

Emergence in liquid crystals: the blue phases

Arnab Samanta

*Department of Mechanical Science and Engineering,
University of Illinois, Urbana, IL 61801*

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Abstract

The blue phases refer to a group of very unique thermodynamically stable phases observed in chiral nematic liquid crystals that exhibit orientational order. These phases are found to appear over a very narrow temperature band in between the isotropic and helical phases of such crystals. In fact, the phase diagram will reveal that there are three such phases. In this essay we will be exploring the origin of such phases using both experimental and theoretical studies. We will be discussing the various aspects of such phases that have already been explained and in addition will also highlight the many unexplained anomalies.

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1 Introduction

Liquid crystals, as the name suggests are substances that exhibit material properties which lie in between conventional liquids and crystalline solids. Unlike isotropic liquids, in liquid crystals some crystal-like ordering exist at least along one spatial direction. Hence, these are systems where some degree of anisotropy should always be present. This is brought about through the constituting molecules being geometrically anisotropic, which are either rod-like or some times disk-like. Liquid crystals, in general, have some degree of orientational order and in some cases partial translational order, although the periodicity of solids is absent. The liquid-crystalline phase is also referred to as a particular case of a *mesophase*.

The fluid mesophases are classified into the *lyotropics* and the *thermotropics* [17]. In this essay we will only be concerned with the latter. Thermotropic liquid crystals undergo phase transitions on being heated. Thus the solid crystal first melts into a turbid liquid-crystalline phase, which becomes clear (isotropic) on further heating. Thermotropic crystals possessing long-range order of the mean molecular orientations, but lacking any long-range translational order are normally classified into *nematics* and *cholesterics*. There are also *smectics* which can have translational order. The constituent molecules in a nematic have inversion symmetry. Even if chiral molecules are present, they are equally distributed among the two handednesses to form what is known as a racemic mixture and so the fluid remains inversion symmetric. Now, when the constituent molecules are chiral with the left and right-handedness not being equally represented, the liquid crystal becomes cholesteric. Following [19], we will refer cholesterics as *chiral nematics*. Chiral nematics are known to show at least two different ordered phases. One of them is called the *helical phase*, while the other is known as the *blue phase*.

The phase diagram of nematic liquid crystals is quite simple, since there exists only one kind of ordered phase in such materials. Chiral nematics on the other hand, at lower temperature, have the helical phase as a stable equilibrium phase. At sufficiently higher temperature they become isotropic liquid. In some chiral nematics, in between these two phases, over a very narrow temperature band of a degree or so blue phases (BPs) appear. Three such blue phases have been identified till now after studying a wide variety of chiral nematic materials. The two low temperature blue phases, called BP I and BP II have cubic symmetry, whereas the highest temperature one, called BP III is amorphous. Although the BP I and BP II phases are commonly seen, the BP III phase is found only in systems with very short pitches. The typical transition temperatures are of the order of several hundred degrees.

In this article, all of the blue phases that we are going to describe belong to the “classical blue phase” league. These are the blue phases of chiral nematic materials. However, blue phases have also been discovered in smectics [11, 6]. The main features of these smectic blue phases are that they exhibit both three dimensional orientational order, like classical cubic blue phases and also the smectic positional order. One of the smectic blue phases has been proven to be hexagonal [15], which shows that these are not merely classical blue phases with smectic fluctuations. These smectic blue phases have been observed in between the isotropic liquid and the so-called *twisted grain boundary phase*. The latter is a new kind of material combining chirality and the smectic order (see for example [5]).

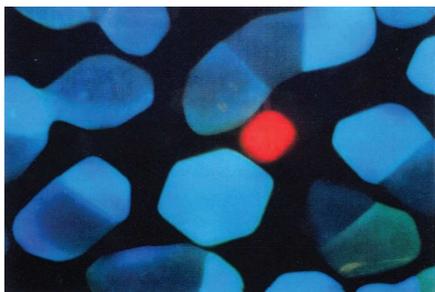


Figure 1: Platelet structure of the BP II phase. Source: Hekimoglu and Conn *Liq. Cryst. Today* 12, 3(2003), 1-2.

