Coarsening in Twist-Bend Nematics

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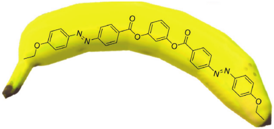
Outline

- Bent Core Liquid Crystals (BCLCs) and their Phases
- Coarsening experiments in BCLCs
- Numerical results
- Experimental implications



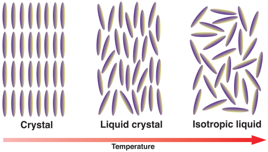
Nishant Birdi (IITD); Sanjay Puri (JNU)
Nigel B. Wilding (University of Bristol)

https://doi.org/10.48550/arXiv.2405.03189 [cond-mat.stat-mech]

Nematic Liquid Crystals

- Liquid crystals (LCs) are intermediate between conventional solids and liquids which combine fluidity with long-range orientational order.

  - In the nematic phase, *calamitic* (rod-shaped) or *discotic* molecules self-align to have directional order, but there is no positional order.



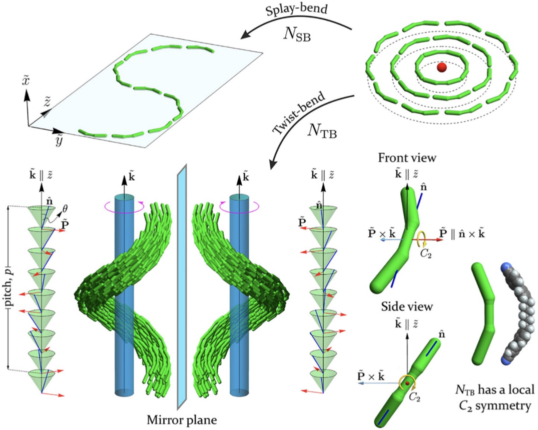
- The average orientation in LCs is described by the sign-invariant unit vector **n** known as the director.

- Fast optical response to tiny electric fields (1-2 V) is the reason for their exploitation in LCD, optical switches and optical imaging.

Modulated phases in BCLCs

- Nm phase becomes unstable due to formation of bend deformations in the **n** field.
- A constant bend field **B** cannot fill space uniformly.
- Geometrical frustrations resolved by formation of:
  (a) $3-d$ chiral *twist bend* structure,
  (b) $2-d$ structure with *splay* distortions.

Meyer (1976); Dozov (2001)

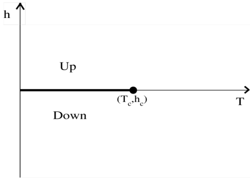


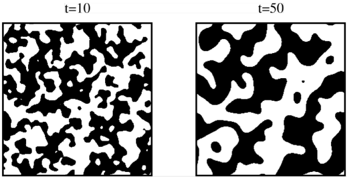
L. Longa and W. Tomczyk, J. Phys. Chem. C 124, 22761 (2020)

Phase ordering dynamics or coarsening

Consider rapid cooling of a magnet from $T > T_c$ to $T < T_c$ at $t = 0$:

This far-from-equilibrium system evolves via the formation of domains.



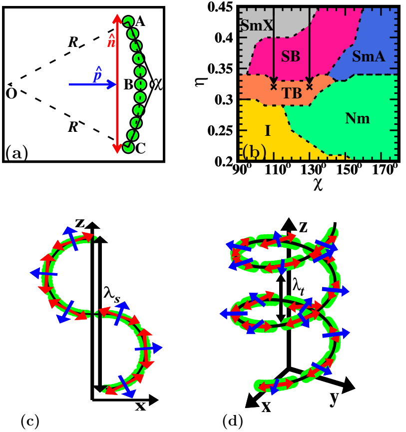


- Domain growth (coarsening) is driven by domain boundaries (defects).
- What is the domain growth law? What is the role of defects?
- Growth laws reveals important details of the free-energy landscape and the relaxation time-scales in the system.

Problems in this area arise from diverse fields, ranging from atmospheric physics to materials science, and metallurgy to astrophysics.

