Onsager-theory-based tensor model for nematic phases of bent-core molecules

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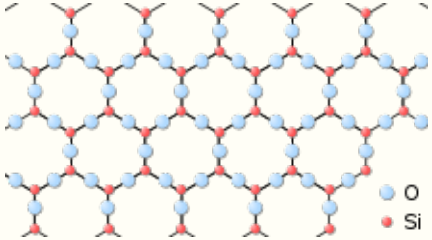
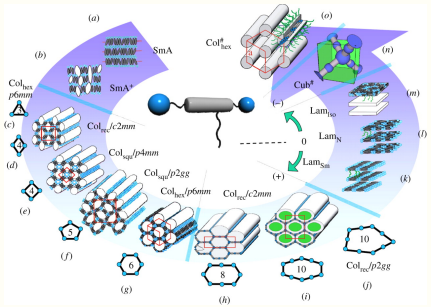
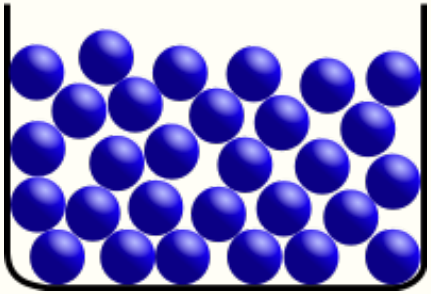
Nov. 27, 2017

Liquid crystals

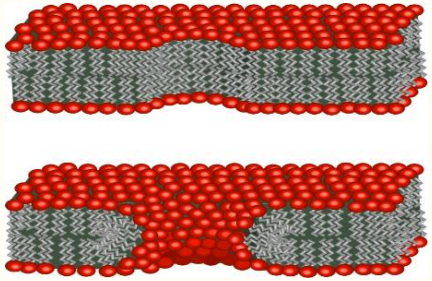
Solid: ordered $\leftrightarrow$ Liquid Crystals $\leftrightarrow$ Liquid: disordered

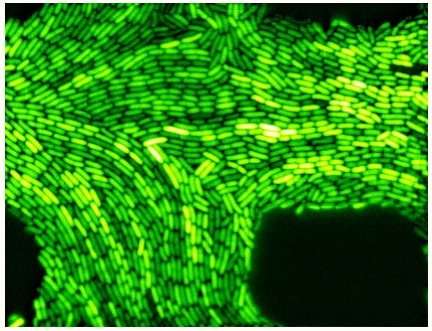


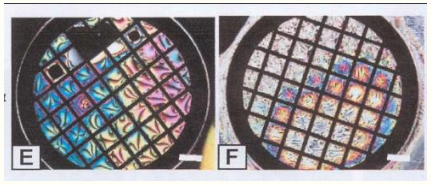




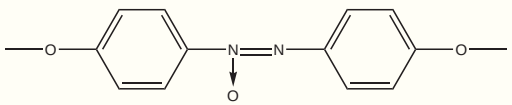
Display, Biology, Medical & Nano- materials



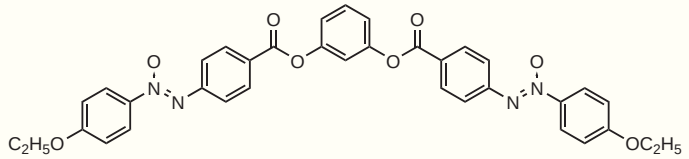




Rigid molecules

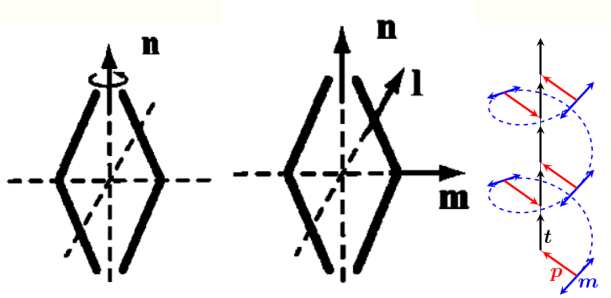


Rod-like molecules (achiral)

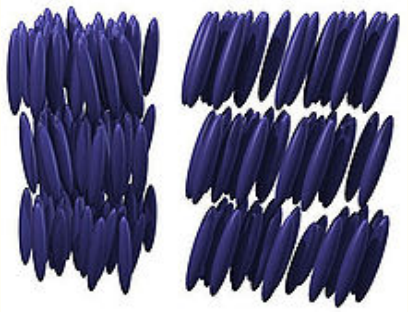


Bent-core molecules

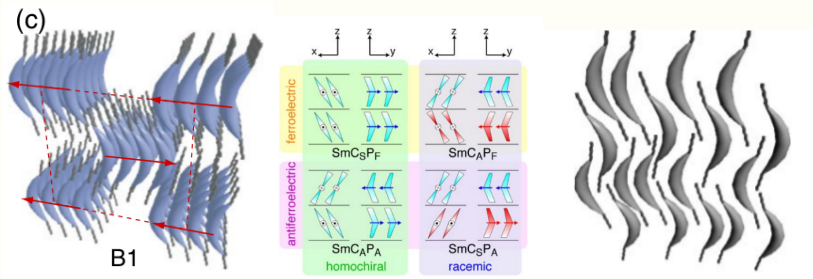
Nematic: only uniaxial



Uniaxial, Biaxial & modulated nematic phases



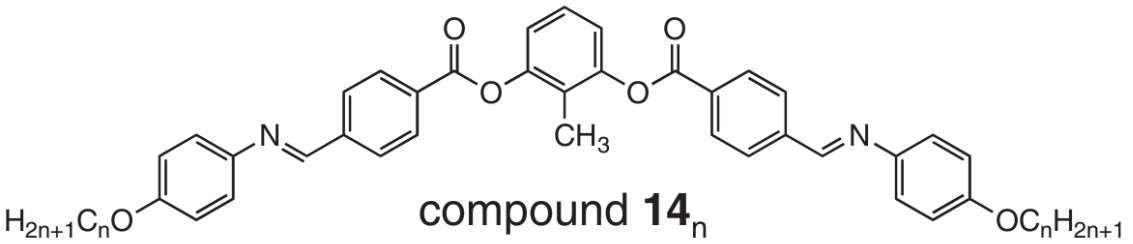
Smectic A & C



Polar & chiral structure

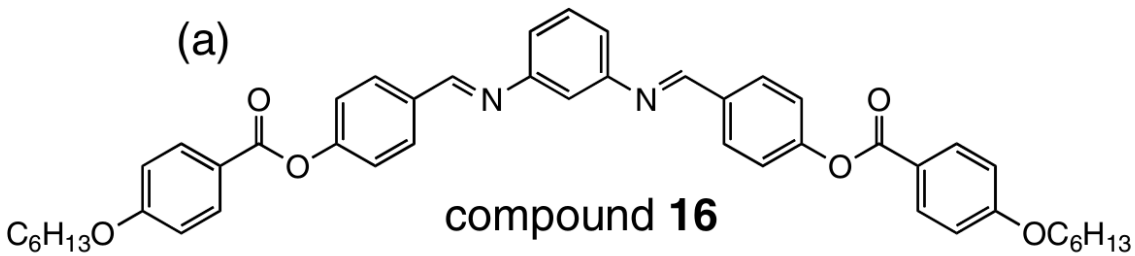
Features of bent-core molecules

Phase behaviors could vary with minor change on molecular architecture.



compound **14**$_n$

n = 8	Cryst.	161	B5	165	B2	172	Iso
n = 9	Cryst.	157	B5	163	B2	168	Iso
n = 10	Cryst.	153	B5	158	B2	167	Iso



compound **16**

Cryst. 134 B1 142 B6 148 Iso

Goal of Modeling: Microscopic interaction $\rightarrow$ Macroscopic phases & properties

Rods: models at different level

- Molecular model: $f(\boldsymbol{x}, \boldsymbol{m})$, $\boldsymbol{m} \in S^2$.

$$\frac{F[f]}{k_B T} = \int \mathrm{d}\boldsymbol{m} f \log f + \frac{c}{2} \int \mathrm{d}\boldsymbol{m}\mathrm{d}\boldsymbol{m'} f(\boldsymbol{m}) G(\boldsymbol{m}, \boldsymbol{m'}) f(\boldsymbol{m'}).$$

  MD/Monte-Carlo: time-consuming; small systems.

