Do DYES *KILL* Liquid Crystal Ordering?

NANO 604
Jon and Sahad

Introduction
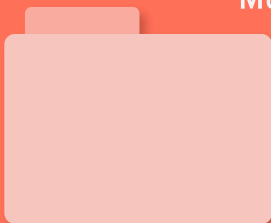
Initialization/
Particle Definition

Settings

Simulation/
Measurements

Conclusions

Presentation Outline

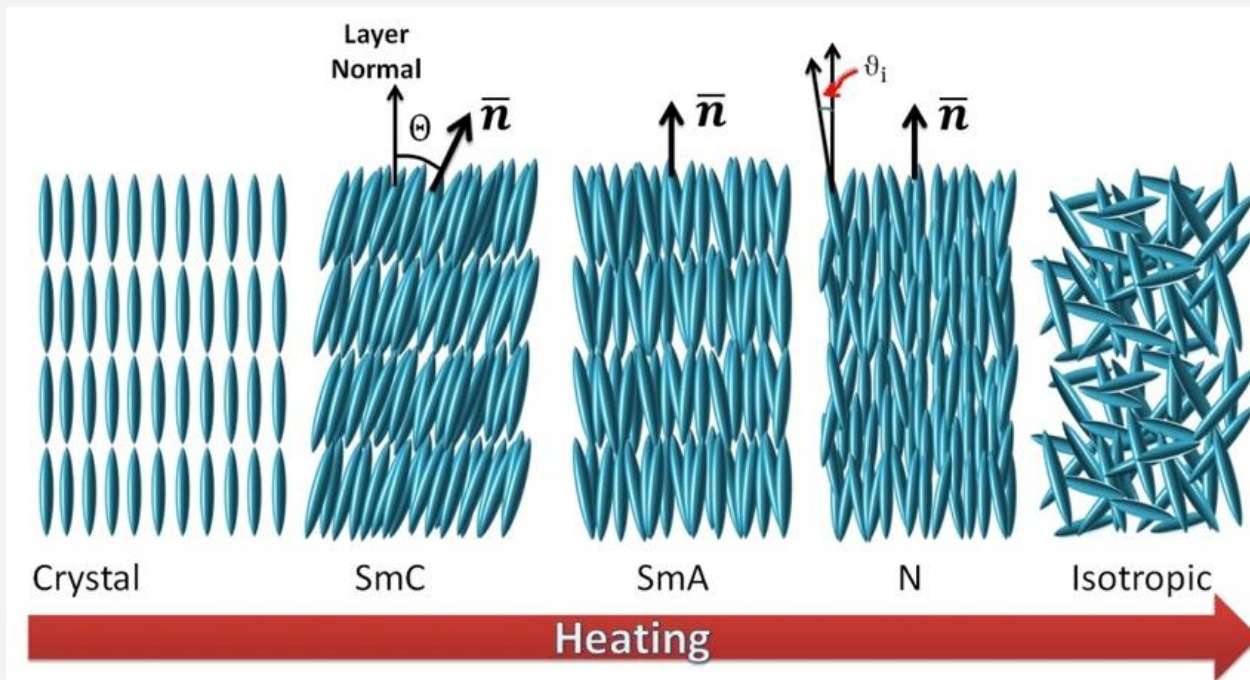Motivations, simulation rationale, results, and next steps

01.

Introduction

Background information and Motivations

Background – Liquid Crystal Phases

[1]

Background – Dichroic Dyes [2]

- Dichroic dyes only absorb light that is polarized parallel to one of their axes.

- This orientation-dependent absorption makes these dyes useful for applications such as liquid crystal displays [3].

- Dichroic dyes can also be used to measure the order of a liquid crystal.
  - The absorption of a dye dissolved in a liquid crystal gives information about the alignment of the dye molecules and thus of the liquid crystal in which it's dissolved.

