PHASE TRANSITIONS IN BIAXIAL BANANA PHASES

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Abstract: We discuss symmetry properties of various phases that can result when biaxial objects with at least one polar axis are orientationally ordered and packed on layers. The possibility of spontaneous splay, bend and twist is also investigated for biaxial nematic, smectic banana and dolphin phases. We further discuss appropriate order parameters and expressions for Ginzburg-Landau free energies for some phase transitions involving these phases.

Keywords: Symmetries. Polar smectics and nematics. Banana smectics. Scalar invariants, spontaneous splay/bend/twist. Phase transitions, order parameters, Ginzburg-Landau free energies.

SYMMETRIES

Because of their unusual physical properties, fluid biaxial smectic phases composed of banana-shaped molecules have recently attracted increasing interest [1–6]. If banana-shaped molecules (i.e. biaxial entities with one polar axis $\hat{\mathbf{m}}$) are organized on layers, the resulting phases are biaxial and polar i.e. they do *not* have $\hat{\boldsymbol{m}} \to -\hat{\boldsymbol{m}}$ invariance, while their other two directions ($\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{l}}$) have $\hat{\boldsymbol{n}} \to -\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{l}} \to -\hat{\boldsymbol{l}}$ invariance. Without loss of generality, we assume $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{l}}$ are perpendicular to $\hat{\boldsymbol{m}}$. In the following, we discuss possible phases when these directions are untilted relative to the layer normal, $\hat{\boldsymbol{k}}$, or tilted once or twice relative to $\hat{\boldsymbol{k}}$ [7].

1) *The Untilted Case:* $\hat{\boldsymbol{n}} \parallel \hat{\boldsymbol{k}}$, $\hat{\boldsymbol{m}} \perp \hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{l}} \perp \hat{\boldsymbol{k}}$ leads to the polar smectic $\mathrm{C_P}$ phase [1] of orthorhombic C_{2v} symmetry.

2) *Two Axes Tilted:*

a. If $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{l}}$ are tilted but $\hat{\boldsymbol{m}}$ stays perpendicular to $\hat{\boldsymbol{k}}$, the smectic C_{B2} phase is obtained. Smectic C_{B2} still has a two-fold polar axis ($\hat{\boldsymbol{m}}$) but no mirror planes i.e. no inversion symmetry. It has monoclinic C_2 symmetry described by the combined $\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{l}} \to -\hat{\boldsymbol{n}}$, $-\hat{\boldsymbol{k}}$, $-\hat{\boldsymbol{l}}$ invariance. The phase is chiral even if the molecules are achiral i.e. have no asymmetric carbons. There exists a pseudoscalar, $\hat{\boldsymbol{m}} \cdot (\hat{\boldsymbol{l}} \times \hat{\boldsymbol{n}})$, which behaves like a scalar under all operations not involving parity and changes sign as soon as behavior under parity is invoked. The presence of such a pseudoscalar allows for the existence of many additional coupling terms, since the behavior under parity can always be fixed by introducing odd powers of the pseudoscalar. In the context of the C_{B2} phase it also expresses the fact that either left or right-handed helices are possible. Neither the chirality nor the helical direction in smectic C_{B2} is fixed by symmetry. The pseudoscalar can be written more generally as $Q_{ij}^{(k)} Q_{jk}^{(2)} \epsilon_{ikl} \hat{m}_l$ with $Q_{ij}^{(k)} = \hat{k}_i \hat{k}_j - (1/3)\delta_{ij}$ and $Q_{ij}^{(2)} = \hat{n}_i \hat{n}_j - \hat{l}_i \hat{l}_j$ the orientational order parameter of the layer normal and the biaxial order parameter of $\hat{\boldsymbol{n}}/\hat{\boldsymbol{l}}$.

b. If $\hat{\boldsymbol{m}}$ and $\hat{\boldsymbol{n}}$ are tilted but $\hat{\boldsymbol{l}}$ remains perpendicular to $\hat{\boldsymbol{k}}$, there is no symmetry axis left, but there is a mirror plane from the $\hat{\boldsymbol{l}} \to -\hat{\boldsymbol{l}}$ invariance. Thus the smectic C_{B1} phase is of monoclinic C_{1h} symmetry, which is not chiral, with a polar direction in the $\hat{\boldsymbol{k}}$-$\hat{\boldsymbol{n}}$ plane.

