

# Macroscopic Properties of Smectic $C_G$ Liquid Crystals

Helmut R. Brand<sup>1 a</sup>, Harald Pleiner<sup>2</sup> and P.E. Cladis<sup>3</sup>,

<sup>1</sup>Theoretische Physik III, Universität Bayreuth, 95440 Bayreuth, Germany.

<sup>2</sup>Max-Planck-Institute for Polymer Research, POBox 3148, 55021 Mainz, Germany.

<sup>3</sup>Advanced Liquid Crystal Technologies, POB 1314, Summit, NJ 07902, U.S.A.

**Abstract.** We discuss the macroscopic behavior of smectic  $C_G$  liquid crystals. Smectic  $C_G$  is the most general tilted smectic phase that is fluid in the layers. It is characterized by global  $C_1$  symmetry. Consequently, it is ferroelectric, pyroelectric and piezoelectric, opening up a number of possible applications for such a phase. As smectic  $C_G$ -phase has a macroscopic hand due to its structure, it is a natural candidate to explain the recent experimental observations of left and right-handed helices in a system composed of achiral molecules. We also discuss critically to what extent smectic  $C_G$  could be important for liquid crystalline phases formed by banana-shaped molecules. Phase transitions involving a smectic  $C_G$  phase and defects of its in-plane director are briefly discussed.

**PACS.** 61.30.-v Liquid crystals – 64.70.Md Transitions in liquid crystals – 77.84.Nh Dielectric, piezoelectric and ferroelectric materials: liquid crystals

## 1 Introduction

The question of the type of electric properties, e.g. ferro- and antiferroelectricity, possible in liquid crystalline materials composed of achiral molecules has recently attracted increasing attention [1-7]. These developments can be traced back, at least in part, to the prediction that suitably bent achiral molecules arranged on smectic layers on average parallel to their bend direction could form a fluid biaxial smectic phase with a macroscopic polarization in the smectic layer planes:  $C_P$  [1,2]. This phase has  $C_{2v}$  symmetry, i.e. a two-fold symmetry axis and a vertical mirror plane perpendicular to the smectic layers and including the two fold axis.

Over the last two years many compounds composed of achiral bent or banana-shaped molecules have been synthesized and investigations of their physical properties begun [3-10]. Among these numerous studies, we highlight two.

By measuring the hysteresis loop and investigating the temperature dependence of the pyroelectric coefficient, Soto Bustamente et al. [3,4] showed that antiferroelectricity is possible in mixtures of achiral side chain liquid crystalline polymers. Quite recently, Sekine et al.[6] described the observation of an equal number of left and right-handed helices in a liquid crystalline phase composed of achiral banana-shaped molecules.

These recent experimental results give rise to a number of important questions. Which biaxial fluid smectic phases (for compounds composed of achiral molecules) can give rise to antiferroelectric, ferroelectric and ferroelectric behavior? How can one obtain left and right-handed helices in fluid smectic phases when the constituents are achiral? How does the smectic  $C_M$  phase, which is a fluid biaxial orthogonal smectic phase [11], fit into this picture? The smectic  $C_M$  phase was first observed in side-on side chain liquid crystalline polymers [12,13].

Its physical properties including its defects [1], its macroscopic and electric behavior [14] as well as phase transitions involving smectic  $C_M$  have been addressed [15,16].

In the present paper we focus on the smectic  $C_G$  phase [11], where the subscript  $G$  stands for general. Smectic  $C_G$  is a biaxial smectic phase that is fluid in the layers and for which none of the principle axes of the second rank tensor characterizing the orientational order includes an angle of 0 or 90° with the planes of the smectic layers. We argue that the smectic  $C_G$  phase is ferroelectric in the bulk and that the structure of this liquid crystalline phase is chiral (in the physical sense) [17], even though its constituents are achiral (in the chemical sense). Thus, this phase comes in a left-handed and a right-handed version. This fact provides a natural explanation for the equal number of left and right-handed helices recently observed [6]. In particular, we discuss the macroscopic properties of smectic  $C_G$  as well as its defect structures. We also sketch properties of some phase transitions involving the smectic  $C_G$  phase. Finally, we suggest ways to distinguish between smectic  $C_G$  and smectic  $C$ , as well as smectic  $C_M$  and  $C_P$ .

## 2 General Symmetry Considerations

In the smectic  $C$  phase, the direction of long range orientational order,  $\hat{n}$ , is tilted with respect to the layer normal,  $\hat{k}$ . In smectic  $C$ , then, the director,  $\hat{n}$ , is not parallel to the layer normal  $\hat{k}$  as it is in the smectic  $A$  phase [11] which has  $D_{\infty h}$  symmetry for achiral compounds. Thus, smectic  $C$  is a phase with global  $C_{2h}$  symmetry [11]: it has a two fold axis parallel to the smectic layers and a horizontal mirror plane perpendicular to the smectic layers and the two fold axis. In smectic  $C$ , the in-plane director  $\hat{c}$ , which is the projection of the director  $\hat{n}$  onto the smectic planes, is not equivalent to  $-\hat{c}$ . As smec-