Weak absorption

Strong absorption
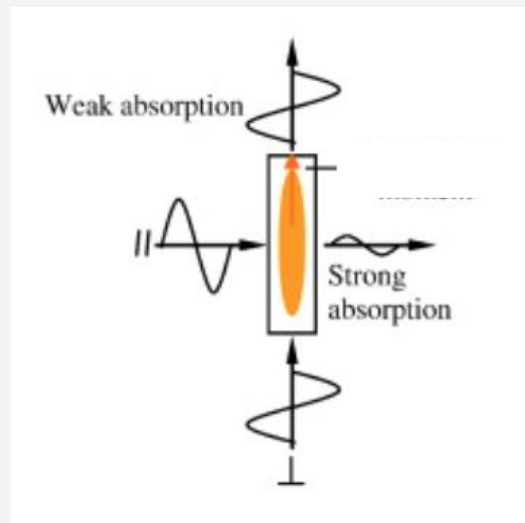
[4]

Simulation Goal

We know that dichroic dyes are used to measure the order parameter of a liquid crystal, but does the inclusion of dichroic dyes affect the order of the liquid crystal being measured?
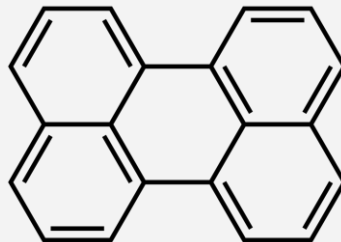
Objective: Investigate the effect of dichroic dyes on the order parameter of a liquid

Implementation: introducing small concentrations of perylene (main constituent of many dyes [3]) into the bulk phase of a common liquid crystal, 4-Cyano-4'-pentylbiphenyl (5CB). Perylene was chosen due to availability of force field parameters.

5CB
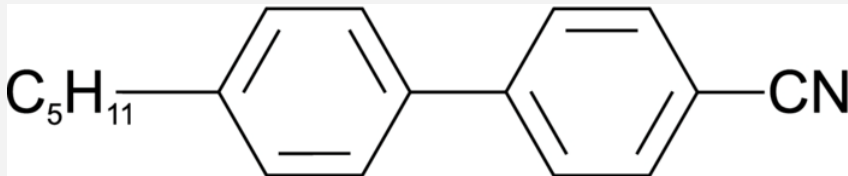
C_5H_{11} ——CN

Perylene

02.

Particle Definition & Initialization

What, Where, and How Many

Particle Models

5CB [5]
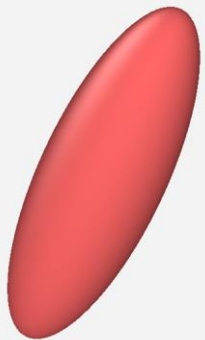
Prolate Ellipsoid

5 Å x 5 Å x 15.5 Å

Mass = 249.4 g/mol

Perylene [6, 7]
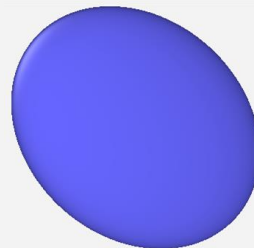
Oblate Ellipsoid

8.2 Å x 10.4 Å x 3.3 Å

Mass = 252.3 g/mol

LAMMPS: atom_style ellipsoid → stores shape, quaternion, and angular momentum
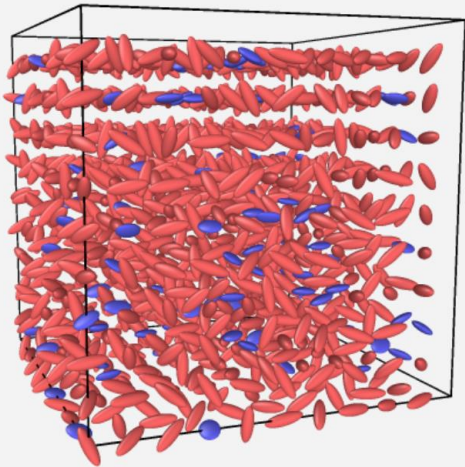
Initial Configuration

- <u>Real units</u> used to match parameters to those in literature

- Particles initially placed <u>15.5 Å apart</u> (largest ellipsoid diameter)
  - <u>Simple cubic</u> lattice so all particles are initially equidistant

- Box dimensions set to 10 x 10 x 10
  - <u>1000 particles</u>; reasonable compromise between sample size and simulation speed
  - Fractions of perylene: 0.001, 0.01, 0.025, 0.05, 0.075, and 0.1 (all tested with four random seeds)

