From Molecular Symmetry to Order Parameters

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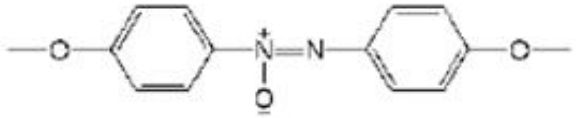
Phenomena and Classical Models

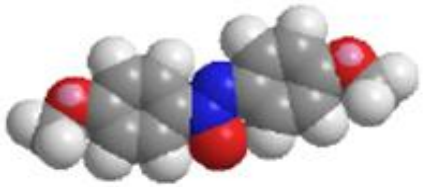
- Molecular symmetry and shape
- Different phases
- Defects
- Classical models

Molecules

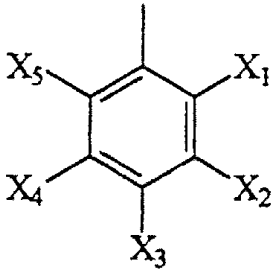
- Rigid rod /disk

PAA



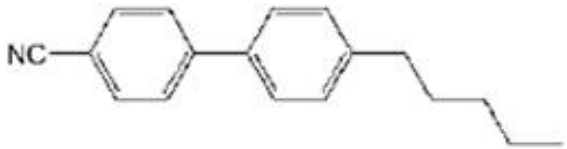


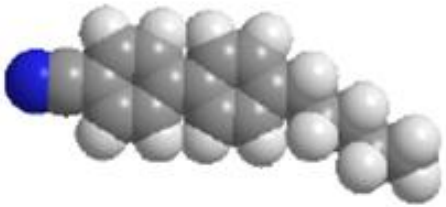
Hexasubstituted Phenylesters



- Polar molecule

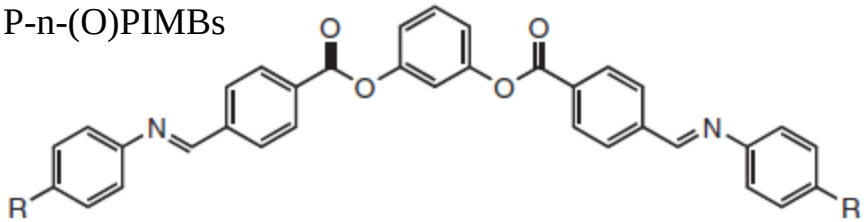
5CB

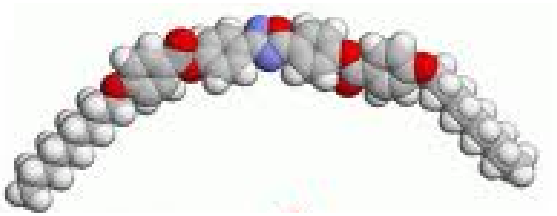




- Bent-core molecule

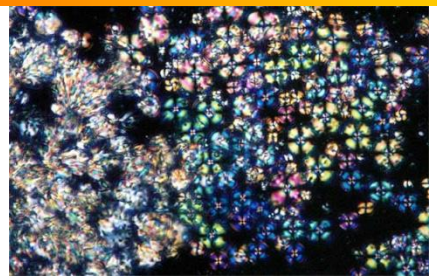
P-n-(O)PIMBs



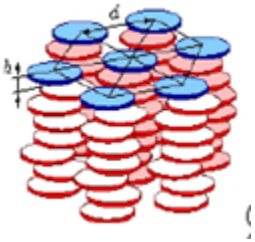


Phases

- Rod:

  I -> N  -phase transition-> S_A -> S_C

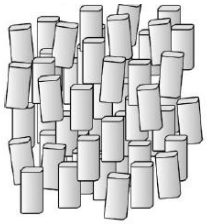
- Disk:

  I -> N -> Col. 

- Polar:

  I -> N* -> S_A* -> S_C* -> Blue

- Bent-core:

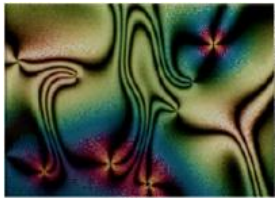
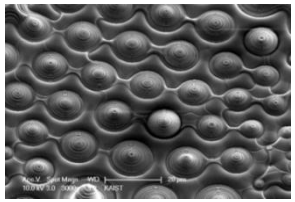
  biaxial nematic 

  I -> B1(Col.) -> B2(SmCP) ->…

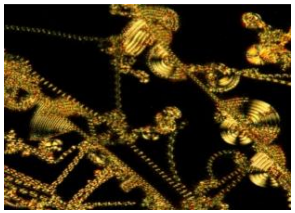
Defects

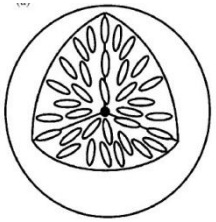
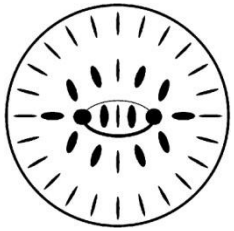
- Classification:

Point defects

Disclination Lines



- Inducement:
  1. Boundary condition
  2. Geometrical restriction

     Hairy ball theorem: There is no nonvanishing continuous tangent vector field on even dimensional n-spheres.
  3. Dynamics

- Question: Can defect be a stable or meta-stable state?

Classic Static Models

Rigid rod	Nematic	Smectic - A	Smectic - C
MM	[Ons], [MS], [Doi], [MG], [McM]	[McM]	
TM	[LG], [BM (LG*)]		
VM	[OF], [Eri], [CL]	[CL]	[CL]

[OF]: C.W. Oseen, *Transactions of the Faraday Society* , 29 (1933).
[Ons]: L. Onsager, *Ann NY. Acad. Sci.*, 51,627, (1949).
[MS]: W. Marer and A. Saupe, *Z. Naturf. a*,14a, 882, (1959); 15a, 287, (1960).
[McM]: W. L. McMillan, *Phys. Rev.* A4, 1238, (1971).
[CL]: J. Chen and T. Lubensky, *Phys. Rev. A*, 14, pp. 1202-1297, (1976).
[Doi]: M. Doi, *Journal of Polymer Science: Polymer Physics Edition*,19,229-243, (1981).
[Eri]: J.L. Ericksen, *Archive for Rational Mechanics and Analysis*,113 2,(1991).
[MG]: G. Marrucci and F. Greco, *Mol. Cryst. Liq. Cryst*, 206, 17-30, (1991).
[LG]: P.G. de Gennes and J. Prost, *Oxford University Press*, USA, (1995).
[BM]: J.M. Ball and A. Majumdar, *Oxford University Eprints archive* (2009).

Disk: Columnar (?)

Classic Static Models

Polar molecule:

Nematic* (Cholesterics) : Continuum theory (Oseen-Frank, etc.), Landau-de Gennes

Blue: de Gennes, P.G., *Mol. Cryst. Liquid Cryst.* 12, 193 (1971). Hornreich, R. M., Kugler, M., and Shtrikman, S. *Phys. Rev. Lett.* 48, 1404 (1982).

Smectic-A*, Smectic-C*: (?)

Bent-Core molecule:

Nematic (Uniaxial, Biaxial) : Geoffrey R. Luckhurst et.al, *Phys. Rev. E* 85 , 031705 (2012)

B1(Columnar): Arun Roy et.al, *PRL* 82, 1466 (1999)

B2(SmCP): Natasa Vaupotic et.al, *PRL* 98, 247802 (2007)

Questions:

- Representation for the configuration space?
- How to choose order parameters?
- Molecular model → Tensor model → Vector model?
- Stability of nematic phases?
- Modeling of smectic phases?

Molecular Symmetry

↓

Order Parameters

Configuration of a rigid molecule

- Body-fixed orthogonal frame $(\hat{O}; \boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$.
  Reference frame $(O; \boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)$.

- Determination of configuration: $\boldsymbol{x}_0 = \hat{O} - O$ and $P \in SO_3$

$$(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3) = (\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3)P$$

- Description of a fixed point on the molecule: coordinates in the body-fixed frame $\hat{\boldsymbol{x}}$.
  Its position in space:

$$\boldsymbol{x} = P\hat{\boldsymbol{x}} + \boldsymbol{x}_0$$

Density functional theory

- Virial expansion: valid when c is small

$$F[f] = F_0 + \frac{k_B T}{V}\left[\int \mathrm{d}P\mathrm{d}\boldsymbol{x} f(\boldsymbol{x}, P)\log f(\boldsymbol{x}, P) + \frac{1}{2}\int \mathrm{d}P\mathrm{d}\boldsymbol{x}\mathrm{d}P'\mathrm{d}\boldsymbol{x'} f(\boldsymbol{x}, P) G(\boldsymbol{x}, P, \boldsymbol{x'}, P') f(\boldsymbol{x'}, P')\right]$$

$$\frac{1}{V}\int \mathrm{d}P\mathrm{d}\boldsymbol{x} f(\boldsymbol{x}, P) = c$$

- Mayer function[1]

$$G(\boldsymbol{x}, P, \boldsymbol{x'}, P') = 1 - \exp(-U(\boldsymbol{x}, P, \boldsymbol{x'}, P')/k_B T)$$

$$U(\boldsymbol{x}, P, \boldsymbol{x'}, P') : \text{pairwise interaction}$$

- Higher density correction: Carnahan-Starling theory[2].

