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Isodesmic self-assembly in lyotropic chromonic systems

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We have developed simple models of chromonic molecules and by carrying out Monte Carlo simulation in a binary mixture of model chromonic and water molecules, have studied the effect of concentration and molecular shape on the pattern of molecular aggregation. We have also computed the free energy change associated with the formation of chromonic columnar aggregates by umbrella sampling. This helps us to verify the isodesmic behaviour which is characteristic of chromonic systems.

1. Introduction

Recently there has been growing interest in a new class of lyotropic liquid crystals (LCs), the 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 [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 coventional 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 shape chromonic molecules stack face-to-face forming columnar aggregates. Although there is no clear understanding of the nature of the forces responsible for this face-to-face stacking, it is generally believed that the π–π interaction of the aromatic cores is the main driving force for molecular face-to-face stacking [1]. Hydrophilic ionic or hydrogen bonding groups at the periphery of the molecules make them water soluble. The two principal chromonic mesophases are chromonic N and M phases. The basic structural unit of both phases is the untilted stack of molecules. The N phase is the nematic phase in which the molecular stacks have 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 have 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.

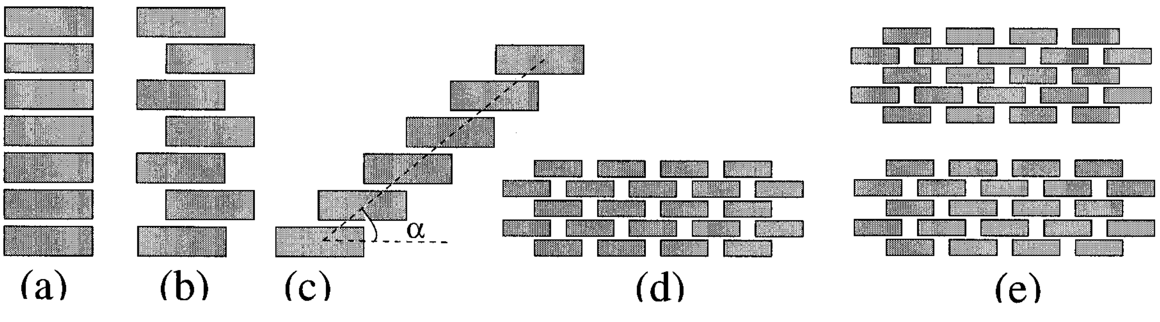

Figure 1. Schematic representations of chromonic columnar aggregates: H-aggregates (*a*) and (*b*), J-aggregates (*c*), brickwork structure (*d*) and layered brickwork (smectic) structure (*e*). The geometric arrangement of the chromonic molecules within the aggregate modifies their spectroscopic properties compared with those of the free monomeric state. The columnar aggregates can shift the absorption spectra towards longer or shorter wavelength depending on the slippage angle α. For less tilted stacks (high α), a blue shift towards shorter wavelength is observed and these are known as H-aggregates. J-aggregates, with larger tilts (low α) give a bathochromic shift (towards red) towards longer wavelength.

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Unlike the conventional amphiphilic system, the chromonic system does not have a critical micellar concentration (CMC). To avoid the unfavourable contact of the hydrophobic part of the molecules with the solvent, the molecules start to stack together forming columns even in very 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 as in conventional amphiphilic systems where micellar aggregates are formed. The micelle has an optimum size depending on the packing parameters which in turn depend on the ratio of the size of the head and tail groups [5]. The chromonic aggregation behaviour is termed 'isodesmic' and contrasts with the 'non-isodesmic' behaviour observed for conventional amphiphilic system. For isodesmic behaviour, the 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 behaviour of simple surfactant systems, where micelle formation is accompanied by a sharp free energy minimum. 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 study, we have developed idealized molecular models of LCLCs which represent the overall shape of the LCLC molecules and capture the nature of their interactions in an approximate way. To understand the self-assembly of chromonic molecules, we have carried out simulations of binary mixtures of LCLC molecules and water, and have studied the effect of concentration, temperature and molecular shape. We have also computed the free energy associated with the addition of each chromonic molecule to a columnar aggregate. The method enables us to test the widely accepted isodesmic behaviour of the chromonic aggregation.

