

The Blue Phase of Cholesteric Liquid Crystals

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The phases of liquid crystals

In 1888, while cooling liquid cholesteric benzoate, Reinitzer [8] reported a very brief bright blue-violet reflection right below the clearing point, which typically defines the transition between the clear isotropic phase and the more turbid liquid-crystalline phase. It wasn't until the mid 1970s that this sighting, as well as many others, was identified to be a new thermodynamically stable phase of certain liquid crystals, aptly named the blue phase (Figure 1).

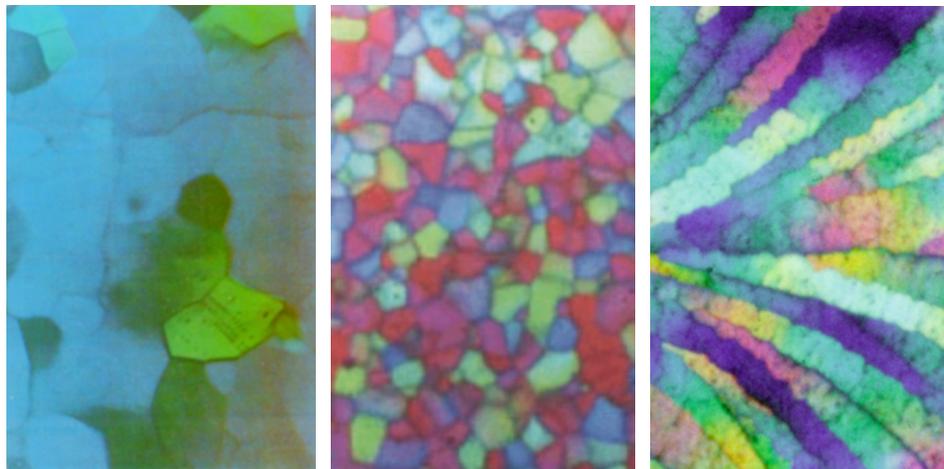


Figure 1. Various "artistic" shots of the first two blue phases (on the left is BP11, the others are undocumented).

Liquid crystals encompass a whole class of substances that exhibit a slew of interesting mesophases, intermediate between the isotropic liquid and the solid crystal. Typically, they are compounds that have very elongated (or more generally anisotropic) molecules that favor strong molecular ordering at low temperatures. The liquid crystalline phases are "liquid" in the sense that the translational symmetry of the centers of mass of their constituent molecules is (mostly) continuous, but they exhibit some crystal-like properties, such as long-range orientational ordering, and in the case of the smectic phase, translational positional ordering in one of the three dimensions. Traditionally, liquid crystals are most readily associated with the smectic and nematic phases, the latter ones becoming the "helical phase" for the case of cholesteric liquid crystals (which have chiral molecules of which either the left- or right-handed species is predominant over the other). Since the discovery of the blue phases, however, it has become apparent that

chiral liquid crystals can have much more complicated and diverse phase diagrams than their nematic counterparts.

The traditional phase diagram for cholesteric liquid crystals has typically been “smectic-helical-isotropic”, in that order, as the temperature is raised. The blue phases are observed in a very narrow ($\sim 1\text{K}$) temperature range between the isotropic and helical phase of cholesteric liquid crystals. Three such phases have been observed, and are all separated by first order transitions: the colorful BPI and BPII and the misty blue BPIII (“blue fog”), respectively in the order at which they appear as the liquid crystal is heated. BPI and BPII both have long-range orientational order which has a 3D cubic symmetry, while the BPIII is isotropic and is only present in very chiral compounds. In addition to these, there are also several *twisted grain boundary* phases [9] between the smectic and the helical phases, in which blocks with smectic ordering are slightly rotated with respect to one another, along a line that is parallel to the smectic layers of all the blocks (creating dislocations between the layers in neighboring blocks). Very recently, there has also been experimental evidence for a *smectic blue phase* (just like the normal blue phases, but with a smectic-like translational symmetry of the molecular mean positions where the smectic “sheets” are not perfect planes, but instead are hypothetically rotated about an axis, as in a screw) [7] in compounds that lack a helical phase (i.e. the smectic blue phases occur directly between the smectic and isotropic phases).

The currently accepted phase diagram for the blue phases as a function of temperature and chirality is shown in Figure 2 (the chirality is varied by adjusting the relative concentrations of left- vs. right-handed molecules). From it, it can be seen that liquid crystals with very low chirality do not exhibit any blue phases. As the chirality is slowly increased, BPI, BPII and finally BPIII come into existence, but BPII then disappears for very chiral substances. Recently, a critical point has been discovered between the BPIII and isotropic phases [5], establishing with certainty that BPIII has the same symmetry as the isotropic liquid. The overall shape of this phase diagram so far seems to be universal, and does not seem to depend on the specificity of the chemical interactions [14].

