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The Q-tensor theory of liquid crystals

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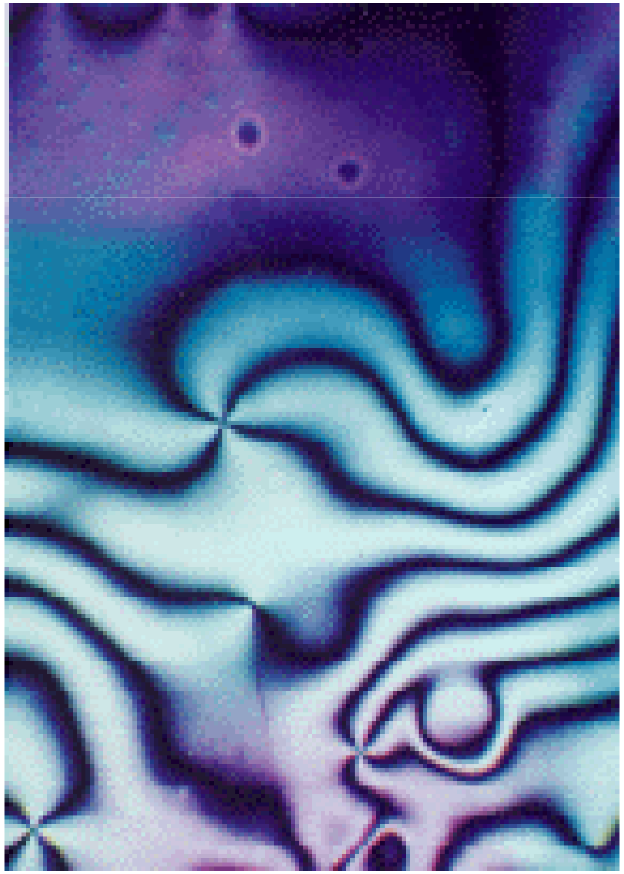


Plan

1. Introduction to liquid crystals. The de Gennes and Oseen-Frank energies.
2. Relations between the theories. Orientability of the director field.
3. The Onsager/Maier-Saupe theory and eigenvalue constraints.

Liquid crystals

A multi-billion dollar industry.

An intermediate state of matter between liquids and solids.

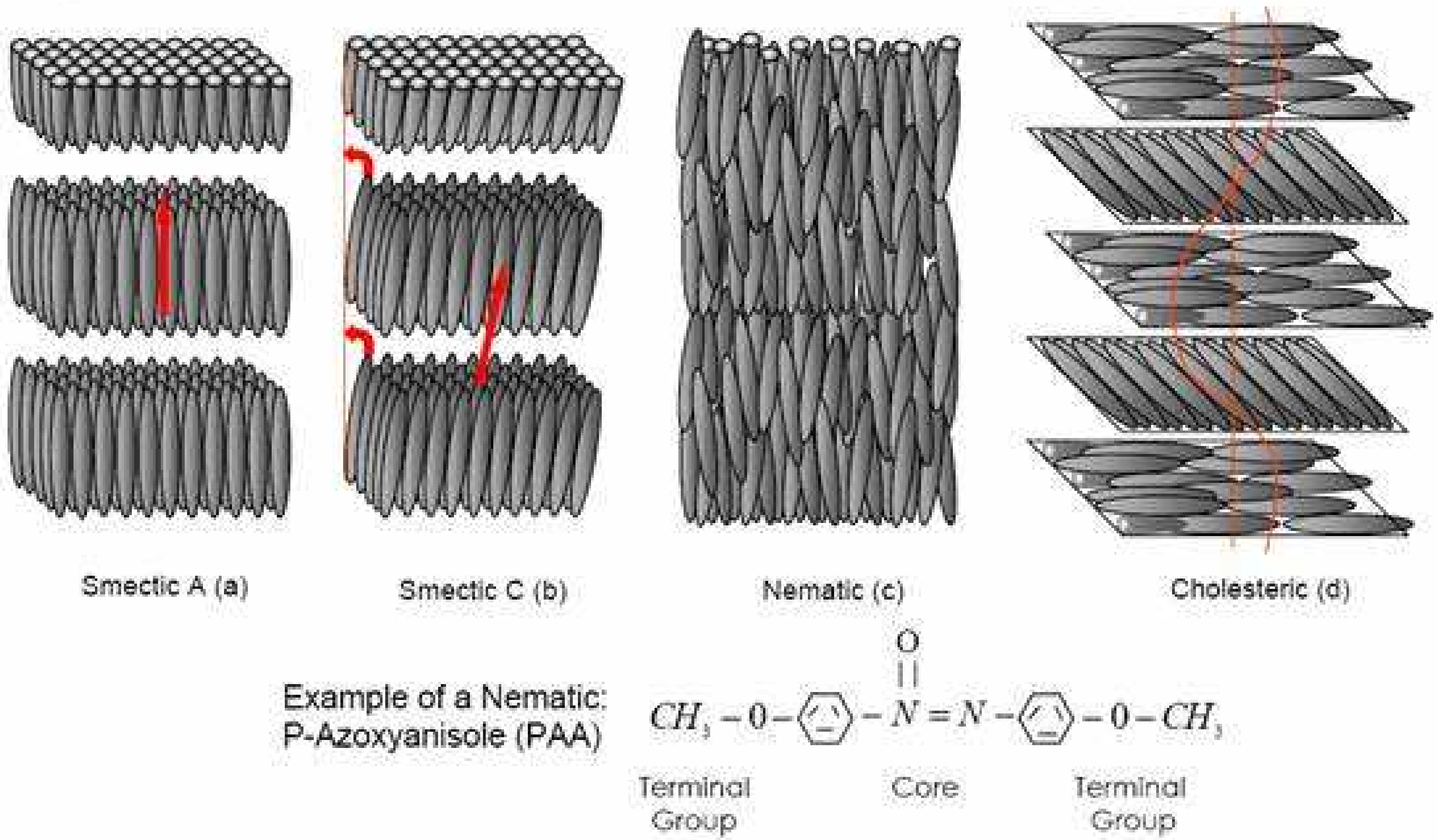
Liquid crystals flow like liquids, but the constituent molecules retain orientational order.

