

Polar Columnar and Tetrahedric Phases: The B7 Phase and Beyond

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Introduction

Motivated by puzzling experimental observations made in compounds composed of banana-shaped molecules, we investigate the symmetries and the physical properties of liquid crystalline columnar phases with a macroscopic polarization in achiral materials [1]. This study is driven by two key observations made for the still poorly understood B7 phase: a) freely suspended films decompose spontaneously into strands [2, 3] and b) several of the textures observed for the B7 phase are reminiscent of textures observed for liquid crystalline columnar phases. Quite recently more experimental evidence was presented [4] for the B7 phase to be columnar.

One of the main results of our analysis [1] is that a chiral phase of C_1 -symmetry results as soon as the macroscopic polarization is inclined with respect to the columnar axes and the 2D lattice directions. We argue that a chiral columnar phase composed of achiral molecules, not previously considered for classic columnar phases, is sufficient to account for many of the unusual physical properties of B7.

Recent experiments on the effect of an external electric field and of temperature variations have also revealed the occurrence of flow close to and in the isotropic phase near the B7 - isotropic phase transition [5]. Consequently, there is a need to look for models which can describe phases that are optically isotropic but not cubic and can show coupling effects between flow and electric fields and/or temperature gradients.

We discuss this [6] for the optically isotropic tetrahedric phase characterized by a third rank tensor order parameter T_{ijk} [7]. We point out that an applied electric field or an applied temperature gradient will lead to flow. Reciprocally we predict that, for example, a shear flow applied to a tetrahedric phase leads to an induced electric field and a temperature gradient.

The hexagonal and rectangular columnar banana phases

Columnar liquid crystal phases are 2-dimensional arrays of columns made of disk-like molecules [8, 9]. The 2-dimensional lattice is either hexagonal or rectangular characterized by two directions, $\mathbf{l}_{1,2}$. The column axis will be called \mathbf{k} . Without a macroscopic polarization, \mathbf{P} , the planes built of $\mathbf{k}/\mathbf{l}_{1,2}$ and $\mathbf{l}_1/\mathbf{l}_2$ are mirror planes. The directions perpendicular to these planes are (at least 2-fold) symmetry axes (there can also be 4- and 6-fold axes). Thus these classical columnar phases, Col_h and Col_r , are of D_{2h} (sometimes D_{4h} and D_{6h}) symmetry. We only consider structures without long-range positional order in the columns, i.e. a 2D crystalline and a 1D fluid behavior.

The symmetry of these phases is reduced when a macroscopic polarization \mathbf{P} is present. As

Table 1: This table shows the symmetries and the physical properties of the classical columnar phases without a macroscopic polarization as well as those of the novel phases discussed here. \mathbf{k} , \mathbf{l}_1 , and \mathbf{l}_2 are the column axis, and the preferred directions of the 2D lattice, respectively.

class	symmetry	polarization \mathbf{P}	2D lattice	first-rank tensor
Col _{h}	D_{6h}	none	hex	none
Col _{r}	D_{2h}	none	rect	none
Col _{P_h}	C_{6v}	parallel to \mathbf{k}	hex	1D along \mathbf{k}
Col _{P_{h2}}	C_{2v}	parallel to \mathbf{l}_1 or \mathbf{l}_2	hex	1D along \mathbf{l}_1 or \mathbf{l}_2
Col _{P_{h1}}	C_{1h}	in the \mathbf{k}/\mathbf{l}_1 , \mathbf{k}/\mathbf{l}_2 , or $\mathbf{l}_1/\mathbf{l}_2$ plane, but oblique to \mathbf{k} , \mathbf{l}_1 , and \mathbf{l}_2	hex	2D in the plane
Col _{P_r}	C_{2v}	parallel to \mathbf{k}	rect	1D along \mathbf{k}
Col _{P_{r2}}	C_{2v}	parallel to \mathbf{l}_1 or \mathbf{l}_2	rect	1D along \mathbf{l}_1 or \mathbf{l}_2
Col _{P_{r1}}	C_{1h}	as in Col _{P_{h1}}	rect	2D in the plane
Col _{P_{i2}}	C_2	parallel to \mathbf{l}_1 or \mathbf{l}_2	any	1D along \mathbf{l}_1 or \mathbf{l}_2
Col _{P_i}	C_1	inclined to any of the planes \mathbf{k}/\mathbf{l}_1 , \mathbf{k}/\mathbf{l}_2 , or $\mathbf{l}_1/\mathbf{l}_2$	any	3D any orientation

long as \mathbf{P} lies in one of the planes $\mathbf{k}/\mathbf{l}_{1,2}$ or $\mathbf{l}_1/\mathbf{l}_2$, this plane still is a mirror plane, while axes perpendicular to this plane are no longer symmetry axes. Such phases are of C_{1h} symmetry and called [1] Col _{P_{h1}} and Col _{P_{r1}} for the hexagonal and rectangular case, respectively. They are of the same symmetry as the C_{B1} smectic banana phase [10, 11].