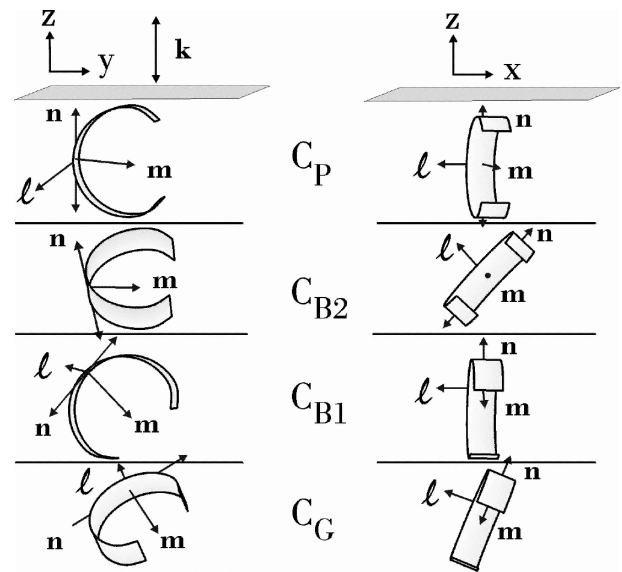
<sup>a</sup> e-mail: cladis@alct.com

tic  $C_M$  [11] is not tilted, its global symmetry is higher ( $D_{2h}$ ). Nevertheless, it is biaxial and fluid in the layers and thus a genuine smectic phase. The in-plane director in smectic  $C_M$ ,  $\hat{\mathbf{m}}$ , is indistinguishable from  $-\hat{\mathbf{m}}$  [1,14,15], a feature that has important consequences for its macroscopic properties and defect structures.

In ref.[1], we suggested the existence of a truly ferroelectric biaxial fluid smectic phase,  $C_P$ , with  $C_{2v}$  symmetry for which there is no horizontal mirror plane but a preferred direction in the layer planes i.e.  $\hat{\mathbf{m}}$ , is distinguishable from  $-\hat{\mathbf{m}}$  (Fig. 1, first row). Thus a macroscopic polarization along this preferred direction is possible leading to a phase that is either ferroelectric or ferrielectric (in the latter case there are two sublayers whose macroscopic polarization is partially compensated) in the bulk. In addition, there is also the possibility that the macroscopic polarizations of the two sublayers is exactly compensated. This case has been discussed in detail by Soto Bustamente et al.[3,4]: there is no net macroscopic polarization resulting in a truly antiferroelectric structure.

One might want to call this truly antiferroelectric phase smectic  $C_A$ , where the subscript  $A$  stands for antiferroelectric. However, this designation has been previously used for the ‘anti-helielectric’ phase in compounds composed of chiral molecules [18]. The term anti-helielectric introduced here complements the term helielectric introduced in ref. [19]. While in the helielectric  $C^*$  phase the polarization is rotating in a spiral fashion perpendicular to the helix axis giving rise to net polarization zero when averaged over many pitch lengths, the case of anti-helielectricity is even more intricate. When going from one layer to the next the macroscopic polarization changes by about  $\pi$ . Thus one has two interpenetrating helices in this case, which both have the same pitch, but again the net polarization is zero when averaged over a sufficiently thick sample. We suggest this phase, which is truly antiferroelectric [3,4], be called smectic  $C_{PA}$ . In this way, we indicate: a) it is a fluid biaxial smectic phase in compounds composed of achiral molecules; b) it has a macroscopic polarization in each of its two sublayers; and c) the macroscopic polarizations of its two sublayers exactly compensate.

Tilting of banana shaped molecules can be done in two different ways. First the preferred direction  $\hat{\mathbf{m}}$  stays untilted and  $\hat{\mathbf{n}}$  and  $\hat{\mathbf{l}}$  (cf. Fig. 1, second row) become tilted. This results in a phase with  $C_2$  symmetry, where  $\hat{\mathbf{m}}$  is the two-fold rotation axis, while the vertical mirror plane is absent due to the tilt. A macroscopic polarization is only possible along the symmetry axis. This ferroelectric phase composed of molecules without chirality has a macroscopic hand due to its structure. If the layers are stacked with alternating polarizations, an antiferroelectric structure is obtained. A different phase is found, if the preferred direction  $\hat{\mathbf{m}}$  (and  $\hat{\mathbf{n}}$ ) is tilted, but  $\hat{\mathbf{l}}$  remains in the smectic layers (cf. Fig. 1, third row). Then the two-fold rotation axis is gone, but the mirror plane (identical to the tilt plane) is still there. This gives a  $C_{1h}$  symmetric phase, where the polarization is restricted to lie in the tilt plane. Thus this phase is ferroelectric with polarization components in the smectic layers as well as perpendicular, and it is achiral. If layers are stacked with opposite  $\hat{\mathbf{m}}$  but the same tilt direction, again an antiferroelectric phase appears (with an in-layer and out-of-layer component of the staggered polarization). If layers with opposite

