# Biaxial Smectic Phases

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## I. Introduction

Phase biaxiality, the spontaneous breaking of rotational symmetry about two distinct directions, is a very rare phenomenon in nematic systems. It has been found in very special lyotropic systems in a very narrow phase space region only [1]. For rod-like molecules no biaxial nematic phase is known. Either the molecules are of an almost-cylindrical shape, then the entropic gain of randomly distributing the secondary axis wins over the energetic gain of ordering them, or they are of a very non-cylindrical shape, which apparently suppresses nematic ordering at all. A mixture of two uniaxial nematics with different preferred directions comes close to the macroscopic dynamic behavior of true biaxial nematics [2], although there are subtle differences [3]. Such a system however, usually modeled as a mixture of rods and plates, seems to phase separate rather than to order nematically.

On the other hand, it is much easier to obtain phase biaxiality in smectic systems. There, the layer normal $\hat{\boldsymbol{k}}$ already exists as a preferred direction due to the layering, although the broken translational symmetry in smectics includes (or slaves) the broken rotational symmetry related to $\hat{\boldsymbol{k}}$. Adding a second preferred direction, $\hat{\boldsymbol{n}}$, due to a (uniaxial) nematic ordering can then lead to biaxiality. If $\hat{\boldsymbol{k}} \parallel \hat{\boldsymbol{n}}$, one has the (uniaxial) smectic A phase, which is of $D_\infty$ symmetry, because there is the $\hat{\boldsymbol{k}} \to -\hat{\boldsymbol{k}}$ (or equivalently the $\hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$) invariance. For $\hat{\boldsymbol{k}} \perp \hat{\boldsymbol{n}}$ an orthorhombic (i.e. untilted) biaxial smectic phase (called smectic $\mathrm{C_M}$ in [4] and realized in a polymeric system [5] with bulky side chains attached side-on) is obtained, which has $D_{2h}$ symmetry [6, 7] according to the independent $\hat{\boldsymbol{k}} \to -\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ invariances. For oblique tilt angles between $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{n}}$ the usual smectic C phase is obtained, which is of monoclinic $C_{2h}$ symmetry due to the combined $\hat{\boldsymbol{k}} \to -\hat{\boldsymbol{k}} \ \wedge \ \hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ invariance.

In the following we will discuss possible smectic phases, where biaxial objects are arranged in a layered fashion. Within the smectic array it seems to be easier to obtain biaxially ordered systems. First we consider biaxial nematic-type and then banana-type objects. Nematic-like objects are e.g. a triad of directions with head and tail indistinguishable, while banana-like means that (at least) one direction is polar (a true vector with an arrow). They can also be viewed as planes (or bricks) in the former, and as directed planes (or directed bricks) in the latter case due to the polar axis present. Of special interest will be single- and twice-tilted phases, which show a host of new smectic phases with quite unusual symmetries and dynamic features [8]. It should be noted that all these phases are smectic C phases in the hydrodynamic sense, since they are described by two extra degrees of freedom in the hydrodynamic limit, a translational and a rotational one.

## II. Smectic Phases with Nematic-type Biaxiality

Here we consider nematic-type constituents forming layers. Biaxially ordered they are characterized by two distinct directions, $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$, which we will assume to be orthogonal. A third direction, $\hat{\boldsymbol{l}} \equiv \hat{\boldsymbol{n}} \times \hat{\boldsymbol{m}}$, completing the tripod can always be defined, but we will not refer to it explicitly below. The case with oblique $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ is slightly more complicated, but does not lead to any other phases than those found in the orthorhombic case.

If one of the axes, say $\hat{\boldsymbol{n}}$, is parallel to the layer normal $\hat{\boldsymbol{k}}$, the other one has to be orthogonal to $\hat{\boldsymbol{k}}$ (Fig.1a) indicating the (orthorhombic) smectic $\mathrm{C_M}$ phase discussed above. If on the other hand one direction (say $\hat{\boldsymbol{m}}$) is orthogonal to the layer normal, the other direction can be oblique (Figs.1b and 1c) giving rise to the common smectic C phase of (monoclinic) $C_{2h}$ symmetry. There is a two-fold rotation axis ($\hat{\boldsymbol{m}}$) and a mirror plane perpendicular to $\hat{\boldsymbol{m}}$ (because of the $\hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ invariance). In order to preserve the angle between $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{n}}$ there is the usual combined $\hat{\boldsymbol{k}} \to -\hat{\boldsymbol{k}} \ \wedge \ \hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ invariance, additionally and independent of the $\hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ invariance. Of course, one could interchange the role of $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{m}}$ without getting anything new.