If in addition \mathbf{P} is parallel to one of the preferred axes, $\mathbf{l}_{1,2}$ or \mathbf{k} , this axis is a symmetry axis (lying within the symmetry plane) of 2-fold (or 4- and 6-fold) symmetry. The resulting columnar banana phases are of C_{2v} (C_{6v}) symmetry and called Col _{P_x} and Col _{P_{x2}} for $\mathbf{P} \parallel \mathbf{k}$ and $\mathbf{P} \parallel \mathbf{l}_{1,2}$, respectively (x stands for h , hexagonal and r , rectangular lattice symmetry). The phases Col _{P_i} and Col _{P_{i2}} are discussed in the following section.

With a hexagonal lattice an arrangement that is antiferroelectric in all 3 lattice directions is not possible. Fig.1 shows the essential frustration by some examples.

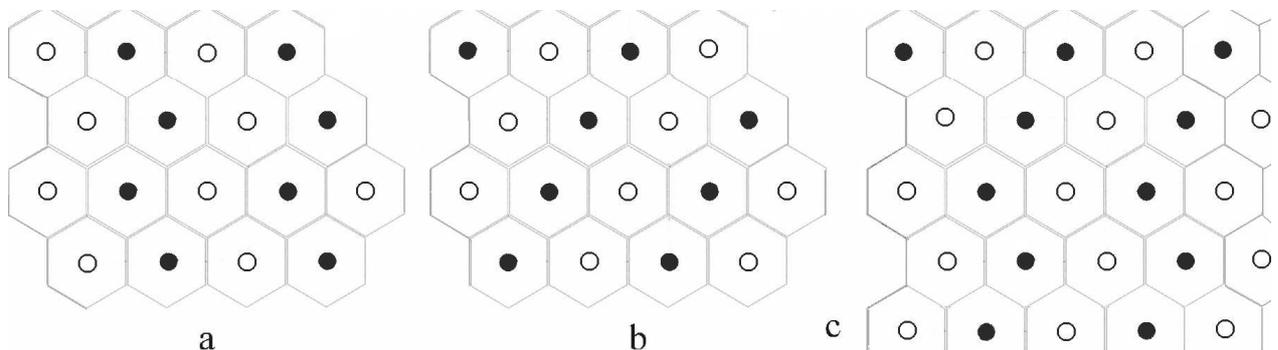


Figure 1: Hexagonal columnar phases with the polarization up (full circles) and down (open circles) the columnar axes. All horizontal rows are antiferroelectric, but different "stacks" lead additionally to a) 2 double-periodic antiferro-, b) 1 ferro- and 1 antiferro-, and c) 1 triple-periodic antiferro- and 1 ferri-electric (2 up and 1 down and vice versa) direction at $\pi/6$.

The inclined columnar banana phase

The phases discussed in the preceding section are non-chiral, since they possess at least a mirror plane. Thus, they cannot be candidates for explaining the B7 phase, which experimentally clearly shows chiral character. This situation is different when we go to the most general case, the Col_{P_i} phase with C_1 symmetry, where the polarization \mathbf{P} is inclined relative to any of the planes $\mathbf{k}/\mathbf{l}_{1,2}$ and $\mathbf{l}_1/\mathbf{l}_2$ (Fig.2 of [1]). It has the same symmetry as the C_G phase possible for