Overview

We consider various theories of static configurations of nematic liquid crystals (de Gennes, Oseen-Frank, Onsager / Maier-Saupe), and relations between them.

Liquid crystals can be of different types. Nematics are the simplest (others are cholesterics, smectics ...) and consist of rod-like molecules (length 2-3 nm) which are ordered so that they have a locally preferred orientation.

The mathematics of liquid crystals involves modelling, variational methods, PDE, algebra, topology, probability ...



http://www.laynetworks.com/Molecular-Orientation-in-Liquid-Crystal-Phases.htm

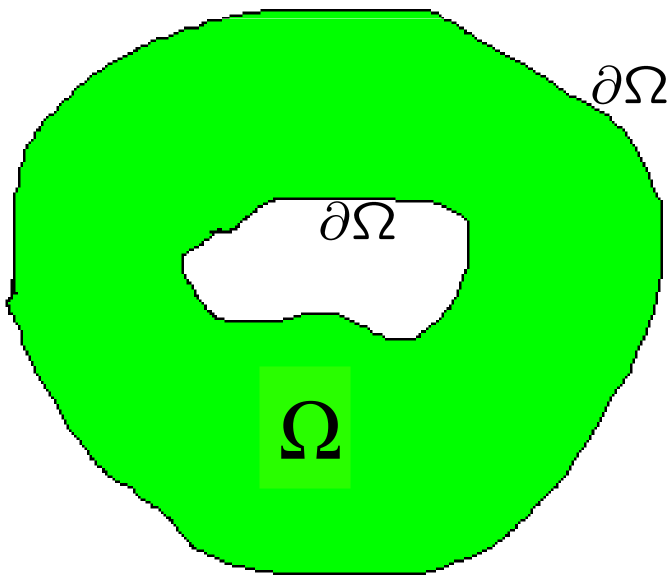
Electron micrograph
