

Structure of Blue Phase III of Cholesteric Liquid Crystals

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We report large scale simulations of the blue phases of cholesteric liquid crystals. Our results suggest a structure for blue phase III, the blue fog, which has been the subject of a long debate in liquid crystal physics. We propose that blue phase III is an amorphous network of disclination lines, which is thermodynamically and kinetically stabilized over crystalline blue phases at intermediate chiralities. This amorphous network becomes ordered under an applied electric field, as seen in experiments.

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Liquid crystals (LCs) offer prime examples of systems with spontaneously broken symmetry that support topological defects of various types [1]. Alongside their technological utility in various optical devices, LCs offer testing grounds for fundamental theories whose counterparts in other fields (such as cosmology, particle physics, and more recently exotic superconductivity [2]) are less directly testable. While many aspects of LC physics are by now understood, some, such as the character of the so-called “blue fog” (blue phase III) have remained unresolved despite efforts spanning several decades.

The simplest liquid crystalline phase is the nematic, in which molecules have a preferred orientational axis (the director) but no translational order. Introduction of molecular chirality causes the director to precess in space. In the simplest resulting phase (the cholesteric) it does so about a single helical axis, thereby creating a 1D periodic structure whose wavelength is the helical pitch. Locally, however, the ordering remains nematic and the cholesteric therefore supports topological line defects, known as disclinations, in which the director executes a rotation of π under a full 2π rotation around the defect line. Within the cholesteric ground state, these excitations are absent.

In many chiral liquid crystals the transition between the cholesteric and isotropic phases occurs through a cascade of weakly first-order transitions to intermediate structures, known as “blue phases” (BPs) and consisting of self-assembled disclination networks [1,3]. At high enough chirality, a simple helical structure is less stable locally than a so-called double-twist cylinder (DTC), in which the director field rotates simultaneously in two directions perpendicular to a cylinder axis. However, DTCs cannot be smoothly patched together to fill the whole of space; disclination lines are required at the interstices between the cylinders. If an external field is used to align the DTCs, the disclinations can form a simple linear array [4], but more generally they meet at junctions forming a multiply connected network. The resulting structure is highly colored (“blue”) since the spacing between defects lies in the optical range. BPs are stable when the free energy gained

by creating DTCs instead of a simple helix is enough to compensate the free energy loss due to defect formation. They therefore occur at high chirality (where DTCs are favored) and for T close to but below T_{IC} (the transition temperature to the isotropic phase) where defect energies are low. Long viewed by many as little more than a curiosity [1], BPs have recently emerged as promising materials for photonics and display devices following their stabilisation over a much larger temperature range than previously possible (about ~ 60 K compared to < 1 K) [5].

Three BPs have been observed experimentally (at zero electric field). Two, BPI and BPII, are highly ordered: their disclination networks form a regular cubic lattice, and their physics is well understood. (Another ordered phase, O_5 , is predicted by theory at high chirality, but not found experimentally.) The last one is known as BPIII, and its structure is one of the unsolved puzzles of liquid crystal physics. Theorists have proposed that BPIII may either be a quasicrystal [6], a spaghettilike tangle of double-twist cylinders [7], an amorphous state formed by BPII domains [8], or a metastable phase [9]. Experiments on the thermodynamics, scattering and electric field response [10–12] remain inconclusive, although electron micrographs appear to favor an amorphous structure and rule out the quasicrystal [3].

In this work we show that computer simulations can help settle this important physical question. Via large scale (supra-unit-cell) simulations, which enable accurate comparison of free energies for both ordered and amorphous structures, we provide strong evidence that BPIII is indeed an amorphous network of disclinations. We show that, within a certain window of chirality and with a standard choice of free energy functional (see below), individual aperiodic structures exist that are more stable than either BPI, BPII, or O_5 . This narrow window lies within the observed range of BPIII, and can only become wider, in line with experiments, if one allows for configurational entropy. (Such entropy arises when there exist multiple aperiodic structures of the same free energy, as seems likely here.) Furthermore, we show that an applied electric field orders our aperiodic BPIII candidate into a different, much

more ordered blue phase. This concurs with longstanding experiments [11,12] which showed evidence of a field-induced transition to a new phase, BPE, whose structure was not previously identified.

The local order in the BPs can be described by a traceless, symmetric, second rank tensor, \mathbf{Q} whose equilibrium thermodynamics is governed by the Landau–de Gennes free energy functional \mathcal{F} , whose form, within the one-elastic constant approximation (discussed later) is standard, and specified in [13]. Within that approximation, the phase behavior of BPs depends on just three dimensionless parameters, a reduced temperature τ , a reduced chirality κ and a reduced field strength \mathcal{E} [14]. Expressions for these in terms of K (the elastic constant), q_0 (the cholesteric wave vector) and other parameters in \mathcal{F} are given in [13]. Good agreement between theoretical [15] and experimental [16] phase boundaries is obtained by taking $\tau \propto (T - T_{IC})$ and κ linear in the mole-fraction of a chiral component (with respective proportionality constants $\simeq 2 \text{ K}^{-1}$ and $\simeq 2$ for one specific mixture [15]).