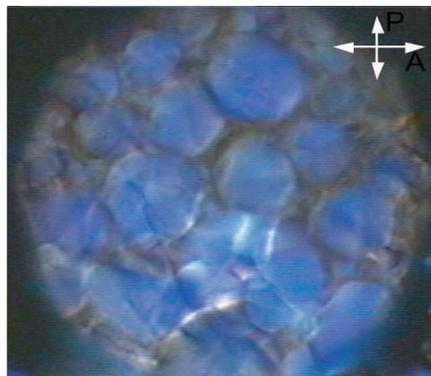


Figure 2: BP_{Sm1} phase observed through polarizing microscopy. Source: Grelet *Liq. Cryst. Today* 12, 4(2003), 1-5.

The most striking feature of these blue phases, as their name suggests, is their display of bright colors (see Figs. 1 and 2). This is in contrast to the isotropic and helical phases lying on either side of the phase diagram which do not possess any such ability. The blue phases have pitches of several thousands of angstroms, which enable them to Bragg-scatter visible light. The BP I and BP II phases consist of brightly colored wrinkled flakes, which are called platelets (Fig.1). These are nothing but domains of crystalline blue phase ordering, and the bright color comes from the scattering in the direction of the observer of those wavelengths which satisfy the Bragg condition. Platelets with changing orientation will show different colors and those that fail to satisfy the Bragg condition appear dark. The colors observed during the earlier experiments were primarily blues or violets, hence the name, but as mentioned the color varies widely across the sample and certainly with changing temperature. The BP III phase, however, is less visually attractive because of its blue-gray appearance and was originally referred to as the “blue fog”.

To understand the importance of the blue phases we might note that blue phases are just one of the intermediate phases found in liquid crystals. Thus to have a clear and complete understanding of the liquid crystal phase diagram, we cannot simply ignore these phases. From the theoretical point of view it serves as a great challenge to the familiar Ginzburg-Landau theory of phase transitions, and as we shall see the theory passes the test with distinction. Still, because of the elusive nature of these phases one might also expect to develop sophisticated experimental (and theoretical) tools to investigate them. Such tools when applied back to liquid crystals might reveal new unknown features. This is precisely what has happened.

2 Experimental observations

The experimental evidence for blue phase goes back to the nineteenth century (1888). In fact, the discovery of blue phase by an Austrian botanist named Friedrich Reinitzer [16] also marked the first sightings of the liquid-crystalline phase itself. But for nearly a century after its discovery these were only regarded as a metastable form of the helical phase. The main argument behind the metastability was the fact

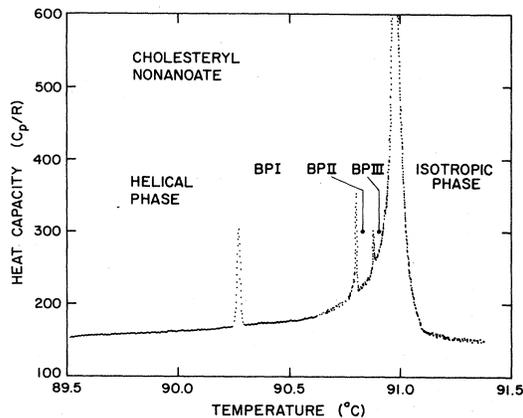


Figure 3: High-resolution heat-capacity measurements for the blue-phase region of cholesteryl nonanoate. Source: [19].

that the blue phase can supercool into helical phase by several degrees, which very often exceeds its entire stability range. Also, within the supercooled range a mere stirring induces phase transition to the helical phase. However, it was later observed that near the high temperature end such a transition could not be achieved, thus providing evidence toward a stable phase. Finally, experiments on several chiral nematics revealed both a change in density and latent heat at the helical–blue phase transition [1], which was good enough to proclaim blue phase as a separate stable phase.

