Two-stage assembly of patchy ellipses: From bent-core particles to liquid crystal analogs

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Plan of the Talk

- Introduction
- Proposed model for patchy colloidal analog of BCLCs
- Interaction potentials for patchy particles
- Exploration of patch parameters on bent-core yield
- State diagram with phase characterization
- Summary and conclusions

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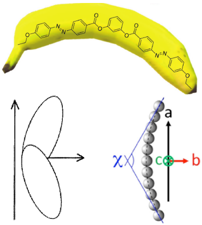
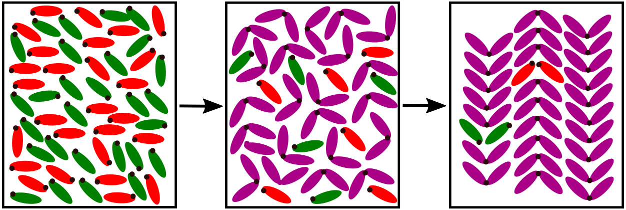
AK Singh et. al., J. Chem. Phys. **161**, 144903 (2024).

Introduction

- Bent-core liquid crystals (BCLCs): Chiral nematic, smectic, splay, and twist-bend phases despite the achiral nature of the BC constituents
- Constituting units of BCLCs:
    - BC molecules
    - Colloidal entities
- Colloidal bent-shape can be observed:
    - By merging two ellipsoids (or sphero-cylinders)
    - Creating bent strings of spherical particles



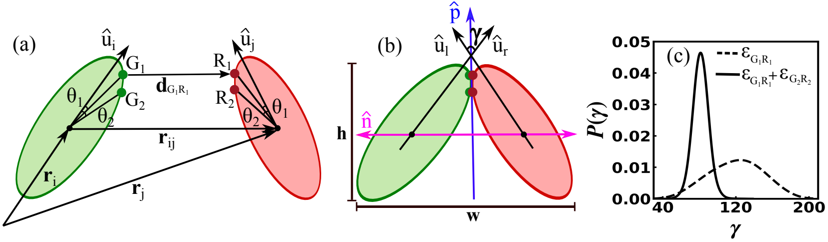
- What if the bent-core entities are themselves formed through the self-assembly of individual colloidal building blocks?



- Need to identify suitable model potentials that lead to the formation of BCs

Proposed model for patchy colloidal analog of BCLCs

- Two-component system (right- and left-handed) with 4 distinct patches



- Elliptic particles interact via "Gay-Berne" interactions
- Patches interact via "inverted Gaussian" interactions
- The only allowed patch-patch interaction is: R_1G_1 & R_2G_2 and others (R_1R_1, R_1R_2, R_1G_2, G_1G_1, G_1G_2, and G_1R_2) are zero
- Two components and *specific* interactions are essential for formation of BCs
- Four patches are adopted to control the flexibility of BCs

Interaction potential for patchy particles

$$V(\hat{u}_1, \hat{u}_2, \vec{r}_{12}) = V_{GB}(\hat{u}_1, \hat{u}_2, \vec{r}_{12}) + V_P(\vec{u}_1, \vec{u}_2, \vec{r}_1, \vec{r}_2)$$

$$V_{GB}(\hat{u}_1, \hat{u}_2, \vec{r}_{12}) = 4\epsilon(\hat{u}_1, \hat{u}_2, \hat{r}_{12}) \left[\left(\frac{\sigma_0}{r_{12} - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}_{12}) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r_{12} - \sigma(\hat{u}_1, \hat{u}_2, \hat{r}_{12}) + \sigma_0} \right)^{6} \right] \quad (1)$$

$$\epsilon(\hat{u}_1, \hat{u}_2) = \epsilon_0 \epsilon_1^{\mu} \epsilon_2^{\nu}$$

where

$$\epsilon_1 = 1 - \frac{\chi'}{2} \left\{ \frac{(\hat{r}_{12}.\hat{u}_1 + \hat{r}_{12}.\hat{u}_2)^2}{1 + \chi' \hat{u}_1.\hat{u}_2} + \frac{(\hat{r}_{12}.\hat{u}_1 - \hat{r}_{12}.\hat{u}_2)^2}{1 - \chi' \hat{u}_1.\hat{u}_2} \right\}, \epsilon_2 = \left[1 - \chi^2 (\hat{u}_1.\hat{u}_2)^2 \right]^{-\frac{1}{2}}$$

