Symmetry and Defects in the C_M Phase of Polymeric Liquid Crystals

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ABSTRACT: Motivated by the recent discovery of a novel biaxial and orthogonal smectic polymeric liquid crystal with in-plane fluid order (smectic C_M), we discuss defects allowed by its symmetry. Smectic C_M has not yet been found in low molecular weight liquid crystals. We point out that the observation of defects provides a useful tool to distinguish smectic C_M from other biaxial and fluid smectic phases known as smectics C and C_2. The structure of a possible ferroelectric, but nonchiral phase (smectic C_P) is briefly discussed.

Introduction

Following the first synthesis in 1978 of liquid crystalline side-chain polymers,[1] many novel materials were synthesized with the electrooptical features of low molecular weight liquid crystal materials combined with the structural properties of polymers.[2,3] Most recently, a fluid smectic phase that is biaxial and orthogonal has been reported for the first time in "side-on" liquid crystalline side-chain polymers and their mixtures with a low molecular weight liquid crystal.[4,5] In the side-chain polymer exhibiting this novel phase, the spacer group tethering a liquid crystal monomer to the polymer backbone is attached to the monomer in a side-on connection much like an umbilical cord.[6] The understanding is that this type of connection promotes the formation of biaxial liquid crystal phases by reducing the monomer's rotational freedom about its long axis.

The new biaxial, fluid, and orthogonal smectic phase was found by cooling a side-on side-chain liquid crystalline polymer, called polymer 1, from a biaxial nematic state.[5] It was identified as biaxial from conoscopic observations in the polarizing microscope and orthogonal and fluid in the layers from X-ray investigations.[5] The new phase was found to occur in mixtures of the polymer (containing a lateral naphthalene group in the side chain; see refs 4 and 5 for details) with a low molecular weight compound[5] for mixtures containing more than about 50% by weight of the polymer.

An intuitive picture is the following: when the fraction of boardlike objects tethered to the polymeric backbone in an umbilic fashion, and thus showing hindered rotation about their long axis, becomes too small, the macrosopic biaxiality of the mixture goes to zero, leaving only uniaxial phases such as uniaxial nematics and smectic A. We note that the parent polymer shows the phase transitions

$$g - 303\ K - C_M - 319\ K - N_{bx} - 326\ K - i$$

and that the polymer and the low molecular weight material are miscible in all proportions.[5] The width of the two phase regions ΔT_c in the mixtures with the low molecular weight compound is $\Delta T_c \sim 2$ K. For the complete phase diagram, we refer to Figure 5 of ref 5. N_{bx} denotes a biaxial nematic phase and the label C_M is explained below. This new phase has all the properties of the smectic phase named smectic C_M by de Gennes[7]

where M refers to MacMillan who first described this phase.

Although a large number of smectic phases is known from studies of low molecular weight systems, the smectic C_M phase has so far only been identified for polymeric liquid crystals.[5] The most familiar[7] low molecular weight smectic liquid crystal phases are the ones showing fluidity in the layers such as smectic C. The possibility emerges that some phases, now classified as smectic C because they are fluid and optically biaxial, may turn out to be actually smectic C_M phases. Therefore, it is useful to give simple criteria based on symmetry arguments to facilitate the identification of smectic phases, in particular smectic C_M, in polymeric and low molecular weight liquid crystals. The powerful link between symmetry arguments and macroscopic physical properties of materials is illustrated by our prediction of a novel ferroelectric fluid polymeric liquid crystal without chiral molecules in another biaxial and fluid smectic phase.

In a mean field approximation,[8] Brand and Pleiner discussed phase transitions involving smectic C_M and investigated the hydrodynamic and electrohydrodynamic properties of both smectic C_M and smectic C^*_M, the chiralized version of smectic C_M that has a spiral structure but no tilt.[9] In a mean field approximation, they find that the biaxial nematic–smectic C_M transition can be continuous.[8] Indeed, DSC measurements[4] in polymer 1 show no evidence of a latent heat at the biaxial nematic–C_M transition. Brand and Pleiner also point out the possibility of continuous A–C_M and C_M–C phase transitions.[8]

So far, defects and their usefulness for identifying smectic C_M liquid crystal phases from macroscopic observations in the polarizing microscope of either polymeric or low molecular weight liquid crystals have not been discussed. Indeed, as mentioned above, C_M may have already been observed but was not identified as such because it is a fluid biaxial smectic phase similar to smectic C.