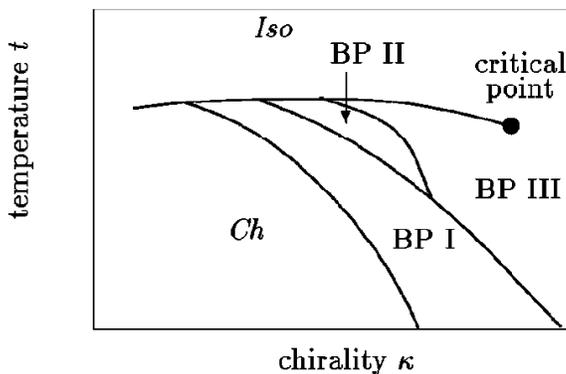


Figure 2. Diagrammatic phase diagram for the 3 blue phases as a function of chirality and temperature (taken from [1]).

Properties of the Blue-Phase.

The blue phases have long been thought to be a metastable incarnation of the helical phase. The reason for this is that they are present only in a very narrow temperature range close to the clearing point of cholesteric liquid crystals and in addition the blue phases can often supercool into the helical phase. Because many of the properties of the blue phases are only slightly different from those of the neighboring helical and/or isotropic phases (with notable exceptions, however), it can be hard at times to tell them apart. For example, at the helical to BPI transition, there is a discontinuous change in the specific volume, but it is of the order of 0.01%. Careful measurements of the specific heat across the transitions provided the first definite evidence that there were indeed a series of distinct stable phases between the helical and isotropic phases of cholesteric liquid crystals. Figure 3 clearly shows the existence of three phases and that the transitions between them are first order, as evidenced by the existence of latent heats (the spikes on the graph).

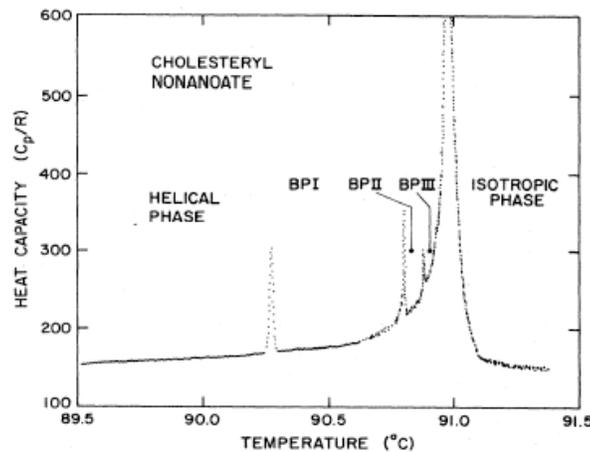


Figure 3. Specific heat as a function of temperature, showing the boundary between the helical, blue and isotropic phases as well as the first order nature of the transitions between them.

The most striking feature of the blue phases is probably their splendid visual appearance (as illustrated in Figure 1). Unlike the more bland smectic, nematic and isotropic phase, the blue phases often come as a display of many colorful platelets, or as in the case of BPIII, as a foggy bluish substance. As we will see later, the blue phases BPI and BPII have 3D orientational ordering with periods of up to 500nm. Because of this huge period of the order of the wavelength of visible light, blue phases can Bragg-scatter light in the visible range, causing a given color to be seen at a given angle. If the blue phase contains many domains that are oriented differently, the color of the light seen by a given observer, at a given angle, will be different for each domain, creating a mosaic of color. In this sense, the microscopic properties of the blue phases (such as the domain size, and periodic lattice spacing, etc., properties which are usually gotten by X-ray measurements) can be directly inferred from measurements using the naked eye!

As beautiful as they may be, the blue phases also have many other unique and extremely interesting properties. Many of these reflect the dual nature of the BP mesophases: they are in some sense both liquid and fully crystalline. Perhaps the most remarkable of these properties is the fact that liquid crystals in the BPI and BPII phases exhibit a non-vanishing static shear modulus (although very small, of order 10^6 less than for normal solids) [4] (Figure 4 show the temperature dependence of a low-frequency shear modulus). This is extremely surprising because the blue phases are completely liquid (from a positional symmetry point of view) and this is the first “liquid” to be discovered that has any resistance to shear. Shear causes an energetically unfavorable modification of the 3D periodic orientational structure of the blue phase, which could be stabilized by a periodic network of singularities (as suggested by theory) which would prevent its reordering. The discontinuities in the elasticity graph of Figure 4 also lent additional credibility to the fact that the blue phases were distinct, thermodynamically stable phases.

