Generalized Orientational Order Parameters: Promises, Possibilities and Perils

Xiaoyu Zheng — Dept. of Math. Sciences, Kent State University

Rolfe Petscheck — Dept. of Physics, Case Western Reserve U.

Sharon Glotzer — Dept. of Chem. Eng., University of Michigan

Michael Shelley — Courant Institute, New York University

Peter Palffy-Muhoray — Liquid Crystal Institute, Kent State University

Motivation

- Generalized Orientational Order Parameters: **WHY??**

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  - 1888: Liquid crystals discovered (Reinitzer)
    - cholesterol esters

rod-like

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  – 1977: Discotic liquid crystals discovered

  - discotics — disk-like

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  - 1996: Bent-core liquid crystals discovered
    - banana — banana-like

Motivation

- Generalized Orientational Order Parameters: **WHY??**

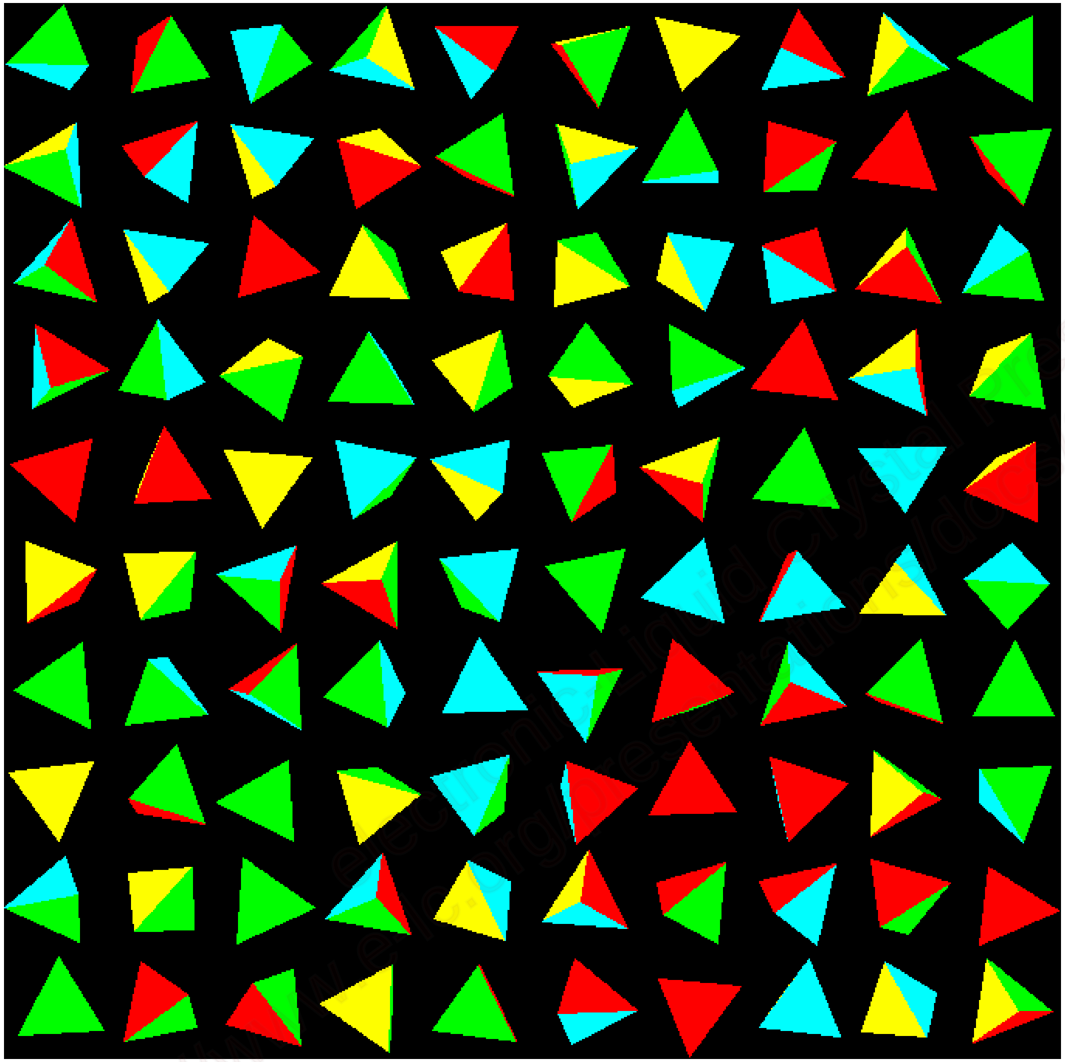
  – 1988: Liquid crystals discovered (Reinitzer)
    - cholesterol esters — rod-like
      - cylindrical

  – 1977: Discotic liquid crystals discovered
    - discotics — disk-like
      - cylindrical

  – 1996: Bent-core liquid crystals discovered
    - banana — banana-like
      - not cylindrical

How do we describe liquid crystals whose constituents have non-cylindrical symmetry??