[1] J. E. Mayer and M. G. Mayer, **Statistical Mechanics**, Wiley, New York, (1940).

[2] N.F.Carnahan and K.E.Starling, **J. Chem. Phys**, 51, 635(1969)

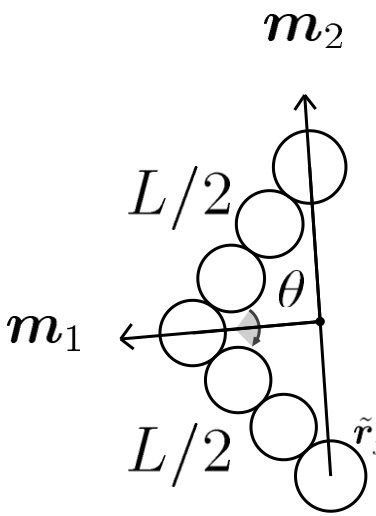
Pairwise interaction

We model the rigid molecule with spheres with radius r_0, distributed in space with probability density $\rho(\hat{\boldsymbol{x}})$.

$$U(\boldsymbol{x}, P, \boldsymbol{x'}, P') = \int\int \mathrm{d}\hat{\boldsymbol{x}}\mathrm{d}\hat{\boldsymbol{x}}'\rho(\hat{\boldsymbol{x}})V_0(|(P\hat{\boldsymbol{x}}+\boldsymbol{x})-(P'\hat{\boldsymbol{x}}'+\boldsymbol{x'})|)$$

- Hardcore potential: $V_0(r) = \begin{cases} 0, & r \geq 2\sigma_0, \\ +\infty, & r < 2\sigma_0. \end{cases}$
  For lyotropic liquid crystal.
- Lennard-Jones potential: $V_0(r) = 4\epsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}]$.
  For lyotropic and thermotropic liquid crystal.

Rod-like and bent-core molecules

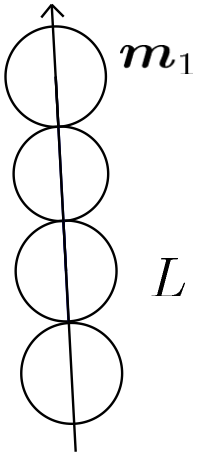


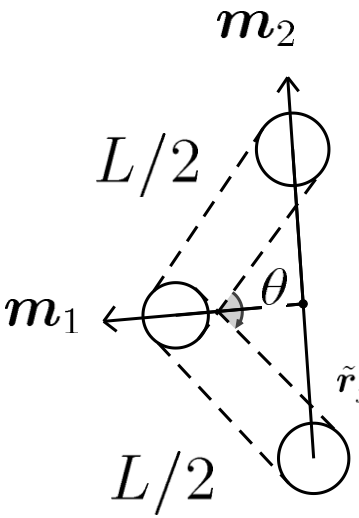
$$\rho(\hat{\boldsymbol{r}}) = \sum_{j=0}^{n} \delta(\hat{\boldsymbol{r}} - \tilde{\boldsymbol{r}}_j)$$

$$\tilde{\boldsymbol{r}}_j = L|s_j| \cos\frac{\theta}{2}\boldsymbol{m}_1 + Ls_j \sin\frac{\theta}{2}\boldsymbol{m}_2,\ s_j = \frac{j}{N} - \frac{1}{2}$$

$$\rho(\hat{\boldsymbol{r}}) = \sum_{j=0}^{n} \delta(\hat{\boldsymbol{r}} - \tilde{\boldsymbol{r}}_j)$$

$$\tilde{\boldsymbol{r}}_j = Ls_j\boldsymbol{m}_1,\ s_j = \frac{j}{N} - \frac{1}{2}$$



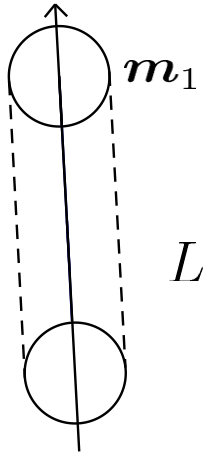


$$\rho(\hat{\boldsymbol{r}}) = \int_{-\frac{1}{2}}^{\frac{1}{2}} \delta(\hat{\boldsymbol{r}} - \tilde{\boldsymbol{r}}(s))$$

$$\tilde{\boldsymbol{r}}_j = L|s| \cos\frac{\theta}{2}\boldsymbol{m}_1 + Ls \sin\frac{\theta}{2}\boldsymbol{m}_2,\ s \in [-\frac{1}{2}, \frac{1}{2}]$$

$$\rho(\hat{\boldsymbol{r}}) = \int_{-\frac{1}{2}}^{\frac{1}{2}} \delta(\hat{\boldsymbol{r}} - \tilde{\boldsymbol{r}}(s))$$

$$\tilde{\ } = Ls\boldsymbol{m}_1,\ s \in [-\frac{1}{2}, \frac{1}{2}]$$



Properties of kernel function

- **Proposition.**

$$G(\boldsymbol{x}, P, \boldsymbol{x'}, P') = G(\boldsymbol{x'}, P', \boldsymbol{x}, P)$$

$$G(\boldsymbol{x}, P, \boldsymbol{x'}, P') = G(\boldsymbol{x} - \boldsymbol{x'}, P, P')$$

$$G(T(\boldsymbol{x} - \boldsymbol{x'}), TP, TP') = G(\boldsymbol{x} - \boldsymbol{x'}, P, P'), \ \forall T \in SO_3$$

- Define homogeneous kernel function

$$G(P, P') = \int \mathrm{d}\boldsymbol{x'} G(\boldsymbol{x} - \boldsymbol{x'}, P, P')$$

$G(P, P')$ is invariant with $\boldsymbol{x}$, thus well-defined.

Spatially homogeneous phases

- $f(\boldsymbol{r}, P) = cf(P)$. Using homogeneous kernel function:

$$\frac{F[f]}{c} = F_0 + k_B T \log c + k_B T \left[\int \mathrm{d}P f(P) \log f(P) + \frac{c}{2} \int \mathrm{d}P \mathrm{d}P' f(P) G(P, P') f(P') \right]$$

- **Proposition.** $G(P, P') = G(P^{-1}P') = G(\bar{P})$, where

$$\bar{P} = (p_{ij})_{3\times 3} = (\boldsymbol{m}_i \cdot \boldsymbol{m}'_j)_{3\times 3}.$$

and $G(\bar{P}) = G(\bar{P}^T)$.

Order parameters

- Molecular symmetries
  $\Rightarrow$ symmetries of kernel function
  $\Rightarrow$ symmetries of $f(P)$
  $\Rightarrow$ choice of order parameters.

- Symmetries of kernel function
  $\Rightarrow$ simplified form of kernel function
  $\Rightarrow$ (with intuitions from experiments and simulations) good approximation of kernel function
  $\Rightarrow$ reduction of order parameters.

- Molecular parameters
  $\Rightarrow$ coefficients in approximate kernel function
  $\Rightarrow$ further reduction of order parameters.

Properties of the homogeneous kernel function

Molecular symmetries lead to symmetries of G.

Theorem.

1. If a molecule is symmetric under T: $\rho(T\hat{\boldsymbol{r}}) = \rho(\hat{\boldsymbol{r}})$,

$$G(PT, P') = G(P, P') = G(P, P'T).$$

2. Reflection symmetry about a plane with normal vector $\hat{\boldsymbol{k}}$
$\Rightarrow G(PJ, P'J) = G(P, P')$
where J represents the rotation of π around $\hat{\boldsymbol{k}}$.

   In particular, when $\hat{\boldsymbol{k}} = \boldsymbol{m}_3$, $G = G(p_{11}, p_{12}, p_{21}, p_{22})$.

Properties of the homogeneous kernel function

Corollary.

- For bent-core molecules, G depends only on $p_{11}, p_{12}, p_{21}, p_{22}$, with

$$G(p_{11}, p_{12}, p_{21}, p_{22}) = G(p_{11}, p_{12}, -p_{21}, -p_{22}) = G(p_{11}, -p_{12}, p_{21}, -p_{22})$$

  and

$$G(p_{11}, p_{12}, p_{21}, p_{22}) = G(p_{11}, p_{21}, p_{12}, p_{22})$$

- For polar rods, G depends only on p_{11}.
- For non-polar rods, G depends only on $|p_{11}|$.

Moments as order parameters

Using moments $\langle \boldsymbol{m}_{i_1} \dots \boldsymbol{m}_{i_l} \rangle$ as order parameters.

Euler-Langrange equation

$$\lambda + f(P) + \int \mathrm{d}P' G(P, P') f(P') = 0$$

Theorem. If the molecule is symmetric under T, $f(P) = f(PT)$.
Corollary.

- For rod-like molecules, odd-order moments of $\boldsymbol{m}_1$ vanish.
- For bent-core molecules, moments with $\boldsymbol{m}_2$ and $\boldsymbol{m}_3$ occuring odd times vanish.

