} (compare, for example, Ref.[23] for the notation) reflecting the fact that there is only a 2-fold rotation axis and a vertical mirror plane left over. This polar biaxial nematic phase appears to be a rather natural candidate for biaxial nematic phases made of banana-shaped molecules. If a second polar axis is added as for the N_{II} phase, the symmetry is reduced further to C_{1h} and only a horizontal mirror plane is left. In the N_{II}-phase the vector of the macroscopic polarization, $\mathbf{P}$, has two non-vanishing components. Such a phase could be possible in case the 'bananas' have two distinguishable 'ends' and that these two different parts are actually ordering macroscopically. Finally there is the - at this stage - rather hypothetical possibility of a biaxial nematic order with three polar directions, N_{III}. This phase has no symmetry left (C_1). It thus allows for chirality in the form of LH and RH versions. The macroscopic polarization in the N_{III} phase has three non-vanishing components. Due to its chiral nature, the N_{III} phase opens the possibility of helix formation in a nematic phase

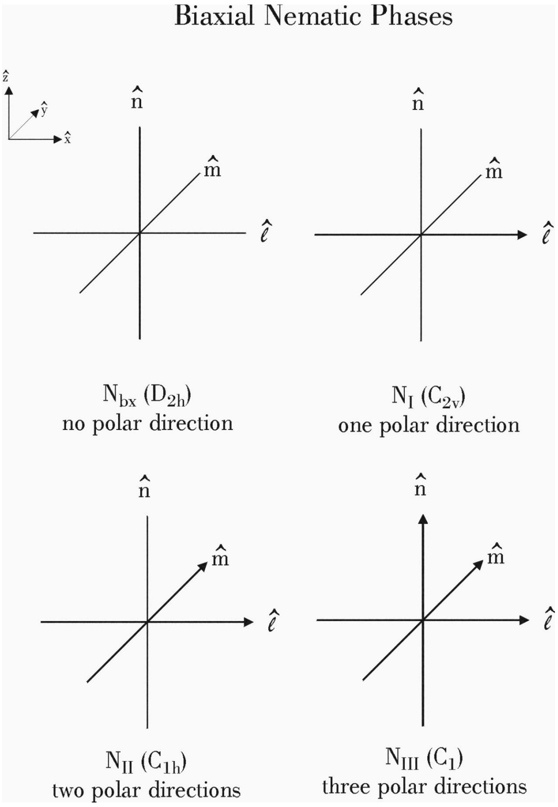

Fig. 1. The four classes of orthogonal biaxial nematic phases. N_{bx} is the classical nonpolar biaxial nematic phase. N_I, N_{II} and N_{III} have one, two and three polar directions, respectively. Note that smectic N_{III} has a macroscopic hand; for symmetries and other physical properties see text and Table 1.

composed of nonchiral molecules. This phenomenon could be easily detected experimentally using optical techniques like polarizing microscopy.
We close this section by pointing out, that the existence of polar directions in the three polar biaxial nematic phases (N_I, N_{II} and N_{III}) allows the construction of scalar invariants such as $\operatorname{div}\hat{\mathbf{l}}$, $\operatorname{div}\hat{\mathbf{m}}$ and $\operatorname{div}\hat{\mathbf{n}}$. As we have shown in Ref.[24] for polar uniaxial nematic phases, the invariant $\operatorname{div}\hat{\mathbf{n}}$ reduces the stability of spatially homogeneous phases and favors the stability of spatially inhomogeneous phases with defects and/or defect lattices (phases with *spontaneous splay*). In Ref.[25] we will investigate the analogues for polar biaxial nematics.

3 Orthogonal fluid biaxial smectic phases

In the last section we have suggested the possibility of polar biaxial nematics. A similar discussion can be given for smectic phases, that are fluid, biaxial and orthogonal. A summary is presented in Table 2 and Fig. 2. Starting from the C_M phase, which is nonpolar and still allows defects of strength $1/2$ in the in-plane director, one sees that in this scheme the smectic C_P phase comes next. It has one polar direction in the layer planes and is ferro- (ferri-) electric in contrast to the smectic C_M phase that is dielectric. Adding a second polar direction in the planes of the fluid smectic layers one arrives at the C_Q phase, which has already a very low symmetry (C_{1h}), while the symmetry of C_P (C_{2v}) and especially of C_M (D_{2h}) is considerably higher.