The most interesting case is that of double tilt, where neither $\hat{\boldsymbol{n}}$ nor $\hat{\boldsymbol{m}}$ are parallel or perpendicular to $\hat{\boldsymbol{k}}$, but make oblique angles (Fig.1d). There is no 2-fold axis left, nor is there a mirror plane. The only symmetry element that remains is inversion symmetry, since the structure is invariant under the combined $\hat{\boldsymbol{k}} \to -\hat{\boldsymbol{k}} \ \wedge \ \hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}} \ \wedge \ \hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ replacement. Thus, this phase is $C_i$-symmetric (monoclinic) and could be called smectic $\mathrm{C_T}$ due to the additional tilt (compared to the SmC phase).

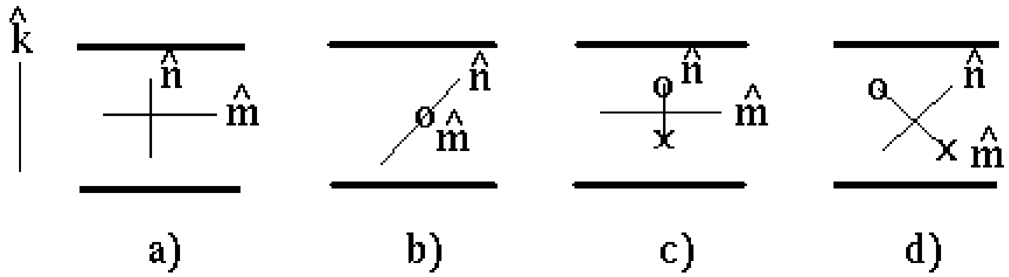


Fig.1 *The biaxial phases obtained by nematic-type ordering: a) the untilted $C_M$ phase, b) the usual smectic C phase, and d) the twice-tilted smectic $C_T$ phase with $C_i$ symmetry; fig. c) is a 90° degree side view of b) and $\hat{\boldsymbol{k}}$ is the layer normal. Here and in the following figures crosses (circles) denote those parts that point out (into) the plane of drawing.*

Hydrodynamically all these phases are described by two symmetry variables, the layer displacement and the the rigid rotation of the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure about the layer normal $\hat{\boldsymbol{k}}$. Since the symmetry is different, the form of the tensors (the number of coefficients they contain) and the kind of couplings among the various variables can be different. E.g., the symmetric second rank tensors (like electric and magnetic susceptibility, heat conduction and electric conductivity, rotational-elastic tensor for the rotational degree of freedom) contain 3, 4, and 6 independent coefficients in the smectic $\mathrm{C_M}$, C, and $\mathrm{C_T}$ phase, respectively, while for the (fourth rank) rotational-elastic tensor of the layer normal (as well as for the viscosity tensor) the numbers are 9, 13, and 21 and for the (third rank) tensor describing rotational-elastic couplings between layer normal and rotational degree of freedom one gets 2, 7, and 13 coefficients, respectively. Note that in the literature for the C and the $C_M$ phases sometimes lower numbers for these coefficients are given, since some of them can be regarded as higher gradient corrections to the elastic modulus and are therefore neglected. In all three cases there is only one true elastic modulus connected with layer compression. For the setup of nonlinear hydrodynamic equations in the monoclinic case see [9], while in [10] the linearized hydrodynamics (including electric behavior) of the orthorhombic phase is discussed.

### III. Smectic Phases with Banana-type Biaxiality

Quite different phases are obtained, when the objects that form the layers are polar. That means there is one direction, $\hat{\boldsymbol{m}}$, that does *not* have a $\hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ invariance. This is realized by using bow- or banana-shaped molecules (Fig.2a). If they are well-oriented, there is a nematic-like direction, $\hat{\boldsymbol{n}}$ with a $\hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ invariance, and in addition the polar direction $\hat{\boldsymbol{m}}$, which will be assumed to be orthogonal to $\hat{\boldsymbol{n}}$ (without loss of generality). 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 (Fig.2b). 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 [11]. It has been called $C_P$ phase in [12] since it is ferroelectric [13], if stacked uniformly. It can be antiferro- or ferri-electric for different stacks (Figs.2c and d). The $C_P$ phase has possibly be seen experimentally [14, 15]. 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.