$$\sigma(\hat{u}_1, \hat{u}_2, \hat{r}_{12}) = \sigma_0 \left[1 - \frac{\chi}{2} \left\{ \frac{(\hat{r}_{12}.\hat{u}_1 + \hat{r}_{12}.\hat{u}_2)^2}{1 + \chi \hat{u}_1.\hat{u}_2} + \frac{(\hat{r}_{12}.\hat{u}_1 - \hat{r}_{12}.\hat{u}_2)^2}{1 - \chi \hat{u}_1.\hat{u}_2} \right\} \right]^{-\frac{1}{2}}$$

$$\chi = (\sigma_{\parallel}^2 - \sigma_{\perp}^2)/(\sigma_{\parallel}^2 + \sigma_{\perp}^2), \chi' = (k'^{1/\mu} - 1)/(k'^{1/\mu} + 1), k' = \epsilon_s/\epsilon_e$$

$$V_{\mathrm{P}}(d) = -\sum_{k \in P_i} \sum_{l \in P_j} \epsilon_{kl} \exp\left[-\frac{1}{2} \left(\frac{d_{kl}}{\alpha} \right)^2 \right] \quad (2)$$

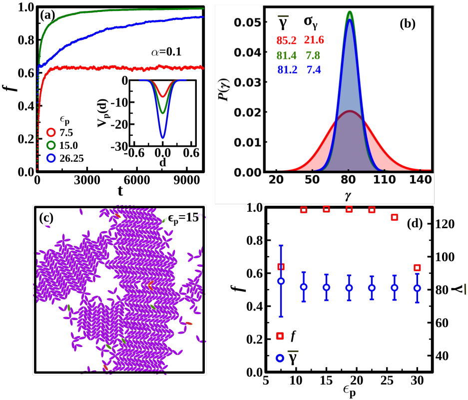
where ϵ_{kl} is patch-patch interaction strength and α is the interaction range.

Parameters for the formation of bent-cores

- **Gay-Berne:** $\sigma_{\|} = 3$, $\sigma_{\perp} = 1$, $\kappa' = 1$, $\mu = 1$ and $\nu = 3$
- **Patch:**
  - $\boldsymbol{\epsilon_p}$: interaction strength
  - $\boldsymbol{\alpha}$: interaction range
  - $\boldsymbol{\theta_1, \theta_2}$: positions
- Initialize the system with 50% right-handed, and 50% left-handed particles.
- MD simulations have been performed in NVT using LAMMPS
- ρ=0.4 and T=1.2 has been fixed for model parameter exploration
- We start with fixed patch positions θ_1=5 and $\theta_2 = 10$

Patch interaction strength ϵ_p

- How ϵ_p affect the BC formation?

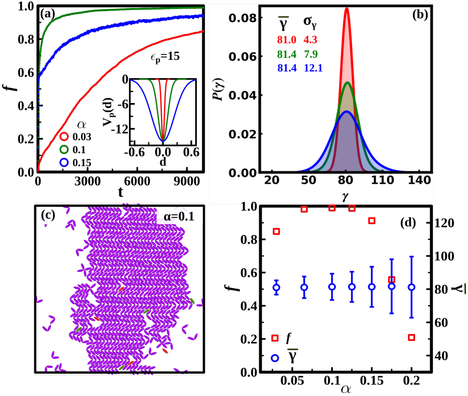


- Favorable observations
  - BC yield f
  - Average bent angle $\bar{\gamma}$ and flexibility
- $\boldsymbol{\epsilon_p = 7.5} \Rightarrow V_P < k_B T$
  - BC yield remains low
  - Bent-angle flexibility is larger
- $\boldsymbol{\epsilon_p = 15} \Rightarrow V_P > k_B T$
  - Keeping building-blocks bonded
  - BC yield close to unity
- $\boldsymbol{\epsilon_p = 30} \Rightarrow V_P >> k_B T$
  - Single bond becomes more stable
  - BC yield reduced via making asters

- For the range of ϵ_p, BC yield is closer to unity with negligible flexibility in γ

Patch interaction range α

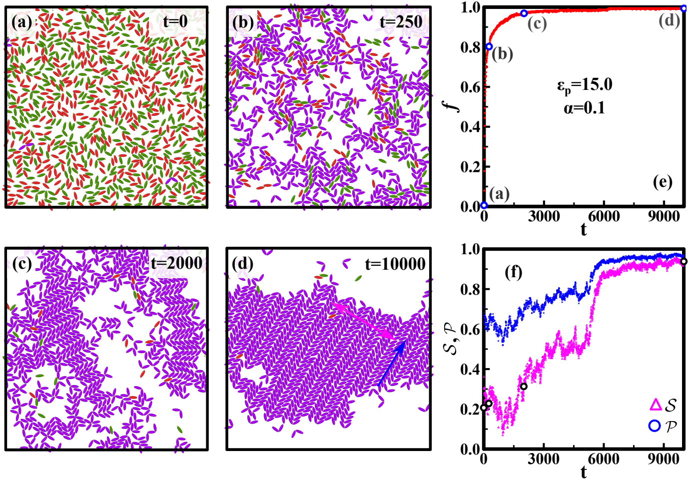
- How α affect the BC formation?



