Self-assembly in Lyotropic Chromonic Liquid Crystals

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Abstract

We have developed a class of idealized models of chromonic molecules which are miscible in water, but which can form aggregates which in turn organize into lyotropic liquid crystal (LC) phases. By carrying out Monte Carlo simulation in a binary mixture of model chromonic and water molecules, we have studied the effect of concentration and molecular shape on the nature of resulting mesophases. We have also computed the free energy associated with the formation of chromonic columnar aggregates by umbrella sampling. Our free energy computation helps us to verify the isodesmic behavior which is characteristic of chromonic systems. For isodesmic behavior the addition of each chromonic molecule to the columnar aggregates is accompanied by a constant free energy increment and the net free energy decreases with increasing column length.

I. INTRODUCTION

Recently there is a growing interest in a new class of lyotropic liquid crystals (LCs), so called lyotropic chromonic liquid crystals (LCLCs) due to their diverse potential application in many areas such as dyes, drugs, nucleic acids, antibiotics and anti-cancer agents \[\text{[1]}\]. Dichroic thin films formed from LCLCs can be used both as alignment layers and polarizers
for LC cells [2]. These materials are fundamentally different from conventional amphiphilic systems: their molecules are disc-like or plank-like rather than rod-like, rigid rather than flexible and aromatic rather than aliphatic. Due to their disc-like molecular shape chromonic molecules stack face to face forming columnar aggregates. Though there is no clear understanding of the nature of forces responsible for this face-to-face stacking, it is generally believed that the $\pi-\pi$ interaction of the aromatic cores is the main mechanism of molecular face-to-face stacking [1]. Hydrophilic ionic groups at the periphery of the molecules make them water soluble. The two principal chromonic mesophases are chromonic $N$ and $M$ phase. The basic structural unit of both phases is the untilted stack of the molecules. The $N$ phase is the nematic phase in which the molecular stacks has orientational order but no positional ordering and is formed when the concentration is low. At higher concentration these molecular stacks arrange themselves in a hexagonal pattern forming the $M$ phase. In recent years, many new chromonic phases has been reported [3,4] which are formed by aqueous cyanine dyes. Some of the liquid-crystalline aggregates formed by the cyanine dyes are shown in Figure 1.

Unlike the conventional amphiphilic system, the chromonic system does not have any critical micellar concentration (CMC). To avoid the unfavorable contact of the hydrophobic part of the molecules with the solvent, the molecules start to stack together forming columns even in dilute solution. As the column length increases, the fraction of the total molecular surface exposed to the solvent decreases. There is widespread experimental evidence that there is no optimum column length or aggregation number like the conventional amphiphilic system forming micellar aggregates. The micelle has a optimum size depending on the packing parameters which in turn depend on the ratio of the size of head and tail group [5]. The chromonic aggregation behavior is termed as ‘isodesmic’ in contrast to the ‘non-isodesmic’ behavior observed for simple amphiphilic system. For isodesmic behavior, addition of each chromonic molecule to the columnar aggregate is accompanied by a constant free energy increment. Therefore, with the increase in column length the free energy gradually decreases, in contrast with the non-isodesmic behavior of simple surfactant system,
where micelle formation is accompanied by sharp free energy minima. The self-assembly of chromonic molecules is governed by many factors such as molecular structure, concentration, temperature, solvent polarity and ionic strength. So far there is no clear understanding of the relationship between molecular structure and the structure of the supramolecular aggregates formed by the LCLC materials. Consequently many different aggregate structures have been proposed based on different experimental results.

In this paper, we have developed idealized molecular models of LCLCs which capture the overall shape of the LCLC molecules and the nature of their interactions in an approximate way. To understand the self-assembly of chromonic molecules, we have carried out simulations of binary mixture of LCLC molecules and water, and have studied the effect of concentration, temperature and molecular shape on the nature of the resulting mesophases. We have also computed the free energy associated with the addition of each chromonic molecule to a columnar aggregate. The method gives us the possibility to test the widely accepted isodesmic behavior of the chromonic aggregation.

The paper is organized as follows: in section 2 we briefly describe our model and the simulation technique. The results on the columnar aggregates, in bulk water, formed by the chromonic molecules are reported in section 3. We describe the method of computation of free-energy by umbrella sampling in section 4. Finally, a summary of the main results and the conclusions drawn from these are given in section 5.

