FLUID BIAXIAL BANANA PHASES: SYMMETRY AT WORK

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Abstract

Fluid biaxial smectics made from compounds without asymmetric carbons but nevertheless with a spontaneous polarization are now known as *banana smectics* because of their molecular shape. Here we show that symmetry changes under parity (**r** → **- r**) are an efficient way to summarize and differentiate their electro-optic properties. Typical of fluid biaxial smectics, there are also a large number of stacking options endowing them with opto-electric properties spanning a broad range of economically viable applications. "Value-added features" of some banana smectics include a faster electro-optic response than found in liquid crystals with a helix structure, their steric property allowing rotations about an axis in a layer plane without compromising smectic layer stability and *ambidextrous chirality*.

Keywords: Fluid biaxial smectic liquid crystals. Helielectric, antiferroelectric, ferroelectric liquid crystals. Scalar invariants, spontaneous splay/bend/twist.

INTRODUCTION

Thermotropic smectic phases are layered structures with layer spacing on the order of 30–100Å. When the in-plane fluidity is isotropic, we have the well-known smectic A phase. When the in-plane fluidity is anisotropic, we can have the equally well-known smectic C phase. Both smectics C and A are dielectrics. The consequence is that while their "turn-on" response in an electric field can be fast (because they are 2-D fluids), the absence of a spontaneous polarization, **P**, means that their "turn-off" response is relatively slow (elastic relaxation). As a result, fluid biaxial smectics exhibiting a spontaneous polarization have long been of interest.

Until recently [1], the only way known to obtain **P** was in compounds composed of molecules with at least one asymmetric carbon. The macroscopic expression of chirality in these compounds is spontaneous twist, a helix structure with a hand and wavenumber $q_o = 2\pi/p_o$. p_o is the helix pitch. q_o is a bulk property that controls the electro-optic response times ("a little bit too slow for video-rate"*) of displays made from cholesterics (e.g. STN displays) and smectic C* (e.g. SSFLCs).

Most recently it was predicted [1] and found [2] that fluid biaxial smectic phases formed by certain compounds without any asymmetric carbons, could nevertheless have a spontaneous polarization, **P**. These phases are now known as *banana smectics* because of their molecular shape. In addition to the well-known properties of fluid biaxial smectic phases exhibited by rod-like molecules (e.g. C*), banana smectics have been shown to have a number of original features [2-13]. Here we use symmetry arguments to summarize and differentiate banana smectics from the more well-known liquid crystal phases. In particular, we argue that some banana phases can support an ambidextrous helix structure.

If q_o describes a right-handed helix, then, $-q_o$ describes a left-handed one. As the mirror image of a right-hand is a left-hand, under parity, $q_o \to -q_o$. q_o is a pseudo-scalar. This property allows scalar invariants (S) in the free energy density expansion in gradients of the director, **n**, where $\mathbf{n}^2 = 1$, for cholesterics and helielectrics such as smectic C* [14] of the form:

$$S_0 = q_o\, \mathbf{n} \cdot curl\mathbf{n} \neq 0$$

to account for spontaneous helix formation. For, under parity, $q_o \to -q_o$ and $\mathbf{n} \cdot curl\mathbf{n} \to -\mathbf{n} \cdot curl\mathbf{n}$. While each quantity has an *odd* number of negative signs, their product, $q_o \mathbf{n} \cdot curl\mathbf{n}$, has an *even* number, meaning S_0 is conserved under parity.