Example: Tetrahedra



orientationally ordered?

how do we know?

would they order?

why would they order?

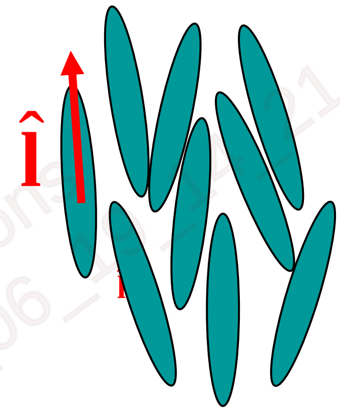
Goal:

- want to describe the behavior of systems of oriented particles with a variety of shapes:
  - small molecules
  - macromolecules
  - nanoparticles
  - biological entities
  - soft colloids
  - macroscopic objects

- need free energy and dissipation as function of order parameter to get
  - phase behavior
  - response to excitations

Paradigm: Nematic LCs

- systems of rod-like molecules



- order parameter

$$\mathbf{Q} = \frac{1}{2}(3 < \hat{\mathbf{l}}\hat{\mathbf{l}} > - \mathbf{I})$$

$$Q = \begin{bmatrix} -\frac{1}{2}(S-P) & 0 & 0 \\ 0 & -\frac{1}{2}(S-P) & 0 \\ 0 & 0 & S \end{bmatrix}$$

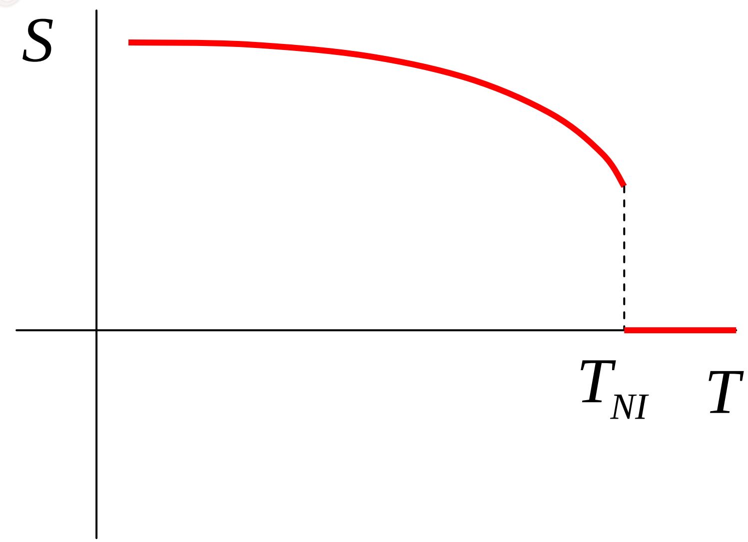
Paradigm: Nematic LCs

- free energy density:

$$\mathcal{F} = \frac{1}{2} A Q^2 - \frac{1}{3} B Q^3 + \frac{1}{4} C (Q^2)^2 + ..$$

- if uniaxial ($P = 0$), then

$$\mathcal{F} = \frac{1}{2} a S^2 - \frac{1}{3} b S^3 + \frac{1}{4} c S^4 + ..$$



Paradigm: Nematic LCs

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$$\mathcal{F} = \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}C(Q^2)^2 + ..$$
$$+\frac{1}{2}K(\nabla Q)^2$$
$$-\frac{1}{2}\Delta\varepsilon QEE$$

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$$T\dot{S} = \gamma(\dot{Q})^2 + \beta(\dot{Q}\nabla v) + \eta(\nabla v)^2$$

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- entropy production:

$$T\dot{S} = \gamma(\dot{Q})^2 + \beta(\dot{Q}\nabla v) + \eta(\nabla v)^2$$

- can get equations of motion and dynamics, etc.

Promise: if we have the right order parameter, can get free energy, etc.

Outline

- generalized orientational order parameters
- eigenvalue expansion of tensors of arbitrary rank
- role of scalar invariants

project
under
construction!