II. THE MODEL

We have modeled chromonic molecules as diamond shaped constituted of 9 (model 1) tangent spheres of diameter \( \sigma \) bonded together (figure 2). We also considered another variant of the model where the chromonic molecules are disk shaped constituted of 7 (model 2) tangent sphere of diameter \( \sigma \) bonded together (figure 2). Model 2 is similar to the model considered by Edwards et. al. [6] with different kind of interactions. In case of model 1 the 7 spheres forming the disc are hydrophobic and the 2 spheres at the two ends are hydrophilic.
In case of model 2, the 6 outer spheres are hydrophilic and the inner sphere at the center of each molecule is treated as hydrophobic. Water molecule is modeled as a sphere.

Attractive interaction between like particles (water-water, hydrophilic-water, and hydrophilic-hydrophilic) is modeled via a Lennard-Jones (LJ) potential:

\[ V(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \]  

where \( r \) is the separating distance between the two interacting particles. The parameter \( \epsilon \) governs the strength of interaction and \( \sigma \) defines a length scale. We have assumed that \( \sigma = 1 \) and \( \epsilon = 1 \) for all interactions. We have taken a cut-off \( r_c = 2.5\sigma \), large enough to include excluded volume effects and attractive forces.

Repulsive hydrophobic-hydrophilic and water-hydrophobic interactions are modeled by a truncated and shifted LJ potential (WCA potential):

\[ V(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} + \epsilon \quad r \leq r_c, \\
= 0 \quad \text{otherwise.} \]  

where \( r_c = 2^{1/6}\sigma \).

For MC studies using LJ potential it is convenient to introduce reduced units. In terms of \( m, \sigma \) and \( \epsilon \), some of the quantities of interest are density \( \rho^* = \rho\sigma^3 \), temperature \( T^* = k_BT/\epsilon \), and pressure \( P^* = P\sigma^3/\epsilon \). The simulation has been carried out both in \( NVT \) (fixed number of particles at constant volume and temperature) and \( NPT \) fixed number of particles at constant pressure and temperature) ensemble. During each MC step either chromonic or water molecules were chosen randomly and displaced using Metropolis criteria. The reorientation move was performed using quaternions \[7\]. We have carried out simulations for different concentrations of the chromonic molecules at different temperatures. The concentration of chromonic is defined as

\[ \phi = \frac{xN_c}{xN_c + N_w} \]  

where \( x \) is the number of atoms constituting a single chromonic molecules, \( N_c \) and \( N_w \) are
the number of chromonic and water molecules respectively, $x$ is 9 for model 1 and 7 for model 2.

III. RESULTS

In order to investigate the spontaneous formation of chromonic aggregates and their morphology, various choices of initial conditions were used. Model chromonic and water molecules are initially dispersed randomly in a $L_x \times L_y \times L_z$ system with periodic boundary condition. Unless specified all of the results shown below are for model 1. Instantaneous snapshots of the columnar aggregates formed by chromonic molecules are shown in figure 3 and figure 4. At low concentration the chromonic molecules form short columns and with the increase in concentration the length and the number of the columnar aggregates increases. At higher concentration they form chain like aggregates.

We have also calculated various positional and orientational pair correlation functions for the chromonic as well as water molecules to characterize the structure of the columnar aggregates. $g^{cc}(r)$ is the radial distribution function of the center of mass of the chromonic molecules and is defined as

$$g^{cc}(r) = \frac{1}{\rho N_c} \left\langle \sum_{i \neq j} \delta(r - r_{ij}^{cc}) \right\rangle \quad (4)$$