2.1 The order of transition in blue phases

The first set of differential scanning calorimetry studies [1] that proved the stability of the blue phases were able to capture a very small but finite change in density at the transition point. The latent heat measured was of the order of 0.01 cal/g, which is only a small fraction of the isotropic–BP transition. These observations indicated a discontinuous or (weakly) first order transition between the helical and blue phase. Later, more accurate measurements detected the presence of a second peak in the heat capacity, thus indicating the presence of the BP II phase. The latent heat for the BP I–BP II transition was found to be very similar to the helical–BP I value. The BP III phase was also discovered soon enough, but it exists over a temperature range of only 0.05K. Nevertheless, BP III showed many optical activities similar to the other two phases with the exception of any Bragg scattering. All the transitions between intermediate blue phases were conclusively agreed to be of first order. The only one which required some debate was the BP III–isotropic transition. But that has also been resolved to be a weakly first order transition using adiabatic scanning calorimetry measurements (see Fig. 3). Although the blue phases undergo some specific heat changes during intermediate transitions, the bulk of it can be seen to be reserved for the blue to isotropic transition.

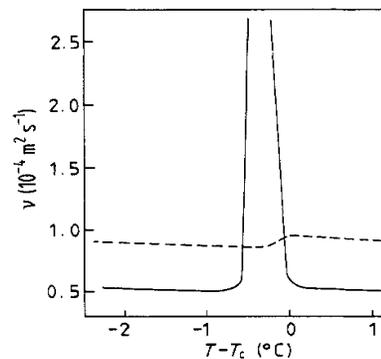


Figure 4: Kinematic viscosity measurement of cholesteryl nonanoate. The solid line is for a concentration ratio that shows BPs. Source: [18].

2.2 Important properties of blue phases

Aside from their ability to produce bright colors the blue phases also possess many other interesting properties. We will be discussing in brief a few of them.

2.2.1 Elastic shear modulus

The blue phases BP I and BP II have periodicity like crystals, thus they are expected to have some properties to resist shear inspite of them being liquids. Measurements in a torsional oscillator have actually confirmed this. Although, the magnitude is roughly a million times smaller than conventional solids at only 10^3 dynes/cm² [3]. This value also seems to agree well with the estimates from dimensional arguments.

2.2.2 Viscoelastic properties

The blue phases have also been measured to have anomalously large bulk viscosities compared to the helical and isotropic phases. Measurements [18] have shown that chiral nematics that do possess a blue phase undergo a sharp increase (up to 10^6 times the helical phase value) in viscosity near the helical–blue transition, as the temperature is raised (see Fig. 4). The value immediately drops as the isotropic phase is reached. The reason for such high magnitudes can generally be attributed to the ordered structures of blue phases. The well-known ability of BP I to supercool is also a result of these viscous properties.

2.2.3 Electric field effects

When blue phases are brought under the influence of external electric field, it gives rise to field-induced transitions with the appearance of new phases. These new phases usually have a two or three-dimensional hexagonal structure. But, phases with tetrahedral symmetry have also been discovered.

2.3 Structure of blue phases

A wide array of experimental (and also theoretical) work has been performed to determine the structure of the blue phases. In all of the experiments across all samples tested, a single space group was found to describe BP I and another one defined BP II. This is quite a surprising achievement considering the very small energy difference separating the individual phases.

The absence of any birefringence property in the lower temperature blue phases was enough to suggest that they certainly cannot be anisotropic, and possibly they have some cubic symmetry. Experimental techniques which included measurements of selective reflection and rotatory power demonstrated the three-dimensional periodicity of BP I and BP II and their local chiral structures. Their pitches were found to be of the same order as the pitch of the helical phase. Later, optical Bragg scattering experiments [13] were able to determine the translational symmetry nature of these phases. Specifically, it was concluded that both BP I and BP II have either a simple cubic (sc) or a body-centered-cubic (bcc) symmetry. Since these phases are also chiral the number of possible space groups that they may have are restricted to six with sc translational symmetry and four with bcc translational symmetry

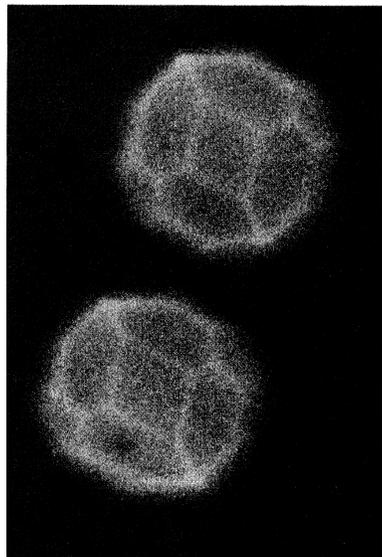


Figure 5: Single crystals of BP I showing well-defined facets. Source: [19].