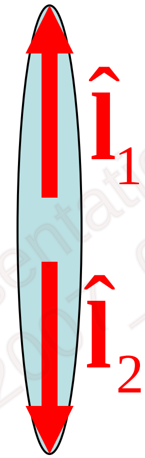
generalized orientational order parameter

Orientational Order Parameter (OOP)

- what is it?
  - configuration: position & orientation
    - OOP: descriptor of orientation
  - orientation of rigid body is defined by three Euler angles: *orientational distribution function* $P(\theta,\phi,\psi)$ has <u>all</u> info.
  - <u>too much</u> information!
- examples of OOP:
  - ferroelectric order parameter: $\mathbf{P} = P\hat{\mathbf{P}} = <\rho\mathbf{r}>$
  - nematic order parameter: $\mathbf{Q} = <\frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I})> = S\hat{\mathbf{n}}\hat{\mathbf{n}}$

Nematic liquid crystals

- orientational coordinate?
  - two equivalent directions:



- expressions which treat these the same:

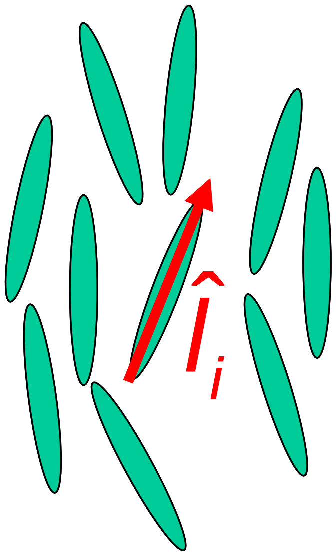
$$\xcancel{\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2} = 0!$$

$$\frac{1}{2}(\hat{\mathbf{l}}_1\hat{\mathbf{l}}_2 + \hat{\mathbf{l}}_2\hat{\mathbf{l}}_1) = -\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1 = -\hat{\mathbf{l}}_2\hat{\mathbf{l}}_2 = -\hat{\mathbf{l}}\hat{\mathbf{l}}$$

$$\xcancel{\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2\hat{\mathbf{l}}_2\hat{\mathbf{l}}_2} \quad \text{not necessary}$$

symmetry allowed orientational coordinate: $\hat{\mathbf{l}}\hat{\mathbf{l}}$

Nematic liquid crystals



- order parameter:
  - expectation value of orientational coordinate
  - subtract isotropic value
  - normalize

$$\langle \hat{\mathbf{l}}\hat{\mathbf{l}} \rangle$$

$$\langle \hat{\mathbf{l}}\hat{\mathbf{l}} \rangle - \mathbf{I}/3$$

$$Q = \langle \frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I}) \rangle$$

- $\langle \hat{\mathbf{l}}\hat{\mathbf{l}} \rangle$ is second rank tensor

- eigenvectors:
  - direction of alignment
- eigenvalues:
  - degree of orientational order

Nematic liquid crystals

$$<\hat{\mathbf{l}}\hat{\mathbf{l}}>=<\begin{bmatrix} l_x^{\,2} & l_x l_y & l_x l_z \\ l_y l_x & l_y^{\,2} & l_y l_z \\ l_z l_x & l_z l_y & l_z^{\,2} \end{bmatrix}>$$

– 6-1 = 5 constants

– trace = 1

- Diagonalize:

$$<\hat{\mathbf{l}}\hat{\mathbf{l}}>=<\begin{bmatrix} l_x^{\,2} & 0 & 0 \\ 0 & l_y^{\,2} & 0 \\ 0 & 0 & l_z^{\,2} \end{bmatrix}>$$

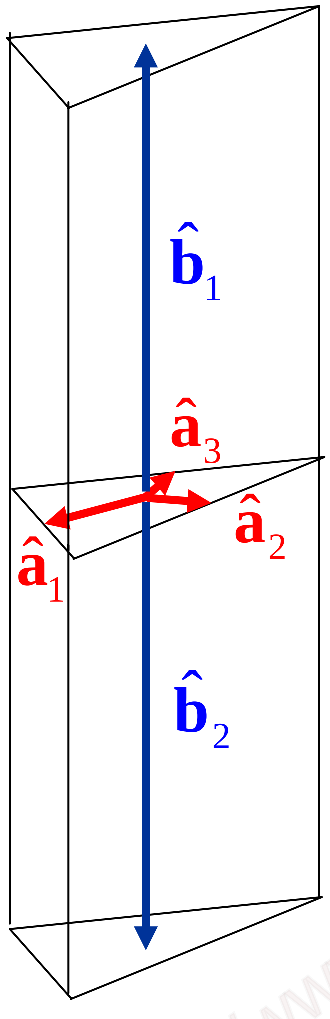
– 3 eigenvalues

– 3 Euler angles

– trace = 1

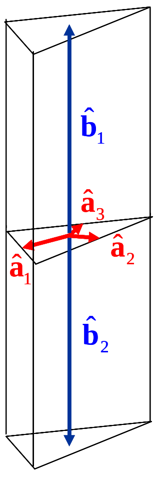
- can represent elements in terms of spherical harmonics

