New Phases in Biaxial liquid crystal polymers

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Outline

- Introduction, experimental motivation, challenges
- Biaxial model
- Steady State symmetries
- Smoluchowski equation, spectral approximation
- Numerical issues: Mesh refinement, time-stepping
- Numerical results
- Conclusions, future work

Introduction: Biaxial Liquid Crystals

Industry: Different time-scales

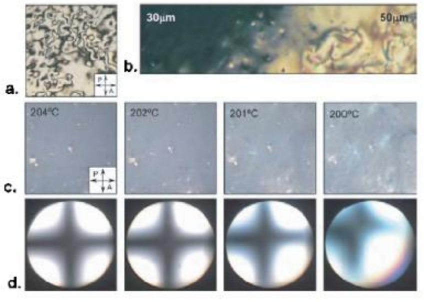
- Display Technologies
- Ultra-fast biaxial switches

Science:

- Rich variety of phases
- Complex intermediate symmetries

"Holy Grail of liquid-crystal science has been found": Nature, **430**, (2004)

Experimental Evidence



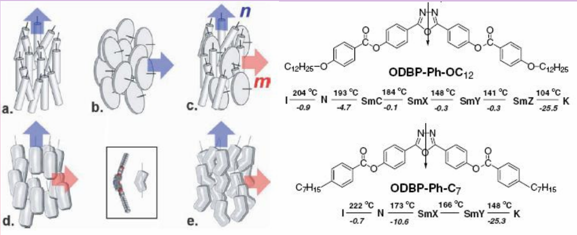
Biaxial nematic sample:

Phys. Rev. Lett. **92**, 145505 (2004)

Phys. Rev. Lett. **92**, 145506 (2004)

- Temperature variation
- NMR spectroscopy

Molecular structures showing phase biaxiality



Goals/Challenges

Goals:

- Develop hydrodynamic theory for biaxial liquid crystals
- Study mesoscale phase/structure with external shear flow

Challenges:

- Degrees of freedom : 6 Independent parameters
- Non-linearity of the solutions
- Multiple solutions: Dynamical solutions sensitive to initial conditions

Model: Excluded Volume Potential

(Sircar and Wang: 2008)

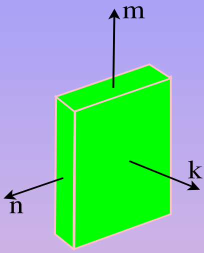
- $V = -\frac{3N}{2}[\xi_0 \mathbf{q}' \cdot \mathbf{M} + \gamma_0(\mathbf{q}' \cdot \mathbf{N} + \mathbf{b}' \cdot \mathbf{M}) + \lambda_0 \mathbf{b}' \cdot \mathbf{N}]$

  $q' = \mathbf{m} \otimes \mathbf{m} \qquad \mathbf{M} =< q' >$

  $b' = \mathbf{n} \otimes \mathbf{n} \qquad \mathbf{N} =< b' >$

  $\xi_0 = 1 + 2\gamma + \lambda, \quad \gamma_0 = 2(\gamma + \lambda), \quad \lambda_0 = 4\lambda$

  N: Dimensionless LCP concentration



(Straley: 1974, Virga: 2003,04,06,07)

- $V = -\beta(\xi \mathbf{q} \cdot \mathbf{Q} + \gamma(\mathbf{q} \cdot \mathbf{B} + \mathbf{b} \cdot \mathbf{Q}) + \lambda \mathbf{b} \cdot \mathbf{B})$

  $q = \mathbf{m} \otimes \mathbf{m} - \frac{1}{3}\mathbf{I} \qquad \mathbf{Q} =< q >$

  $b = \mathbf{n} \otimes \mathbf{n} - \mathbf{k} \otimes \mathbf{k} \qquad \mathbf{B} =< b >$

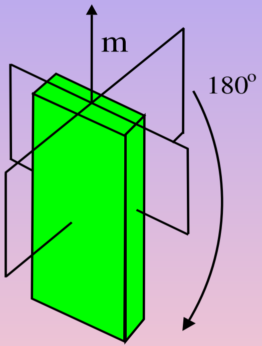
  $\beta = \frac{1}{k_B T}, (\gamma, \lambda)$ = material parameters