3) *Three Axes Tilted*: If all three axes are tilted such that no pair of them forms a plane with $\hat{\boldsymbol{k}}$, then no symmetry is left at all: triclinic C_1 symmetry. This lowest symmetry smectic C phase, C_G, has a polar axis at an arbitrary direction to $\hat{\boldsymbol{k}}$ and is chiral even when the molecules composing this phase are achiral. As in smectic C_{B2}, neither the chirality nor the helical direction in smectic C_G is fixed by symmetry.

Illustrations of the symmetries of these phases can be found in [7–9] and their special properties are listed in Table I.

The phases without inversion symmetry, C_{B2} and C_G, have 3 linear twist contributions ($\hat{\boldsymbol{n}} \cdot curl\, \hat{\boldsymbol{n}}$, $\hat{\boldsymbol{m}} \cdot curl\, \hat{\boldsymbol{m}}$, $\hat{\boldsymbol{l}} \cdot curl\, \hat{\boldsymbol{l}}$) in the gradient energy giving rise to spontaneous twist (helices). The existence of a polar axis implies the linear splay term $div\,\hat{\boldsymbol{m}}$ in the gradient energy. The general C_G phase admits, in addition, the 2 splay terms $div\,\hat{\boldsymbol{n}}$ and $div\,\hat{\boldsymbol{l}}$, but C_{B1} only one additional independent one, $(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{n}})div\,\hat{\boldsymbol{n}}$. In the C_G phase there are 6 linear distortion terms of the 'mixed' type, $\hat{\boldsymbol{n}}\cdot curl\,\hat{\boldsymbol{m}}$, $\hat{\boldsymbol{m}}\cdot curl\,\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{l}}\cdot curl\,\hat{\boldsymbol{m}}$, $\hat{\boldsymbol{m}}\cdot curl\,\hat{\boldsymbol{l}}$, $\hat{\boldsymbol{l}}\cdot curl\hat{\boldsymbol{m}}$, and $\hat{\boldsymbol{m}}\cdot curl\,\hat{\boldsymbol{l}}$. These terms do or do not contribute to splay, bend or twist deformations, depending on the specific distortion considered.[1] In C_{B1} there are 4 mixed terms ($\hat{\boldsymbol{n}}\cdot curl\hat{\boldsymbol{m}}$, $\hat{\boldsymbol{m}}\cdot curl\hat{\boldsymbol{n}}$, $(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{l}})\cdot curl\,\hat{\boldsymbol{l}}$, $(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{n}})\cdot curl\,\hat{\boldsymbol{n}}$), of which only the two latter ones survive the $\hat{\boldsymbol{l}}$, $\hat{\boldsymbol{n}}\to-\hat{\boldsymbol{l}}$, $-\hat{\boldsymbol{n}}$ invariance of the C_{B2} phase. These two terms are non-zero for a helical structure.

phase class	local sym.	untilted axes	comp. of P	spont. splay	spont. 'mixed'	spont. twist
C	C_{2h}	**1**	**none**	**no**	**no**	**no**
$\mathbf{C}_T$	C_i	**0**	**none**	**no**	**no**	**no**
$\mathbf{C}_{B2}$	C_2	**1** polar	**1 (in)**	1	2	3
$\mathbf{C}_{B1}$	C_{1h}	**1**	**2**	2	4	**no**
$\mathbf{C}_G$	C_1	**0**	**3**	3	6	3

Table I: Properties of the tilted banana phases in comparison with tilted non-polar phases C and C_T.

It should be noted that upon complete linearization in deviations from a ground state (e.g. $\delta\hat{\boldsymbol{l}}\equiv\hat{\boldsymbol{l}}-\hat{\boldsymbol{l}}_{eq}$) some of the above terms may not be linearly independent from others. This does not mean that those terms can be discarded, since the energy density is required at least to quadratic order.

The existence of linear twist terms generally leads to defect-free helical or conical-helical structures. Linear splay terms taken separately can lead to inhomogeneous textures with large defect areas. Therefore such textures may not be energetically favorable. Taken together with linear terms of the 'mixed' type, linear splay can lead to bend-splay textures with minimal defect areas [10], so that the gain by the linear terms may still overcome the defect energy. Examples are discussed elsewhere [11].