The paper is organized as follows: in § 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 § 3. We describe the method of computation of free-energy by umbrella sampling in § 4. Finally, a summary of the main results, and the conclusions drawn from these, are given in § 5.

2. The model

We have modelled chromonic molecules in two ways: firstly as diamond shaped units (model 1) made up from nine touching spheres of diameter σ (figure 2). Secondly, as a variant of the model where the chromonic molecules are disk shaped units consisting of seven (model 2) touching spheres of diameter σ (figure 2). Model 2 is similar to the model considered by Edwards *et al.* [6] but with different kinds of interaction. In the case of model 1 the seven spheres forming the disc are hydrophobic and the two spheres at the ends are hydrophilic. In the case of model 2, the six outer spheres are hydrophilic and the central sphere is treated as hydrophobic. Water molecules are modelled as spheres.

The attractive interaction between like units (water–water, hydrophilic–water, and hydrophilic–hydrophilic) is modelled via a Lennard–Jones (LJ) potential:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

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

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

$$\begin{aligned} V(r) &= 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon \quad \text{where } r \leqslant r_c, \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{2}$$

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

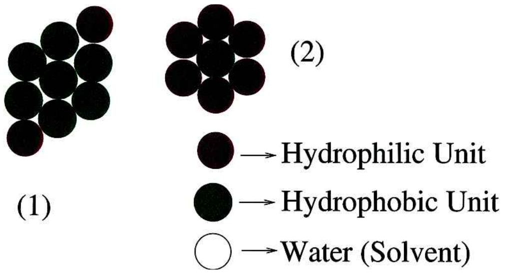


Figure 2. A schematic representation of model chromonic and water molecules. We have modelled chromonic molecules in two simple ways: (1) as a diamond pattern of seven touching hydrophobic spheres with hydrophilic spheres at each end; (2) as a disc of six hydrophilic spheres in contact with a central hydrophobic sphere. In both the cases the units are coplanar and all the spheres are of the same size.

For MC studies using a LJ potential, it is convenient to work in reduced units. In terms of σ and ε, some of the quantities of interest are density $\rho^* = \rho\sigma^3$, temperature $T^* = k_B T/\varepsilon$, and pressure $P^* = P\sigma^3/\varepsilon$. 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 chromonic molecules at different temperatures. The concentration is defined as

$$\phi = \frac{xN_c}{xN_c + N_w} \qquad (3)$$

where x is the number of spherical units constituting a single chromonic molecule, nine for model 1 and seven for model 2 and N_c and N_w are the number of chromonic and water molecules respectively.

3. 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 figures 3 and 4. At low concentration the chromonic molecules form short columns, and with increase in concentration the length and the number of 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 the water molecules to characterize the structure of the columnar aggregates. $g^{cc}(\mathbf{r})$ is the radial distribution function of the centre of mass of the chromonic molecules and is defined as

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

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

$$g_1^{cc}(\mathbf{r}) = \frac{1}{\rho N_c g^{cc}(\mathbf{r})}\left\langle \sum_{i\neq j} P_2(\mathbf{u}_i^{cc} \quad \mathbf{u}_j^{cc})\delta(\mathbf{r} - \mathbf{r}_{ij}^{cc})\right\rangle \qquad (5)$$

$$g_1^{cc}(\mathbf{r}) = \frac{1}{\rho N_c g^{cc}(\mathbf{r})}\left\langle \sum_{i\neq j} P_2(\mathbf{pu}_i^{cc} \quad \mathbf{pu}_j^{cc})\delta(\mathbf{r} - \mathbf{r}_{ij}^{cc})\right\rangle \qquad (6)$$