$g^{ss}(r)$ is the same for solvent molecules (water) and is defined in an analogous way. $g_1^{cc}(r)$ and $g_2^{cc}(r)$ are the orientational correlation functions and are defined as

$$g_1^{cc}(r) = \frac{1}{\rho N g^{cc}(r)} \left\langle \sum_{i \neq j} P_2(u_i^{cc} \cdot u_j^{cc}) \delta(r - r_{ij}^{cc}) \right\rangle, \quad (5)$$

$$g_2^{cc}(r) = \frac{1}{\rho N g^{cc}(r)} \left\langle \sum_{i \neq j} P_2(p_i^{cc} \cdot p_j^{cc}) \delta(r - r_{ij}^{cc}) \right\rangle, \quad (6)$$

where $r_{ij}^{cc}$ is the relative separation of the center of the $i$th and $j$th chromonic molecules, $p_i^{cc}$ and $u_i^{cc}$ are a unit vectors lying parallel and perpendicular to the plane of the the $i$th chromonic molecule, $P_2(x) = 3/2 \cos^2(x) - 1/2$ is the second Legendre polynomial, and the sums range over all pairs of molecules.
In practice, we work either with fully angle-averaged correlation functions, e.g.

\[ g^{cc}(r) = \frac{1}{4\pi} \int d\Omega \ g^{cc}(r, \Omega), \]  

or with cylindrically-averaged correlation functions, e.g.

\[ g^{cc}(r_\parallel, r_\perp) = \frac{1}{2\pi} \int_0^{2\pi} d\phi \ g^{cc}(r_\parallel, r_\perp, \phi). \]  

Here, \( r_\parallel \) and \( r_\perp \) denote the components of \( r \) parallel and perpendicular to the orientation of the disc at the origin of the coordinate frame (see figure [10](a)), i.e. \( r_\parallel = r \cdot u^{cc} \) and \( r_\perp = |r - (r \cdot u^{cc})u^{cc}| \), and \( \phi \) is the azimuthal orientation of \( r \) about \( u^{cc} \). \( g^{cc}_1(r) \), \( g^{cc}_2(r) \) and \( g^{cc}_1(r_\parallel, r_\perp) \) are defined in an analogous way.

In figure 5 we have plotted spherically averaged correlation function \( g^{cc}(r) \) for different chromonic concentration and the first peak at \( r = 1.12\sigma \) signify strong positional correlation between chromonic molecules. Successive small peaks at \( r = 2.2\sigma, 3.3\sigma \) etc. indicate that the molecules aggregate in a columnar fashion as in figure 1(a) or (b).

The pair correlation between water molecules plotted in figure 6 exhibits the expected liquid like behavior with short range positional order.

More detailed structural informations for the chromonic aggregate emerges from the two-dimensional correlation function \( g^{cc}(r_\parallel, r_\perp) \) and \( g^{cc}_1(r_\parallel, r_\perp) \), shown in figure 7. With the reference chromonic molecule situated at the origin the three prominent peaks at \( r_\perp \sim 1.1, 2.2, 3.3 \) indicate that the chromonic molecules form columnar aggregates and the molecules within the columns is organized as in figure 1(a). Due to close packing effect the center of mass of the chromonic molecules within the columns can be shifted with respect to another by \( \sigma \) which is reflected in the broadening of the peaks around \( r_\parallel \pm 1.0 \). Examination of \( g^{cc}_1(r_\parallel, r_\perp) \) reveals a strong intensity (\( \sim 1.0 \)) peak around \( r_\parallel \pm 1.0 \) which indicates that the chromonic molecules within the columns are parallel to each other.

We also compute average the aggregation number to study its dependence on chromonic concentration. We identify two chromonic molecules belonging to a cluster if the distance separating two monomers belonging to two chromonic molecules is \( \leq 2.5\sigma \). From the cluster
size distribution we have calculated the average aggregation number through the following equation:

\[
<L> = \frac{\sum s^2N(s)}{\sum sN(s)}
\]  

(9)

where \(N(s)\) is the number of cluster of size \(s\). In figure 8 we have shown the average aggregate size \(< L >\) as a function of chromonic concentration. At low concentration \(< L > \sim \phi^{0.6}\). At higher concentration the dependence of \(< L >\) on \(\phi\) is stronger than power law. Similar behavior is observed for conventional lyotropic systems [8,9].

Since in our simulation we do not observe the formation of regular columnar aggregates as shown in figure 1, we have simulated pre-assembled single and multiple columnar aggregates to test the stability of columnar aggregates. The simulation was done in \(NVT\) ensemble. The columnar aggregates remain stable over simulation time, in contrast to model 2 in which case pre-assembled columnar aggregates break and the system becomes isotropic. In addition our simulation with model 2 do not exhibits the spontaneous formation of columnar aggregates (figure 9). This indicates that we need to make judicious choice of the ratio of number of hydrophilic and hydrophobic units, an overall hydrophobicity of the chromonic molecules being necessary for the spontaneous self-assembly.