Steady State solution symmetry

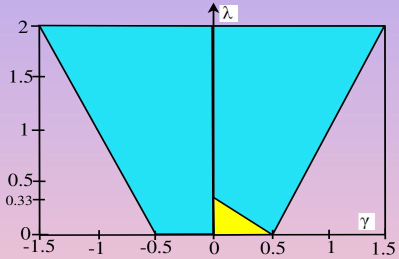
$$\mathbf{k}^* = \mathbf{k}, \quad \gamma_1^* = \frac{1+2\gamma-3\lambda}{|1+6\gamma+9\lambda|}, \lambda_1^* = \frac{1-2\gamma+\lambda}{|1+6\gamma+9\lambda|}, \beta_1^* = \frac{1}{4}\beta|1+6\gamma+9\lambda|$$

$$\mathbf{n}^* = \mathbf{n}, \quad \gamma_2^* = \frac{2\gamma+3\lambda-1}{|1-6\gamma+9\lambda|}, \lambda_2^* = \frac{1+2\gamma+\lambda}{|1-6\gamma+9\lambda|}, \beta_2^* = \frac{1}{4}\beta|1-6\gamma+9\lambda|$$

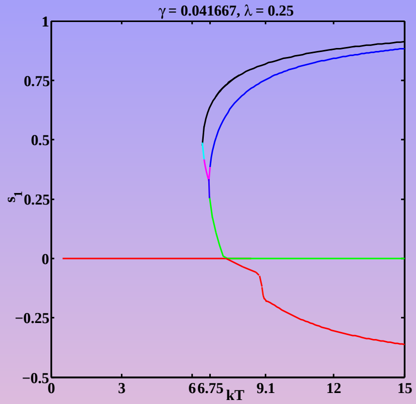
$$\mathbf{m}^* = \mathbf{m}, \quad \gamma_3^* = -\gamma, \qquad \lambda_3^* = \lambda, \qquad \beta_3^* = \beta$$



Rotational + Reflective symmetry

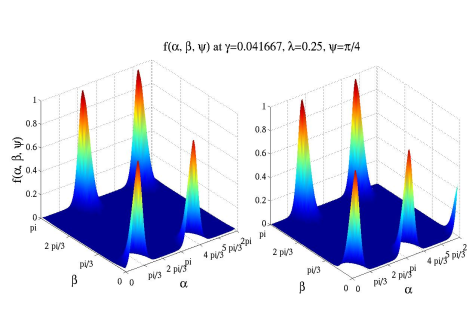


Degenerate steady-state solutions



- $s_1 = \langle D^2_{20} \rangle$
- $f = \frac{1}{\mathcal{Z}} e^{-V}, \frac{1}{\mathcal{Z}} = \langle e^{-V} \rangle$

- Solutions marked black,blue at $1/(k_B T)$=9.1 (N=6.06)



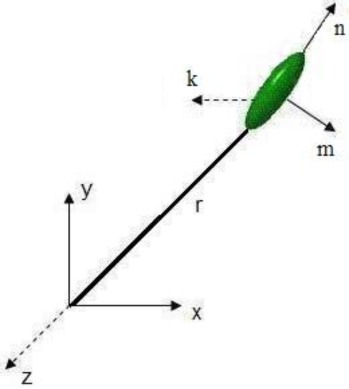
Smoluchowski Equation: Rotating Frame

- $\frac{d}{dt}f = \mathbf{L}^* \cdot (D_r \mathbf{L}\mu f) - \mathbf{L}^* \cdot (\mathbf{g}f)$

$\mathbf{L} = \mathbf{m}L_m + \mathbf{n}L_n + \mathbf{k}L_k$ (Angular momentum)

$\mu = \ln f + \frac{1}{kT}V$ (chemical potential)

Unknowns: PDF:**f**, $\mathbf{M} = \langle \mathbf{mm} \rangle, \mathbf{N} = \langle \mathbf{nn} \rangle$



Flow vector:

$\vec{g} = i[\frac{\mathbf{m}}{r_b^2+r_c^2}(\mathbf{K} : (r_b^2\mathbf{nk} - r_c^2\mathbf{kn})) + \frac{\mathbf{n}}{1+r_c^2}(\mathbf{K} : (r_c^2\mathbf{km} - \mathbf{mk})) + \frac{\mathbf{k}}{1+r_b^2}(\mathbf{K} : (\mathbf{mn} - r_b^2\mathbf{nm}))]$