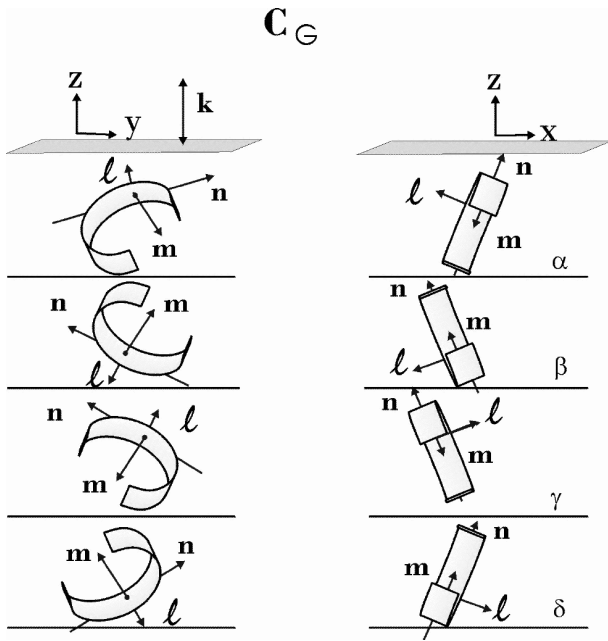


**Fig. 1.** Plot of the classes of fluid biaxial phases that are ferroelectric: the untilted phase  $C_P$ , the phases tilted with respect to one direction,  $C_{B2}$  and  $C_{B1}$ , and the doubly tilted phase  $C_G$ . Note that smectic  $C_{B2}$  and  $C_G$  have a macroscopic hand; for symmetries and other physical properties see text and Table 1.

tilt direction, but the same  $\hat{\mathbf{m}}$  are stacked, this phase is antiferroelectric perpendicular, but ferroelectric within, the layers, while stacking layers with opposite tilt and opposite  $\hat{\mathbf{m}}$  gives ferroelectricity perpendicular, and antiferroelectricity within, the layers. Since these phases are expected to arise predominantly for compounds composed of banana-shaped molecules, they could be called  $C_{B2}$  and  $C_{B1}$ , respectively.

So far, we have focused on biaxial fluid smectic phases where at least one of the principle axes of the bananas lies within the smectic layers. If we drop this restriction, the smectic  $C_G$  phase [11] results (Fig. 1, fourth row). In smectic  $C_G$  all three principle axes include an angle with the smectic layers different from 0 and  $90^\circ$  (double tilted structure). As a result, smectic  $C_G$  has, in general, global  $C_1$  symmetry, the lowest possible symmetry: triclinic [20].  $C_1$  symmetry means that this phase has no symmetry at all and that therefore a macroscopic polarization exists that can point in any direction i.e. is not determined by any symmetry element. The low symmetry, ( $C_1$ ), of the  $C_G$  phase has a large number of important consequences [20] for the macroscopic properties of smectic  $C_G$  that we discuss in detail in the next section. In particular, any smectic  $C_G$  phase should be ferroelectric in the bulk.

We stress that we use the term ‘ferroelectric’ for all phases that show a non-vanishing spontaneous polarization in the bulk. This implies automatically such phases to be pyroelectric and piezoelectric as well (for piezoelectricity this statement cannot be inverted). We do not make a distinction between pyroelectric and ferroelectric phases based on hysteretic switchability (of the latter) – as is done sometimes. Since ‘switchability’ is neither a feature based on symmetry arguments nor a property of the phase itself (e.g. a surface stabilized smectic  $C^*$  is switchable, but the phase is helielectric and not ferroelectric), such a distinction is not useful when discussing material



**Fig. 2.** Sketch of the right-handed ( $\alpha, \beta$ ) and left-handed ( $\gamma, \delta$ ) versions of smectic  $C_G$ . Note that the existence of a *macroscopic handedness* of the  $C_G$  phase follows quite similarly as the *microscopic handedness* for an asymmetric carbon atom on a molecular scale.

properties (and classifying phases) by symmetry considerations only.

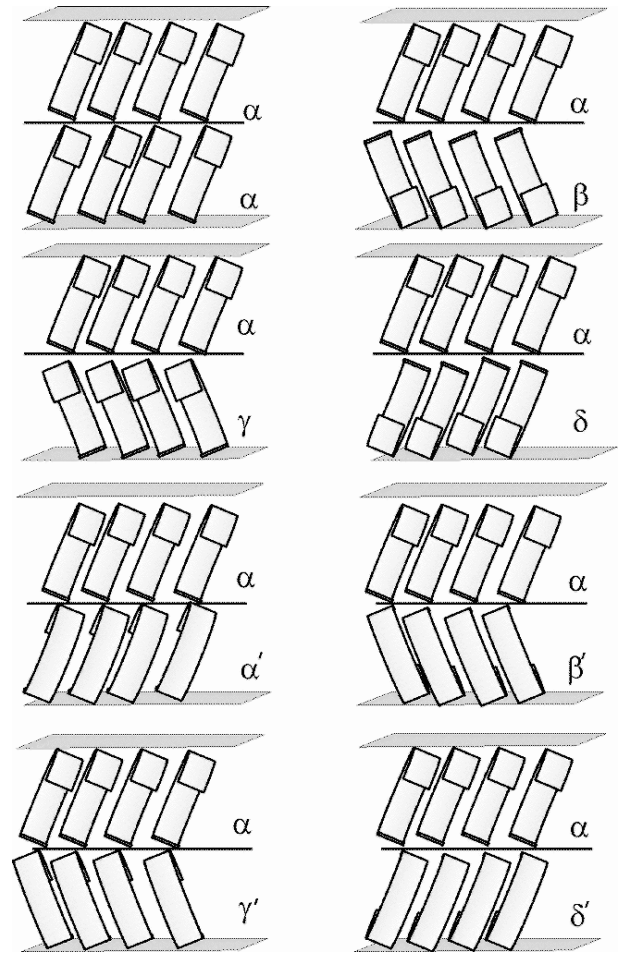
Inspecting Fig. 2 closely, one realizes that this phase has a macroscopic handedness, although the molecules (constituents) themselves do not.