Table 2
The expected defect structures and the electrical hysteresis properties for the four different classes of orthogonal biaxial smectic phases composed of achiral molecules[a]

Class of phase	Symmetry	Strength of defects	Electro-optic response	LH and RH helices
C_M	D_{2h}	Half integer	Dielectric	No
C_P	C_{2v}	Integer	Ferroelectric, $\mathbf{P} = (P_x, 0, 0)$	No
C_Q	C_{1h}	Integer	Ferroelectric, $\mathbf{P} = (P_x, P_y, 0)$	No
C_R	C_1	Integer	Ferroelectric, $\mathbf{P} = (P_x, P_y, P_z)$	Yes

[a] Again we focus on the phases that are either dielectric or ferro- (ferri-) electric.

As a next and final step one can add a third polar direction perpendicular to the layers and is left with a phase with no symmetry (C_1): the smectic C_R phase. At this stage, however, one should add a word of caution. Fluid smectic phases with a polar direction parallel to the layer normal are in the bulk very likely unstable to the formation of defects in the smectic layering. The same can be expected to apply, if one starts with the smectic C_M phase or the smectic C_P phase and adds a polar direction parallel to the layer normal.

It seems worthwhile to point out that some of the phase transitions between the various types of biaxial nematic phases and orthogonal fluid smectic phases can be of second order in mean field approximation. For the smectic C_M - biaxial nematic transition this has been described in Ref.[21] and such a phase transition has been observed experimentally [19]. A similar type of analysis applies to the phase transitions $N_I - C_P$, $N_{II} - C_Q$ and $N_{III} - C_R$. In each case, as already analyzed for the smectic C_M - N_{bx} transition, one is putting objects with an increasing number of polar axes ($N_{bx} - N_I - N_{II} - N_{III}$) onto smectic layers ($C_M - C_P - C_Q - C_R$). We close this section by noting that for banana-shaped molecules the C_P phase and, to a lesser extent, the C_Q phase are good candidates for polar orthogonal smectic phases to be observed experimentally in such materials. In section 6 we will argue that the smectic C_Q phase might actually show spontaneous bend.

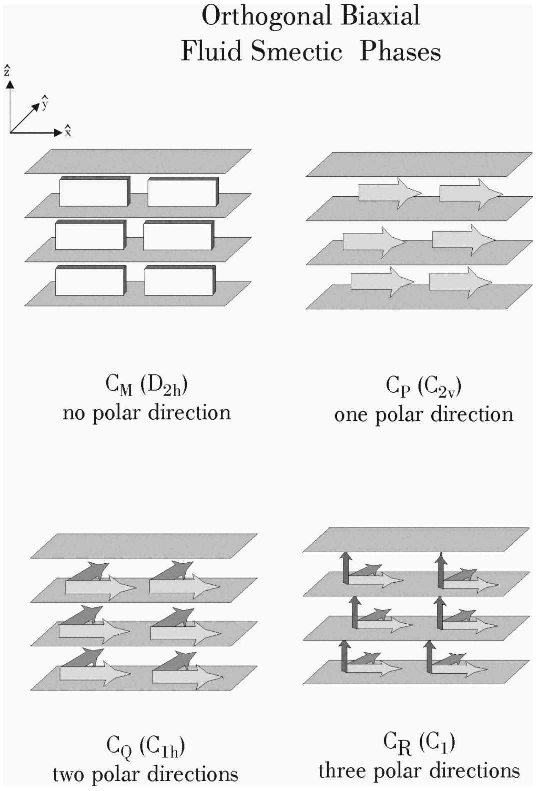

Fig. 2. The four classes of orthogonal biaxial smectic phases with in-plane fluidity are plotted. The nonpolar smectic C_M phase and smectic C_P with one polar direction in the layer planes have already been discussed previously (compare refs.[14,16,20,21]). Smectic C_Q and C_R have two and three polar directions, respectively. We note that smectic C_R has a macroscopic hand; for symmetries and other physical properties see text and Table 2.