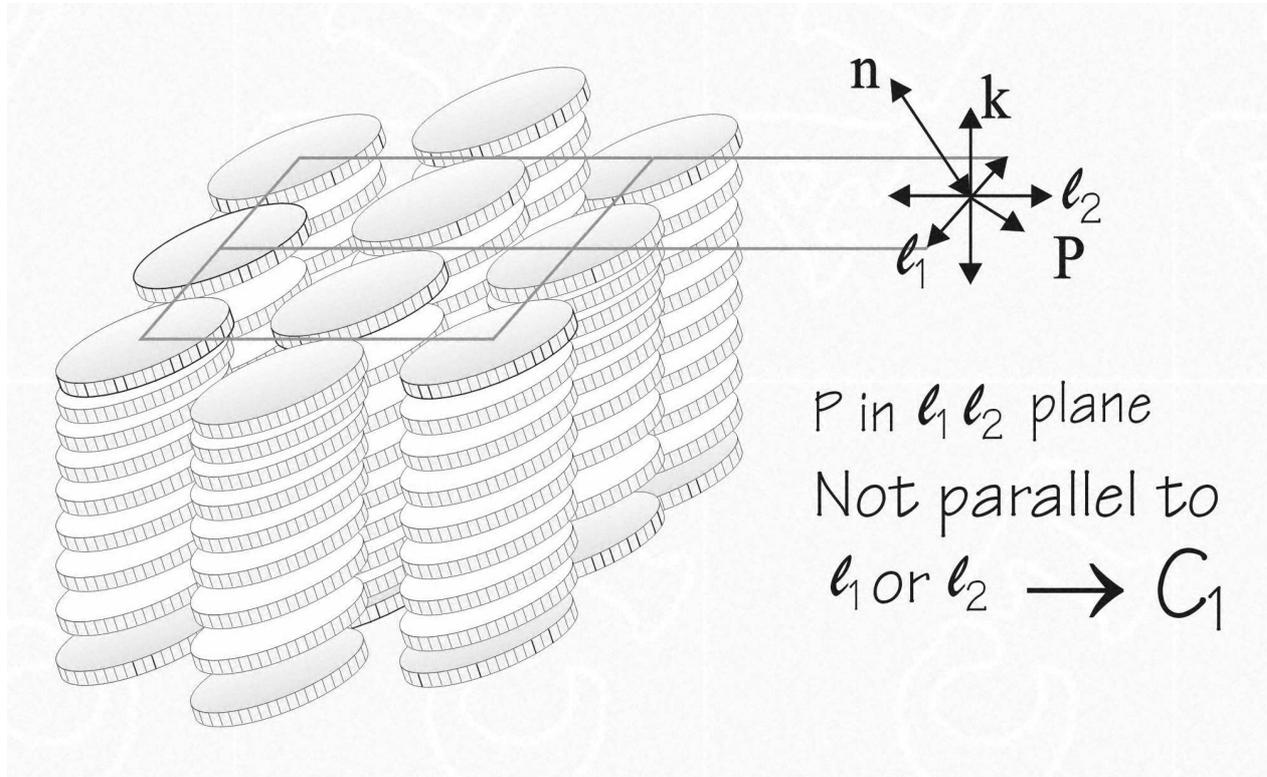


Figure 2: The local structure of the Col_{P_i} phase for disk-shaped objects with \mathbf{k} the column axis, \mathbf{P} the macroscopic polarization perpendicular to the disk axis \mathbf{n} , and $\mathbf{l}_{1,2}$ the non-polar symmetry directions in the planes of 2D positional order. \mathbf{P} is not parallel to \mathbf{l}_1 or \mathbf{l}_2 . The Col_{P_i} phase has no mirror plane and is, therefore, chiral.

smectic phases formed by banana-shaped molecules [10]. The Col_{P_i} phase is chiral as is manifest by the existence of a pseudoscalar: with the polarization $\mathbf{P} = P_0 \hat{\mathbf{p}}$ (P_0 is the magnitude and $\hat{\mathbf{p}}$ the direction of the polarization) the scalar $\tilde{q} = [\hat{\mathbf{p}} \cdot (\mathbf{k} \times \mathbf{l}_1)] [\hat{\mathbf{p}} \cdot (\mathbf{k} \times \mathbf{l}_2)] [\hat{\mathbf{p}} \cdot (\mathbf{l}_1 \times \mathbf{l}_2)]$ changes sign under spatial inversion. For $\hat{\mathbf{p}} \rightarrow -\hat{\mathbf{p}}$ the chirality changes from, say, right- to left-handed. The chirality can, but need not, show up in helical structures which would be right- as well as left-handed (ambidextrous chirality), since the structure is made of achiral molecules. Thus it emerges that tilted columnar phases with a polarization and C_1 symmetry are a natural candidate for B7. It is a columnar structure whose symmetry cannot be further lowered when anti-ferroelectric aspects are included.