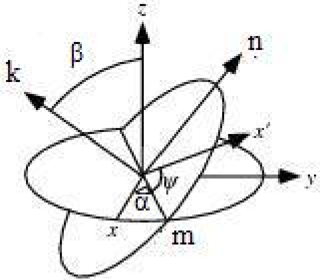
$K = (\nabla v)_{ij}$, (r_b, r_c) = aspect ratios

Spectral Approximation: Wigner Functions

- $f = \sum_{Lmn} C_{Lmn}(t)\mathcal{D}^L_{m,n}(\alpha,\beta,\gamma)$
- $\mathcal{D}^L_{m,n} = e^{-i(m\alpha+n\psi)}$

$$\sqrt{(L+m)!(L-m)!(L+n)!(L-n)!}$$

$$\sum_s \frac{(-1)^s(\cos\beta/2)^{2L+n-m-2s}(-\sin\beta/2)^{m-n+2s}}{(L-m-s)!(L+n-s)!(s+m-n)!s!}$$



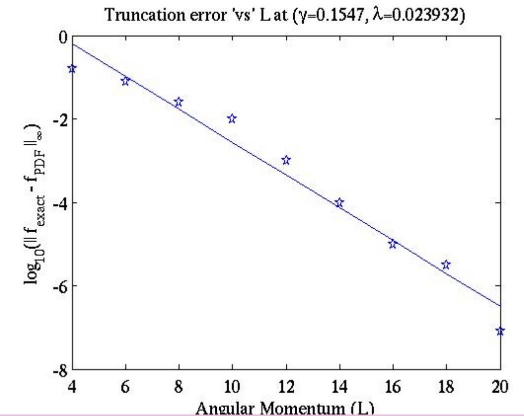
- Coupling of Angular Momentum:

$$\mathcal{D}^{j_1}_{\mu_1,m_1}\mathcal{D}^{j_2}_{\mu_2,m_2} =$$

$$\sum_{|j_1-j_2|}^{j_1+j_2} C(j_1,j_2,j,\mu_1,\mu_2)C(j_1,j_2,j,m_1,m_2)\mathcal{D}^j_{\mu_1+\mu_2,m_1+m_2}$$

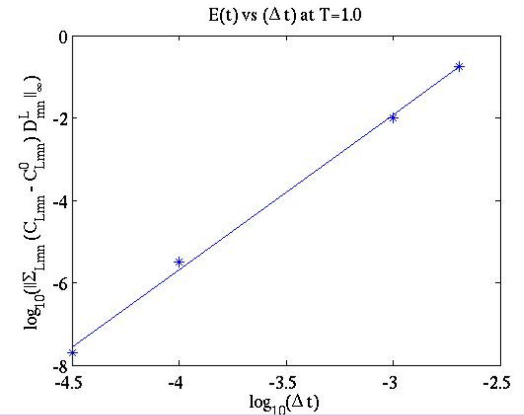
Mesh refinement

- $|m|, |n| \leq L, \quad L \geq 4$
- Number of unknown coefficients = $O(L^3)$
- Theoretical error $\sim \mathcal{O}(1/L!)$
- L=10: 1771 Modes Error $< 2\%$
  L=20: 12341 Modes Error $< 10^{-5}\%$

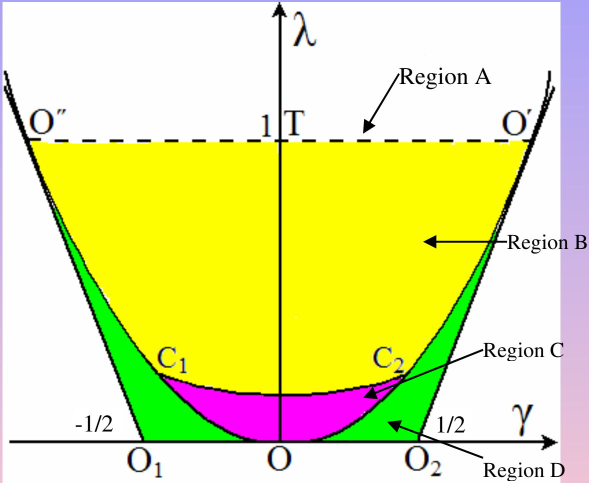


- 4-step Runge-Kutta
- $\triangle t = 10^{-3}$: Error $< 1\%$

  (L = 10)