IV. FREE ENERGY COMPUTATION BY UMBRELLA SAMPLING

To calculate the free energy associated with the formation of columnar aggregates we have calculated the free energy of association in pulling apart two chromonic molecules by using umbrella sampling [10]. The distance \(r_c\) separating two chromonic molecules were confined (figure 10) by means of a harmonic potential of the form:

\[
U(r) = \frac{1}{2}k(r - r_c)^2
\]

(10)

where \(r_c\) is the equilibrium distance imposed between the center of mass of two chromonic molecules. The equilibrium distance were varied from \(1.1\sigma\) to \(7\sigma\) in steps of \(0.1\sigma - 0.2\sigma\).
Note that the equilibrium distance between two chromonic molecules can not be less than \( \sigma \). From the individual biased average probabilities, \( P(r) \), obtained for each \( r_c \), unbiased free energy \( (F) \) can be constructed self-consistently using the weighted histogram analysis method (WHAM) \[11,12\]. We have performed MC simulation at constant pressure for 25 windows. The value of the spring constant used was \( k = 200 \). We have performed some simulation with higher values of spring constant \( k = 2000 \) and found qualitatively similar free energy behavior. The probability distribution of the distance \( r \) separating two chromonic molecules is,

\[
P(r) = \langle \delta(r - r_c) \rangle = \frac{1}{Z} \int d\mathbf{r}^N \delta[r - r_c] \exp[-\beta V(\mathbf{r}^N)]\] (11)

for values of \( r \) for which \( P(r) \) is exceedingly small. Here, \( \delta \) is a Dirac delta function, \( N \) is the number of particles, \( \mathbf{r}^N \) denotes the set of particle coordinates, \( \beta = 1/(k_B T) \), where \( k_B \) is Boltzmann’s constant and \( T \) is the absolute temperature, \( V(\mathbf{r}^N) \) is the potential energy, and \( Z \) is a normalization factor (the configurational partition function). However, problem arises due to the fact that to \( P(r) \) becomes exceedingly small for values of \( r \) which give significant contribution to the free energy. Umbrella sampling makes use of a biasing potential to sample the region of phase space for which \( P(r) \) is exceedingly small. The distribution of \( r \) in the presence of a biasing potential is

\[
P'(r) = \frac{1}{Z'} \int d\mathbf{r}^N \delta[r - r_c] \exp[-\beta[V(\mathbf{r}^N) + U(r)]]
\]

\[
= \frac{Z}{Z'} \exp[-\beta U(r)] P(r),
\] (12)

where \( Z' \) is the partition function for the biased Hamiltonian. From this it follows that

\[
P(r) = \frac{Z'}{Z} \exp[\beta U(r)] P'(r).
\] (13)

Thus, the distribution function \( P(r) \) can be obtained (to within a multiplicative constant) from a measurement of the biased distribution \( P'(r) \). The Helmholtz free energy \( F \) as a function of \( r \) can then be obtained (to within an additive constant) from
By piecing together the relative free energies measured using a number of biasing potentials, it is possible to construct $F(r)$ over any specified range of $r$.

We have computed the potential of mean force of bringing two initially separated chromonic molecules on top of each other by the above method and the result is shown in figure 11. This case is referred to column 2 (figure 10(a)). From the free energy curve we see that there is strong attraction between chromonic molecules at short distance, leading to face-to-face chromonic aggregation. Both energetic and entropic factors lead to this attraction: by stacking on top of each other the unfavorable hydrophobic interaction with water molecules is reduced and this stacking results in a net increase in the volume available to the water molecules and thereby increasing their entropy. At intermediate separation water molecules form solvation shells between the two chromonic molecules which results in a depletion repulsion between the chromonic molecules and thereby increasing the free energy barrier between them. At larger separation two chromonics do not interact with each other and so the potential of mean force levels off. However, at this stage we are unable to separate the entropic and energetic contribution in the free energy.

We have also computed different orientational pair correlations $g^c_{1c}(r)$ and $g^c_{2c}(r)$ between the two chromonic molecules and are shown in figure 12.