We employ a 3D hybrid lattice Boltzmann (LB) algorithm [15,17–19] to solve the Beris-Edwards equations. The evolution of the \mathbf{Q} tensor [20] is

$$D_t \mathbf{Q} = \Gamma \left(\frac{-\delta \mathcal{F}}{\delta \mathbf{Q}} + \frac{1}{3} \text{Tr} \left(\frac{\delta \mathcal{F}}{\delta \mathbf{Q}} \right) \mathbf{I} \right). \quad (1)$$

Here, Γ is a collective rotational diffusion constant and D_t is a material derivative for rodlike molecules [20]. The term in brackets is the molecular field, \mathbf{H} , which ensures that \mathbf{Q} evolves towards a minimum of the free energy. The fluid velocity field obeys the continuity equation and a Navier-Stokes equation with a stress tensor generalised to describe liquid crystal hydrodynamics, and discussed elsewhere [17].

Though these equations represent the true dynamics, we use them here simply to find free energy minima. Thus, as in previous work we additionally allow a so-called “red-shift” in which the parameters in \mathcal{F} are dynamically updated at fixed τ , κ , \mathcal{E} [13]. This exploits a scaling among those parameters to ensure that the system is not frustrated by periodic boundaries: in particular, for any cubic BP, a lattice parameter emerges that truly minimizes \mathcal{F} . The accuracies of their computed free energies $F \equiv \min(\mathcal{F})$ are (at least for $\mathcal{E} = 0$) thus limited only by discretization. This is chosen to fully resolve the defects [13], whose core energy is finite, and set by \mathcal{F} itself.

In computing the free energy of periodic structures (BPI, BPII and O_5) we apply a perturbation of the appropriate symmetry to a uniform state and then evolve dynamically [13]. This delivers an accurate F value in each such phase, of which the lowest can be chosen, but (in common with all other methods for computing free energies of ordered phases) we cannot rule out others of still lower \mathcal{F} . To address BPIII, we also need to generate aperiodic candidates. Here our strategy is similar: we start from various different aperiodic initial conditions, evolve each dynamically, and choose that of lowest \mathcal{F} [13]. As shown

below, this beats all three periodic structures within a certain parameter window. Because we cannot exhaust all possible initial conditions, our free energy is an upper bound on aperiodic states; further exploration can thus only widen that stability window. In practice, all the aperiodic candidates we generated look similar. Our conclusions about the character of BPIII are thus likely robust.

To minimize finite size effects, we simulate very large systems (in contrast to [15]). Typically, we used 128^3 lattices, which accommodates 8 half pitches in each direction. Selected simulations with 256^3 lattices confirm the results which we report below. As shown in [19], it is easy to generate aperiodic structures by placing a localized nucleus of BPI or II in a cholesteric or isotropic matrix. However, the lowest \mathcal{F} values we have so far found are instead achieved by initialising the system in the cholesteric phase in the presence of a low density (typically about 1–2% in volume) of randomly placed doubly twisted droplets. Once initialized, the system is relaxed dynamically until it reaches a quiescent end-state.

For low chirality ($\kappa < 1.5$), the initial defects are washed out to leave a cholesteric phase. However, for a large regime of intermediate chiralities ($1.75 \leq \kappa \leq 3$), our simulations show an intriguing dynamics, through which the dilute doubly twisted regions grow and rearrange dramatically to form a whole network of disclinations, which very slowly creeps to an amorphous end-state (Fig. 1, top). Its amorphous character is confirmed by the structure factor $C(\mathbf{k})$ (Fig. 1, bottom). The ring in $C(\mathbf{k})$ is set by the average distance between the branch-points in the defect network, whereas the small residual peaks (which break spherical symmetry) are likely due to