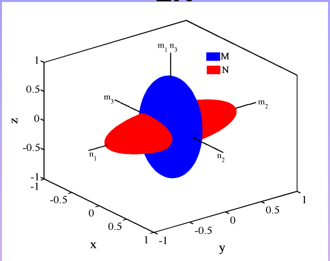


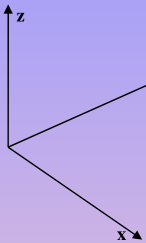
Shear flow results: Material parameter region



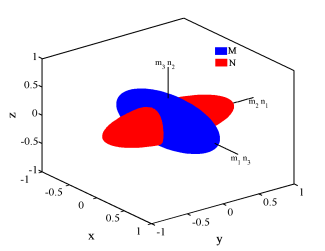
Steady orientational phases: LR, FA, OS

LR

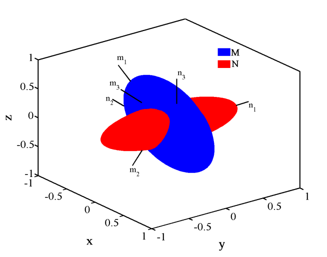




FA

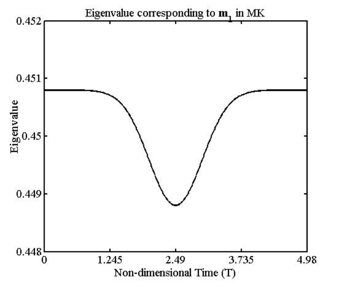


OS

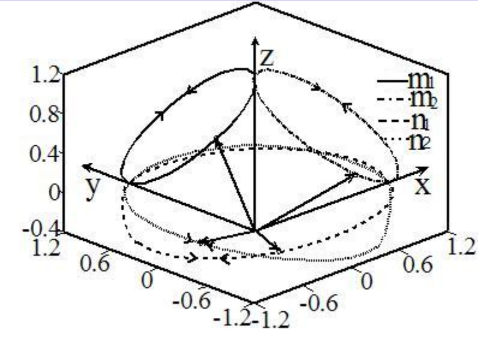


Periodic phase: MK

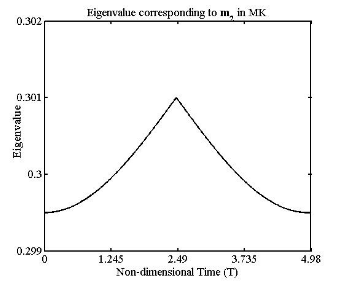
Eigenvalue of $\mathbf{m_1}$ $\rightarrow$



Trajectory of m_1, m_2, n_1, n_2



Eigenvalue of $\mathbf{m_2}$ $\rightarrow$

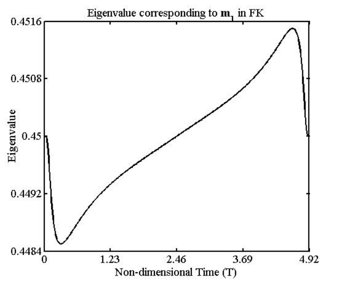


Periodic phase: MK

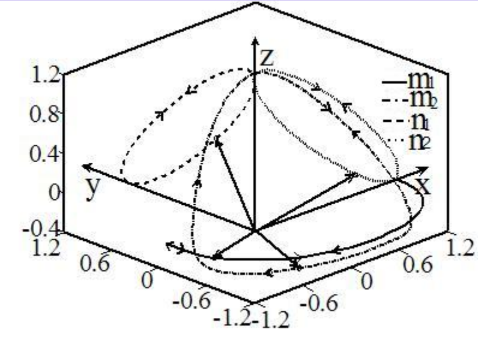
- Angle between m_1 and n_1 oscillates between 40^o and 140^o
- Blue: **M**, Red: **N**

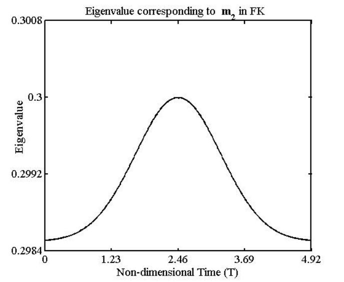
Periodic phase: FK

Eigenvalue of $\mathbf{m_1}$ $\longrightarrow$



Trajectory of m_1, m_2, n_1, n_2



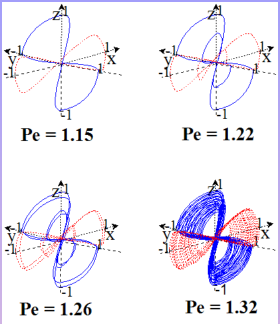


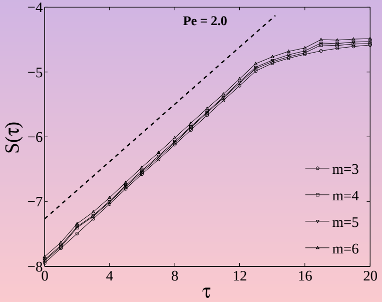
Eigenvalue of $\mathbf{m_2}$ $\longrightarrow$