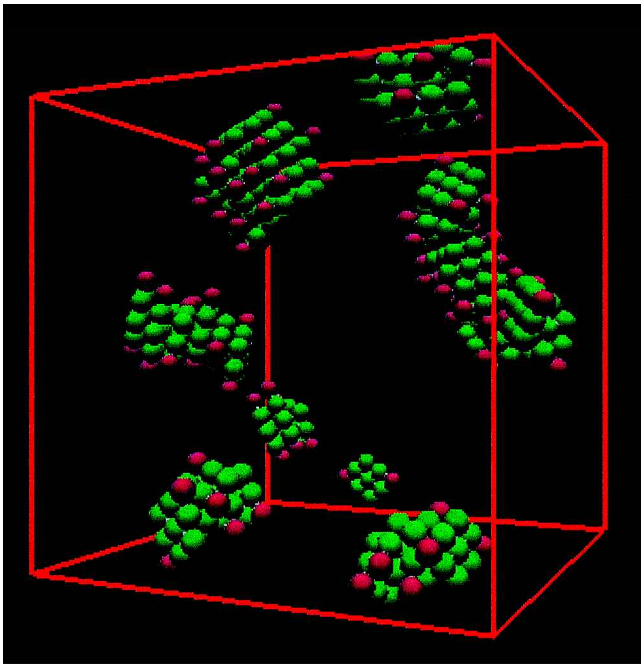


Figure 3. The beginning of chromonic aggregate formation (for model 1). Starting from an initial isotropic state, with isolated solute molecules, columnar aggregate formation occurs at relatively low concentrations. This figure shows the beginning of column formation for parameters: $\phi = 0.081$, $N_c = 50$, $N_W = 5100$, $T^* = 1.0$, $P^* = 1.0$, in reduced units. For clarity the water molecules are not shown.

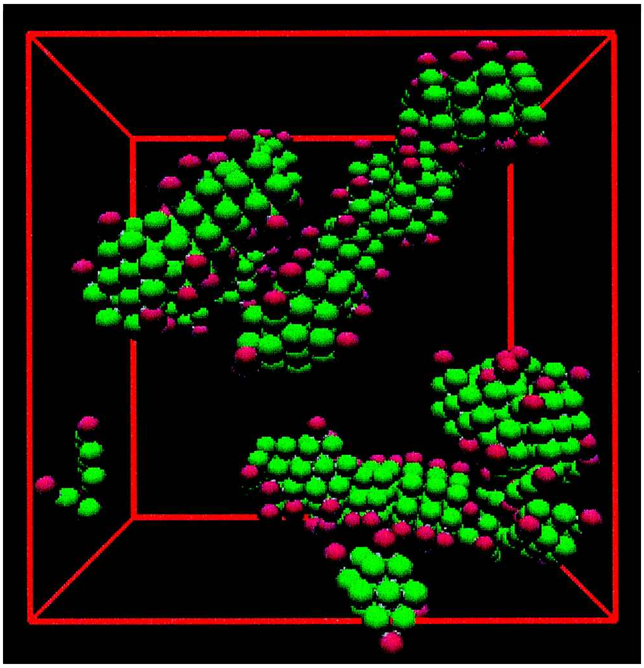


Figure 4. Chromonic aggregation at higher concentration (for model 1). Here the concentration of chromonic molecules has been raised to $\phi = 0.137$ ($N_c = 90$). All other parameters are the same as for figure 3. Note the decrease in the number of individual isolated solute molecules.

where $\mathbf{r}_{ij}^{cc}$ is the relative separation of the centre of the ith and jth chromonic molecules, $\mathbf{pu}_i^{cc}$ and $\mathbf{u}_i^{cc}$ are unit vectors lying parallel and perpendicular to the plane of the ith 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.

$$g^{cc}(r) = \frac{1}{4\pi}\int d\Omega g^{cc}(r, \Omega) \tag{7}$$

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

$$g^{cc}(r_{\parallel}, r_{\perp}) = \frac{1}{2\pi}\int_0^{2\pi} d\phi g^{cc}(r_{\parallel}, r_{\perp}, \phi). \tag{8}$$

