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Fluid Biaxial Banana Smectics: Symmetry at Work

P. E. Cladis[1], H. R. Brand[2] and H. Pleiner[3]

[1]Advanced Liquid Crystal Technologies, POB 1314, Summit, NJ 07902, USA

[2]Theoretical Physics III, University of Bayreuth, 95440 Bayreuth, Germany

[3]Max-Planck-Institute for Polymer Research, 55021 Mainz, Germany

Perhaps one of the most surprising results in the past 10 years was the prediction of Brand *et al*. {1} that fluid biaxial smectics made from compounds without asymmetric carbons could, by symmetry, have a spontaneous polarization, P, in the layer plane. They called this construct, which can be either ferroelectric or antiferroelectric, smectic C_P. Advances gained from their prediction include the development of highly efficient electrets for broad-band telecommunications {2, 3} as well as a basic nonlinear model {4} for TLAFs, *thresholdless antiferroelectrics* {5}, now seen in beautiful, CMOS compatible, active matrix liquid crystal displays {6} (figure 1).

Fluid biaxial smectics made from compounds without asymmetric

In this issue:

Figure 1. Casio's 2.5-inch diagonal 832×´230 active matrix TLAF prototype. The drive voltage is ±2.5 V; time to scan one line, 60 µs; and contrast ratio over 300. The upper right is a front view. The other images show no grey scale inversion nor colour change even when the viewing angle is as in the lower right [6]. Courtesy T.Yoshida: tyoshida@drd.hlb.casio.co.jp

carbons but nevertheless with a spontaneous polarization, **P**, are now known as *banana smectics* because of their molecular shape [7–19]. How their symmetry changes under parity ($\mathbf{r} \rightarrow -\mathbf{r}$) is an efficient way to summarize and differentiate their electro-optic properties [1, 16–19].

Typical of fluid biaxial smectics, there are a large number of stacking options endowing banana smectics with opto-electric properties spanning an extremely broad range of economically viable applications. 'Value-added features' of some banana smectics include: (a) a faster electro-optic response than liquid crystals with a helix structure; (b) their steric property allowing possible rotations about an axis in a layer plane with minimal changes in the smectic layer spacing; and (c) *ambidextrous chirality*.

Thermotropic smectic phases are layered structures with layer spacing on the order of 30–100 Å. 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 2D fluids), the absence of a spontaneous polarization, **P**, means that their 'turn-off' response is relatively slow (elastic relaxation).

For fluid biaxial smectic liquid crystals composed of molecules with at least one asymmetric carbon, the macroscopic expression of chirality is spontaneous twist, a helix structure with a hand and wavenumber $q_o = 2\pi/p_o$. p_o is the helix pitch. 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, $q_o \rightarrow -q_o$. 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* [20] of the form:

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

to account for spontaneous helix formation. For, under parity, $q_o \rightarrow -q_o$ and $\mathbf{n} \bullet \mathrm{curl}\ \mathbf{n} \rightarrow -\mathbf{n} \bullet \mathrm{curl}\ \mathbf{n}$. While each have an *odd* number of

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negative signs, their product, q_o**n**•curl **n**, has an *even* number, meaning S_0 is conserved under parity.

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).

Here, in the light of parity, we give a synopsis of biaxial fluid smectic phases with no polar vectors and those with one or two polar vectors [19]. Recent more complete accounts of the physical properties, scalar invariants and phase transitions of fluid biaxial smectics can be found in [16–18].

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 (figure 2(*a*), 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 ($\mathbf{r} \rightarrow -\mathbf{r}$) symmetry (figure 2(*a*), 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 [20].