A model for a new biaxial, orthogonal smectic phase, smectic C_P, is shown in Figure 1. In this model, the unit cell is a bilayer with orthorhombic symmetry, C_{2v}: it lacks one of the three possible mirror planes. As is well-known,[10] bulk ferroelectricity is associated with C_{2v} symmetry with polarization P (in Figure 1) parallel to the 2-fold axis. We note that such a structure is *ferroelectric without chiral molecules* (Figure 1).

At the other extreme, we point out that the biaxial orthogonal fluid smectic phase observed in the nonchiral main-chain liquid crystalline polymers BB5, BB7, BB9, etc.[11,12] *also* has C_{2v} symmetry, but *antiferroelectric* order.

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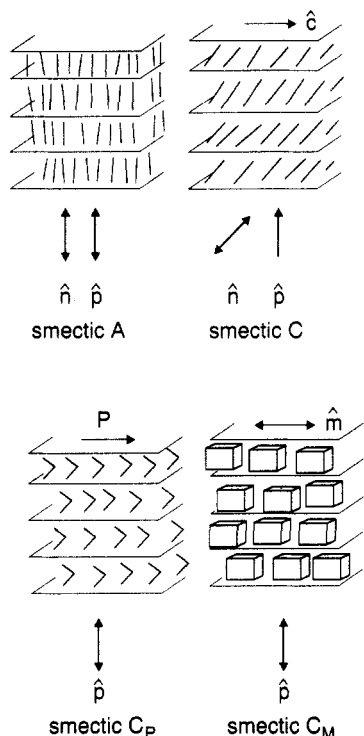‡ Kyushu Institute of Technology.
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Figure 1. Structure of smectics A, C, C$_P$, and C$_M$.

Both the C$_P$ phase suggested here and the phase found by Watanabe and Hayashi[11,12] (that they call smectic C$_2$) have a chevron structure. One can easily imagine ferrielectric phases bridging the gap between ferroelectricity and antiferroelectricity, that have also C$_{2v}$ symmetry.

Since smectic C$_P$ and smectic C$_M$ both have orthorhombic symmetry, they have the same number of elastic constants and viscous coefficients, even though X-ray measurements show differences in their point symmetry.

Thus the discovery of C$_P$ would be the first time that a nonchiral material shows a truly ferroelectric liquid crystal phase.

General Properties of Smectic C$_M$

Here we point out that the knowledge of smectic C$_M$ defects and their properties is useful for distinguishing between smectic A, nematic, and most importantly, the optically biaxial smectic C and C$_P$ phases. In particular, we suggest that differences in the in-plane symmetry of the different smectic phases are most simply revealed by observations of defects in the polarizing microscope of freely suspended films. In freely suspended smectic films, defects in the layering are absent and the sample is most conveniently viewed in a direction parallel to the layer normal. We stress that defects of the in-plane director can also be obtained in bulk samples or in drops on free surfaces. In these cases, however, it is more difficult to show that one has only a defect in the in-plane director and not a combined defect in the layering and in the in-plane director. Because polymer dynamics is slow relative to low molecular weight materials, these systems also present an opportunity for studying, e.g., coarsening dynamics and the associated scaling laws for topological defects on experimentally accessible time scales.

Smectic C$_M$ has D_{2h}, smectic C$_P$ has C_{2v}, and smectic C phase has C_{2h} point (local) symmetry. The usual nematic and smectic A liquid crystals have uniaxial symmetry, $D_{\infty h}$. Nematics have broken continuous rotational symmetry with a preferred direction, characterized by a director, $\hat{n}$, a unit vector, that does not distinguish between head and

tail.[7] In smectic A, a layered state, the layer normal is a unit vector $\hat{p}$ that is indistinguishable from $-\hat{p}$. In the plane of its layers, smectic A is an isotropic liquid[7] and the director $\hat{n}$ is parallel to $\hat{p}$ (see Figure 1).