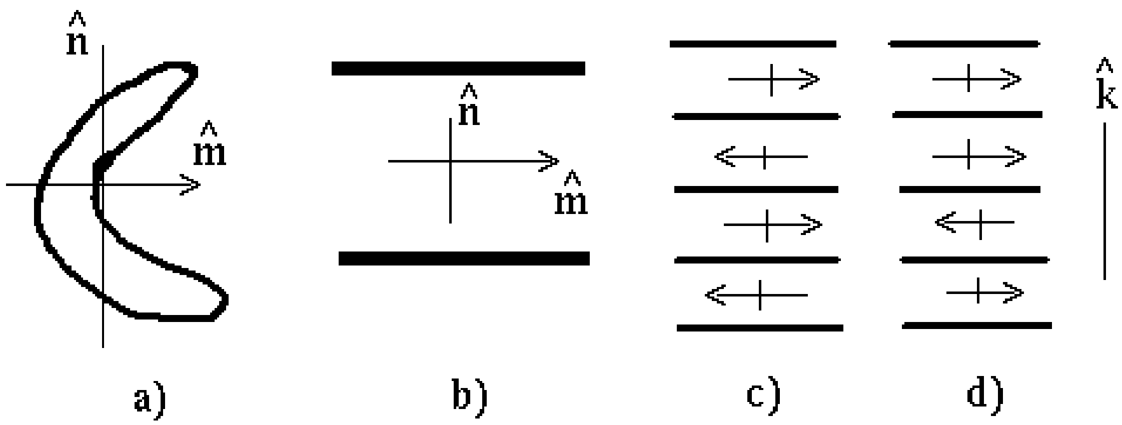


Fig.2 *a) Polar bananas, b) the untilted ferroelectric smectic $C_P$ phase, c) its antiferroelectric, and d) its ferrielectric variant.*

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 $C_P$ 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 [5], if the bulky side-chains have a dipole moment along their side-on spacers.

Even more interesting phases are obtained when $\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{m}}$, or both are tilted. Let us start with 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 $C_{B2}$ 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.3). 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 $C_{B2}$ phases the additional tilt of $\hat{\boldsymbol{n}}$ is responsible for chirality.

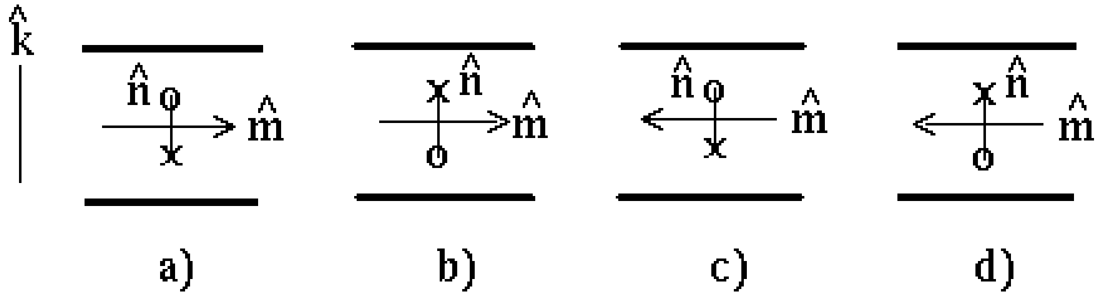


Fig.3 *a) The smectic $C_{B2}$ phase, with in-plane polarisation and $\hat{\boldsymbol{n}}$ tilted, b) a variant of it with different handedness, c) and d) the respective forms with opposite polarisation.*

Taking the Fig.3a 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.3b shows a right-handed version of this phase. Of course, chirality can lead to a helical stacking and the phase is then heli-electric (like C* [16]). However, since both versions are completely equivalent, one has to expect to 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). Another difference to conventional C* phases comes from the possibility to stack layers antiferroelectrically. Stacking variants of Fig.3a with 3c (or 3b with 3d) alternatively, one gets a locally antiferroelectric structure with $\hat{\boldsymbol{n}}$ synclinic. Stacking 3a with 3b (3d) the local structure is ferroelectric (antiferroelectric) with $\hat{\boldsymbol{n}}$ anticlinic. In any case, globally the polarisation (or staggered polarisation in the antiferroelectric case) is in-plane helical. Such a phase seems to have been described and discussed in [17].