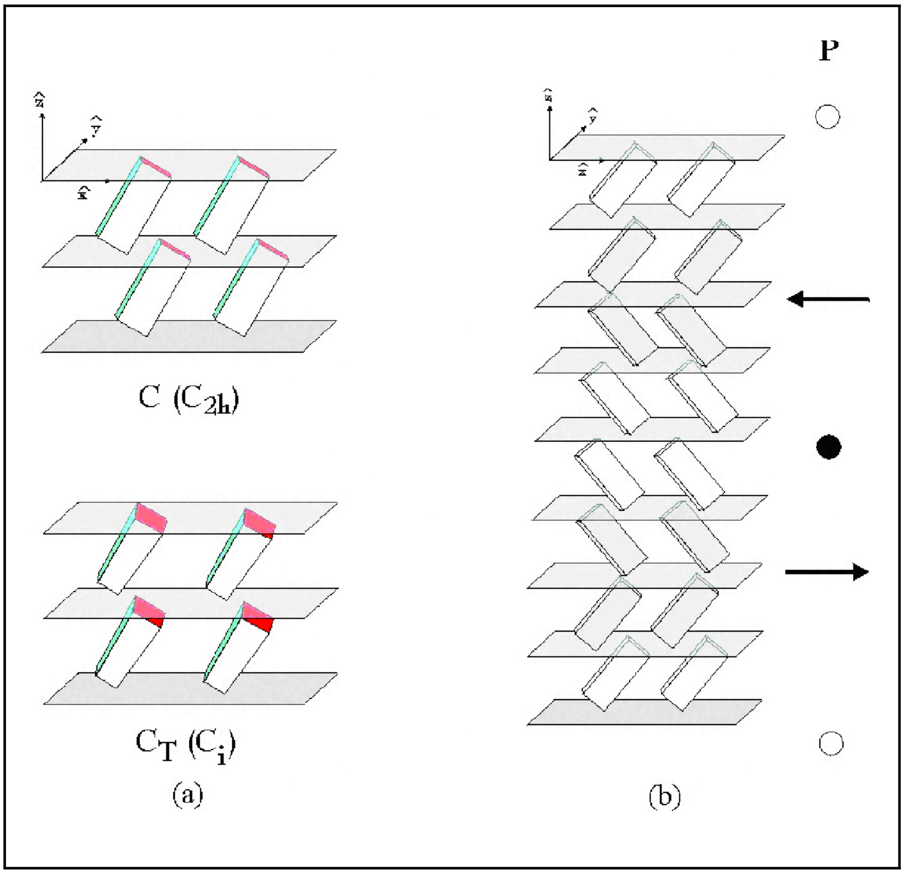

Figure 2. (*a*) Smectic C (top) and smectic C_T (bottom). (*b*) Antiferroelectric with two layers CA alternating with two layers C* [4]. Eight layer P modulation on right. O: **P** "in" and •: **P** "out".

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 infrared 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.

Antihelielectric planks on planes

Stacking chiral C-type planks in pairs with opposite **P** on neighbouring layers, results in antiferroelectric liquid crystals called smectic