In classical smectic C phases, which are fluid and biaxial, the average direction of the molecules, the director $\hat{n}$, is at a constant tilt angle to the layer normal $\hat{p}$. The projection of $\hat{n}$ in the plane of the layers is called $\hat{c}$. The smectic C ground state is invariant only under the *simultaneous* replacements $\hat{p} \rightarrow -\hat{p}$ and $\hat{c} \rightarrow -\hat{c}$. Because of the tilt, these replacements cannot be made separately (see Figure 1).

For an overview of defects in liquid crystals other than smectic C$_M$, see ref 13. Various textures are shown and explained in ref 14.

In contrast to classical smectic C, smectic C$_M$ has no tilt and $\hat{p}\|\hat{n}$. The in-plane preferred direction is characterized[8] by a director, $\hat{m}$, that is orthogonal to the layer normal $\hat{p}$. The ground state is invariant under the replacement $\hat{p} \rightarrow -\hat{p}$ or $\hat{m} \rightarrow -\hat{m}$ *separately*[8] (see Figure 1). As we will see in the following, this difference along with the higher local symmetry of C$_M$ allows for a convenient qualitative optical distinction between smectic C and smectic C$_M$ in freely suspended films.

As for smectic C$_P$, the operation $\hat{p} \rightarrow -\hat{p}$ leaves the ground state invariant; an operation equivalent to $\hat{m} \rightarrow -\hat{m}$ does not exist. This gives rise to the possibility for a spontaneous polarization, P, in the plane of the layers for smectic C$_P$ (see Figure 1).

Defects of the In-Plane Director

First, we consider line defects in smectics associated with the in-plane director, either $\hat{m}$ in C$_M$ or $\hat{c}$ in C when the smectic layers are flat: i.e. $\hat{p}$ is fixed. These defects, called disclination lines or disclinations, are shown in Figure 4.2 of ref 7. On a circuit around a disclination line, the director changes its "inclination" (rotates) by $2\pi S$ where S defines the strength of the line. For $\hat{m} \rightarrow -\hat{m}$ symmetry, the lowest order defects are the Möbius defects, $S = \pm^1/_2$. In the absence of this symmetry, the lowest order defects are $S = \pm 1$.

When viewed between crossed polarizers in a direction parallel to the defect line, disclinations of strength $S = \pm^1/_2$ are characterized by two black brushes while defects of strength $S = \pm 1$ are characterized by four black brushes. Besides the number of brushes radiating from a defect line, to identify defect strength, it is also important to check the rate of rotation of the brushes as the sample is turned between crossed polarizers. For example, if the defect line is at an angle to the field of view, then, because of the more complicated optics this implies, a defect of strength $S = 1$ could show two brushes, not all four brushes normally associated with it. On the other hand, when a defect of strength $S = 1$ is rotated between crossed polarizers, the four brushes do not move while brushes associated with defects $S \neq 1$ are "mobile".

While defects of strength $S = \pm 1$ are equivalent to a defect-free topology[15] in uniaxial nematics, this is not the case for biaxial nematics. This is because, e.g., allowing a singularity in $\hat{n}$ to escape into the third dimension introduces a singularity in $\hat{m}$ in biaxial nematics.

In smectic phases, there is a strong coupling between $\hat{n}$ and $\hat{p}$ so escape into the third dimension introduces dislocations in the layered structure. Defects of strength $S = \pm 1$ in smectic systems have a singular core in contrast to defects of this strength in uniaxial nematics. Thus, if no dislocations are introduced in the layering, disclination energies scale like S^2 making, e.g., two $S = ^1/_2$ defects less

energetic than one topologically equivalent $S = 1$ defect. But, an $S = 1$ will decay into two $S = \frac{1}{2}$ defects if, and only if, $S = \pm\frac{1}{2}$ disclinations are allowed by symmetry.

Because of the nematic-like $\hat{m} \rightarrow -\hat{m}$ equivalence in smectic C_M, $\hat{m}$ can have defects of strength $S = \pm\frac{1}{2}$ and $S = \pm1$, just as in uniaxial nematic liquid crystals. In contrast to smectic C_M, in the classical tilted smectic C phase, $\hat{c}$ is not equivalent to $-\hat{c}$. Therefore, only defects of strength $S = \pm1$ (2π rotations) are possible for the in-plane director, $\hat{c}$, and no $S = \pm\frac{1}{2}$ defects (π rotations) are allowed by its symmetry.[16]

This difference leads to the suggestion of how to distinguish smectic C and smectic C_M from the observations of defects in the polarizing microscope: if one observes that a fluid, optically biaxial smectic phase has defects of strength $S = \pm\frac{1}{2}$, it cannot be a classical smectic C phase, but possibly it will be a smectic C_M phase with no tilt.