Polynomial approximations of kernel function

- Approximate G by a polynomial of p_{ij}.
  A term $p_{i_1 j_1} \dots p_{i_n j_n}$ leads to a product of two moments in the energy functional:

$$\langle \boldsymbol{m}_{i_1} \dots \boldsymbol{m}_{i_n} \rangle : \langle \boldsymbol{m}_{j_1} \dots \boldsymbol{m}_{j_n} \rangle$$

- By Euler-Langrangian equation, f is fully determined by these moments. They naturally become order parameters.

- Where to truncate is decided by the results of experiments and numerical simulations.

Polynomial approximations of kernel function

Symmetries of G decide non-vanishing terms.

- Rod-like molecules(nonpolar): p_{11}^2.
- Polar rods: p_{11}, p_{11}^2.
- Bent-core molecules:

  Below second order: $p_{11}, p_{11}^2, p_{22}^2, (p_{12}^2 + p_{21}^2)$.

  Third order: $p_{11}^3, p_{11}p_{22}^2, p_{11}(p_{12}^2 + p_{21}^2), p_{11}p_{12}p_{21}$.

The coefficients of these terms rely on temperature and molecular parameters. They also affect the choice of order parameters.

Rod-like molecules

- **Theorem.**[1,2,3] For Maier-Saupe potential of rods $G = cp_{11}^2$, f is axially symmetric:

$$\left\langle \mathbf{m}_1\mathbf{m}_1 - \frac{1}{3}\mathbf{I} \right\rangle = s(\mathbf{nn} - \frac{1}{3}\mathbf{I}). \boxed{+b(\mathbf{n}'\mathbf{n}' - \frac{1}{3}\mathbf{I})}$$

- The only order parameter is s.
- Consistent with experiments: uniaxial nematic is the only homogeneous phase found other than isotropic phase.

[1] H. Liu, H. Zhang and P. Zhang, **Comm. Math. Sci.**, 2005.

[2] I. Fatkullin and V. Slastikov, **Nonlinearity**, 2005.

[3] H. Zhou, H. Wang, M. G. Forest and Q. Wang, **Nonlinearity**, 2005.

Polar rods

- **Theorem.**[1] For polar rods $G = c_1 p_{11} + c_2 p_{11}^2$,

  1. $\langle \boldsymbol{m}_1 \rangle$ parallels to one of the eigenvectors of $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$.
  2. $\langle \boldsymbol{m}_1 \rangle = 0$ if $c_1 \leq 1$

- $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle = \frac{1}{3}\boldsymbol{I} + s(\boldsymbol{n}\boldsymbol{n} - \frac{1}{3}\boldsymbol{I}) + b(\boldsymbol{n}'\boldsymbol{n}' - \frac{1}{3}\boldsymbol{I})$ with $\boldsymbol{n} \perp \boldsymbol{n}'$.
  $\langle \boldsymbol{m}_1 \rangle = s_1 \boldsymbol{k}$ with $\boldsymbol{k} = \boldsymbol{n}, \boldsymbol{n}'$ or $\boldsymbol{n} \times \boldsymbol{n}'$.
  Three order parameters: s, b, s_1.

- Numerical results indicate stable phases give uniaxial $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$, suggesting two order parameters are sufficient.

[1] G.Ji, Q.Wang H.Zhou and P.Zhang, **Physics of Fluids**, 18, 123103 (2006).

Bent-core molecules

- **Theorem.** For bent-core molecules,

$$G = c_1 p_{11} + c_2 p_{11}^2 + c_3 p_{22}^2 + c_4 (p_{12}^2 + p_{21}^2)$$

  1. $\langle \boldsymbol{m}_1 \rangle = 0$ if $c_1 \leq 1$
  2. If $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$ and $\langle \boldsymbol{m}_2 \boldsymbol{m}_2 \rangle$ can be diagnolized simultaneously, $\langle \boldsymbol{m}_1 \rangle$ parallels to one of the eigenvectors of $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$.
  3. $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$ and $\langle \boldsymbol{m}_2 \boldsymbol{m}_2 \rangle$ can be diagnolized simultaneously when $c_1 \leq 1$ and $c_4^2 = c_2 c_3$.

- Assume that $\langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$ and $\langle \boldsymbol{m}_2 \boldsymbol{m}_2 \rangle$ can be diagnolized simultaneously, five order parameters are sufficient for bent-core molecules.

Molecular Model

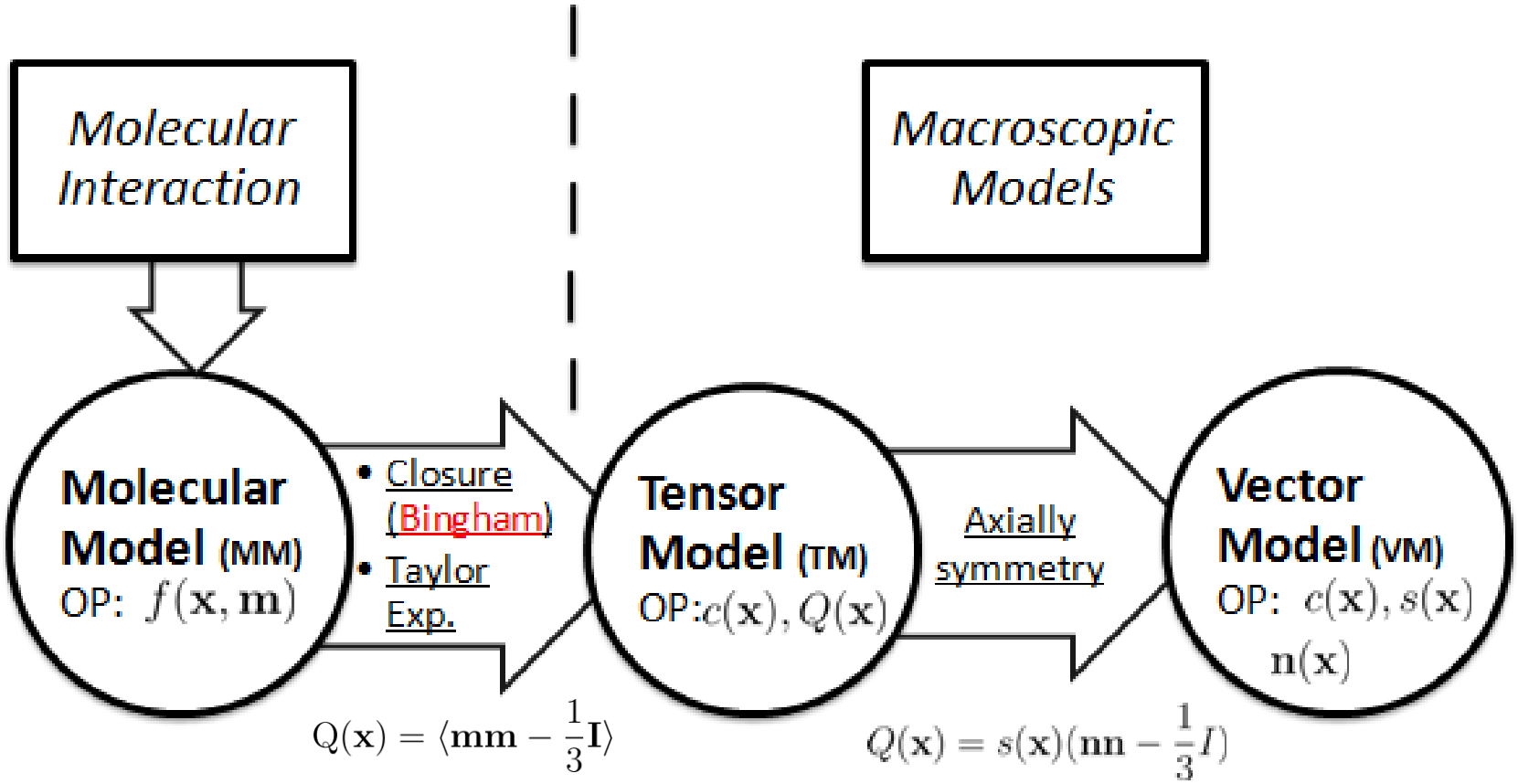
→

Tensor Model

→

Vector Model

Modelling



OP: Order Parameter

Bingham Closure

There are a variety of Closure Models:

- The quadratic closure (Doi closure):
- Two Hinch–Leal closures;
- Bingham closure:

$$f(\mathbf{x}, \mathbf{m}) = \frac{1}{Z} \exp(B_Q : \mathbf{mm})$$

where Z is the normalization constant:

$$Z(B_Q) = \int_{|\mathbf{m}|=1} \exp(B_Q : \mathbf{mm}) \, \mathrm{d}\mathbf{m}$$

$$Q = \int_{|\mathbf{m}|=1} \left(\mathbf{mm} - \frac{1}{3}\mathbf{I}\right) f_0 \, \mathrm{d}\mathbf{m} = \int_{|\mathbf{m}|=1} \left(\mathbf{mm} - \frac{1}{3}\mathbf{I}\right) \frac{1}{Z} \exp(B_Q : \mathbf{mm}) \, \mathrm{d}\mathbf{m}$$