Here, $r_{\parallel}$ and $r_{\perp}$ denote the components of $\mathbf{r}$ parallel and perpendicular to the orientation of the disc at the origin of the coordinate frame [see figure 10 (*a*)], i.e. $r_{\parallel} = \mathbf{r} \cdot \mathbf{u}^{cc}$ and $r_{\perp} = |\mathbf{r} - (\mathbf{r} \cdot \mathbf{u}^{cc})\mathbf{u}^{cc}|$, and ϕ is the azimuthal orientation of $\mathbf{r}$ about $\mathbf{u}^{cc}$. $g_1^{cc}(r)$, $g_2^{cc}(r)$ and $g_1^{cc}(r_{\parallel}, r_{\perp})$ are defined in an analogous way.

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

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

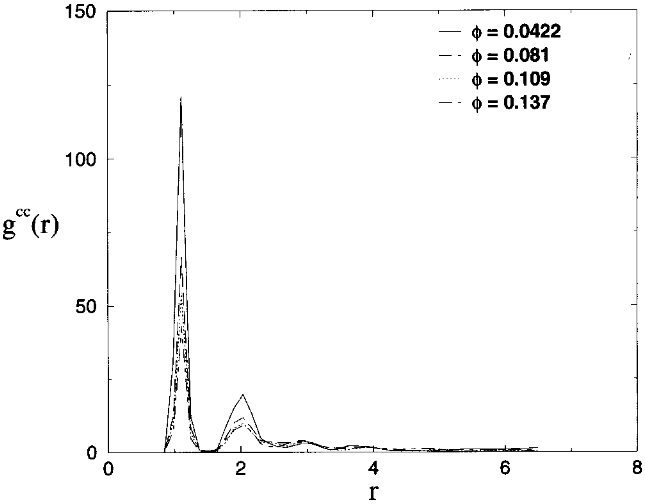


Figure 5. The pair correlation between the centres of mass of the chromonic molecules as a function of concentration ϕ. The separation r is given in units of the diameter σ of the modelling spheres.

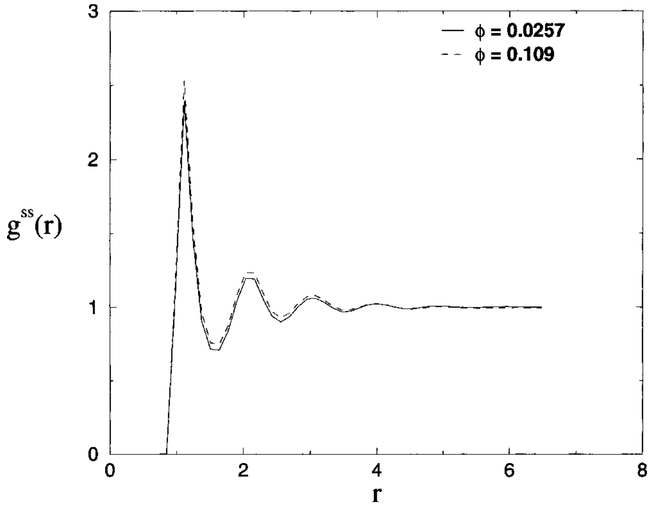
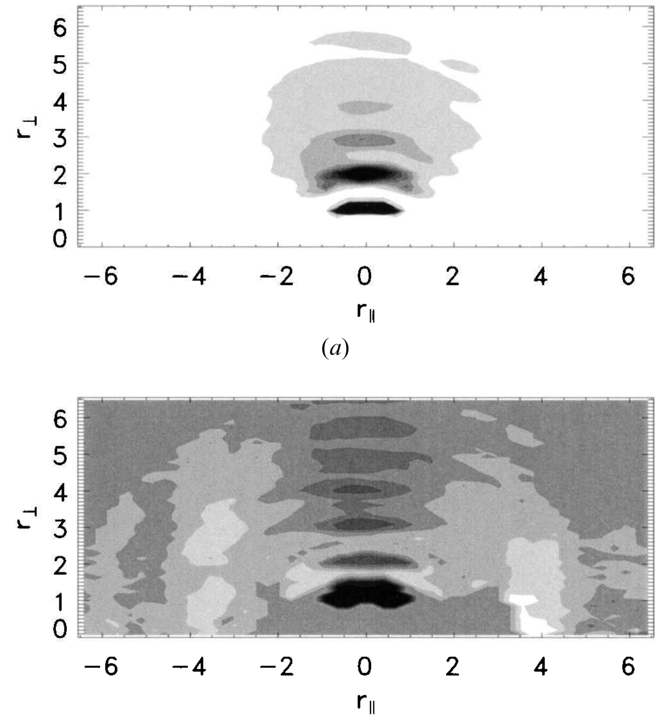