From the $g^c_{1c}(r)$ we see that at the minimum separation ($r = 1.0826\sigma$) the two chromonic molecules are parallel and stacked together. However, their in-plane unit vectors make an angle to each other as is evident from $g^c_{2c}(r)$. As the separation increases they start loosing their orientational correlations.

Next we compute free energy of association of a chromonic molecules onto a columnar aggregates formed by two chromonics (referred to as column 3, figure 10(b)) and three chromonic molecules (referred to as column 4, figure 10(c)) respectively. Within the columnar aggregate, the separation and orientation of the two chromonics are kept fixed which was computed at the location of the free energy minima for the column 2 case (see figure
The computed free energy is shown in figure 13. The free energy curves have the same features as in the case column 2 (figure 11). At large separation chromonic molecules do not see each other and consequently free energy reaches a plateau at larger separation. At intermediate separation the chromonic molecules start interacting with each other and start expelling the water molecules form the region between them to aggregate on top of each other and this leaves more room for the water molecules. This way water molecules gain entropy and chromonic molecules gain energetically (less contact with water molecules). This depletion effect eventually leads single chromonic molecules going on top of the existing columnar aggregates of length 2 or 3. Such type of depletion attraction and repulsion has been found between macromolecules immersed in a fluid of much smaller particles [13–15]. As in the case of column 2, we have also computed the orientational pair correlation for column 3 and 4. In case of column 3, the behavior is similar to the case of column 2. However for column 4, now the chromonic molecules remain perfectly parallel both within and perpendicular to the chromonic plane. The presence of three chromonic molecules within the aggregate strongly influence the fourth one which is coming on top of it.

V. SUMMARY AND CONCLUSION

We have developed a class of idealized model for the chromonic molecules. Simple site-interaction models represent a useful class of models for the study of the chromonic liquid crystalline self-assembly. For sufficiently hydrophobic molecular models formation of columnar aggregates is observed. Our free energy computation for different length of columnar aggregates gives valuable insight. However, more effort is required to test the isodesmic hypothesis. Future work will focus on improving configurational sampling (via rigid-body molecular dynamics) and on investigations of chemically realistic models of chromonic LCs.
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FIG. 1. Schematic representations of chromonic columnar aggregates, H-aggregates (a and b), J-aggregates (c), brickwork structure (d) and layered brickwork (smectic) structure (e)
FIG. 2. A schematic representation of model chromonic and water molecules.
FIG. 3. Starting from an isotropic initial condition we get columnar aggregates. The parameters are: $\phi = 0.081$, $N_c = 50$, $N_W = 5100$, $T^* = 1.0$ $P^* = 1.0$, all in reduced units. For clarity the water molecules have not been shown.
FIG. 4. Same as in figure 3. The parameters are: $\phi = 0.137$, $N_c = 90$, $N_W = 5100$, $T^* = 1.0$, $P^* = 1.0$, all in reduced units. For clarity the water molecules have not been shown.
FIG. 5. Pair correlation between the center of mass of the chromonic molecules for different chromonic concentration.
FIG. 6. Pair correlation for water molecules for different chromonic concentration.
FIG. 7. Two dimensional correlation between the center of mass of the chromonic molecules (a) \(g^{cc}(r_{\parallel}, r_{\perp})\) and (b) 
\(g_1^{cc}(r_{\parallel}, r_{\perp})\). The parameters are same as in figure [4].
FIG. 8. Average aggregation number $\langle L \rangle$ as a function of chromonic concentration $\phi$. 
FIG. 9. Simulation with model 2 does not give rise to columnar aggregates. The chromonic density is $\phi = 0.12$. Other parameters are the same as in figure 8.
FIG. 10. Three different cases for which the free energy has been computed. (a) column 2, (b) column 3 and (c) column 4.
FIG. 11. Free energy as a function of the distance separating the center-of-mass of two chromonic molecules for the case 10(a).
FIG. 12. Orientational pair correlations between two chromonic molecules for the case 10(a).
FIG. 13. Free energy as a function of the distance separating the center-of-mass of two chromonic molecules for the case shown in figure 10(b) and (c).
FIG. 14. Orientational pair correlations between chromonic molecules (a) for the case shown in figure 10(b) and (b) for the case shown in figure 10(c).