Biaxial Smectic Banana Phases

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Introduction

Smectic phases made up of banana-shaped molecules have drawn increasing interest recently [1–7] due to their unusual properties. If banana-shaped molecules are put into a layer in an ordered fashion, they are biaxial, where (at least) one axis ($\hat{\boldsymbol{m}}$) is polar (i.e. *not* having a $\hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ invariance), while the other ($\hat{\boldsymbol{n}}$) can be taken as a nematic-type direction (with $\hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ invariance). We assume $\hat{\boldsymbol{n}}$ to be perpendicular to $\hat{\boldsymbol{m}}$ without loss of generality. In the following we will discuss what kind of phases are possible, when such molecules are either untilted, or tilted once or twice [8].

The untilted case (either $\hat{\boldsymbol{n}}$ or $\hat{\boldsymbol{m}}$ is parallel to the layer normal $\hat{\boldsymbol{k}}$) leads to the polar smectic C_P phase [1] of orthorhombic C_{2v} symmetry [9]. If $\hat{\boldsymbol{n}}$ (but not $\hat{\boldsymbol{m}}$) is tilted, the smectic C_{B2} phase is obtained that still has a two-fold polar axis, but no longer a mirror plane. It is of the monoclinic C_2 symmetry and chiral, although the molecules are achiral. If $\hat{\boldsymbol{m}}$ and $\hat{\boldsymbol{n}}$ are tilted, but lie in the same plane with $\hat{\boldsymbol{k}}$, there is no symmetry axis left, but there is still a mirror plane. This smectic C_{B1} phase is of monoclinic C_{1h} symmetry with a polar direction in the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{n}}$ plane, but no chirality. If both, $\hat{\boldsymbol{n}}$ as well as $\hat{\boldsymbol{m}}$ are tilted, but do not form a plane with $\hat{\boldsymbol{k}}$, then no symmetry is left at all (triclinic C_1 symmetry). This most general smectic C phase, C_G, has a polar axis at an arbitrary direction and is chiral although the molecules are achiral. Neither the chirality nor the helical direction is fixed by symmetry.

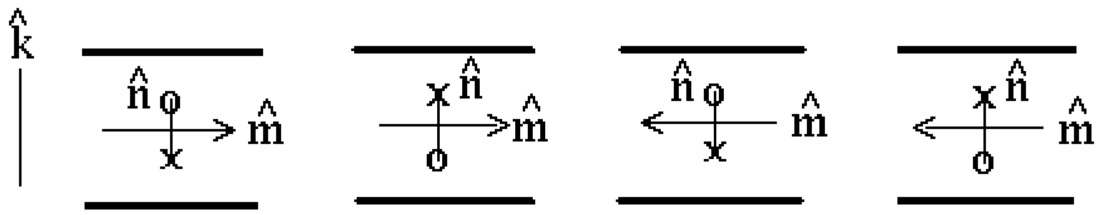
However, in smectic phases the layers can be stacked upon each other non-uniformly, i.e. with the polar axis oriented alternately or helically from layer to layer giving rise to antiferroelectricity and helielectricity, respectively. Such non-uniform stacks can show a global symmetry and behavior, which is quite different from the local one of a single layer. Due to the richness of tilted banana phases, there is a vast number of different possibilities, how layers can be stacked together. However, due to lack of space we will only briefly discuss this topic.

Smectic Phases with Banana-type Biaxiality

SMECTIC C_P PHASE: In the untilted case, where $\hat{\boldsymbol{n}}$ is parallel to the layer normal $\hat{\boldsymbol{k}}$, the polar direction lies in the layer planes. This phase has a two-fold rotation axis (along the $\hat{\boldsymbol{m}}$ direction) and a mirror plane that contains the polar axis $\hat{\boldsymbol{m}}$, resulting in a C_{2v} (orthorhombic) symmetry [10]. It has been called C_P phase in [1] since it is ferroelectric [11], if stacked uniformly. It can be antiferro- or ferri-electric for different stacks. The C_P phase has possibly be seen experimentally [3,4]. In contrast to a chiral C^* phase, the C_P phase is achiral and does not show any helix. Thus, there is no need for unwinding any helix by surface forces or external fields before switching.