Molecular Theory

Energy:

$$F = \int \rho(\mathbf{x},\mathbf{m}) \ln \rho(\mathbf{x},\mathbf{m}) \mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x} + \frac{\alpha}{2} \int \rho(\mathbf{x},\mathbf{m}) G(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}') \rho(\mathbf{x}',\mathbf{m}') \mathrm{d}\mathbf{m}'\mathrm{d}\mathbf{x}'\mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x}.$$

where

$$G(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}') = \begin{cases} 0, & \text{molecule}(\mathbf{x},\mathbf{m}) \text{ is disjoint with molecule}(\mathbf{x}',\mathbf{m}') \\ 1, & \text{joint with each other.} \end{cases} \quad \text{(hard core)}$$

or

$$G(\mathbf{m},\mathbf{m}',\mathbf{x}-\mathbf{x}') \text{ is derived from the Lennard-Jones potential.}$$

Let $\mathbf{r} = \mathbf{x} - \mathbf{x}'$. Using Taylor expansion:

$$\rho(\mathbf{x}',\mathbf{m}') = \rho(\mathbf{x},\mathbf{m}') + \mathbf{r} \cdot \nabla \rho(\mathbf{x},\mathbf{m}') + \frac{1}{2}\mathbf{r}\mathbf{r} : \nabla^2 \rho(\mathbf{x},\mathbf{m}') + \cdots .$$

Molecular Theory

$$F = \int \rho(\mathbf{x},\mathbf{m}) \ln \rho(\mathbf{x},\mathbf{m}) \mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x}$$
$$+ \frac{\alpha}{2} \int \rho(\mathbf{x},\mathbf{m}) G(\mathbf{m},\mathbf{m}',\mathbf{r}) \rho(\mathbf{x},\mathbf{m}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{m}'\mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x}$$
$$+ \frac{\alpha}{2} \int \rho(\mathbf{x},\mathbf{m}) G(\mathbf{m},\mathbf{m}',\mathbf{r}) \mathbf{r} \cdot \nabla \rho(\mathbf{x},\mathbf{m}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{m}'\mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x}$$
$$+ \frac{\alpha}{4} \int \rho(\mathbf{x},\mathbf{m}) G(\mathbf{m},\mathbf{m}',\mathbf{r}) \mathbf{r}\mathbf{r} : \nabla^2 \rho(\mathbf{x},\mathbf{m}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{m}'\mathrm{d}\mathbf{m}\mathrm{d}\mathbf{x} + \cdots .$$

Calculate $\int G(\mathbf{m},\mathbf{m}',\mathbf{r})\mathrm{d}\mathbf{r}, \quad \int G(\mathbf{m},\mathbf{m}',\mathbf{r})\mathbf{r}\mathrm{d}\mathbf{r}, \quad \int G(\mathbf{m},\mathbf{m}',\mathbf{r})\mathbf{r}\mathbf{r}^T\mathrm{d}\mathbf{r}, \quad \cdots .$

Bingham closure, truncation, → Tensor models.

Hard-core potential: Everything can be calculated exactly.

Interaction Region under Hard-Core Potential for Rodlike Molecules

EXAMPLE: Rigid rods with length *L* and diameter *D*. Both ends are half spheres.

For two rods with the direction **m** and **m'**, the interaction region is composed of three parts:

Body-body part: a parallelepiped whose intersection on one direction is a diamond

Body-end part: four half cylinders

End-end part: four corners, which compose a sphere with diameter *2D* together

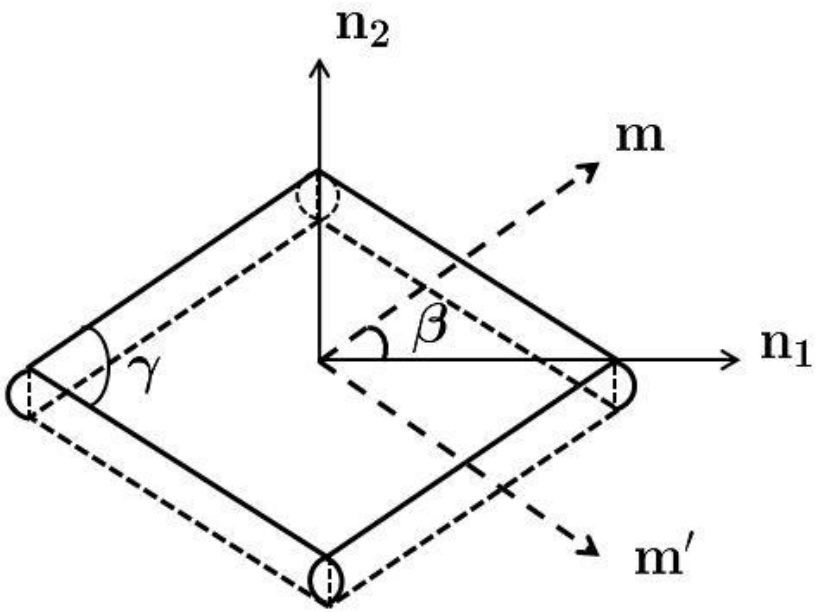


Figure: *Interaction region of hard rods under hard-core potential*

The Onsager Model and the Maier-Saupe Potential

The volume of interaction region:

$$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\ \mathrm{d}\mathbf{r} = 2L^2 D|\sin\gamma| + 2\pi D^2 L + \frac{4\pi}{3} D^3.$$

Taking Leading order in the situation $L >> D$, ➔ Onsager model:

$$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\ \mathrm{d}\mathbf{r} \approx 2L^2 D|\sin\gamma|.$$

If the kernel function is based on the Lennard Jones petential, in the sense of leading order, we have

$$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\ \mathrm{d}\mathbf{r} \approx H(L, D, T, \cos\gamma),$$

here T is the temerature. Expanding H (L,D,T, $\cos\gamma$) in orthognal polynomials w.r.t the last variable, we can obtain Maier-Saupe potential:

$$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\ \mathrm{d}\mathbf{r} \approx H_1(L, D, T) - H_2(L, D, T) P_2(\cos\gamma),$$

Second Moment

Return to the hard-core potential:

- First moment: $$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\mathbf{r}\ \mathrm{d}\mathbf{r} = 0.$$
- Second moment:

$$\int G(\mathbf{m}, \mathbf{m}', \mathbf{r})\mathbf{r}\mathbf{r}\ \mathrm{d}\mathbf{r} = L^4 D(A_1\mathbf{n}_1\mathbf{n}_1 + A_2\mathbf{n}_2\mathbf{n}_2 + A_3\mathbf{n}_3\mathbf{n}_3),$$

where the specific chosen Cartesian Coordinate is given by

$$\begin{cases} \mathbf{n}_1 = (\mathbf{m} + \mathbf{m}')/|\mathbf{m} + \mathbf{m}'|, \\ \mathbf{n}_2 = (\mathbf{m} - \mathbf{m}')/|\mathbf{m} - \mathbf{m}'|, \\ \mathbf{n}_3 = (\mathbf{m} \times \mathbf{m}')/|\mathbf{m} \times \mathbf{m}'|, \end{cases}$$

and ($\eta = D/L$)

$$A_1 = \left(\frac{\sin\gamma}{3} + \frac{2\pi\eta}{3} + \frac{4(\pi-\gamma)\eta^2}{3} + \frac{\pi\eta^3}{2}\right)\cos^2\beta + \left(\frac{4\sin\gamma\ \eta^2}{3} + \frac{\pi\eta^3}{2} + \frac{4\pi\eta^4}{15}\right),$$

$$A_2 = \left(\frac{\sin\gamma}{3} + \frac{2\pi\eta}{3} + \frac{4\gamma\eta^2}{3} + \frac{\pi\eta^3}{2}\right)\sin^2\beta + \left(\frac{4\sin\gamma\ \eta^2}{3} + \frac{\pi\eta^3}{2} + \frac{4\pi\eta^4}{15}\right),$$

$$A_3 = \frac{2\sin\gamma\eta^2}{3} + \frac{\pi\eta^3}{2} + \frac{4\pi\eta^4}{15}.$$

Decomposition of Second Moments

Furthermore,

$$\int G(\mathbf{m},\mathbf{m}',\mathbf{r})\mathbf{r}\mathbf{r}\ \mathrm{d}\mathbf{r}$$
$$=B_1(\mathbf{m},\mathbf{m}')\mathbf{I}+B_2(\mathbf{m},\mathbf{m}')(\mathbf{m}\mathbf{m}+\mathbf{m}'\mathbf{m}')+B_3(\mathbf{m},\mathbf{m}')(\mathbf{m}\mathbf{m}'+\mathbf{m}'\mathbf{m}),$$

where $(\sin\gamma=|\mathbf{m}\times\mathbf{m}'|)$

$$B_1(\mathbf{m},\mathbf{m}')=L^4D\left(\frac{2\sin\gamma\eta^2}{3}+\frac{\pi\eta^3}{2}+\frac{4\pi\eta^4}{15}\right),$$

$$B_2(\mathbf{m},\mathbf{m}')=L^4D\left(\frac{\sin\gamma}{6}+\frac{\pi\eta}{3}+\frac{\pi\eta^2}{3}+\frac{\pi\eta^3}{4}+\frac{2}{3\sin\gamma}\eta^2\right),$$

$$B_3(\mathbf{m},\mathbf{m}')=L^4D\left(\frac{(\pi-2\gamma)\eta^2}{3}-\frac{2\cos\gamma}{3\sin\gamma}\eta^2\right).$$

$$\frac{2\eta^2}{3}\frac{1}{|\mathbf{m}\times\mathbf{m}'|}\Big(\mathbf{m}\mathbf{m}+\mathbf{m}'\mathbf{m}'-(\mathbf{m}\cdot\mathbf{m}')(\mathbf{m}\mathbf{m}'+\mathbf{m}'\mathbf{m})\Big).$$

