

Low-symmetry liquid crystals

Stefano Turzi

Dip. Matematica, Politecnico di Milano, Italy

25/03/2014

Workshop on LC-flows, Pavia (Italy), 24-25 March 2014

ACKNOWLEDGEMENTS

- Geoffrey Luckhurst (School of Chemistry, Southampton, UK)
- Tim Sluckin (School of Mathematics, Southampton, UK)
- David Chillingworth (School of Mathematics, Southampton, UK)
- Reiner Lauterbach (Faculty for Mathematics, University of Hamburg)
- Tung To (School of Mathematics, Southampton, UK)
- Shohei Naemura (Electronic Display Research Centre, Tottori University, Japan)

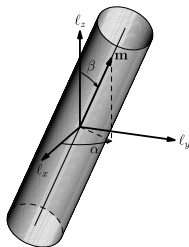
- Orientational order parameters
- Molecular field (MF) theory vs. Landau theory:
classical results for D_{2h} molecules
- Counting the second-rank invariants in absence of
any symmetry

- **Orientational order parameters**
- Molecular field (MF) theory vs. Landau theory:
classical results for D_{2h} molecules
- Counting the second-rank invariants in absence of
any symmetry

ORIENTATIONAL ORDER PARAMETERS (UNIAXIAL - $D_{\infty h}$)

Spherical expansion (multi-pole expansion):

$$f(\mathbf{m}) = \sum_{l=0}^{+\infty} \sum_{k=-l}^l f_{lk} Y_{lk}(\mathbf{m}),$$



Cartesian 2nd-rank moments ($l=2$):

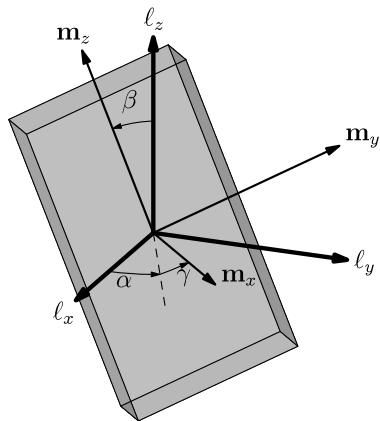
$$\mathbf{Q} = \left\langle \mathbf{m} \otimes \mathbf{m} - \frac{1}{3} \mathbf{I} \right\rangle = S \left(\ell_z \otimes \ell_z - \frac{1}{3} \mathbf{I} \right) + p (\ell_x \otimes \ell_x - \ell_y \otimes \ell_y).$$

Link: $S = \sqrt{\frac{4\pi}{5}} \langle Y_{20} \rangle, \quad p = \sqrt{\frac{4\pi}{15}} \langle Y_{22} + Y_{2-2} \rangle.$

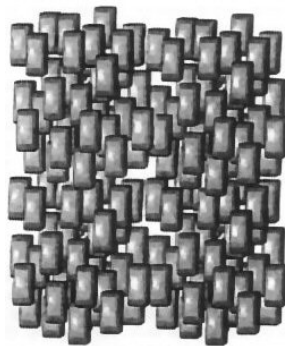
Q: How to extend the Cartesian definition to higher-rank tensors?

A: S. Turzi, *J. Math. Phys.*, **52**, 053517 (2011).

PROTOTYPICAL LOW-SYMMETRY



D_{2h} molecule



D_{2h} phase

ORIENTATIONAL ORDER PARAMETERS (D_{2h} INCLUDED)

Spherical expansion

$$f(R) = \sum_{j=0}^{+\infty} \sum_{k', k=-j}^j \frac{2j+1}{8\pi^2} f_{k'k}^j \mathcal{D}_{k'k}^{(j)}(R).$$

where $\mathcal{D}^{(j)}(R)$ (Wigner matrices) are $(2j+1) \times (2j+1)$ irreducible matrix representations of $SO(3)$. Then, Peter-Weyl Theorem says

Theorem

The functions defined by the matrix entries

$$\sqrt{2j+1} \mathcal{D}_{k'k}^{(j)}(R), \quad j \geq 0, \quad |k|, |k'| \leq j,$$

form *a complete orthonormal system in $L^2(SO(3))$ (with respect to the normalised invariant measure).*

ORIENTATIONAL ORDER PARAMETERS (D_{2h} INCLUDED)

Spherical expansion

$$f(R) = \sum_{j=0}^{+\infty} \sum_{k', k=-j}^j \frac{2j+1}{8\pi^2} f_{k'k}^j \mathcal{D}_{k'k}^{(j)}(R).$$

where $\mathcal{D}^{(j)}(R)$ (Wigner matrices) are $(2j+1) \times (2j+1)$ irreducible matrix representations of $SO(3)$. Then, Peter-Weyl Theorem says

Theorem

The functions defined by the matrix entries

$$\sqrt{2j+1} \mathcal{D}_{k'k}^{(j)}(R), \quad j \geq 0, \quad |k|, |k'| \leq j,$$

form a complete orthonormal system in $L^2(SO(3))$ (with respect to the normalised invariant measure).

Via orthogonality, $f_{k'k}^j = \langle \mathcal{D}^{(j)}(R)^* \rangle$. These are, by definition, the orientational order parameters.

ORIENTATIONAL ORDER PARAMETERS (CARTESIAN)

By contrast, the **traditional Cartesian definition** employs the *Saupe ordering super-matrix*:

$$S_{ab}^{AB} = \ell_A \cdot \frac{3}{2} \left\langle \mathbf{m}_a \otimes \mathbf{m}_b - \frac{1}{3} \delta_{ab} \mathbf{I} \right\rangle \ell_B,$$

$(\mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3)$ is the orthonormal frame set in the molecule, (ℓ_1, ℓ_2, ℓ_3) is the orthonormal frame set in the phase.

ORIENTATIONAL ORDER PARAMETERS (CARTESIAN)

By contrast, the **traditional Cartesian definition** employs the *Saupe ordering super-matrix*:

$$S_{ab}^{AB} = \ell_A \cdot \frac{3}{2} \left\langle \mathbf{m}_a \otimes \mathbf{m}_b - \frac{1}{3} \delta_{ab} \mathbf{I} \right\rangle \ell_B,$$

$(\mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3)$ is the orthonormal frame set in the molecule, (ℓ_1, ℓ_2, ℓ_3) is the orthonormal frame set in the phase.

However, in general this is not compatible with the 2^{nd} -rank spherical definition: it must be symmetrised^a:

$$\mathbf{Q}_{ab} = \left\langle \frac{1}{2} (\mathbf{m}_a \otimes \mathbf{m}_b + \mathbf{m}_b \otimes \mathbf{m}_a) - \frac{1}{3} \delta_{ab} \mathbf{I} \right\rangle$$

^aS. Turzi, *J. Math. Phys.*, **52**, 053517 (2011)

KEY EXAMPLE (D_{2h})

When the D_{2h} symmetry for both the molecules and the phase is exploited:

order parameter	measures the alignment of	limiting value
$S = S_{zz}^{ZZ}$	major mol. w.r.t. major lab	1
$D = S_{xx}^{ZZ} - S_{yy}^{ZZ}$	minor mol. w.r.t. major lab	0
$P = S_{zz}^{XX} - S_{zz}^{YY}$	major mol. w.r.t. minor lab	0
$C = (S_{xx}^{XX} - S_{yy}^{XX}) - (S_{xx}^{YY} - S_{yy}^{YY})$	minor mol. w.r.t. minor lab	3

Isotropic phase: $S = D = P = C = 0$

uniaxial nematic phase: usually S, D ; non-zero, $P = C = 0$

Biaxial nematic phase: usually S, D, P, C non-zero

KEY EXAMPLE (D_{2h})

