Computer Simulation of Liquid Crystals

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Outline

Various kinds of liquid crystal:

- Thermotropic

- Lyotropic

- Phase behavior of a special kind of thermotropic liquid crystal (Banana molecules and mixture of banana and rods)

- Self-assembly in surfactant solution (Lyotropic system)

- Self-assembly in chromonic liquid crystal (a special class of lyotropic system)

- Interfacial surface tension in liquid-crystal system (surfactant layer in between water and oil interface)
What are liquid crystals?

- **isotropic**
- **nematic**
- **smectic A**
- **smectic C**

Phase changes as a function of temperature:

- Molecular orientational order (MOO)
- MOO + 1d positional order
- MOO + 1d positional order + tilt order
Symmetry breaking with bent-core molecule

Spontaneous chiral symmetry breaking with achiral molecules
Motivation

molecular structure  \rightarrow prediction  \rightarrow statistical mechanics

\leftarrow design  \leftarrow macroscopic properties
Hard-core spherocylinders

Phase transition driven only by entropic effects, at a given density:

$$\Delta S^{\text{trans}} > \Delta S^{\text{orient}}$$  $$\Delta S^{\text{trans} \perp} > \Delta S^{\text{orient} \parallel}$$
Achiral banana (bent-core) molecules exhibit spontaneous polar and chiral ordering

What is the minimal molecular model that captures polar and/or chiral symmetry breaking?

Are excluded volume interactions sufficient?

Very few materials exhibit both polar smectic and nematic phases

What is the degree of molecular bending compatible with a nematic ordering?

The overwhelming majority of banana materials have an antiferroelectric ground state

Is there some fundamental mechanism that favors antipolar ordering in banana phases?
A minimal model of rod/banana mixtures

We have studied mixtures of rod-shaped molecules (hard spherocylinders) and bow-shaped molecules (hard spherocylinder dimers) via Monte Carlo simulation.

This model enables us to investigate the role of excluded volume (entropic) effects in rod/banana mixtures.
Rigid body Monte Carlo

Sphere Cylinder Prolate ellipsoid disk spherocylinder

Each MC moves consists of translation and rotation of molecules. Rotation is performed through Quaternion.

Move is accepted with Boltzmann criteria if there is no overlap

Whole exercise is to devise efficient algorithm to do the overlap check
Quaternion dynamics

The quaternion are related to the Euler angles as follows:

\[ q_o = \cos \frac{\theta}{2} \cos(\phi + \psi)/2 \]
\[ q_1 = \sin \frac{\theta}{2} \cos(\phi + \psi)/2 \]
\[ q_2 = \sin \frac{\theta}{2} \sin(\phi + \psi)/2 \]
\[ q_3 = \cos \frac{\theta}{2} \sin(\phi + \psi)/2 \]

The quaternion satisfy the constraint

\[ q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1 \]

The Euler angle rotation matrix can be written as

\[
\begin{pmatrix}
q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1q_2 + q_0q_3) & 2(q_1q_3 - q_0q_2) \\
2(q_1q_2 - q_0q_3) & q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_2q_3 + q_0q_1) \\
2(q_1q_3 - q_0q_2) & 2(q_2q_3 - q_0q_1) & q_0^2 + q_1^2 - q_2^2 + q_3^2
\end{pmatrix}
\]
Overlap test for sphere

Two hard spheres of radius $R_1$ and $R_2$ overlap if the distance between the center of the two spheres $r_{12}$ is less than $\sigma_{12} = R_1 + R_2$

In simulation we do not compare $r_{12}$ with $\sigma_{12}$ but $r_{12}^2$ with $\sigma_{12}^2$. Later test is cheaper computationally.

In general above test can be decomposed into sequence of several smaller test. In this case the steps are

What happens if we have molecules composed of $n$ hard spheres : In this case the overlap between two molecules can be broken down into $n^2$ hard sphere tests

Overlap test for spherocylinders

Just as a sphere can be defined as the set of points that are within a distance $R$ from a given origin (center of sphere). The spherocylinder can be thought of as set of points that are within a distance $R$ from a line segment of length $L$. We can draw around every point on this line segment a sphere of radius $R$ that contains all points that are within a distance $R$ from that point.