Triangular Prism



- cross-section: equilateral
- $\hat{a}$'s are unit vectors from center of 'mass' to centers of rectangular faces
- $\hat{a}_1$, $\hat{a}_2$ and $\hat{a}_3$ are equivalent
- $\hat{b}$'s are unit vectors from center of mass to centers of triangular faces
- $\hat{b}_1$, $\hat{b}_2$ and $\hat{b}_3$ are equivalent

Triangular Prism: multipole expansion

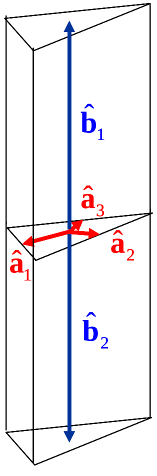


$$P(\theta,\phi,\psi) = P(\hat{\mathbf{a}}_1, \hat{\mathbf{b}}_2)$$

expand:

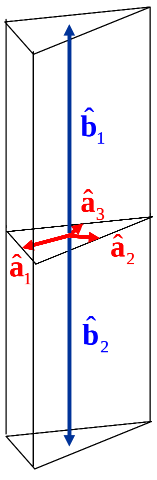
or:

Triangular Prism



$$P(\hat{\mathbf{a}}_1, \hat{\mathbf{b}}_2) = P(\hat{\mathbf{a}}_1, \hat{\mathbf{b}}_1) = \frac{1}{2}(P(\hat{\mathbf{a}}_1, \hat{\mathbf{b}}_2) + P(\hat{\mathbf{a}}_1, \hat{\mathbf{b}}_1))$$

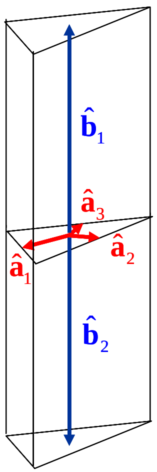
Triangular Prism



$$P(\hat{\mathbf{a}}_1,\hat{\mathbf{b}}_2)=\frac{1}{3}(P(\hat{\mathbf{a}}_1,\hat{\mathbf{b}}_2)+P(\hat{\mathbf{a}}_2,\hat{\mathbf{b}}_2)+P(\hat{\mathbf{a}}_3,\hat{\mathbf{b}}_2))$$

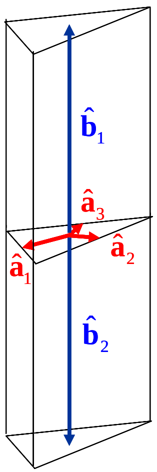
symmetry allowed orientational coordinates: $\hat{\mathbf{b}}\hat{\mathbf{b}}$ and $\hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}}$.

Triangular Prism



- order parameters:
  - expectation values of orientational coordinates $<\hat{\mathbf{b}}\hat{\mathbf{b}}>$ $<\hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}}>$
- $<\hat{\mathbf{b}}\hat{\mathbf{b}}>$ is second rank tensor
  - same as nematic (could use $<\hat{\mathbf{a}}\hat{\mathbf{a}}>$ since $<\hat{\mathbf{a}}\hat{\mathbf{a}}>=\frac{1}{2}(I-<\hat{\mathbf{b}}\hat{\mathbf{b}}>)$)
- $<\hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}}>$ is third rank tensor
  - eigenvectors?
  - eigenvalues?