- Tensor model: $Q = \int \mathrm{d}\boldsymbol{m}\ (\boldsymbol{mm} - I/3) f(\boldsymbol{m}) = \langle \boldsymbol{mm} - I/3 \rangle$. Sketch of f.
  Landau-de Gennes.

$$F[Q] = \int \mathrm{d}\boldsymbol{x}\ a_2 \mathrm{tr}(Q^2) - a_3 \mathrm{tr}(Q^3) + a_4 (\mathrm{tr}(Q^2))^2$$
$$+ L_1 |\nabla Q|^2 + L_2 \partial_i Q_{jk} \partial_j Q_{ik} + L_3 \partial_i Q_{ik} \partial_j Q_{jk} + L_4 Q_{ij} \partial_i Q_{kl} \partial_j Q_{kl}.$$

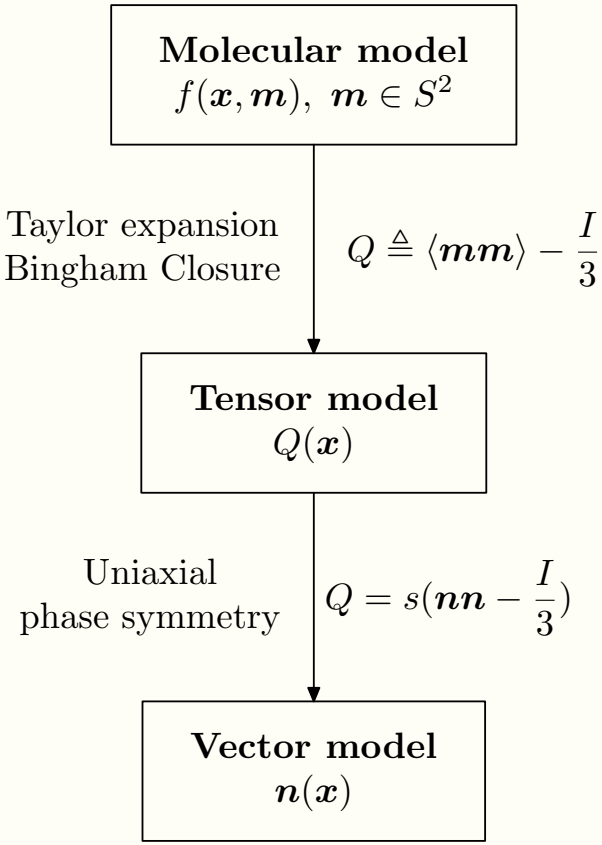
  Connection between phenomenological coefficients and molecular interaction?

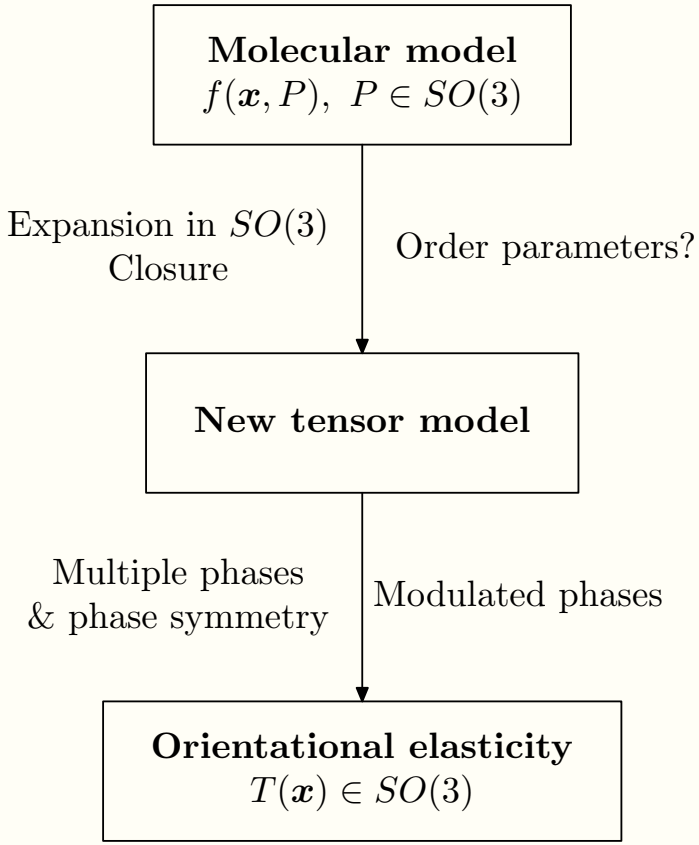
- Vector model: uniaxial $Q = s(\boldsymbol{nn} - I/3)$. Oseen-Frank.

$$F[\boldsymbol{n}] = \frac{1}{2} \int \mathrm{d}\boldsymbol{x}\ K_1 (\nabla \cdot \boldsymbol{n})^2 + K_2 (\boldsymbol{n} \cdot (\nabla \times \boldsymbol{n}))^2 + K_3 |\boldsymbol{n} \times (\nabla \times \boldsymbol{n})|^2.$$

  K_i: measurable elastic constants.
  Elasticity for the uniaxial nematic phase.

Systematic modeling





- Molecular symmetry $\longrightarrow$ Order parameters & Form of tensor model
- Phase symmetry $\longrightarrow$ Form of orientational elasticity
- Molecular parameters $\longrightarrow$ Coefficients in tensor model $\longrightarrow$ Elastic constants

J. Han, Y. Luo, W. Wang, P. Zhang and Z. Zhang, ARMA(2015).

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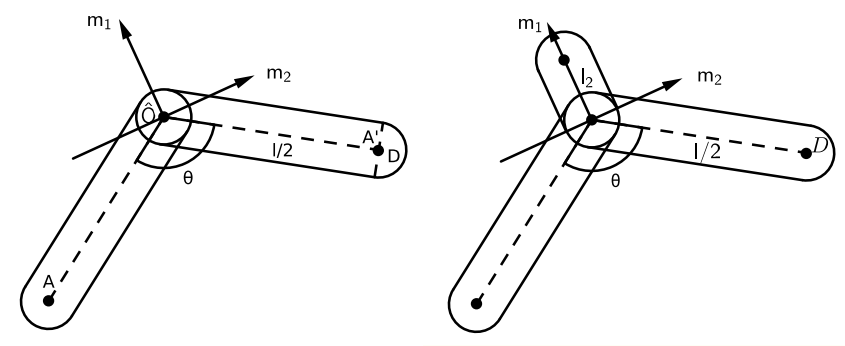
Representation of orientation



- Body-fixed frame: $(\hat{O}; \boldsymbol{m}_i)$. Density: $f(\boldsymbol{x}, P)$.