So a spherocylinder can be considered as the union of all spheres around points on a line segment $L$. The test for the overlap between two spherocylinders can be done by computing the shortest distance between two line segments that form the core of the spherocylinders. If this distance of closest approach is less than $D_{12} = R_1 + R_2$, the two spherocylinders overlap.

Main task is to determine the distance of closest approach for the two line
We want to determine the minimum distance between two finite line segments $i$ and $j$ with orientations $\hat{u}_i$ and $\hat{u}_j$ and centers $r_i$ and $r_j$. We can describe any point on line $i$ parametrically as

$$r_i(\lambda) = r_i + \lambda \hat{u}_i$$

Line $j$ is given by

$$r_j(\mu) = r_j + \mu \hat{u}_j$$

The vector distance between these two points is given by

$$r_{ij}(\lambda, \mu) = (r_i - r_j) + \lambda \hat{u}_i - \mu \hat{u}_j$$

Now we want to determine the values of $\lambda$ and $\mu$ for which the distance $r_{ij}$ is minimum. A simple method to find these values of $\lambda$ and $\mu$ is the following. Construct the dot product of $r_{ij}$ with $\hat{u}_i$ and $\hat{u}_j$. The shortest distance vector must be perpendicular to both $\hat{u}_i$ and $\hat{u}_j$.

Our task is to solve the following equations

$$\begin{align*}
(r_i - r_j) \cdot \hat{u}_i &= -\lambda \hat{u}_i \cdot \hat{u}_j + \mu \hat{u}_j \cdot \hat{u}_i \\
(r_i - r_j) \cdot \hat{u}_j &= -\lambda \hat{u}_i \cdot \hat{u}_j + \mu \hat{u}_j \cdot \hat{u}_i
\end{align*}$$
Solving for $\lambda$ and $\mu$ we have

$$
\begin{bmatrix}
\lambda_0 \\
\mu_0
\end{bmatrix} = \frac{1}{1 - \left( \hat{u}_i \cdot \hat{u}_j \right)^2} \begin{bmatrix}
-u_i \cdot r_{ij} + \left( \hat{u}_i \cdot \hat{u}_j \right) \left( \hat{u}_j \cdot r_{ij} \right) \\
+ \hat{u}_j \cdot r_{ij} - \left( \hat{u}_i \cdot \hat{u}_j \right) \left( \hat{u}_i \cdot r_{ij} \right)
\end{bmatrix}
$$

If the spherocylinders are parallel

$$
r_{ij} \cdot \hat{u}_i = r_{ij} \cdot \hat{u}_j,
$$

$$
\lambda_0 = \frac{1}{1 - \left( \hat{u}_i \cdot \hat{u}_j \right)^2} \left( -u_i \cdot r_{ij} + \left( \hat{u}_i \cdot \hat{u}_j \right) \left( \hat{u}_j \cdot r_{ij} \right) \right)
$$

$$
= \frac{-u_i \cdot r_{ij} \left( 1 - \hat{u}_i \cdot \hat{u}_j \right)}{\left( 1 + \hat{u}_i \cdot \hat{u}_j \right) \left( 1 - \hat{u}_i \cdot \hat{u}_j \right)} = \frac{-u_i \cdot r_{ij}}{2}
$$

$$
\mu_0 = \frac{\hat{u}_j \cdot r_{ij}}{2}
$$
If the spherocylinders are perpendicular

\[ z_{ij} = \frac{L_i}{2} + \frac{L_j}{2} + D \]
The thermodynamic properties of the hard spherocylinder system depend on the length to breadth ratio $L / D$ and the reduced density $\rho^* = \rho v_0$, where $\rho$ is the molecular number density and $v_0$ is the spherocylinder volume.
Model

Hard spherocylinder dimers

Three-parameter model:

*length / breadth ratio*: $L / D$

*opening angle*: $\Psi$

*reduced density or pressure*: $\rho^* = \rho \nu_0$

or $P^* = \beta P \nu_0$

We study the phase diagram as a function of pressure and opening angle for $L / D = 5$

by NPT Monte Carlo simulation
Isotropic fluid (I)
Nematic (N)
Polar smectic A (SmAP)
Smectic A (SmA)
Columnar (Col)
Polar crystal (XP)
Crystal (X)

No chiral (tilted) smectic phase found.