Triangular Prism



- order parameters: $< \hat{\mathbf{b}}\hat{\mathbf{b}} >$ – nematic

  $< \hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}} >$ – new

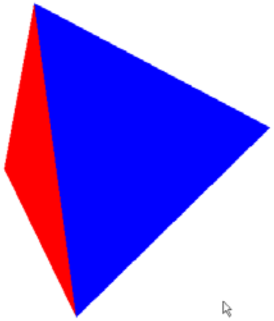
$$\hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}} = \{a_x^3, a_y^3, a_z^3, \\ a_x^2 a_y, a_x^2 a_z, a_y^2 a_x, a_y^2 a_z, a_z^2 a_x, a_z^2 a_y \\ a_x a_y a_z\}$$

- 10 constants
- decompositon ?

$$< \hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}} >_{iso.} = 0$$

- can represent elements in terms of spherical harmonics

Tetrahedron



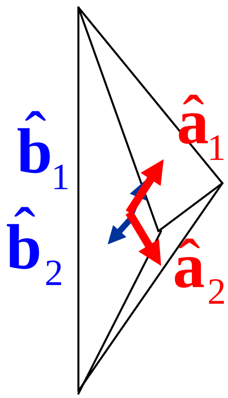
- expect $<\hat{n}\hat{n}\hat{n}\hat{n}>$

*in agreement with:

L.G. Fel, *Phys. Rev.* E **52**, 702 (1995)

H.R. Brand, H. Pleiner and P.E. Cladis, *Eur. Phys. J.* E, **7**, 163 (2002)

Irregular tetrahedron



same symmetry
as banana

- Here $c\hat{\mathbf{c}} = \hat{\mathbf{a}}_1 + \hat{\mathbf{a}}_2 + \hat{\mathbf{b}}_1 + \hat{\mathbf{b}}_2 \neq 0$

- order parameters are: $< \hat{\mathbf{c}} >$

$$< (\hat{\mathbf{a}}_1 - \hat{\mathbf{a}}_2)(\hat{\mathbf{a}}_1 - \hat{\mathbf{a}}_2) > \quad < (\hat{\mathbf{b}}_1 - \hat{\mathbf{b}}_2)(\hat{\mathbf{b}}_1 - \hat{\mathbf{b}}_2) >$$

$$< \mathbf{a}_1\mathbf{a}_1\mathbf{a}_1 + \mathbf{a}_2\mathbf{a}_2\mathbf{a}_2 > \quad < \mathbf{b}_1\mathbf{b}_1\mathbf{b}_1 + \mathbf{b}_2\mathbf{b}_2\mathbf{b}_2 >$$

- …..etc.

- in agreement with:

T.C. Lubensky and L. Radzihovsky, *Phys. Rev*. E **66**, 031704 (2002)

Procedure to define orientational order parameters

- identify groups of equivalent vectors based on symmetry
  - i.e. $\{\hat{\mathbf{b}}_1, \hat{\mathbf{b}}_2\}$ and $\{\hat{\mathbf{a}}_1, \hat{\mathbf{a}}_2, \hat{\mathbf{a}}_3\}$ for triangular prism
- evaluate $P(\hat{\mathbf{a}}, \hat{\mathbf{b}}) = \frac{1}{N} \sum_{i,j} P(\hat{\mathbf{a}}_i, \hat{\mathbf{b}}_j)$ summing over all equivalent vectors
- order parameters are expectation values of lowest order orientational coordinates
  - i.e. $< \hat{\mathbf{b}}\hat{\mathbf{b}} >$ and $< \hat{\mathbf{a}}\hat{\mathbf{a}}\hat{\mathbf{a}} >$ for triangular prism

Outstanding questions

- decomposition of higher order tensors
  - generalization of eigenvectors & eigenvalues, or??
- measurement of higher order OOPs
  - nonlinear susceptibilities, or ??
- what is phase behavior of systems with such order parameters?

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eigenvalue expansion
of
tensors of arbitrary rank

Standard eigenvalue problem

– Given $\mathbf{A}$, find $\mathbf{x}$ and λ

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$$

- in indicial notation,

$$A_{\alpha\beta} x^r_\beta = \lambda x^r_\alpha .$$

&

$$x^l_\alpha A_{\alpha\beta} = \lambda x^l_\beta .$$

and then we can write

$$A_{\alpha\beta} = \sum_i \lambda_i \hat{x}^r_{i\alpha} \hat{x}^l_{i\beta} .$$

Standard eigenvalue problem

- essential features:
  - eigenvalues λ_i are independent of coordinate system

- tensor $\leftrightarrow$ purse; eigenvalues $\leftrightarrow$ money inside

Standard eigenvalue problem

- essential features:
  - eigenvalues λ_i are independent of coordinate system

- free energy has the form

$$\mathcal{F} = \frac{1}{2} a A_{\alpha\beta} A_{\alpha\beta} + \frac{1}{3} b A_{\alpha\beta} A_{\beta\gamma} A_{\gamma\alpha} + \frac{1}{4} c (A_{\alpha\beta} A_{\alpha\beta})^2 + ..$$

  - and

$$A_{\alpha\beta} A_{\alpha\beta} = \lambda_1^{\ 2} + \lambda_2^{\ 2} + \lambda_3^{\ 2} \qquad A_{\alpha\beta} A_{\beta\gamma} A_{\gamma\alpha} = \lambda_1^{\ 3} + \lambda_2^{\ 3} + \lambda_3^{\ 3}$$

- Minimize free energy, get phase behavior.