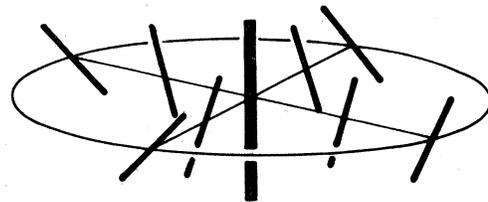


Figure 6: The orientation of the director field in a double twist structure. Source: [19].

[19]. In order to ascertain the correct choice, a substantial number of these phases in different materials were subjected to very sophisticated experimentations. The conclusion was that BP I has a bcc O^8 structure, while BP II has a sc O^2 structure. These experiments were able to visualize the three-dimensional single crystal structures of these phases (Fig. 5). In spite of all these, it should be mentioned that there is actually no theory which disallows the appearance of other different structures in other materials that are yet to be tested [19].

Although the structures of the low temperature phases have largely been resolved, BP III still remains a mystery. The only feature definitely known is that this phase is amorphous without any long range symmetry and it also has a locally chiral structure. But then the large latent heat release at the BP III–isotropic transition (Fig 3) also indicated that a substantial ordering takes place here. It also does not help that the experimental evidences for BP III are conflicting. Accordingly, two different structures are being proposed [17], each of which has its own experimental backers. One of them says this phase consists of the so-called double twist cylinders, which are a tangle of low-energy cylinders of ordered material. The other approach has been to apply the quasi-crystal ordering concept to study BP III. The simplest three-dimensional quasi-crystalline structure turned out to be a regular icosahedron. There is not yet a consensus on which is the actual model and so further elaborate experiments are necessary.

3 Theoretical models

Any physical process observed through experiments needs to be validated via theoretical models and the blue phases are no exception. Extensive theoretical models have been developed to explain the various experimental data. Some are in good agreement, while the rest are not, and surely there remains many open questions.

The most widely used theoretical device to explain a system undergoing phase transitions is obviously the Ginzburg-Landau theory of phase transitions. Indeed, correct theoretical description of blue phases remains one of the more glowing achievements of such theory [9].

3.1 Ginzburg-Landau theory

Ginzburg-Landau theory essentially requires the assumption that the liquid-crystalline order be a perturbation upon the isotropic state. Then the free-energy density needs to be expanded in terms of the powers of the order parameter and its spatial derivatives, while neglecting the higher-order terms.

3.1.1 Order parameter

The first step in such a theory is then a proper choice of the order parameter. For most liquid crystals a scalar or a vector order parameter is inapplicable since liquid crystals are mostly composed of anisotropic molecules. These systems show orientational order below a critical temperature. Macroscopically, this order evidences itself as an anisotropy in the system's second-order tensor properties, which may be the dielectric or the diamagnetic tensor. A tensor, \mathbf{Q} can therefore be an appropriate order parameter. This is nothing but the anisotropic part of the dielectric tensor. And so

$$Q_{ij} \equiv \epsilon_{ij} - \frac{1}{3} \text{tr}(\epsilon) \delta_{ij} \neq 0. \quad (1)$$

The symmetric traceless quantity \mathbf{Q} vanishes in the disordered phase and is non-zero in any phase possessing orientational order.

3.1.2 Free energy

We have remarked that the transition from isotropic to anisotropic phase is essentially of the first order. This, in fact, permits blue phase ordering to be described from a simple mean-field theory and thus neglecting any fluctuations. However, there have also been studies which take fluctuations into account [2]. In such theories by simply considering the spatial periodicity of the anisotropic phase it has been shown that the net effect of large fluctuations is to disrupt the onset of such phase from the isotropic phase. In such a situation the free energy of the isotropic phase has to be lower than other competing structures, if it has to survive. But, if a new structure with a lower energy appears then a first-order phase transition takes place from the isotropic to that new phase [4]. Thus, spatial periodicity arguments together with the fluctuation theory can also predict the existence of intermediate blue phases.