We point out that in the ferroelectric smectic C_P phase introduced above, $S = \pm\frac{1}{2}$ defects in the in-plane director are ruled out by symmetry, since the in-plane director in C_P as well as in C distinguishes head and tail.

We also note, that the C_2 phase discussed above[11,12] does not show $S = \pm\frac{1}{2}$ defects, but rather dispirations, i.e. combined defects in the layering and the in-plane director.[17,18] In contrast, smectic C_M can show true $S = \pm\frac{1}{2}$ disclinations without additional defects in the layering. This is because smectic C_M has D_{2h} symmetry, while the C_2 phase of refs 13 and 14 has C_{2v} symmetry. Thus, smectic C_M is unique among the fluid biaxial smectic phases in allowing for the existence of $S = \pm\frac{1}{2}$ defects in the in-plane director.

Defects Involving Layering and the In-Plane Director

While the energy to compress or dilate layers is large, for layered systems with fluid in-plane order, curvature energy to deform layers is small. The most famous defects for smectic phases with in-plane fluidity are focal conic defects observed as singularities in the layering along lines known as Dupin cyclides.[7,19-21] When many occur, the resulting texture is known as a *fan texture*. The important property of focal conics is that they conserve microscopic layer spacing when the layers are curved. Because layer curvature energy is small, focal conic defects are easily observed with a polarizing light microscope without special attention to sample preparation and become "broken" when the layer spacing changes as, for example, at a smectic A (unbroken fans) to C (broken fans) phase transition. For the C phase, additional problems from tilt mismatch (see Figure 25 of ref 16) at focal conic line singularities provide another argument for why fan textures are broken in the C phase but not in the A phase.[14]

Because of its $\hat{m}$ to $-\hat{m}$ symmetry, smectic C_M does not have a matching problem. Furthermore, the C_M layer spacing, similar to smectic A, is close to the fully extended monomer length. On the basis of these two properties, we expect an unbroken fan texture for smectic C_M, as is indeed observed.[22] Thus, differences in fan texture provide a qualitative macroscopic distinction between smectic C and C_M.

Smectic phases with in-plane fluidity can also have edge and screw dislocations.[19,20] For systems with in-plane anisotropy, layer defects may or may not be associated with defects of the in-plane structure, providing another way to distinguish between a C_M phase and A, C_P, or C phases.

For example, in an edge dislocation, the singular line (edge line) perpendicular to the layer normal $\hat{p}$ can be decomposed[21] into two half-integer ($+\frac{1}{2}$ and $-\frac{1}{2}$) disclinations of the layer normal, $\hat{p}$. In this description, that is all that can happen for smectic A with $\hat{p}\|\hat{n}$. In a C_M phase, whether $\hat{m}$ shows a defect or not depends on its orientation relative to the edge line. If $\hat{m}$ is parallel to the edge line, there is no defect and $\hat{m}$ is constant everywhere, while when $\hat{m}$ is perpendicular to the edge line, it makes a half-integer disclination of the same sign as $\hat{p}$. The latter type of edge dislocation is expected to cost more energy and, therefore, should occur less frequently than the first one.[9]

In smectic C, however, splitting an edge dislocation into two disclinations of the layer normal, $\hat{p}$, always has the geometrical implication of defects for the director $\hat{n}$. $\hat{c}$ perpendicular to the edge line creates a disclination[13] for $\hat{n}$, while $\hat{c}$ parallel to the edge line creates an energetic tilt inversion wall[14,16] for $\hat{n}$ where the tilt angle changes sign (see, e.g., Figure 4 of ref 16). While tilt inversion defects may also play a role in the broken fan texture observed when a smectic A phase transforms to a smectic C phase, being very energetic, electron microscopy techniques are likely required to observe them.

