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Reappraisal of The Optical Textures of Columnar Phases in Terms of Developable Domain Structures with Relaxed Constraints and a Rationale for The Striated Texture

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Abstract: Optical textures pictured in the seminal 1974 textbook, *The Microscopy of Liquid Crystals*, by Norman Hartshorne, have been reappraised. Some of these, which were described by Hartshorne (and many others) as *confused focal conics*, were of chromonic and discotic phases, which had not been identified at that time—and would now be recognized as developable domain structures of columnar phases. It is suggested that the rigorous constraint of isometry in these is relaxed in regions of the director field under high stress. A rationale for the characteristic striated appearance of columnar textures is proposed, in which the molecular columns are bundled together, forming twisted ropes within the domains. It is also suggested that the regular alternation of opposing domains in M ribbons minimizes the slippage of columns required as the mesophase develops, and an explanation of the characteristic multi-pole appearance of the brushes in the optical textures of columnar structures is proposed.

Keywords: Hartshorne; Bouligand; liquid crystals; optical textures; developable domains; columnar hexagonal phases

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1. Preface

This article is divided into three numbered parts, Section 1, which includes the Introduction and background, Section 2, which describes the reappraisal of Norman Hartshorne's inferences drawn from his observed optical textures in light of subsequent published work, and Section 3, which contains original material: new tentative hypotheses for the striated texture and the multi-nucleated appearance of discontinuities in the optical textures of columnar structures.

In the years between 1930 and his death in 1982, Norman Hartshorne was among a small handful of internationally recognized experts on optical microscopy in general and of liquid crystals in particular. In 1974, he wrote the first book dealing specifically with the optics of mesophases, *The Microscopy of Liquid Crystals*, Volume 48 in *The Microscope Series* [1]. This comprehensive small volume covered the optical microscopy of the then-known world of liquid crystals, lyotropic and thermotropic. It included descriptions of mesophases which would now be recognized as developable domain structures of columnar phases [2,3]. Previously, his textbook, *Crystals and the polarizing microscope*, co-authored by the geologist, Allan Stuart, [4] was regarded as the definitive volume on the subject (and ran to seven editions). In his later life, after retiring as Reader in Physical Chemistry at the University of Leeds, he ran courses in optical microscopy under the banners of both the Royal Microscopical Society and the London branch of the McCrone Research Institute.

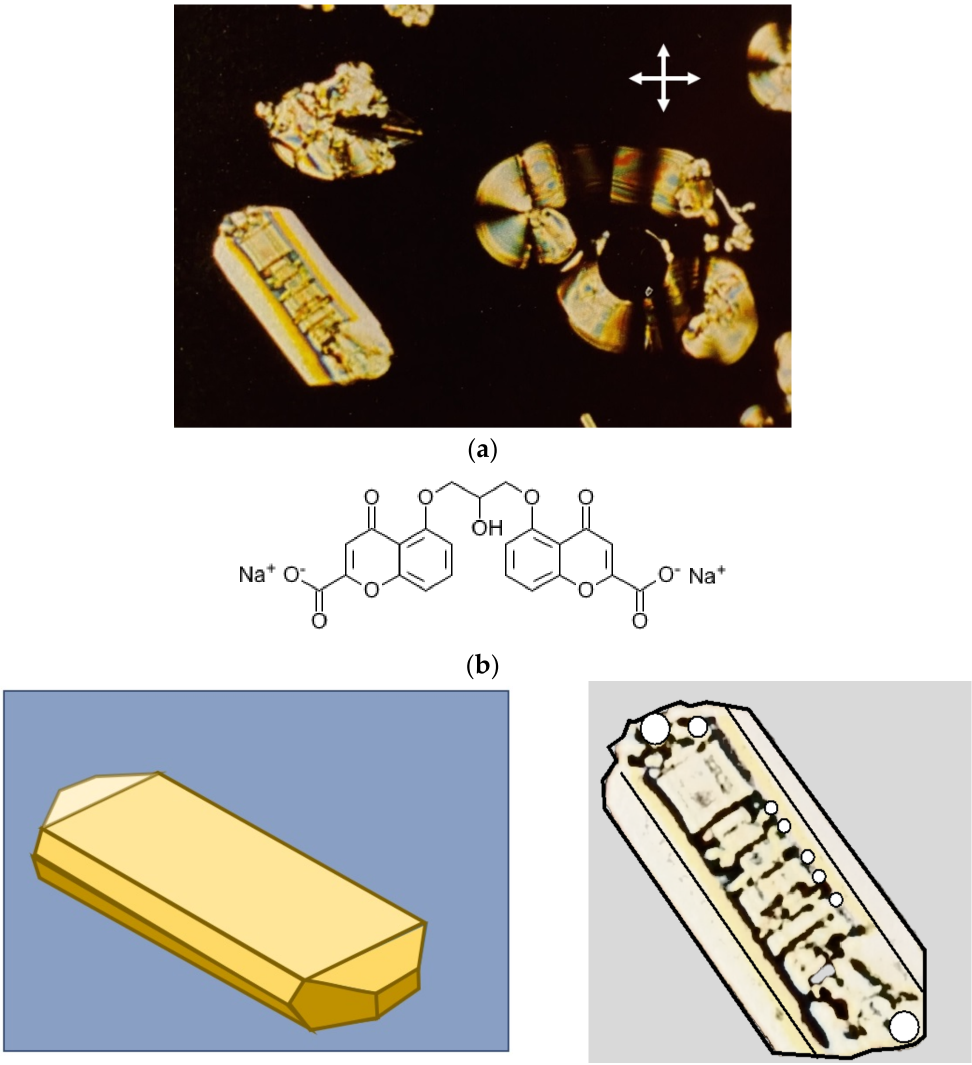
The came at a time of rapid expansion of the subject [5]. Prior to this, things had been relatively simple and neatly compartmentalized into lyotropic mesogens, which were largely the possession of the soap and detergent industry, and the thermotropics, which were synthesized by organic chemists and studied by a few physicists. Their only property, which was seen as being exploitable at that time, was the thermochromic nature, of cholesteric phases, for temperature mapping, in medicine (for detecting cancerous growths) and for military night vision devices [6]. There were occasional far-sighted papers such as Bernal and Fankuchen's article on the mesophase formed by the tobacco mosaic virus in 1941 [7], but these were isolated and were in no way mainstream liquid crystal literature works. Reviews of liquid crystals rarely mentioned carbonaceous phases or biological materials other than lipids. The aggregation of dye molecules in solution was not mentioned in the context of liquid crystalline phases. Each area had its own terminology, and the papers dealing with them were usually published in different journals. The first specialist journal dealing with liquid crystals, *Molecular Crystals* (which was to evolve into Molecular Crystals and Liquid Crystals), appeared in 1966. Its rival journal, *Liquid Crystals*, started in 1986, and *Liquid Crystals Today* in 1990.