When the D_{2h} symmetry for both the molecules and the phase is exploited:

order parameter	measures the alignment of	limiting value
$S = S_{zz}^{ZZ}$	major mol. w.r.t. major lab	1
$D = S_{xx}^{ZZ} - S_{yy}^{ZZ}$	minor mol. w.r.t. major lab	0
$P = S_{zz}^{XX} - S_{zz}^{YY}$	major mol. w.r.t. minor lab	0
$C = (S_{xx}^{XX} - S_{yy}^{XX}) - (S_{xx}^{YY} - S_{yy}^{YY})$	minor mol. w.r.t. minor lab	3

In terms of Wigner functions:

$$S = \langle \mathcal{D}_{00}^{(2)} \rangle = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle,$$

$$P = \sqrt{6} \langle \text{Re } \mathcal{D}_{20}^{(2)} \rangle,$$

$$D = \sqrt{6} \langle \text{Re } \mathcal{D}_{02}^{(2)} \rangle,$$

$$C = 3 \langle \text{Re} \{ \mathcal{D}_{22}^{(2)} + \mathcal{D}_{2-2}^{(2)} \} \rangle.$$

A CARTESIAN GENERAL ROUTE TO OPS

In the standard construction of the $SO(3)$ -irreps, $\mathcal{D}^{(j)}(R) \in L(V^{(j)})$, where $V^{(j)}$ is the $(2j+1)$ -dimensional vector space spanned by the spherical harmonics Y_{jm} , $m = -j, \dots, +j$, of order j .

However, any $(2j+1)$ -dimensional vector space should work

$V^{(j)}$ = vector space of **totally symmetric and traceless tensors** of order j on $W = \mathbb{R}^3$.
 $\dim V^{(j)} = 2j+1$

Now define the group action on $\mathbf{v}_1 \otimes \dots \otimes \mathbf{v}_j \in W^{\otimes j}$ as

$$D(R)(\mathbf{v}_1 \otimes \dots \otimes \mathbf{v}_j) = R\mathbf{v}_1 \otimes \dots \otimes R\mathbf{v}_j,$$

and extend by linearity to $W^{\otimes j}$ and then to $V^{(j)}$. R is the standard rotation matrix in \mathbb{R}^3

A CARTESIAN GENERAL ROUTE TO OPS

In the standard construction of the $SO(3)$ -irreps, $\mathcal{D}^{(j)}(R) \in L(V^{(j)})$, where $V^{(j)}$ is the $(2j+1)$ -dimensional vector space spanned by the spherical harmonics Y_{jm} , $m = -j, \dots, +j$, of order j .

However, any $(2j+1)$ -dimensional vector space should work

$V^{(j)}$ = vector space of **totally symmetric and traceless tensors** of order j on $W = \mathbb{R}^3$.
 $\dim V^{(j)} = 2j+1$

Now define the group action on $\mathbf{v}_1 \otimes \dots \otimes \mathbf{v}_j \in W^{\otimes j}$ as

$$D(R)(\mathbf{v}_1 \otimes \dots \otimes \mathbf{v}_j) = R\mathbf{v}_1 \otimes \dots \otimes R\mathbf{v}_j,$$

and extend by linearity to $W^{\otimes j}$ and then to $V^{(j)}$. R is the standard rotation matrix in \mathbb{R}^3

Theorem

For all j , $D(R) : V^{(j)} \rightarrow V^{(j)}$ is irreducible, therefore it is equivalent to $\mathcal{D}^{(j)}(R)$.

A CARTESIAN GENERAL ROUTE TO OPS

The Peter-Weyl Theorem holds also for $D^{(j)}(R)$: the orthonormal basis is now expressed in terms of the unit vectors defining the molecular frame. For example, when $j = 2$,

$$\mathbb{E}_{-2}^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_2 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_2), \quad \mathbb{E}_{-1}^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_1),$$

$$\mathbb{E}_0^{(2)} = \sqrt{\frac{3}{2}} \left(\mathbf{m}_3 \otimes \mathbf{m}_3 - \frac{1}{3} \mathbf{I} \right), \quad \mathbb{E}_1^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_1 - \mathbf{m}_2 \otimes \mathbf{m}_2),$$

$$\mathbb{E}_2^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_2 + \mathbf{m}_2 \otimes \mathbf{m}_1).$$

A CARTESIAN GENERAL ROUTE TO OPs

The Peter-Weyl Theorem holds also for $D^{(j)}(R)$: the orthonormal basis is now expressed in terms of the unit vectors defining the molecular frame. For example, when $j = 2$,

$$\mathbb{E}_{-2}^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_2 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_2), \quad \mathbb{E}_{-1}^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_1),$$

$$\mathbb{E}_0^{(2)} = \sqrt{\frac{3}{2}} \left(\mathbf{m}_3 \otimes \mathbf{m}_3 - \frac{1}{3} \mathbf{I} \right), \quad \mathbb{E}_1^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_1 - \mathbf{m}_2 \otimes \mathbf{m}_2),$$

$$\mathbb{E}_2^{(2)} = \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_2 + \mathbf{m}_2 \otimes \mathbf{m}_1).$$

$$f(R) = \sum f_{ab}^{(j)} D_{ab}^{(j)}(R), \quad D_{ab}^{(j)}(R) = \mathbb{E}_a^{(j)} \cdot D(R) \mathbb{E}_b^{(j)}$$

And the j^{th} -rank OPs are defined in terms of the averages $\langle D_{ab}^{(j)}(R) \rangle$.

A CARTESIAN GENERAL ROUTE TO OPs

The Peter-Weyl Theorem holds also for $D^{(j)}(R)$: the orthonormal basis is now expressed in terms of the unit vectors defining the molecular frame. For example, when $j = 2$,

$$\begin{aligned}\mathbb{E}_{-2}^{(2)} &= \frac{1}{\sqrt{2}} (\mathbf{m}_2 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_2), & \mathbb{E}_{-1}^{(2)} &= \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_3 + \mathbf{m}_3 \otimes \mathbf{m}_1), \\ \mathbb{E}_0^{(2)} &= \sqrt{\frac{3}{2}} \left(\mathbf{m}_3 \otimes \mathbf{m}_3 - \frac{1}{3} \mathbf{I} \right), & \mathbb{E}_1^{(2)} &= \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_1 - \mathbf{m}_2 \otimes \mathbf{m}_2), \\ \mathbb{E}_2^{(2)} &= \frac{1}{\sqrt{2}} (\mathbf{m}_1 \otimes \mathbf{m}_2 + \mathbf{m}_2 \otimes \mathbf{m}_1).\end{aligned}$$

$$f(R) = \sum f_{ab}^{(j)} D_{ab}^{(j)}(R), \quad D_{ab}^{(j)}(R) = \mathbb{E}_a^{(j)} \cdot D(R) \mathbb{E}_b^{(j)}$$

And the j^{th} -rank OPs are defined in terms of the averages $\langle D_{ab}^{(j)}(R) \rangle$.

Advantages: (1) purely real OPs (in contrast to Wigner's), (2) easier account for molecular and phase symmetries, (3) easier to determine from simulation numerical results.

SAUPE ORDERING SUPER-MATRIX

From these construction, after some algebra, we can also prove the following expansion of the probability function

$$f(R) = \sum_{j=0}^{+\infty} \sum_{\mathbf{a}, \mathbf{A}} {}^{(j)}S_{\mathbf{a}}^{\mathbf{A}} R_{a_1, A_1} R_{a_2, A_2} \cdots R_{a_j, A_j}$$

where the ${}^{(j)}S_{\mathbf{a}}^{\mathbf{A}}$ are the “ordering super-matrices” and are (non-trivially) related to the $\langle D_{ab}(R) \rangle$ of the same rank.