S. Puri & V. Wadhwan (eds.), Kinetics of Phase Transitions, CRC Press, 2009

MD simulations with curved spherocylinders:



(b) Adapted from P. Kubala, W. Tomczyk & M. Cieśla, J. Mol. Liq. 367, 120156 (2022)

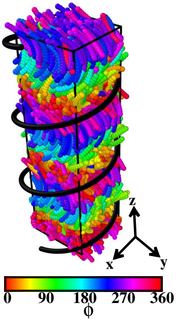
- BC unit: 11 beads; bend angle χ;
  Beads i, j (from distinct units) interact via Weeks-Chandler-Anderson potential:

$$E_{ij} = 4\epsilon \left\{ \left[\frac{\sigma}{r_{ij}}\right]^{12} - \left[\frac{\sigma}{r_{ij}}\right]^{6} \right\} + \epsilon;\; r_{ij} < 2^{1/6}\sigma$$

- In the TB phase:
  $\hat{\boldsymbol{n}} = [\cos(q_t z)\sin\theta, \sin(q_t z)\sin\theta, \cos\theta]$
  $\hat{\boldsymbol{p}} = [\sin(q_t z), -\cos(q_t z), 0]$
  $q_t = 2\pi/\lambda_t$; θ: conical angle between $\hat{\mathbf{n}}$ and $\hat{\mathbf{z}}$.
- In the SB phase:
  $\hat{\boldsymbol{n}} = [0, \sin(\theta' \sin(q_s z)), \cos(\theta' \sin(q_s z))]$
  $\hat{\boldsymbol{p}} = [0, -\cos(\theta' \sin(q_s z)), \sin(\theta' \sin(q_s z))]$
  $q_s = 2\pi/\lambda_s$; θ': maximum angle between $\hat{\mathbf{n}}$ and $\hat{\mathbf{z}}$ in the SB plane.

Equilibrated TB phase after SmX→ TB quench

- $\chi = 110^\circ$; $\eta = 0.32$,
- $N = 3200$; $t = 10^8$ MD steps
- Elongated box



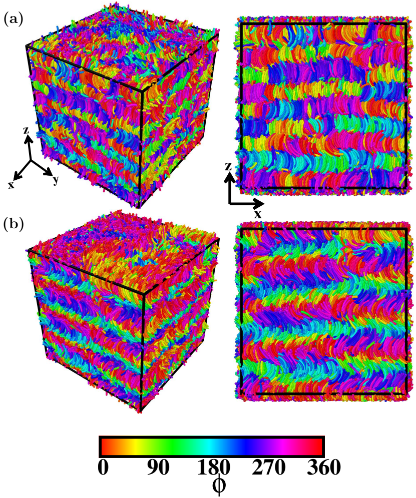
- ϕ: angle that the projection of $\hat{\boldsymbol{p}}$ on the *xy*-plane makes with the *x*-axis.

Order parameters

- Bend $\boldsymbol{B} = \hat{\boldsymbol{n}} \times (\nabla \times \hat{\boldsymbol{n}})$.
- Splay $\mathcal{S} = \hat{\boldsymbol{n}}(\nabla \cdot \hat{\boldsymbol{n}})$.
- Twist $\mathcal{T} = \hat{\boldsymbol{n}} \cdot (\nabla \times \hat{\boldsymbol{n}})$.
- In the TB phase: $\boldsymbol{B}, \mathcal{T} \neq 0$ and $\mathcal{S} = 0$. Continuously changing ϕ and corresponding colors will indicate development of helical order.
- In the SB phase: $\boldsymbol{B}, \mathcal{S} \neq 0$ and $\mathcal{T} = 0$. Alternating colors will indicate the S-shaped SB structures.

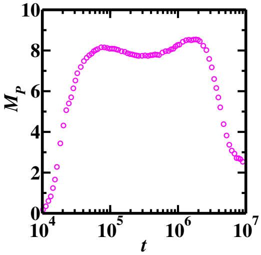
Non-equilibrium coarsening: SmX → TB

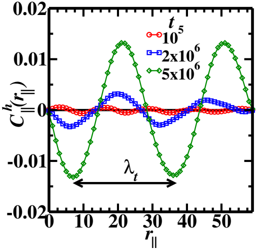
Evolution snapshots and *xy*-slices:



- $\chi = 110^\circ$, $\eta = 0.32$, $N = 9 \times 10^4$, $k_B T/\epsilon = 1.0$ and $L_s \simeq 117.443\sigma$.
- (a) $t = 2 \times 10^6$. The layers with alternating colors indicate S-shaped SB structures.
- (b) $t = 5 \times 10^6$. Continuously changing ϕ indicates development of helical order characteristic of the TB structure.
- Is there an intermediate SB phase enroute the TB phase?