In the following decades, the situation became rapidly more complex. Chromonic phases were identified [8–10], and discotic thermotropic phases appeared [11–13], in spite of Vorländer apparently "proving" that they were impossible [14]. Liquid crystal displays had started to cover the world. There was increased funding for liquid crystal research, and the rate of publication of articles about mesophases began to increase exponentially. The fascinating complexities of blue phases, banana-shaped mesogens, twist grain boundaries, and liquid crystalline elastomers were all well below the horizon, waiting to be discovered.

Over the years since the 1970s, there has been a sequence of invaluable textbooks on the optical textures of liquid crystals, including those listed in [15–17], but Hartshorne's book is of particular historical importance because of the work it stimulated. It was written when discotic and chromonic phases had been produced and studied, but not yet characterized and recognized as radically new families of liquid crystals. He had accurately described their optical textures and optical properties (i.e., their optical textures, birefringence, and refractive indices) in detail, but he was not able to deduce their structures. Like everyone else at that time, he was attempting to define them in terms of the known mesophase structures, i.e., the nematic and smectic thermotropic states and the lyotropic neat and middle phases.

The frontispiece of Hartshorne's book (the only colour illustration in the volume) is shown in Figure 1a. His caption reads: "These batonnets and spherulites are characteristic of the lyotropic mesophase, M, of disodium chromoglycate (INTAL), Fisons new anti-asthma drug. They are formed on cooling an aqueous solution saturated at about 65–70° to about 50°".

The features identified here as "spherulites" would now be recognized as developable domain structures [2,3] formed by M phase columns curving into circular arcs. I suggest that the richly decorated straight-sided polygon (resembling a miniature item of art deco jewellery), described as a "batonnet", is actually a single crystal of Intal, with added surface detail formed from epitaxially positioned strands and circles of the M phase. Note that the larger circular decorations tend to occur above the edges and corners of the crystal, whereas the linear and rectangular features lie in lines on the horizontal surface of the crystal, usually along prominent crystallographic axes. I interpret the complete anulus, shown on the lower right of the photograph, as a ring of chromonic M phase, formed around an air bubble.



(**a**)

(**b**)

(**c**)

(**d**)

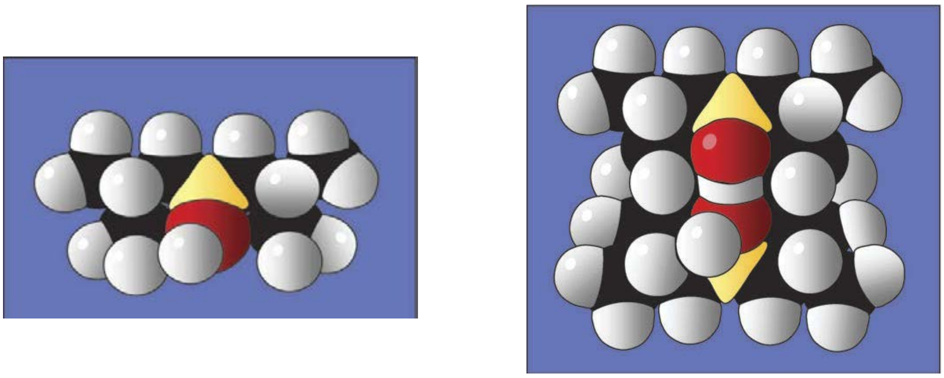
Figure 1. (**a**) A reproduction, with the permission of Microscope Publications, of the frontispiece in Hartshorne's 1974 textbook, *The Microscopy of Liquid Crystals*, [1] showing regions of the mesophase of Intal forming in the isotropic liquid [1]. (**b**) The molecular structure of the Intal. (**c**) The habit of a single crystal of Intal. (**d**) Enhanced image of the decorated "batonnet" in (**a**), with some circular features outlined.

2. Introduction

2.1. Diisobutylsilane Diol and Intal

I described previously how I came to be given an early copy of Hartshorne's book in 1974, at one of his courses in London (where, to my considerable embarrassment, I had to give the introductory lecture when he became ill) [8].

The early chapters of this book contained the standard groundwork for that time: basic microscopy, hot stages, birefringence, lyotropics and thermotropics, optical textures—schlieren patterns of nematics and focal conics—director fields of smectics, cholesteric phases, etc., with familiar drawings, such as those of Dupin cyclides and the polygonal texture of smectic phases. However, the final chapter was surprising and certainly not what you would expect to find in a textbook intended for beginners in the field. It was entitled simply *Some unusual mesophase systems*. Norman Hartshorne was highlighting material for further investigation. Its fifteen pages covered two topics. The first was the optical textures of the mesophases of the small thermotropic mesogen, di-isobutyl silane diol, shown in Figure 2 [12]. Its compact molecules did not resemble those of any known mesogen and did not look in any way suitable for mesophase formation. It occurred to me that the mesogenic units of the discotic phase might actually be the hydrogen-bonded dimers shown in Figure 2b.



(**a**) (**b**)

Figure 2. Molecular models of the monomer of diisobutyl silane diol (**a**) and the dimer (**b**) that was proposed as the structural unit of the discotic phase [12].

The second half of the chapter described the lyotropic phases formed by aqueous solutions of the then new anti-asthmatic drug, produced by Fisons. This was disodium chromoglycate, commercially known in the U.K. as Intal (from **Int**erference with **Al**lergy) and in the USA as Chromolyn. The first compound was arguably the first discotic mesogen to be characterised [12], and the second became the archetypal chromonic liquid crystalline mesogen [11,12].