PRE 67, 011703 (2003)
Final configurations for $\Psi = 90^\circ$

- **Isotropic**
  - $P^* = 1$

- **SmAP**
  - $P^* = 7$

- **Crystal**
  - $P^* = 15$
Final configurations for $\psi = 165^\circ$

<table>
<thead>
<tr>
<th>Phase</th>
<th>$P^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic</td>
<td>1</td>
</tr>
<tr>
<td>Nematic</td>
<td>5</td>
</tr>
<tr>
<td>SmAP</td>
<td>9</td>
</tr>
<tr>
<td>Crystal</td>
<td>15</td>
</tr>
</tbody>
</table>
Polar and nonpolar smectic A phases

$SmAP$ (in-layer polarity)  
$\Psi = 165^\circ$

$SmA$ (no polarity)  
$\Psi = 172.5^\circ$
Nature of the SmAP phase

Free energy calculation using umbrella sampling
\( \Psi = 120^\circ \) at \( P^* = 7.5 \) (middle of the SmAP phase)

Entropic effects stabilize the antipolar SmAP phase
Sawtooth Model

- **High entropy**
- **Low entropy**

\[ \beta F(\cos\Theta) / N \]

\[ \Theta (^\circ) \]

\[ 0 \quad 0.5 \quad 1 \]

\[ 0 \quad 0.05 \quad 0.1 \quad 0.15 \quad 0.2 \]

\[ \cos \Theta \]
Liquid Crystals are Exotic Solvents

- Nematics impose orientational order on non-spherical solutes
- Smectics impose one-dimensional positional order (as well as orientational order) on solutes
  - Enhancement of polymerization rate (C.A. Guymon et al., Science 275, 57 (1997))
- Smectic C solvents impose polar orientational order on low-symmetry solutes
  - Chiral solutes contribute to ferroelectric polarization

nanophase segregation in a smectic solvent

intralamellar segregation

interlamellar segregation
An orientational transition of bent-core molecules in an anisotropic matrix

Induced anticlinic ordering for $L_{\text{ban}} / D = 5$ and $c_{\text{ban}} = 3\%$

Anticlinic ($\text{SmC}_A$) ordering is induced for intermediate opening angles.

For small opening angles, the system exhibits SmA ordering, with half of each banana molecule intercalated between smectic layers.

PRL, 88, 065504 (2002)
Sergeants and Soldiers

- A low concentration of longer bow-shaped molecules can induce anticlinic ordering
Anticlinic ordering is observed for $100^\circ \leq \psi < 150^\circ$

The anticlinic tilt angle approximately shows the ‘ideal’ dependence $\theta = (\pi - \psi) / 2$ over this range.

Molecular tilt leads to a decrease in layer spacing over this range.
The entropic cost of a 30° tilt in the hard spherocylinder system is modest (~ 0.1 \( k_B T / \text{molecule} \))
Estimated transition point

free energy density:
\[ f = \frac{1}{2} K (\nabla \theta)^2 + \frac{1}{2} a \theta^2 \]
decay length:
\[ \xi = (K / a)^{1/2} \]
hard ellipsoids, dense nematic phase (B. Tjipto-Margo et al., JPC 96, 3942 (1992))
\[ K \sim 1 - 10 \frac{k_B T}{D} \]
hard spherocylinders, SmA phase (M. A. Glaser and N. A. Clark, unpublished)
\[ a \sim 0.1 \frac{k_B T}{D^3} \]
this gives
\[ \xi \sim 10 D \]
we expect a transition to the SmCA phase for \( \rho_{ban} \sim 1 / (d \xi^2) \), or
\[ c_{ban} \sim 0.01 \]
For large opening angles, banana molecules are segregated within smectic layers.

For small opening angles, banana molecules are segregated between smectic layers.