Instead of tilting the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure in Fig.2b about $\hat{\boldsymbol{m}}$, which has lead to the $C_{B2}$ 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.4).

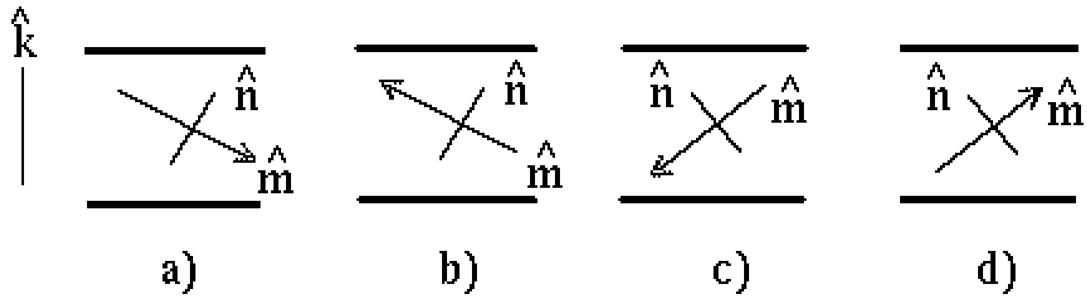


Fig.4 *The smectic $C_{B1}$ phase, where the polarisation lies in the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{n}}$-plane, thus having also a component perpendicular to the layers. Shown are all four different modifications concerning the polarization.*

This plane is of course a mirror plane, but there is no symmetry axis left and the phase (called $C_{B1}$ 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 $C_P$ phase of Fig.2 is obtained). Thus the $C_{B1}$ 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.4a with 4b results in a completely antiferroelectric structure, while 4a with 4c gives a structure that is antiferro- in, but ferroelectric across, the layers; while for 4a stacked with 4d there is ferro- in, and antiferroelectricity across, the layers.

Tilting the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{m}}$ structure in Fig.2b about *two* different axis results in the most general smectic C phase possible, the smectic $C_G$ phase mentioned already briefly in [4]. 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.5). 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 $C_{B1}$ and $C_{B2}$ 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. Fig.5 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.

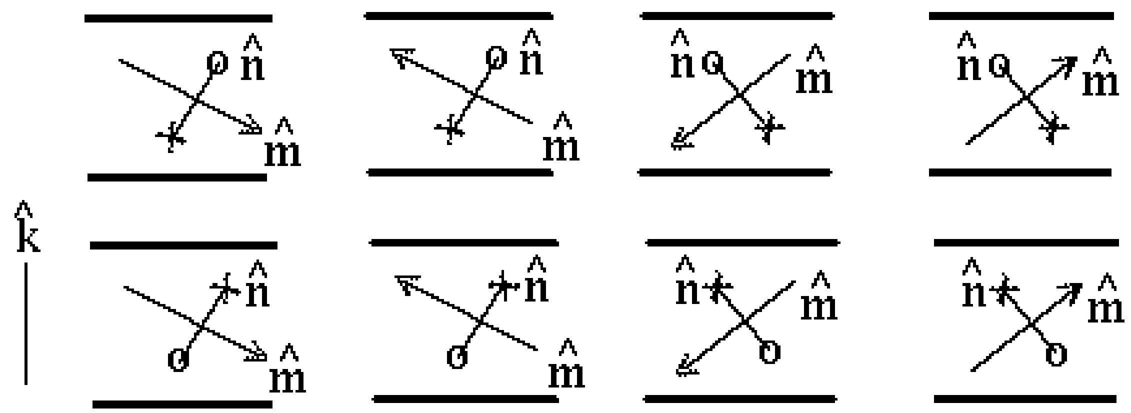


Fig.5 *The most general smectic $C_G$ phase with 8 different modifications concerning the polarisation, handedness and inclination.*

Hydrodynamically all these banana 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 about the layer normal $\hat{\boldsymbol{k}}$. If there is a helix, the latter can be replaced by the helix displacement along the helical axis [18]. However, due to the very low symmetries involved [19], 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].

Some of the new banana phases discussed in [20] or at the recent 'Banana Workshop' at the TU Berlin may turn out to be phases discussed above.

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