In 1974, reading and re-reading Hartshorne's book, it dawned on me that although his observations would almost certainly be faultless, his interpretations of them might not necessarily be correct and that he might not have taken into consideration the possibility that he was dealing with radically new types of the mesophase that did not conform to any of the then-known structures. Perhaps the familiar terms such as *spherulites*, *batonnets*, and *focal conics*, which he had used, were not appropriate. Puzzlingly, in his comments about the two mesophases formed by Intal, he described the textures of the more dilute N phase as resembling those formed by small-molecule **thermotropic** nematic phases and the textures of the M phase as resembling those of **lyotropic** middle phases, with hexagonal arrays of cylindrical micelles, as shown in Figure 3. In this, he was perfectly correct, of course, but he did not comment on the apparently paramorphotic relationship between their two textures nor suggest that both mesophases were built out of the same stacks of molecules, nor appreciate that there was something unusually precise about the curvature of the director field within the domains in the optical texture. In addition, he specifically commented on the unusual fine detail of striations that develop with time, but did not suggest any explanation.

Bearing in mind the similarity of the optical texture of the M phase of Intal and the middle phase of conventional lyotropic systems, I wondered if they were both composed of cylindrical columns, as sketched in Figure 3.

It seemed almost heresy to question the work of such a monumental figure, and it was not until I had talked the matter over with George Gray at Hull that I decided to risk proposing new models for both systems [8,11] and eventually coined the term "chromonic".

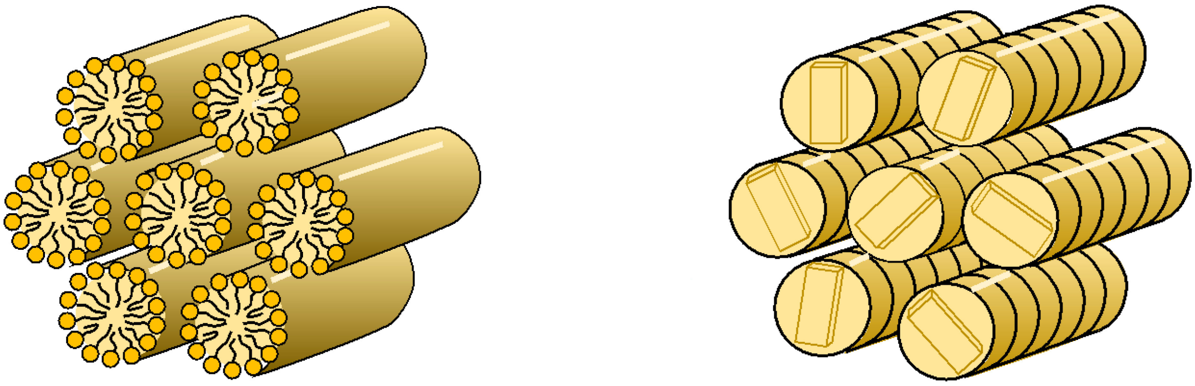

(**a**) (**b**)

Figure 3. Stylized representations of hexagonal columnar phases. (**a**) The M1 middle phase of an amphiphile/water system, showing a hexagonal array of cylindrical micelles in an aqueous continuum. The wavy radial lines represent more-or-less fluid aliphatic chains, and the small peripheral circles around each cylinder represent the hydrophilic head groups, with ionic or hydrogen bonding properties. (**b**) The hexagonal columnar structure of the chromonic M phase, showing the stacked aromatic molecules held face-to-face by π–π interactions. The rectangles drawn on the face of the discs indicate the random orientation of the stacks of aromatic groups in the columns. The peripheral hydrophilic groups attached to the aromatic cores make the columns soluble in the water continuum.

2.2. Developable Domains

The crucial factor determining the structures of developable domains is that columnar structures *splay* requires relatively high energy and the easiest distortion is *bend*. This leads to textures composed of units termed *developable domains* (discussed below), with isometric packing, of a hexagonal array, where the closest separation of the columns is constant throughout the structure.

A developable surface is a smooth surface that can be flattened onto a plane in some way by folding, bending, rolling, cutting, or gluing, without distortion (i.e., it can be bent without stretching or compression). Cylinders and cones have developable surfaces. All developable surfaces are ruled surfaces, but the converse is not necessarily true. The sphere is not a developable surface, and cartography is forced to be a two-stage process. First, part of the Earth's surface is projected onto a developable surface (a cylinder in the case of the Mercator projection) and, hence, onto a plane.

The cylinder-to-plane transformation is sketched in Figure 4a; industrial examples occur in large-scale engineering, such as shipbuilding, where plates (curved in one dimension) for the hulls of vessels are formed from flat sheets of metal in a rolling mill. An ancient example of the use of developable domains is the cylindrical seal used for authenticating official documents, shown in Figure 4b. This was rolled across wet clay, sealing a document, to identify the contents.

Isometry: Structures are said to be isometric if the distances of the closest approach between all neighbouring columns are constant and equal. The sketches shown Figures 5 and 6 illustrate the distinction between isometric and equidistant arrangements.


(**a**) (**b**)

Figure 4. (**a**) An example of a developable surface, where a cylinder is unrolled into a plane. This surface is also ruled, and the pattern of parallel straight lines drawn on the cylinder surface is preserved during the transformation. Figure (**b**) shows an ancient Mesopotamian cylindrical seal (dating to about 5000 BC) and its imprint. [18].