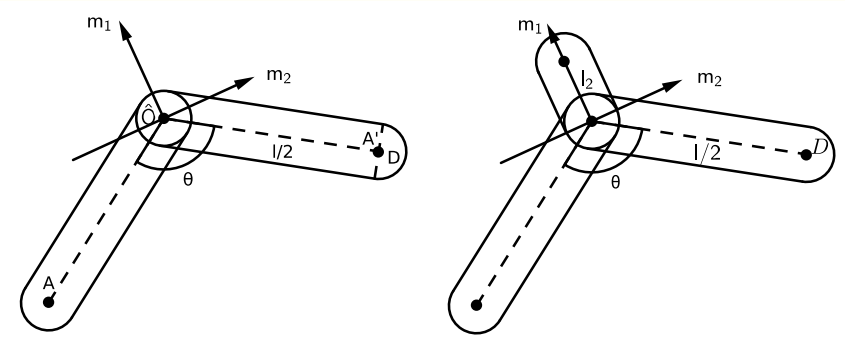
$$P = (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3) = \begin{pmatrix} m_{11} & m_{21} & m_{31} \\ m_{12} & m_{22} & m_{32} \\ m_{13} & m_{23} & m_{33} \end{pmatrix} \in SO(3).$$

- Representation by Euler angles:

$$\begin{pmatrix} \cos\alpha & -\sin\alpha\cos\gamma & \sin\alpha\sin\gamma \\ \sin\alpha\cos\beta & \cos\alpha\cos\beta\cos\gamma - \sin\beta\sin\gamma & -\cos\alpha\cos\beta\sin\gamma - \sin\beta\cos\gamma \\ \sin\alpha\sin\beta & \cos\alpha\sin\beta\cos\gamma + \cos\beta\sin\gamma & -\cos\alpha\sin\beta\sin\gamma + \cos\beta\cos\gamma \end{pmatrix}.$$

$$\mathrm{d}P = \frac{1}{8\pi^2}\sin\alpha \mathrm{d}\alpha\mathrm{d}\beta\mathrm{d}\gamma.$$

Order parameters: intuitive



- Body-fixed frame: $(\hat{O}; \boldsymbol{m}_i)$. Density: $f(\boldsymbol{x}, P)$.

$$P = (\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3) = \begin{pmatrix} m_{11} & m_{21} & m_{31} \\ m_{12} & m_{22} & m_{32} \\ m_{13} & m_{23} & m_{33} \end{pmatrix} \in SO(3).$$

- Tensors for bent-core molecules: $\boldsymbol{m}_2 \to -\boldsymbol{m}_2$ symmetry.
  First order: $\boldsymbol{p} = \langle \boldsymbol{m}_1 \rangle$. Necessary for polar order.
  Second order: $Q_1 = \langle \boldsymbol{m}_1 \boldsymbol{m}_1 \rangle$, $Q_2 = \langle \boldsymbol{m}_2 \boldsymbol{m}_2 \rangle$. Need both for biaxial nematic phase.
  $(Q_3 = \langle \boldsymbol{m}_3 \boldsymbol{m}_3 \rangle = I - Q_1 - Q_2)$

Molecular model

Let $\boldsymbol{r} = \boldsymbol{x}' - \boldsymbol{x}$.

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

Concentration: $c(\boldsymbol{x}) = \int \mathrm{d}P f(\boldsymbol{x}, P) = c_0$.

Orientational density: $\rho(\boldsymbol{x}, P) = f(\boldsymbol{x}, P)/c(\boldsymbol{x})$.

- Kernel function: $G(\boldsymbol{r}, P, P') = 1 - \exp(-U(\boldsymbol{r}, P, P')/k_B T)$.
- $U(\boldsymbol{r}, P, P')$: pairwise molecular interaction.

  Hardcore:

  $$U = \begin{cases} +\infty, & \text{if two molecules touch,} \\ 0, & \text{elsewhere.} \end{cases}$$

  Lennard-Jones; Electromagnetics, ...

Spatial and orientational expansion

- Expand f about $\boldsymbol{r} = \boldsymbol{x}' - \boldsymbol{x}$. Spatial moments

$$M^{(k)}(P, P') = \int G(\boldsymbol{r}, P, P') \underbrace{\boldsymbol{r} \ldots \boldsymbol{r}}_{k \text{ times}} \mathrm{d}\boldsymbol{r}.$$

$$\frac{F[f]}{k_B T} = \int \mathrm{d}P \mathrm{d}\boldsymbol{x} f \log f + \sum_k \frac{1}{2k!} \int \mathrm{d}\boldsymbol{x} \mathrm{d}P \mathrm{d}P' f(\boldsymbol{x}, P) M^{(k)}(P, P') \nabla^k f(\boldsymbol{x}, P').$$

- Expand $M^{(k)}(P, P')$. Determined by molecular symmetry & truncation. Relative orientation: $\bar{P} = P^{-1}P' = (p_{ij})_{3\times 3} = (\boldsymbol{m}_i \cdot \boldsymbol{m}'_j)$.

$$\begin{aligned}
\hat{M}^{(0)} &= c_{00} + c_{01}p_{11} + c_{02}p_{11}^2 + c_{03}p_{22}^2 + c_{04}(p_{12}^2 + p_{21}^2), \\
\hat{M}^{(1)} &= -c_{10}(\boldsymbol{m}_1 - \boldsymbol{m}'_1) - c_{11}p_{11}(\boldsymbol{m}_1 - \boldsymbol{m}'_1) - c_{12}(p_{21}\boldsymbol{m}_2 - p_{12}\boldsymbol{m}'_2), \\
\hat{M}^{(2)} &= -\left(c_{20} + c_{21}p_{11} + c_{22}p_{11}^2 + c_{23}p_{22}^2 + c_{24}(p_{12}^2 + p_{21}^2)\right) I \\
&\quad - c_{25}(\boldsymbol{m}_1\boldsymbol{m}_1 + \boldsymbol{m}'_1\boldsymbol{m}'_1) - c_{26}(\boldsymbol{m}_2\boldsymbol{m}_2 + \boldsymbol{m}'_2\boldsymbol{m}'_2) \\
&\quad - (c_{27} + c_{28}p_{11})(\boldsymbol{m}_1\boldsymbol{m}'_1 + \boldsymbol{m}'_1\boldsymbol{m}_1) - c_{29}p_{22}(\boldsymbol{m}_2\boldsymbol{m}'_2 + \boldsymbol{m}'_2\boldsymbol{m}_2) \\
&\quad - c_{2,10}\left[p_{12}(\boldsymbol{m}_1\boldsymbol{m}'_2 + \boldsymbol{m}'_2\boldsymbol{m}_1) + p_{21}(\boldsymbol{m}_2\boldsymbol{m}'_1 + \boldsymbol{m}'_1\boldsymbol{m}_2)\right].
\end{aligned}$$

Separate variables

The term $-p_{12}^2 I$ in $\hat{M}^{(2)}$ generates $\nabla(cQ_1) : \nabla(cQ_2)$.

$$\int \mathrm{d}\boldsymbol{x}\mathrm{d}P\mathrm{d}P' \; -(\boldsymbol{m}_1 \cdot \boldsymbol{m}_2')^2 I : f(\boldsymbol{x}, P)\nabla^2 f(\boldsymbol{x}, P')$$

$$= -\int \mathrm{d}\boldsymbol{x} \left(c(\boldsymbol{x}) \int \mathrm{d}P m_{1i} m_{1j} \rho(\boldsymbol{x}, P) \right) \partial_{kk} \left(c(\boldsymbol{x}) \int \mathrm{d}P' m'_{2i} m'_{2j} \rho(\boldsymbol{x}, P') \right)$$

$$= -\int \mathrm{d}\boldsymbol{x} \left(c(\boldsymbol{x}) \left\langle m_{1i} m_{1j} \right\rangle \right) \partial_{kk} \left(c(\boldsymbol{x}) \left\langle m_{2i} m_{2j} \right\rangle \right),$$

=(integration by parts, boundary terms discarded)

$$= \int \mathrm{d}\boldsymbol{x} \partial_k \left(c(\boldsymbol{x}) Q_{1ij} \right) \partial_k \left(c(\boldsymbol{x}) Q_{2ij} \right).$$

Free energy

Nematic phases: $c = c_0$.

$$\frac{F[\boldsymbol{p}(\boldsymbol{x}), Q_1(\boldsymbol{x}), Q_2(\boldsymbol{x})]}{k_B T}$$

$$= \int \mathrm{d}\boldsymbol{x} \Big\{ c(\boldsymbol{b}\cdot\boldsymbol{p} + B_1 : Q_1 + B_2 : Q_2 - \log Z) \quad \rightarrow \text{Quasiequilibrium Closure}$$

$$+ \frac{c^2}{2}(c_{01}|\boldsymbol{p}|^2 + c_{02}|Q_1|^2 + c_{03}|Q_2|^2 + 2c_{04}Q_1 : Q_2)$$

$$+ c^2(c_{11}p_j\partial_i Q_{1ij} + c_{12}p_j\partial_i Q_{2ij})$$

$$+ \frac{c^2}{4}\left[c_{21}|\nabla\boldsymbol{p}|^2 + c_{22}|\nabla Q_1|^2 + c_{23}|\nabla Q_2|^2 + 2c_{24}\partial_i Q_{1jk}\partial_i Q_{2jk}\right.$$

$$+ 2c_{27}\partial_i p_i \partial_j p_j + 2c_{28}\partial_i Q_{1ik}\partial_j Q_{1jk}$$

$$\left. + 2c_{29}\partial_i Q_{2ik}\partial_j Q_{2jk} + 4c_{2,10}\partial_i Q_{1ik}\partial_j Q_{2jk}\right] \Big\}.$$