Question: can we generalize this?

– consider $\mathbf{Ax} = \lambda \mathbf{x}$

if $\mathbf{A}$ is of rank 4.

If $\mathbf{x}$ is a vector, then λ must be a rank 2 tensor.

If $\mathbf{x}$ is a rank two tensor, then λ must be a scalar.

$$\text{rank}(\mathbf{x}) = \frac{1}{2}\text{rank}(\mathbf{A})$$

We need to solve:

$$A_{\alpha\beta\gamma\delta} x^{r}_{\gamma\delta} = \lambda x^{r}_{\alpha\beta}$$

Strategy:

- original

$$A_{\alpha\beta\gamma\delta} x^{r}_{\gamma\delta} = \lambda x^{r}_{\alpha\beta}$$

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$$A_{\alpha\beta\gamma\delta} x^{r}_{\gamma\delta} = \lambda x^{r}_{\alpha\beta}$$

scalar product

Strategy:

- original

$$A_{\alpha\beta\gamma\delta} x^r_{\gamma\delta} = \lambda x^r_{\alpha\beta}$$

- observe

$$B_{\alpha\beta} C_{\alpha\beta} = \tilde{\mathbf{B}} \cdot \tilde{\mathbf{C}}.$$

scalar product

$$\tilde{\mathbf{B}} = (B_{11}, B_{12}, B_{13}, B_{21}, B_{22}, B_{23}, B_{31}, B_{32}, B_{33})$$

$$\tilde{\mathbf{C}} = (C_{11}, C_{12}, C_{13}, C_{21}, C_{22}, C_{23}, C_{31}, C_{32}, C_{33}).$$

Strategy: unfold

$$A_{\alpha\beta\gamma\delta} x^{r}_{\gamma\delta} = \lambda x^{r}_{\alpha\beta}$$

- unfold:

vector in 9D $\tilde{x}^{r}_{\phi} = x^{r}_{\gamma\delta},$

rank 2 tensor in 9D $\tilde{A}_{\theta\phi} = A_{\alpha\beta\gamma\delta}.$

standard eigenvalue problem in 9D $\tilde{A}_{\theta\phi}\tilde{x}^{r}_{\phi} = \lambda \tilde{x}^{r}_{\theta},$

Strategy: unfold

$$A_{\alpha\beta\gamma\delta} x^r_{\gamma\delta} = \lambda x^r_{\alpha\beta}$$

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standard eigenvalue problem in 9D $\tilde{A}_{\theta\phi} \tilde{x}^r_{\phi} = \lambda \tilde{x}^r_{\theta},$

- solve for eigenvalues, eigenvectors;

Strategy: unfold, solve then fold

- fold:

$$x^r_{\gamma\delta} = \tilde{x}^r_{\phi}$$

$$A_{\alpha\beta\gamma\delta} = \tilde{A}_{\theta\phi}$$

$$A_{\alpha\beta\gamma\delta} x^r_{\gamma\delta} = \lambda x^r_{\alpha\beta}$$

- have eigenvalues, eigentensors.

Eigenvalue expansion:

- also have

$$A_{\alpha\beta\gamma\delta} = \sum_{i=1}^{9} \lambda_i \hat{x}^r_{i\alpha\beta} \hat{x}^l_{i\gamma\delta}$$

  - left and right eigentensors belonging to different eigenvalues are orthogonal;

$$A_{\alpha\beta\gamma\delta} A_{\gamma\delta\alpha\beta} = \sum_{i=1}^{9} \lambda_i^{\ 2}$$

Can extend to even rank *r* in D-dim.