4 Tilted fluid smectic phases without or with one polar direction

The best known and characterized tilted fluid smectic phase is undoubtedly the classical smectic C phase, which is biaxial and can be characterized by a tilt angle of the director $\hat{\mathbf{n}}$ with respect to the layer normal $\hat{\mathbf{k}}$. This gives rise to C_{2h} symmetry globally and dielectric behavior. Turning to objects now which order orientationally in two and thus three directions, one can introduce - in addition to the layer normal $\hat{\mathbf{k}}$ - the triad of unit vectors $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ just as for biaxial nematics. Let us start with the case that $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ are all nonpolar. Naturally again phases of the classical smectic C type discussed above are possible. If one is tilting, however, $\hat{\mathbf{l}}$, $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ by an angle that is different from $0°$ and $90°$ with respect to the layer normal $\hat{\mathbf{k}}$ ('double tilt'), then there is no mirror plane and no symmetry axis left. Nevertheless there is one type of symmetry left over: inversion symmetry. This means that there is still invariance under $\hat{\mathbf{l}} \to -\hat{\mathbf{l}}$, $\hat{\mathbf{m}} \to -\hat{\mathbf{m}}$ and $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$ simultaneously. This phase, C_T, has C_i (or S_2) symmetry and is thus triclinic in nature. Since this phase still has inversion symmetry and is achiral, it is dielectric and does not have ferroelectric or even piezoelectric properties [23].

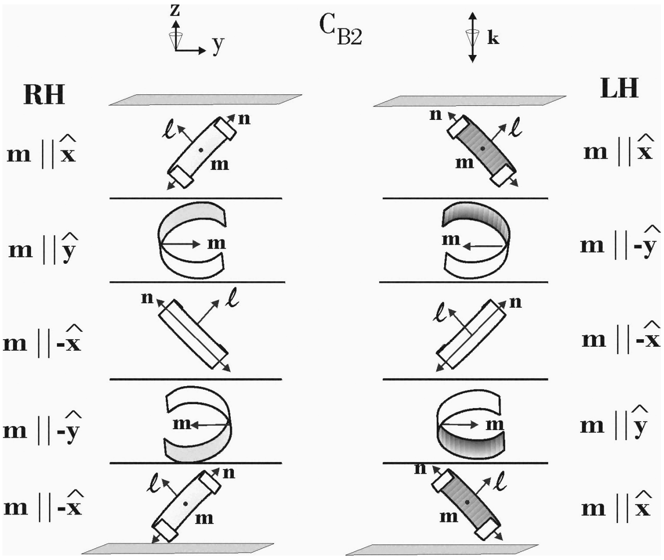

Fig. 3. Sketch of the RH and LH helical versions of the smectic C_{B2} phase composed of achiral molecules.

Table 3
The summary of the behavior of all tilted fluid smectic phases composed of achiral molecules without any or with one polar direction including electro-optic properties

Class of phase	Symmetry	Strength of defects	Electro-optic response	LH and RH helices
C	C_{2h}	Integer	Dielectric	No
C_T	C_i	Integer	Dielectric	No
C_{B2}	C_2	Integer	Ferroelectric, $\mathbf{P} = (P_x, 0, 0)$	Yes
C_{B1}	C_{1h}	Integer	Ferroelectric, $\mathbf{P} = (P_x, 0, P_z)$	No
C_G	C_1	Integer	Ferroelectric, $\mathbf{P} = (P_x, P_y, P_z)$	Yes

The situation with respect to the electric and the electromechanical properties changes drastically if one of the three directions, say the $\hat{\mathbf{m}}$ direction, is polar as it can be the case for banana-shaped molecules. The properties of the resulting phases together with these of smectic C and smectic C_T are presented in Table 3. The discussion in the remainder of this section follows closely Ref.[16]. Tilting of banana shaped molecules can be done in two different ways. First the preferred direction $\hat{\mathbf{m}}$ stays untilted and $\hat{\mathbf{n}}$ and $\hat{\mathbf{l}}$ become tilted. This results in a phase with C_2 symmetry, where $\hat{\mathbf{m}}$ is the two-fold rotation axis, while the vertical mirror plane is absent due to the tilt. This phase has been denoted by C_{B2} in Ref.[16]. A macroscopic polarization is only possible along the symmetry axis. This ferroelectric phase composed of molecules without chirality has a macroscopic hand due to its structure. It stacking properties will be discussed in detail in next section (section 5). We note that smectic C_{B2} is the banana phase discussed in Ref.[5].