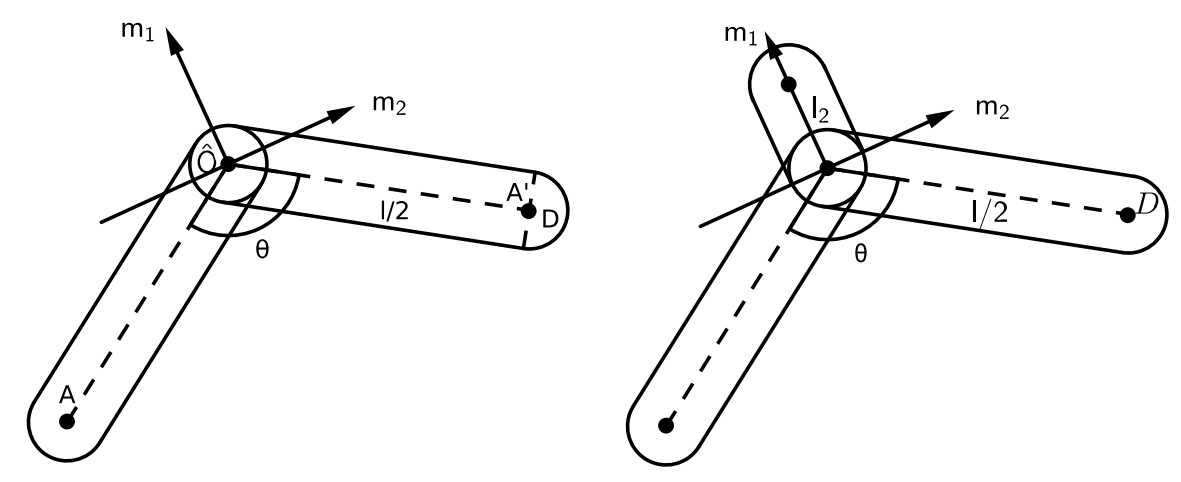
c_{kj}: those in $\hat{M}^{(k)}$.

Coupling of $\boldsymbol{p}$ and $\partial_i Q_{\alpha ij} \Rightarrow$ Modulated phases

Jie Xu and Pingwen Zhang. Sci. China Math.(2014).

Jie Xu, Fangfu Ye and Pingwen Zhang, MMS, in revision, arXiv:1408:3722v2.

Coefficients



- Minimize

$$\int_{SO_3} \mathrm{d}\bar{P} ||M^{(k)}(P, P'; \{l, D, \theta\}) - \hat{M}^{(k)}(P, P'; \{c_{kj}\})||_F^2,$$

- Functions of molecular parameters: $c_{kj} = l^{k+3} c_{kj}(\eta, \theta)$, $\eta = D/l$.
- Nondimensionalization: $\boldsymbol{x} \to \boldsymbol{x}/l$, $c \to \alpha = \pi c(l + l_2)D^2/4$.
  Dimensionless molecular parameters: volume fraction α, thickness η, bending angle θ, and l_2/l.

Quasiequilibrium Closure Approximation

Minimize the entropy term with given value of $(\boldsymbol{p}, Q_1, Q_2)$.

$$\rho(P) = \frac{1}{Z} \exp(\boldsymbol{b} \cdot \boldsymbol{m}_1 + B_1 : \boldsymbol{m}_1\boldsymbol{m}_1 + B_2 : \boldsymbol{m}_2\boldsymbol{m}_2).$$

$$(\boldsymbol{p}, Q_1, Q_2) = \frac{1}{Z} \int \mathrm{d}P \ \rho(P)(\boldsymbol{m}_1, \boldsymbol{m}_1\boldsymbol{m}_1, \boldsymbol{m}_2\boldsymbol{m}_2).$$

Approximation: shared eigenframe $T(\boldsymbol{x}) \in SO(3)$ (proved for homogeneous phases*),

$$\boldsymbol{p} = T(s, 0, 0)^T, \qquad \boldsymbol{b} = T(b_1, 0, 0)^T,$$
$$Q_1 = T\mathsf{diag}(q_{11}, q_{12}, q_{13})T^T, \qquad B_1 = T\mathsf{diag}(b_{11}, b_{12}, 0)T^T,$$
$$Q_2 = T\mathsf{diag}(q_{21}, q_{22}, q_{23})T^T, \qquad B_2 = T\mathsf{diag}(b_{21}, b_{22}, 0)T^T.$$

Physical range of eigenvalues:

$$q_{ij} > 0, s^2 < q_{11},$$
$$q_{11} + q_{12}, q_{11} + q_{21}, q_{12} + q_{22}, q_{21} + q_{22} < 1,$$
$$q_{11} + q_{12} + q_{21} + q_{22} > 1.$$

Bijection: $(s, q_{ij}) \leftrightarrow (b_1, b_{ij}) \ \Rightarrow \rho(P)$ is determined by the tensors.

*Jie Xu and Pingwen Zhang, Comm. Math. Sci.(2017)

Reduce to rod-like molecules

When $\theta = \pi$.

- Pairwise interaction: coefficients involving $\boldsymbol{p}$ and Q_1 are zero.
- Entropy: Bingham closure.
- Free energy:

$$\frac{F[Q_2]}{k_B T} = \int \mathrm{d}\boldsymbol{x} \Big\{ c(B_2 : Q_2 - \log Z) + \frac{c^2}{2} c_{03} |Q_2|^2 + \frac{c^2}{4} \left(c_{23} |\nabla Q_2|^2 + 2 c_{29} \partial_i Q_{2ik} \partial_j Q_{2jk} \right) \Big\}.$$

Contents

Nematic phases (restrained to 1D periodic)

- Isotropic phase (I): $\boldsymbol{p} = 0$, $Q_1 = Q_2 = \frac{I}{3}$.
- Uniaxial nematic phase (N): $\boldsymbol{p} = 0$. $Q_3 = \langle \boldsymbol{m}_3 \boldsymbol{m}_3 \rangle = I - Q_1 - Q_2$.

$$Q_i = s_i(\boldsymbol{n}\boldsymbol{n} - \frac{I}{3}) + \frac{I}{3}, \quad i = 1, 2, 3.$$

  Only one s_i positive. $s_i > 0 \to N_i$.

- Biaxial nematic phase (B): $\boldsymbol{p} = 0$; $q_{ii} > q_{ij}$ $(j \neq i)$.
- Twist-bend phase (N_{tb}). (s, q_{ij}) constant, $\boldsymbol{p} \neq 0$. Chiral.

$$T(x) = (\boldsymbol{n}_1, \boldsymbol{n}_2, \boldsymbol{n}_3) = \begin{pmatrix} 0 & \cos\gamma & \sin\gamma \\ \cos\frac{-2\pi x}{L} & -\sin\gamma\sin\frac{-2\pi x}{L} & \cos\gamma\sin\frac{-2\pi x}{L} \\ \sin\frac{-2\pi x}{L} & \sin\gamma\cos\frac{-2\pi x}{L} & -\cos\gamma\cos\frac{-2\pi x}{L} \end{pmatrix}.$$

  L: pitch; γ: cone angle.

  Red: $\boldsymbol{n}_1$; Blue: $\boldsymbol{n}_2$.

Phases diagram w.r.t molecular parameters

Include all the nematic phases confirmed experimentally.