of nematic phase

http://www.netwalk.com/~laserlab/lclinks.html

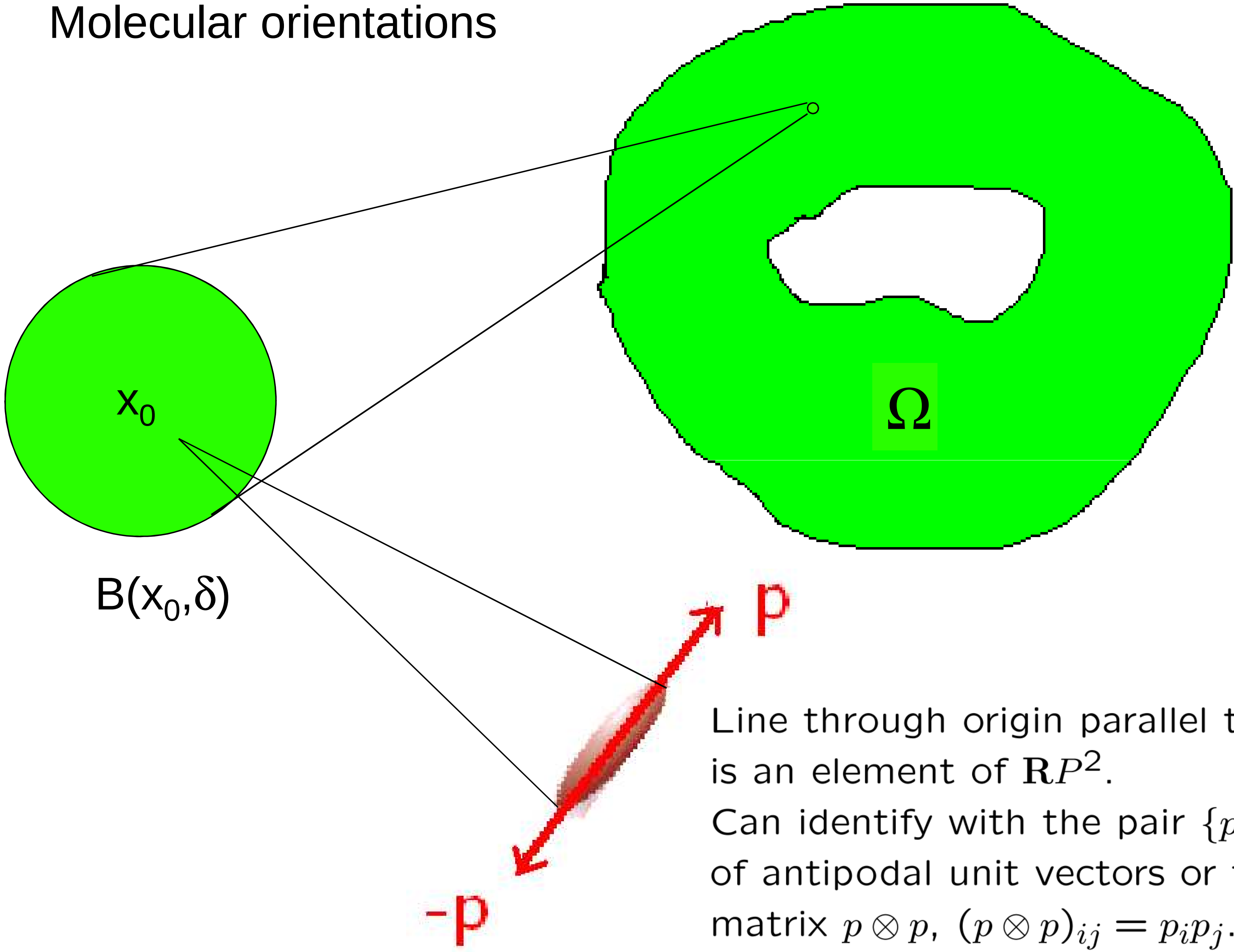
Review of Q-tensor theory

Consider a nematic liquid crystal filling a container $\Omega \subset \mathbf{R}^3$, where Ω is connected with Lipschitz boundary $\partial\Omega$.

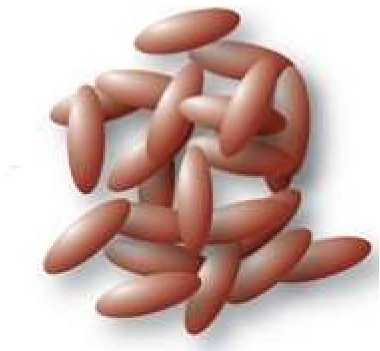
The topology of the container can play a role.

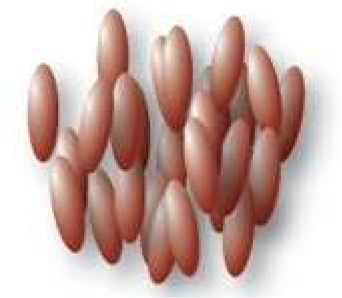


Molecular orientations



Line through origin parallel to p is an element of $\mathbf{R}P^2$.
Can identify with the pair $\{p, -p\}$ of antipodal unit vectors or the matrix $p \otimes p$, $(p \otimes p)_{ij} = p_i p_j$.