For comparison we have added in Table I the ordinary smectic C phase of C_{2h}-symmetry, obtained by tilting 2 axes of a non-polar triad

[1] Note: bend is a vector quantity so cannot appear alone linearly, since scalar quantities are required for the free energy density.

with respect to the smectic layering. If all three (non-polar) axes are tilted, the C_T phase with C_i-symmetry (only inversion symmetry left) results. Without any polar axis and due to the inversion symmetry left, no linear terms in the gradient energy are allowed.

In biaxial smectic phases, layers can be stacked with the polar axis oriented alternately or helically from layer to layer giving rise to ferri- and antiferroelectricity, to heli- and antihelielectricity etc. For the chiral cases $\mathrm{C_{B2}}$ and $\mathrm{C_G}$ the stacking can involve alternately left- and right-handed layers leading to globally achiral phases. Thus, such stacking can show a global symmetry and behavior that is quite different from the local one of a single layer. Tilted banana phases are richer than the known usual biaxial smectics in their stacking options.

phase class	**sym-metry**	**polar axes**	**defect strength**	**spont. splay**	**spont. 'mixed'**	**spont. twist**
$\mathbf{N}_{\mathrm{bx}}$	D_{2h}	**0**	**half int.**	**no**	**no**	**no**
$\mathbf{N}_{\mathrm{I}}$	C_{2v}	**1**	**integer**	1	2	**no**
$\mathbf{N}_{\mathrm{II}}$	C_{1h}	**2**	**integer**	2	4	**no**
$\mathbf{N}_{\mathrm{III}}$	C_1	**3**	**integer**	3	6	3

Table II: Properties of biaxial nematic phases with different numbers of polar axes.

Besides these smectic C phases (they all have an in-plane nematic-like degree of freedom - i.e. are 2D anisotropic liquids), some of which have been detected experimentally, there are other, up to now hypothetical, phases. It is conceivable that nematic-like phases without layering exist. If only one of the non-polar axes is ordered, an ordinary uniaxial nematic is obtained. If the polar axis is ordered (but not the other two), one gets a uniaxial polar nematic ($\mathrm{N_p}$) phase, that shows spontaneous splay and may form non-homogeneous textures [12]. If two (and thus three) axes are ordered, a biaxial nematic phase ($\mathrm{N_I}$) with one polar direction ($\hat{\boldsymbol{m}}$) is found, that not only gives rise to linear splay, $div\,\hat{\boldsymbol{m}}$, but also to linear 'mixed'-type terms, $\hat{\boldsymbol{m}}\cdot(\hat{\boldsymbol{n}}\times curl\,\hat{\boldsymbol{n}})$, $\hat{\boldsymbol{m}}\cdot(\hat{\boldsymbol{l}}\times curl\,\hat{\boldsymbol{l}})$ [8]. If biaxial dolphin-like objects with two polar axes ($\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{m}}$) are ordered, a phase $\mathrm{N_{II}}$ of C_{1h}-symmetry is obtained ($\hat{\boldsymbol{l}} \to -\hat{\boldsymbol{l}}$ invariance). There are 2 linear splay terms, $div\,\hat{\boldsymbol{m}}$ and $div\,\hat{\boldsymbol{n}}$, 4 linear bend-like terms, $\hat{\boldsymbol{m}}\cdot(\hat{\boldsymbol{l}}\times curl\hat{\boldsymbol{l}})$, $\hat{\boldsymbol{n}}\cdot(\hat{\boldsymbol{l}}\times curl\,\hat{\boldsymbol{l}})$, $\hat{\boldsymbol{n}}\cdot(\hat{\boldsymbol{m}}\times curl\,\hat{\boldsymbol{m}})$, $\hat{\boldsymbol{m}}\cdot(\hat{\boldsymbol{n}}\times curl\,\hat{\boldsymbol{n}})$, but no linear twist terms, because of the inversion symmetry. The (hypothetical) case of 3 polar axes results in a general C_1-symmetric phase (N_{III}).

Another possibility to prepare phases with low symmetry is to put biaxial objects that have more than one polar axis into layers. Even untilted, two polar axes result in C_{1h}-symmetric $C_{Q^{(\prime)}}$ phases, while with 3 polar axes no symmetry is left (C_R phase), cf. Table III.

