On the origin and structure of liquid crystalline Blue Phase III: A computer simulation study

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The origin and structure of self assembled chiral liquid crystalline Blue Phase III (BPIII) have remained an enigma despite efforts spreading over decades. We report here an off-lattice NVT molecular dynamics simulation study of a system of polar chiral ellipsoidal molecules, which spontaneously exhibits BPIII , considering coarse-grained attractive-repulsive pair interaction appropriate for anisotropic liquid crystal mesogens. We have observed that suitable selection of chiral and dipolar strengths not only gives rise to thermodynamically stable BPIII but novel Smectic and Bilayered BPIII as well. Further, we have demonstrated that occurrence of BPIII and its layered counterparts depend crucially on molecular elongation.

Chirality, characterized by broken reflection symmetry, is an essential issue for understanding major physical problems belonging mostly, to all length scales, viz. massive cosmological objects, mesoscopic biological components, nano systems, subatomic particles etc. Chiral liquid crystal systems may provide an arena to testify fundamental reasons behind these chirality related important physical phenomena analogically, where, in general, basic comprehension is unachievable even with ardous experimental procedures. Though non-chiral liquid crystalline phases are well understood, theoretical studies related to chiral phases are rare. Among chiral phases, the origin and structure of the BPIII phase still remains as a long standing puzzle, despite extensive endeavour [1].

Chiral liquid crystals, in addition to broken rotational and translational (optional) symmetries, belong to the symmetry group that lacks reflection symmetry. Chiral liquid crystal molecules exhibit translationally disordered cholesteric phase where the nematic director precesses about the helical axis. The isotropic-cholesteric phase transition can go through a cascade of intermediate Blue Phases. Experimental evidences [1-4] indicate that though the BPI and the BPII possess cubic structure for the double twist cylinders, the BPIII, the so called ‘blue fog’ [3, 5], seems to be amorphous. Apparently the BPIII does not exhibit Bragg scattering [6] whereas it is attributed with strong optical activity alongwith thermodynamic stability but is lacking birefrangence and having mechanical properties more like isotropic phase. Here, the fact to be noted is that experimental explorations have been very much hindered by the occurrence of the BPIII phase in an extremely narrow temperature (or other factors affecting phase transitions) interval and optical effects are manifested only at very short wave length range. Additionally, study of chain-length size of the chiral molecules is important for many technological devices [7, 8], lipid bilayer cell-membranes [9], chiral drugs [10] etc. Even in biological membranes, it has been found that, larger chainlength of cholesterol molecules, separately or mixed with phospholipids, is beneficial for health [11].

Theoretical [1, 12, 14] models proposing amorphous ‘spaghetti’ like arrangement of double-twist cylinders, or amorphous network of disclinations helped in determining phase properties. However, a complete understanding of these behaviours requires the information depicting molecular arrangement at microscopic level responsible for giving rise to the BPIII, which is yet to be achieved. Here, we have considered systems composed of molecules interacting through chiral, dipolar and attractive-repulsive van-der-Waals’ type interactions. In this MD simulation study, microscopic structure of spontaneous self-assembled BPIII including its layered and novel bilayered counterparts have been realized. We also have found that molecular elongation supports more efficient self assembly, thus acts as a stimulating molecular feature to widen stability region.

A coarse-grained model of a polar chiral molecule of prolate ellipsoidal shape has been used in this NVT Molecular Dynamics study. In this work, the pair potential acting between two such molecules i and j has been taken as [15, 16],

\[
U(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) = -c 4 \epsilon (\hat{r}_{ij} \cdot \hat{u}_i) \rho_{ij}^{-7} \{ \hat{u}_i \times \hat{u}_j \} (\hat{u}_i \cdot \hat{u}_j) \\
+ \frac{1}{r_{ij}^3} [\mathbf{p}_{d_i} \cdot \mathbf{p}_{d_j} - \frac{3}{r_{ij}^2} (\mathbf{p}_{d_i} \cdot \mathbf{p}_{d_j}) (\mathbf{p}_{d_i} \cdot \mathbf{p}_{d_j})] \\
+ 4 \epsilon (\hat{r}_{ij} \cdot \hat{u}_i, \hat{u}_j) (\rho_{ij}^{-12} - \rho_{ij}^{-6})
\]

(1)

The first, second and third terms in equation [1] represent the chiral, dipole-dipole and Gay-Berne [17] interactions respectively. \(\hat{r}_{ij}\) is the separation between the centers of mass of the molecules i and j, \(\hat{u}_i\) and \(\hat{u}_j\) represent the orientations of the molecular long axes of respective molecules with respect to the lab axis.