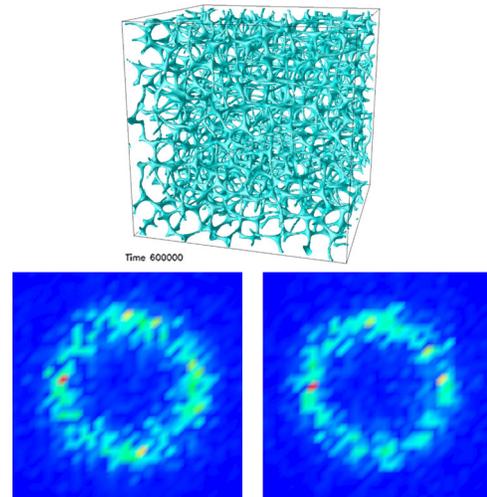


FIG. 1 (color online). Top: End-state disclination network at $\tau = -0.25$, $\kappa = 2.5$: The picture shows the isosurface $q(\mathbf{r}) = 0.12$, with q the largest eigenvalue of \mathbf{Q} . Inside each tube is a disclination line (on which q takes a minimum value). Bottom: Structure factor $C(\mathbf{k}) \equiv |q(\mathbf{k})|^2$, on cuts along $k_y = 0$ (left) and $k_x = 0$ (right) with wave vectors $k_x/q_0, k_z/q_0 \in [-4, 4]$ and $k_y/q_0, k_z/q_0 \in [-4, 4]$, respectively.

residual finite size or periodic boundary effects. The amorphous network approaches equilibrium through very slow local rearrangements of the disclination junctions; the end-state in Fig. 1 is very close to kinetic arrest, in at least a local minimum of \mathcal{F} . Notably, four disclination lines meet at most junctions, so that, as suggested by experiment [10], the structure is locally closer to that of BPII than BPI.

Remarkably, for larger values of the chirality ($\kappa > 3$) our simulations attain a much more regular state, closely resembling O_5 which (see below) minimizes our chosen \mathcal{F} at very high κ . (In O_5 itself, whose free energy we have computed precisely, eight disclination lines merge at each junction [13].) Therefore, our methodology is capable in principle of finding a periodic disclination lattice, if kinetically accessible. We believe that the kinetic propensity to form a disordered disclination network for intermediate chiralities indeed reflects a real physical property, although our limited simulation times (≈ 1 ms [13]) may well exaggerate the stability window of amorphous structures in the (κ, τ) plane.

A crucial question is whether our BPIII candidate structure is only kinetically, or also thermodynamically stable. To answer this, we have carefully compared $F(\kappa, \tau)$ for BPIII with those of BPII and O_5 , for a range of chiralities κ at selected values of τ . (BPI is not competitive in the κ range of interest here.) As an example, curves for $F(\kappa, -0.25)$ are shown in Fig. 2. We see that there is a small but finite chirality window in which the BPIII-network is the thermodynamic equilibrium phase. We find it remarkable that any single aperiodic structure can out-compete such periodic ones when minimizing the relatively simple Landau-de Gennes free energy. In particular, this minimization takes no account of order-parameter fluctuations about the local minimum, which might help stabilize BPIII [21], nor the configurational entropy associated with having many such minima. (These neglected contributions should be small—of order $k_B T$ per unit cell while the free energy differences in Fig. 2 are typically of order 100–1000

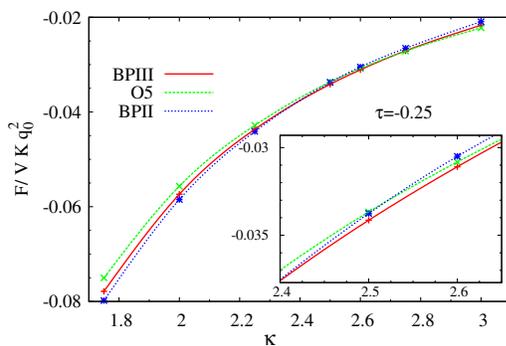


FIG. 2 (color online). Free energy densities (V is the volume) vs chirality κ at $\tau = -0.25$ for BPII, our candidate for BPIII, and O_5 . The inset shows a blowup of the region where our BPIII is the equilibrium phase. Our free energy densities are expressed in units of $K q_0^2$ (see [13] for the mapping between simulation and real units).

times larger [13].) However, the thermodynamic stability window in BPIII is smaller than the kinetic one—agreeing with the idea that amorphous structures should form more easily dynamically than highly ordered counterparts, which require long and complicated process to annihilate any dislocations and overcome relatively high energy barriers. The window of thermodynamic stability might also be broadened by relaxing the one-elastic constant approximation, particularly if this raises the free energy of O_5 relative to the other states. This certainly merits further study, given the experimental absence of that phase.

All the above arguments support our assignment of the amorphous network seen in Fig. 1 as the theoretically elusive BPIII, stable at larger κ than BPII, but locally similar to it [3]. Experiments on BPIII in electric fields also point to a field-induced transition between BPIII and another structure which has been named BPE [11,12]. BPE was found to give rise to a sharper peak in the scattering data consistent with an enhanced ordering (unfortunately Refs. [11,12] do not provide further experimental data on the structure of BPE). It is therefore interesting to ask what happens when our amorphous structure is subjected to an electric field. In our simulations we can follow the evolution of the \mathbf{Q} tensor and of the disclination network in an external field \mathcal{E} , and also compute $C(k)$; if a crystalline phase emerges, it will exhibit Bragg peaks.