- Imparts the flexibility to the γ
- For $\alpha = 0.03$:
  - Probability of making bond reduces
  - Negatively affects the dynamics
- For $\alpha = 0.1$:
  - Probability of making bonds is high
  - Contribute to a larger BC yield
- For $\alpha = 0.15$:
  - Coexistence of BCs and asters
  - Larger fluctuations in bent-angle

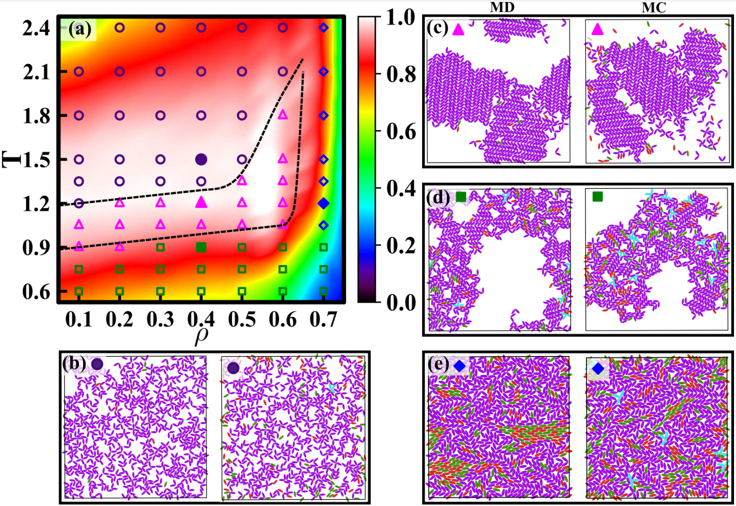
- For fixed θ_i, sizable region in (ϵ_p-α) parameter space for BC yield close to 1

Two-stage self-assembly for optimal parameters



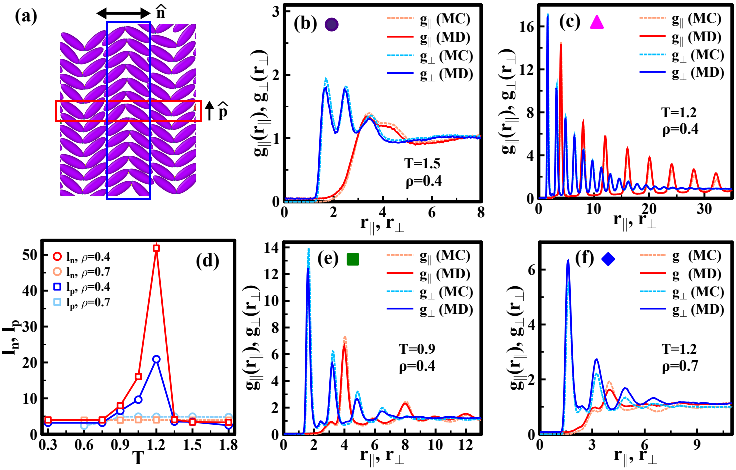
- For optimal parameters $\boldsymbol{\epsilon_p = 15, \alpha = 0.1}$
- Quenched from isotropic state $T = 2.0 \rightarrow T = 1.2$
- Opposite monomers form BCs: Due to attractive patches
- BCs arranged in liquid crystalline phases; Due to GB interactions
- Two-stage self-assembly observed in our model

State diagram



- Formation of BCs in isotropic sate: $U_{GB} < k_B T$
- Smectic antiferroelectric phase in large ordered domains
- Low temperature: Locally aligned region of BCs due to frozen clusters
- High density: Particles lack the free volume → dense disordered phase

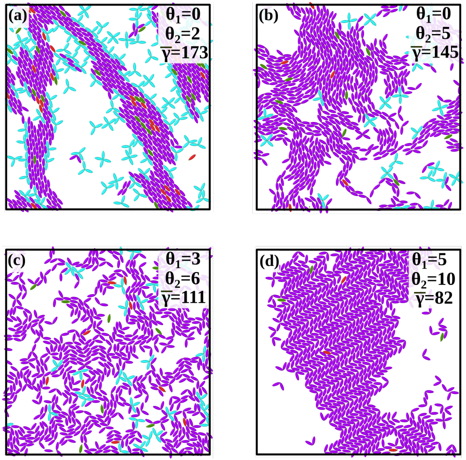
Pair correlation function



- T=1.5, PCF shows no order along nematic (n) and polar (p) order
- T=1.2, the PCF along n and p have long-ranged order [Sm-AF]
- T=0.9, the PCF along n and p have short-range order [AS1]
- High density (ρ=0.7), PCF also show short-range order [AS2]

How patch positions θ_i control phases?