That means, that smectic  $C_G$  has macroscopically a hand in the bulk with two possibilities, namely left-handed ( $\alpha, \beta$ ) and right-handed ( $\gamma, \delta$ ) versions, as sketched in Fig. 2. It contains as a natural special case the  $C_{B2}$  phase discussed above.

While such a behavior is well known from solids [21], this is the first time it is discussed for liquid crystal phases, in particular, for smectic phases with in-plane fluidity. The combination of these two properties, macroscopic handedness of the *phase* (in contrast to the chirality of the molecules involved in chiral smectic phases such as smectic  $C^*$  [11]) and in-plane fluidity, makes it plausible that such a phase will form statistically an equal number of left and right-handed helices macroscopically. And this is precisely what has been observed by Sekine et al. [6].

In Fig. 3 we show the wide range of possibilities that emerges when two layers of the different forms of smectic  $C_G$  are associated.

We note, that all the other biaxial fluid smectic phases discussed in this section, namely smectic  $C$ ,  $C_M$ ,  $C_P$ ,  $C_{B1}$  and  $C_{PA}$  do not possess a macroscopic hand. There is thus no reason to observe any helices, not even an equal number of left and right-handed helices, in these phases in compounds composed of achiral molecules. It appears then that smectic  $C_G$  and  $C_{B2}$  are the only candidates known to date that can account for the experimental observations of Sekine et al. [6].



**Fig. 3.** Fig. 3 shows some of the possibilities that emerge when two layers of different forms of smectic  $C_G$  are associated. Also shown are forms, where the molecules are facing into the drawing plane ( $\alpha', \beta', \gamma', \delta'$ ) instead of out. Stackings like ( $\alpha, \alpha$ ) are ferroelectric, while ( $\alpha, \delta'$ ) are antiferroelectric. Novel are ( $\alpha, \beta$ ) stackings that are ferroelectric within the layers and antiferroelectric perpendicular to them. Vice-versa for ( $\alpha, \gamma'$ ). These possibilities are also found in the  $C_{B1}$  phase which is contained in  $C_G$  as a special case. More novel behavior is found for ( $\alpha, \gamma$ ) and ( $\alpha, \alpha'$ ) stackings which are ferroelectric perpendicular to the layers as well as in one direction within the layers, but antiferroelectric in the other layer direction. Vice-versa, ( $\alpha, \delta$ ) and ( $\alpha, \beta'$ ) are ferroelectric in one direction in the layers and antiferroelectric in the other layer direction as well as perpendicular to the layers.

### 3 Macroscopic and Electric Properties of $C_G$

Since smectic  $C_G$  has in general  $C_1$  symmetry, there exists [20] a polar vector  $p_i = (p_x, p_y, p_z)$ , whose direction is not determined by simple symmetry considerations. This implies that, in contrast to  $C_P$  and  $C^*$ , the direction of macroscopic polarization is not fixed in a special symmetry direction. For  $C_P$  it has to be in a specific direction set by the mirror-plane and by the two fold axis. For one layer of smectic  $C^*$ , the polar direction and thus the direction of the polarization  $\mathbf{P}$  is also fixed by symmetry considerations [11].

In the  $C_G$  phase one can construct 3 independent, non coplanar vectors,  $\hat{\mathbf{m}}$ ,  $\hat{\mathbf{k}} \times \hat{\mathbf{m}}$ , and  $\hat{\mathbf{n}} \times \hat{\mathbf{m}}$  and the actual polarization is a linear combination of those. Now chirality can also be seen easily, since the triple product made of these three polar vectors is a pseudoscalar:  $\tilde{q} = \hat{\mathbf{m}} \cdot [(\hat{\mathbf{k}} \times \hat{\mathbf{m}}) \times (\hat{\mathbf{n}} \times \hat{\mathbf{m}})] = \hat{\mathbf{m}} \cdot (\hat{\mathbf{k}} \times \hat{\mathbf{n}})$ . For  $\hat{\mathbf{m}}$  to  $-\hat{\mathbf{m}}$  the chirality changes from, say, right- to left-handed, which can also be seen from Fig. 1.

Because smectic  $C_G$  possesses a polar vector, it has rather interesting macroscopic electric and electromechanical properties. For that part of the generalized free energy we obtain in lowest order

$$\Phi = \int d\tau [\epsilon_{ij}^E E_i E_j + P_i E_i + E_i (\zeta_i^T \delta T + \zeta_i^p \delta p + \zeta_i^c \delta c) + d_{ij} E_i \nabla_j u_z] \quad (3.1)$$

The contribution  $\sim \epsilon_{ij}^E$  is the usual dielectric term, which contains six independent coefficients for triclinic symmetry. The next term is the one characteristic for all ferroelectric materials. The terms  $\sim \zeta_i^T$ ,  $\zeta_i^p$  and  $\zeta_i^c$  are related to pyroelectric effects, pressure electric effects and to an electric response resulting from a concentration change in mixtures. All three first rank tensors are of the structure  $\zeta_i^\alpha = \zeta^{i\alpha} p_i$  and thus contain three independent coefficients each. The last term in Eq. (3.1) is related to piezoelectric effects coupling the electric field to gradients of the layer displacement  $\mathbf{u} \cdot \hat{\mathbf{k}}$ . Since we have a layered structure (smectic), which is fluid in the layers, only first order gradients of  $u_z$  contribute (when  $\hat{\mathbf{z}}$  corresponds to the direction of the layer normal) to lowest order in the gradients. Thus  $d_{ij}$  contains six independent coefficients for smectic  $C_G$  (assuming  $\nabla \times \mathbf{E} \equiv 0$ ).