Orthogonal polynomial expansion

Let $x = \mathbf{m}' \cdot \mathbf{m}$, and $P_k(x)$ is the k-th Legendre polynomial, then:

$$|\mathbf{m} \times \mathbf{m}'| = \sqrt{1-x^2} = \frac{\pi}{4} - \frac{5\pi}{32} P_2(x) - \frac{9\pi}{256} P_4(x) + \cdots ,$$

$$\frac{1}{|\mathbf{m} \times \mathbf{m}'|} = \frac{1}{\sqrt{1-x^2}} = \frac{\pi}{2} + \frac{5\pi}{8} P_2(x) + \cdots ,$$

$$\frac{\arcsin x}{x} = \frac{\pi \ln 2}{2} + \frac{5\pi}{16}(3 - 4\ln 2) P_2(x) + \cdots .$$

Hence

$$\frac{1}{L^4 D} B_1(\mathbf{m}\cdot\mathbf{m}') = \frac{\pi\eta^2}{6} + \frac{\pi\eta^3}{2} + \frac{4\pi\eta^4}{15} - \frac{2\eta^2}{3}\cdot\frac{5\pi}{32} P_2(\mathbf{m}\cdot\mathbf{m}') - \frac{2\eta^2}{3}\cdot\frac{9\pi}{256} P_4(\mathbf{m}\cdot\mathbf{m}') \underbrace{+\cdots}_{\text{dropped}} ,$$

$$= \alpha_{11} + \alpha_{12} P_2(\mathbf{m}\cdot\mathbf{m}') + \alpha_{13} P_4(\mathbf{m}\cdot\mathbf{m}')$$

$$\frac{1}{L^4 D} B_2(\mathbf{m}\cdot\mathbf{m}') = \frac{\pi}{24} + \frac{\pi\eta(1+2\eta)}{3} + \frac{\pi\eta^3}{4} + (-\frac{5\pi}{3\cdot 64} + \frac{5\pi\eta^2}{12}) P_2(\mathbf{m}\cdot\mathbf{m}') \underbrace{+\cdots}_{\text{dropped}} ,$$

$$= \alpha_{21} + \alpha_{22} P_2(\mathbf{m}\cdot\mathbf{m}'),$$

$$\frac{1}{L^4 D} B_3(\mathbf{m}\cdot\mathbf{m}') = \eta^2 \mathbf{m}\cdot\mathbf{m}' \Big((\frac{\pi\ln 2}{3} - \frac{\pi}{3}) + (\frac{5\pi}{24} - \frac{5\pi\ln 2}{6}) P_2(\mathbf{m}\cdot\mathbf{m}') \Big) \underbrace{+\cdots}_{\text{dropped}} ,$$

$$= \alpha_{31} + \alpha_{32} P_2(\mathbf{m}\cdot\mathbf{m}').$$

Validity?

Stronger Singularity of Higher Moments

The complete fourth moment includes terms with high order coefficients like

$$\frac{1}{|\mathbf{m}\times\mathbf{m}'|^3}(\mathbf{mmmm}+\mathbf{m}'\mathbf{m}'\mathbf{m}'\mathbf{m}'),$$

$$\frac{1}{|\mathbf{m}\times\mathbf{m}'|^3}(\mathbf{mmm}'\mathbf{m})_{\mathrm{symmetric}},$$

$$\frac{\mathbf{m}\cdot\mathbf{m}'}{|\mathbf{m}\times\mathbf{m}'|^3}(\mathbf{mmmm}'+\mathbf{m}'\mathbf{m}'\mathbf{m}'\mathbf{m})_{\mathrm{symmetric}}.$$

Here $(\cdot)_{\mathrm{symmetric}}$ means the symmetrization of the concerning tensor. Notice that the sum of the above terms is not singular, but the Legendre polynomial expansion of

$$\frac{1}{\sin^3\gamma},\quad \frac{\cos\gamma}{\sin^3\gamma}$$

does not work. Taylor expansion works.

Q-tensor Model

Denote:

$$c(\mathbf{x}) = \int \rho(\mathbf{x}, \mathbf{m}) \mathrm{d}\mathbf{m}, \qquad \rho(\mathbf{x}, \mathbf{m}) = c(\mathbf{x}) f(\mathbf{x}, \mathbf{m}).$$

Introduce:

$$Q_{2ij}(\mathbf{x}) = \int (m_i m_j - \frac{1}{3}\delta_{ij}) f(\mathbf{x}, \mathbf{m}) \mathrm{d}\mathbf{m},$$

$$Q_{4ijkl}(\mathbf{x}) = \int \Big(m_i m_k m_j m_l - \frac{1}{7}\big(m_i m_j \delta_{kl} + m_i m_k \delta_{jl} + m_i m_l \delta_{jk} + m_k m_l \delta_{ij} + m_j m_l \delta_{ik} + m_j m_k \delta_{il}\big) + \frac{1}{35}\big(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}\big)\Big) f(\mathbf{x}, \mathbf{m}) \mathrm{d}\mathbf{m}.$$

With the complete second moment and leading order of the fourth moment, we can finally obtain a Q-tensor model based on the hardcore potential.

Q-tensor Model

$$
\begin{aligned}
& F[c(\mathbf{x}), Q_2(\mathbf{x})] \\
& = \int c(\ln c + B_Q : Q_2 - \ln Z)\mathrm{d}\mathbf{x} + \frac{\alpha}{2}\int E_1 c^2 + E_2|cQ_2|^2 + E_3|cQ_4|^2 \ \mathrm{d}\mathbf{x} \\
& \quad + \frac{\alpha}{2}\int \Big\{ J_1|\nabla c|^2 + J_2|\nabla(cQ_2)|^2 + J_3|\nabla(cQ_4)|^2 + J_4\ \partial_i(cQ_{2ij})\partial_j(c) \\
& F^{(1)}_{\text{elastic}} \quad + J_5\Big(\partial_i(cQ_{ik})\partial_j(cQ_{jk}) + \partial_i(cQ_{jk})\partial_j(cQ_{ik})\Big) + J_6\ \partial_i(cQ_{4ijkl})\partial_j(cQ_{2kl}) \\
& \quad + J_7\Big(\partial_i(cQ_{4iklm})\partial_j(cQ_{4jklm}) + \partial_i(cQ_{4jklm})\partial_j(cQ_{4iklm})\Big) \\
& F^{(2)}_{\text{elastic}} \quad + N_1|\nabla^2 c|^2 + N_2\ \partial_{ij}(cQ_{2ij})\partial_{kk}(c) \\
& \quad + N_3\ \partial_{ij}(cQ_{4ijkl})\partial_{kl}(c) + N_4\ \partial_{ij}(cQ_{2ij})\partial_{kl}(cQ_{2kl})\Big\}\mathrm{d}\mathbf{x}.
\end{aligned}
$$

Here $E_1 - E_3, J_1 - J_8, N_1 - N_4$ only depend on η. B_Q, Z, Q_4 is determined by Q_2 with Bingham closure.

- Lytropic liquid crystals.
- Only has two dimensionless parameters: $\alpha = \pi L^2 D c_0$ and $\eta = D/L$.

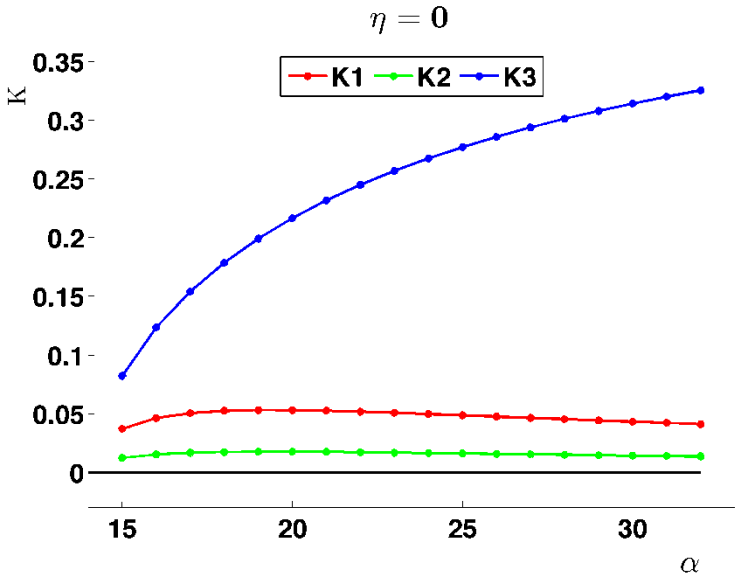
Vector Model

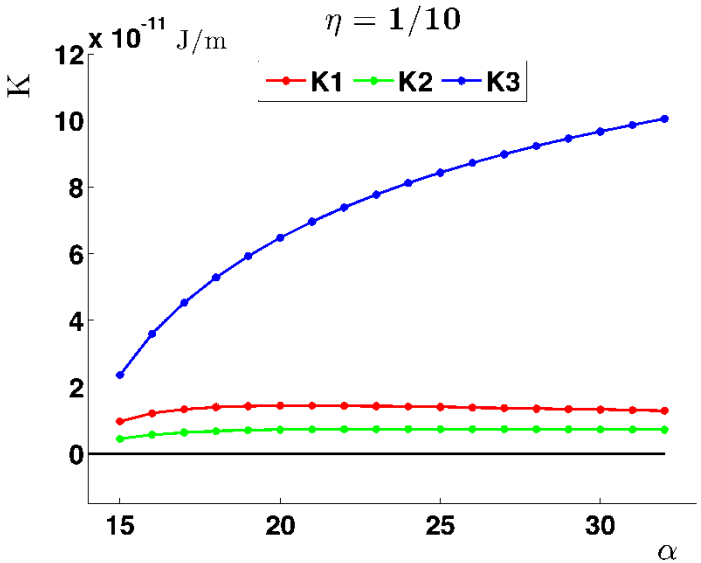
- Constant density ($c(\mathbf{x}) = c_0$ is constant);
- Uniaxial approximation; $\Longrightarrow$ Oseen-Frank Energy
- Neglect higher order derivatives energy (i.e. $F^{(2)}_{elastic}$).