The free energy density for twist can be written: $f_2 = ½K_2[(\mathbf{n} \cdot curl\mathbf{n})^2 + 2S_0]$. The state without a helix, $\mathbf{n} \cdot curl\mathbf{n} = 0$ and $f_2 = 0$, is then no longer a minimum energy state. The true ground state has $\mathbf{n} \cdot curl\mathbf{n} = -q_o$, denoting spontaneous helix formation. It is energetically more favourable than no helix formation because, with $\mathbf{n} \cdot curl\mathbf{n} = -q_o$, $f_2 = -½K_2 q_o^2 < 0$. As free energies are only defined up to additive constants, usually $\tilde{f}_2 \equiv f_2 + ½K_2 q_o^2 = ½K_2[\mathbf{n} \cdot curl\mathbf{n} + q_o]^2$ is used to describe the constant helix ground state. When $\mathbf{n} \cdot curl\mathbf{n}$ depends on space, as it does for example to stabilize Blue Phases, other terms in the free energy density must also be considered.

* *A View of Two Years Progress in the Liquid Crystal Industry*, Nikkei Business Publications, Inc. 1992 Video in Japanese.

Another example of parity at work discussed by Pleiner and Brand [15] clarifies situations exhibiting spontaneous splay. Their argument also applies to banana liquid crystal phases. They considered a polar nematic for which there is a polarization vector, **p**. For, under parity, $\mathbf{p} \to -\mathbf{p}$ is not conserved but $S_1 = \text{div}\,\mathbf{p}$ is conserved. That is:

$$S_1 = \text{div}\,\mathbf{p} \neq 0$$

is a scalar invariant when there is a polarization vector, **p**.

S_1 is not associated with the spontaneous appearance of a space filling, defect free periodic structure, as is S_0. To make a liquid crystal phase exhibiting a spontaneous periodic space filling structure and which involves spontaneous splay, one needs symmetry features supporting, in addition, spontaneous bend and/or twist.

In the light of parity, we discuss here fluid biaxial smectic phases with no polarization vectors and those with one and two polarization vectors. Intrigued by recent observations of textures with rectangular symmetry in smectic B_7 [4], we mention briefly how the symmetry of fluid biaxial smectic phases with two polarization vectors can support spontaneous splay, bend and twist. Recent more complete accounts of the physical properties, scalar invariants and phase transitions of banana smectics can be found in [11-13].

PLANKS ON PLANES: NO POLAR VECTORS

A natural model for fluid biaxial smectics with no polarization vectors is provided by situating an array of planks on layers. When the planks are inclined so that one of their axes is at an angle to the layer normal, we have a smectic C phase with C_{2h} symmetry (Fig. 1a *top*). With two axes inclined to the layer normal we have smectic C_T with C_i symmetry. Smectic C_T has no mirror planes nor two-fold axes, but it does have inversion ($\mathbf{r} \to -\mathbf{r}$) symmetry (Fig. 1a *bottom*).

While symmetry distinguishes smectic C_T from C, they are not so easy to tell apart in the polarizing microscope. However, smectic C* and C_T^* have quite different electro-optic properties.

Locally C* has C_2 symmetry with its spontaneous polarization vector, **P**, in the plane of the layers. Because C* is chiral (has a hand), it has globally D_∞ symmetry. Smectic C* is helielectric [14].

In contrast, smectic C_T^* has locally C_1 and globally C_∞ symmetry. As a result, its polarization vector, **P**, is at an angle to the smectic layers. In its simplest stacking, C_T^* is helielectric in the plane of its layers and ferroelectric perpendicular to them (conical helielectric).

As ferroelectrics are always pyroelectric, a change in temperature results in a change in **P**. For example, locally heating C_T^* could result in a rotation of **P** to be more (or less) perpendicular to the layers. The resulting change in intensity of electric fields, e.g. perpendicular to the smectic planes, can then be detected and used to convert a heat signal to an electric signal.

An example where this may be useful is for the conversion of an infra-red optical signal carried by a fibre optic element to an electric signal carried by copper wires. In the telecommunications industry, inexpensive opto-electric transducers are needed to bring broad band information carried by optical fibres to buildings wired for electricity. While smectic C_T^* can do the job, its helix structure tends to slow its response.