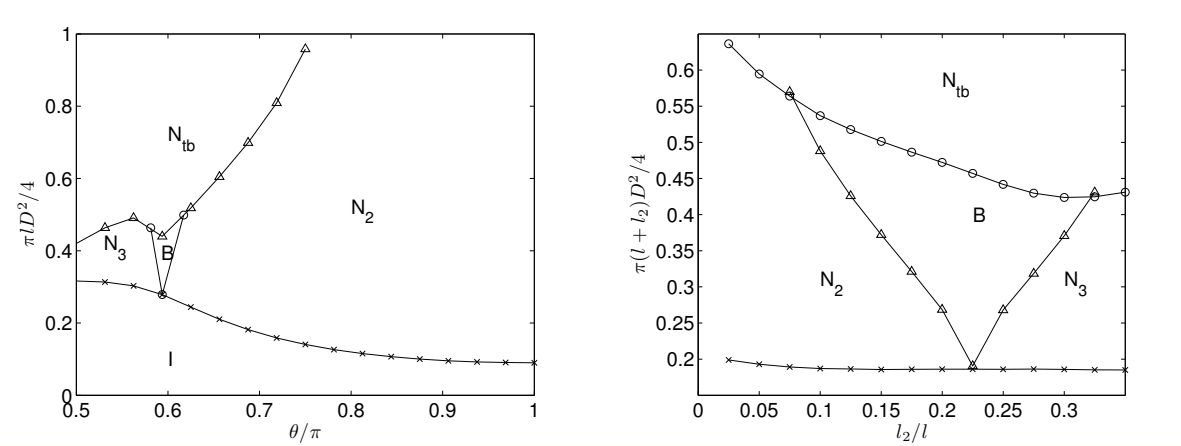


Figure : Bent-core molecules ($\eta = 1/40$) and star molecules ($\eta = 1/40$, $\theta = 2\pi/3$).

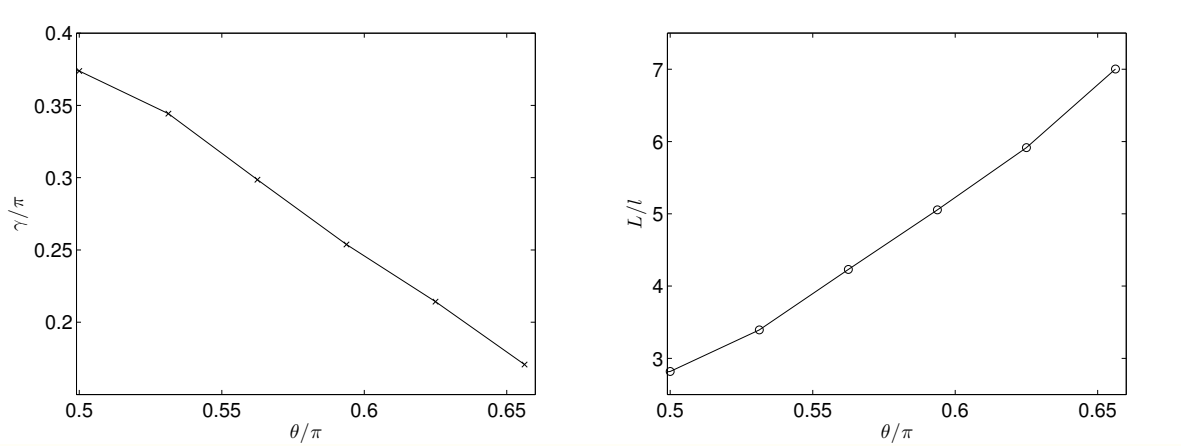


Figure : Cone angle and pitch of bent-core molecules ($\eta = 1/40$, $\alpha = 0.7$).

Orientational elasticity

Phase symmetry $\Rightarrow$ elasticity.

- Uniaxial nematic phase: Oseen-Frank.

$$F_{OF} = \int \mathrm{d}\boldsymbol{x}\ \frac{1}{2}\left[K_1(\nabla\cdot\boldsymbol{n})^2 + K_2(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_3|\boldsymbol{n}\times(\nabla\times\boldsymbol{n})|^2\right].$$

- Derivatives of $T(\boldsymbol{x}) = (\boldsymbol{n}_1(\boldsymbol{x}), \boldsymbol{n}_2(\boldsymbol{x}), \boldsymbol{n}_3(\boldsymbol{x}))$: nine degrees of freedom.

$$D_{11} = n_{1i}n_{2j}\partial_i n_{3j},\ D_{12} = n_{1i}n_{3j}\partial_i n_{1j},\ D_{13} = n_{1i}n_{1j}\partial_i n_{2j},$$
$$D_{21} = n_{2i}n_{2j}\partial_i n_{3j},\ D_{22} = n_{2i}n_{3j}\partial_i n_{1j},\ D_{23} = n_{2i}n_{1j}\partial_i n_{2j},$$
$$D_{31} = n_{3i}n_{2j}\partial_i n_{3j},\ D_{32} = n_{3i}n_{3j}\partial_i n_{1j},\ D_{33} = n_{3i}n_{1j}\partial_i n_{2j}.$$

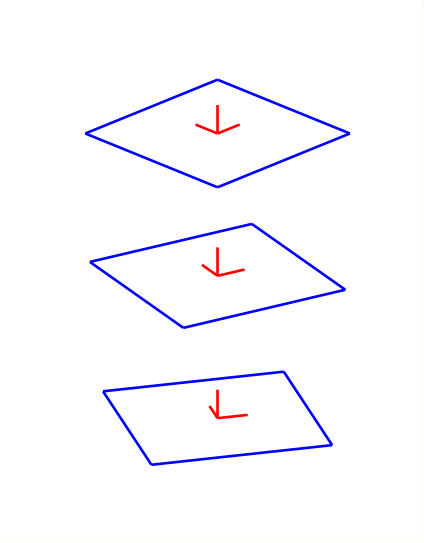
- Biaxial nematic phase: $\boldsymbol{n}_i \to -\boldsymbol{n}_i$ symmetry.

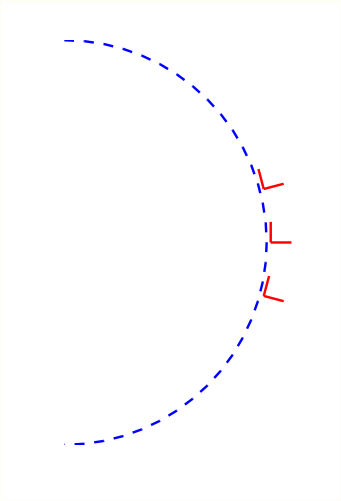
$$F_{Bi}[T(\boldsymbol{x})] = \int \mathrm{d}\boldsymbol{x}\ \frac{1}{2}\Big[K_{1111}D_{11}^2 + K_{2222}D_{22}^2 + K_{3333}D_{33}^2 \longrightarrow \mathbb{T}_i$$
$$+K_{1212}D_{12}^2 + K_{2121}D_{21}^2 + K_{2323}D_{23}^2$$
$$+K_{3232}D_{32}^2 + K_{3131}D_{31}^2 + K_{1313}D_{13}^2 \longrightarrow \mathbb{S}_i\mathbb{B}_j$$
$$+ K_{1221}D_{12}D_{21} + K_{2332}D_{23}D_{32} + K_{1331}D_{13}D_{31}\Big].$$

Elastic constants

Patterns:

Twist: $D_{ii} \neq 0$, Splay & Bend: $D_{jk} \neq 0$,





- Twelve elastic constants.
- If Q_i uniaxial: Biaxial elasticity $\Rightarrow$ Oseen-Frank.