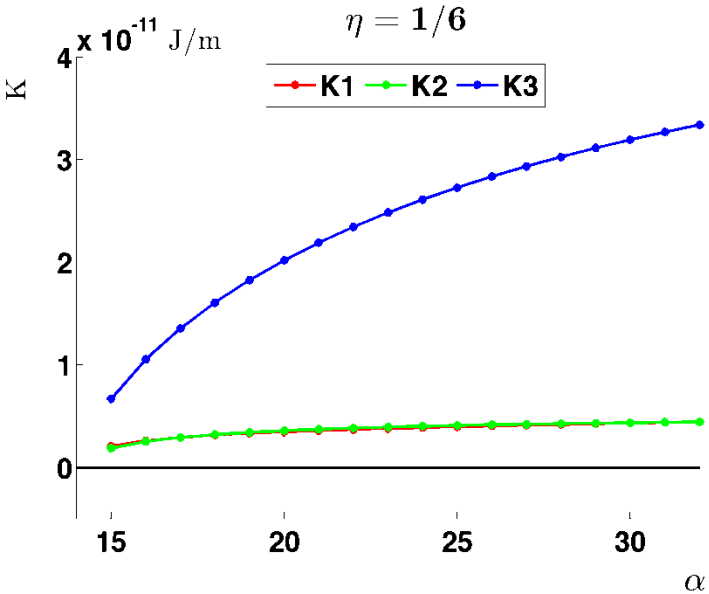
$$F^{(1)}_{elastic} = \frac{1}{2}\left(K_1(\nabla\cdot\mathbf{n})^2 + K_2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + K_3|\mathbf{n}\times(\nabla\times\mathbf{n})|^2\right),$$

$$\begin{aligned}
K_1 =& 2K_BTL^4Dc_0^2\pi\Big\{\Big(\frac{15}{224} - \frac{1131\eta^2}{784} + \frac{24\ln 2\eta^2}{49}\Big)S_2^2 + \Big(-\frac{221\eta^2}{64\cdot 49} + \frac{115\ln 2\eta^2}{49}\Big)S_4^2 \\
&+ \Big(-\frac{15}{224} + \frac{75\eta^2}{49} - \frac{90\ln 2\eta^2}{49}\Big)S_2S_4\Big\}, \\
K_2 =& 2K_BTL^4Dc_0^2\pi\Big\{\Big(-\frac{95\eta^2}{784} + \frac{5}{7\cdot 32} + \frac{15\eta^2\ln 2}{49}\Big)S_2^2 + \Big(\frac{495\eta^2}{64\cdot 49} + \frac{15\ln 2\eta^2}{49}\Big)S_4^2 \\
&+ \Big(-\frac{5}{224} + \frac{25\eta^2}{49} - \frac{30\ln 2\eta^2}{49}\Big)S_2S_4\Big\}, \\
K_3 =& 2K_BTL^4Dc_0^2\pi\Big\{\Big(\frac{15}{224} - \frac{1131\eta^2}{784} + \frac{24\ln 2\eta^2}{49}\Big)S_2^2 + \Big(-\frac{2155\eta^2}{64\cdot 49} + \frac{150\ln 2\eta^2}{49}\Big)S_4^2 \\
&+ \Big(\frac{20}{224} - \frac{100\eta^2}{49} + \frac{120\ln 2\eta^2}{49}\Big)S_2S_4\Big\}.
\end{aligned}$$