- <u>Periodic boundary conditions</u> in all dimensions
  - We are simulating a segment of a bulk solution

- Initial temperature set to <u>298 K</u> (within 5CB's nematic range [8])
  - Initial distribution set to be <u>Gaussian</u>; closer to Maxwell-Boltzmann than a uniform distribution
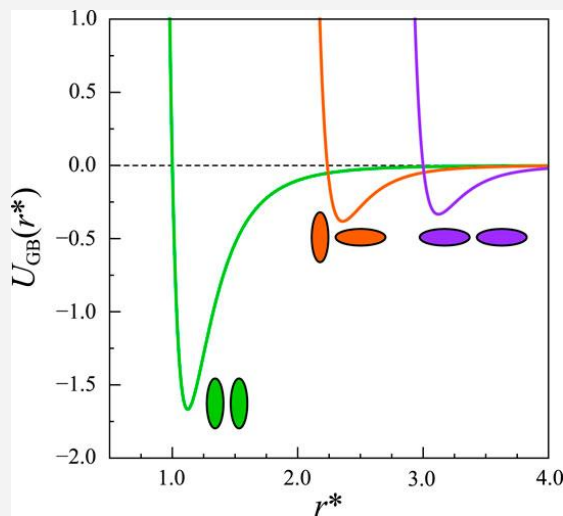
03.

Settings

Interaction Potentials and
LAMMPS Parameters

Gay-Berne (GB) Potential [9]

$$U(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}) = U_r(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}, \gamma) \cdot \eta_{12}(\mathbf{A}_1, \mathbf{A}_2, \upsilon) \cdot \chi_{12}(\mathbf{A}_1, \mathbf{A}_2, \mathbf{r}_{12}, \mu)$$

$$U_r = 4\epsilon(\varrho^{12} - \varrho^6) \quad \varrho = \frac{\sigma}{h_{12} + \gamma\sigma}$$


[10]

- Commonly <u>used to model ellipsoidal particles</u> in literature
- <u>pair_style parameters:</u>
  - gamma = shift for potential minimum (typically 1)
  - upsilon = exponent for eta orientation-dependent energy function
  - mu = exponent for chi orientation-dependent energy function
  - cutoff = global cutoff distance for interactions
- <u>We used the following:</u>
  - gamma, upsilon = 1 (from literature references) [5-7]
  - mu = 2 (from literature references) [5-7]
  - cutoff = 18 Å; smallest cutoff with negligible energy drift
  - Neighbor list built by binning with skin thickness = 2.6 Å

Gay-Berne (GB) Potential

[10]
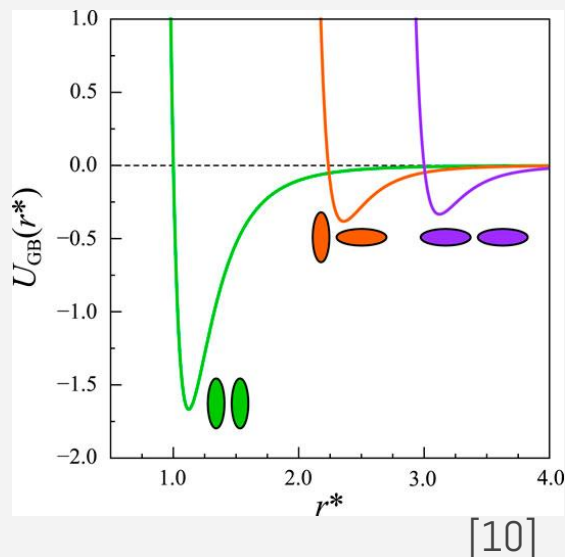
- <u>Pair coefficients</u> needed in LAMMPS:
  - ε = well depth (energy units)
  - σ = minimum effective particle radii (distance units)
  - $\varepsilon_{i,a}$ = relative well depth of type I for side-to-side interactions
  - $\varepsilon_{i,b}$ = relative well depth of type I for face-to-face interactions
  - $\varepsilon_{i,c}$ = relative well depth of type I for end-to-end interactions
  - $\varepsilon_{j,a}$ = relative well depth of type J for side-to-side interactions
  - $\varepsilon_{j,b}$ = relative well depth of type J for face-to-face interactions
  - $\varepsilon_{j,c}$ = relative well depth of type J for end-to-end interactions
  - cutoff (distance units); optional