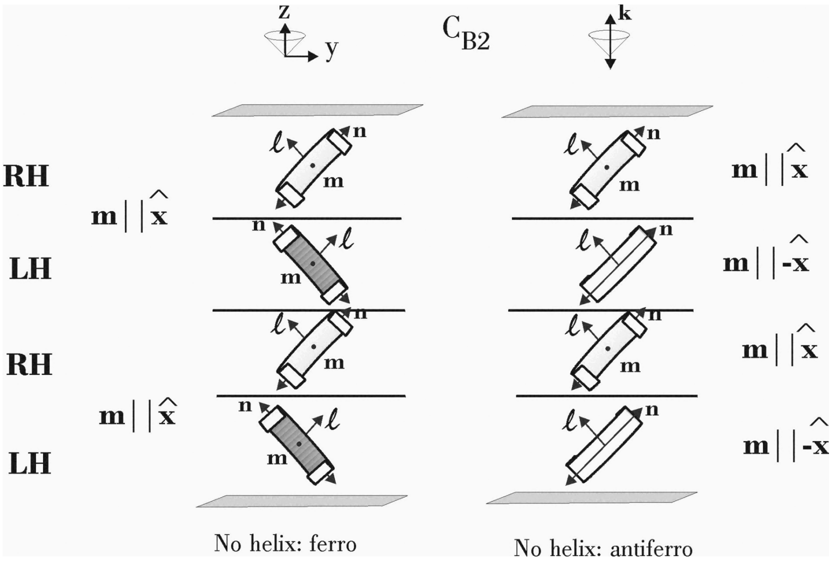

Fig. 4. Alternating stackings of left-handed (LH) and right-handed (RH) layers can be used to generate macroscopically ferroelectric (on the left) and antiferroelectric (on the right) arrangements of C_{B2} layers with no helix macroscopically.

A different phase is found, if the preferred direction $\hat{\mathbf{m}}$ (and $\hat{\mathbf{n}}$) is tilted, but $\hat{\mathbf{l}}$ remains in the smectic layers. Then the two-fold rotation axis is gone, but the mirror plane (identical to the tilt plane) is still there. This gives a C_{1h} symmetric phase (called C_{B1} in Ref.[16]), where the polarization is restricted to lie in the tilt plane. Thus this phase is ferroelectric with polarization components in the smectic layers as well as perpendicular, and it is achiral. If layers are stacked with opposite $\hat{\mathbf{m}}$ but the same tilt direction, an antiferroelectric phase appears (with an in-layer and out-of-layer component of the staggered polarization). If layers with opposite tilt direction, but the same $\hat{\mathbf{m}}$ are stacked, this phase is antiferroelectric perpendicular, but ferroelectric within, the layers, while stacking layers with opposite tilt and opposite $\hat{\mathbf{m}}$ gives ferroelectricity perpendicular, and antiferroelectricity within, the layers.

So far, we have focused on biaxial fluid smectic phases where at least one of the principle axes of the bananas lies within the smectic layers. If we drop this restriction, the smectic C_G phase [17] results. In smectic C_G all three principle axes include an angle with the smectic layers different from 0 and 90° (double tilted structure). As a result, smectic C_G has, in general, global C_1 symmetry, the lowest possible symmetry: triclinic [20]. C_1 symmetry means that this phase has no symmetry at all and that therefore a macroscopic polarization exists that can point in any direction i.e. is not determined by any symmetry element. The low symmetry, (C_1), of the C_G phase has a large number of important consequences [23] for the macroscopic properties of smectic C_G [16]. In particular, any smectic C_G phase with C_1 symmetry globally should be ferroelectric in the bulk.

We stress that we use the term 'ferroelectric' for all phases that show a non-vanishing spontaneous polarization in the bulk. This implies automatically such

phases to be pyroelectric and piezoelectric as well (for piezoelectricity this statement cannot be inverted). We do not make a distinction between pyroelectric and ferroelectric phases based on hysteretic switchability (of the latter) – as is done sometimes. Since 'switchability' is neither a feature based on symmetry arguments nor a property of the phase itself (e.g. a surface stabilized smectic C* is switchable, but the phase is helielectric and not ferroelectric), such a distinction is not useful when discussing material properties (and classifying phases) by symmetry considerations only.
Inspecting the symmetry of C_G closely, one realizes that this phase has a macroscopic handedness, although the molecules (constituents) themselves do not. That means, that smectic C_G has macroscopically a hand in the bulk with two possibilities, namely left-handed and RH versions. It contains as a natural special case the C_{B2} phase discussed above [16].