  If we set $\boldsymbol{n} = \boldsymbol{n}_1$.

$$K_{2323} = K_{3232} = K_1,\ K_{2222} = K_{3333} = K_2,\ K_{1212} = K_{1313} = K_3,$$

$$K_{2332} = 2(K_2 - K_1),\ K_{1111} = K_{2121} = K_{3131} = K_{1221} = K_{1331} = 0.$$

Elastic constants

- For uniaxial & biaxial nematics: $\boldsymbol{p} = 0$, $Q_i = T\text{diag}(q_{i1}, q_{i2}, q_{i3})T^T$.
  Let q_{ij} be equilibrium values $\Longrightarrow$ Elasticity of T
- $K = K(q_{ij}, c_{2k})$. Solve $q_{ij} = q_{ij}(c_{0k}) \Rightarrow K = K(c_{0k}(\alpha, \eta, \theta), c_{2k}(\alpha, \eta, \theta))$

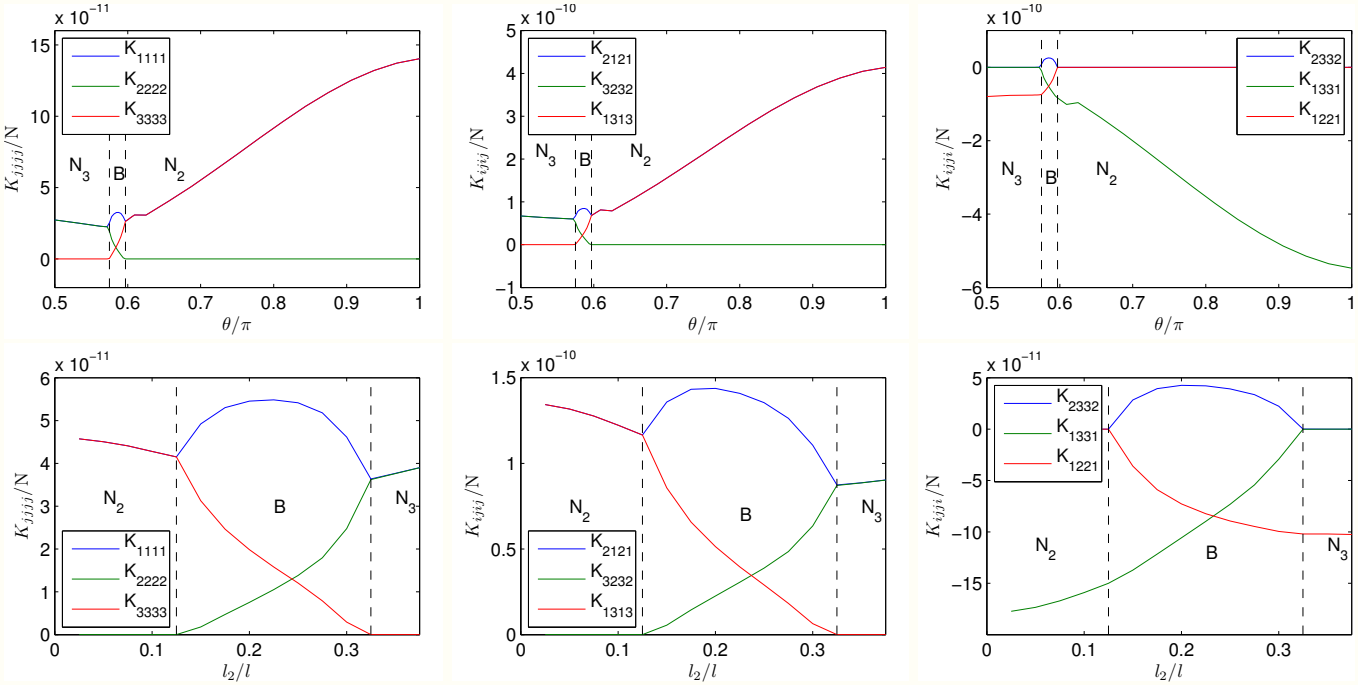


Figure : Elastic constants with $\eta = 1/20$, $cl^2D = 20.0$ and $\theta = 2\pi/3$ (star molecules).

Jie Xu and Pingwen Zhang. Liquid Crystals, online.

Contents

Molecular model

- Differential operators on $SO(3)$

  $L_j = \partial_{X'_j}$: derivative along infinitesimal rotation about $\boldsymbol{m}_j$.

$$L_1 = \frac{\partial}{\partial\gamma},$$
$$L_2 = \frac{-\cos\gamma}{\sin\alpha}\left(\frac{\partial}{\partial\beta} - \cos\alpha\frac{\partial}{\partial\gamma}\right) + \sin\gamma\frac{\partial}{\partial\alpha},$$
$$L_3 = \frac{\sin\gamma}{\sin\alpha}\left(\frac{\partial}{\partial\beta} - \cos\alpha\frac{\partial}{\partial\gamma}\right) + \cos\gamma\frac{\partial}{\partial\alpha}.$$

  $L = (L_1, L_2, L_3)$: 'gradient' in $SO(3)$.

- Smoluchowski equation:

$$\frac{\partial f}{\partial t} + \nabla\cdot(\boldsymbol{v}f) = \nabla\cdot(\boldsymbol{J}f\nabla\mu) + L\cdot(\boldsymbol{D}fL\mu) - L\cdot(\boldsymbol{g}f),\ \mu = \frac{\delta F}{\delta f}.$$

  Navier-Stokes:

$$\rho_s\left(\frac{\partial\boldsymbol{v}}{\partial t} + \boldsymbol{v}\cdot\nabla\boldsymbol{v}\right) = -\nabla p + \nu\Delta\boldsymbol{v} + \nabla\cdot(\tau_e + \tau_v) + \boldsymbol{F}_e,$$
$$\nabla\cdot\boldsymbol{v} = 0.$$

Molecular model

- Molecule consists of spheres.
- Sphere–fluid friction $\boldsymbol{F} = \zeta \boldsymbol{v}$ Molecular architecture $\Longrightarrow$ Rotational convection $\boldsymbol{g}$ Diffusion coefficients $\boldsymbol{D} = D_0 \boldsymbol{I}^{-1}$ $\boldsymbol{J} = \sum \gamma_j^{-1} \boldsymbol{m}_j \boldsymbol{m}_j$ viscous stress τ_v
- Moment of inertia: $\boldsymbol{I} = \mathrm{diag}(I_{11}, I_{22}, I_{33})$
  bent-core: $\propto l^2 \mathrm{diag}(4\sin^2\frac{\theta}{2}, \cos^2\frac{\theta}{2}, 1 + 3\sin^2\frac{\theta}{2})$;
  star: depend on l, l_2, θ.
- Rotation: $\kappa = \nabla \boldsymbol{v}$.

$$\begin{aligned}\boldsymbol{g} =& (\kappa : \boldsymbol{m}_2\boldsymbol{m}_3)\boldsymbol{m}_1 - (\kappa : \boldsymbol{m}_1\boldsymbol{m}_3)\boldsymbol{m}_2 \\ &+ \frac{1}{I_{11} + I_{22}}(I_{22}\kappa : \boldsymbol{m}_1\boldsymbol{m}_2 - I_{11}\kappa : \boldsymbol{m}_2\boldsymbol{m}_1)\boldsymbol{m}_3.\end{aligned}$$

Molecular model

- Viscous stress:

$$\tau_v = c\zeta\kappa : \Big[I_{22} \langle \boldsymbol{m}_1\boldsymbol{m}_1\boldsymbol{m}_1\boldsymbol{m}_1 \rangle + I_{11} \langle \boldsymbol{m}_2\boldsymbol{m}_2\boldsymbol{m}_2\boldsymbol{m}_2 \rangle + \frac{I_{11}I_{22}}{I_{11}+I_{22}} \langle (\boldsymbol{m}_1\boldsymbol{m}_2 + \boldsymbol{m}_2\boldsymbol{m}_1)(\boldsymbol{m}_1\boldsymbol{m}_2 + \boldsymbol{m}_2\boldsymbol{m}_1) \rangle \Big].$$

- Principle of virtual work $\Longrightarrow$ Elastic stress τ_e & Body force $\boldsymbol{F}_e$

  Elastic stress: $\tau_e^{\alpha\beta} = ck_BT \left\langle \alpha_i^{\alpha\beta} L_i \mu \right\rangle$,

$$\alpha_1 = \boldsymbol{m}_2\boldsymbol{m}_3, \quad \alpha_2 = -\boldsymbol{m}_1\boldsymbol{m}_3,$$

$$\alpha_3 = \frac{1}{I_{11}+I_{22}} (I_{22}\boldsymbol{m}_1\boldsymbol{m}_2 - I_{11}\boldsymbol{m}_2\boldsymbol{m}_1).$$

  Body force: $\boldsymbol{F}_e = -ck_BT \langle \nabla\mu \rangle$.