5CB [5]

- ε = 3.6 kcal/mol; Increased to match perylene (originally 0.475 kcal/mol, but literature model included point charges)

- σ = 2.5 Å
- $\varepsilon_{i,a}$ = 1
- $\varepsilon_{i,b}$ = 1
- $\varepsilon_{i,c}$ = 0.2
- $\varepsilon_{j,a}$ = 1
- $\varepsilon_{j,b}$ = 1
- $\varepsilon_{j,c}$ = 0.2

Perylene [6,7]

- ε = 3.6 kcal/mol; doubled from literature value to encourage alignment over shorter runs

- σ = 1.65 Å
- $\varepsilon_{i,a}$ = 1
- $\varepsilon_{i,b}$ = 1
- $\varepsilon_{i,c}$ = 0.19
- $\varepsilon_{j,a}$ = 1
- $\varepsilon_{j,b}$ = 1
- $\varepsilon_{j,c}$ = 0.19

Mix [5-7]

- ε = 3.6 kcal/mol; in.ellipse.gayberne used highest value from the two species

- σ = 2.075
  - $(\sigma_{5CB} + \sigma_{perylene})/2$
- $\varepsilon_{i,a}$ = 1
- $\varepsilon_{i,b}$ = 1
- $\varepsilon_{i,c}$ = 0.2
- $\varepsilon_{j,a}$ = 1
- $\varepsilon_{j,b}$ = 1
- $\varepsilon_{j,c}$ = 0.19

Timestep and Integration Method

- <u>Timestep = 1 fs</u>
  - Allows us to run reasonably long simulations in a dense system
  - Simulation appears to be stable at this timstep (energy conservation will be discussed)

- Integration method: <u>Störmer-Verlet time integration algorithm (default)</u> [11]

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2$$

$$v(t + \Delta t) = v(t) + \frac{1}{2}(a(t) + a(t + \Delta t))\Delta t$$

Thermostats and Barostats

Our runs consisted of the following steps:

Description	Time (fs)	Code
Pressurization to achieve target density	12,500	fix 1 all npt/asphere temp 298 298 100 iso 21.57 150 1000 & mtk no pchain 0 tchain 1
Hold at final pressure to equilibrate	12,500	fix 1 all npt/asphere temp 298 298 100 iso 150 150 1000 & mtk no pchain 0 tchain 1
NVT run at 298 K to analyze order parameter	105,000	fix 1 all nvt/asphere temp 298 298 100
NVE run for error check	10,000	fix 1 all nve/asphere

The default <u>Nose-Hoover</u> thermostat and barostat were used.
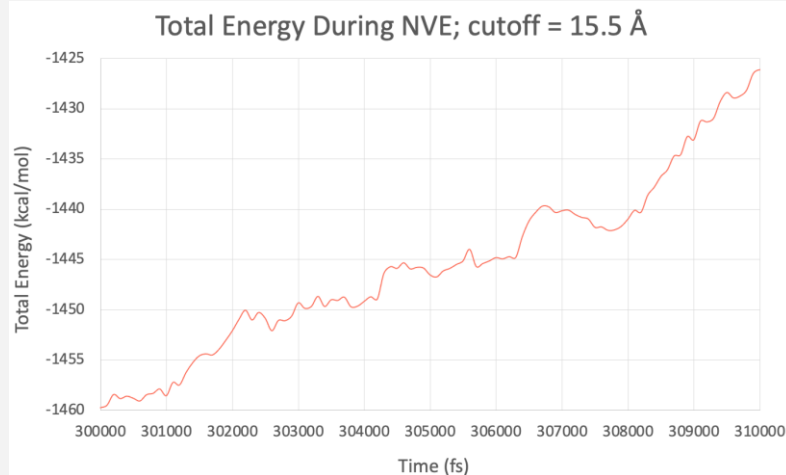
04.