In addition to these linear electric and electromechanical effects, the symmetry of  $C_G$  also allows for second harmonic generation. The corresponding contribution  $\Phi_{SHG}$  reads

$$\Phi_{SHG} = \int d\tau \chi_{ijk}^{(2)} E_i E_j E_k \quad (3.2)$$

where  $\chi_{ijk}^{(2)}$  contributes 10 independent coefficients.

In addition to the static effects discussed so far, one can set up the macroscopic dynamics of smectic  $C_G$ , including dissipative and reversible parts, using the usual procedure. It turns out, that in particular the dissipative contributions bring along a host of coefficients due to the low symmetry of smectic  $C_G$ .

Here we just focus on one coupling, namely the coupling between flow (velocity gradients) and the macroscopic polarization, which can lead to the possibility to align the in-plane component of the polarization,  $\mathbf{P}$ , by a flow in the layer planes or, vice versa, a motion of the in-plane component of the polarization can lead to a flow the planes of the layers. In general this coupling (which is reversible, since it is associated with vanishing entropy production) is of the form

$$\sigma_{ij}^R = \dots + \xi_{ijk} P_k \quad (3.3)$$

$$J_k^P = \dots - \xi_{ijk} \nabla_i v_j \quad (3.4)$$

As one can see from Eq. (3.3), the reversible part of the stress tensor,  $\sigma_{ij}^R$ , acquires a contribution proportional to the

macroscopic polarization and from Eq. (3.4) it follows that the polarization current,  $J_k^P$ , contains a coupling to velocity gradients,  $\nabla_i v_j$ . In the most general case, the third rank tensor  $\xi_{ijk}$  has 18 independent components. Most of the coupling terms will involve either a component of  $\mathbf{P}$  out of the planes or an out of plane component of the velocity. These will lead to rather complicated deformations involving the smectic layers. If both, the velocity gradients and the polarization are in the planes, however, an analogue of flow alignment [11] can arise for  $\mathbf{P}$  and thus lead, for example, to the coupling

$$J_x^P = \xi_{xyx} \nabla_y v_x \quad (3.5)$$

Undoubtedly the best possibility to detect this coupling and the other in-plane contributions will be the study of freely suspended smectic films [22,23] in the  $C_G$  phase.

## 4 Defects of the in-plane Director in Smectic $C_G$

The preferred direction in the planes of the layers in smectic  $C_G$  is a polar vector  $\hat{\mathbf{c}}$ , which distinguishes between head and tail. Correspondingly there are no defects of strength  $S = (2n + 1)/2$  (where  $n$  is an integer) in smectic  $C_G$ , but only defects of integer strength  $S = n$ . Thus the situation for defects of the in-plane director is the same as for smectic  $C$  and smectic  $C_P$ . This has to be contrasted with the orthogonal biaxial smectic  $C_M$  phase, whose symmetry allows for defects of half integer strength for the in-plane director.

It also seems important to discuss in this connection the truly antiferroelectric phase  $C_{PA}$  for which the polarizations of the two alternating sets of layers exactly cancel [3,4,24,25]. In this case half integer defects of the in-plane director should be possible, since there is no overall polar direction - remembering that a double layer has zero net polarization. Due to its intricate structure, however, the antiferroelectric phase  $C_{PA}$  offers a unique possibility. Applying an external electric field  $\mathbf{E}$  the two subsets of polarization will no longer exactly cancel and there will be a field-induced net polarization left over. As a consequence we expect in such a situation only defects of integer strength to be stable. Therefore the prediction is that, starting with a sample in the smectic  $C_{PA}$  phase containing defects of half integer strength, the application of a sufficiently strong external electric field should lead to the combination of these half integer defects to form defects of integer strength exclusively. Or, as an alternative, they could just disappear.

## 5 Phase Transitions involving Smectic $C_G$

The key features characterizing the ordering of a smectic  $C_G$  phase are its layering and the fact that it is a polar phase, which has a macroscopic polarization  $\mathbf{P}$ . As it is well known from solid state physics, this macroscopic polarization  $\mathbf{P}$  can also serve as the order parameter of certain phase transitions, for example of the paraelectric - ferroelectric phase transition in many solids. In the following we want to outline, what can be said from general and simple symmetry arguments about phase transitions involving a smectic  $C_G$  phase. Throughout

we will confine ourselves to the mean field approximation thus ignoring fluctuation effects.

There are phase transitions between a smectic  $C_G$  phase and other smectic phases including smectic  $A$ ,  $C$ ,  $C_M$  and  $C_P$  (all fluid in the layer planes). For smectic  $A$ ,  $C$  and  $C_M$  one starts with a layered phase that shows the appropriate orientational order, but no polar order, i.e. there is no macroscopic polarization. Correspondingly the macroscopic polarization  $\mathbf{P}$ , where  $\mathbf{P}$  has in general three independent components, emerges as a natural candidate for the order parameter describing the phase transitions  $A-C_G$ ,  $C-C_G$  and  $C_M-C_G$ . Assuming that a Ginzburg-Landau expansion makes sense (that is, assuming that the phase transition is not strongly first order) the corresponding Ginzburg-Landau energy for the terms containing the macroscopic polarization  $P_i$  is of the following structure

$$\begin{aligned} \Phi = \Phi_0 + \int d\tau [ & a\mathbf{P}^2 + c_{ijkl}P_iP_jP_kP_l + d_{ijkl}(\nabla_iP_j)(\nabla_kP_l) \\ & + e_{ijkl}P_iP_j\nabla_kP_l ] \end{aligned} \quad (4.1)$$