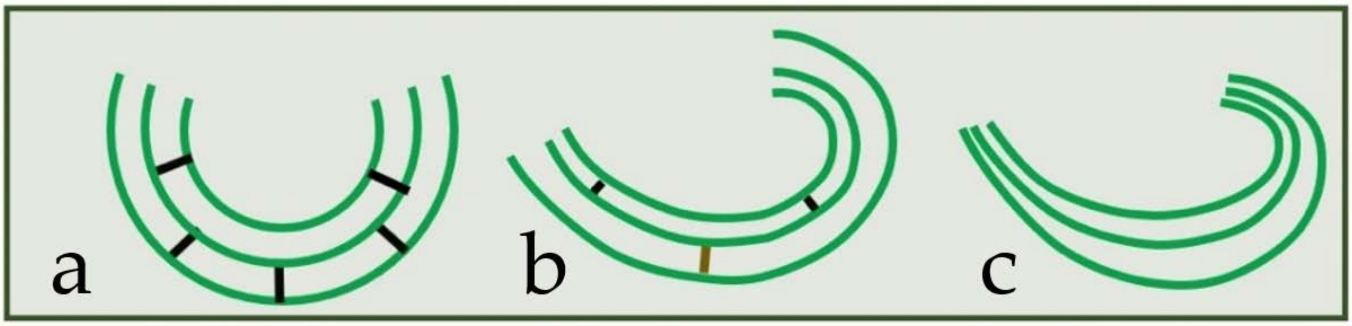


Figure 5. Isometric and equidistant structures in two dimensions. (**a**) shows an isometric arrangement, where the distances of the closest approach between all neighbouring columns are constant and equal. Note that the columns lie in a family of concentric circular arcs. (**b**) shows an equidistant array, where the distances of the closest approach are constant along the length of a pair of neighbouring fibrils, but are not equal throughout a domain. The pattern shown in (**c**) is neither isometric nor equidistant. Redrawn from Atkinson et al. [19].

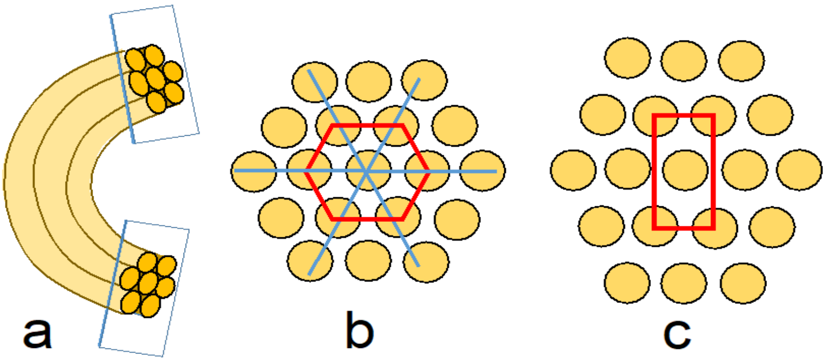


Figure 6. Isometric and equidistant structures in three dimensions. (**a**) A fragment of a developable domain structure, where all columns are curved in arcs of circles, but not splayed or twisted, and where the distribution of columns in any perpendicular plane shows the same hexagonal lattice of column axes. If the hexagonal distribution shown in (**b**) is distorted, for example into a centred rectangular lattice, as shown in (**c**), the structure becomes equidistant, but is no longer isometric. Redrawn from Atkinson et al. [19].

2.3. Compression Structures

The middle phase (M) of lyotropic systems was so-called because it occurs in the concentration range between that of the neat phase and of the isotropic liquid. It shows a range of paramorphotic optical textures, depending on how the mesophase had been created. In particular, the herringbone texture, shown in Figure 7a, appears when the concentrated isotropic solution is cooled. Until about 1980, it was widely assumed that every optical texture not immediately recognizable as a schlieren texture of a nematic phase was a focal conic image from a smectic phase. The explanation given for textures of this kind, was that the solute molecules are at their lowest energy state when they are packed in layers. This view was abandoned when it became accepted that the middle phases were columnar. It was then argued that it was energetically favourable for an isolated molecule to become intercalated within an existing column. When elongating columns become crowded in a confined space, they are forced to meander and, ultimately, to buckle sharply into zig-zag layers. As sketched in Figure 8, they are pictured as compressed springs, with the energy gain from the molecular intercalation being sufficient to cope with the energy cost of any concomitant long-range distortion of the director field that this may cause.

Herringbone textures, produced by internally generated compressive forces or by externally imposed stress, occur over a wide range of dimensions from µm in liquid crystalline materials to meters in geological strata, which have been subjected to massive tectoidal forces. Figure 7a shows the herringbone texture of the M phase of Intal, formed by cooling a concentrated solution of the isotropic liquid. Figure 7b shows a geological formation with strata distorted into chevron bands by external compression [20].

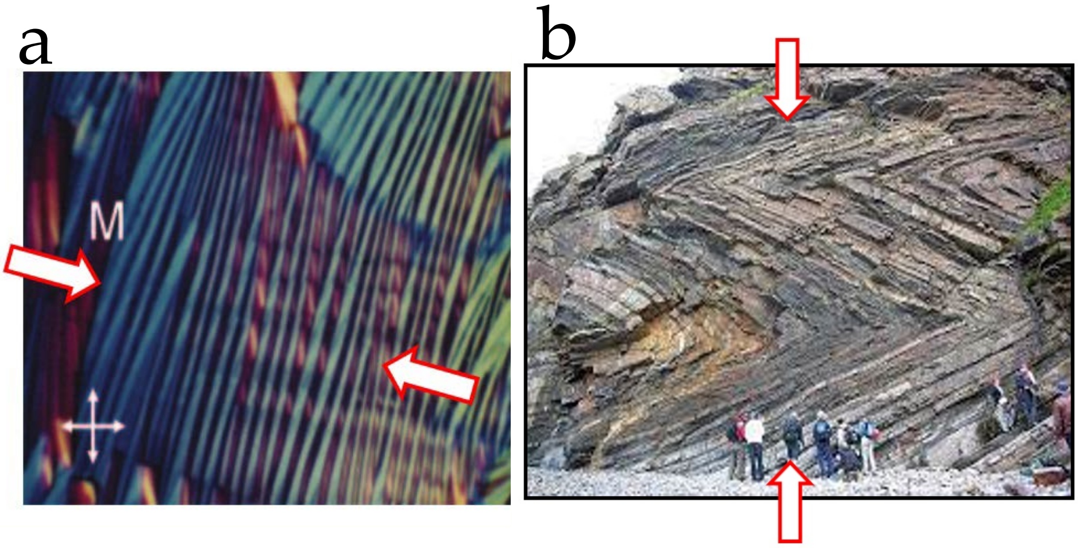


Figure 7. Herringbone textures. (**a**) shows the optical texture of the M phase of Intal. (**b**) shows the chevron distortion of strata in the cliff at Millhook Haven in North Cornwall Cornwall [20]. The arrows indicate the direction of the compressive stress.