There is a variant of the C_P phase, $C_{P'}$, where the polar axis is parallel to the layer normal. This may be hard to achieve in reality, but it is a theoretical possibility and distinct from the longitudinal ferroelectric phases previously discussed [13] in that $C_{P'}$ is biaxial. While the symmetry of $C_{P'}$ is the same as that of C_P, it can lead to a different result in one case under the tilt operation. The C_G phase is obtained when tilting either C_P or $C_{P'}$ twice. Tilting the polar axis $\hat{\mathbf{m}}$ and the nonpolar axis $\hat{\mathbf{n}}$ while keeping $\hat{\mathbf{l}}$ fixed results in the C_{B1} phase for both C_P and $C_{P'}$. In contrast, if the polar direction of C_P, $\hat{\mathbf{m}}$, stays in the layer planes, while $\hat{\mathbf{l}}$ and $\hat{\mathbf{n}}$ are tilted, the C_{B2} phase results, while nothing changes for the symmetry of the $C_{P'}$ phase when the orientation of $\hat{\mathbf{m}}$ is fixed and the orientations of $\hat{\mathbf{l}}$ and $\hat{\mathbf{n}}$ are tilted - i.e. simply rotated in the layer plane.

phase class	**local sym.**	**polar axes**	**polari-zation**	**spont. splay**	**spont. 'mixed'**	**spont. twist**
$\mathbf{C}_M$	D_{2h}	**0**	**no**	**no**	**no**	**no**
$\mathbf{C}_P$	C_{2v}	**1**	**1D in**	1	2	**no**
$\mathbf{C}_{P'}$	C_{2v}	**1**	**1D out**	1	2	**no**
$\mathbf{C}_Q$	C_{1h}	**2**	**2D in**	2	4	**no**
$\mathbf{C}_{Q'}$	C_{1h}	**2**	**2D**	2	4	**no**
$\mathbf{C}_R$	C_1	**3**	**3D**	3	6	3

Table III: Properties of the biaxial untilted smectic phases with different numbers of polar axes.

The C_Q dolphin phase also comes in two variants: unprimed (both polar directions are in-plane) and primed (only one of the two polar axes is in-plane). They both have the same symmetry. However, if they are tilted once, the C_Q phase always leads to a C_1-symmetric phase (called C_{DG}), while in $C_{Q'}$ tilting the two polar axes about the non-polar one preserves C_{1h} symmetry (leading to a C_{D1} phase) and only tilting about the in-plane polar vector gives rise to a C_1-symmetric general C_{DG} phase.

From a symmetry point of view these untilted smectic phases are very similar to the biaxial nematic counterparts (Table II), although hydrodynamically they are different. The smectic phases are all C phases with two symmetry variables (layer displacement and in-plane nematic reorientation), while the biaxial nematic ones have 3 orientational hydrodynamic degrees of freedom.

PHASE TRANSITIONS

Among the various phases discussed, there are numerous interesting phase transitions. We briefly discuss some of them. For a phase transition, where the macroscopic polarization $\boldsymbol{P}$ arises for the first time, the order parameter is a vector: $\boldsymbol{P} = P_0 \hat{\boldsymbol{m}}$. P_0 is the strength of the ordering, and $\hat{\boldsymbol{m}}$ the polar axis. The corresponding Ginzburg-Landau functional reads [7]

$$\begin{aligned}\Phi &= \Phi_0 + \int d\tau [a\boldsymbol{P}^2 + c_{ijkl} P_i P_j P_k P_l + d_{ijkl} (\nabla_i P_j)(\nabla_k P_l) \\ &\quad + e_{ijkl} P_i P_j \nabla_k P_l + f_{ij} \nabla_j P_i] \qquad (1)\end{aligned}$$

where the form of the material tensors depends on the symmetry of the starting phase. For the isotropic to $\mathrm{N_p}$ transition one gets $c_{ijkl} = (c/3)(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj})$, $d_{ijkl} = d_1 \delta_{ik}\delta_{jl} + (d_2/2)(\delta_{ij}\delta_{kl} + \delta_{kj}\delta_{il})$, $f_{ij} = f\delta_{ij}$, while e_{ijkl} is of the same form as c_{ijkl}.