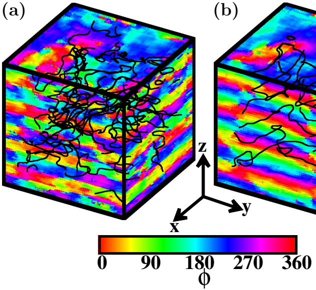
Characterization of SB and TB phase:

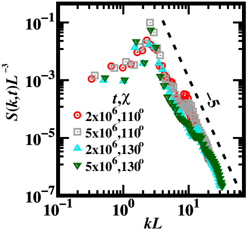




- Define an order parameter $M_P = \int |n_z(z) - \langle n_z(z)\rangle| dz$.
  It is positive in the SB phase and zero in the TB phase.
- Evaluation indicates that SmX-TB kinetic transformation traverses an intermediate SB state.
- Chirality or correlation along the helical axis:
  $C^h_\parallel(r_\parallel) = \sum_{i\neq j} c_{ij_\parallel} [(\hat{\boldsymbol{n}}_i \times \hat{\boldsymbol{n}}_j) \cdot \hat{\boldsymbol{r}}_{ij_\parallel}](\hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{n}}_j)$,
  where $c_{ij_\parallel} = \delta(r_{ij_\parallel} - r_\parallel)/\sum_{i\neq j} \delta(r_{ij_\parallel} - r_\parallel)$;
  $r_{ij_\parallel}$ is the separation between the i and j molecules along the helical axis.
- $C^h_\parallel$ confirms the helical order at late times.

Bend field morphologies and β lines:



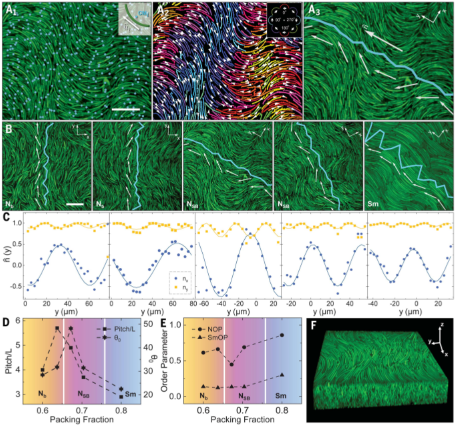


- Bend field $\boldsymbol{B} = \hat{\boldsymbol{n}} \times (\nabla \times \hat{\boldsymbol{n}})$ at $t =$ (a) 2×10^6, and (b) 5×10^6. β *lines* are defect regions where $\boldsymbol{B} \simeq 0$.

- With time, the helical ordering grows due to annihilation of β-lines. On the time-scales of our simulation, the beta lines do not exhibit marked anisotropy. They are reminiscent of vortex strings in 3-d liquid crystals or the XY model.

- Log-log plot of the scaled structure factor of $\boldsymbol{B}$-fields exhibits generalized Porod behaviour: $S(k,t) \sim k^{-5}$ at large k. (Experimental signature of the beta lines.)

Relevance with experiments



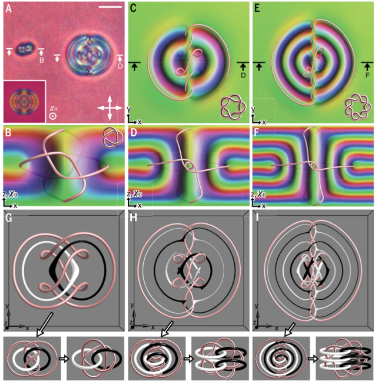
C. Fernandez-Rico, M. Chiappini, T. Yanagishima, H. de Sousa, D. G. A. L. Aarts, M. Dijkstra, and R. P. A. Dullens, Science 369, 950 (2020).

- Droplets of diluted aqueous dispersions of straight rods of SU-8 photoresist exhibited temperature driven buckling that resulted in BCs with controlled bent-core angle χ.

- A rich phase diagram in the $\chi - \eta$ plane was observed comprising of biaxial nematic, SB nematic, and polar and anti-polar smectic-like structures.

- Notably, simplistic rigid BCs used in our simulations seem to provide a good model for the buckled SU-8 photoresist rods.

Suggestions for future work:



J.-S. B. Tai and I. I. Smalyukh, Science 365, 1449 (2019)

- Of immense motivation is understanding the new class of topological defects in chiral LCs called *heliknotons*.
- They are energetically stable micrometer-sized knots of beta lines that are spatially localized but freely diffusing, and self-assemble into crystalline lattices.
- An important future step is to adapt our model to have flexible BC entities that can yield such topological defects and identify their signatures.