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Orthoconic liquid crystals — A case study

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ABSTRACT

Since the early investigations on liquid crystals it was realized how the confining surfaces often determine the textures and even properties of the material. This influence is particularly complex and important for chiral materials. When we come to chiral smectics the surfaces may have dramatic effects. These are illustrated on the ferroelectric liquid crystals; they then again increase in importance for the antiferroelectric liquid crystals where the most recent example is given by the orthoconic liquid crystals.

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1. History

In 1910 Charles Mauguin in Paris pioneered the study of liquid crystals (or Lehmann liquids as they were often called at that time) in that he was the first to show, beyond doubt, that the nematic liquid crystal (the name nematic was given later by Friedel) is a true anisotropic liquid [1]. It is a 3D fluid that is *oriented* in space. It is birefringent, uniaxial positive, with an optic axis that is strongly influenced by the substrates between which it is enclosed. A little later he started systematic investigations on how certain substrates, for instance mica, oriented the optic axis and was able to obtain homogeneous preparations of nematics with the optic axis everywhere parallel to a certain crystal direction along the two identical substrates. On twisting the two substrates relative to each other he was able to observe that the optic axis next to the substrates seemed to be fixed to the surface, thus giving the optic axis a helicoidal structure in the bulk between the two substrates [2]. In other words, there must exist a thin film of liquid crystal at the surface, in which, as simply expressed, the long axis of the rodlike molecules has a strongly preferred direction dictated by the surface. Around ten years later François Grandjean, also in Paris, studied the more complicated case of aligning a cholesteric liquid crystal by a surface [3]. A cholesteric is likewise a 3D fluid but has an inherent periodical structure (it is a chiral form of nematic) in which the long axis of the molecule is strongly twisted around a common direction, the twist axis. He found that the cholesteric tends to align such that the molecules are parallel to the substrates, as with the typical nematic case. Therefore the twist takes place

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going from one substrate to the other with the helical axis perpendicular to the substrates. This alignment condition is commonly called "Grandjean texture". With some skill he also managed to get the opposite alignment such that the helix axis lies *parallel* to the substrate. It turns out, however that this surface condition, that would be quite useful in many modern devices, is not very stable — it has the tendency to relax back to the Grandjean texture. The reason is easy to understand: this condition is not supported by any simple surface. A supporting surface for this case would have to be periodic, with the right periodicity, and possibly also chiral. This example may illustrate the importance of surfaces for the alignment of liquid crystals. By modern techniques one can achieve planar alignment (optic axis homogeneously parallel to the substrate), perpendicular (often called homeotropic) alignment (optic axis homogeneously perpendicular to the substrate), or even alignment with the optic axis tilted a certain angle — but it is very hard to create a surface supporting a periodic condition. This will be important in the discussion below.

In 1911 Friedel and Grandjean in Saint-Étienne [4,5] and then Grandjean 1916 in Paris [6] made their breakthrough studies that disclosed the nature of the other important class of liquid crystals, the smectic. A smectic is a layered liquid crystal. The kind of smectic that they studied had the rodlike molecules (and the optic axis) perpendicular to the layer, each layer forming a kind of 2D fluid. There is fluidity in the layer but not across it. Thus, along the optic axis there is a quasi-crystalline periodicity in one dimension. This smectic, now called smectic A, naturally aligns with the layers parallel to the substrates, but it is also possible to get the molecules to align along the substrates such that the layers stand perpendicular to them ("bookshelf texture"). Already in the 1920s Daniel Vorländer in Halle insisted that there are other kinds of smectics but the evidence for this came only in the 1960s with the investigations by the later Halle group of Sackmann, Arnold and Demus [7]. In fact, the most important of these, the smectic C, where the molecules tilt a certain angle with respect to the smectic layer normal, was not identified until 1970 by Arora, Fergason and Saupe [8]. This led to a new interest in smectics, and especially after the new breakthrough that came in 1974 with R. B. Meyer's recognition that the chiral version of smectic C, now usually written smectic C*, must have an intrinsic electric polarization. Meyer called this phase ferroelectric (although in the ferroelectric community it would rather be called helielectric) and the intrinsic polarization was demonstrated shortly after [9]. Meyer's insight is particularly striking because, with the basic symmetry operation valid for all liquid crystals known at that time — that the sign of the director $\boldsymbol{n}$ (loosely representing the average of molecular directions) can be inversed without affecting the system — most liquid crystals cannot be polar. Thus the nematic phase is non-polar and you have to reduce the symmetry down to a tilted smectic *and* break the mirror symmetry in order to allow a polarization vector $\boldsymbol{P}$ compatible with invariance under $\boldsymbol{n} \rightarrow -\boldsymbol{n}$. On the other hand, if this condition was not valid, in principle any liquid crystal phase could be polar.