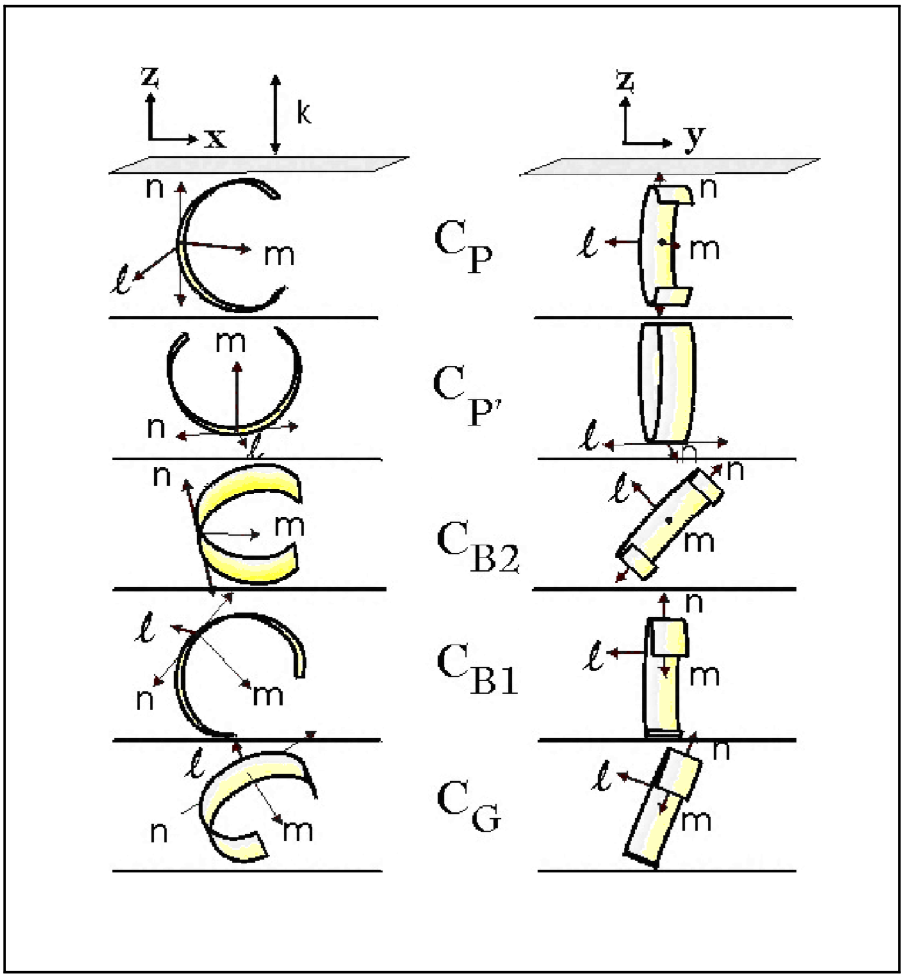

Figure 3. Minimal banana smectics.

C_A [21, 22]. This type of stacking is correlated with a large tilt angle for the planks [22].

In smectic C_A, when **P** is modulated over two layers, its threshold field is large [4]. It has been shown [5], however, that the threshold field can be reduced to within the range of CMOS compatible drive electronics by mixing C_A with C*. This has led to antiferroelectric displays called TLAFs [6]. TLAFs have antiferroelectric liquid crystal hallmarks: a wide *isotropic* viewing angle (figure 1) and fast 'turn-off response' [22, 23]. In the light of one model [4] where the threshold field is zero for a ~50% C*/CA mixture, this is interpreted as a **P** modulation over more than two layers (figure 2(*b*)).

Table 1. After [16].

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

Minimal banana smectics: one polar vector

Banana smectics are a new avenue to develop smart materials from fluid biaxial smectics [1, 16–19]. Figure 3 shows the minimal banana smectic phases which have one polarization vector, **P** ∥ **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 [17, 18]. The reference frame attached to the minimal bananas in figure 3 is [**l**, **m**, **n**] with **m** ∥ **P**. The layer normal is **k**. Their properties are summarized in table 1 along with those of smectic C.

Smectic C_P

In the case of smectic C_P [1], the banana has **n** ∥ **k** and **m** ⊥ **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 **m** ∥ **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 [3] 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

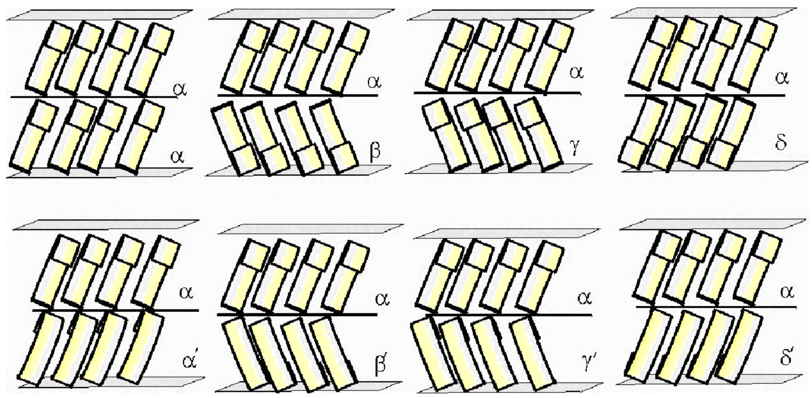

Figure 4. Smectic C_G's many 2-layer stackings.