Figure 6. The pair correlation for water molecules for different concentrations of chromonic molecules. We see the liquid-like behaviour with short range positional order.

More detailed structural information for the chromonic aggregate emerges from the two-dimensional correlation function $g^{cc}(r_{\parallel}, r_{\perp})$ and $g_1^{cc}(r_{\parallel}, r_{\perp})$, shown in figure 7.



(*a*)

(*b*)

Figure 7. Two-dimensional correlation between the centre of mass of the chromonic molecules (*a*) $g^{cc}(r_{\parallel}, r_{\perp})$ and (*b*) $g_1^{cc}(r_{\parallel}, r_{\perp})$. 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. The parameters are same as in figure 4.

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 are organized as in figure 1 (*a*). Due to the close packing effect, the centre of mass of the chromonic molecules within the columns can be shifted with respect to one another by σ, which is reflected in the broadening of the peaks around $r_{\parallel} \pm 1.0$. Examination of $g_1^{cc}(r_{\parallel}, r_{\perp})$ reveals a strong intensity (~ 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 computed the average aggregation number, to study its dependence on concentration. We identify two chromonic molecules belonging to a cluster if the distance separating them is $\leqslant 2.5\sigma$. From the cluster size distribution we have calculated the average aggregation number through the equation:

$$\langle L \rangle = \sum s^2 N(s) / \sum sN(s) \qquad (9)$$

where $N(s)$ is the number of clusters of size s. In figure 8 we show (on a logarithmic scale) the average aggregate size $\langle L \rangle$ as a function of chromonic concentration. At low concentration $\langle L \rangle \sim \phi^{0.6}$. At higher concentration the dependence of $\langle L \rangle$ on ϕ is stronger than this power law. Similar behaviour is observed for conventional lyotropic systems [8, 9]. At higher concentrations, the enormous growth is not well understood. With increasing concentration, short columns aggregate to form chain-like aggregates (a kind of worm-like micelle). There is an indication that long chain-like aggregates tend to exhibit stronger excluded volume interactions compared with smaller aggregates [10]. This leads to stronger excluded volume interactions at higher concentration which enhance the growth of micelles.

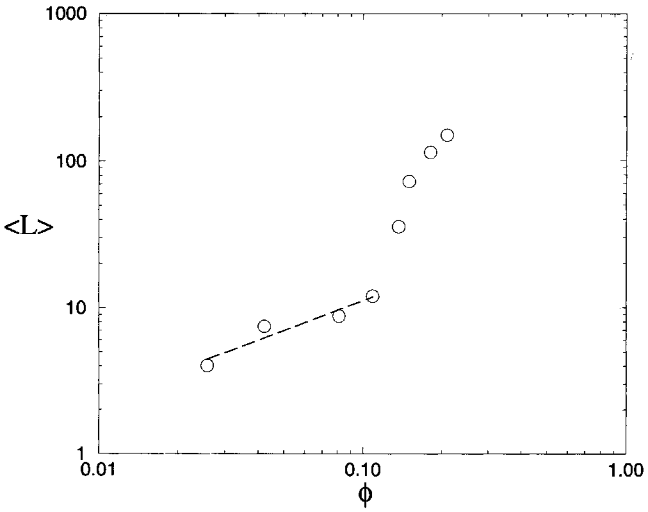


Figure 8. Average aggregation number $\langle L \rangle$ as a function of chromonic concentration ϕ.