The polar part of a molecule has been represented by a single terminal point dipole, positioned at 0.5σ distance from one terminal point, the orientation of which has been fixed at an angle of 90° relative to the molecular long axis. The dipole moment vectors of respective point dipoles are \(\mathbf{p}_{d_i} \equiv \mu^+ \hat{u}_{d_i}\) and \(\mathbf{p}_{d_j} \equiv -\mu^+ \hat{u}_{d_j}\) where \(\mu^+ = (\mu^2 / \epsilon_0 \sigma_0^2)^{1/2}\) is the magnitude of the dipole moment in reduced unit; ‘d’ suffix suprises to the dipole. The long-range correction of the dipolar interaction has been taken care of by standard Reaction Field technique [18]. In our study, the values of cut-off radius \(r_{RF}\) and continuous dielectric constant \(\epsilon_{RF}\) have been taken as \(r_{RF} = 0.5\) and \(\epsilon_{RF} = 1.5\) [19] respectively.

The GB parameters \(\kappa\) (length to breadth ratio), \(\kappa'\) (strength ratio) and the relative well depth controlling parameters \(\mu\)
and $\nu$ have been taken as 3.0, 1/5, 1 and 2 respectively. Scaled density $\rho^* \left( \rho^* = \frac{N \rho}{\rho_0} \right)$ has been set to 0.30 for $\kappa = 3$. For each system, an well equilibrated isotropic phase has been used as the initial configuration and then the scaled temperature ($T^* \equiv k_B T / \varepsilon_0$, $k_B$ = Boltzmann constant) has been decreased gradually to study the phase change. For a particular system at each temperature step, the initial configuration has been a previous higher temperature equilibrium phase and simulation run of $5 \times 10^5$ steps has been performed to obtain the equilibrium configuration. At each MD step, average energy of the system has been calculated and its variation with MD steps remains within 2% RMS fluctuation about a mean value at equilibrium. Average values have been calculated from next $5 \times 10^4$ steps after equilibrium. As the twisted cylindrical domains remain oriented at random in the BPIII, so have no biasing in twist directionality, we have used conventional cubic periodic boundary condition.

For characterization of the phases, suitable distribution functions have been computed. For different system sizes: $N = 864$ & 1372 with $\kappa = 3.0$, phase properties have been studied for some selected discrete values of the chiral strength parameter $c$. The results obtained are qualitatively similar for all system sizes. The value of the reduced dipole moment $\mu^*$ has been set fixed at a typical value 1.0 [16]. For $c = 3.0$ & 4.0, Blue phases have been generated from a higher temperature isotropic phase by decreasing temperature. To find out the orientational correlations between molecules, longitudinal orientational correlation functions $S_{220}(r_{\parallel}^*/d)$ and $S_{221}(r_{\parallel}^*/d)$ have been calculated as functions of the intermolecular separation $r_{\parallel}^*$, in units of $\sigma_0$, measured along an appropriately selected reference axis and further scaled by a selected distance $d$ which is related to the periodicity of the phase studied [15]. The reference axis has been chosen perpendicular to one of the cubic simulation box sides. The plots of $S_{220}(r_{\parallel}^*/d)$ and $S_{221}(r_{\parallel}^*/d)$ show qualitatively the same variation as that of a Blue phase (figure 2) but the plots are not smooth. Here, these functions are calculated considering minimum image convention and taking half of the box length as the scaling length $d$. But, for other chiral phases obtained with lower $c$ values, these plots are quite smooth and show sinusoidal variation [15, 16]. Snapshot of a typical configuration obtained for $\kappa = 3.0$, $c = 3.0$ has been shown in figure 2a. Careful observation of the configurations obtained in these cases reveals that the double twist cylinders are not extended straight from a box face to the opposite face. Here in the case of BPIII long cylinders are oriented in a random fashion.

FIG. 1: Different phases formed: (a) BPIII with $\kappa = 3.0$, $c = 3.0$, $\mu^* = 1.0$, (b) Bilayered BPIII with $\kappa = 4.0$, $c = 3.0$, $\mu^* = 1.6$, (c) BPIII with $\kappa = 4.0$, $c = 4.0$, $\mu^* = 1.0$, (d) BPIII, $\kappa = 5.0$, $c = 3.0$, $\mu^* = 1.0$, (e) Bilayered BPIII, $\kappa = 5.0$, $c = 3.0$, $\mu^* = 1.4$, (f) BPIII, $\kappa = 5.0$, $c = 5.0$, $\mu^* = 1.0$.