The starting phase (smectic  $A$ ,  $C$  and  $C_M$ , respectively) reflects itself in the different number of coefficients involved in the fourth rank tensors  $c_{ijkl}$ ,  $d_{ijkl}$  and  $e_{ijkl}$ , but not in its overall structure. The term in front of  $\mathbf{P}^2$  need not be a second rank tensor, which would be the most general ansatz. As we are dealing with the first phase transition involving the macroscopic polarization  $\mathbf{P}$  (not to be confused with the electric dipole moment of the molecules), the prefactor of  $\mathbf{P}^2$  can be chosen to be a scalar without loss of generality. The direction of  $\mathbf{P}$  in the low symmetry phase is determined by the values of the coefficients contained in  $c_{ijkl}$ . We also note that the  $C_M-C_G$  transition is characterized, in addition, by a tilt angle (similar to the  $A-C$  transition) and for the  $A-C_G$  transition there is, in addition, a tilt angle as well as biaxial nematic order. For example, it turns out that for the smectic  $A$  - smectic  $C_G$  transition the fourth rank tensor  $c_{ijkl}$  contains in the bulk three independent coefficients,  $d_{ijkl}$  brings along five and  $e_{ijkl}$  four. The contribution proportional to  $e_{ijkl}$ , which only exists for systems with a vector order parameter (with a true vector), is well known to favor incommensurate and modulated phases for certain combination of parameter values in the Ginzburg-Landau energy from solid ferroelectrics [26]. As can be seen from Eq. (5.1) the Ginzburg-Landau energy does not have a contribution cubic in  $\mathbf{P}$  and, thus, all these phase transitions can be of second order offering a new chance to test in detail the theory of phase transitions on a number of systems.

For the smectic  $C_G$  - smectic  $C_P$  transition the situation is slightly different. While the overall structure of Ginzburg-Landau energy is the same as for the other three phase transitions just discussed, the order parameter changes, since smectic  $C_P$  has already a macroscopic polarization with a fixed direction of the polarization  $P_0 = |\mathbf{P}_0|$  in the plane of the layers. Correspondingly the polarization  $\mathbf{P}$  in eq.(5.2) must be replaced for the smectic  $C_P-C_G$  phase transition by  $\delta\mathbf{P} = \mathbf{P} - \mathbf{P}_0$  with  $\delta\mathbf{P} \cdot \mathbf{P}_0 = 0$ . Thus the order parameter for this transition has only two components instead of three. We note that the order parameter are the components  $\delta\mathbf{P}$  of the macroscopic polarization  $\mathbf{P}$ , which are perpendicular to the macroscopic polarization  $\mathbf{P}_0$  that exists already in the  $C_P$ -

phase. The new symmetry elements are thus characterized by  $\delta\mathbf{P}$ , a macroscopic quantity, which should not be confused with the electric dipole moment.

The isotropic - smectic  $C_G$  phase transition is more complicated. First it is very likely that it is a (rather strongly) first order transition, where a Ginzburg-Landau treatment is less significant. Second, at that transition the layering and the orientational order have to emerge simultaneously such that the polar order is created. Therefore one needs an order parameter that describes the strength of the smectic layering as well as an order parameter that gives the biaxial and oblique orientational order leading together to the polar order. Thus the appropriate Ginzburg-Landau parameters of the quadratic terms (say  $a$  and  $a'$ ) have to vanish in the vicinity of (the fictitious second order phase transition)  $T^*$ , otherwise the system would not make an isotropic - smectic  $C_G$  transition, but rather e.g. an isotropic - smectic  $A$  transition. We note that an isotropic - ferroelectric transition has never been observed in a system that is fluid in all three spatial dimensions.

Another phase transition of interest would be a biaxial nematic - smectic  $C_G$  transition. This phase transition bears at first sight some resemblance with the biaxial nematic - smectic  $C_M$  transition found in side-on liquid crystalline side chain polymers [13] and analyzed in mean field approximation in ref.[15]. It turned out that this latter phase transition can be of second order and that it can be thought of as putting books onto a shelf. As outlined in Sec. 2, the situation for biaxial nematic - smectic  $C_G$  is slightly different, since the smectic layers are intersecting all unit vectors of the triad characterizing the biaxial nematic order under an angle that is different from 0 and 90°. This leads to the polar ordering and we have to consider the macroscopic polarization  $\mathbf{P}$  as an additional order parameter in addition to the complex scalar function  $\psi$  characterizing the smectic layering. Thus the order parameter characterizing the biaxial nematic - smectic  $C_G$  transition is rather different from the order parameter used to describe biaxial nematic -  $C_M$ . Analyzing the former transition along similar lines as the latter one [15], we find that the smectic  $C_G$  - biaxial nematic transition can also be of second order, since a cubic invariant cannot be constructed for the Landau functional using  $\psi$  and  $\mathbf{P}$  as order parameters.