5 Stacking possibilities of phases with C_2 symmetry in each smectic layer

In this section we address the question, which physical properties can be obtained when layers of the smectic C_{B2} phase discussed in the last section are stacked in various ways. We will focus especially on the resulting macroscopic electric properties and on the question whether the emerging structure has macroscopically a hand or not. This presentation complements to a certain extent the discussion of the various types of stacking we have given in Ref.[16] for the case when two layers of different forms of smectic C_G are associated.
To fix notation we have plotted in Fig.3 the left-handed (LH) and right-handed (RH) versions of smectic C_{B2}. Both versions are helielectric [26] and have therefore macroscopically - when averaged over many pitches - no net polarization. In Fig.4 we show how one can obtain truly ferroelectric and antiferroelectric properties using combinations of pairs of LH and RH layers. From Fig.4 we see that there is no helix present macroscopically in both cases. In Fig.5 we demonstrate how to obtain stackings that have no net handedness as well as no net polarization macroscopically. Note that in this case one also has again alternating layers of opposite handedness. In Fig.6 we have plotted an antihelielectric [16] arrangement associated with one handedness. To obtain this antihelielectric configuration all one has to do is to superpose the RH helix shown on the left of Fig.3 with the same helix shifted by half a pitch for alternating layers. We note that for chiral materials antihelielectric phases have been called antiferroelectric in the past [27]. These phases should not be confused with truly antiferroelectric phases, however, which are well known in solid state physics since decades [23,28]. In Fig.7 we plot the effect of an external electric field on one of the two configurations of mixed LH and RH layers presented in Fig.5. We see that due to the effect of an external electric field walls are generated periodically in space for the mixed configuration shown. We speculate that these frustrated regions probably flip as the external electric field is increased.

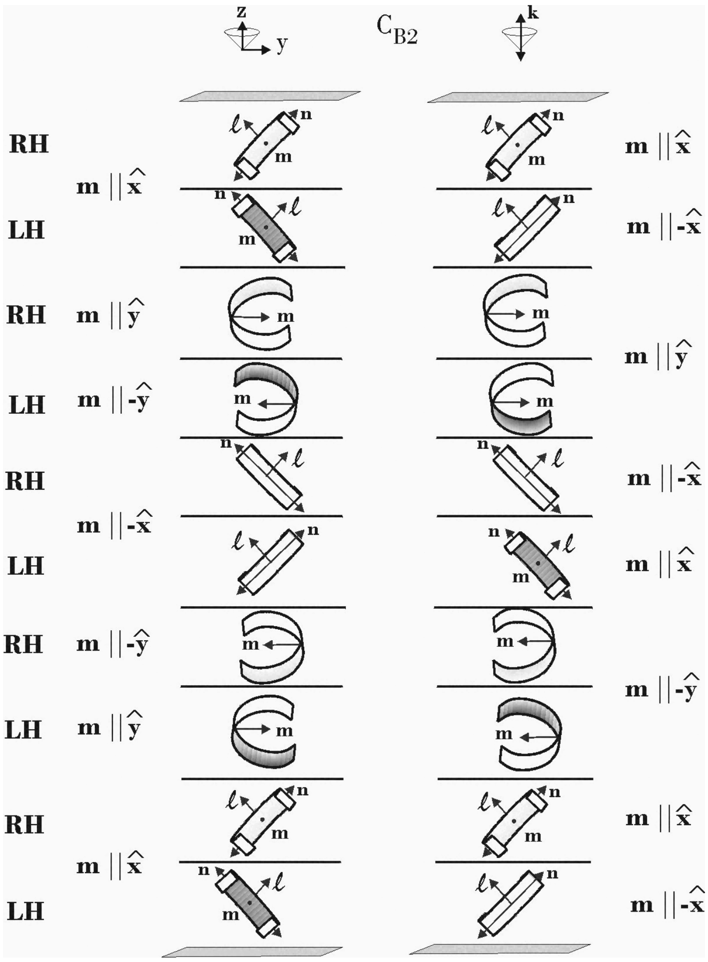

Fig. 5. LH and RH C_{B2} layers can also be stacked in an alternating fashion such that there is macroscopically no net handedness as well as no net macroscopic polarization or staggered polarization.