By stepwise increasing \mathcal{E} from 0 to 0.65, we found that the disclination network in Fig. 1 melts away leaving a nematic state. (This holds for positive dielectric anisotropy [13].) We then performed a long simulation at $\mathcal{E} = 0.55$, close to but below the threshold beyond which the system becomes nematic. The time evolution of our BPIII, stable at zero field, is shown in Fig. 3. This shows an interesting rearrangement of the defect texture, through which the junction points rotate and finally reconstruct to yield a topologically distinct phase, with helical disclinations lying along layers stacked perpendicular to the electric field (which is vertical). The disclination lines in two consecutive layers are turned by 90° , so that they show a square arrangement when viewed along the field direction. As in experiments, we find that our amorphous BPIII candidate undergoes a field-induced transition to an ordered disclination network which we provisionally identify as BPE. It would be interesting to perform additional experiments to test such an identification. Our candidate BPE appears related to, but distinct from, other field- or confinement-induced BPs previously reported [4,22], with strong crystalline order (albeit with some defects remaining) as confirmed by its structure factor.

In conclusion, we have presented large scale simulations of the cholesteric blue phases. We have given strong evidence that in a region of the temperature-chirality plane, instead of a periodic BP, an aperiodic one is selected kinetically. Moreover, and strikingly, within the (one-elastic constant) Landau-de Gennes free energy [13], we have found a finite window of chirality in which this amorphous network is thermodynamically more stable

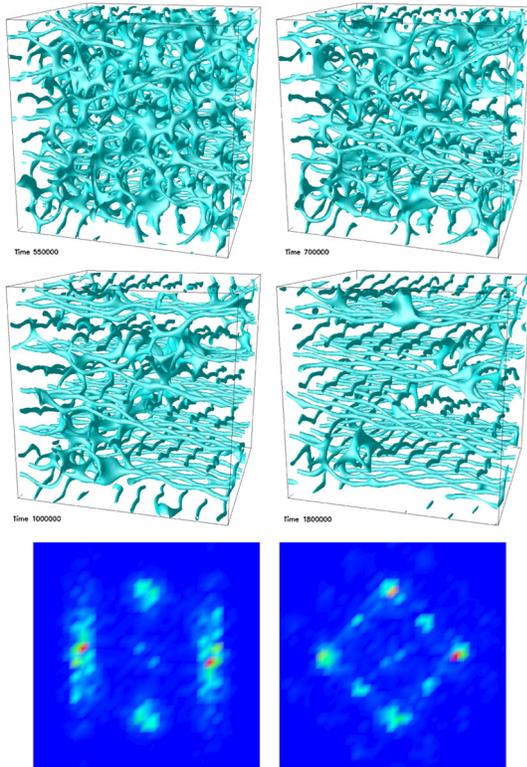


FIG. 3 (color online). Isosurfaces of $q = 0.12$ at $\tau = 0.2$, $\kappa = 2.0$, $\mathcal{E} = 0.55$: The sequence shows the transition from the amorphous BPIII-network to a field-induced BPE. The field direction, z , is vertical. Times shown are $t \approx 0.15, 0.3, 0.6$ and 1.4 ms (taking one time step ≈ 1 ns). Bottom row: Structure factor $C(\vec{k})$ at the end of the run. The pictures show a cut through the 3D data at $k_y = 0$ (in the (k_x, k_z) plane, left) and $k_z = 0$ [in the (k_x, k_y) plane, right], with scales as in Fig. 1.

than the competing crystalline blue phases, BPI, BPII and O_5 . These facts suggest that our kinetically and thermodynamically stable network is none other than the blue fog, BPIII. This view is strengthened by the study of the field response of this structure, which reconstructs into an ordered phase at intermediate values of the electric field, slightly smaller than those at which the disclination network melts to give a field-oriented nematic phase.

We believe our simulations shed important light on the structure of BPIII, which we propose is an amorphous disclination network which is locally close to BPII. Several open questions remain or are stimulated by our results. First, one should characterize statistically the phase transition from the blue phase to the isotropic phase: this may be possible by adding thermal noise to simulations like the ones reported here. Second, use of more accurate scattering and visualization techniques should allow tests of our candidate structure for BPE (see Fig. 3). Finally, if the large energy scales that separate the various BP topologies (of order $100\text{--}1000k_B T$ per unit cell [13]) also control reconstruction of the defect network within BPIII itself, one may expect that in some materials, even when

thermal noise is allowed for, such reconstruction cannot be achieved on any reasonable time scale. If so, BPIII will represent another elusive entity: an “equilibrium glass.”

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