## 6 Differences in the Physical Properties of smectic $C_G$ versus smectic $C_P$ , $C_{PA}$ , $C_M$ , $C_{B1}$ and $C$

After characterizing the physical properties of  $C_G$ , the question arises how does one distinguish such a phase from other biaxial fluid smectic phases composed of achiral molecules, namely  $C_P$ ,  $C_{PA}$ ,  $C_M$ ,  $C_{B1}$ ,  $C_{B2}$  and  $C$ . In addition, it is important to know how to distinguish these four classes among each other. And, of course, it is important to have tools that can be implemented easily like polarizing microscopy or electro-optic techniques. In Sec. 2 we have discussed, that  $C_G$  comes naturally with macroscopic handedness in a left-handed and in a right-handed version, since the structure of the phase is chiral. This is not the case for  $C_P$ ,  $C_{PA}$ ,  $C_M$ ,  $C_{B1}$ , and  $C$ . Thus, if an equal number of left and right-handed helices is observed in

a biaxial fluid smectic phase, the prime candidates are smectic  $C_G$  and  $C_{B2}$ , since there is no obvious reason for  $C_P$ ,  $C_{PA}$ ,  $C_M$ ,  $C_{B1}$  and  $C$  to show a tendency towards helix formation, when composed of achiral molecules.

This leaves us with the task to distinguish by simple means  $C_P$ ,  $C_{PA}$ ,  $C_M$  and  $C$ . As we have seen in Sec. 4,  $C_M$  and  $C_{PA}$  can show defects of half integer strength for the in-plane director due to their overall symmetry, whereas smectic  $C$  and  $C_P$  can only reveal defects of integer strength of the in-plane director. A simple way to discriminate between a classical  $C$  phase and a  $C_P$  phase is the evaluation of a  $P - E$  hysteresis loop. While a smectic  $C$  phase is dielectric, smectic  $C_P$  is ferroelectric or ferroelectric and thus is expected to show the corresponding hysteresis in the  $P - E$  loop, well known in solid state physics. Using the same technique also smectic  $C_M$  and  $C_{PA}$  can be distinguished, since  $C_M$  is dielectric, while  $C_{PA}$  is truly antiferroelectric. The analysis given in this section up to now is summarized in Table 1.

We would also like to point out that there exist many other techniques which are useful to discriminate between the various classes. One are x-ray investigations in the wide angle regime of well-oriented samples. The classic  $C$  phase, for example, shows two crescents that are tilted with respect to the equator asymmetrically. In contrast smectic  $C_M$  is an orthogonal phase that shows four lobes located symmetrically above and below the equator. This latter type of behavior has clearly been demonstrated by Watanabe's group [25, 27-29] for main chain liquid crystalline polymers as well as for a special class of low molecular weight compounds.

## 7 Conclusions and Perspective

In this manuscript we discussed the macroscopic properties and the defect structures of smectic  $C_G$  as well as the phase transitions involving this most general biaxial smectic phase with fluidity in the smectic layers, which has very low symmetry:  $C_1$ . We note that we have looked previously [30-32] at cholesteric and chiral smectic structures, mainly for polymers, that can also have in certain cases  $C_1$  symmetry locally. But due to the chirality of the molecules the overall symmetry of these liquid crystalline structures is typically  $C_\infty$ .

Apart from characterizing the macroscopic physical properties of the  $C_G$  phase we have made concrete suggestions how to distinguish experimentally  $C_G$  from  $C_M$ ,  $C_P$ ,  $C_{PA}$  and  $C$  phases by using the defect structures of the in-plane director, the presence or absence of left and right-handed helices as well as measurements of the hysteresis loop. We have summarized the corresponding results to be expected in Table 1. From these three types of behavior, it emerges that among these five different classes the polymer mixtures studied by Soto Bustamente et al. [3,4] fall into class  $C_{PA}$ , the banana-shaped molecules analyzed by Sekine et al. [6] are a very good (and the first) candidate for  $C_G$  or  $C_{B2}$ , since they show an equal number of left and right-handed helices, and the side-on side chain liquid crystalline polymers studied by Leube and Finkelmann [12,13] belong to class  $C_M$ , as discussed previously [1,14,15].

There are clearly several open questions and future challenges. One of them is to find more compounds showing a

smectic  $C_G$  phase. Another important question is to sort out which ones of the liquid crystalline phases formed by the various classes of banana-shaped molecules [5-10,18] are ferro- or ferro-electric ( $C_P$ ) and which ones are truly antiferroelectric and thus of class  $C_{PA}$  showing defects of half integer strength of the in-plane director.

Another interesting question is to what extent can the various compounds be mixed to optimize properties of technological interest. For example, for the anti-helielectric phases [18] it has been possible to reduce the threshold field for electro-optic effects by more than a factor of two by doping them with a helielectric  $C^*$  phase [33]. A recent effective internal field model [34] accounts quantitatively for the observed changes in the threshold field and will undoubtedly also be helpful to characterize electro-optic properties of mixtures involving banana-shaped molecules.

A wide open area of research is clearly the problem to what extent the concepts that have been useful to achieve interesting electro-optical properties in banana-shaped low molecular weight materials can be carried over to side chain as well as to main chain liquid crystalline polymers and elastomers containing such molecules.

*Acknowledgements:* It is a pleasure for P.E.C. to thank the Alexander von Humboldt Foundation for the award of an Alexander von Humboldt Research Prize. Partial support of H.R.B. by the Deutscher Akademischer Austauschdienst through PROCOPE 312/pro-gg is also gratefully acknowledged.