- unfold
- find eigenvales and eigentensors
- fold

$$A_{\alpha'\beta'\ldots\nu'\alpha\beta\ldots\nu} = \sum_{i=1}^{D^{r/2}} \lambda_i \hat{x}^{r}_{i\alpha'\beta'\ldots\nu'} \hat{x}^{l}_{i\alpha\beta\ldots\nu}$$

$$A_{\alpha'\beta'\ldots\nu'\alpha\beta\ldots\nu} A_{\alpha\beta\ldots\nu\alpha'\beta'\ldots\nu'} = \sum_{i=1}^{D^{r/2}} \lambda_i^2 .$$

Tensors of odd rank

- have

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$$

$$\mathrm{rank}(\mathbf{x}) = \frac{1}{2}\mathrm{rank}(\mathbf{A})$$

- but rank($\mathbf{A}$) is odd!

Tensors of odd rank

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???????

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so

- make rank even by
  - augmenting rank with Levi-Civita
  - diminishing rank with Levi-Civita

Tensors of odd rank

– separate into tensors odd and even on outermost indices:

$$A_{\alpha\beta\gamma} = A^{s}_{\alpha\beta\gamma} + A^{a}_{\alpha\beta\gamma},$$

$$A^{s}_{\alpha\beta\gamma} = \frac{1}{2}(A_{\alpha\beta\gamma} + A_{\gamma\beta\alpha})$$

$$A^{a}_{\alpha\beta\gamma} = \frac{1}{2}(A_{\alpha\beta\gamma} - A_{\gamma\beta\alpha}).$$

Odd rank: symmetric part

– augment $$B_{\alpha\beta\gamma\delta} = A^s_{\alpha\nu\gamma}\varepsilon_{\beta\nu\delta}$$

– find eigenvalues & eigentensors as before

- $\tilde{\mathbf{B}}$ is odd; one eigenvalue is zero, other 8 are imag. & c.c.

– eigenvalue expansion

$$A^s_{\alpha\eta\gamma} = \frac{1}{2}\sum_{i=1}^{4}\lambda^s_{+i}\varepsilon_{\beta\eta\delta}\left(\hat{x}^r_{+i\alpha\beta}\hat{x}^l_{+i\gamma\delta} - \hat{x}^l_{+i\alpha\beta}\hat{x}^r_{+i\gamma\delta}\right)$$

&

$$A^s_{\alpha\eta\gamma}A^s_{\gamma\eta\alpha} = -\sum_{i=1}^{4}(\lambda^s_i)^2$$

Odd rank: antisymmetric part

– diminish

$$C_{\beta\delta} = A^a_{\alpha\beta\gamma}\varepsilon_{\delta\alpha\gamma}$$

– find eigenvalues & eigentensors as before

– eigenvalue expansion

$$A^a_{\eta\beta\mu} = \frac{1}{2}\sum_{i=1}^{3}\lambda_i^a \varepsilon_{\delta\eta\mu}\hat{x}^r_{i\beta}\hat{x}^l_{i\delta}$$

P.P-M and Xiaoyu Zheng, *e-LC. org*

Summary

- can find eigenvalues, etc. for tensors of arbitrary rank!

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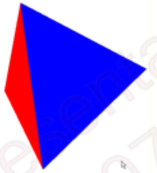
- what about tetrahedral LCs?



Summary

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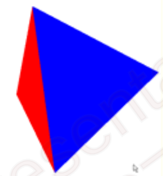


- order parameter: $$\mathbf{t} = \frac{1}{4} < (\hat{\mathbf{a}}_1\hat{\mathbf{a}}_1\hat{\mathbf{a}}_1 + \hat{\mathbf{a}}_2\hat{\mathbf{a}}_2\hat{\mathbf{a}}_2 + \hat{\mathbf{a}}_3\hat{\mathbf{a}}_3\hat{\mathbf{a}}_3 + \hat{\mathbf{a}}_4\hat{\mathbf{a}}_4\hat{\mathbf{a}}_4) >$$
- 4 eigenvalues
- corresponding phases??

the role of scalar invariants

Question:

- do eigenvalues tell the whole story?
  - yes, in case of
    - ferroelectrics (rank 1)
    - nematics (rank 2)
  - in general…..??? (peril?)