SAUPE ORDERING SUPER-MATRIX

From these construction, after some algebra, we can also prove the following expansion of the probability function

$$f(R) = \sum_{j=0}^{+\infty} \sum_{\mathbf{a}, \mathbf{A}} {}^{(j)}S_{\mathbf{a}}^{\mathbf{A}} R_{a_1, A_1} R_{a_2, A_2} \cdots R_{a_j, A_j}$$

where the ${}^{(j)}S_{\mathbf{a}}^{\mathbf{A}}$ are the “ordering super-matrices” and are (non-trivially) related to the $\langle D_{ab}(R) \rangle$ of the same rank.

Property

${}^{(j)}S_{\mathbf{a}}^{\mathbf{A}}$ are totally symmetric and traceless separately in the lower and upper indices.

The standard Saupe super-matrix, to be purely second-rank, should be symmetrised:

$${}^{(2)}S_{ab}^{AB} = \ell_A \cdot \left\langle \frac{1}{2} (\mathbf{m}_a \otimes \mathbf{m}_b + \mathbf{m}_b \otimes \mathbf{m}_a) - \frac{1}{3} \delta_{ab} \mathbf{I} \right\rangle \ell_B$$

- Orientational order parameters
- Molecular field (MF) theory vs. Landau theory: classical results for D_{2h} molecules
- Counting the second-rank invariants in absence of any symmetry

MF THEORY FOR UNIAXIAL MOLECULES (MAIER-SAUPE)

- One of the first and well-established theories.
- It is based on the definition of a potential of mean torque (mean field potential)

$$U_{mf}(\vartheta) = -u_{200}S(3\cos^2\vartheta - 1)/2.$$

- Derivation: (a) truncation of the pair potential; (b) variational analysis using dominant order parameter

MF THEORY FOR UNIAXIAL MOLECULES (MAIER-SAUPE)

- One of the first and well-established theories.
- It is based on the definition of a potential of mean torque (mean field potential)

$$U_{mf}(\vartheta) = -u_{200}S(3\cos^2\vartheta - 1)/2.$$

- Derivation: (a) truncation of the pair potential; (b) variational analysis using dominant order parameter

Helmholtz free energy

$$F = U - T\mathcal{S} = \underbrace{-\frac{1}{2}u_{200}S^2}_{\text{internal energy}} + \underbrace{k_B T \int_0^\pi f(\vartheta) \log f(\vartheta) \sin\vartheta d\vartheta}_{\text{entropic contribution}}.$$

MF THEORY FOR UNIAXIAL MOLECULES (MAIER-SAUPE)

- One of the first and well-established theories.
- It is based on the definition of a potential of mean torque (mean field potential)

$$U_{mf}(\vartheta) = -u_{200}S(3\cos^2\vartheta - 1)/2.$$

- Derivation: (a) truncation of the pair potential; (b) variational analysis using dominant order parameter

$$\delta F = 0 \text{ w.r.t } f(\vartheta) \quad \Rightarrow \quad f(\vartheta) = \frac{1}{Z} \exp\left(-\frac{U_{mf}(\vartheta)}{k_B T}\right)$$

MF THEORY FOR UNIAXIAL MOLECULES (MAIER-SAUPE)

- One of the first and well-established theories.
- It is based on the definition of a potential of mean torque (mean field potential)

$$U_{mf}(\vartheta) = -u_{200}S(3\cos^2\vartheta - 1)/2.$$

- Derivation: (a) truncation of the pair potential; (b) variational analysis using dominant order parameter

$$\delta F = 0 \text{ w.r.t } f(\vartheta) \quad \Rightarrow \quad f(\vartheta) = \frac{1}{Z} \exp\left(-\frac{U_{mf}(\vartheta)}{k_B T}\right)$$

The OPs are found by solving *numerically* the self-consistency equation

$$S = \int_0^\pi \frac{3\cos^2\vartheta - 1}{2} f(\vartheta) \sin\vartheta d\vartheta.$$

Potential of mean torque

$$U_{mf}(R) = - \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \mathcal{D}_{-pn}^{(2)}(R).$$

MF THEORY - EXTENSION TO BIAxIAL NEMATICS

Potential of mean torque

$$U_{mf}(R) = - \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \mathcal{D}_{-pn}^{(2)}(R).$$

Helmholtz free energy

$$F = U - T\mathcal{S} = \underbrace{-\frac{1}{2} \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \langle \mathcal{D}_{-pn}^{(2)} \rangle}_{\text{internal energy}} + \underbrace{k_B T \int_{SO(3)} f(R) \log f(R) d\mu(R)}_{\text{entropic contribution}}.$$

MF THEORY - EXTENSION TO BIAxIAL NEMATICS

Potential of mean torque

$$U_{mf}(R) = - \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \mathcal{D}_{-pn}^{(2)}(R).$$

Probability distribution function

$$\delta F = 0 \quad \text{w.r.t } f(R) \quad \Rightarrow \quad f(R) = \frac{1}{Z} \exp\left(-\frac{U_{mf}(R)}{k_B T}\right)$$

MF THEORY - EXTENSION TO BIAxIAL NEMATICS

Potential of mean torque

$$U_{mf}(R) = - \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \mathcal{D}_{-pn}^{(2)}(R).$$

Probability distribution function

$$\delta F = 0 \quad \text{w.r.t } f(R) \quad \Rightarrow \quad f(R) = \frac{1}{Z} \exp\left(-\frac{U_{mf}(R)}{k_B T}\right)$$

The OPs are found by solving *numerically* the self-consistency equations

$$\langle \mathcal{D}_{pm}^{(2)} \rangle = \int_{SO(3)} \mathcal{D}_{pm}^{(2)}(R) f(R) d\mu(R).$$

MF THEORY - INTERNAL ENERGY

Considering the D_{2h} symmetry for the molecule and the phase:

Internal energy

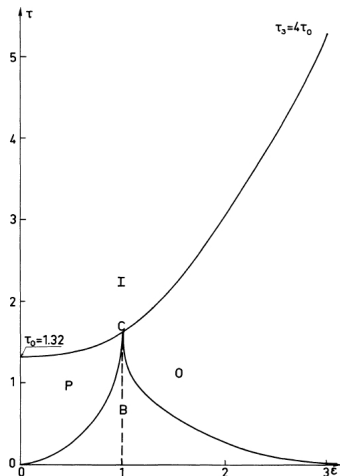
$$U = -\frac{1}{2} \left[u_{200} \left(S^2 + \frac{1}{3} P^2 \right) + u_{220} \sqrt{\frac{8}{3}} \left(SD + \frac{1}{3} PC \right) + u_{222} \frac{2}{3} \left(D^2 + \frac{1}{3} C^2 \right) \right].$$

Expansion coefficients u_{2mn}

- Form a super-tensor
- Represent the anisotropic interactions
- Are reduced by molecular symmetry
- D_{2h} : only two measures of biaxiality survive, u_{220}/u_{200} and u_{222}/u_{200} .

MOLECULAR FIELD THEORY PREDICTIONS

N. Boccara, R. Medjani, and L. de Seze, *J. Phys.*, **38**, 149–151 (1977).



Geometric mean approximation

$$(u_{220})^2 = u_{222} u_{200},$$

$$\epsilon = \sqrt{6} \frac{u_{222}}{u_{200}},$$

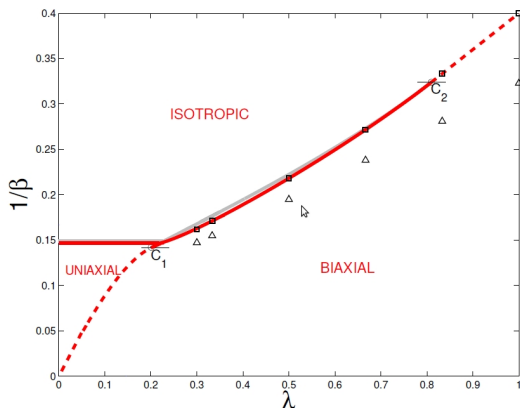
$$\tau \propto T$$

Features:

- $N_U^\pm - I$ First order
- $N_B - I$ Second order (Landau point)
- $N_U^\pm - N_B$ Second order

MOLECULAR FIELD THEORY PREDICTIONS

A.M. Sonnet, E.G. Virga, and G.E. Durand, *Phys. Rev. E*, **67**, 061701 (2003).