In what follows, we will totally neglect any fluctuations (following [19]). We know that to determine the equilibrium structure one clearly needs to minimize the free energy. We will identify two different sets of terms contained in free energy density. One set which contains the derivatives of the order parameter is called the *gradient* free energy density, and the other set which do not contain such terms is called the *bulk* free energy density. Now the main difficulty while minimizing this

free energy density is that in case of chiral nematics the bulk and the gradient free energy densities are minimized by different forms of the order parameter. The bulk free energy is minimized by a *uniaxial* \mathbf{Q} , while the gradient one is done by a *biaxial* form. The competition between these two forms of energy is what gives rise to the “compromise” structures near the transition point which we are calling blue phases.

Up to fourth-order the bulk free-energy density is given by

$$f_{\text{bulk}} = c \text{tr}(\mathbf{Q}^2) + b \text{tr}(\mathbf{Q}^3) + a [\text{tr}(\mathbf{Q}^2)]^2. \quad (2)$$

Here the parameter c can have either sign. But a should be positive from stability requirements. The cubic coefficient, b determines whether the transition is of first or second order. When b is nonzero, the order parameter shows a jump to a nonzero value and then c is positive. This is what we know to occur in ordinary nematics where ordering is driven entirely by bulk free energy and where the coefficient b makes the transition first order. Now, for a non-vanishing b , the bulk free energy density is minimized at any point by a uniaxial tensor. Mathematically, this means the matrix \mathbf{Q} has a pair of degenerate eigenvalues. Thus both \mathbf{n} and $-\mathbf{n}$, which are directions orthogonal to the director, are identical and hence this configuration is called the *uniaxial helix*. The anisotropy of the ordered liquid has a rod-like symmetry in this case.

The gradient free-energy density on the other hand has the form

$$f_{\text{grad}} = K_1 [(\nabla \times \mathbf{Q})_{ij} + \frac{4\pi}{p_0} Q_{ij}]^2 + K_0 [(\nabla \cdot \mathbf{Q})_i]^2, \quad (3)$$

where the curl term appears only in chiral nematics, p_0 is the pitch of the helical phase and K_1, K_0 are two elastic constants. When the elastic constants are both positive, the gradient free energy is surely positive. It reaches its minimum for any \mathbf{Q} under the following condition

$$\nabla \times \mathbf{Q} = -\frac{4\pi}{p_0} \mathbf{Q}. \quad (4)$$

f_{grad} is minimized by a structure of the order parameter, which like the uniaxial helix is constant in directions normal to the director and also rotates uniformly along the director axis. Locally, however, this structure is totally different. In this case there are three distinct eigenvalues and the geometry is different along all three directions. This anisotropy has a brick-like symmetry. Note that this clearly relates to the platelets, we mentioned while discussing the blue phase structure. This configuration is called the *biaxial helix*. Biaxiality is important in understanding the blue phase ordering, especially at the high-chirality limit to be discussed subsequently. One thing that we would like to point out here is that the overall symmetry of the ordered phase may or may not reflect the individual symmetry of the constituent molecules, and molecules with brick-like symmetry can in fact form a uniaxial liquid.

The full free-energy density is then

$$f = f_{\text{bulk}} + f_{\text{grad}}, \quad (5)$$

where f_{bulk} and f_{grad} are respectively given by (2) and (3). The minimization of the full free energy is still an open problem, since its two components favor separate

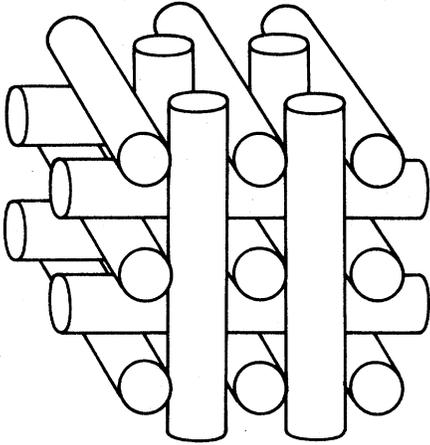


Figure 7: The arrangement of double-twist cylinders in the O^2 structure. Source: [19].