 Intralamellar-interlamellar transition for $L_{\text{ban}} / D = 2.5$ and $c_{\text{ban}} = 3\%$
Nanophase segregation in rod/banana mixtures

- Monte Carlo simulations of mixtures of hard spherocylinders and hard bananas (spherocylinder dimers)
- Excluded volume interactions can produce nanophase segregation of bow-shaped molecules
- In other words, nanophase segregation can be entropy-driven
Number density profiles for $L_{ban}/D = 2.5$

A transition from intralamellar to interlamellar nanophase segregation is observed near $\psi = 130^\circ$.
Intralamellar-interlamellar transition for \( L_{\text{ban}} / D = 2.5 \) and \( c_{\text{ban}} = 3\% \)

No anticlinic ordering is observed.

A sharp transition from intralamellar to interlamellar nanophase segregation occurs near \( \psi = 130^\circ \)
Orientational distributions of bananas for $L_{\text{ban}} / D = 2.5$

Molecular director:

$$\cos \theta = n \cdot z$$

Bow vector:

$$\cos \theta = m \cdot z$$

For small opening angles, most banana molecules are ‘half segregated’, with some molecules ‘fully segregated’
Self-assembly in surfactant oligomers
(Molecular Dynamics)
Simple model for surfactant oligomers to understand the relationship between molecular structure and the resulting mesophases for surfactant oligomers in solution.

The thermodynamics of self-assembly of chromonic liquid crystals.

Surface tension study of the Hexadecane benzene sulfonate

Coarse grained description for Hexadecane benzene sulfonate
Goal

• To gain a deeper understanding of the various parameters which cause different supramolecular aggregates to form.

• To design molecules with specific aggregate properties.

• Qualitatively study the phase behavior

• To compare our simulation results with available experimental results to validate our model

Ref:


Gemini surfactant: an example of surfactant oligomer

CTMABr

![Gemini surfactant structure](image)

Conventional single tail surfactant

Some of the advantage of gemini surfactants

- Micellization at low concentration (low CMC)
- Significant decrease in surface tension
- Best efficiency in the adsorption
- Lower value of craft point (better solubility)

Gemini has two head groups connected by a spacer of variable length

C16-s-16 2Br-\)
Solution of Amphiphiles

Concentration of surfactant below the critical micelle concentration.

http://www.pharmacy.umaryland.edu/faculty/ghollenb/pchem/colloids/colloids%20revised.ppt
Solution of Amphiphiles

Concentration of surfactant below the critical micelle concentration.
Solution of Amphiphiles

Concentration of surfactant below the critical micelle concentration.
Association Colloids

Concentration above the critical micelle concentration.
Phase diagram

JCP, 91, 2479 (1989)
Gemini surfactant: Our previous modeling efforts


Maiti et. al. EPL, 41, 183 (1998)
Gemini surfactant: Our previous modeling efforts

Cross-linked micelles

Model

Hydrophobic-water, hydrophilic-hydrophobic interactions: repulsive WCA potential:

\[ V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \varepsilon \quad \text{for} \quad r < r_c = 2^{1/6}\sigma \]

= 0 \quad \text{for} \quad r > r_c = 2^{1/6}\sigma

Water-water, hydrophilic-water, hydrophilic-hydrophilic interactions - attractive Lennard-Jones (LJ) potential:

\[ V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]
We have performed MD simulation with constant pressure (NPT) using Berendsen manostat with variable box shape. Temperature was kept constant using Berendsen thermostat (weak coupling to a external heat bath).