6 On the possibility of spontaneous bend in polar biaxial nematics and polar orthogonal fluid smectic phases

Towards the end of Section 2 we have indicated the possibility that polar biaxial nematics might show phases with spontaneous splay. Naturally the same applies for the polar preferred directions in the planes of the layers for smectic C_P, C_Q and C_R. In this section we discuss that one can have, in addition, in all three fluid smectic phases not only spontaneous splay, but also spontaneous bend.

In an uniaxial nematic the bend contribution to Frank's free energy is given by $K_3(\hat{\mathbf{n}} \times \mathrm{curl}\, \mathbf{n})^2$. To construct a true scalar that is linear in the gradients of preferred directions for the two directions in the planes of the layers, it is clear that one needs at least one polar direction. In the case of the C_P-phase one can construct one scalar that is invariant under parity: $(\hat{\mathbf{m}} \times \mathrm{curl}\, \mathbf{m}) \cdot \hat{\mathbf{l}}$ with the polar direction $\hat{\mathbf{l}}$. The situation changes when going to C_Q. Denoting the two polar directions in the planes of the

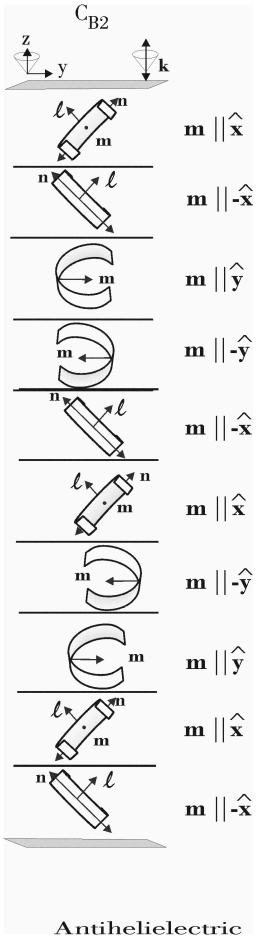

Fig. 6. Antihelielectric arrangement of C_{B2} layers. This scenario can be achieved by stacking the RH helix of Fig.3 for alternating layers with the same RH helix shifted by half a pitch.

fluid layers by $\hat{\mathbf{l}}$ and $\hat{\mathbf{m}}$, one can construct

$$(\hat{\mathbf{l}} \times \operatorname{curl} \mathbf{l}) \cdot \hat{\mathbf{m}} \qquad \text{and} \qquad (\hat{\mathbf{m}} \times \operatorname{curl} \mathbf{m}) \cdot \hat{\mathbf{l}}$$

Taking into account that $\hat{\mathbf{l}}$ and $\hat{\mathbf{m}}$ are two orthogonal unit vectors: $\hat{\mathbf{l}} \cdot \hat{\mathbf{m}} = 0$ or linearized, using $\hat{\mathbf{l}} = \hat{\mathbf{l}}^0 + \delta \mathbf{l}$ and $\hat{\mathbf{m}} = \hat{\mathbf{m}}^0 + \delta \mathbf{m}$

$$\hat{\mathbf{m}}^0 \cdot \delta \mathbf{l} + \hat{\mathbf{l}}^0 \cdot \delta \mathbf{m} = 0$$

one can easily convince oneself that the two scalars constructed are completely equivalent. Thus spontaneous bend as well as spontaneous splay are possible in smectic C_Q and smectic C_R.
At this point it is useful to recall that one can induce splay-bend walls by applying e.g. a magnetic field to a uniaxial nematic. From the fact that smectic C_Q and C_R can show splay *and* bend spontaneously, the fascinating possibility arises that one can get phases, which show an intrinsic length scale for the in-plane directions. This length scale is set by a balance between the terms linear and quadratic in the