In addition, rotating plank shaped molecules so that **P** is perpendicular to the layers (say), forces a change in the layer spacing. In a worst case scenario, such rotations will irreversibly destabilize flat layer structures thereby reducing the useful lifetime of C_T^* as an opto-electric transducer. It is conceivable that this particular limitation posed by "planks on planes" can be finessed by banana smectics.

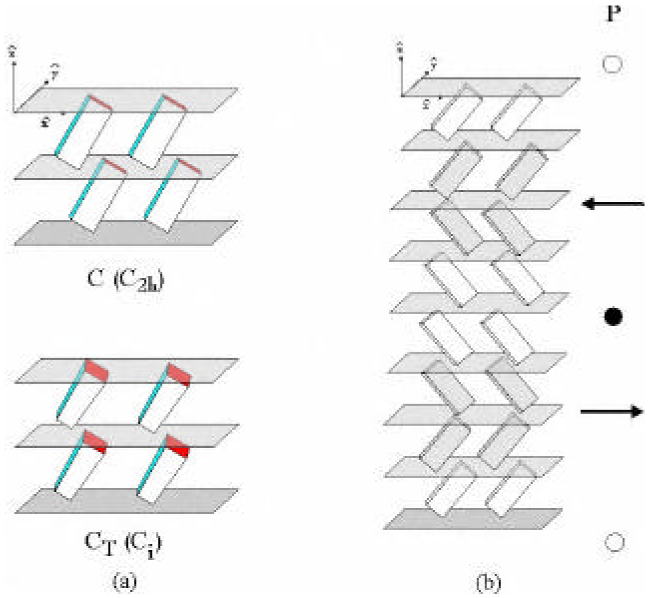

Fig. 1. a) Smectic C (*top*) and smectic C_T (*bottom*). b) Antiferroelectric with two layers C_A alternating with two layers C* [16]. Eight layer P modulation on right. o: **P** "in" and •: **P** "out".

Antihelielectric Planks on Planes

Stacking chiral C-type planks in pairs with opposite **P** on neighboring layers, results in antiferroelectric liquid crystals called smectic C_A [17,18]. This type of stacking is correlated with a large tilt angle for the planks [18].

In smectic C_A, when **P** is modulated over two layers, its threshold field is large [16]. It has been shown [19], however, that the threshold field can be reduced to within range of CMOS compatible drive electronics by mixing C_A with C*. This has led to antiferroelectric displays called TLAFs [20]. TLAFs have antiferroelectric liquid crystal hallmarks: a wide *isotropic* viewing angle and fast “turn-off response” [18,21]. In the light of one model [16] where the threshold field is zero for a ~50% C^*/C_A mixture, this is interpreted as a **P** modulation over more than two layers (Fig. 1b).

MINIMAL BANANA SMECTICS: ONE POLAR VECTOR

Banana smectics are a new avenue to develop smart materials from fluid biaxial smectics [1, 11-13]. Fig. 3 shows the minimal banana smectic phases that have one polarization vector, $\mathbf{P} \| \mathbf{m}$, even when composed of molecules with no asymmetric carbons. We call them “minimal banana smectics” to distinguish them from the “peelable bananas” or dolphin smectics which have two polar vectors [12,13]. The reference frame attached to the minimal bananas in Fig. 2 is $[\mathbf{l}, \mathbf{m}, \mathbf{n}]$ with $\mathbf{m} \| \mathbf{P}$. The layer normal is **k.** Their properties are summarized in Table 1 along with those of smectic C for comparison.

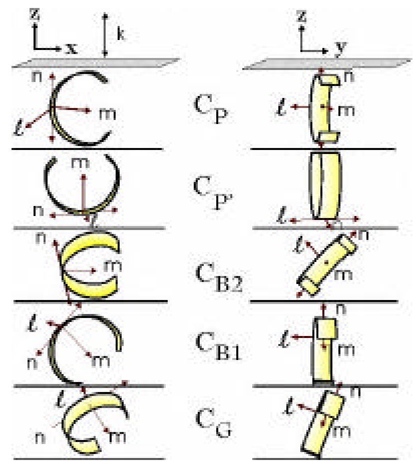

Fig. 2. Minimal banana smectics.

