Recent Work on Biaxial Nematic in Thermotropics

- Our Focus: Detailed light scattering studies of fluctuations associated with biaxial ordering in the tetrapodes.

Materials

- Ge-3 ring tetrapode
- Ge-4 ring tetrapode

Schematic representation with biaxial ordering in the tetrapodes.

Approach

Light Scattering "Dark Uniaxial Geometry"

- In principle, cross-section for director (Ι) fluctuations vanishes. In practice, a small mosaic in Ί or slight optical misalignment will lead to "leakage" of the intrinsically strong director scattering.
- "Dark uniaxial" geometry offers best chance to see order parameter mode associated with biaxiality.

Summary

- Our light scattering study supports the existence of a biaxial nematic phase in liquid crystalline tetrapodes, and reveals weakly first-order isotropic-nematic phase transition, weakly first-order nematic-nematic phase transition in 4-ring tetrapode and second-order nematic-nematic phase transition in 3-ring tetrapode.

Data and Results

Data and Analysis of Time Correlation Function of Scattered Intensity

Ge-4 ring Tetrapode

- Faster mode detected in N_b phase is non-hydrodynamic (q-independent).
- Slower mode is hydrodynamic (I (I - q^2)) associated with leakage of Ί director fluctuations.

Ge-3 ring Tetrapode

- Blue lines: Representative data for intensity correlation functions taken in – Top Panel: Isotropic phase; Bottom Panel: Nematic phases.
- Red lines: Fits to single exponential decay (I and N_b phases) and double exponential decay (N_s phase).

Result of Temperature Scan at q = 17249 cm⁻¹

- Linear T dependence of Γ_0 and Γ_1 confirmed.
- T_1 slows down with T but does not vanish at the observed transition (T = T_m) in 4-ring and does vanish in 3-ring tetrapode.
- This indicates the N_s - N_b transition is first order in the 4-ring and second order in 3-ring tetrapode.
- S order parameter fluctuations are ~ 15 times slower in Ge-3 ring than in Ge-4 ring.
- P order parameter fluctuations are ~ 30 times slower in Ge-3 ring than in Ge-4 ring.
- Director fluctuations are ~ 100 times slower in Ge-3 ring than in Ge-4 ring.
- Interpretation: Orientational motion of mesogens is more hindered in the tetrapode with smaller mesogenic cores.

Landau-deGennes Theory

- Order Parameter Invariants:
  \[ A_0 = (35/3)^2 + P^2/2, \quad A_1 = -3P^2/2 - P^4/4 \]

- Free Energy:
  \[ F = 2A_2 + b_2A_4 + c_4A_6 + d_6A_8 + e_8A_{10} + \cdots \]
  \[ = \beta S^2 + \gamma (S'^2) + \delta (S'^2)^2 + \epsilon (I^2) + \zeta (I^2)^2 + \cdots \]

- Results for Relaxation Rates:
  \[ \Gamma_0 = 3a_0 (T - T_m) + 2b_0, \quad \Gamma_1 = 2a_0 (T - T_m) + 2b_0 (T - T_m) \]

- Intensity of Biaxial Director (Ι) Fluctuations (N_s phase):
  \[ I_0 = (3a_0)^2 + P^2 + P^4 (T - T_m) \]

References

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