FIG. 2: Plots of (a) $S_{220}(r_{\parallel}^*/d)$, (b) $S_{221}(r_{\parallel}^*/d)$ for $\kappa = 3.0$ and $\kappa = 5.0$. 
Snapshots depicting the configurations within five consecutive layers of same thickness perpendicular to one box axis has been provided in figure 3 where circles are drawn to show the cross-sections of some of the double twist cylinders. In figure shifting of the cylindrical cross-section (encircled) positions in different planes indicates cylinder twist in BPIII. In case of other BPs it goes straight from one face to the opposite face to the breadth ratio.

To study length dependence we have considered \( \kappa \) (length to breadth ratio) = 4.0 and 5.0 in addition to \( \kappa = 3.0 \) case.

Values of \( \rho^* \) which have different values for different \( \kappa \)'s have been taken equal to 0.19 for \( \kappa = 4.0 \) and 0.12 for \( \kappa = 5.0 \). Again, like \( \kappa = 3.0 \) for both \( \kappa = 4.0 \) and 5.0, to check chiral strength effect, we simulated three systems keeping \( c = 3.0, 4.0 \) and 5.0 values respectively. These double twist cylinders are not straight as in the cases of blue phases I and II, but they are tangled, as seen from the configurations. Also, at higher value of \( \kappa \), stable equilibrium blue phase has been realized at higher value of scaled temperature. For further investigation, the simulation box has been divided into some planar layers and then \( S_{220}(r^*_0/d) \) and \( S_{221}(r^*_0/d) \) have been calculated for all the planes separately, considering \( r^*_0 \) in a direction parallel to the planes. Plots of these functions show multiple peaks, not coinciding at same points for all of the layers, as formed in BPI and BPII, but they are at different points for different layers (figure 4). The number of peaks are more for higher values of \( c \) showing higher pitch values. Snapshots of the configuration are presented in figure 5 dividing the simulation box in five planar layers perpendicular to \( x \)-axis for better understanding of the twist of the double twist cylinders. From these analyses, it can be concluded that number of double twist cylinders increases with the increase in the chiral strength parameter \( c \). These double twist cylinders are found to be intertwined to form spaghetti-like structures as speculated for BPIII.

With further decrease in temperature, formation of smectic layers have started to develop in addition to orientational arrangement of the BPIII phase. For a system with higher value of \( \kappa \), smectic layers have started forming more efficiently at relatively higher value of the scaled temperature.

Additionally, we checked the effect of dipole strength on layer formation. Surely, the presence of dipoles give more stability to the smectic layers. Interestingly, for a higher value of \( \mu^* \) novel bilayered smectic BPIII (figure 15 and 16) has been formed, by decreasing temperature from a
FIG. 5: Snapshots of the configuration in five separate consecutive layers dividing the simulation box perpendicular to x-axis for a system with $\kappa = 5.0$ and $c = 3.0$. Dipoles are not shown for clarity. Colour variation in small smectic domains indicates twisted arrangement of molecules.

relatively higher temperature phase. Plots of $g(z^*)$ and $g_d(z^*)$ (figure 6), where the former is the correlation function for molecular center of masses as a function of the projection ($z^*$) of separation vector along the axis of a cylindrical domain considered around each molecule and the latter is the same for dipoles, are drawn. For $\kappa = 4.0$ (figure 6a) cylindrical domain of length $5\sigma_0$ and radius $4\sigma_0$ has been taken whereas for $\kappa = 5.0$ (figure 6b) they are $7\sigma_0$ and $5\sigma_0$ respectively. In both cases, the peaks of comparable heights for both the functions occur at nearly same positions for lower values of $\mu^*$, but when the value of $\mu^*$ increases the peaks of comparable heights for $g_d(z^*)$ occur alternately indicating the presence of small bilayered smectic domains in the BPIII. As the smectic domains are small, we have obtained fewer peaks for these plots.

In this simulation study, it has been found that higher chiral strength in the system induces intertwining of double twist cylinders which eventually gives rise to BPIII. Additionally, it has been observed that higher value of dipole moment can induce bilayer in smectic BPIII. Change in phase properties with increase in molecular length has also been studied. The observation is that the BPIII-Isotropic transition temperature is higher for a system with higher molecular length. Greater the molecular length, the required value of $c$ is lower at which BP III is formed. We also have observed that, molecular elongation favours efficacious formation of the smectic BPIII, whereas, increased dipolar strength is the key to give rise to novel bilayered BPIII. This work reveals microscopic interactions responsible for the realization of BPIII, taking into account realistic attractive-repulsive interactions and giving both positional and orientational freedom to the molecules and at the same time, this work indicates the way to minimize present experimental hurdle due to significantly narrow stability region of the BPIII phase. We hope, the present coarse-grained simulation study will help in fundamental theoretical understanding of the molecular level arrangement in BPIII phase and the coveted structure-property relationship.
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