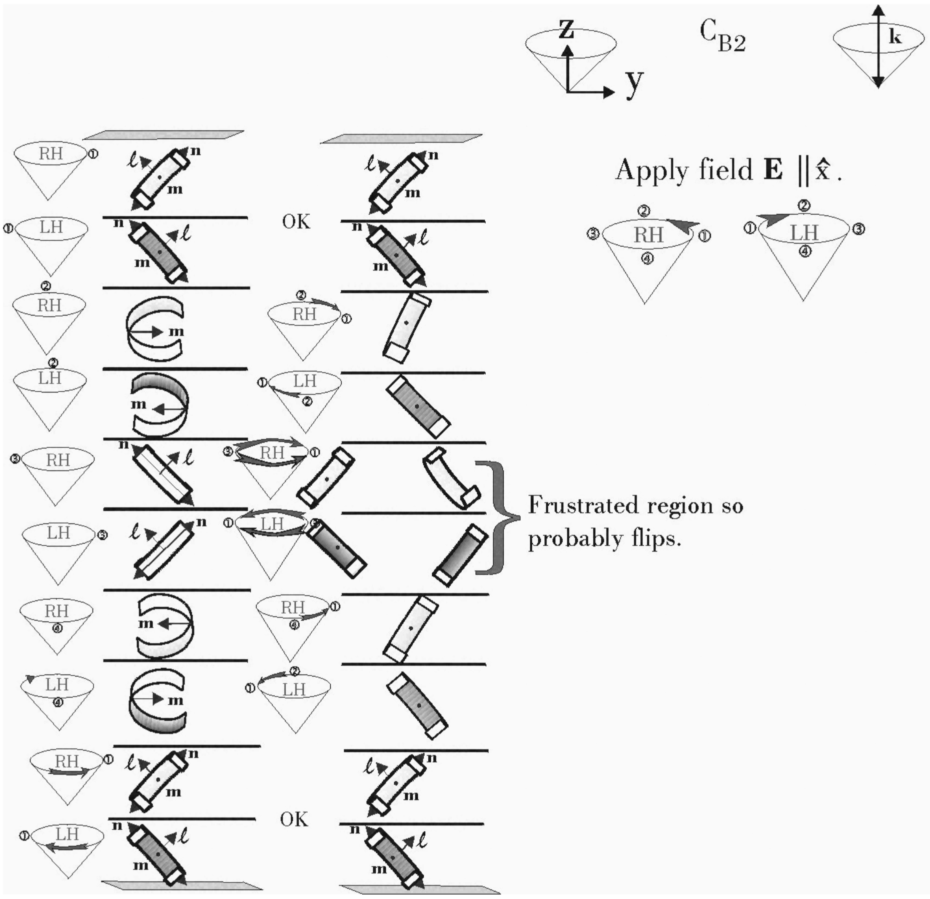

Fig. 7. Effect of an external electric field applied parallel to the layering for one of the two mixed configurations depicted in Fig.5. We note that upon application of an electric field a spatially periodic set of walls is generated for the configuration shown.

gradients of $\hat{\mathbf{m}}$ and $\hat{\mathbf{l}}$. The simplest nontrivial geometric possibility is the formation of stripes composed of splay-bend walls. A more detailed discussion of these phenomena will be given elsewhere [25].

Now we switch briefly to the question of spontaneous bend for polar biaxial nematic phases. As it is easily checked, one can generate scalar quantities containing only two of the three directions:

$$\hat{\mathbf{l}}\cdot(\hat{\mathbf{m}}\times\mathrm{curl}\,\mathbf{m}),\ \hat{\mathbf{l}}\cdot(\hat{\mathbf{n}}\times\mathrm{curl}\,\mathbf{n}),\ \hat{\mathbf{m}}\cdot(\hat{\mathbf{l}}\times\mathrm{curl}\,\mathbf{l}),\ \hat{\mathbf{m}}\cdot(\hat{\mathbf{n}}\times\mathrm{curl}\,\mathbf{n}),\ \hat{\mathbf{n}}\cdot(\hat{\mathbf{l}}\times\mathrm{curl}\,\mathbf{l})$$

and

$$\hat{\mathbf{n}}\cdot(\hat{\mathbf{m}}\times\mathrm{curl}\,\mathbf{m})$$

Let us assume first that e.g. $\hat{\mathbf{l}}$ is polar whereas $\hat{\mathbf{m}}$ and $\hat{\mathbf{n}}$ are not (case of the N_I phase). Then the first two scalar quantities are true scalars, while the last four do not exist in N_I. If e.g. $\hat{\mathbf{l}}$ and $\hat{\mathbf{m}}$ are polar whereas $\hat{\mathbf{n}}$ is not, then the first four of the six quantities just written down are true scalars, whereas the last two do not exist in N_{II}. Thus it is possible for N_{II} to construct two different scalars related to spontaneous bend. If all three directions are polar, all six scalar quantities written down are true scalars. We therefore arrive at the conclusion that for all three types of polar biaxial nematics (N_I, N_{II} and N_{III}) an occurrence of *spontaneous bend and splay* is possible. A thorough discussion of the implications of this result will be given in Ref.[25].