Sonnet, Virga, Durand limit

$$u_{220} = 0.$$

Features:

- $N_U - I$ First order
- $N_B - I$ Either first or second order (tricritical point)
- $N_U - N_B$ Either first or second order (tricritical point)

LANDAU THEORY OF PHASE TRANSITIONS

Landau (or Landau-de Gennes...) theory

- It's a **polynomial** expansion of F in terms of the system **invariants**;
- Expansion coefficients are **phenomenological scalars** and **temperature independent** ($n > 2$);
- Usually it gives a clearer insight into the phase sequences;
- Can be incorporated into a continuum theory.

LANDAU THEORY OF PHASE TRANSITIONS

Landau (or Landau-de Gennes...) theory

- It's a **polynomial** expansion of F in terms of the system **invariants**;
- Expansion coefficients are **phenomenological scalars** and **temperature independent** ($n > 2$);
- Usually it gives a clearer insight into the phase sequences;
- Can be incorporated into a continuum theory.

However, despite some interesting works [Allender, Lee 1984, Allender et al. 1985, Virga et al. 2008], standard Landau free energies seem not to provide us with phase diagrams in qualitative agreement with MF predictions. Contrariwise, Landau-de Gennes potential is standard for uniaxial nematics.

LANDAU THEORY OF PHASE TRANSITIONS

Landau (or Landau-de Gennes...) theory

- It's a **polynomial** expansion of F in terms of the system **invariants**;
- Expansion coefficients are **phenomenological scalars** and **temperature independent** ($n > 2$);
- Usually it gives a clearer insight into the phase sequences;
- Can be incorporated into a continuum theory.

However, despite some interesting works

[Allender, Lee 1984, Allender et al. 1985, Virga et al. 2008], standard Landau free energies seem not to provide us with phase diagrams in qualitative agreement with MF predictions. Contrariwise, Landau-de Gennes potential is standard for uniaxial nematics.

Possible reasons

- (technical problem): too many phenomenological coefficients (up to 14 [Virga et al. 2008])
- (more fundamental issue): the tensorial nature of the coefficients is neglected and, as a consequence, some invariants are omitted.

LANDAU THEORY OF PHASE TRANSITIONS

Landau (or Landau-de Gennes...) theory

- It's a **polynomial** expansion of F in terms of the system **invariants**;
- Expansion coefficients are **phenomenological scalars** and **temperature independent** ($n > 2$);
- Usually it gives a clearer insight into the phase sequences;
- Can be incorporated into a continuum theory.

However, despite some interesting works [Allender, Lee 1984, Allender et al. 1985, Virga et al. 2008], standard Landau free energies seem not to provide us with phase diagrams in qualitative agreement with MF predictions. Contrariwise, Landau-de Gennes potential is standard for uniaxial nematics.

Can we derive a Landau-like theory consistent with MF predictions?

A LANDAU-LIKE THEORY (KKLS^{1,2})

We present the method only for the “simple” case (= one order parameter):

$$S = \langle \frac{1}{2}(3 \cos^2 \vartheta - 1) \rangle = \langle P_2(\cos \vartheta) \rangle .$$

MF free energy:

$$F = -\frac{1}{2} u_{200} S^2 + k_B T \int_0^\pi f(\vartheta) \log f(\vartheta) \sin \vartheta d\vartheta \quad (1)$$

KKLS method

- 1 Determine the “most unbiased” probability distribution, given the knowledge of the order parameters \Rightarrow max. entropy principle.

$$f(\vartheta) = \frac{1}{Z(\eta)} e^{\eta P_2(\cos \vartheta)} . \quad (2)$$

η is the Lagrangian multiplier for the constraint: $S = \langle P_2(\cos \vartheta) \rangle$.

- 2 Partition function: $Z(\eta) = \int_0^\pi e^{\eta P_2(\cos \vartheta)} \sin \vartheta d\vartheta$

¹[Katriel, Kvetsel, Luckhurst and Sluckin, 1986]

²[Ball and Majumdar, 2010]

A LANDAU-LIKE THEORY (KKLS)

$$F = -\frac{1}{2} u_{200} S^2 + k_B T \int_0^\pi f(\vartheta) \log f(\vartheta) \sin \vartheta d\vartheta \quad (3)$$

KKLS method

- ③ The MF free energy becomes (still a function of S and η):

$$F = -\frac{1}{2} u_{200} S^2 + k_B T S \eta - k_B T \log Z(\eta). \quad (4)$$

- ④ The order parameter is related to $Z(\eta)$ by

$$S = \frac{1}{Z} \frac{\partial Z(\eta)}{\partial \eta}. \quad (5)$$

- ⑤ Expand (5) in terms of η , then invert the series to obtain an expansion of η in terms of S :

$$\eta = a_1 S + a_2 S^2 + a_3 S^3 + \dots \quad (6)$$

- ⑥ Insert (6) into the **MF free energy** (4) and expand $\Rightarrow F = F(S)$.

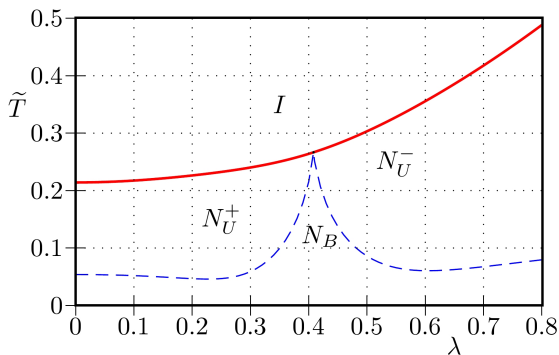
BIAXIAL FREE ENERGY (D_{2h})³

$$\begin{aligned} F/u_{200} = & \frac{5}{2} \left(\tilde{T} - \frac{1}{5} \right) \left(S^2 + \frac{1}{3} P^2 \right) + \frac{5}{6} \left(\tilde{T} - \frac{2}{5} \lambda^2 \right) \left(D^2 + \frac{1}{3} C^2 \right) \\ & - \sqrt{\frac{2}{3}} \gamma \left(SD + \frac{1}{3} PC \right) - \frac{25}{21} \tilde{T} S (S^2 - P^2) \\ & + \frac{25}{21} \tilde{T} \left(SD^2 - \frac{1}{3} SC^2 - \frac{2}{3} PDC \right) \\ & + \frac{425}{196} \vartheta \left[\left(S^2 + \frac{1}{3} P^2 \right)^2 + \frac{1}{9} \left(D^2 + \frac{1}{3} C^2 \right)^2 + \frac{2}{3} \left(SD + \frac{1}{3} PC \right)^2 \right] \\ & + \frac{325}{588} \tilde{T} (SC - PD)^2 . \end{aligned}$$

$$\tilde{T} = k_B T / u_{200}, \quad \gamma = u_{220} / u_{200}, \quad \lambda^2 = u_{222} / u_{200} .$$

³[Luckhurst, Naemura, Sluckin, Thomas and Turzi 2012]

COMPARISON WITH MF TOPOLOGIES



Geometric mean approximation

$$(u_{220})^2 = u_{222} u_{200},$$

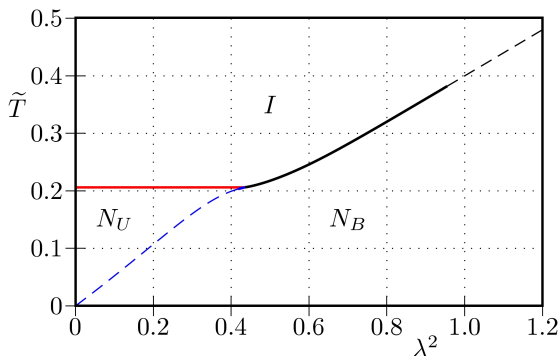
$$\lambda^2 = u_{222} / u_{200},$$

$$\tilde{T} = k_B T / u_{200}.$$

Features:

- $N_U^\pm - I$ First order
- $N_B - I$ Second order (Landau point)
- $N_U^\pm - N_B$ Second order

COMPARISON WITH MF TOPOLOGIES



Sonnet, Virga, Durand limit

$$\begin{aligned}u_{220} &= 0, \\ \lambda^2 &= u_{222} / u_{200}, \\ \tilde{T} &= k_B T / u_{200}.\end{aligned}$$

Features:

- $N_U - I$ First order
- $N_B - I$ Either first or second order (tricritical point)
- $N_U - N_B$ Either first or second order (tricritical point)

DISTINGUISHING FEATURES OF THE KKLS METHOD

- No knowledge of the system symmetry or the invariants is required (although still useful!).
- Limited number of unknown coefficients
- These are not purely phenomenological, but are related to the molecular anisotropy via the inter-particle potential.
- The tensorial nature of the molecular interactions is taken into account.
- The temperature dependence is not limited to 2nd-degree terms.
- Results consistent (in a limited range of temperature) with MF predictions.

OUTLINE

- Orientational order parameters
- Molecular field (MF) theory vs. Landau theory: classical results for D_{2h} molecules
- Counting the second-rank invariants in absence of any symmetry

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.
- 2 All C^∞ G -invariant functions are C^∞ functions of *invariant polynomials* (G finite or compact).

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.
- 2 All C^∞ G -invariant functions are C^∞ functions of *invariant polynomials* (G finite or compact).
- 3 In LCs, *the second-rank OP* is a map

$$\mathbb{Q} = \langle D^{(2)}(R) \rangle : V^{(2)} \rightarrow V^{(2)},$$

where $V^{(2)}$ =vector space of symmetric traceless tensors.

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.
- 2 All C^∞ G -invariant functions are C^∞ functions of *invariant polynomials* (G finite or compact).
- 3 In LCs, *the second-rank OP* is a map

$$\mathbb{Q} = \langle D^{(2)}(R) \rangle : V^{(2)} \rightarrow V^{(2)},$$

where $V^{(2)}$ =vector space of symmetric traceless tensors.

- 4 The scalar order parameters are the matrix entries of these map, with respect to the chosen Lab axes.

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.
- 2 All C^∞ G -invariant functions are C^∞ functions of *invariant polynomials* (G finite or compact).
- 3 In LCs, *the second-rank OP* is a map

$$\mathbb{Q} = \langle D^{(2)}(R) \rangle : V^{(2)} \rightarrow V^{(2)},$$

where $V^{(2)}$ =vector space of symmetric traceless tensors.

- 4 The scalar order parameters are the matrix entries of these map, with respect to the chosen Lab axes.
- 5 We are lead to study the homogeneous invariant polynomials wrt to the $SO(3)$ action on $V^{(2)}$ (still need to identify the correct full group, however).

INVARIANTS

- 1 Invariant functions: $f : V \rightarrow \mathbb{R}$, $gf(\mathbf{v}) = f(D(g^{-1})\mathbf{v}) = f(\mathbf{v})$, for all $g \in G$ and $\mathbf{v} \in V$.
- 2 All C^∞ G -invariant functions are C^∞ functions of *invariant polynomials* (G finite or compact).
- 3 In LCs, *the second-rank OP* is a map

$$\mathbb{Q} = \langle D^{(2)}(R) \rangle : V^{(2)} \rightarrow V^{(2)},$$

where $V^{(2)}$ =vector space of symmetric traceless tensors.

- 4 The scalar order parameters are the matrix entries of these map, with respect to the chosen Lab axes.
- 5 We are lead to study the homogeneous invariant polynomials wrt to the $SO(3)$ action on $V^{(2)}$ (still need to identify the correct full group, however).
- 6 The construction of the full algebra of the invariants is unrealistic (we will see why), however, thanks to Molien, we can count the number of polynomial invariants for each degree!

PROPERTIES OF THE RING \mathcal{R} OF INVARIANTS

- 1 Theorem (Hilbert): \mathcal{R} is generated by a finite set of fundamental invariants
- 2 Theorem (Cohen-Macaulay condition): There exist *primary* invariants K_m with $m = 1, 2, \dots, n$ and *secondary* invariants J_k with $k = 1, 2, \dots, r$ such that

$$\mathcal{R} = \bigoplus_{k=0}^r J_k \mathbb{C}[K_1, K_2, \dots, K_n],$$

with $J_0 = 1$.

- 3 An *arbitrary* invariant can be written as:

$$I = \sum_{k=0}^r J_k p_k(K_1, K_2, \dots, K_n),$$

with p_k polynomial in the K_m .

- 4 Primary invariants K_m are *algebraically independent*.
- 5 Secondary invariants J_k are *linearly independent*, but are algebraic functions of the K_m .

MOLIEN THEOREM

Let $P_k(V; \mathbb{R})$ denote the space of homogeneous polynomials $p: V \rightarrow \mathbb{R}$ of degree k , we set

$$d_k = \dim \{p \in P_k(V; \mathbb{R}) : p \text{ is invariant}\}$$

= number of linearly independent invariants of degree k .

Theorem (Molien)

Let G be finite or compact, the generating function is

$$R_G^V(t) = \sum_{k=0}^{+\infty} d_k t^k = \int_G \frac{1}{\det(\mathbf{I} - tD(g))} dg.$$

MOLIEN THEOREM

Let $P_k(V; \mathbb{R})$ denote the space of homogeneous polynomials $p: V \rightarrow \mathbb{R}$ of degree k , we set

$$\begin{aligned}d_k &= \dim \{p \in P_k(V; \mathbb{R}) : p \text{ is invariant}\} \\ &= \text{number of linearly independent invariants of degree } k.\end{aligned}$$

Theorem (Molien)

Let G be finite or compact, the generating function is

$$R_G^V(t) = \sum_{k=0}^{+\infty} d_k t^k = \int_G \frac{1}{\det(\mathbf{I} - tD(g))} dg.$$

G finite:

$$R_G^V(t) = \frac{\sum_{k=0}^r t^{\deg J_k}}{\prod_{m=1}^n (1 - t^{\deg K_m})}$$

EXAMPLE

Given $V = V^{(2)}$ = **symmetric traceless matrices**, $G = SO(3)$ acting irreducibly on $V^{(2)}$ via the $j = 2$ representation $D^{(2)}(R)$, the Molien generating function is

$$R_{SO(3)}^{V^{(2)}}(t) = \frac{1}{(1-t^2)(1-t^3)} = 1 + t^2 + t^3 + t^4 + 2t^6 + t^7 + \dots$$

EXAMPLE

Given $V = V^{(2)}$ = **symmetric traceless matrices**, $G = SO(3)$ acting irreducibly on $V^{(2)}$ via the $j = 2$ representation $D^{(2)}(R)$, the Molien generating function is

$$R_{SO(3)}^{V^{(2)}}(t) = \frac{1}{(1-t^2)(1-t^3)} = 1 + t^2 + t^3 + t^4 + 2t^6 + t^7 + \dots$$

There are two algebraically independent generators (primary invariants):

$$\text{tr}(\mathbf{Q}^2), \quad \det(\mathbf{Q}) = \frac{1}{3} \text{tr}(\mathbf{Q}^3).$$

EXAMPLE

Given $V = V^{(2)}$ = **symmetric traceless matrices**, $G = SO(3)$ acting irreducibly on $V^{(2)}$ via the $j = 2$ representation $D^{(2)}(R)$, the Molien generating function is

$$R_{SO(3)}^{V^{(2)}}(t) = \frac{1}{(1-t^2)(1-t^3)} = 1 + t^2 + t^3 + t^4 + 2t^6 + t^7 + \dots$$

There are two algebraically independent generators (primary invariants):

$$\text{tr}(\mathbf{Q}^2), \quad \det(\mathbf{Q}) = \frac{1}{3} \text{tr}(\mathbf{Q}^3).$$

The number of invariant polynomials for each given degree are:

deg	2	3	4	5	6	7 ...
Number	1	1	1	0	2	1 ...