**Parameters:**

- Between N=25,000 and 35,000 particles with Nw water molecules and Ns surfactant molecules of length Ls
- Ls = 5 for single chain surfactant, 12 for dimeric surfactant, 19 for trimeric surfactant
- T* = 1.0, P* = 1.0, σ = 1, ε = 1.0, k = 30, r₀ = 1.2 σ
- 2-3x10⁵ MD steps for equilibration and another 10⁵ steps for production (velocity verlet algorithm with dt between 0.005-0.01)
- Surfactant mole fraction c = Ns/(Ns+Nw)
- Surfactant monomer fraction cs = NsLs/(NsLs+Nw)
Movie time: Micelle formation

Correspondence to real units:

3-4 CH2 groups making one tail bead
So $0.31 \text{nm} < \sigma < 0.37 \text{nm}$
$0.42 \text{kJ/mol} < \varepsilon < 3.5 \text{ kJ/mol}$

We use $\sigma = 0.34 \text{ nm}$
$\varepsilon = 2.5 \text{ kJ/mol}$

$M = 36 \text{ g/mol}$

$\delta t = (m \sigma^2 / \varepsilon)^{1/2} = 1.3 \text{ ps}$

$T = 300 \text{K}$
Equilibrium structure at different conc.:

Single chain surfactant

Dimeric surfactant

\[
c = 0.000208 \quad c = 0.002618 \quad c = 0.00497 \quad c = 0.00719
\]
Critical Micellar concentration (CMC)

Various ways to determine CMC in simulation:

- Plot Free surfactant mole fraction as a function of surfactant mole fraction \(c\) and fit it to a line of unit slope. The point at which slope changes corresponds to CMC.

- Monitor the change in physical property of micellar solution (like concentration of the solution) as a function of the surfactant mole fraction. Change in the slope corresponds to CMC.
Critical Micellar concentration (CMC)

Free surfactant mole fraction as a function of surfactant mole fraction $c$. The solid line of unit slope is the results for a solution of monomer only.

As the solvent molecules are replaced by long surfactant molecules, the volume increases to maintain the same pressure resulting decrease in density. Below CMC individual chain collapse onto itself. Above CMC inside cluster they are much more elongated. This leads to the change in slope of the density plot.

Total number density $\rho^*$ as a function of surfactant mole fraction.
Critical Micellar concentration (CMC)

Dimeric (Gemini) surfactant have remarkably low cmc’s compared with the corresponding monomeric surfactant of equivalent chain length. For trimeric surfactant it is even lower. These are in qualitative agreement with available expt. Data.
Critical Micellar concentration (CMC)

\( R_g \) of an individual surfactant increases as a function of surfactant concentration. As an increasing number of surfactants are incorporated in the micelles, they become elongated and the volume occupied by a surfactant is larger for higher aggregation numbers. So the volume excluded to a free monomer due to the presence of free surfactants is more than the volume excluded to a monomer by an aggregate formed by the surfactants. So larger aggregates are favored since they reduce the total excluded volume.
Micelle size and Shape

The shape tensor of the micelle

\[ G_{mn} = \frac{1}{S} \left[ \sum_i S \left( r_{mi} - R_m \right) \left( r_{ni} - R_n \right) \right], m, n = x, y, z \]

\( \sum_1 = \frac{S}{S} \left[ \sum_i \left( r_{mi} - R_m \right) \left( r_{ni} - R_n \right) \right] \]

S cluster size and R CM of the cluster

Ratio of the eigenvalues of G (g_1, g_2, g_3 in descending order) determine the shape of the micelles. And sum of them give \(<R_G^2>\).

\[ R_{gc} \sim s^{1/3}. \] This indicates almost Spherical shape in this conc. regime

For \( N_s < 75 \), \( g_1/g_2 \sim 1.1-2.0 \)

And \( g_2/g_3 \sim 1.1-1.3 \)
Micelle size and Shape

Average cluster size \( \langle L \rangle_W = \frac{\sum s^2 N(s)}{\sum sN(s)} \)

for \( c >> \text{cmc} \)

\( \alpha = 0.98 +/- 0.06 \) for single chain

\( \alpha = 1.27 +/- 0.22 \) for dimeric

\( \alpha = 1.39 +/- 0.19 \) for trimeric

Our growth exponent is very close to the prediction by Schurtenberger et. al. Langmuir, 12, 2894 (1996)

For dimeric and trimeric surfactants, the repulsive interactions between the head groups are screened due to the presence of spacer groups and the micelle size can grow faster compared to their single chain counterpart.
Sphere to cylinder Transition