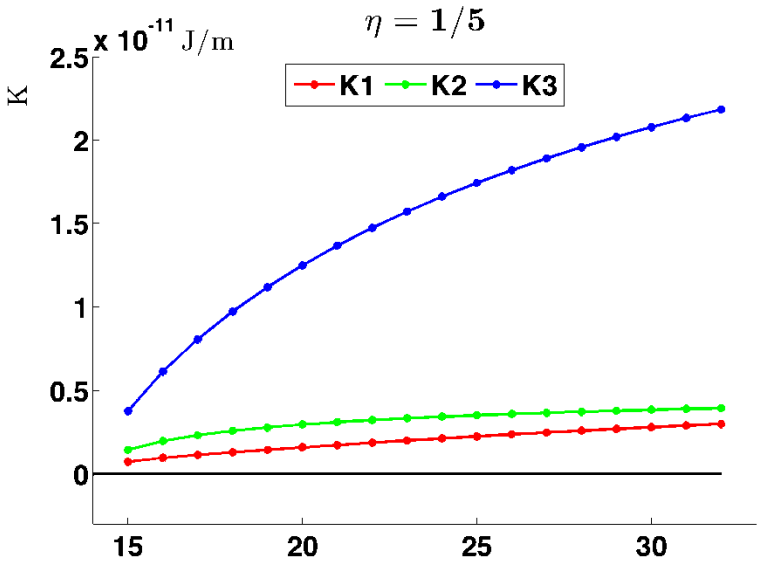
Stability of Nematic Phase

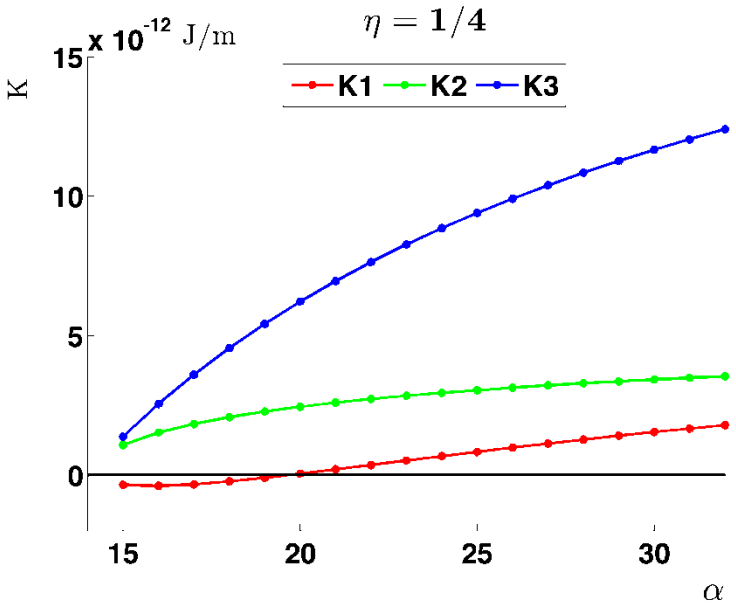


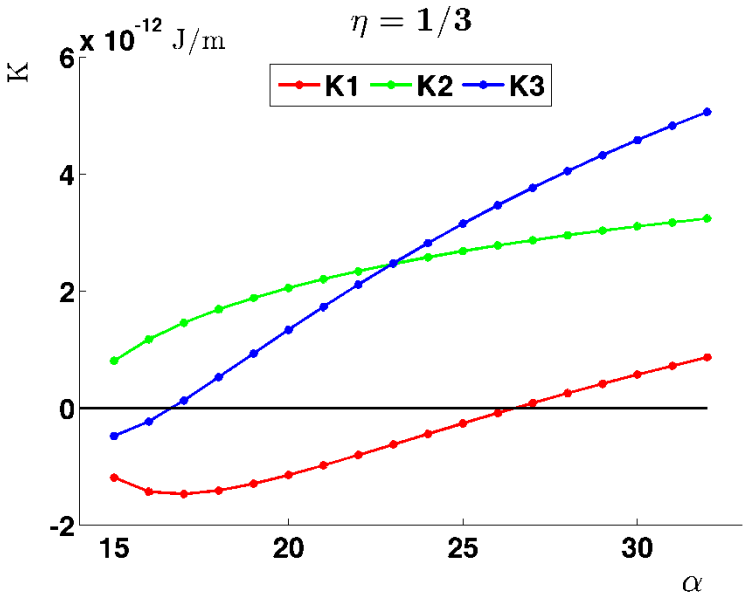




Stability of Nematic Phase







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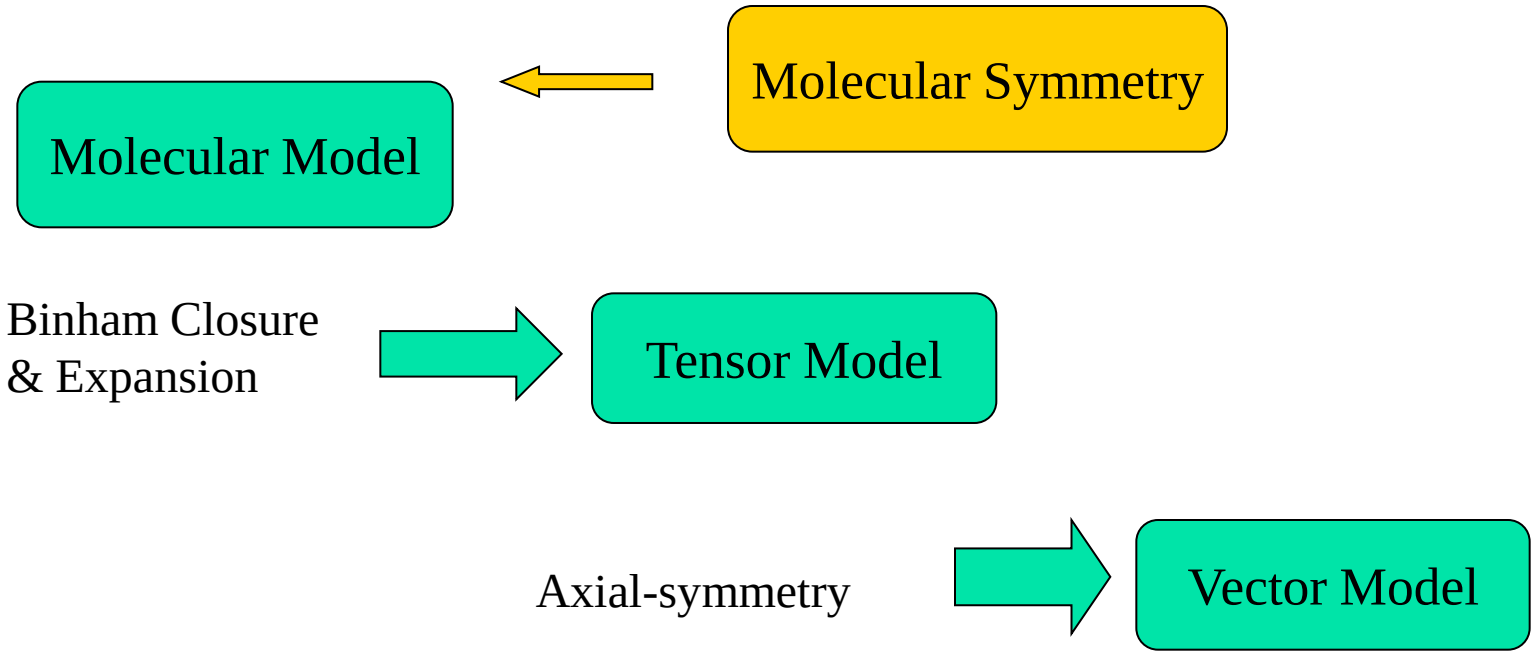
- Saupe, A. Z. *Naturforsch.* 15a, 1960
- Durand, G., Léger, L., Rondelez, F., and Veyssie, M. *Phys. Rev. Lett.*, 1969
- Orsay Liquid Crystal Group, *Liquid crystals and ordered fluids*, 1970.

The whole procedure can by applied to different-shape molecules.



Modeling for Smectic Liquid Crystals

1-Demensional Model for Smectic Liquid Crystals

Assume

- $Q_2 = s_2(\mathbf{nn} - \frac{1}{3}\mathbf{I})$;(uniaxial)
- $\mathbf{n} = (\cos\theta, \sin\theta, 0)$ is a constant vector;
- The density $c(\mathbf{x})$ only varies along x direction.

$\Rightarrow$ 1-Demensional Model for Smectic Phase

$$
\begin{aligned}
&F_{\eta,c_0}[\theta, h, c(x), s_2(x)] \\
=&\frac{1}{h}\Bigg\{\int_{-h}^{h} c(\ln c + \frac{2}{3}bs_2 - \ln Z)\,\mathrm{d}x \\
&+\frac{\alpha}{2}\int_{-h}^{h}\Big\{\tilde{E}_1 c^2 + \tilde{E}_2(cs_2)^2 + \tilde{E}_3(cs_4)^2 + \tilde{J}_1(c')^2 + \tilde{J}_2\big((cs_2)'\big)^2 + \tilde{J}_3\big((cs_4)'\big)^2 + \tilde{J}_4\ c'(cs_2)' \\
&\qquad + \tilde{J}_5(cs_2)'(cs_4)' + \tilde{N}_1(c'')^2 + \tilde{N}_2\ c''(cs_2)'' + \tilde{N}_3\ c''(cs_4)'' + \tilde{N}_4((cs_2)'')^2\Big\}\mathrm{d}x\Bigg\}.
\end{aligned}
$$

Here $\tilde{E}_1 \sim \tilde{E}_3, \tilde{J}_1 \sim \tilde{J}_5, \tilde{N}_1 \sim \tilde{N}_4$ depend on η and θ, and b, Z, s_4 is determined by s_2 under Bingham closure.

Other Related Works

Simulation

Simulation for Thermotropic Liquid Crystals

With the kernel function based on the Lennard-Jones potential, we can use the molecular model to study **thermotropic liquid crystals** in homogeneous situation.

- Boyle temperature
- Phase diagram
- Phase separation

The approach is applicable to different-shaped molecules, but the difficulty in complete molecular model is the calculation of high dimensional integral:

- Rigid rods & Polarized molecules:

$$\underset{\text{(kernel)}}{2} + \underset{\text{(space)}}{3} + \underset{\text{(direction)}}{3} = 8 \ \text{dimension}$$

- Disks:

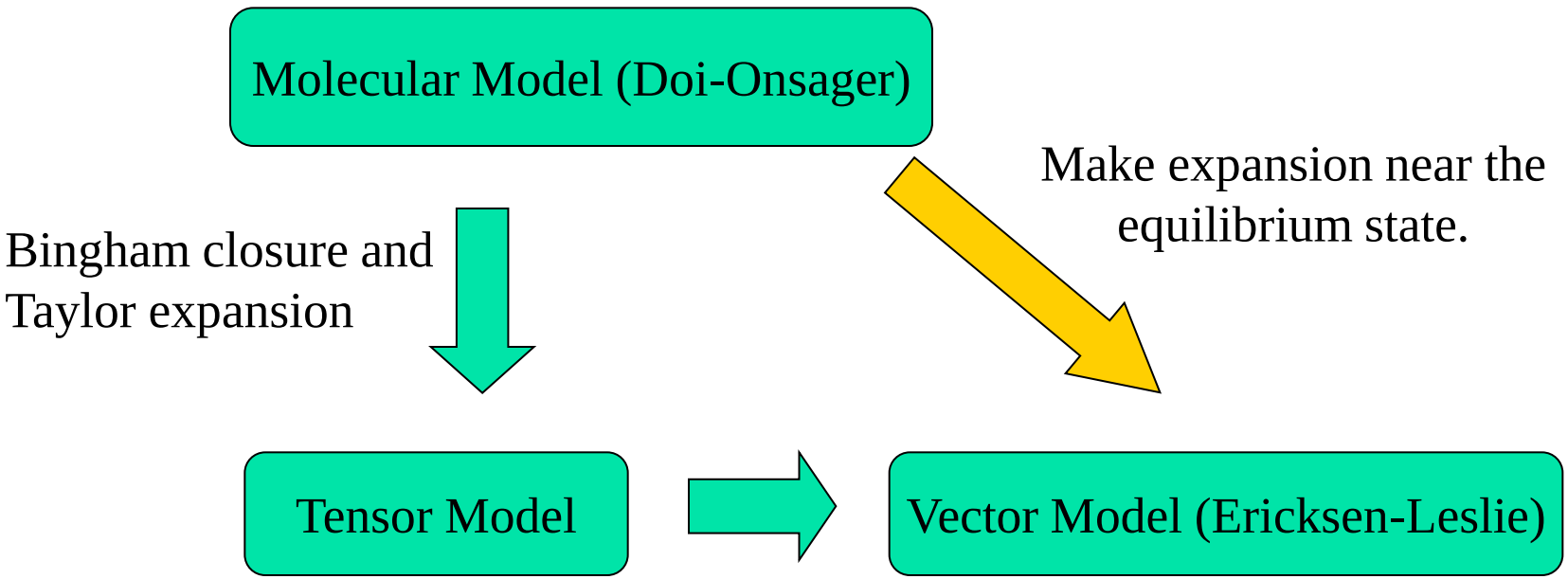
$$\underset{\text{(kernel)}}{4} + \underset{\text{(space)}}{3} + \underset{\text{(direction)}}{3} = 10 \ \text{dimension}$$

- Bent-core molecules:

$$\underset{\text{(kernel)}}{2} + \underset{\text{(space)}}{3} + \underset{\text{(direction)}}{5} = 10 \ \text{dimension}$$

Analysis

Dynamics



We can not assume axial-symmetry constrain as static case.
Have to make expansion near the equilibrium state.