① $\mathbb{Q} = \langle D^{(2)}(R) \rangle : V^{(2)} \rightarrow V^{(2)} \quad \Rightarrow \quad \mathbb{Q} \in \mathbb{M}_{5 \times 5}(\mathbb{R})$

- ② Maximum entropy principle leads to a Maxwell-Boltzmann distribution

$$f(R) = Z(\boldsymbol{\eta})^{-1} \exp(\boldsymbol{\eta} \cdot D^{(2)}(g)).$$

- ③ $\boldsymbol{\eta}$ is the Lagrangian multiplier for $\langle D^{(2)}(R) \rangle = \mathbb{Q}$, and

$$Z(\boldsymbol{\eta}) = \int_{SO(3)} \exp(\boldsymbol{\eta} \cdot D^{(2)}(g)).$$

- ④ $\mathbb{Q} = \nabla_{\boldsymbol{\eta}} \log Z(\boldsymbol{\eta})$; define $W(\boldsymbol{\eta}) = \nabla_{\boldsymbol{\eta}} \log Z(\boldsymbol{\eta})$.

- ⑤ The entropy is: $\mathcal{S}(\boldsymbol{\eta}) = k(\log Z(\boldsymbol{\eta}) - \boldsymbol{\eta} \cdot W(\boldsymbol{\eta}))$

Proposition [Chillingworth, 2013]

The partition function $Z(\boldsymbol{\eta})$ and **the entropy** $\mathcal{S}(\boldsymbol{\eta})$ are invariant under

- 1 the action of $SO(3)$ on $\mathbb{M}_{5 \times 5}(\mathbb{R})$ by left composition

$$\mathbf{A} \mapsto D^{(2)}(g)\mathbf{A};$$

- 2 transposition in $\mathbb{M}_{5 \times 5}(\mathbb{R})$

The group G generated by (1) and (2) is $G = SO(3) \times SO(3) \rtimes Z_2$. **Every element of G can be written in the form: $(M, N)\tau^\alpha$** , with $M, N \in SO(3)$ and $\alpha = 0, 1$ subject to the multiplication rules

$$\tau^2 = 1, \quad \tau(M, N) = (N^T, M^T)\tau.$$

The group G acts on $\mathbb{M}_{5 \times 5}(\mathbb{R})$ by ρ , where

$$\rho((M, N)) : \mathbf{A} \mapsto D^{(2)}(M)\mathbf{A}D^{(2)}(N^T)$$

$$\rho(\tau) : \mathbf{A} \mapsto \mathbf{A}^T$$

SKETCH OF THE PROOF

Let $h \in SO(3)$,

$$Z(D^{(2)}(h)\boldsymbol{\eta}) = \int_{SO(3)} \exp(D^{(2)}(h)\boldsymbol{\eta} \cdot D^{(2)}(g)) dg = \int_{SO(3)} \exp(\boldsymbol{\eta} \cdot D^{(2)}(h^{-1}g)) dg = Z(\boldsymbol{\eta})$$
$$Z(\boldsymbol{\eta}^T) = \int_{SO(3)} \exp(\boldsymbol{\eta}^T \cdot D^{(2)}(g)) dg = \int_{SO(3)} \exp(\boldsymbol{\eta} \cdot D^{(2)}(g^{-1})) dg = Z(\boldsymbol{\eta})$$

Therefore, $W(\boldsymbol{\eta}) = \nabla_{\boldsymbol{\eta}} \log Z(\boldsymbol{\eta})$ is *equivariant*: $W(D^{(2)}(h)\boldsymbol{\eta}) = D^{(2)}(h)W(\boldsymbol{\eta})$, and the entropy

$$\mathcal{S}(\boldsymbol{\eta}) = k(\log Z(\boldsymbol{\eta}) - \boldsymbol{\eta} \cdot W(\boldsymbol{\eta}))$$

is *invariant*: $h\mathcal{S}(\boldsymbol{\eta}) = \mathcal{S}(D^{(2)}(h)\boldsymbol{\eta}) = \mathcal{S}(\boldsymbol{\eta})$, $\tau\mathcal{S}(\boldsymbol{\eta}) = \mathcal{S}(\boldsymbol{\eta}^T) = \mathcal{S}(\boldsymbol{\eta})$.

Furthermore, let $g = \tau h \tau$

$$g\mathcal{S}(\boldsymbol{\eta}) = \mathcal{S}((D^{(2)}(h)\boldsymbol{\eta}^T)^T) = \mathcal{S}(\boldsymbol{\eta}D^{(2)}(h^T)) = \mathcal{S}(\boldsymbol{\eta})h^T,$$

Therefore, also the action of $SO(3)$ by *right composition* must be included.

MOLIEN RATIONAL FUNCTION

The symmetries (1) and (2) for non-symmetric nematic liquid crystals which can be described by second-rank OPs are therefore captured by the action of the group $G = SO(3) \times SO(3) \rtimes Z_2$ on $\mathbb{M}_{5 \times 5}(\mathbb{R}) \sim \mathbb{R}^{25}$.

Challenge

It is quite a challenge to perform the Molien integral, but we finally did it [Chillingworth, Lauterbach, Turzi]! However, I omit the terrible computations...

MOLIEN RATIONAL FUNCTION

The symmetries (1) and (2) for non-symmetric nematic liquid crystals which can be described by second-rank OPs are therefore captured by the action of the group $G = SO(3) \times SO(3) \rtimes Z_2$ on $\mathbb{M}_{5 \times 5}(\mathbb{R}) \sim \mathbb{R}^{25}$.

$$R_G^{\mathbb{M}_{5 \times 5}(\mathbb{R})}(t) = \frac{N(t)}{D(t)}$$

$N(t)$ is a **polynomial in t of degree 113 with positive integer coefficients**, which we do not report for brevity;














$$D(t) = (1 - t^2)(1 - t^3)(1 - t^4)^3(1 - t^5)(1 - t^6)^2(1 - t^7)^2(1 - t^8)^2 \times \\ \times (1 - t^9)^2(1 - t^{10})^2(1 - t^{11})(1 - t^{12})(1 - t^{13})$$

There are 19 primary invariants and 1 453 926 048 secondary invariants [Chillingworth, Lauterbach, Turzi].