As the concentration is increased due to the screening of repulsive head group interactions the surfactant now have a preference for local cylindrical packing.
Closed-Loop micelles

Formation of closed loop micelles in worm-like micellar system has been theoretically predicted and observed expt. In surfactant tetramer solution Zana et al. Langmuir, 16, 141 (2000)

Formation of closed-loop micelles require delicate balance between the volume of hydrophobic tail \(v\), length of hydrophobic tail \(l\) and the effective surface area per head group \(a\) to achieve desired packing parameter \(P = \frac{v}{la}\). Such fine tuning happens with surfactant oligomers

Our simulation gives first direct evidence of the formation of closed-loop micelles for both dimeric and trimeric surfactant at intermediate concentration

\[c = 0.027\quad c = 0.0345\]
Structure of micelles

Radial pair correlation function for the head groups for dimeric surfactant at two different conc.

C = 0.0026 (spherical micelles)
C = 0.011735 (cylindrical micelles)

- Closer packing of head groups in cylindrical micelles (larger 1st peak)
- In spherical micelles head groups are surrounded by water (appearance of second peak) apart from other heads.
**Diffusivity**

Diffusion constant $D$ is related to the mean-square displacement (MSD) by

$$D = \frac{\sum [r_i(t) - r_i(0)]^2}{6N \alpha t}$$

$R_i(t)$ and $r_i(0)$ are the CM of $i$-th chain at time $t$ and $t=0$ respectively

For dimeric and trimeric surfactant $D^*$ shows two distinct regimes:

- For low $c$ $D^*$ remains independent of $c$. Here micelles are spherical shape.
- After that $D^*$ decreases very fast following $c^{-\delta}$ with $\delta = 0.38$ for both dimeric and trimeric

This is in qualitative agreement with expt. Data Zana et. al. PRL, 81, 228 (1998)
Self-assembly in Lyotropic Chromonic systems
(Rigid body Monte Carlo)
Motivation

The thermodynamics of self-assembly of chromonic liquid crystals is poorly understood

- Chromonic LCs differ significantly from conventional aliphatic lyotropics.
- Hierarchical self-assembly
- Self-assembly of columnar aggregates is thought to be isodesmic (in contrast to conventional aliphatic lyotropics)

Dichoric thin films formed from chromonic LCs can be used both as alignment layers and polarizers for LC cells

Oleg Lavrentovich, LCI, Kent State University

Novel materials composed of plank- or disk-like molecules in organic solvents (lyomesophases, or organic lyotropics) exhibit similar hierarchical structures.
Various phases formed by chromonic

In contrast to the conventional amphiphilic molecules, chromonic molecules are:

- Plank-like rather than rod-like
- Rigid rather than flexible
- Aromatic rather than aliphatic

Schematic representations of the chromonic columnar aggregates, H-aggregates (a and b), J-aggregates (c), brickwork structure (d), and layered brickwork structure (smectic) (e).
They form isotropic (I), nematic (N) and columnar and hexagonal (M) phases

Some of the molecules forming chromonic phases

CI Direct Blue. This forms a chromonic N phase
Model building

(1) Chromonic – rigid molecules composed of hydrophobic and hydrophilic interaction sites

(2) Solvent – Lennard-Jones fluid

Hydrophobic-water, hydrophilic-hydrophobic interactions: repulsive WCA potential:

\[ V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \varepsilon \quad \text{for} \quad r < r_c = 2^{1/6}\sigma \]

= 0 \quad \text{for} \quad r > r_c = 2^{1/6}\sigma

Water-water, hydrophilic-hydrophilic interactions - attractive Lennard-Jones (LJ) potential:

\[ V_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]
NPT Monte Carlo (MC) simulations of chromonic/solvent mixtures with varying concentration of chromonic molecules

Each MC move consists of translation and rotation of chromonic solvent molecules. Rotation is performed through Quaternion.