Sketches like that in Figure 8a give the impression that the meandering pattern is a continuous sine wave, distinct from the zig-zag herringbone pattern, which is clearly divided into domains. However, this is not the case for narrow stripes of the mesophase, where the meandering wave is not sinusoidal and is composed of alternating domains, as will be described below.

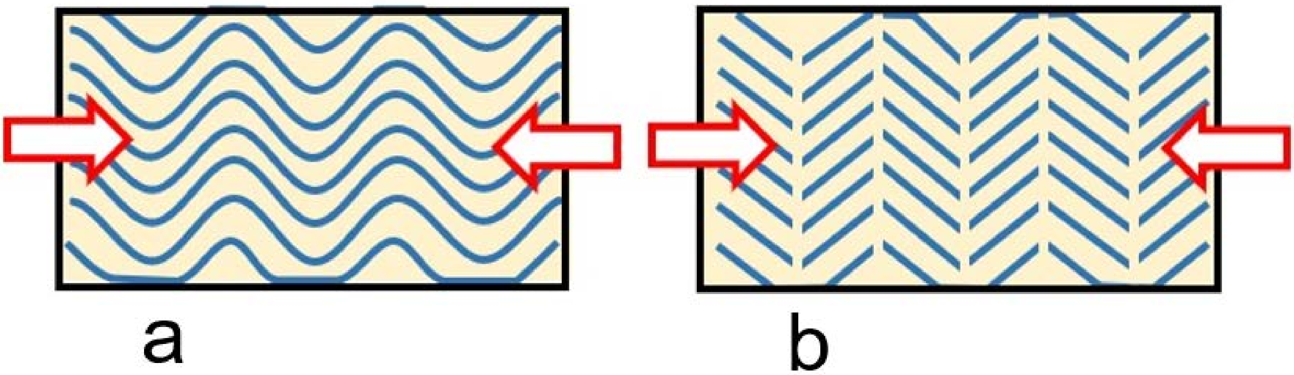


Figure 8. The development of the herringbone texture from the smoothly curved meandering pattern (**a**) to the broken zig-zag drawn in (**b**).

2.4. Optical Textures of Columnar Mesophase Stripes

For columnar phases confined between a slide and cover slip, the only plane in which the director field can meander in response to the compressive forces is that perpendicular to the viewing direction. In a recent publication by Bramble et al. [21], a technique for producing straight narrow stripes of the mesophase is described. This uses a prepared substrate, with alternating surface bands of a wetting and de-wetting nature, and when the mesophase is spread over the surface, it separates into distinct bands. In this case, the mesophase is constrained in both width and thickness, as sketched in Figure 9. The variety of director field patterns spontaneously created is shown in Figure 10. Although the stripes are not all identical in appearance (presumably because of minor irregularities in the dimensions of the prepared surface and the thickness of the mesogen stripe), all the textures appear to consist of developable domains. Note the interesting "egg and dart" texture of stripes **e** and **f** and the overspill region of **g**.

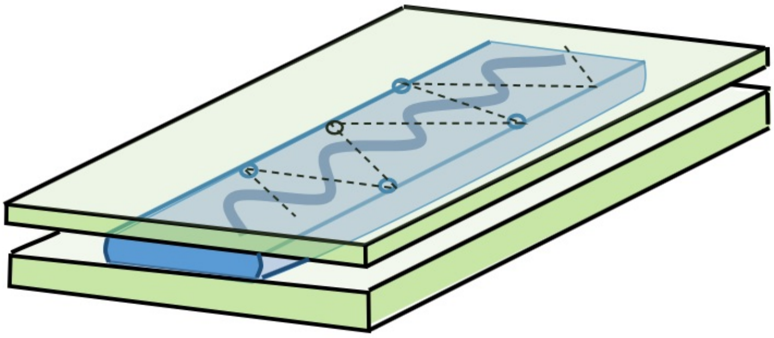
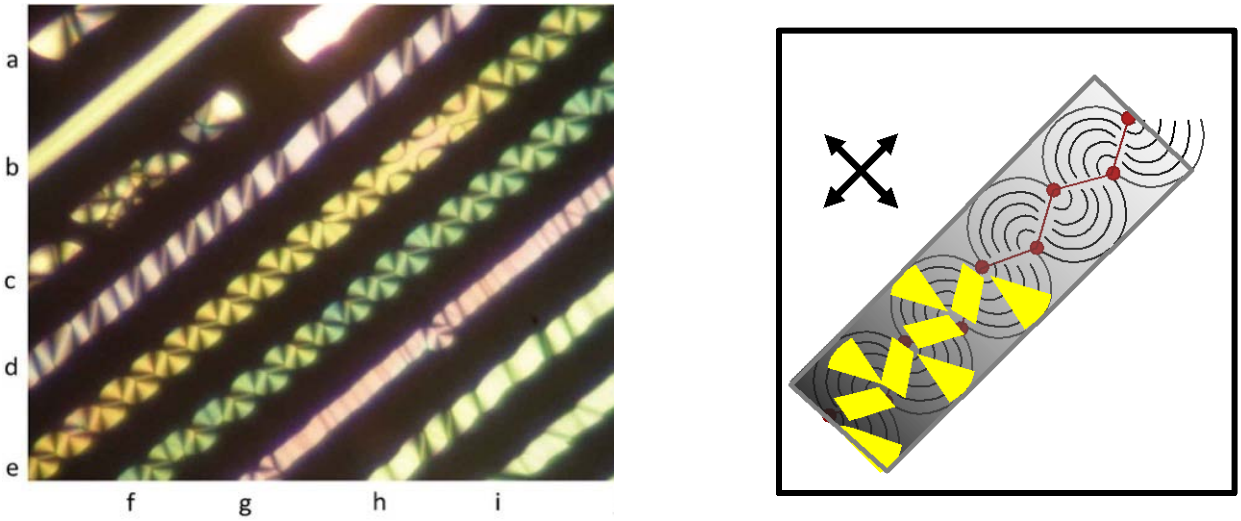


Figure 9. The developable domain structure of a thin band of a columnar mesophase, held between a slide and cover slip. Note that the only plane in which the director field can meander in response to the compressive forces is perpendicular to the viewing direction, causing all the domains to appear as nested arcs of concentric circles. The broken lines indicate domain boundaries, and the small circles show the positions of the poles of the concentric director fields. Redrawn from [21].