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 the 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 does not exhibit the spontaneous formation of columnar aggregates (figure 9). This indicates that we need to make a judicious choice of the ratio of the number of hydrophilic and hydrophobic units; an overall hydrophobicity of the chromonic molecules being necessary for the spontaneous self-assembly.

4. 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 [11]. The distance r_c separating two chromonic molecules were confined (figure 10) by means of a harmonic potential of the form:

$$U(r) = \frac{1}{2} k (r - r_c)^2 \qquad (10)$$

where r_c is the equilibrium distance imposed between the centre of mass of two chromonic molecules. The equilibrium distances were varied from 1.1σ to 7σ in

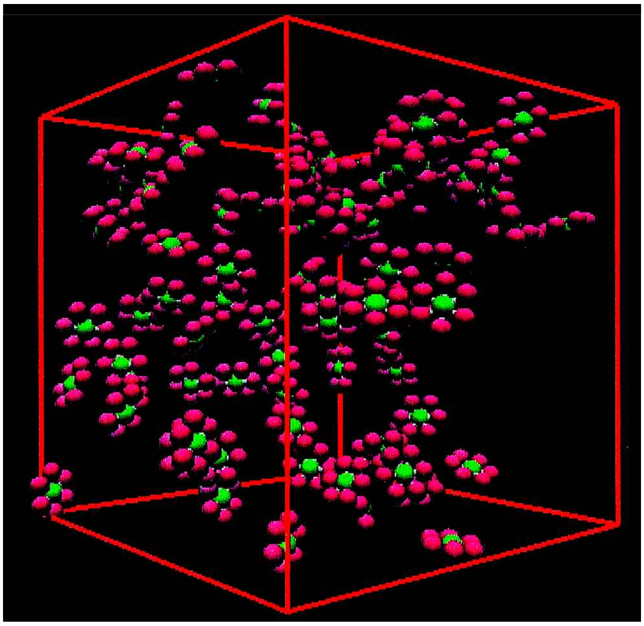


Figure 9. Simulation with model 2 does not give rise to columnar aggregates. The chromonic density is $\phi = 0.12$. Other parameters are the same as in figure 3.

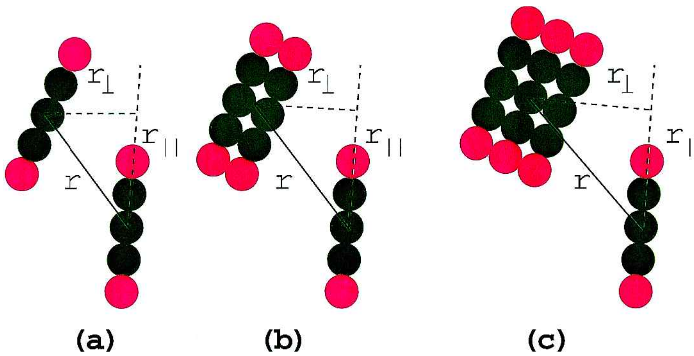


Figure 10. Three different cases for which the free energy has been computed: (*a*) column 2, (*b*) column 3 and (*c*) column 4.

steps of 0.1σ–0.2σ. Note that the equilibrium distance between two chromonic molecules cannot be less than σ. 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) [12, 13]. 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 simulations with higher values of the spring constant, $k = 2000$, and found qualitatively similar free energy behaviour. The probability distribution of the distance r separating two chromonic molecules is

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

for values of r for which $P(r)$ is exceedingly small. Here, δ 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, a problem arises because $P(r)$ 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

$$P'(r) = \frac{1}{Z'} \int \mathrm{d}\mathbf{r}^N \delta[r - r_c)] \exp\{-\beta[V(\mathbf{r}^N) + U(r)]\} = \frac{Z}{Z'} \exp[-\beta U(r)] P(r) \qquad (12)$$

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

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

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

$$F(r) = -k_B T \ln[P(r)]. \qquad (14)$$

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 as 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 unfavourable hydrophobic interaction with water molecules is reduced and this stacking results in a net increase in the volume available to the water molecule, thereby increasing their entropy. At intermediate separations, water molecules form solvation shells between the two chromonic molecules which results in a depletion repulsion between them thereby increasing the 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 $g_1^{cc}(r)$ and $g_2^{cc}(r)$ between the two chromonic molecules; these are shown in figure 12.