Class	Symmetry	Electro-optics	Helix
C	C_{2h}	dielectric	no
C_P	C_{2v}	ferro or ferri-electric **P** = $(P_x, 0, 0)$	no
$C_{P'}$	C_{2v}	ferro or ferri-electric **P** = $(0, 0, P_z)$	no
C_{B2}	C_2	ferro or ferri-electric **P** = $(P_x, 0, 0)$	yes
C_{B1}	C_{1h}	ferro or ferri-electric **P** = $(P_x, 0, P_z)$	no
C_G	C_1	ferro or ferri-electric **P** = (P_x, P_y, P_z)	yes

Table 1 after [11]

Smectic C_P

In the case of smectic C_P [1], the banana has $\mathbf{n} \| \mathbf{k}$ and $\mathbf{m} \perp \mathbf{k}$. C_P has vertical mirror planes and a 2-fold axis, i.e. C_{2v} symmetry. The 2-fold axis which lies in the mirror plane is $\mathbf{m} \| \mathbf{P}$. C_P can be either ferroelectric or antiferroelectric depending upon how it is stacked.

The symmetry of C_P provides physical arguments for recent patents awarded to Deutsche Telekom [22] for highly efficient electrets made from smectic liquid crystal polymers and monomers composed of molecules without any asymmetric carbons. An external electric field uniformly orients **P** in the plane of layers. The material is then cooled below the glass transition to "freeze in" the "poled" state. The large pyroelectric properties of their material exclude it being a dielectric, such as smectics A or C which have no polarization vectors. The fact that their material has no asymmetric carbons excludes it from being smectic C*. The fact that the large electric field can be stored indefinitely in the glassy state excludes the presence of free electrons in their electrets.

Smectic $C_{P'}$

In $C_{P'}$, the bananas are oriented with their polar direction $\mathbf{P} \| \mathbf{m} \| \mathbf{k}$ [12,13]. Like smectic C_P, $C_{P'}$ has vertical mirror planes and a 2-fold axis, i.e. C_{2v} symmetry. The 2-fold axis which lies in the mirror plane is $\mathbf{m} \| \mathbf{P}$. $C_{P'}$ can also be either ferroelectric or anti-ferroelectric depending upon how it is stacked. With no in-plane polarization, $C_{P'}$ may have been observed in some highly symmetric bananas.

Smectic C_{B2}: No mirror planes and Ambidextrous Helices

Rotating **n** and **l** in C_P around $\mathbf{m} \| \mathbf{P}$ removes all mirror planes giving rise to a chiral structure called smectic C_{B2} [11]. The C_{B2} structure is unchanged when $\mathbf{l} \rightarrow -\mathbf{l}$ *and* $\mathbf{n} \rightarrow -\mathbf{n}$ together. In contrast, the C_P structure is invariant when $\mathbf{l} \rightarrow -\mathbf{l}$ and $\mathbf{n} \rightarrow -\mathbf{n}$ separately. The pseudo-scalar for phases without mirror symmetry and one polar vector, **m**, is: $\tilde{q} \equiv (\mathbf{l} \times \mathbf{n}) \cdot \mathbf{m}.$ As a result, a scalar invariant can be constructed for C_{B2} [12]:

$$S_2 = (\mathbf{l} \times \mathbf{n}) \cdot \mathit{curl}\, \mathbf{m} \neq 0.$$

As $(\mathbf{l} \times \mathbf{n})$ can be either parallel or anti-parallel to **m**, S_2 represents an *ambidextrous helix*. The spontaneous appearance of both left and right-handed helices is possible in bulk smectic C_{B2}.

Besides $S_2 \neq 0$, smectic C_{B2} has two other twist scalar invariants [13]. Thus, while S_2 is a scalar invariant in the free energy for smectic C_{B2}, neither its hand nor the direction of its helix structure is fixed by symmetry.