For the smectic A to smectic $\mathrm{C_P}$ transition, $\boldsymbol{P}$ has to lie in the plane $\boldsymbol{P} \perp \hat{\boldsymbol{k}}$. As a result, the material tensors above the Kronecker deltas involving $\boldsymbol{P}$ have to be replaced by $\delta^{tr}_{ij} = \delta_{ij} - \hat{k}_i \hat{k}_j$, e.g. $d_{ijkl} = (d_1 \delta^{tr}_{ik} + d_3 \hat{k}_i \hat{k}_k)\delta^{tr}_{jl} + (d_2/2)(\delta^{tr}_{ij}\delta^{tr}_{kl} + \delta^{tr}_{kj}\delta^{tr}_{il})$. Similarly, at the N to N_I transition, where the new polar axis $\hat{\boldsymbol{m}}$ occurs perpendicular to the non-polar director $\hat{\boldsymbol{n}}$, the transverse Kronecker is $\delta^{tr}_{ij} = \delta_{ij} - \hat{n}_i \hat{n}_j$.[2]

For the polar uniaxial to biaxial transition ($\mathrm{N_p}$ to $\mathrm{N_I}$) the other non-polar axes order. This is described by a two-dimensional symmetric second-rank tensor $Q^{(2)}_{ij} = \eta(\hat{n}_i \hat{n}_j - \hat{l}_i \hat{l}_j)$, with η the strength of this ordering.

[2]Note that the Ginzburg-Landau energy does not depend on the azimuthal orientation of $\hat{\boldsymbol{m}}$ (w.r.t. $\hat{\boldsymbol{n}}$ or $\hat{\boldsymbol{k}}$ for N or C_P, respectively), which is a hydrodynamic Goldstone mode.

For the smectic phase transitions involving one additional tilt direction, e.g. smectic C_P to C_{B2}, C_P to C_{B1}, C_{B1} to C_G, C_{B2} to C_G and C to C_T, the order parameter is simply the tilt angle (ordering strength), since the tilt direction is already fixed by symmetry (in contrast to the usual smectic A to C transition). The transition is described by the Ginzburg-Landau functional (with ψ real)

$$\Phi = \Phi_0 + \int d\tau[a\psi^2 + c\psi^4 + d_{ij}(\nabla_i\psi)(\nabla_j\psi) + L_g^{(1)}] \qquad (2)$$

where $L_g^{(1)}$ contains the linear gradient terms. Eq.(2) shows a $\psi \to -\psi$ symmetry, since tilt in opposite directions is energetically equivalent, but leads to different states. For the smectic C_P to C_{B2} transition, e.g., opposite tilts denote the discrimination between left- and right-handed variants, which are indeed energetically equivalent. Thus these phase transitions can be of second order.

The high (low) symmetry phase is obtained for $a > 0$ ($a < 0$). The tensor $d_{ij} = d_1\hat{n}_i\hat{n}_j + d_2\hat{l}_i\hat{l}_j + d_3\hat{m}_i\hat{m}_j + d_4O_{ij}$ is of the monoclinic form with $O_{ij} \equiv \hat{n}_i\hat{l}_j + \hat{l}_i\hat{n}_j$ for the C and C_{B2} phases, $O_{ij} \equiv \hat{m}_i(\hat{\boldsymbol{m}} \times \hat{\boldsymbol{n}})_j + \hat{m}_j(\hat{\boldsymbol{m}} \times \hat{\boldsymbol{n}})_i$ for the C_{B1} phase, and of the orthorhombic form ($d_4 \equiv 0$) for the C_P phase as starting point.