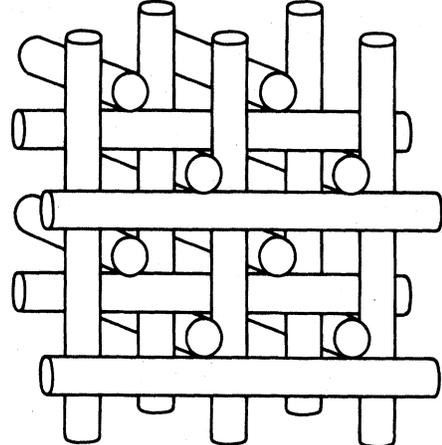


Figure 8: The arrangement of double-twist cylinders in the O^8 structure. Source: [19].

minimization structures.

3.2 Two limiting cases

In what follows in this section, we will be studying two of the limiting cases of Ginzburg-Landau theory, which makes it possible to extract many of the experimentally observed blue-phase structures.

3.2.1 Low chirality limit

Denoting chirality by κ , this is the case when $\kappa \rightarrow 0$, which happens when the pitch, $p_0 \rightarrow \infty$. In this situation f_{bulk} dominates. This is easily seen as follows. For infinite pitch the second term in (3) vanishes and also the right hand of (4). Thus any constant tensor \mathbf{Q} minimizes f_{grad} , and a uniaxial \mathbf{Q} certainly does that which also, as we have seen, minimizes f_{bulk} . The gradient free energy in this case becomes zero. Note that in the low-chirality limit ($\kappa = 0$) there is actually no blue phase and the structure is, as expected, uniaxial. The low-chirality model [14] will assume chirality to be low enough so that the order parameter is only weakly biaxial, but which nevertheless causes new phases to appear.

Low-chirality limit is important since typical values of κ found in many systems actually conform to this limit. As pointed out, this model assumes the free-energy density to be uniaxial, even though the chirality is not actually zero, but then a relaxation to biaxiality is expected to result in only small corrections. The main task here is to determine what kind of uniaxial structure may have a lower free energy than the helical phase, so that it may exist beyond the transition temperature. It turns out [14] that the *double-twist* structure of the director (see Fig. 6) indeed does that. The structure is so-called since the director rotates simultaneously along two directions orthogonal to each other. This assumption is, however, not without trouble. It is not possible to built structures which are locally double twist that extend across an entire region of space. Thus, quite evidently, regions of double

twist will be separated by less favorably aligned structures. Then a structure with locally double twist configuration can only be stable if the free-energy gain in the double twist zones more than offset the loss outside those zones. One way to do this is by varying the amplitude (denoted here by λ) of the order parameter. Reducing the amplitude in those non-double twist regions lowers the gradient free energy, which is good, but its effect on bulk free energy is undesirable, since f_{bulk} does not prefer variations in amplitude. Since, in the low chirality limit it is the bulk free energy which dominates, such variations are possible only up to a certain threshold. Below which no blue phases may appear.

Construction of stable structures then calls for a slight alteration of the perfect double twist structure. Instead of a double twist structure which varies constantly in amplitude we consider an imperfect double twist structure, which has some constant amplitude until some radius, and is zero beyond. This is because a double twist structure is always preferable near the director axis and up to a certain radius, but in addition, for the above configuration to be stable the isotropic phase (the zero amplitude domain) needs to be of lower energy than the helical phase. This has been proved to be true over a certain range of κ [7]. The resulting stable structure then consists of double twist cylinders floating in a sea of isotropic phase. When the cylinders are not arranged in a periodic fashion we get the double twist model of amorphous BP III, mentioned earlier. The periodic arrangements result in the tight-binding blue phase models for BP I and BP II.