Depending on stacking sequence one can obtain ferro- as well as anti-ferroelectricity without a helical structure; helielectric and antihelielectric structures without any net polarization and even more complex arrangements [12]. Thus, while smectic C_{B2} has C_2 symmetry in one layer, globally, its symmetry can be D_∞, similar to that of C* only when it makes a simple helix structure and in its simplest stacking.

Smectic C_{B1}

Some of the limitations of smectic C_{B2} may not be present in smectic C_{B1} where **n** and **m** are at an angle to **k**, $\mathbf{l} \perp \mathbf{k}$ and $\mathbf{P} \| \mathbf{m}$ [11]. C_{B1} can be obtained by rotating **n** and **m** in the C_P or $C_{P'}$ phase about $\mathbf{l}$. Smectic C_{B1} has a mirror plane (like C_P) but no symmetry axis and therefore C_{1h} symmetry. Its structure is not chiral (no helix) so its electro-optic properties are either ferro or antiferroelectric with a potentially larger pyroelectric coefficient than smectic C_P. In this context, studies of C_P ($C_{P'}$) $\leftrightarrow$ C_{B1} phase transitions would be helpful [13].

Smectic C_G

In smectic C_G, where G stands for "general" [23], neither **l, m** nor **n** are zero or 90° to **k**. Smectic C_G is chiral because it has no mirror planes, even when its molecular composition has no asymmetric carbons. As in the case of smectic C_{B2}, neither the chirality nor the helical direction in C_G is fixed by symmetry. A striking feature of smectic C_G is the number of ways it can stack in layers [11]. With C_1 symmetry, C_G supports spontaneous splay, bend and twist [13].

<u>Stacking Ambidextrous Bananas</u>

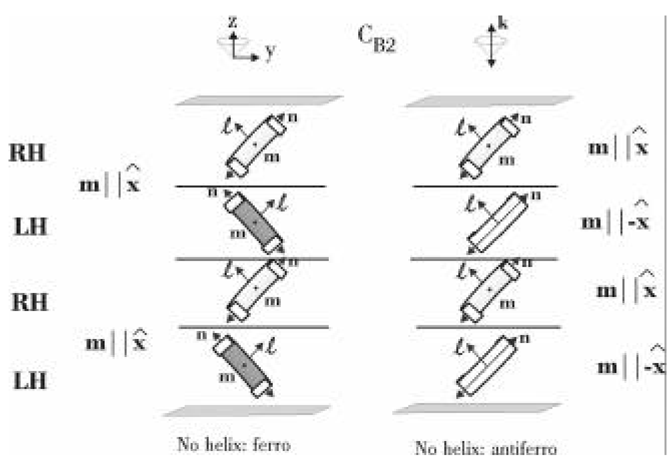

Fig. 3. Ferro and antiferroelectric stacking with no net chirality for C_{B2} [12].

The presence of both hands can result in a number of situations. The simplest is phase separated regions of left and right handed helices. One can also imagine a bilayer packing of left and right handed layers with no net hand (Fig. 3) or even interpenetrating left and right handed helices. The options seem limitless. In most cases, smectic C_{B2} is expected to be an ambidextrous helielectric or antihelielectric with pitch $p_o \sim 1$-10μm because $S_2 \neq 0$. Despite a macroscopic length scale (p_o), the characteristic time associated with ambidextrous helielectric smectic C_{B2}

will likely be faster than C* with fewer defects. The “turn-off” time of ambidextrous antihelielectric C_{B2} may even be faster than that of C_A.