Reference [21] also contains a description of a different preparation, which has a preferred normal alignment of the columns at the mesophase/air boundary, as shown in Figure 11a. This shows a region of a stripe containing a single disclination viewed between crossed polars, with a red 1λ plate inserted. Figure 11b shows the inferred director field. Note the range of the yellow and blue areas, which indicates that there are regions of gentle splay extending on both sides of the singularity, over a range of about 200 µm, which gradually bring the director field back to a normal alignment at the edge of the mesophase stripe. Clearly, the constraint against splay, which gives rise to developable domains, can be overridden when the opportunity arises.



(a) **(b)**

Figure 10. Taken from Bramble et al. [21], photographed at 150° in reflection mode, between crossed polars. (**a**) Stripes of a columnar Col$_h$ mesophase spontaneously aligned on a patterned silicon substrate with alternate 25 µm-wide bands of a wetting and non-wetting surface. (**b**) An analysis of the director field of the egg and dart patterns in stripes e and f, in terms of the developable domain. The red lines joining them indicate the domain boundaries.

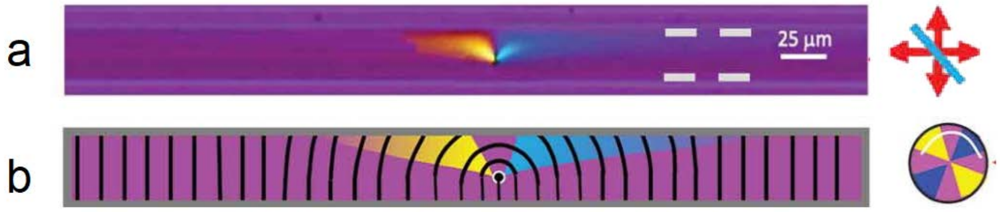


Figure 11. (**a**) shows the appearance of a 25 µm-wide stripe of a columnar mesophase around a single disclination (extending upwards from the centre line of the stripe), when viewed between crossed polars with a red 1λ plate inserted. In Figure (**b**), the black lines have been added to indicate the inferred director field. Note the distribution of the yellow and blue areas, indicating the extent of the regions of splay extending from the singularity. The orientation diagram shown on the right shows the alignments corresponding to the blue, magenta, and yellow regions of the image. The white arc indicates the range of orientations within the director field of the sample. Taken from Bramble et al. [21].

3. Discussion

3.1. Slippage

The rationale for the developable domain concept, proposed by Yves Bouligand [2], assumes that the molecular columns are effectively smooth and featureless and that they are easily bent and can slide past each other when a domain is growing. This picture must be reasonably valid; otherwise, the structure would not be able to assemble with columns bending with such a wide range of radii of curvature within each domain. However, it is perhaps also reasonable to assume that there is at least some small periodic lateral interaction between the columns, which causes them to prefer to assemble in register and to stop them building up a cumulative offset strain along the stripe. This could explain why developable domains are usually paired, as indicated in Figure 12. In these two highly stylized sketches, the dashed lines indicate columns of molecules in a hexagonal array, showing how sequences of alternating domains could build up within a parallel region of the director field, without requiring any large-scale slippage between the columns.

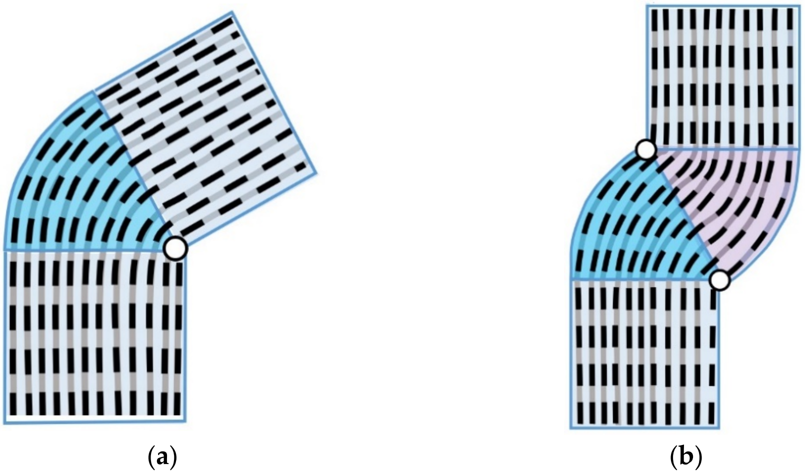


Figure 12. In these highly stylized sketches, the broken lines indicate columns of molecules in an M phase structure. The lines have been drawn in this fashion to make the lateral positioning clear. Note the way in which a pairing of domains maintains the long-range register between the columns. In Figure (**a**), the columns are drawn in register at the bottom of the figure and slide out of phase as they curve through the wedge of the developable domain. In Figure (**b**), the addition of an apposed domain cancels the effect of the first and brings the columns back into register. Note that the long stripes of the developable domain structure shown in Figure 10 contain a balanced pairing of segments.

3.2. Striations

Lyotropic middle (hexagonal) phases, chromonic M ribbons, and the triangulated plates and ribbons of columnar discotics have all been found decorated with patterns of striations, which follow the course of the director field, as shown in Figure 13. No other optical texture is categorized by features of this kind. Although the striations appear to be at more-or-less equal spacing, the blocks of colour in the optical textures often show abrupt and apparently random changes, as shown in Figure 1b. (They are very different from the regular banding patterns associated with the helicoidal layered structures of cholesteric, N* phases, where there is a smooth sinusoidal variation of intensity.) The presence of these striations has been commented on repeatedly, but, as far as I am aware, no detailed explanation has been offered for their presence.