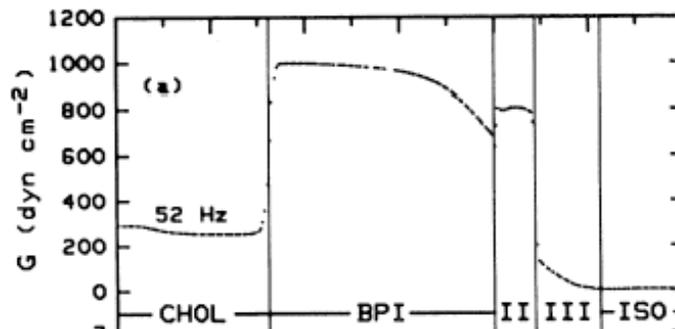


Figure 4. (a) Shear elasticity G (at 52Hz) of the blue, cholesteric (helical), and isotropic phases of cholesteryl nonanoate as a function of temperature [4].

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TO BE SCANNED]

Figure 5. Viscosity vs. temperature near the clearing point of cholesteryl –nonanoate/-chloride mixtures at a concentration ratio that exhibits (full line) and does not exhibit (dotted line) a blue phase [11].

Additionally, the blue phases have been measured to display a strikingly large viscosity. Anomalous viscosities near the clearing point have been observed for a very long time. Measurements of the viscosity[11] for a mixture of substances with concentrations ratios that do and do not exhibit a blue phase show that the presence of a blue phase is correlated with an up to 10^6 -fold increase in the viscosity over that of the neighbouring helical phase (Figure 5). The mixture that did not have a blue phase did not exhibit the high viscosity. This phenomenon lends further weight to the possibility of a 3D extended ordered structure in the blue phase,

As a very surprising culmination of the evidence supporting a 3D periodic structure of the first two blue phases, single crystals of BPI floating in the isotropic liquid have been grown that macroscopically exhibit the internal structure of that blue phase [1]. The single crystals show very clear faces (for a “liquid”), and the shape of the crystal would indicate a cubic symmetry.

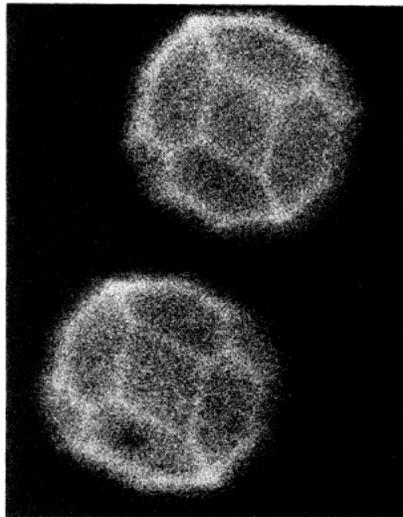


Figure 6. Micrograph of crystals (0.1-0.2mm) of BPI floating in the isotropic phase [1].

Theory

In order to claim that we have a successful theory of the blue phase, we must find a logical explanation that accounts for the observations stated above. We must be able to find an energetically favorable structure that is only stable very close to the clearing point for cholesteric liquid crystals. Furthermore, from this structure must naturally arise a periodicity with a very large unit cell, since experiment overwhelmingly seems to support this, even though the liquid crystal remains “liquid,” in that it can be poured. Finally, we can use to our advantage the fact that it seems that we are only dealing with first order transitions, to, on one hand, help us select the right range of constants in our Landau free energy, and on the other, to justify that we can ignore fluctuations and assume that mean field theory will give us a physically relevant answer.

The first two blue phases are well described by current theoretical tools, whereas BPIII is still poorly understood. The structures of BPI and BPII can be derived using the same Landau-Ginzburg free energy that is used to describe the more common phases of liquid crystals; these theoretical steps are reviewed in [10,13]. From these analyses, it emerges that the blue phases occur when there is a high level of frustration between locally and globally favored structures. In these cases, the “compromise” structures cannot always be easily extended to all space, and thus we get networks of defects that separate isolated stable regions. These networks can lead to quite intricate structure that are periodic at a large length scale, such as seen in the BPI and BPII phases. The detailed theory behind the blue phases can be quite involved, but at the most basic level, it is quite informative. I will thus attempt to summarize the important lines from an “intuitive” point of view, and omit most of the mathematical derivations and proofs.