DOLPHIN SMECTICS: TWO POLAR VECTORS

Orthogonal “peelable banana” and dolphin smectics are denoted smectics $C_{Q'}$ and C_Q, respectively [12,13]. Both have the same symmetry (C_{1h}) and

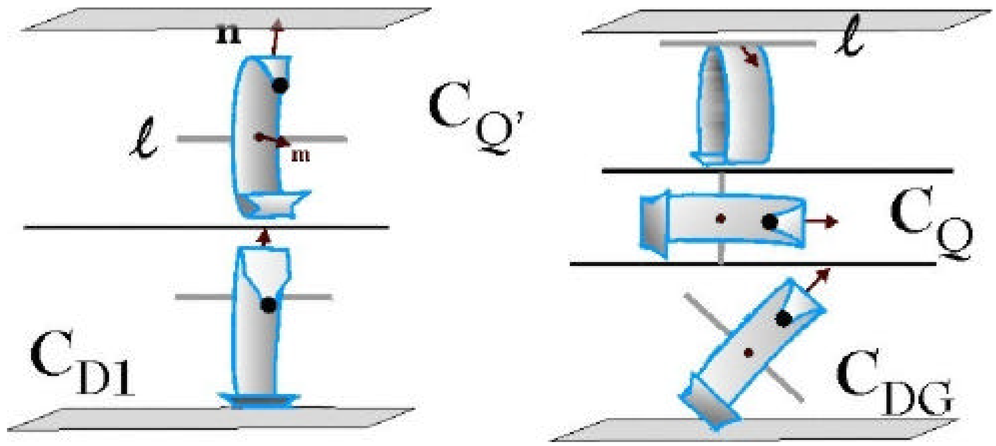

Fig. 4. Dolphin smectics with two polar vectors, **n** and **m**. In smectic $C_{Q'}$, either **m** or **n** is ⊥ **k**. In C_Q, both are ⊥ **k**.

two polar vectors, here **m** and **n** (Fig. 4). They differ in that in smectic C_Q, both **n** and **m** are ⊥ **k** while in smectic $C_{Q'}$ only one of them is ⊥ **k.** A general account of these phases and their phase transitions is given in [13].

The two variants of $C_{Q'}$ show that while they both have the same symmetry, their layer spacings would be different (Fig. 4 *top*). Tilting C_Q about **n** or **m** always leads to a phase with C_1 symmetry, called smectic C_{DG}. Tilting smectic $C_{Q'}$ about its polar axis **m** also leads to smectic C_{DG} (Fig. 4 *lower right*). But, tilting $C_{Q'}$ about its one non-polar axis, **l**, leads to a phase with C_{1h} symmetry called smectic C_{D1}.

Smectic C_{D1} has the possibility of spontaneous splay and bend while smectic C_{DG} has the possibility of spontaneous splay, bend and twist [12,13]. Banana and dolphin smectics thus pose some outstanding questions [24]. For example, what is the ground state when there is spontaneous splay, bend and twist or even only spontaneous splay and bend? Indeed, do dolphin smectics have a simple ground state? The results of Pelzl et al. [5] suggest that there are many different states with energies very close to that of the ground state.

CONCLUSIONS

By identifying the essential features of biaxial fluid smectic phases, parity provides a compact framework to finely differentiate their characteristic properties. Here we have considered biaxial fluid smectics with:

1. **No Polar Vectors**: exemplified as “planks on planes”. We highlighted the novel smectic C_T^* phase which is a conical helielectric. A simple “8-layer model” for C_A is presented to account for thresholdless antiferroelectricity.
2. **One Polar Vector**: exemplified by minimal bananas with many stacking options. Minimal bananas are a novel route for fluid biaxial smectic phases to have a polarization, **P**, in materials without asymmetric carbons. Minimal bananas can exhibit either spontaneous ambidextrous twist or no net twist. There is an important aspect concerning the geometric properties of bananas: due to their shape they can be rotated in the layer planes about the axis perpendicular to **P** with a relatively small change in the layer spacing. This appears to be an attractive feature for applications exploiting their large pyroelectric properties.
3. **Two Polar Vectors**: referred to as “peelable” bananas, or dolphin smectics. “Peelable” bananas or “dolphin smectics” may be required to account for the stable smectic B_7 phase of Pelzl et al. [5].

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