Simulation/ Measurements

Error Checks, Steady-State, and Particle Alignment

Error Check

- As previously discussed, every run ended with 10,000 fs in NVE to confirm energy conservation.
  - Cutoff increased from 15.5 Å to 18 Å to avoid energy drift

Total Energy During NVE; cutoff = 15.5 Å

Total Energy During NVE; cutoff = 18 Å
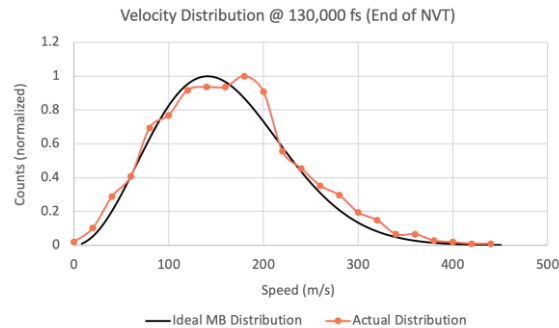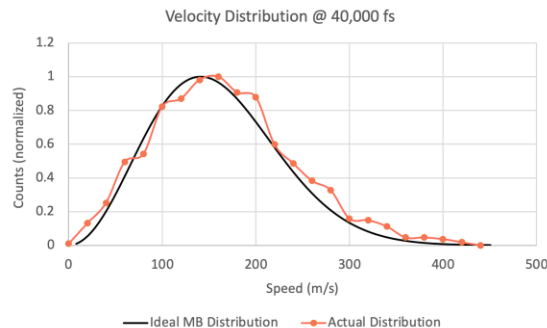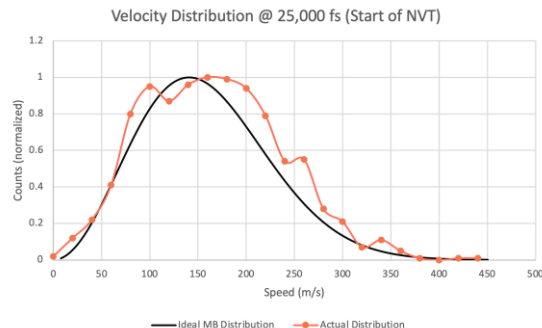(0.1% perylene)

Error Check

- As previously discussed, every run ended with 10,000 fs in NVE to confirm energy conservation.
  - Cutoff increased from 15.5 Å to 18 Å to avoid energy drift

Total Energy During NVE; cutoff = 15.5 Å

Total Energy During NVE; cutoff = 18 Å
(10% perylene)
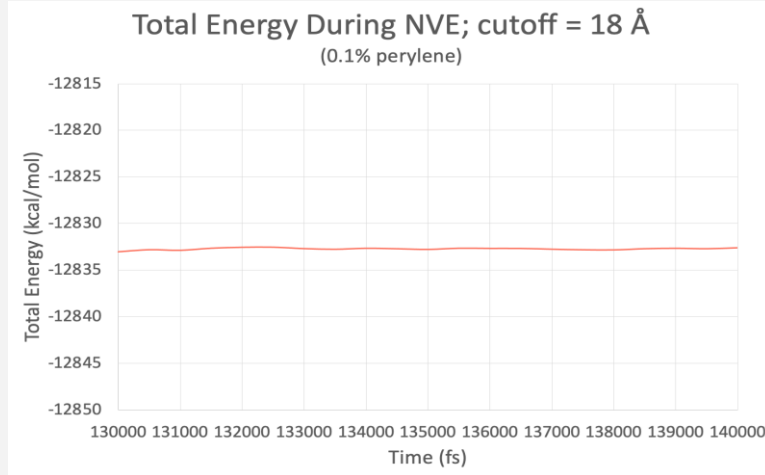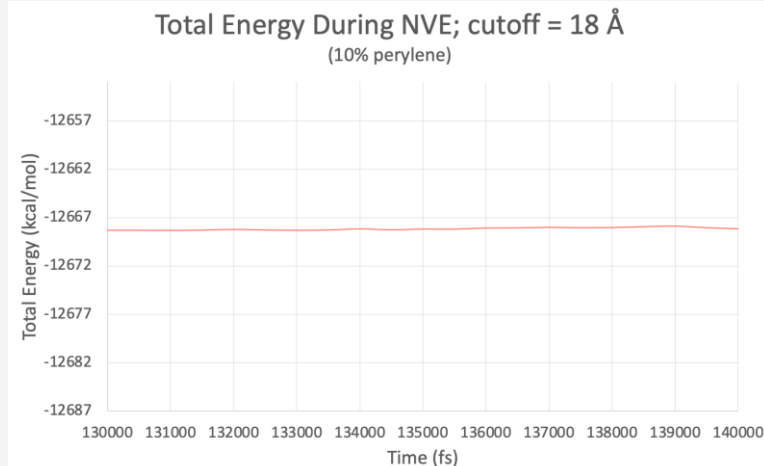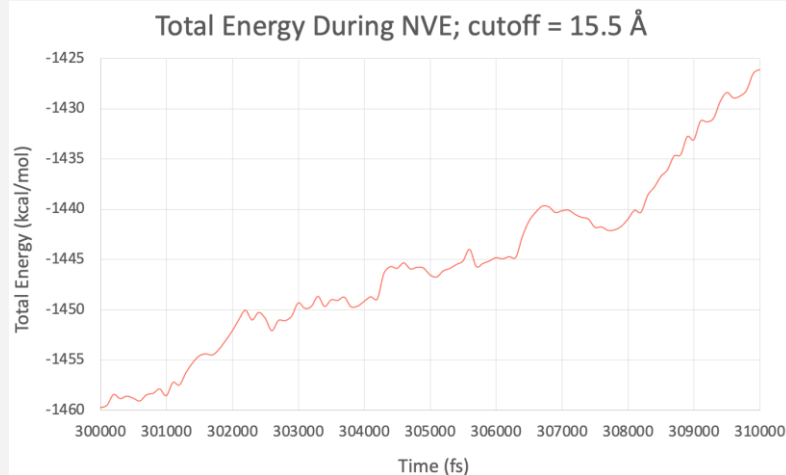
Steady State Check