When the double twist cylinders are arranged in a periodic array with simple cubic translational symmetry we get the O^2 space group which describes the BP II phase, as shown in Fig. 7. This arrangement, although it fills out at least $3\pi/16$ (58.9%) of the space with zones that has a lower free energy than the helical phase, introduces singularity in between two such zones. These are the π -dislocations and are found in all such structures built using double twist cylinders. There is a singularity since the gradient free energy diverges at the core of such dislocations. The compromise is then to vary λ in such a way that it vanishes at the dislocation cores and thus results in a non-singular core of isotropic liquid. Similarly one may also get O^8 space group corresponding to BP I, by arranging the cylinders into a body centered cubic array fashion (Fig. 8).

3.2.2 High chirality limit

For short pitch, the stability analysis for the helical phase predicts that the helical ordering disappears through a second-order transition to the isotropic phase. But, that is never observed in practice, where the second order transition is replaced by a series of first order transitions that result in the intermediate blue phases. For very low pitch or when the chirality is very high the gradient free energy dominates. As mentioned earlier this energy is minimized by a biaxial helix order parameter or a linear combinations of the same. In the $\kappa \rightarrow \infty$ limit, the helical phase order parameter becomes a single biaxial helix. The blue phases are then a linear combination of biaxial helices differing from each other by translation and/or rotation. It turns out (see for example [8]) that such a phase with a cubic f_{bulk} has lower free energy compared to both the helical and isotropic phases at sufficiently low temperature. As the temperature drops further the order parameter grows and the quartic terms in the bulk free energy become more dominant. Then it can be shown

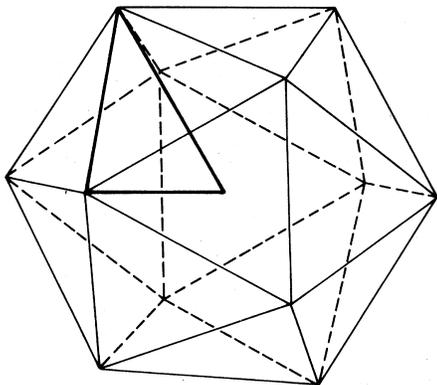


Figure 9: The wave vectors of the icosahedral model. Source: [19].

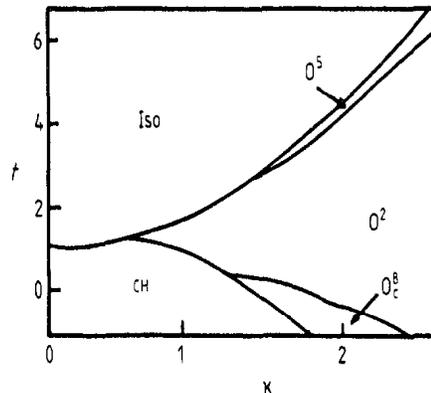


Figure 10: A theoretical phase diagram. Source: [17].

that the helical phase becomes more favorable. In this manner the high chirality limit identifies the existence of blue phases.

To determine which space groups are dominant in this limit one can carry out a detailed minimization procedure of the free energy terms [19]. It shows the space group O^5 to be the most favorable high-temperature form for blue phases in this high-chirality limit. This is the ordered state (BP II) where the isotropic liquid first condenses into. When the temperature is further dropped a O^8 structure (for BP I) appears with a lower free energy. But, this structure turns out to be unstable in this limit. Instead, a structure with hexagonal symmetry seems to be stable all along the region where the O^8 structure is favored over O^5 . It is interesting to note that the O^8 space group, although unstable here, is predicted by both the high and low chirality limit analysis. On the other hand, the O^5 structure has never been observed experimentally. When κ is not infinity, but still moderately high, there seems to be a possibility for the O^2 structure to also appear, which then becomes more stable than the helical phase. So there is a possibility that this structure might also fit inside the chirality-temperature phase diagram along with the other structures described.

As for BP III, the only structure suggested in this limit has the translational symmetry of an icosahedral quasicrystal as shown in Fig. 9. The argument put forward here is that the 30 wave vectors directed along the 15 twofold axes of an icosahedron should contain quite a few many trios that sum to zero, which would let the cubic bulk free energy compete more favorably with the bcc phases. Actual calculations, however, show otherwise [19]. There have been many attempts to tweak the above structure so that it becomes more favorable energetically, but this problem is still far from being resolved.