Periodic phase: FK

- Angle between m_1 and n_1 oscillates between 40^o and 140^o
- Blue: **M**, Red: **N**

Period-doubling chaotic Phase: CH





Label	Pe	$F = \frac{Pe_i - Pe_{i-1}}{Pe_{i+1} - Pe_i}$
PDL_1	1.161	...
PDL_2	1.225	1.575
PDL_3	1.266	1.819
PDL_4	1.289	1.951
PDL_5	1.300	...
PDR_1	2.472	...
PDR_2	2.381	2.299
PDR_3	2.341	1.988
PDR_4	2.321	...

Table: $F \rightarrow 1.958$

Stretching function:

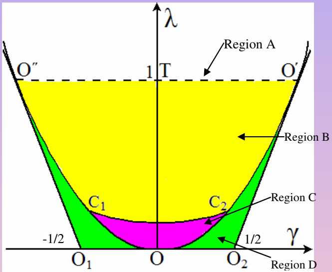
Phys. Lett. A, **185** pp 77-87 (1994)

$$\leftarrow S(\tau) = \frac{1}{T}\sum_{t=1}^{T} ln(\frac{1}{|\epsilon|}\sum(x_{t+\tau} - x_{\epsilon+\tau}))$$

$$(\lambda_1 \sim 0.228)$$

Variation in *Pe*. (N, λ, γ) fixed

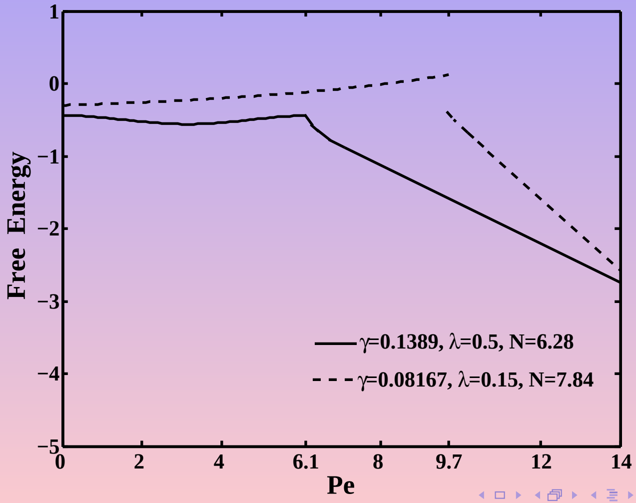
- Region A: **LR** $\rightarrow$ **FA**
- Region B: **LR** $\rightarrow$ **MK** $\rightarrow$ **FK** $\rightarrow$**FA**
- Region C: **LR** $\rightarrow$ **MK** $\rightarrow$ **OS** $\rightarrow$ **FK** $\rightarrow$**FA**
- Region D: **MK** $\rightarrow$ **OS** $\rightarrow$ **FK** $\rightarrow$**FA**
  MK $\rightarrow$ **CH** $\rightarrow$ **FK** $\rightarrow$**FA**



Nature of Phase transition: Region B $\leftrightarrow$ C

Free energy: $\int_\Omega [k_B T \ln f + \frac{V}{2}] f d\mathbf{m}$

- 1^{st} order $\leftrightarrow$ 2^{nd} order transition from Region (B)$\leftrightarrow$(C)



Conclusions

- Dynamical Analog: Shear flow beaks downs the rotational symmetry
- Low shear: **LR** phase High shear: **FA**

  Intermediate shear: **OS** phase
- Presence of 2 new periodic phases: **MK**, **FK**
- Choas **CH** in Region(D): Non-convex potential
- Change in the nature of the phase transition: Region (B)$\longrightarrow$(C)

What's next ?

"Extended nematics"
Biaxial LCPs

V-Shaped/biaxial blends

Dynamical phases, Optical Properties, Dipole-dipole interaction

Defect dynamics

Defect pattern recognition

LCP momentum transport Eqns. (Navier-Stokes)

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Questions....