'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 $\mathbf{P} \parallel \mathbf{m} \parallel \mathbf{k}$ [17–19]. 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 $\mathbf{m} \parallel \mathbf{P}$. $C_{P'}$ can also be either ferroelectric or antiferroelectric 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}

Rotating $\mathbf{n}$ and $\mathbf{l}$ in C_P around $\mathbf{m} \parallel \mathbf{P}$ removes all mirror planes giving rise to a chiral structure called smectic C_{B2} [16]. C_{B2} symmetry is unchanged when $\mathbf{l} \to -\mathbf{l}$ *and* $\mathbf{n} \to -\mathbf{n}$ together. In contrast, C_P symmetry is invariant when $\mathbf{l} \to -\mathbf{l}$ and $\mathbf{n} \to -\mathbf{n}$ separately. A scalar invariant can then be constructed for C_{B2} [17]:

$$S_2 = (\mathbf{l} \times \mathbf{n}) \bullet \mathrm{curl}\ \mathbf{m} \neq 0.$$

As $(\mathbf{l} \times \mathbf{n})$ can be either parallel or anti-parallel to $\mathbf{m}$, 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 [18]. 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 ferroelectricity, as well as antiferroelectricity without a helical structure; helielectric and antihelielectric structures without any net polarization and even more complex arrangements [17, 19]. Thus, while smectic C_{B2} has C_2 symmetry in one layer, globally, its symmetry can be D_∞, similar to that of C*, only e.g. when it makes a simple helix structure and is in its simplest stacking.

Smectic C_{B1}

Some of the limitations of smectic C_{B2} may not be present in smectic C_{B1}, where $\mathbf{n}$ and $\mathbf{m}$ are at an angle to $\mathbf{k}$, $\mathbf{l} \perp \mathbf{k}$ and $\mathbf{P} \parallel \mathbf{m}$ [16]. 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 opto-electric properties are either ferroelectric or antiferroelectric with a potentially larger pyroelectric coefficient than smectic C_P. In this context, studies of C_P (or $C_{P'}$) $\leftrightarrow$ C_{B1} phase transitions would be helpful [18].

Smectic C_G

In smectic C_G, where G stands for 'general' [24], neither $\mathbf{l}$, $\mathbf{m}$ nor $\mathbf{n}$ are zero or 90° to $\mathbf{k}$. Smectic C_G is chiral, 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 smectic C_G is fixed by symmetry. A striking feature of smectic C_G is the number of ways it can stack just two of its layers (figure 4) [16].

Stacking ambidextrous bananas

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 or even interpenetrating left- and right-handed helices [19]. The options seem limitless. In any case, as $S_2 \neq 0$, smectic C_{B2} is expected to be an ambidextrous helielectric or antihelielectric with pitch $p_o \sim 1$–$10\ \mu$m.

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 [19]. The 'turn-off' time of ambidextrous antihelielectric C_{B2} may even be faster than that of C_A.

'Peelable bananas' and dolphins: two polar vectors

Orthogonal 'peelable banana' and dolphin smectics are denoted smectics $C_{Q'}$ and C_Q, respectively [17, 18]. Both have the same symmetry and *two* polar vectors one of which, **m**, is in the plane of the layers. They differ in that in smectic C_Q, the second polar vector (i.e. **l**) is also in the plane of the layers while in smectic $C_{Q'}$ it is perpendicular to the layers (i.e. **n**). Tilting C_Q always leads to a phase with C_1 symmetry, called smectic C_{DG}, which is like C_G but with two polar vectors, **m** and **l**. Tilting smectic $C_{Q'}$ about its polar axis **m** also leads to smectic C_{DG}. But, tilting $C_{Q'}$ about its one non-polar axis, **l**, leads to a phase with C_{1h} symmetry called smectic C_{D1}, like C_{B1} but with two polar vectors, **n** and **m** for 'peelable bananas'.

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