4 Phase diagram

Assembling all the aspects of the blue phases discussed, we are now in a position to construct the temperature-chirality phase diagram. The theoretical phase diagram shown in Fig. 10 clearly shows the various space groups and this can be compared with the experimental data of Fig. 11. Note that these comparisons are done only

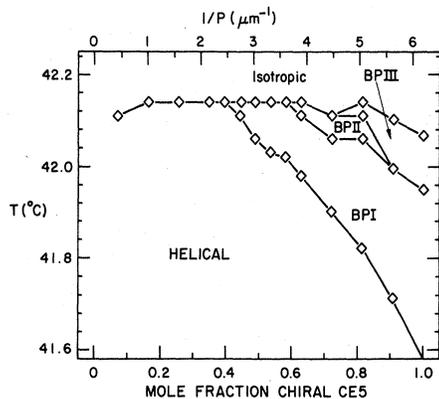


Figure 11: Phase diagram obtained via experiments on CE5. Source: [19].

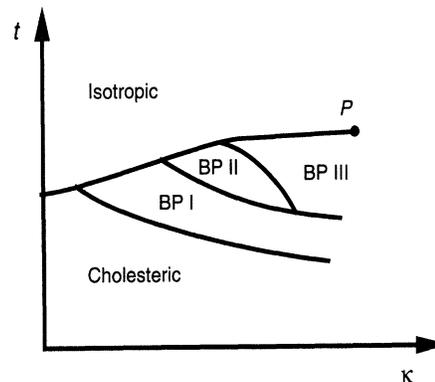


Figure 12: A schematic phase diagram showing the location of the isotropic–BP III critical point (P). Source: [12].

on a qualitative basis. As noted in the previous sections O^8 and O^2 structures are clearly identified with BP I and BP II respectively. At the high chirality limit, the theory in addition predicts the O^5 structure over a narrow region. This kind of phase diagram has been recently augmented with the discovery of a critical point [10] in between the BP III and the isotropic phase. This phenomenon has only been observed in highly chiral liquid crystals. Clearly, it suggests a liquid–gaslike critical point in the temperature–chirality plane [12] of liquid crystals. There probably exists a one-to-one correspondence between the BP III–isotropic and the liquid–gas transitions. Also, it implies that the isotropic and BP III phases have the same isotropic symmetry, contrary to the predicted icosahedral and double twist structures, discussed before. A simple phenomenological model has been constructed supporting this argument using a pseudoscalar order parameter, $(\nabla \times \mathbf{Q}) \cdot \mathbf{Q}$ [12]. A schematic of the currently accepted phase diagram is shown in Fig. 12. It is then also of interest to investigate the other blue phases using this new order parameter to see if the O^5 space group gets eliminated.

5 Concluding remarks

Liquid crystals belong to that class of physical systems which are interesting both from the point of view of their underlying physics and also from their industrial applications. The worldwide liquid-crystal-display industry will surely testify to that. And, blue phases remain one of the most exotic phases of such matter. In this essay we have mainly tried to demonstrate how the simple Landau theory is able to explain most of the anomalies that appear for these phases. Also, from the knowledge of space-group symmetries most of the features of BP structures have been identified. But, these approaches have their own problems. A complete understanding of the BP structures require knowledge of the spatial molecular distribution function. Simple space-group studies cannot lead to that. Neither can a mean-field theory, which neglects fluctuations, accurately compute the latent heat ratios in a typical order–disorder transition. Thus, the phase diagrams we compared were also largely qualitative. The issue of the O^5 structure remains, since it has

never been observed experimentally. The mystery of BP III also needs to be resolved sooner than later. One extension that is clearly possible is to extend the Landau theory to include higher-order terms in the free-energy expansion. Such procedures might enable closer comparisons with experimental data. On the other hand, the experimental field that is expected to show the most promise in the near future is that of NMR spectroscopy [9]. Interestingly, the methods developed to analyze the blue phases were good enough to discover other new phases of liquid crystals, such as the smectic blue phase and the twisted grain boundary phase, mentioned before. And the current crop of research in this field seems to be more focused on these new phases, instead of solving some of the more traditional puzzles.

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