For years only a few smectic C* materials were available but the activity in synthetic chemistry increased considerably after the observation of spontaneous ferroelectric domains in thin bookshelf preparation of smectic C* by Clark and Lagerwall in 1980 [10]. This allowed very fast switching between two symmetrically stable states and created immediate interest for display applications. In the following years many chemistry groups, not least in Japan, tried to synthesize new materials with ever increasing value of spontaneous polarization, in the belief that this would lead to faster switching. While this is not really the case (higher polarization tends to go along with higher viscosity) this led finally to the discovery of the antiferroelectric liquid crystals in 1989, simultaneously in Paris by Galerne and Liébert and by the Fukuda group in Tokyo [11–13].

2. Ferroelectric liquid crystals

In Fig. 1 is shown the smectic C* structure at the top, each smectic layer represented by a cone on which the molecule (more accurately the *director*, the local average of the molecular directions) has a freedom to move with the tilt angle θ prescribed. The local polarization $\boldsymbol{P}$ is always perpendicular to the plane that includes the director and the layer normal. The lack of mirror symmetry in smectic C* allows a local vector property (the polarization), but it also allows a helical distribution of this polarization by which it cancels itself in the bulk. The helix has a somewhat analogous role to the splitting up of the polarization in opposite domains in a solid ferroelectric. The appearance of spontaneous domains in thin bookshelf samples of smectic C* can now be understood as follows. As explained earlier there is no surface that supports a helicoidally varying director along the surface. The surface forces the director to be aligned homogeneously in a certain direction or, depending on the specific surface treatment, at least in the plane of the surface. In the bulk, however, the distribution is helical, as this is the inherent structure of the smectic C* phase. Between each surface and the main part of the bulk there must therefore be a region rich on orientational defects. These are line disclinations with a distance in between corresponding to the helical pitch (or half the pitch, depending on the type of surface anchoring) mediating the incompatible structures. When the surfaces are brought closer together (the critical distance should be of the order of the helical pitch, which is about 1 μm) the helix will be elastically unwound by the surface torques, leaving only two directions of the director compatible both with being on the cone and being on the substrate surface. The unwinding of the helix costs less energy than the structure gains by getting rid of the line defects. While the helical state is the ground state of the bulk, the non-helical state is the ground state of this *surface-stabilized* smectic C*. This state represents the lowest energy (equilibrium condition) and is hence stable in the absence of any applied field. The two director orientations correspond to polarization $\boldsymbol{P}$ up and down as shown in the lower part of the figure. The spontaneous up and down domains have now replaced the helix. In the virgin state the domains of each sign sum up to equal area, but if we apply a field across the sample, all uncomfortable domains will, above a certain threshold, switch over to the opposite direction. As can be seen, this corresponds to switching the slow axis of the dielectric tensor by twice the tilt angle, 2θ. With "slow axis" we here mean the tensor axis representing the highest dielectric value (and thus the highest refraction index). For the electro-optics of smectic C* (the phase is biaxial) this axis is the effective optic axis, while the two real optic axes are irrelevant. As the tilt angle can be made typically 22–23°, this is a powerful electro-optic effect giving a very good dark state between crossed polarizers and a very high contrast. The helix-unwound structure is bistable and is called surface-stabilized ferroelectric

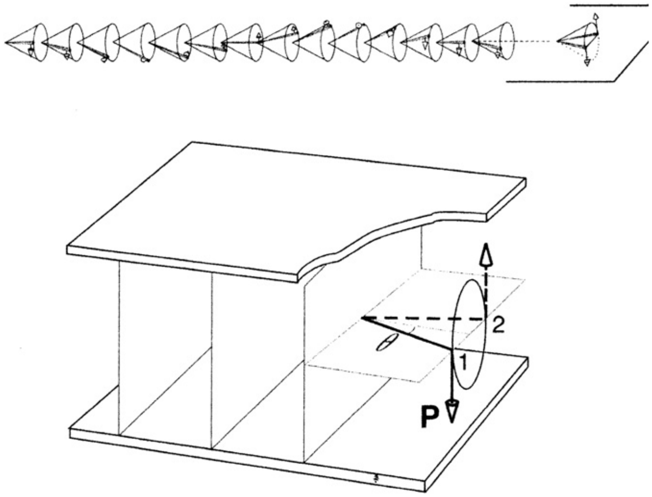

Fig. 1. Smectic C* in its natural form (top left) and in the surface-stabilized structure due to the confining cell surfaces in a display. The constraint for the molecule to be on the cone but also along the surface results in two permitted directions, the bistable states (top right).

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