Because Col_{P_i} possesses a polar vector, it has interesting macroscopic electric and electromechanical properties. In the free energy they show up as

$$\Phi = \int d\tau [\epsilon_{ij}^E E_i E_j + P_i E_i + E_i (\zeta_i^T \delta T + \zeta_i^p \delta p + \zeta_i^c \delta c) + d_{ijk} E_i \nabla_j u_k + \chi_{ijk}^{(2)} E_i E_j E_k] \quad (1)$$

where the contribution $\sim \epsilon_{ij}^E$ is the usual dielectric term with six independent coefficients for triclinic (C_1) symmetry [12]. The next term is characteristic of all ferroelectric materials. The

terms $\sim \zeta_i^T, \zeta_i^P$ and ζ_i^c relate to pyroelectric effects, pressure electric effects and to an electric response resulting from a concentration change in mixtures. The second last term in Eq.(1) is related to piezoelectric effects coupling the electric field to in-plane deformations of the lattice built by the columns. This results in 9 independent piezoelectric constants for C_1 symmetry. In addition to these linear electric and electromechanical effects, the last term describes second harmonic generation, where $\chi_{ijk}^{(2)}$ contributes 10 independent coefficients.

Assuming that the orientation of the entities, which form the columns, are not only characterized by the polarization \mathbf{P} , but in addition by a (non-polar) direction \mathbf{n} (which can be viewed as the normal of disk-like objects and which can be taken as perpendicular to \mathbf{P}), then the Col_{P_i} is easily realized by a single tilt of the disks: If \mathbf{P} is not along one of the lattice axes $\mathbf{l}_{1,2}$ (Fig.2) a C_1 -symmetric structure arises.¹ We note one important difference in this respect between smectic and columnar phases. For columnar phases, tilting the disk-shaped objects once is sufficient to reach the lowest symmetry level, while in the smectic C_G phase, banana-shaped molecules are tilted twice, i.e. about two different orthogonal axes.

It should be noted however, that the homogeneous state as depicted in Fig.2 might not be the true ground state of that phase, because – due to the low C_1 symmetry – there are a host of possible first order gradient invariants in the free energy, allowing for spontaneous twist, splay and splay-bend structures [13] possibly leading to textured and frustrated structures.

The tetrahedric phase

In the tetrahedric phase one has – in addition to the usual fields describing isotropic fluids – a third rank tensor T_{ijk} characterizing the tetrahedric order. Note that we deal only with the so-called nonchiral tetrahedric phase, T_d , made by achiral molecules. T_{ijk} is symmetric in all indices and traceless $T_{iik} = 0$, i.e. it does not contain any vectorial quantity. Since it transforms under an $l = 3$ representation of spherical harmonics, it is odd under parity and thus allows coupling terms not possible in ordinary simple liquids. It can be written as [7] $T_{ijk} = \sum_{\alpha=1}^4 n_i^\alpha n_j^\alpha n_k^\alpha$ in terms of the 4 unit vectors n_i^α that form a tetrahedron ($\sum_{\alpha=1}^4 n_i^\alpha = 0$). A tetrahedron has no inversion symmetry and so does the tetrahedric phase. In the absence of any vector this requires a 3-rank tensor as order parameter. Since a 3-rank tensor cannot influence the form of 2-rank material tensors, like the dielectric tensor, the tetrahedric phase appears to be isotropic optically. However, there are other material properties described by higher-ranked tensors, like viscosity, where the non-isotropic nature of this phase becomes manifest.

In addition, the existence of T_{ijk} allows couplings described by 3-rank material tensors not possible in ordinary isotropic phases. When comparing the tetrahedric phase to an ordinary isotropic phase in the dynamic regime, we have additional reversible contributions [6]

$$\sigma_{ij}^R = \dots - \Gamma_1 T_{ijk} E_i - \Gamma_2 T_{ijk} \nabla_i T - \Gamma_3 T_{ijk} \nabla_i c \quad (2)$$

$$j_i^{eR} = \dots + \Gamma_1 T_{ijk} A_{jk} \quad (3)$$

$$j_i^{\sigma R} = \dots + \Gamma_2 T_{ijk} A_{jk} \quad (4)$$

$$j_i^{cR} = \dots + \Gamma_3 T_{ijk} A_{jk} \quad (5)$$

to the stress tensor, the electric, entropy, and concentration current, respectively. From inspecting Eqs.(2–5), we see that velocity gradients (A_{ij})- including shear and extensional flows - couple to electric fields (E_i) as well as to temperature and concentration gradients ($\nabla_i T$ and $\nabla_i c$).

¹When \mathbf{P} is parallel to \mathbf{l}_1 (or \mathbf{l}_2) a C_2 -symmetric phase ($\text{Col}_{P_{i2}}$) is obtained similar to the C_{B2} smectic banana phases. In that case \mathbf{P} is the 2-fold axis and $\tilde{q} = [\hat{p} \cdot (\mathbf{k} \times \mathbf{n})][\hat{p} \cdot (\mathbf{k} \times \mathbf{l}_2)][\hat{p} \cdot (\mathbf{n} \times \mathbf{l}_2)]$.