For the C_P to C_{B2} transition ψ (or rather $\sin\psi$) is $\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}}$, while the gradient part L_g^1 contains the new linear twist terms that are non-zero in C_{B2} but zero in C_P, $L_g^1 = (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{n}})(\hat{\boldsymbol{n}}\times\hat{\boldsymbol{l}})\cdot\hat{\boldsymbol{m}}\,(e_1\,\hat{\boldsymbol{n}}\cdot curl\,\hat{\boldsymbol{n}} + e_2\,\hat{\boldsymbol{m}}\cdot curl\,\hat{\boldsymbol{m}} + e_3\,\hat{\boldsymbol{l}}\cdot curl\,\hat{\boldsymbol{l}})$. For the C_P to C_{B1} transition $\sin\psi = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}}$ and $L_g^{(1)} = (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})\,[e_1\,(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{l}})\cdot curl\,\hat{\boldsymbol{m}} + e_2\,\hat{\boldsymbol{m}}\cdot curl\,(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{l}})] + e_3\,(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{n}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})\,div\,\hat{\boldsymbol{n}}$. At the C_{B1} to C_G transition $\sin\psi = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}}$ gets non-zero as well as one additional splay, three twist and two 'mixed'-type terms $L_g^{(1)} = (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{n}})(\hat{\boldsymbol{n}}\times\hat{\boldsymbol{l}})\cdot\hat{\boldsymbol{m}}\,(e_1\,\hat{\boldsymbol{n}}\cdot curl\,\hat{\boldsymbol{n}} + e_2\,\hat{\boldsymbol{m}}\cdot curl\,\hat{\boldsymbol{m}} + e_3\,\hat{\boldsymbol{l}}\cdot curl\,\hat{\boldsymbol{l}}) + (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})(e_4\,div\,\hat{\boldsymbol{l}} + e_5\,\hat{\boldsymbol{n}}\cdot curl\,\hat{\boldsymbol{l}} + e_6\,\hat{\boldsymbol{l}}\cdot curl\,\hat{\boldsymbol{n}})$, while for C_{B2} to C_G $\sin\psi = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}}$ and two new linear splay and 4 'mixed'-type contributions arise $L_g^{(1)} = (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{l}})[e_1 div\,\hat{\boldsymbol{l}} + e_3(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{l}})\cdot curl\,\hat{\boldsymbol{m}}] + (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{n}})[e_2\,div\,\hat{\boldsymbol{n}} + e_4(\hat{\boldsymbol{m}}\times\hat{\boldsymbol{n}})\cdot curl\,\hat{\boldsymbol{m}}] + (\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{m}})[e_5(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{l}})\cdot curl\,\hat{\boldsymbol{l}} + e_6(\hat{\boldsymbol{k}}\times\hat{\boldsymbol{n}})\cdot curl\,\hat{\boldsymbol{n}}]$. At the C to C_T transition no linear gradient terms are possible, and $L_g^{(1)} = 0$.

The phase transition from C_P to a C_G phase involves two tilts, one is a rotation about $\hat{\boldsymbol{l}}$ and the second about $\hat{\boldsymbol{m}}$. Since finite rotations about different axes are generally non-commutative, the result depends on the sequence of the rotations. Thus one cannot use two scalar tilt angles as order parameters for that transition, as two scalars always commute. Since two subsequent rotations about different axes can always be described as an effective rotation (about some other axis) the orientation of the triad in C_G is given by the general orientational order parameter Q_{ij}^G and Q_{ij}^P is the orientational order parameter in the C_P phase. We choose $Q_{ij} \equiv Q_{ij}^G - Q_{ij}^P$ as order parameter for the $C_P - C_G$ transition. It contains two angles defining the orientation of the effective rotation axis (w.r.t. $\hat{\boldsymbol{k}}$), one rotation angle, and 2 ordering strengths denoting a possible jump in the uniaxial as well as biaxial order parameter modulus at that transition.

We obtain for the free energy

$$\begin{aligned}\Phi &= \Phi_0 + \int d\tau [a Q_{ij} Q_{ij} + b_{ijklmn} Q_{ij} Q_{kl} Q_{mn} \\ &\quad + c_{ijklmnpq} Q_{ij} Q_{kl} Q_{mn} Q_{pq} + d_{ijklmn} (\nabla_i Q_{jk})(\nabla_l Q_{mn}) + L_g^{(1)}] \end{aligned} \tag{3}$$

where $L_g^{(1)}$ contains all the new linear gradient terms, which are nonzero in C_G.