Screw dislocations, where the singular line (the screw line) is parallel to the layer normal $\hat{p}$, are frequently seen in freeze fracture electron microscopy.[20] In the A phase the director is constant everywhere (except for one small core region that we disregard in this discussion) and shows no defect. The same holds for a C phase and also for a C_M phase. As there is no qualitative difference for screw dislocations in these phases, they are not expected to be useful for discriminating between smectic C_M and smectic A or C.

Conclusions and Perspectives

Many compounds classified as smectic C solely on the basis of their in-plane fluidity and optical biaxiality may turn out to be actually smectic C_M or even C_P phases. A combination of the study of defects (presented here), of the phase transitions involving a possible C_M phase,[8] and of the hydrodynamic and electrohydrodynamic properties[9] will be useful to find more examples of smectic C_M and an example of C_P in both polymeric and low molecular weight liquid crystals. We have pointed out that C_M is unique among biaxial smectic phases in that stable $S = \pm\frac{1}{2}$ disclinations can occur without the introduction of dislocations in the layer structure. This can be most conveniently and easily checked by polarizing microscope observations. This method has been used by Takanishi et al.[17,18] to demonstrate that a dislocation always accompanies $S = \pm\frac{1}{2}$ disclinations in the biaxial orthogonal smectic phase found in the main-chain polymer BB5.

The occurrence of the smectic C_M phase seems much easier to achieve in a controlled way, however, in side-on side-chain liquid crystalline polymers than in low molecular weight materials or even in the more common end-on side-chain liquid crystalline polymers, where the mesogenic units are attached at one end of the mesogen to the spacer connecting to the polymeric backbone. This feature can be traced back to the design of the side-on side-chain liquid crystalline polymers: the molecules are attached to the polymeric backbone in such a way as to prevent their rotation about their long axis, thus giving rise only to biaxial phases. In fact, this concept was pioneered by Hessel and Finkelmann[6] in their search for biaxial nematic phases in thermotropic liquid crystalline polymers. Therefore, it appears completely natural that the smectic phase below

a biaxial nematic phase in these polymers is also biaxial and thus of the C_M type and not of the usual uniaxial smectic A type prevalent in end-on side-chain polymers and in low molecular weight materials. On the basis of this reasoning, we expect that the smectic C_M phase will be most conveniently obtained in side-on side-chain liquid crystalline polymers and, consequently, in sufficiently concentrated mixtures with the more common end-on side-chain polymers or even low molecular weight materials.[5]

After this analysis one might ask whether it is also possible to observe smectic C_M and its defects in main-chain liquid crystalline polymers in which the mesogenic units are incorporated into the polymeric backbone. While a C_M phase has not yet been reported, perhaps partly because one has not applied the concept outlined above for side-chain polymers to main-chain polymers, it seems worthwhile to notice that already in 1988 Watanabe and Hayashi[11,12] discussed, on the basis of their X-ray analysis, a fluid orthorhombic biaxial phase. They suggested that the occurrence of such a phase is favored over smectic A and C in the odd homologues of the BBn series[11,12] by packing arguments. In this case the picture is that molecules in one layer tilt in one direction and in the next layer they tilt in the opposite direction, thus giving rise to a chevron structure that is orthorhombic, i.e. a fluid biaxial smectic phase. The resulting overall symmetry is, however, not D_{2h}, as for smectic C_M, but rather C_{2v}. We point out here that the model presented by Watanabe and Hayashi[11,12] implies antiferroelectricity in the nonchiral compound, a suggestion that should surely be checked experimentally by looking at a P – E loop on a sample of this compound.

We note, that the study of defects and their motion, for example in an external electric field, has become of interest recently also outside the field of liquid crystalline polymers, namely in block copolymers,[23] where one has observed defects that are similar to those observed in smectic liquid crystalline polymers.

In the present paper, we have presented general symmetry arguments that apply to low molecular weight liquid crystals as well as they do to polymeric liquid crystals. Hessel and Finkelmann[6] have shown that the polymeric structure can be used to control the rotations of the mesogenic units, leading to novel ordered structures that are more difficult to obtain in nonpolymeric materials.

For example, we pointed out here, for the first time, the possibility of a side-on side-chain liquid crystalline polymer that is ferroelectric in the bulk without chiral molecules. Development of such a material would open the door for new optoelectronic applications that will emerge when ferroelectricity in a liquid crystalline material is coupled with the structural advantages provided by polymers.

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