This leads to the simple experimentally testable predictions to enable a distinction between the novel tetrahedric phase and the usual isotropic liquid. Applying, for example, a simple shear flow in the $y - z$ -plane, that is $A_{jk} = S\delta_{jy}\delta_{kz}$ with the shear rate S , to a tetrahedric phase, we read off from Eq.(4) that this results in a reversible heat current of the form

$$j_i^{\sigma R} = \Gamma_2 T_{iyz} S = \Gamma_2 \frac{4S}{3\sqrt{3}} \delta_{ix} \quad (6)$$

using of the explicit form of T_{ijk} [7]. This result shows that a shear flow applied in a given plane leads to a heat current in the direction perpendicular to this plane. Analogously we obtain from Eq.(3)

$$j_x^{eR} = \Gamma_1 \frac{4S}{3\sqrt{3}}, \quad j_y^{eR} = 0 = j_z^{eR} \quad (7)$$

This demonstrates that there is, in addition to the heat current, also a reversible electric current set up in the direction perpendicular to the shear plane. The same applies for the appearance of a concentration current in mixtures: in a tetrahedric phase a shear flow leads to a segregation of the subspecies involved.

Reciprocally, one can apply an electric field or a temperature gradient (or a concentration gradient) to a sample in the tetrahedric phase and ask how the flow behavior is affected. Applying, for example, an electric field \mathbf{E} in the z -direction, one obtains for the only non-vanishing component of the stress tensor (Eq.(2))

$$\sigma_{yx}^R = \sigma_{xy}^R = -\Gamma_1 \frac{4E_z}{3\sqrt{3}} \quad (8)$$

This result shows that an electric field applied in a specific direction gives rise to a shear stress in the plane perpendicular to this direction. And this shear stress can in turn lead for spatially varying situations - via the dynamic equation for the linear momentum density or the velocity field - to a flow in the plane perpendicular to the direction of the applied field. The same applies to external gradients of temperature and concentration.

An important implication of the new reversible dynamic contributions discussed here, is that the analysis of the electric Frederiks transition must include also dynamic effects. A static analysis based on energy considerations only as that given in [7] is insufficient for the tetrahedric phase.

The B7 phase and its isotropic neighbor

In the last section we discussed how the new terms in the tetrahedric phase coupling flow to an external electric field as well as to temperature gradients could be experimentally detected. Here we suggest that a good candidate for the tetrahedric phase may be the isotropic liquid state above the B7 phase for the following reasons.

First of all, we note that all experiments undertaken so far show, that the B7 phase has several types of local order. This includes some degree of positional order, be it smectic or columnar. Simultaneously, with the onset of translational order there is also an onset of orientational order - typically characterized by the order parameter Q_{ij} , a traceless second rank tensor [14, 15]. Therefore to describe the isotropic - B7 phase transition minimal ingredients include order parameters for the onset of translational and orientational order, just as for the only recently studied case of the smectic A - isotropic phase transition in Landau approximation [16].

Second, the transition enthalpy observed at the B7 - isotropic transition [3, 5] is comparable to that typically obtained for isotropic - columnar phase transitions in other classes of low

molecular weight materials including compounds made of pyramidic molecules [17]. This points to the fact that major rearrangements in the degree of order take place at this transition.

Third, one observes pronounced dielectric behavior along with flow [5]. A completely open question for the B7 phase is the role and importance of a macroscopic polarization, \mathbf{P} . There appears to be no conclusive experimental evidence as yet for the occurrence of a substantial linear electro-optic effect.

The most significant similarity is clearly the response of the isotropic phase in the vicinity of the isotropic - B7 phase boundary. Applying an electric field leads to hydrodynamic flow of significant strength [5]. When the field is turned off, this flow subsides. The same is true for temperature variations. When temperature changes are applied to a sample in the vicinity of the isotropic - B7 phase transition, this leads again to a considerable amount of flow, which stops after the temperature gradients have disappeared [5]. Such phenomena are not observed at the phase transitions between the isotropic phase and a large number of other liquid crystalline phases including, for example, nematic, smectic A, smectic C, smectic B and hexagonal columnar phases.

To decide unequivocally whether the isotropic phase above the B7 phase is actually a good candidate for the tetrahedratic phase or not, two steps seem to be important. First, the nature of the ordering in the B7 phase must be identified, in particular with respect to the existence of a macroscopic polarization \mathbf{P} . And second, it would be crucial to investigate in detail the behavior of the isotropic phase above the B7 phase under external electric fields and temperature gradients in the absence of the B7 phase.

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