Following the review of Wright and Mermin [13], we will examine the blue phases by using the Landau free energy arising from the low order expansion in powers of the dielectric anisotropy tensor Q_{ij} , which is just a function of the dielectric tensor ϵ_{ij} that is defined to vanish in the isotropic phase ($Q_{ij} = \epsilon_{ij} - 1/3 \text{tr}(\epsilon)\delta_{ij}$). The general Landau energy f , in this case, (to be used as a general reference for reading the rest of this paper) is:

$$f = f_{bulk} + f_{gradient} + \int \cdot f_{surface terms}$$

with,

$$f_{bulk} = a \frac{T - T_c}{T_c} \text{tr} Q^2 + b \text{tr} Q^3 + c \text{tr} Q^4$$

$$f_{gradient} = K_1 \int (\nabla_i Q)_{ij} + \frac{4}{p_o} \int Q_{ij}^2 + K_o [(\nabla \cdot Q)_i]^2$$

where, a , b and $c > 0$ (given that we will only consider transitions that are first order), and K_o and K_1 are the elastic coefficients of bending of the liquid crystal, and p_o is the pitch that the liquid crystal would have in the helical phase at the given temperature. (In the helical phase, the molecules within a given plane all have the same orientation parallel to that plane, but because of chiral interactions, the alignment of the planes above and below are slightly rotated. The axis perpendicular to those plane (and to the alignment in general) is called the *pitch axis*, and the length scale at which the system is *exactly* periodic along this axis is the *pitch*). The cross-terms that contain the curl term are only present in cholesteric substances.

The need for non-uniform phases (as opposed to smectic, nematic, helical) can be readily seen by examining the structures that minimize the bulk and gradient free energy respectively. It can be shown [13], that the bulk free energy is minimized by a Q that has two degenerate eigenvalues. If one thinks about the local dielectric tensor in a material with aligned elongated polar molecules, it is obvious that the dielectric tensor will have different eigenvalues in the direction along the director (along which the molecules point), and in the directions orthogonal to it. A pair of degenerate eigenvalues implies on a microscopic (but not necessarily “molecular”) scale, that the directions orthogonal to

the director are indistinguishable from a dielectric point of view. This configuration is called the *uniaxial helix*, which is the natural configuration for rod-shaped molecules. On the other hand, the gradient free energy is minimized by a Q with three very distinct eigenvalues. This is the *biaxial helix*, which is the configuration for a compound which locally has a different geometry in all three directions (e.g.: an irregular rectangular prism or, alternatively, small rectangular “platelets”). The “axiality” of the order parameter need not reflect the symmetries of the individual molecules, since the order parameter reflects local *average* orientation, and biaxial particles can give rise to uniaxial ordering and vice-versa. A biaxial Q reflects molecular orientation about two axes, and when this is the case, one cannot express the free energy in terms of the director alone, since the director only contains orientational information along one axis. Biaxiality plays an important role in the blue phases, and they can only be explained by the given form of f when one goes beyond the implicit uniaxial approximation which is standard in basic liquid crystal theories.

In the limit of non-chiral nematics, the pitch is infinite, and we can see from $f_{gradient}$ that the positive-definite gradient free energy then only depends on spatial derivatives of Q . Thus the only constraint arising from the gradient terms is that Q be uniform while f_{bulk} selects for uniaxiality; this gives us the nematic phase. Typical liquid cholesteric liquid crystals have rather large pitches, and a common starting point of many theories of the blue phase, is to consider them to be slight perturbations of the helical phase in which the uniaxial order parameter is permitted to have a slight degree of biaxiality. This new order parameter is always more stable than the uniaxial one for cholesterics, however when the biaxiality is slight, and the temperature is low enough, its effects are negligible and the resulting phase can be considered to be to an excellent approximation, the “helical” one. This is not the case, however, when we approach the clearing point.

Meiboom *et al.* [6] discovered that the local free energy of most cholesterics could be reduced by a “double twist” structure in which the director twists simultaneously about two independent directions (see Figure 7). Such a structure cannot not be stably extended across all space, and its presence would necessarily require energetically unfavorable disclinations (which is a singularity of the orientational ordering) between separate double twist regions. Meiboom *et al.* noted, however, that as the liquid crystal approaches the isotropic transition, the energy cost of disclinations lowers, and that sufficiently close to the transition, a network of double twist structures stitched together by disclinations might be globally more stable than the helical phase.