  Depend on I_{ii} & μ.

  $\mu = \delta F/\delta f$ determined by molecular architecture.

Jie Xu and Pingwen Zhang, JNNFM, online.

Tensor model

- Multiply the Smoluchowski equation with $\boldsymbol{m}_1$, $\boldsymbol{m}_1\boldsymbol{m}_1$, $\boldsymbol{m}_2\boldsymbol{m}_2$ and integrate over SO_3, assume c is constant,

$$\frac{\partial A}{\partial t} + \boldsymbol{v} \cdot \nabla A = \mathcal{N}_A + \mathcal{M}_A + \mathcal{V}_A, \qquad A \in \{\boldsymbol{p}, Q_1, Q_2\}.$$

  $\mathcal{N}_A$: spatial diffusion; $\mathcal{M}_A$: rotational diffusion; $\mathcal{V}_A$: rotational convection.

- $\mathcal{M}_A$, $\mathcal{V}_A$, τ_e, τ_v, $\boldsymbol{F}_e$: functions of tensors up to 4th order.

  $\mathcal{N}_A$: functions of tensors up to 6th order.

  Express high-order tensors: quasiequilibrium closure approximation.

$$\rho(P) = \frac{1}{Z} \exp(\boldsymbol{b} \cdot \boldsymbol{m}_1 + B_1 : \boldsymbol{m}_1\boldsymbol{m}_1 + B_2 : \boldsymbol{m}_2\boldsymbol{m}_2).$$

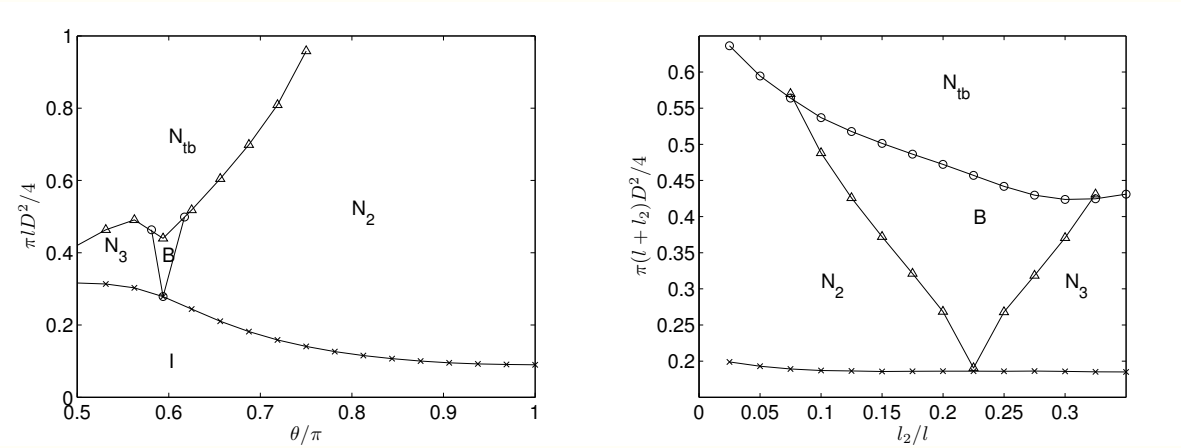
- Advantage: keep energy dissipation.

  Energy dissipation of molecular model:

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\left(\int \mathrm{d}\boldsymbol{x}\frac{\rho}{2}|\boldsymbol{v}|^2 + k_B T \int \mathrm{d}\nu f \log f + F_r\right) \\
&= \int \mathrm{d}\boldsymbol{x}\mathrm{d}\nu f \left[-k_B T\left((L\mu)^T D_0 \boldsymbol{I}^{-1} L\mu - (\nabla\mu)^T \boldsymbol{J}\nabla\mu\right)\right. \\
&\left. -2\eta\frac{\kappa+\kappa^T}{2} : \frac{\kappa+\kappa^T}{2} - \kappa : \tau_{vf}\right].
\end{aligned}$$

Shear flow problem

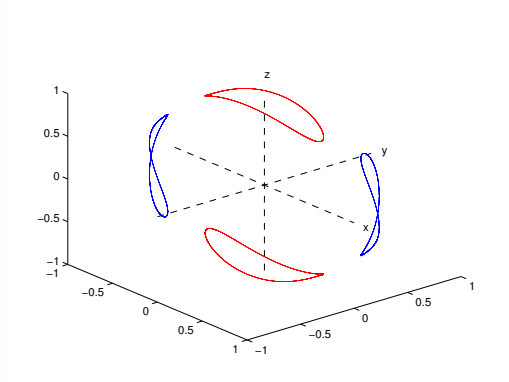
- Assume $\kappa_{12} = \partial_y v_x = k$ constant, $(\boldsymbol{p}, Q_1, Q_2)$ spatially homogeneous.
  Solve Smochulowski equation only.
- Rescale $\tilde{t} = (\zeta l^2/48 k_B T)^{-1} t$, $\tilde{\boldsymbol{x}} = \boldsymbol{x}/l$.
  Dimensionless parameters: k, $\alpha = \pi c D^2 (l + l_2)/4$, θ, l_2/l, $\eta = D/l$.
- Choose $\eta = 1/40$, $\alpha = 0.33, 0.39$.
  Alter θ, l_2/l: N_2–B–N_3 transition.



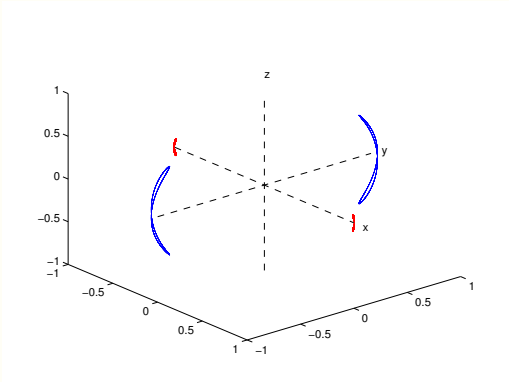
- Classification of flow modes: motion of the principal eigenvectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$.
  In equilibrium $\boldsymbol{q}_1 \perp \boldsymbol{q}_2$; In shear flow, they are approximately vertical.

Flow modes

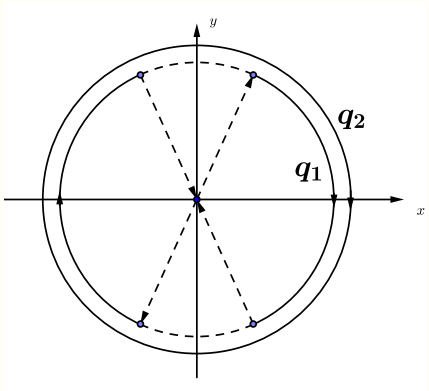
- Steady states.
  - Log-rolling (LR): $\boldsymbol{q}_2$ along z (vortex), $\boldsymbol{q}_1$ in x-y (shear plane).
  - Flow-aligning (FA): $\boldsymbol{q}_2$ in x-y near x, $\boldsymbol{q}_1$ may be in x-y near y (FA-y) or along z (FA-z).
- Periodic modes.



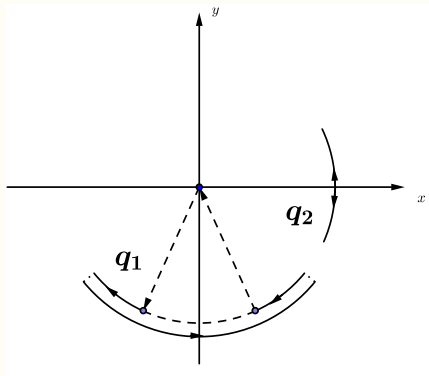
Kayaking (K-Q_1 or K-Q_2)



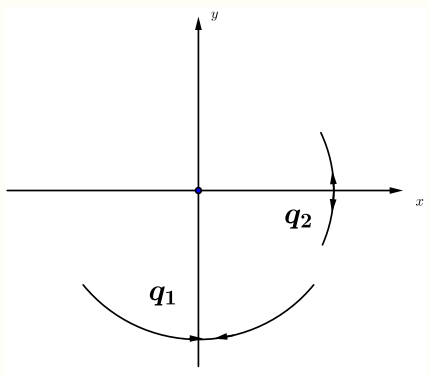
Double splayed (DS)



Tumbling (T)



Wagging-alternating (W-A)



Wagging-wagging (W-W)

Flow mode sequences when k increases

Molecular model:

- N_2 region: LR — K-Q_2 — T — W-A — W-W — FA-y — FA-z.
  Some may be missing. No switch.
  Look at $\boldsymbol{q}_2$: similar to rod-like molecules.
- N_3 region: FA-z.