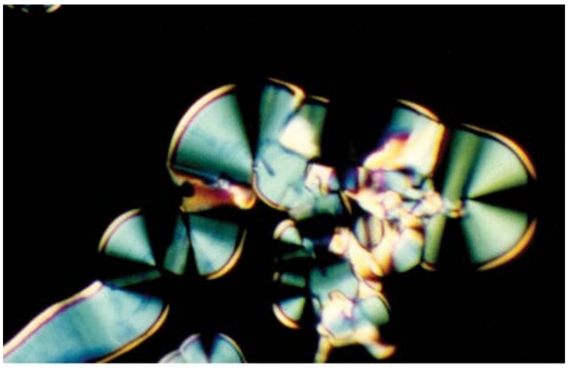


Figure 13. A ribbon of developable domains of the columnar phase of Intal, formed when the isotropic solution is cooled. Note the pattern of striations following the alignment of the director field.

Hartshorne comments that:

> "The well-developed striated textures shown by M phases are frequently displayed by M phases between crossed polars, particularly when they have formed slowly or have aged somewhat". [1] page 114

3.3. Helical Bundles

In their beautifully illustrated geometrical analysis of assemblies of one-dimensional filaments, Atkinson et al. comment:

> "The relatively restrictive geometry of equidistant fields raises interesting questions about the relationship between the problem of packing finite versus infinite equidistant curves . . . . The structure of finite equidistant bundles may be much less constrained than equidistant fields. Discrete equidistant bundles of this sort have ready applications to physical systems, from collagen triple helices and other dense packed biological systems". [19]

They discussed the geometry of "almost equidistant" arrays, by relaxing the strict isometric constraints of Bouligand's developable domain structure [2,3]. The examples they discussed were for toroids, which are of relevance to the structures of "spherical" viruses, where the closed loop of nucleic acid is constrained within an icosahedral capsid. Here, space is very constricted, and there is no room for the nucleic acids to adopt an unstrained developable domain structure; furthermore, there is considerable distortion in addition to bending. I suggest that in the region near the poles in director fields such as those pictured in Figure 10, pressure from the outer regions of the director field causes the inner regions near the dislocations, where the director field is highly curved, to become highly distorted.

Bearing this in mind, I suggest that the relatively slow reorganization process, which produces striations, involves the consolidation of the structure into twisted bundles of columns—perhaps with equidistant rather than isometric structures—as sketched in Figure 14.

Each individual strand within a twisted multistrand helix is a coiled coil structure, sometimes called a *gyre*. The formations of helices and gyres are both ways of relieving twist strain—as is apparent when an elastic band is twisted under tension and then, relaxed. If the molecular units are non-chiral, there may be an alternation, or random mixture of clockwise and anti-clockwise helices, as Bernal and Fankuchen found in the mesophase formed by concentrated dispersions of the tobacco mosaic virus [7].

As mentioned by Atkinson et al. [19], multiple helices are common in biological polymer systems. They listed the double chains of DNA, actin fibrils, which spontaneously wrap around each other to form a double helix, and collagen fibres, which are three-stranded helices. To this list, one could add xylan (a linear polysaccharide in the cell walls of green algae), which is also a three-stranded helix [22].

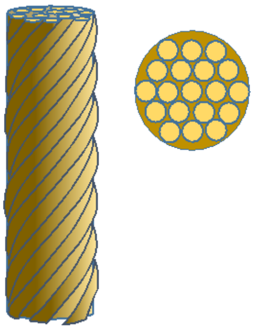
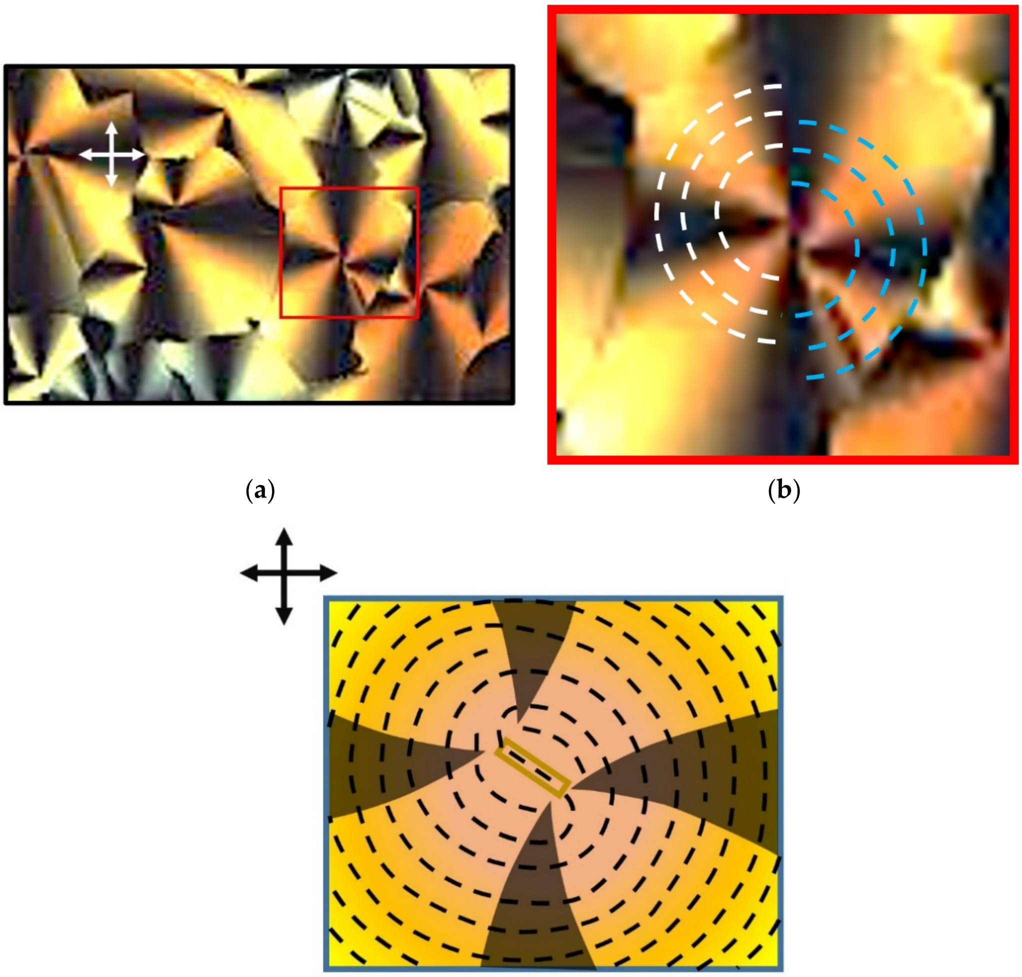


Figure 14. A sketch of a helical bundle of columns, which, it is proposed, slowly forms within columnar developable domain structures, giving rise to the straited appearance. Redrawn from Atkinson et al. [19].