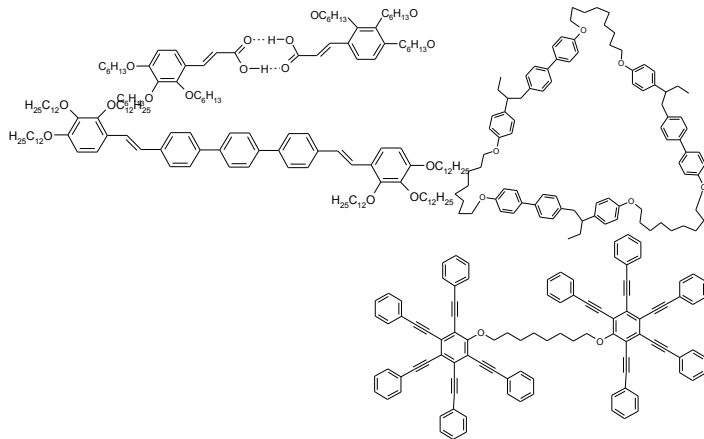
MOLIEN SERIES

$$R_G^{\mathbb{M}_{5 \times 5}(\mathbb{R})}(t) = 1 + t^2 + t^3 + 4t^4 + 5t^5 + 14t^6 + 20t^7 + 52t^8 + 90t^9 + 201t^{10} + 371t^{11} + 792t^{12} + 1485t^{13} + 2977t^{14} + 5557t^{15} + 10620t^{16} + 19354t^{17} + 35467t^{18} + O(t^{19}).$$

REFERENCES

-  S. Turzi, *J. Math. Phys.*, **52**, 053517 (2011).
-  N. Boccara, R. Medjani, and L. de Seze, *J. Phys.*, **38**, 149–151 (1977).
-  A.M. Sonnet, E.G. Virga, and G.E. Durand, *Phys. Rev. E*, **67**, 061701 (2003).
-  D.W. Allender and M.A. Lee, *Mol. Cryst. Liq. Cryst.*, **110**, 331 (1984).
-  D.W. Allender, M.A. Lee and N. Hafiz, *Mol. Cryst. Liq. Cryst.*, **124**, 45 (1985).
-  G. De Matteis, A.M. Sonnet and E.G. Virga *Continuum Mech. Thermodyn.*, **20**, 347 (2008).
-  J. Katriel, G.F. Kventsel, G.R. Luckhurst and T.J. Sluckin, *Liq. Cryst.*, **1**, 165 (1986).
-  J. Ball and A. Majumdar, *Mol. Cryst. Liq. Cryst.*, **525** (2010).
-  G.R. Luckhurst, S. Naemura, T.J. Sluckin, T.B.T. To and S. Turzi, *Phys. Rev. E*, **84**, 011704 (2011).
-  G.R. Luckhurst, S. Naemura, T.J. Sluckin, K.S. Thomas and S. Turzi, *Phys. Rev. E*, **85**, 031705 (2012).
-  S. Turzi and T. Sluckin, *SIAM J. Appl. Math.*, **73** 1139–1163 (2013).
-  D. Chillingworth, *Nonlinearity*, submitted (2014).
-  D. Chillingworth, R. Lauterbach and S. Turzi, in preparation.

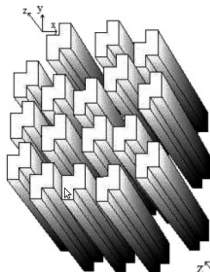
STRUCTURE OF BIAxIAL MESOGENIC MOLECULES



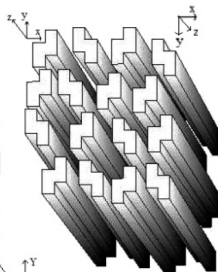
Lower symmetry biaxial nematics (C_{2h})

ORIENTATIONAL ORDER PARAMETERS

C_{2h}

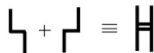


(a)



(b)

D_{2h}



(c)

A sketch of the idealised organisation of elongated molecules with C_{2h} point group symmetry in a biaxial nematic phase with (a) C_{2h} symmetry and (b) D_{2h} symmetry.

ORIENTATIONAL ORDER PARAMETERS

		phase		
		$D_{\infty h}$	D_{2h}	C_{2h}
molecule	$D_{\infty h}$	$S = S_{zz}^{ZZ}$	$P = (S_{zz}^{XX} - S_{zz}^{YY})$	$-\sqrt{\frac{2}{3}} S_{zz}^{XY}$
	D_{2h}	$D = (S_{xx}^{ZZ} - S_{yy}^{ZZ})$	$C = \begin{matrix} (S_{xx}^{XX} - S_{yy}^{XX}) \\ -(S_{xx}^{YY} - S_{yy}^{YY}) \end{matrix}$	$-\frac{2}{3} (S_{xx}^{XY} - S_{yy}^{XY})$
	C_{2h}	$\sqrt{\frac{2}{3}} S_{xy}^{ZZ}$	$\frac{2}{3} (S_{xy}^{XX} - S_{xy}^{YY})$	$\frac{2}{3} (S_{xy}^{XY} + S_{xy}^{YX})$

C_{2h} phase

- Three new OPs.
- In the limit of high order $\frac{2}{3} (S_{xy}^{XY} + S_{xy}^{YX})$ is large, while the other two tend to vanish.

ORIENTATIONAL ORDER PARAMETERS

		phase		
		$D_{\infty h}$	D_{2h}	C_{2h}
molecule	$D_{\infty h}$	$S = S_{zz}^{ZZ}$	$P = (S_{zz}^{XX} - S_{zz}^{YY})$	$-\sqrt{\frac{2}{3}} S_{zz}^{XY}$
	D_{2h}	$D = (S_{xx}^{ZZ} - S_{yy}^{ZZ})$	$C = (S_{xx}^{XX} - S_{yy}^{XX}) - (S_{xx}^{YY} - S_{yy}^{YY})$	$-\frac{2}{3} (S_{xx}^{XY} - S_{yy}^{XY})$
	C_{2h}	$\sqrt{\frac{2}{3}} S_{xy}^{ZZ}$	$\frac{2}{3} (S_{xy}^{XX} - S_{xy}^{YY})$	$\frac{2}{3} (S_{xy}^{XY} + S_{xy}^{YX})$

In terms of (symmetry adapted) Wigner functions:

$$\langle R_{00} \rangle = S = \langle \mathcal{D}_{00}^{(2)} \rangle = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle$$

$$\langle R_{22}^s \rangle = C/3 = \langle \text{Re} \{ \mathcal{D}_{22}^{(2)} + \mathcal{D}_{2-2}^{(2)} \} \rangle$$

$$\langle R_{22}^a \rangle = \frac{2}{3} (S_{xy}^{XY} + S_{xy}^{YX}) = \langle \text{Re} \{ \mathcal{D}_{22}^{(2)} - \mathcal{D}_{2-2}^{(2)} \} \rangle$$

SIMPLIFIED MOLECULAR FIELD THEORY

$$F = U - T\mathcal{S} = \underbrace{-\frac{1}{2} \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \langle \mathcal{D}_{-pn}^{(2)} \rangle}_{\text{internal energy}} + \underbrace{k_B T \int_{SO(3)} f(R) \log f(R) d\mu(R)}_{\text{entropic contribution}}.$$

In principle, C_{2h} symmetry reduces the number of independent expansion coefficients down to six: u_{200} , u_{220} , u_{2-20} , u_{222} , u_{2-22} and u_{2-2-2} .

SIMPLIFIED MOLECULAR FIELD THEORY

$$F = U - T\mathcal{S} = \underbrace{-\frac{1}{2} \sum_{m,n} u_{2mn} \sum_p \langle \mathcal{D}_{pm}^{(2)} \rangle \langle \mathcal{D}_{-pn}^{(2)} \rangle}_{\text{internal energy}} + \underbrace{k_B T \int_{SO(3)} f(R) \log f(R) d\mu(R)}_{\text{entropic contribution}}.$$

In principle, C_{2h} symmetry reduces the number of independent expansion coefficients down to six: u_{200} , u_{220} , u_{2-20} , u_{222} , u_{2-22} and u_{2-2-2} .

Too complicated! Can we simplify the model?

As in the Sonnet-Virga-Durand limit ($u_{220} = 0$), we simplify the MF theory including only the contributions of the **three** dominant OPs: $\langle R_{00} \rangle$, $\langle R_{22}^s \rangle$ and $\langle R_{22}^a \rangle$.