Question:

- do eigenvalues tell the whole story?
  - yes, in case of
    - ferroelectrics (rank 1)
    - nematics (rank 2)
  - in general…..???
- another approach:

group theory

scalar invariants

Tetrahedral order

- order parameter

$$\mathbf{t} = \frac{1}{4} < (\hat{\mathbf{a}}_1\hat{\mathbf{a}}_1\hat{\mathbf{a}}_1 + \hat{\mathbf{a}}_2\hat{\mathbf{a}}_2\hat{\mathbf{a}}_2 + \hat{\mathbf{a}}_3\hat{\mathbf{a}}_3\hat{\mathbf{a}}_3 + \hat{\mathbf{a}}_4\hat{\mathbf{a}}_4\hat{\mathbf{a}}_4) >$$

- fully symmetric traceless third rank tensor

4 scalar invariants:

• tensors	scalars	order
$t_{\alpha\beta\gamma}$	t^2	2
$Q_{\alpha\beta} = t_{\alpha\mu\nu} t_{\beta\mu\nu}$	Q^2	4
$v_{\alpha} = t_{\alpha\mu\nu} Q_{\mu\nu}$	v^2	6
$p_{\alpha\beta} = \varepsilon_{\alpha\mu\nu} v_{\mu} Q_{\beta\nu}$	p^2	10

pseudotensor

4 scalar invariants:

tensors	scalars	order
$t_{\alpha\beta\gamma}$	t^2	2
$Q_{\alpha\beta} = t_{\alpha\mu\nu} t_{\beta\mu\nu}$	Q^2	4
$v_\alpha = t_{\alpha\mu\nu} Q_{\mu\nu}$	v^2	6
$p_{\alpha\beta} = \varepsilon_{\alpha\mu\nu} v_\mu Q_{\beta\nu}$	p^2	10

do these scalars correspond to the 4 eigenvalues?

4 scalar invariants:

tensors	scalars	order
$t_{\alpha\beta\gamma}$	t^2	2
$Q_{\alpha\beta} = t_{\alpha\mu\nu} t_{\beta\mu\nu}$	Q^2	4
$v_\alpha = t_{\alpha\mu\nu} Q_{\mu\nu}$	v^2	6
$p_{\alpha\beta} = \varepsilon_{\alpha\mu\nu} v_\mu Q_{\beta\nu}$	p^2	10

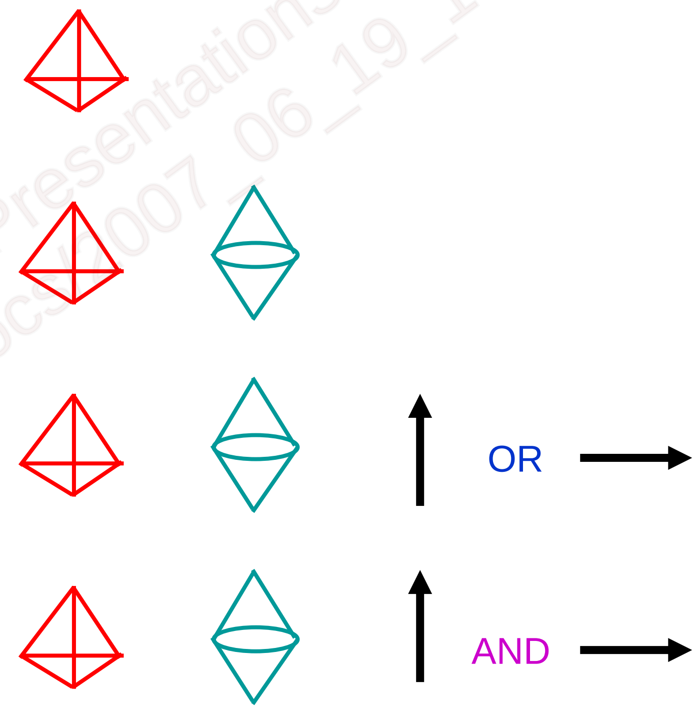
do these scalars correspond to the 4 eigenvectors?

perhaps not; secular equation for unfolded augmented matrix is 9th order!

Phase sequence possibility:

- tensors | scalars | order

tensors		scalars
$t_{\alpha\beta\gamma}$		$t^2 \neq 0$
$Q_{\alpha\beta} = t_{\alpha\mu\nu} t_{\beta\mu\nu}$	&	$Q^2 \neq 0$
$v_\alpha = t_{\alpha\mu\nu} Q_{\mu\nu}$	&	$v^2 \neq 0$
$p_{\alpha\beta} = \varepsilon_{\alpha\mu\nu} v_\mu Q_{\beta\nu}$	&	$p^2 \neq 0$



Summary

- proposed procedure to define orientational order parameters for variety of shapes
- provided scheme for eigenvalue decomposition for tensors of arbitrary rank
- identified scalar invariants of tetrahedral order parameter
- Questions:
  - identify phases & connections with scalar invariants
  - relate order parameter to experimental measurements