A phase of the same C_{2v} symmetry is obtained, if $\hat{\boldsymbol{m}}$ is along the layer normal $\hat{\boldsymbol{k}}$, and $\hat{\boldsymbol{n}}$ is perpendicular to the latter. The only difference to the $\mathrm{C_P}$ phase is that this phase has a polarization across, instead of within the layers. Experimentally such a phase could be realized by the polymeric system of [12], if the bulky side-chains have a dipole moment along their side-on spacers.

Smectic $\mathrm{C_{B2}}$ Phase: Next we discuss the case that $\hat{\boldsymbol{n}}$ is tilted with respect to the layer normal $\hat{\boldsymbol{k}}$, but the polarisation $\hat{\boldsymbol{m}}$ stays perpendicular to it. This phase, called smectic $\mathrm{C_{B2}}$ in [8], still has a two-fold rotation axis ($\hat{\boldsymbol{m}}$), but no mirror plane at all, since $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{m}}$ and $\hat{\boldsymbol{n}}$ do not lie in one plane (Fig.1). In such C_2-symmetric (monoclinic) phases the direction of the polarisation is fixed by symmetry (similar to the smectic C* case). C_2 symmetry also implies chirality (optical activity), since there is no inversion center. In the standard smectic C* phases the chirality of the molecules itself breaks the mirror symmetry (of the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{m}}$ plane) while in the $\mathrm{C_{B2}}$ phases the additional tilt of $\hat{\boldsymbol{n}}$ is responsible for chirality.



a) b) c) d)

Fig.1 *a) The smectic* $\mathrm{C_{B2}}$ *phase, with in-plane polarisation and* $\hat{\boldsymbol{n}}$ *tilted, b) a variant of it with different handedness, c) and d) the respective forms with opposite polarisation. Crosses (circles) denote out-of- (into-)paper components.*

Taking the Fig.1a to be a left-handed variant (take $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{m}}$ and the out-of-paper component of $\hat{\boldsymbol{n}}$) then Fig.1d is also left-handed, while Figs.1b and 1c show right-handed version of this phase. Of course, chirality can lead to a helical stacking and the phase is then heli-electric (like C* [13]). However, since both versions are completely equivalent, one can find both, left- and right-handed helices, statistically distributed in a given sample (in contrast to C* phases, where the molecules' handedness chooses one type of chirality). It is also possible that layers of opposite handedness are stacked together leading to globally achiral phases. Another difference to conventional C* phases comes from the possibility to stack layers antiferroelectrically. Stacking variants of Fig.1a with 1c (or 1b with 1d) alternatively, one gets locally antiferroelectric structures, which are globally achiral. Stacking 1a with 1d (or 1b with 1c) the local structures are again antiferroelectric but globally chiral. The last possibility, locally ferroelectric and globally achiral, results from stacks 1a with 1b (or 1c with 1d). In any case, the polarisation (or staggered polarisation in the antiferroelectric case) is in-plane. Such a phase has been described and discussed in [5].