The transition from the biaxial nematic phases N_I, N_{II}, N_{III} to the orthogonal smectic phases C_P, C_Q, C_R, respectively, are characterized by the occurrence of layers. The layer normal, however, is not arbitrary but fixed to one of the nematic axes (say $\hat{\boldsymbol{n}}$). Thus the order parameter is a complex scalar Ψ (just as for the uniaxial nematic - smectic A transition) and

$$\Phi = \Phi_0 + \int d\tau \, [a|\Psi|^2 + c|\Psi|^4 + d_{ij} (\tilde{\nabla}_i \Psi)(\tilde{\nabla}_j \Psi)^*] \tag{4}$$

(with $\tilde{\nabla}_i = \nabla_i + 2\pi i d_0^{-1} \hat{n}_i$, where d_0 is the layer spacing) which allows for the possibility that these transitions can be of second order in mean field approximation. The tensor d_{ij} is of orthorhombic (N_I), monoclinic (N_{II}) and triclinic (N_{III}) form. There are no linear gradient terms in (4), since the phases involved support the same types of linear gradient terms (cf. Tables II and III).

For transitions involving the macroscopic polarization as well as tilt angles (smectic A to C_{B1} and C_{B2}) one has to combine different order parameters. Regarding the smectic A phase (of banana molecules) as one with nematic order of $\hat{\boldsymbol{n}}$ ($\parallel \hat{\boldsymbol{k}}$), but disordered $\hat{\boldsymbol{l}}$ and $\hat{\boldsymbol{m}}$ (both in the planes of the layers), the transition to C_{B2} or

C_{B1} consists of tilting $\hat{\boldsymbol{n}}$ (w.r.t. $\hat{\boldsymbol{k}}$) described by $\psi = \psi_0 exp(i\phi)$ (like at the smectic A to C transition) and additionally by the occurrence of a polarization $\boldsymbol{P} = P_0 \hat{\boldsymbol{m}}$, perpendicular to $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{n}}$ ($\hat{\boldsymbol{m}} \parallel \hat{\boldsymbol{k}} \times \hat{\boldsymbol{n}}$) or in the $\hat{\boldsymbol{n}}/\hat{\boldsymbol{k}}$ plane ($\hat{\boldsymbol{m}} \parallel \hat{\boldsymbol{k}} - \hat{\boldsymbol{n}}(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{n}})$), respectively.

If one starts from the nematic phases, one needs order parameters describing the layering, the polarization (beginning with non-polar uniaxial nematics) and the tilt directions. The most frequently observed phase transition is from the isotropic phase to a fluid tilted smectic banana phase requiring all order parameters: nematic, smectic layering, polarization as well as tilt directions.

SUMMARY

The banana and dolphin phases constitute a new class of liquid crystalline phases with unique symmetries and thus material properties. These low symmetry phases also allow for various textures involving spontaneous splay, bend and twist, although the molecules are achiral. There are new types of phase transitions, of which the most interesting are the ones, where the polar ordering takes place. Here new effects and unusual textures can be expected. This is also true for transitions involving the new linear gradient terms discussed above.

References

[1] H.R. Brand, P.E. Cladis, and H. Pleiner, Macromolecules **25**, 7223 (1992).

[2] T. Niori, F. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J.Mater.Chem. **6**, 1231 (1996).

[3] E.A. Soto Bustamente, S.V. Yablonskii, B.I. Ostrovskii, L.A. Beresnev, L.M. Blinov, W. Haase, Liq.Cryst. **21**, 829 (1996).

[4] D.R. Link, G. Natale, R. Shao, J.E. McLennan, N.A. Clark, E. Körblova, D.M. Walba, Science **278**, 1924 (1997).

[5] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi, H. Takezoe, J. Mat. Chem. **7**, 1307 (1997).

[6] D. Shen, S. Diele, I. Wirt, and C. Tschierske, Chem. Commun. **1998**, 2573 (1998).

[7] H.R. Brand, P.E. Cladis, and H. Pleiner, Eur.Phys.J. **B6**, 347 (1998).

[8] H.R. Brand, P.E. Cladis, and H. Pleiner, Int. J. Engin. Sci., in print (1999).

[9] P.E. Cladis, H.R. Brand, and H. Pleiner, these Conference Proceedings

[10] P.E. Cladis, M. Kléman, and P. Pieranski, C.R.Acad.Sci. (Paris) B **273**, 275 (1971)

[11] H.R. Brand, P.E. Cladis, and H. Pleiner, submitted for publication.

[12] H. Pleiner and H.R. Brand, Europhys. Lett. **9**, 243 (1989).

[13] R.G. Petschek and K.M. Wiefling, Phys.Rev.Lett., **59**, 343 (1987).