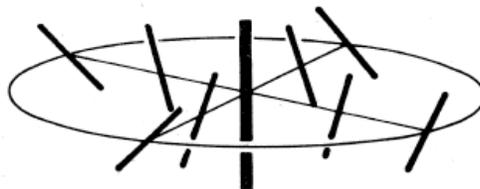


Figure 7. “Double twist” structure of the director. The director rotates when moving along both the pitch axis and the direction perpendicular to it. The arrangement is symmetrical around a central axis.

The double twist cylinder shown in Figure 7 can be perfectly extended along its symmetry axis, but in the radial direction, it must have a finite average extent, since the double twist cannot be extended over all space. Because of this, we will consider that the double twist structures will be locally preserved in long cylindrical regions (Figure 9a), which are then arranged in periodical arrays. Regions of energetically favored double twist structure must inevitably be complemented by compromised areas that are less ideally oriented, and have strong variations in $tr(Q)$, which are penalized by the bulk free energy (because of deviations from the optimal $tr(Q)$). As the radius of the tubular regions is increased, the variations in $tr(Q)$ must become sharper, and the chosen radius is the one at which the gradient energy of the interstitial regions becomes larger than that of the helical phase, had it been present. It turns out, that this radius is roughly equal to the pitch of the material (had it been in the helical phase) [13].

For materials with a large pitch, it is thus possible to create structures that have orientational order that is periodic over great distances (in this case 100-5000Å). It turns out that it is not possible to arrange double twist cylinders in a 3D array without introducing some disclinations (for an example, see Figure 9b). The actual arrangement of the cylinders that is chosen by the system results from a compromise between picking the structure that maximizes the volume of the liquid crystal that is in the favored double twist structure, while minimizing the amount and size of the disclinations between the cylinders. Depending on the temperature, these energetic considerations give rise to the experimentally observed simple cubic symmetrical structures for BPI, and bcc symmetrical structures for BPII (Figure 9).

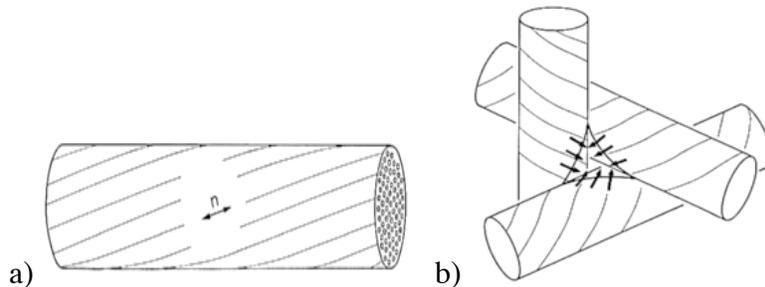


Figure 8. (a) A cylindrical region of double twist structure (which is stable up to a certain maximum radius). (b) Intersection of three double twist cylinders with an interstitial disclination.

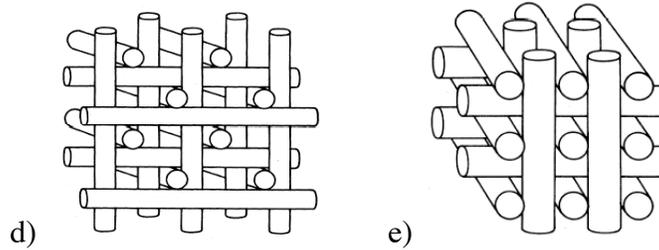


Figure 9. Arrangement of double twist cylinders as they are believed to exist in (c) BPI and (d) BPII.

Discussion

Aside from being a curiosity of nature, the blue phase proves to be quite an interesting system for studying the properties of systems oriented molecules. Before their discovery, it seemed as though the Landau theory of liquid crystals was complete. It was only because of this novel phase that the liquid crystal community went back to the theory and reconsidered the approximations that had been made (such as the uniaxial helix form of the order parameter Q). A careful reexamination of the same free energy revealed that many previously overlooked phases were possible, and indeed predicted, by it.

In this regard, the blue phases are extremely interesting because they permit us to test thermal phase transition models that are much more complicated than what is usually seen. The stable structure is a compromise between many competing interactions that lead to frustration giving rise to a fundamentally non-uniform phase in regions of great stability coexist with regions of very unfavorable gradients and defects, but that is still globally the most stable phase. Most importantly, though, is that these structure arise in localized regions of parameter space of the *same* simple free energy that described the much simpler phases. The techniques and insights gathered from the analysis of the blue phase give us a much greater understanding of the energetics of liquid crystals, and have permitted such developments as the theoretical predictions of new liquid crystalline phases (such as the twisted grain boundary phase, to name one example).

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