3.4. Multi-Pole Nucleation

There is another unexplained characteristic feature of developable domain optical textures. When columnar phases are formed from the isotropic liquid, they often appear to grow from a small nucleus and expand outwards. However, as shown in Figure 15, at higher magnification, the nucleus does not appear to be a single sharp point, as seen in the optical textures of small-molecule nematic schlieren patterns. It is revealed as two pairs of points about 1 μm apart joined by a short length of a straight line. This is evident in the optical textures of the columnar phases of nucleic acids, shown in Figure 15 [23].

The postulated way in which the multiple nuclei are formed is shown in Figure 15c. In this, the director field is a consequence of the same mechanical properties of a mesophase as those that give rise to developable domains. To create a radiating pattern from a single point would involve an energetically prohibitive level of splay, and multi-pole nucleation provides a way of avoiding this.



(**a**) (**b**)

(**c**)

Figure 15. (**a**). The optical texture of the chromonic liquid crystalline phase formed by a concentrated aqueous solution of short-stranded DNA. Taken from [23]. Note the faint, straight line in the middle of the outlined square, which appears to join the two pairs of poles centring the pattern of striations. Furthermore, note the way in which the four dark brushes curve as they approach the poles (a pattern that is repeated in other parts of the micrograph). (**b**) An enlarged view of the square outlined in (**a**), with the pattern of striations superimposed. (**c**) A stylized sketch of the optical texture in the region of the multipole nucleus, stressing the curvature of the dark extinguished areas of the optical texture and showing the proposed pattern of the director field around the complex nucleus.

The helical bundle and the developable domain structure are the only two patterns of columns that are strictly equidistant [19], and the sketch in Figure 16 shows the postulated director field between the helical germ and the outer region (which might be first established as a developable domain and, then, revert to a striated array of bundles of helical columns).

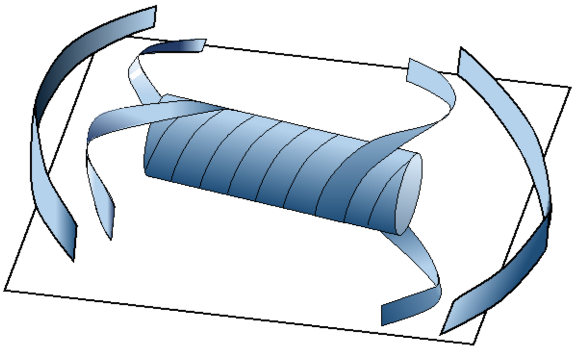


Figure 16. Taken from [21]. A stylized sketch of the proposed director field pattern when the mesophase region is extending outwards from a helically wound core. Note that the ribbons drawn in this figure are intended to give a three-dimensional impression of the alignment within the director field. They are not intended to imply that the striations are caused by ribbon-like fibrils.

3.5. Helical Fibrils

Some additional support for the hypothesis of helical bundles comes from the study by Khan et al. of the triphenylene mesogen 2,3,6,7,10,11-hexakishexyloxytriphenylene (HAT6) [24]. This compound is a bona fide columnar mesogen, exhibiting a nematic and a hexagonal columnar mesophase with the familiar developable domain optical textures. However, when it is mixed with an acetonitrile-based solvent, it forms a gel state in a thermally reversible "physical" process. (In this context, the word "physical" means without any covalent bonding being involved, and the forces involved in the cross-linking are considered to be hydrogen bonding or π–π interactions.) The gel is composed of an open network of strands of columnar material, as shown in Figure 17. Note the banded appearance of the strands viewed between crossed polars, indicating helical twisting.

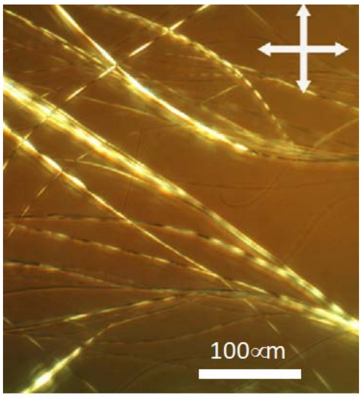


Figure 17. The open mesh of the gel phase of HAT 6 fibres dispersed in an acetonitrile-based solvent, viewed between crossed polars. Note the appearance of a helical gyre structure in the fibres. From Khan et al. [24]. I am indebted to Professor Richard Bushby for drawing my attention to this work.

4. Retrospect

In 1974, based on its optical texture as described by Norman Hartshorne [1], page 127, I concluded that the mesophase of diisibutyl silane diol might be composed of an array of columns of dimeric units. I observed that this phase appeared to have the mechanical properties of a sheet of paper, which can be curved in one direction, but which cannot then be curved in a different direction without being torn [12]. This picture falls short of the concept of developable domains, but points in that direction. I did not possess the geometrical insight of Yves Bouligand, and his publication did not to appear until six years later [2,3]. Furthermore, I had not considered the significance of the striations decorating the domains in the optical textures of columnar mesophases nor noticed that, in the M ribbons of Intal, the director tends to follow either straight lines or is curved into apparently precise arcs of circles.

The great fictional detective created by Arthur Conan Doyle solved cases that baffled everyone else, by his powers of close observation of apparently inconsequential detail:

"It has long been an axiom of mine that the little things are infinitely the most important" Sherlock Holmes, to Dr Watson in *A case of identity* [25].

Then, he followed a process of inductive reasoning, wherever it led (ignoring any preconceptions). In retrospect, I see that I had clearly learned little from my extensive reading of the Sherlock Holmes stories in my childhood.

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Dedication: to Norman Hartshorne with thanks for his patient and quietly inspiring Teaching, which gave me the same love of optical microscopy that had dominated his scientific life.

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