Simulations carried out at $T^* = 1.0$, $P^* = 1.0$, in dense liquid phase of the LJ system

Free energy of association of small chromonic aggregates measured via umbrella sampling to test isodesmic assumption
columnar aggregate formation:

Beginning of chromonic columnar aggregate formation:
\[ \phi = 0.081, N_c = 50, N_w = 5100 \]

Chromonic columnar aggregate at higher concentration formation:
\[ \phi = 0.081 (N_c = 90) \]

At low conc. The chromonic molecules form short columns, and with increase in conc. The length and number of aggregates increases.
columnar aggregate formation:

To probe the formation of columnar aggregates we compute positional pair correlation function $g^{cc}$ between the CM of chromonic molecules.

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

First peak at $r = 1.12\sigma$ signifies strong positional correlation between chromonic molecules. Successive small peaks at $r = 2.2 \sigma$, $3.3 \sigma$, etc indicate they form columnar aggregates.
To probe the orientation of chromonic in columnar aggregates we compute orientational correlation function $g^{cc}$ and $g_1^{cc}$

$$g^{cc}(r||, r\perp) = \frac{1}{2\pi} \int_0^{2\pi} d\phi g^{cc}(r||, r\perp, \phi)$$

$$g_1^{cc}(r) = \frac{1}{\rho N_c g^{cc}(r)} \sum_{i \neq j} \sum P_2(u_i^{cc} \cdot u_j^{cc}) \delta(r - r_i^{cc} - r_j^{cc})$$

Peaks at $r\perp \sim 1.1, 2.2, 3.3$ indicate columnar aggregate. Strong intensity peak around $r|| \sim 1.0$ indicate parallel arrangement in the column.
Average aggregation number:

Average cluster size \( \langle L \rangle = \frac{\sum s^2 N(s)}{\sum s N(s)} \)

- At low concentration \( \langle L \rangle \sim \phi^{0.6} \)
- Higher concentration shows stronger dependence on \( \phi \)
- At high conc. Short columns aggregates to form chain like aggregates.
- Chain like aggregates tends to exhibit stronger excluded volume interactions leading to enhanced growth of micelles (PRB, 46, 6061 (1992))
columnar aggregate formation:

Simulation with eight columnar aggregates: at the end of simulation columnar aggregates go to isotropic $N_c=256$, $N_w=2304$

Initial str.          Final str.

Columnar aggregates with model (a) remain stable over simulation time
Umbrella sampling (Torrie and Valleau 1977)

Umbrella sampling attempts to overcome the sampling problem by modifying the potential function so that the unfavorable states are sampled sufficiently. The modification of the potential can be written as a perturbation and is given by

$$V(r^N) = V_0(r^N) + U(r^N)$$

$U(r^N)$ is the Umbrella potential and could be a function of some order parameter or reaction coordinate. Quite often it is taken to be Quadratic form

$$U(r) = \frac{1}{2}k(r - r_0)^2$$

For configuration that are far from the equilibrium state $r_0$ the Umbrella Potential will be large and so a simulation using the modified potential will be biased along some relevant reaction coordinate away
Umbrella Sampling

The probability distribution is given by

\[ P(r) = \frac{1}{Z} \int dr^N \delta[r - r_0] \exp[-\beta V(r^N)] \]

The probability distribution in the presence of Umbrella potential is given by

\[ P'(r) = \frac{1}{Z'} \int dr^N \delta[r - r_0] \exp[-\beta (V(r^N) + U(r))] \]

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

Thus the original distribution function \( P(r) \) can be obtained (to within a multiplicative constant)

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

The Helmholtz free energy

\[ F(r) = -k_BT \ln[P(r)] \]
Calculating potential of mean force of two chromonic liquid crystal in water
Free energy for larger column (3 and 4)

- Strong attraction at short distance leading face to face chromonic aggregation.
- Plateau at larger distance
- Increase in free energy at intermediate distance due to respective solvation shells interactions

By stacking on top of each other the unfavorable hydrophobic interactions with water molecules is reduced and this stacking results in a net increase in the volume available to the water molecules thereby increasing their entropy (depletion force).
Orientation within the column

- At the minimum separation ($r=1.1\sigma$) the two chromonic are parallel and stacked together (see g1).
- Their in-plane unit vector make an angle to each other as seen from g2.
- With increase in separation they loose their orientation correlations.
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