SIMPLIFIED MOLECULAR FIELD THEORY

MF internal energy

$$U = -\frac{1}{2} u_{200} (\langle R_{00} \rangle^2 + 2\lambda_s \langle R_{22}^s \rangle^2 + 2\lambda_a \langle R_{22}^a \rangle^2).$$

Two relative biaxial coefficients

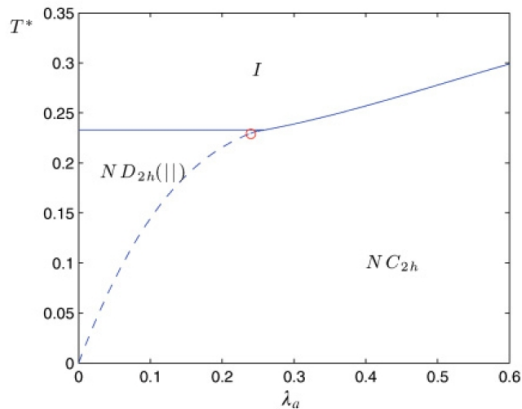
$$\lambda_s = \frac{\operatorname{Re}\{u_{222}\} + u_{2-22}}{2 u_{200}}, \quad \lambda_a = \frac{\operatorname{Re}\{u_{222}\} - u_{2-22}}{2 u_{200}}.$$

- λ_s drives the appearance of $\langle R_{22}^s \rangle$ (D_{2h} phase).
- λ_a drives the appearance of $\langle R_{22}^a \rangle$ (C_{2h} phase).

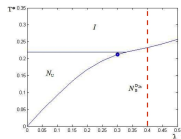
Free energy: $F = U - T\mathcal{S}$

Two competing effects: the internal energy is minimised at high order, the entropic term $-T\mathcal{S}$ is minimised at low order ($f = \text{const.}$).

MOLECULAR FIELD THEORY PREDICTIONS: $\lambda_s = 0.4$



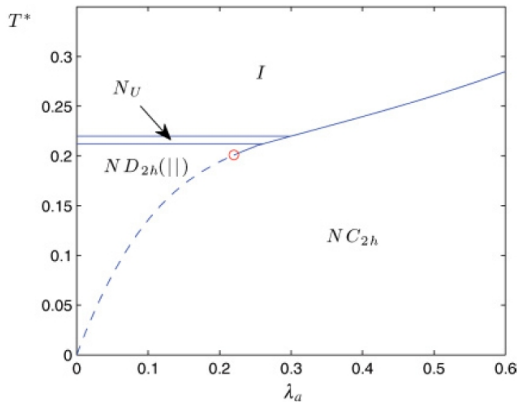
$$\lambda_s = 0.4$$



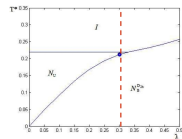
Features:

- Phase sequence at $\lambda_a = 0$: $I - ND_{2h}(\parallel)$;
- $I - ND_{2h}(\parallel)$ first order;
- $ND_{2h}(\parallel) - NC_{2h}$ either first or second order (tricritical point)
- $I - NC_{2h}$ first order;
- transition temperature of $I - ND_{2h}(\parallel)$ does not change as λ_a is increased (λ_a does not contribute to the orientational order of the phase involved);
- transition temperatures of $I - NC_{2h}$ and $ND_{2h}(\parallel) - NC_{2h}$ increase as λ_a is increased (the appearance of the NC_{2h} phase is facilitated).

MOLECULAR FIELD THEORY PREDICTIONS: $\lambda_s = 0.3$



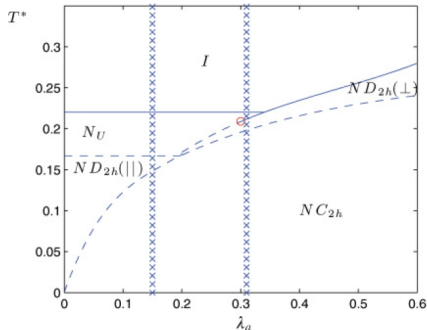
$\lambda_s = 0.3$



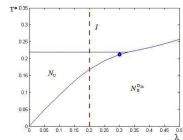
Features:

- Phase sequence at $\lambda_a = 0$:
 $I - N_U - ND_{2h}(\parallel)$;
- $I - N_U$ and $N_U - ND_{2h}(\parallel)$ are first order;
- $ND_{2h}(\parallel) - NC_{2h}$ either first or second order (tricritical point)
- $I - NC_{2h}$ first order;
- transition temperatures of $I - N_U$ and $N_U - ND_{2h}(\parallel)$ do not change as λ_a is increased (λ_a does not contribute to the orientational order of the phases involved);
- transition temperature of $I - ND_{2h}(\parallel)$ increases as λ_a is increased (the appearance of the NC_{2h} phase is facilitated).

MOLECULAR FIELD THEORY PREDICTIONS: $\lambda_s = 0.2$



$$\lambda_s = 0.2$$

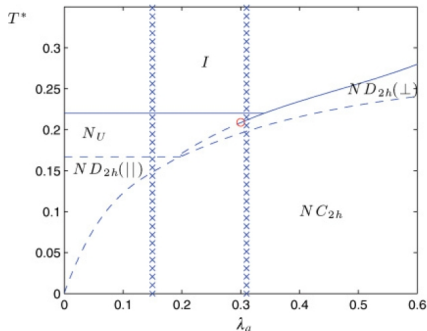


Features:

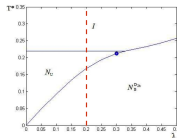
- Phase sequence at $\lambda_a = 0$: $I - N_U - ND_{2h}(||)$;
- $I - N_U$ and $N_U - ND_{2h}(||)$ are first order;
- **New phase: $ND_{2h}(\perp)$.** When $\lambda_a > \lambda_s$, $\langle R_{22}^a \rangle$ appears at a higher temperature than $\langle R_{22}^s \rangle$.

	$\langle R_{00} \rangle$	$\langle R_{22}^s \rangle$	$\langle R_{22}^a \rangle$
N_U	$\neq 0$	0	0
$ND_{2h}()$	$\neq 0$	$\neq 0$	0
NC_{2h}	$\neq 0$	$\neq 0$	$\neq 0$
$ND_{2h}(\perp)$	$\neq 0$	0	$\neq 0$

MOLECULAR FIELD THEORY PREDICTIONS: $\lambda_s = 0.2$



$$\lambda_s = 0.2$$



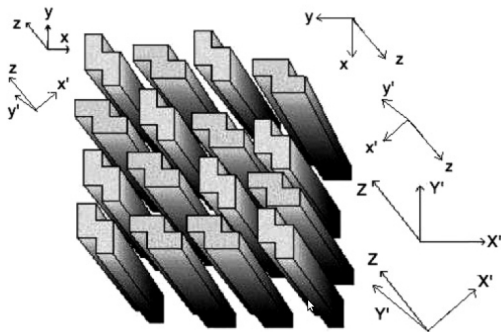
Features:

- Phase sequence at $\lambda_a = 0$: $I - N_U - N D_{2h}(\parallel)$;
- $I - N_U$ and $N_U - N D_{2h}(\parallel)$ are first order;
- **New phase: $N D_{2h}(\perp)$.** When $\lambda_a > \lambda_s$, $\langle R_{22}^a \rangle$ appears at a higher temperature than $\langle R_{22}^s \rangle$.

	$\langle R_{00} \rangle$	$\langle R_{22}^s \rangle$	$\langle R_{22}^a \rangle$
N_U	$\neq 0$	0	0
$N D_{2h}(\parallel)$	$\neq 0$	$\neq 0$	0
$N C_{2h}$	$\neq 0$	$\neq 0$	$\neq 0$
$N D_{2h}(\perp)$	$\neq 0$	0	$\neq 0$

Is $N D_{2h}(\perp)$ a phase with C_{2h} symmetry?

A NEW BIAxIAL PHASE MAY APPEAR



Still a phase with D_{2h} symmetry!



CONCLUSIONS

- Even the simplified (=no coupling) theory shows a rich phase behaviour
- Transitions are both first and second order and show tricritical points
- Our MF theory has more surprises especially as non-trivial phases are expected.