Assuming that one has three polar directions (case of the N_{III} phase), then one can construct easily the following additional scalar quantities:

$$\hat{\mathbf{l}} \cdot (\hat{\mathbf{m}} \times \operatorname{curl} \mathbf{n}), \;\; \hat{\mathbf{m}} \cdot (\hat{\mathbf{n}} \times \operatorname{curl} \mathbf{l}) \text{ and } \hat{\mathbf{n}} \cdot (\hat{\mathbf{l}} \times \operatorname{curl} \mathbf{m})$$

Inspection of the three scalar quantities written down reveals that these scalars are related to the possibility of spontaneous twist as it can occur in phases with C_1 symmetry. Rewriting the first term as $(\hat{\mathbf{l}} \times \hat{\mathbf{m}}) \cdot \operatorname{curl} \mathbf{n}$, one notices that the bracket is parallel to $\hat{\mathbf{n}}$. Thus for N_{III} spontaneous splay, twist and bend are possible.
We close this section by pointing out that the possibility of spontaneous bend has, to our knowledge, never been discussed before for a bulk 3D liquid crystalline phase.

7 Conclusions and perspective

In this manuscript we have investigated how the presence of one or more polar directions influences the symmetry and the macroscopic properties of biaxial nematic phases (phases with three-dimensional fluidity) and of biaxial orthogonal or tilted smectic phases (systems with anisotropic in-plane fluidity). As result we find that even for one polar direction the symmetry of the phase is reduced drastically to C_{2v} and for three polar directions even to C_1 (no symmetry left).
We mention in passing that we have looked previously at cholesteric and chiral smectic structures [29-31], that can also have C_1 symmetry locally, especially in polymeric systems. It must be emphasized, however, that in these cases the molecules were chiral, which in turn gave as typical overall symmetry of the liquid crystalline structures C_∞.
One of the major consequences of the study presented here is, by its design, a guide for the synthetic chemists to identify the phase structure of biaxial liquid crystalline phases with 2D or 3D fluidity. But naturally it is also a challenge to actually synthesize compounds with the phases predicted here. Clearly it would be rather exciting to find a smectic phase with in-plane fluidity, which shows stripes or rectangular patterns spontaneously, because two polar directions supply this system (C_Q) with spontaneous bend and splay. Even more stimulating would be the observation of a biaxial nematic phase (N_{III}), which allows the existence of spontaneous splay, bend *and* twist.
Two other major features also emerge from the present investigations. First of all there are many possible smectic phases, even concentrating on achiral molecules as constituents, that are biaxial and fluid in the planes of the smectic layering. And secondly, even given the structure locally, one can produce phases with different

overall symmetry, that is globally, just by stacking the layers in different ways. As an example, we have discussed in this paper the case of the C_{B2} phase, which has C_2 symmetry locally. Solely by stacking the two basic versions (LH and RH), one can generate phases that are ferroelectric, antiferroelectric, helielectric and antihelielectric or compose other stackings that have globally neither a helix nor a net polarization.
For the several as yet unidentified fluid smectic phases found in compounds composed of banana-shaped molecules [1-12], the physical properties discussed here - including symmetry, defects and electric properties - can serve as tools to actually identify the phases without emphasizing at this point in time questions of notation. To optimize properties of technological interest, it will also be useful to find out to what extent the many compounds generated over the last few years are miscible. One promising direction is the study of mixtures of compounds showing helielectric and antihelielectric phases. Recently, for example, we have put forward an effective internal field model [32], which accounts quantitatively for the observation of the reduction by more than a factor of two in the threshold field [33], when an antihelielectric phase with a fairly large threshold is doped with a helielectric C^* phase. Clearly this direction of research can help to increase the applicability of antihelielectric phases in the domain of electro-optics such as for displays.

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