- How θ_i affect the BC phases?



- Patch placements:
  - bent-angle γ
  - bent-core yield f
  - distinct phases and their textures
- (a) $\boldsymbol{\theta_1 = 0}$, $\boldsymbol{\theta_2 = 2}$
  - nematic phase
  - lower BC yield along with asters
- (b) $\boldsymbol{\theta_1 = 0}$, $\boldsymbol{\theta_2 = 5}$
  - texture in splay-bend phase
- (c) $\boldsymbol{\theta_1 = 3}$, $\boldsymbol{\theta_2 = 6}$
  - texture in splay-bend phase
- (d) $\boldsymbol{\theta_1 = 5}$, $\boldsymbol{\theta_2 = 10}$
  - texture in Sm-AF phase

- The interplay of α, θ_i can be expected to yield a range of γ and novel phases

Summary and conclusion

- For fixed θ_1, θ_2, α, the window of ϵ_p values for which the BC yield f is close to unity
- Similarly, with all other parameters fixed, we obtain high BC yields for a wide range of values of α
- For optimal choices of parameter, self-assembly occurs in two stages
- State diagram with isotropic and smectic antiferroelectric phases
- The variation of patch positions explored the various phases
- The extension of our work in 3D, could produce interesting liquid crystalline phases

Thank You

Characterization tools

- **Angle distribution**
- Bent-core angle: $\gamma = \cos^{-1}\left(\frac{\vec{u}_1 . \vec{u}_2}{|\vec{u}_1||\vec{u}_2|}\right)$
- $\vec{u}_1$ is the orientation of right-handed particle
- $\vec{u}_2$ is the orientation of left-handed particle
- **Pair correlation function (PCF):** For isotropic system

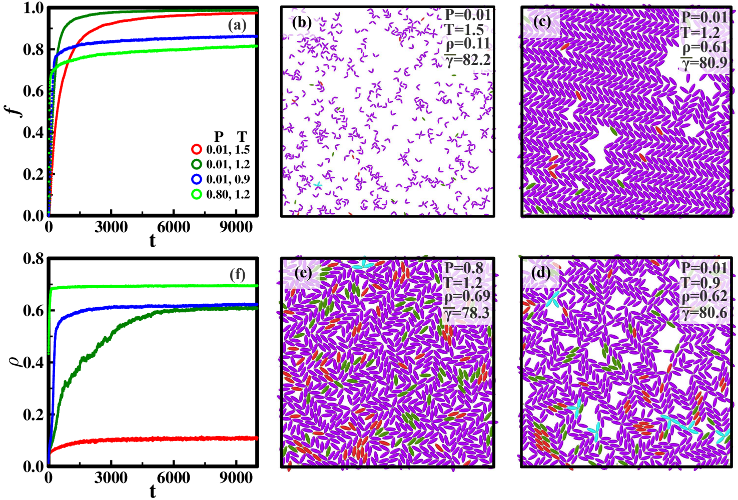
$$g(r) = \frac{\rho(r)}{\rho} = \frac{\langle n(r) \rangle}{(2\pi r \Delta r)\rho} = \frac{L^2}{N^2}\left\langle \sum_{\substack{i,j \\ i \neq j}}^{N} \frac{\delta(r - r_{ij})}{\pi[(r + \Delta r)^2 - r^2]} \right\rangle$$

- **Directed PCF:** For anisotropic system

$$g_{\parallel}(r_{\parallel}) = \frac{L^2}{N^2}\left\langle \sum_{\substack{i,j \\ i \neq j}}^{N} \frac{\delta(r_{\parallel} - r_{ij,\parallel})\theta(\sigma/2 - r_{ij,\perp})}{\sigma h} \right\rangle$$

- Separation along director: $r_{ij,\parallel} = |\vec{r_{ij}} . \hat{n}|$
- Separation perpendicular to director: $r_{ij,\perp} = |\vec{r_{ij}} - (\vec{r_{ij}} . \hat{n})\hat{n}|$
- $\hat{n}$ is local nematic order.
- Similar is applied for polar order.

Observed phases in NPT ensemble



- Similar morphologies are also observed in the NPT ensemble with pressure-tuned to achieve corresponding densities