Tensor model:

- N_2 region: part of the sequence at lower shear rates.
- N_3 region: FA-z.

B region: star molecules with $\theta = 2\pi/3$. Only molecular model.
Let l_2/l vary. Delicately dependent on shape.

- 0.125: LR — K-Q_2 — W-W — FA-y — FA-z;
- 0.15, 0.175: LR — K-Q_2 — W-W — FA-y — K-Q_1 — FA-z;
- 0.2: LR — W-W — FA-y — K-Q_2 — K-Q_1 — FA-z;
- 0.225: K-Q_2 — W-W — FA-y — K-Q_2 — LR — FA-z;
- 0.25: K-Q_2 — W-W — FA-y — LR — FA-z;
- 0.275: DS — FA-y — LR — FA-z.

Contents

Fast algorithm for Bingham closure

Smoluchowski equation for rods: $Q = \langle \boldsymbol{mm} \rangle$, $R = \langle \boldsymbol{mmmm} \rangle$,

$$(Q_t)_{ij} = \left[-6(Q_{ij} - \frac{\delta_{ij}}{3}) + \alpha(Q_{ik}Q_{kj} - Q_{kl}R_{ijkl}) \right] + \kappa_{ik}Q_{kj} + Q_{ik}\kappa_{kj} - \kappa_{kl} : R_{ijkl}.$$

- Bingham distribution $f_B = \frac{1}{Z} \exp(B : \boldsymbol{mm})$, such that

$$Q = \langle \boldsymbol{mm} | f_B \rangle , \; R = \langle \boldsymbol{mmmm} | f_B \rangle .$$

  Compute $R = R(B(Q))$.

- Polynomial fitting. Error $\approx 10^{-4}$.

$$\begin{aligned} R_{ijkl} =& \beta_1 S(\delta_{ij}\delta_{kl}) + \beta_2 S(\delta_{ij}Q_{kl}) + \beta_3 S(Q_{ij}Q_{kl}) \\ &+ \beta_4 S(\delta_{ij}Q_{km}Q_{ml}) + \beta_5 S(Q_{ij}Q_{km}Q_{ml}) + \beta_6 S(Q_{im}Q_{mj}Q_{kn}Q_{nl}). \end{aligned}$$

M. Grosso, P. L. Maffettone, F. Dupret, Rheol. Acta(2000).

Fast algorithm for Bingham closure

Sometimes need to compute $B \leftrightarrow Q$.

- Diagonalize: $f = \frac{1}{Z} \exp(b_1 m_1^2 + b_2 m_2^2),\ b_1, b_2 \leq 0.$

$$q_i(b_1, b_2) = \frac{1}{Z} \int \mathrm{d}\boldsymbol{m} \exp(b_1 m_1^2 + b_2 m_2^2) m_i^2.$$

- Direct computation: 2D integration.
- Piecewise rational approximation: 'integration free'

  $B \to Q, \langle \boldsymbol{mmmm} \rangle, \langle \boldsymbol{mmmmmm} \rangle, \ldots$.

  Absolute error $< 5 \times 10^{-8}$ & 10^4 times faster than numerical integration.

Yixiang Luo, Jie Xu and Pingwen Zhang. J. Sci. Comput., online.

Package: https://github.com/yixiangLuo/Bingham-moment-function/

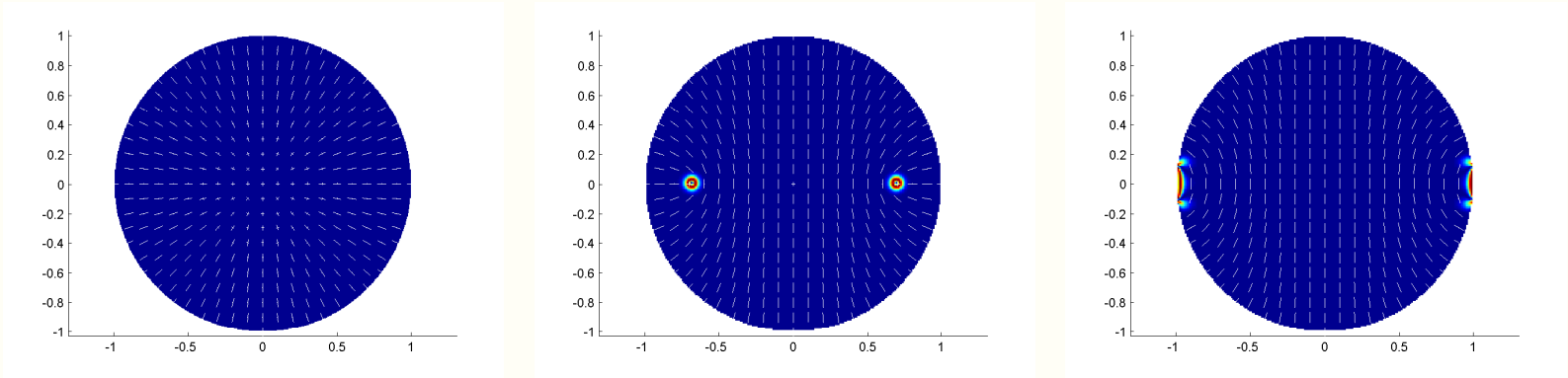
Application: Defects of rod-like molecules in a sphere

Free energy

$$F = \int_\Omega \mathrm{d}x\mathrm{d}y\mathrm{d}z \left[(B : (Q + \frac{I}{3}) - \log Z) - \frac{1}{2}\alpha_1 |Q|^2 + \frac{1}{2}\alpha_2 |\nabla Q|^2 \right] + F_p,$$

Surface energy: let $Q \approx \lambda(\boldsymbol{r})(\boldsymbol{rr} - I/3)$.

$$F_p = \int_{\partial\Omega} \mathrm{d}S \, [Q_{11}xy - Q_{12}(x^2 - \frac{1}{3})]^2 + [Q_{12}z - Q_{13}y]^2 + [Q_{22}xy - Q_{12}(y^2 - \frac{1}{3})]^2 + [Q_{12}z - Q_{23}x]^2,$$



(a) Radial hedgehog (b) Ring disclination (c) Sphere ring band

Typically take 1 hour. Would take >1 year without fast algorithm.

Summary & Future works

From molecular theory to tensor model:

Molecular symmetry $\longrightarrow$ Order parameters & Form of free energy

Molecular parameters $\longrightarrow$ Coefficients

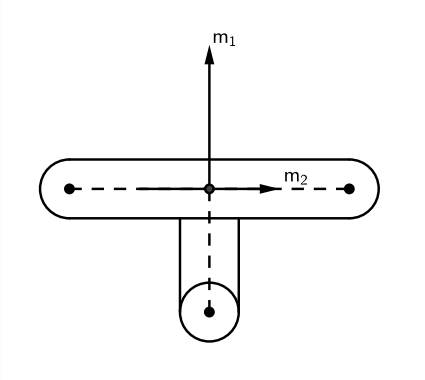
Nematic phase diagram & Elasticity

Dynamic model; shear flow problem

Fast algorithm for Bingham closure

- High-dimensional structures; Defects; Fast closure approximation for bent-core molecules.
- Same molecular symmetry, Different shape & interactions

  Same Model, Different coefficients



- Include concentration variation $\Rightarrow$ Extend to smectics.