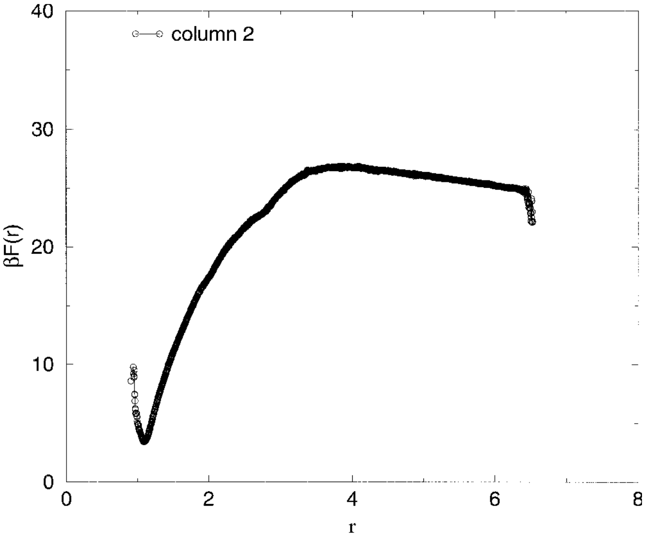


Figure 11. Free energy as a function of the distance separating the centre of mass of two chromonic molecules for the case in figure 10 (*a*).

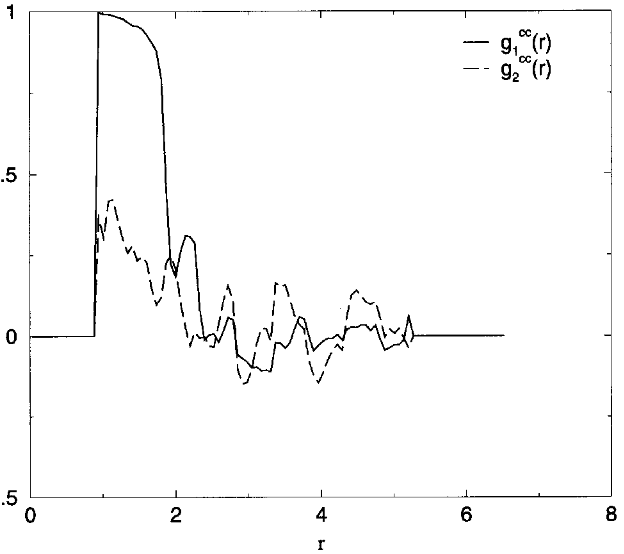


Figure 12. Orientational pair correlations between two chromonic molecules for the case in figure 10 (*a*).

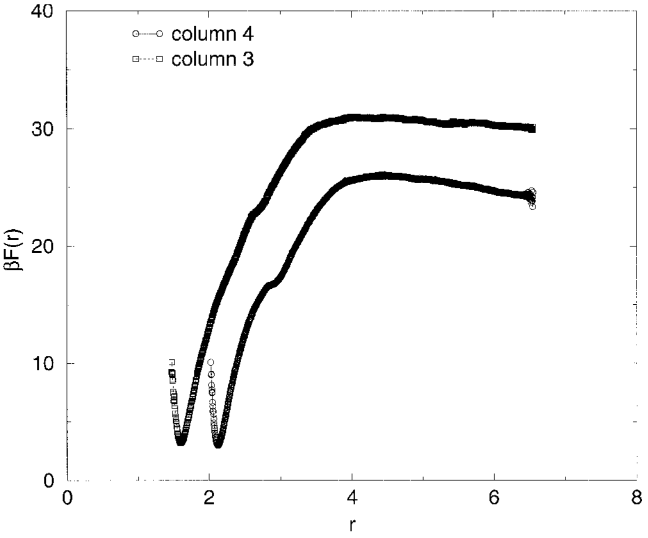


Figure 13. Free energy as a function of the distance separating the centre of mass of two chromonic molecules for the case shown in figures 10 (*b*) and (*c*).