Dynamical Model

Total energy:

$$E(Q) = \int -\ln Z_Q + Q : B_Q + \frac{\alpha}{2}\big(-|Q|^2 + G\varepsilon|\nabla Q|^2\big)\mathrm{d}\mathbf{x}.$$

Dynamical Q-tensor system:

$$\begin{aligned}
\frac{\partial Q}{\partial t} + \mathbf{v}\cdot\nabla Q &= \gamma_\perp\Big\{\Delta Q - \alpha\big(\Delta(M_Q^{(4)} : Q) - \frac{1}{3}\mathbf{I}\Delta(Q:Q)\big)\Big\} \\
&+ (\gamma_\parallel - \gamma_\perp)\Big\{(\nabla^2 : M_Q^{(4)} - \frac{1}{3}\mathbf{I}\nabla^2 : Q) - \alpha\big(\nabla^2 : (M_Q^{(6)} : Q) - \frac{1}{3}\nabla^2 : (M_Q^{(4)} : Q)\big)\Big\} \\
&+ \frac{1}{De}\Big(-6Q + 2\alpha\big[\frac{2}{3}Q + \frac{2}{3}G\varepsilon\Delta Q + 2Q\cdot Q + G\varepsilon(\Delta Q\cdot Q + Q\cdot\Delta Q) \\
&- 2\big(Q + G\varepsilon\Delta Q\big) : M_Q^{(4)}\big]\Big) + \big(\kappa\cdot Q + Q\cdot\kappa^T + \frac{2}{3}\mathbf{D} - 2\kappa : M_Q^{(4)}\big), \\
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v} &= \frac{\gamma}{Re}\Delta\mathbf{v} + \frac{1-\gamma}{2Re}\nabla\cdot(\mathbf{D} : M_Q^{(4)}) + \frac{1-\gamma}{DeRe}\Big\{\nabla\cdot\Big[-3Q \\
&+ 2\alpha\big\{\frac{1}{3}(Q + G\varepsilon\Delta Q) + Q\cdot Q + G\varepsilon Q\cdot\Delta Q - (Q + G\varepsilon\Delta Q) : M_Q^{(4)}\big\}\Big] + G\varepsilon Q : \nabla\Delta Q\Big\}.
\end{aligned}$$

- Deduced from the molecular model;
- Keep two kinds of diffusion: translational and rotational diffusion;
- Could derive Ericksen-Leslie model from it.

Dynamical Model Reduction

Molecular Model (Doi-Onsager) → Vector Model (Ericksen-Leslie)

$$f = f_0(\mathbf{m}\cdot\mathbf{n}(t,\mathbf{x})) + Def_1 + De^2 f_2 + De^3 f_3 + De^3 f_R, \quad \mathbf{v} = \mathbf{v}_0 + De\mathbf{v}_1 + De^2\mathbf{v}_2 + De^3\mathbf{v}_R.$$

Formal derivation ([KD], [EZ]): $(\mathbf{n}(t,\mathbf{x}), \mathbf{v}_0(t,\mathbf{x}))$ satisfies the Ericksen-Leslie equations.

Rigorous proof ([WZZ]): The remainder terms can be controlled.

Theorem (Convergence):
There exists $\varepsilon_0 > 0$, such that if $0 < De < \varepsilon_0$, and $(f_R, \mathbf{v}_R)$ are bounded at the initial time, then they will be bounded on $[0, T]$ before the singularity appears.

[KD] N. Kuzuu and M. Doi, **Journal of the Physical Society of Japan**, 52(1983), 3486-3494.
[EZ] W. E and P. Zhang, **Methods and Appications of Analysis**, 13(2006), 181-198.
[WZZ] Wei Wang, Pingwen Zhang and Zhifei Zhang, *The small Deborah number limit of the Doi-Onsager equation to the Ericksen-Leslie equation*, **arXiv:1206.5480,** submitted.

Defects

Defects on Spherical Surface

• Hairy ball theorem: There is no nonvanishing continuous tangent vector field on even dimensional n-spheres.

There must be defects if Liquid crystals are confined on the spherical surface .

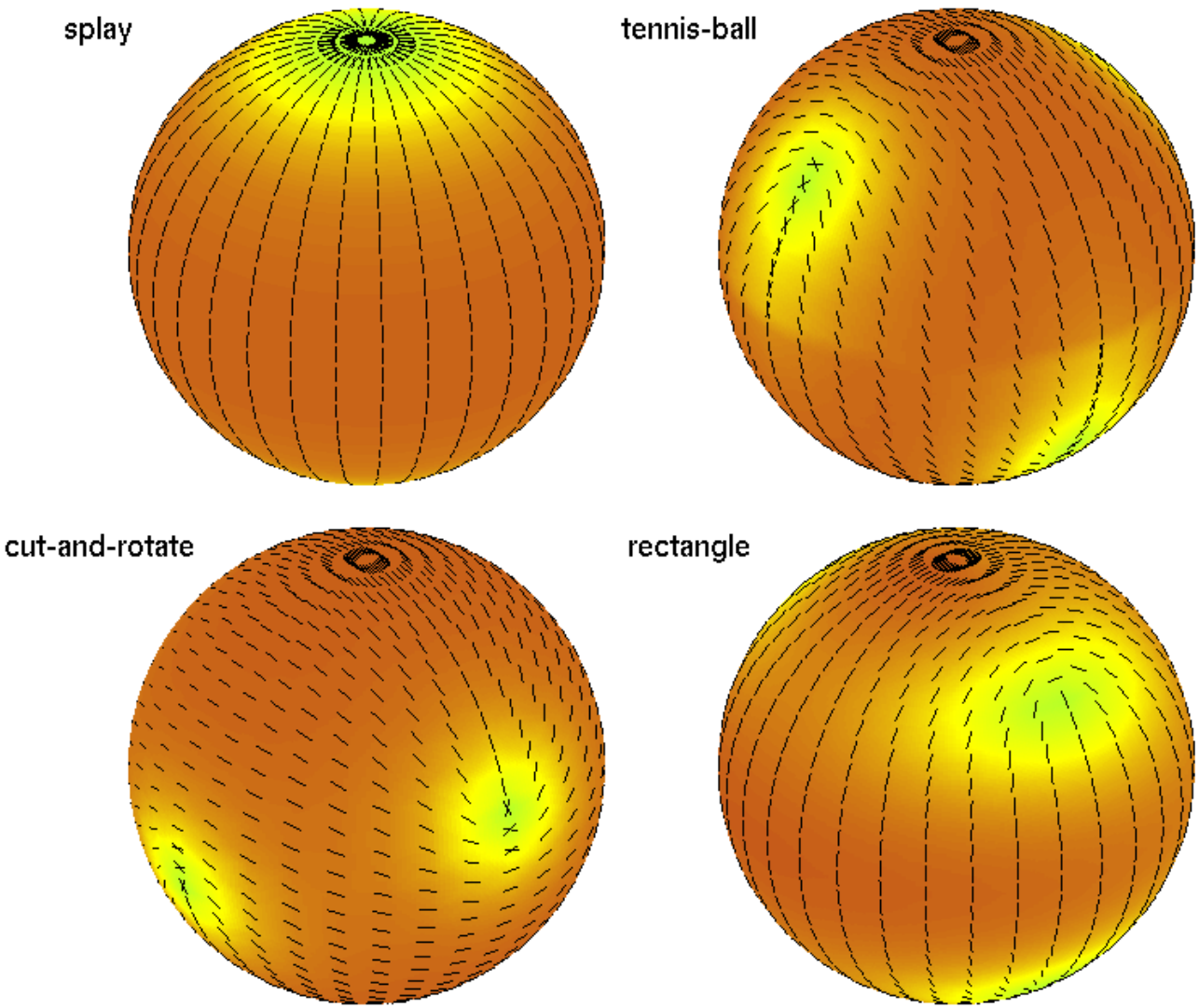
• Poincaré-Hopf theorem: The sum of indexes of all the defects must equal to the Euler characteristic number of the closed surface-two for a spherical surface.

[Ne] D. R. Nelson, **Nano Lett. 2**,1125(2002).
[KRV] S. Kralj, R. Rosso, and E. G. Virga, **Soft Matter 7**, 670(2011).
[ZJC] W. Y. Zhang, Y. Jiang, J. Z. Y. Chen, **Phys. Rev. Lett.** 108, 057801(2012).

Captured Configurations

Models:

- Molecular Model
- Tensor Model
- SCFT



Question: Which is more stable?

Collaborators

Professors:

Jeff Chen
Modelling &
Simulation

Weinan E
Modelling
& Analysis

Zhifei Zhang
Analysis

Students:

Hong Cheng
Simulation

Jiequn Han
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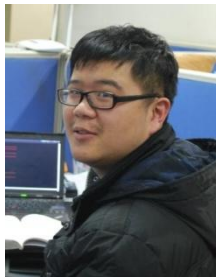
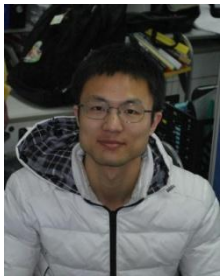


Yi Luo
Modelling



Yang Qu
Simulation

Wei Wang
Modelling
& Analysis

Jie Xu
Modelling &
Simulation

Weiquan Xu
Simulation

Shiwei Ye
Simulation