Smectic $\mathrm{C_{B1}}$ Phase: Instead of tilting the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure about $\hat{\boldsymbol{m}}$, which has lead to the $\mathrm{C_{B2}}$ phase discussed above, one can rotate it about $\hat{\boldsymbol{n}} \times \hat{\boldsymbol{m}}$, which gives a phase, where $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ are both tilted with respect to the layer normal $\hat{\boldsymbol{k}}$, but where these three directions all lie in one plane (Fig.2). This plane is of course a mirror plane, but there is no symmetry axis left and the phase (called $\mathrm{C_{B1}}$ in [8]) has C_{1h} (monoclinic) symmetry. It is achiral and does not show helices due to the mirror plane. By symmetry the polarisation ($\hat{\boldsymbol{m}}$) is forced to lie in the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{n}}$ plane, but within this plane it can have any direction depending on temperature, pressure, chemistry etc. (For the special cases $\hat{\boldsymbol{m}} \perp$ or $\parallel \hat{\boldsymbol{k}}$, the $\mathrm{C_P}$ phase is obtained). Thus the $\mathrm{C_{B1}}$ phase can be ferroelectric with a component of the polarisation out of the layer planes. However, there are four different ways of stacking the various modifications on top of each other. Alternating the variants of Fig.2a with 2b (or 2c with 2d) results in a completely antiferroelectric structure, while 2a with 2c (or 2b with 2d) gives a structure that is antiferro- in, but ferroelectric across, the layers; while for 2a stacked with 2d (or 2b with 2c) there is ferro- in, and antiferroelectricity across, the layers.

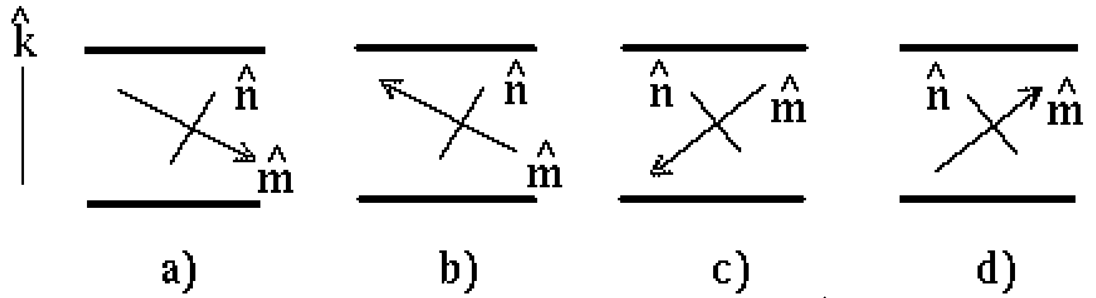


Fig.2 *The smectic* $\mathrm{C_{B1}}$ *phase, where the polarisation lies in the* $\hat{\boldsymbol{k}}/\hat{\boldsymbol{n}}$*-plane, thus having also a component perpendicular to the layers. Shown are all four different modifications concerning the polarization.*

Smectic $\mathrm{C_G}$ Phase: Tilting the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure about *two* different axes results in the most general smectic C phase possible, the smectic $\mathrm{C_G}$ phase mentioned already briefly in [14]. The directions $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ are tilted with respect to the layer normal $\hat{\boldsymbol{k}}$, but do not form a common plane with it (Fig.3). Thus, there is no mirror plane, no rotation axis left, and no inversion symmetry, because of the polar direction, i.e. this phase has no symmetry element at all, a situation that is called C_1 symmetry (triclinic) by crystallographers. The polarisation is not fixed by symmetry, but can have any direction depending on temperature, pressure, chemistry etc., i.e. generally there is a component across the layers and two within the layers (say parallel and perpendicular to the tilt direction of $\hat{\boldsymbol{n}}$). Of course, this phase comprises all the intricacies of the $\mathrm{C_{B1}}$ and $\mathrm{C_{B2}}$ phases. It is chiral, which leads to helices with arbitrary handedness and arbitrary helical direction. There are ferro- and antiferroelectric, as well as complicated mixed stacks possible, where e.g. ferroelectricity (antiferroelectricity) holds in 0, 1, 2, or 3 (3, 2, 1, or 0) directions, say across the layers, parallel, and perpendicular to the tilt direction of $\hat{\boldsymbol{n}}$ within the layers. All these different stacks can be globally chiral or achiral. Fig.3 shows the 8 different possibilities of arranging the polarisation, the inclination (the tilt direction of $\hat{\boldsymbol{n}}$ out of the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{m}}$ plane) and the handedness.