- Stability confirmed by comparing velocity profiles to <u>Maxwell-Boltzmann (MB) distribution</u>

- Quite similar to MB at start of NVT stage (25,000 fs); others equilibrated soon after.

- <u>40,000 fs chosen as starting point for measurements</u> to ensure steady state.
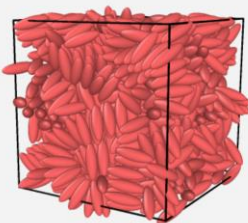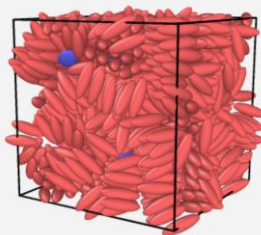
Particle Ordering

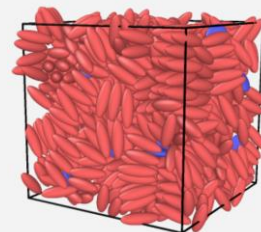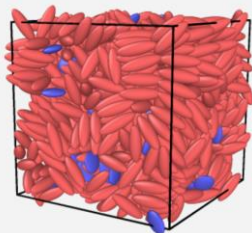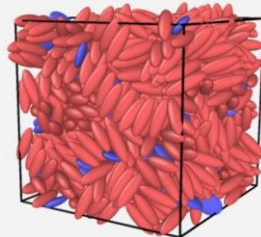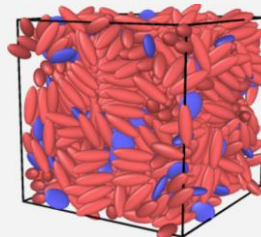<u>Screenshots from 40,000 fs</u> for various perylene concentrations:

0.1%
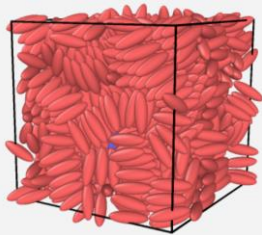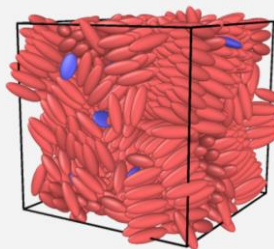
1%

2.5%

5%

7.5%

10%

Particle Ordering

Screenshots from 130,000 fs (end of NVT) for various perylene concentrations:

0.1%

1%

2.5%
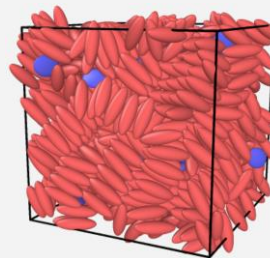
5%
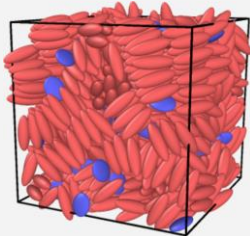
7.5%
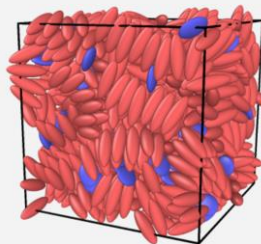
10%
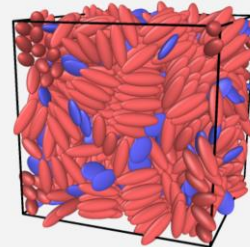
Measurements – Order Parameter

- We analyzed the ordering of the ellipsoidal particles using the **nematic order parameter** for the 5CB particles:

$$S = \left\langle P_2 \left(\cos \theta \right) \right\rangle = \left\langle \frac{3 \cos^2 \theta - 1}{2} \right\rangle$$

[12]

- θ = angle between long molecular axis and the director, which represents the direction of global order in the system
- 1 = all prolates facing one direction; -½ = completely ordered oblate ellipsoids
- Developed Python code for calculating S using particle simulation library [13]

Measurements – Order Parameter

- Highest ordering achieved at .025 perylene
    - Optimal π-π stacking at this fraction

- Beyond .025, π-π stacking inhibits global order

- Trend is maintained throughout simulation

- Expected overall downward trend (Resembles S versus Temperature plot of nematogen)

- Large standard deviation suggests absence of nematic phase (perhaps due to perylene's comparable dimensions)
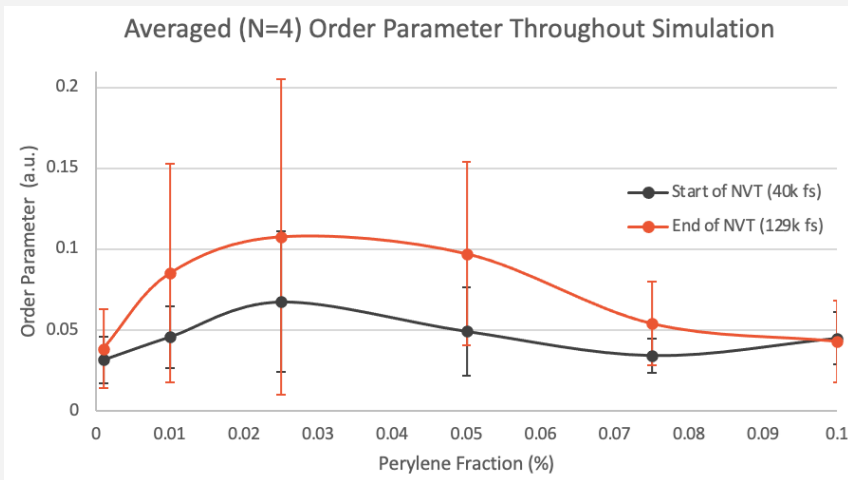
05.

Conclusions

Progress and Next Steps

Conclusions

- Examined if dichroic dyes adversely affect order parameter (S) of Liquid Crystals

- Developed a drift-minimized, steady-state simulation to measure order vs. dye fraction

- Simulation drift ≤ 1kCal/mol/10,000 fs; velocity profile matches Maxwell-Boltzmann distribution

- Small dye fractions increase order; larger fractions destroy ordering and the LC phase

  - Perhaps due to comparable dimensions between dye and LC

  - Overall order parameter trend did not reflect expected results

Potential Improvements

- Longer simulations
  - Increase timestep
  - Run for more timesteps

- Tweak potentials to observe nematic phase and decrease error bars

- More accurate model of 5CB (e.g., chain flexibility, incorporating point charges since polar)

- Optimize parameters to run at 1 atm (i.e., more realistic conditions)

- Incorporate models for other perylene-based dyes

- Attempt energy minimization during run

Thanks!

Do you have any questions?

References

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