From the $g_1^{cc}(r)$ 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 $g_2^{cc}(r)$. As the separation increases they start losing their orientational correlations.

Next we compute the free energy of association of chromonic molecules onto a columnar aggregate formed by two chromonics [referred to as column 3, figure 10 (*b*)] and three chromonic molecules [referred to as column 4, figure 10 (*c*)]. 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 11). The computed free energy is shown in figure 13.

The free energy curve has the same features as in the case of column 2 (figure 11). At large separation, chromonic molecules do not see each other and consequently the free energy reaches a plateau at larger values. At intermediate separation, the chromonic molecules start interacting with each other and start expelling the water molecules from the region between them so that they are able to aggregate on top of each other and this leaves more room for the water molecules. In this way water molecules gain entropy and chromonic molecules gain energetically (less contact with water molecules). This depletion effect eventually leads to single chromonic molecules settling on top of the existing columnar aggregates of length 2 or 3. Such a type of depletion attraction and repulsion has been found between macromolecules immersed in a fluid of much smaller particles [14–16]. As in the case of column 2, we have also computed the orientational pair correlation for columns 3 and 4 (see figure 14). In the case of column 3, the behaviour is similar to that of column 2. However for

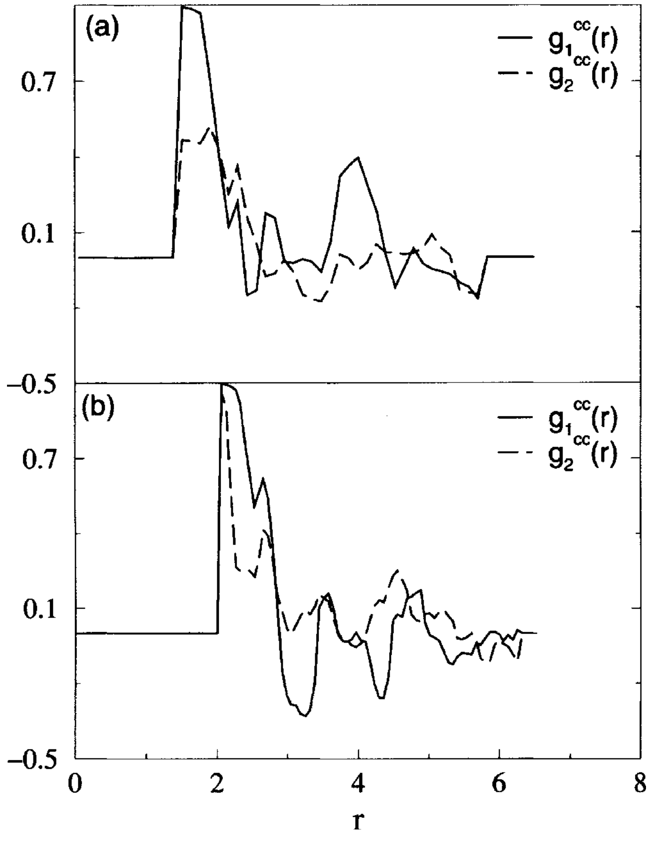


Figure 14. Orientational pair correlations between chromonic molecules (*a*) for the case shown in figure 10 (*b*), and (*b*) for the case shown in figure 10 (*c*).

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 docking on top of it.

5. Summary and conclusion

We have developed a class of idealized model for chromonic molecules. Simple site-interaction models represent a useful class of models for the study of the chromonic liquid crystalline self-assembly. For sufficiently high net hydrophobic molecular models the formation of columnar aggregates is observed. Our free energy computation for different lengths of columnar aggregates gives valuable insight. However, more work is required to test the isodesmic hypothesis. Future work will focus on improving configurational sampling (via rigid-body molecular dynamics) and on the development of more chemically realistic models of chromonic LCs.

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