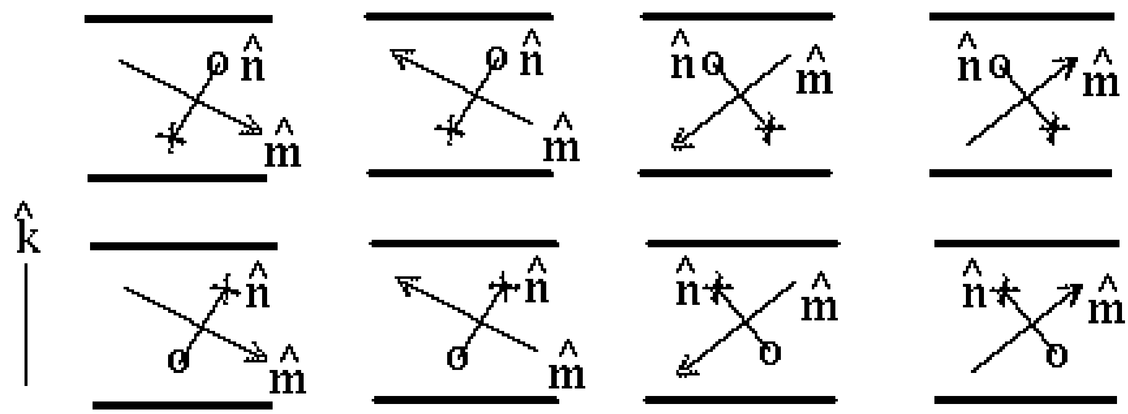


Fig.3 *The most general smectic* $\mathrm{C_G}$ *phase with 8 different modifications concerning the polarisation, handedness and inclination (crosses/circles denote out-of-/ into-paper components).*

Smectic Phases with Nematic-type Biaxiality

If instead of bananas biaxial nematic-like objects are put into layers, the resulting phases are never polar, since inversion symmetry is always present. The untilted case is the C_M phase with D_{2h} symmetry [14], both single tilted cases are equivalent to the ordinary C phase (C_{2h} symmetry), while the twice tilted phase C_T has C_i symmetry [18], where inversion symmetry is the only symmetry left.

Hydrodynamics

Hydrodynamically all these phases are generally smectic C phases described by two symmetry variables, the layer displacement and the rigid rotation of the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure (the $\hat{\boldsymbol{c}}$ director) about the layer normal $\hat{\boldsymbol{k}}$. Rotations of the layer normal and bend of the layers are described by gradients of the displacement variable. A nonlinear description for arbitrarily large layer and director distortions is given in [15] for the case of an ordinary C phase. If there is a helix, the director rotations can be replaced by the helix displacement along the helical axis [16]. However, due to the very low symmetries involved [17], due to complicated ferro- and antiferroelectric stacks, and due to possibly very complicated helical structures, the actual description can be very complicated, especially if external electric fields are involved. Some aspects are discussed in [8].

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[9] We use Schönflies notation, which is related to other notations by D_{2h} = 2/m 2/m 2/m = mmm; C_{2v} = 2mm = mm; C_{2h} = 2/m; $C_2 = 2$; $C_{1h} = C_S$ = m; $C_i = \bar{1}$; $C_1 = 1$.

[10] This is in contrast to the smectic C phase with C_{2h} symmetry, where the mirror plane is *perpendicular* to the preferred direction $\hat{\boldsymbol{k}} \times \hat{\boldsymbol{n}}$, rendering the latter non-polar.

[11] We use the term 'ferroelectric' in the Statistical Mechanics sense, i.e. any phase showing a finite spontaneous polarisation is called ferroelectric, whether it is switchable or not. The latter feature is not connected with symmetries and therefore not discussed here.

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[17] The only low symmetry phase not covered by biaxial smectic phases would be of D_2 ($= V = 222$) symmetry showing 3 two-fold axes, but no mirror plane, thus being chiral but not ferroelectric.

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