## References

1. H.R. Brand, P.E. Cladis, H. Pleiner, *Macromolecules* **25**, 7223 (1992).
2. P.E. Cladis, H.R. Brand, *Liq. Cryst.* **14**, 1327 (1993).
3. E.A. Soto Bustamente, S.V. Yablonskii, B.I. Ostrovskii, L.A. Beresnev, L.M. Blinov, W. Haase, *Chem. Phys. Lett.* **260**, 447 (1996).
4. E.A. Soto Bustamente, S.V. Yablonskii, B.I. Ostrovskii, L.A. Beresnev, L.M. Blinov, W. Haase, *Liq. Cryst.* **21**, 829 (1996).
5. T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, *J. Mat. Chem.* **6**, 1231 (1996).
6. T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S.W. Choi, H. Takezoe, *J. Mat. Chem.* **7**, 1307 (1997).
7. D.R. Link, G. Natale, R. Shao, J.E. McLennan, N.A. Clark, E. Körblova, D.M. Walba, *Science* **278**, 1924 (1997).
8. S.V. Shilov, H. Skupin, F. Kremer, T. Wittig, R. Zentel, *Phys. Rev. Lett.* **79**, 1686 (1997).
9. K.J.K. Semmler, T.J. Dingemans, E.T. Samulski, *Liq. Cryst.*, in print (1998).
10. Abstracts of the workshop 'Banana-shaped liquid crystals: chirality by achiral molecules' held at the Technische Universität Berlin, Dec.10-11, 1997, edited by G. Heppke.
11. P.G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).
12. H. Leube, H. Finkelmann, *Makromol. Chem.* **191**, 2707 (1990).
13. H. Leube, H. Finkelmann, *Makromol. Chem.* **192**, 1317 (1991).
14. H.R. Brand, H. Pleiner, *J. Phys. II France* **1**, 1455 (1991).
15. H.R. Brand, H. Pleiner, *Makromol. Chem. Rapid Commun.* **12**, 539 (1991).
16. P. Schiller, H. Schlacken, *Liq. Cryst.*, in print (1998).

- 17 Throughout the present paper we use the word ‘chiral’ according to its meaning in a physics context: ‘characteristic of an object that cannot be superposed upon its mirror image’. This use must be distinguished from its common use in chemistry, where it refers to a molecular property: ‘the handedness of an asymmetric molecule’. Compare, for example, *The McGraw-Hill Dictionary of Scientific and Technical Terms*, Fifth Edition, S.P. Parker, Editor in Chief (McGraw-Hill, New York, 1994).
- 18 A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, J. Mater. Chem. **4**, 997 (1994).
- 19 H.R. Brand, P.E. Cladis, and P.L. Finn, Phys. Rev. **A31**, 361 (1985).
- 20 W.P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand, New York, 1958).
- 21 Compare, for example, N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt-Saunders, Philadelphia, 1976), or ref.[20].
- 22 P.E. Cladis, Y. Couder, H.R. Brand, Phys. Rev. Lett. **55**, 2945 (1985).
- 23 P.E. Cladis, P.L. Finn, H.R. Brand, Phys. Rev. Lett. **75**, 1528 (1995).
- 24 J. Watanabe, M. Hayashi, Macromolecules **21**, 278 (1988).
- 25 J. Watanabe, M. Hayashi, Macromolecules **22**, 4083 (1989).
- 26 J.W. Felix, D. Mukamel, R.M. Hornreich, Phys. Rev. Lett. **57**, 2180 (1986).
- 27 J. Watanabe, S. Kinoshita, J. Phys. II France **2**, 1237 (1992).
- 28 J. Watanabe, Y. Nakata, K. Simizu, J. Phys. II France **4**, 581 (1994).
- 29 J. Watanabe, H. Komura, T. Niiori, Liq. Cryst. **13**, 455 (1993).
- 30 H. Pleiner, H.R. Brand, Mol. Cryst. Liq. Cryst. **148**, 271 (1993).
- 31 H. Pleiner, H.R. Brand, J. Phys. II France **3**, 1397 (1993).
- 32 H. Pleiner, H.R. Brand, Europhys. Lett. **28**, 579 (1994).
- 33 S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, A. Fukuda, J. Mater. Chem. **6**, 671 (1996).
- 34 P.E. Cladis, H.R. Brand, Ferroelectrics, in print (1998).

**Table 1:**

| class of phase | symmetry | strength of defects | electro-optic response                                    | L.H. & R.H. helices |
|----------------|----------|---------------------|---|---------------------|
| $C_M$          | $D_{2h}$ | half integer        | dielectric  | no                  |
| $C_P$          | $C_{2v}$ | integer             | ferro- or ferrielectric<br>$\mathbf{P} = (P_x, 0, 0)$     | no                  |
| $C$            | $C_{2h}$ | integer             | dielectric  | no                  |
| $C_{B2}$       | $C_2$    | integer             | ferro- or ferrielectric<br>$\mathbf{P} = (P_x, 0, 0)$     | yes                 |
| $C_{B1}$       | $C_{1h}$ | integer             | ferro- or ferrielectric<br>$\mathbf{P} = (P_x, 0, P_z)$   | no                  |
| $C_G$          | $C_1$    | integer             | ferro- or ferrielectric<br>$\mathbf{P} = (P_x, P_y, P_z)$ | yes                 |

Table 1: The expected defect structures and the electrical hysteresis properties are presented for the six different classes of smectic  $C$  phases composed of achiral molecules. In this Table we concentrate on the phases that are either dielectric or ferro- (ferri-) electric.