The distribution of orientations of molecules in $B(x_0, \delta)$ can be represented by a probability measure on $\mathbf{R}P^2$, that is by a probability measure μ on the unit sphere S^2 satisfying $\mu(E) = \mu(-E)$ for $E \subset S^2$.

For a continuously distributed measure $d\mu(p) = \rho(p)dp$, where dp is the element of surface area on S^2 and $\rho \geq 0, \int_{S^2} \rho(p)dp = 1$, $\rho(p) = \rho(-p)$.

The first moment $\int_{S^2} p \, d\mu(p) = 0$.
The second moment

$$M = \int_{S^2} p \otimes p \, d\mu(p)$$

is a symmetric non-negative 3×3 matrix satisfying $\mathrm{tr} M = 1$.

Let $e \in S^2$. Then

$$\begin{aligned} e \cdot Me &= \int_{S^2} (e \cdot p)^2 d\mu(p) \\ &= \langle \cos^2 \theta \rangle, \end{aligned}$$

where θ is the angle between p and e.

If the orientation of molecules is equally distributed in all directions, we say that the distribution is *isotropic*, and then $\mu = \mu_0$, where

$$d\mu_0(p) = \frac{1}{4\pi} dS.$$

The corresponding second moment tensor is

$$M_0 = \frac{1}{4\pi} \int_{S^2} p \otimes p \, dS = \frac{1}{3} \mathbf{1}$$

(since $\int_{S^2} p_1 p_2 \, dS = 0$, $\int_{S^2} p_1^2 \, dS = \int_{S^2} p_2^2 \, dS$ etc and $\mathrm{tr}\, M_0 = 1$.)

The *de Gennes Q-tensor*

$$Q = M - M_0$$

measures the deviation of M from its isotropic value.

Note that

$$Q = \int_{S^2} \left(p \otimes p - \frac{1}{3}\mathbf{1} \right) \, d\mu(p)$$

satisfies $Q = Q^T, \ \operatorname{tr} Q = 0, \ Q \geq -\frac{1}{3}\mathbf{1}$.

Remark. $Q = 0$ does not imply $\mu = \mu_0$.
For example we can take

$$\mu = \frac{1}{6} \sum_{i=1}^{3} (\delta_{e_i} + \delta_{-e_i}).$$

Since Q is symmetric and $\operatorname{tr} Q = 0$,

$$Q = \lambda_1 n_1 \otimes n_1 + \lambda_2 n_2 \otimes n_2 + \lambda_3 n_3 \otimes n_3,$$

where $\{n_i\}$ is an orthonormal basis of eigenvectors of Q with corresponding eigenvalues $\lambda_1, \lambda_2, \lambda_3$ with

$$\lambda_1 + \lambda_2 + \lambda_3 = 0.$$

Since $Q \geq -\frac{1}{3}\mathbf{1}$, $-\frac{1}{3} \leq \lambda_i \leq \frac{2}{3}$.

Conversely, if $-\frac{1}{3} \leq \lambda_i \leq \frac{2}{3}$ then M is the second moment tensor for some μ, e.g. for

$$\mu = \sum_{i=1}^{3} (\lambda_i + \frac{1}{3}) \frac{1}{2} (\delta_{n_i} + \delta_{-n_i}).$$

If the eigenvalues λ_i of Q are distinct then Q is said to be *biaxial*, and if two λ_i are equal *uniaxial*.

In the uniaxial case we can suppose $\lambda_1 = \lambda_2 = -\frac{s}{3}$, $\lambda_3 = \frac{2s}{3}$, and setting $n_3 = n$ we get

$$Q = -\frac{s}{3}(\mathbf{1} - n \otimes n) + \frac{2s}{3} n \otimes n.$$

Thus

$$Q = s(n \otimes n - \frac{1}{3}\mathbf{1}),$$

where $-\frac{1}{2} \leq s \leq 1$.

Note that

$$\begin{aligned} Qn \cdot n &= \frac{2s}{3} \\ &= \langle (p \cdot n)^2 - \frac{1}{3} \rangle \\ &= \langle \cos^2\theta - \frac{1}{3} \rangle, \end{aligned}$$

where θ is the angle between p and n. Hence

$$s = \frac{3}{2} \langle \cos^2\theta - \frac{1}{3} \rangle.$$

$$s = -\frac{1}{2} \Leftrightarrow \int_{S^2} (p \cdot n)^2 d\mu(p) = 0$$

(all molecules perpendicular to n).

$$s = 0 \Leftrightarrow Q = 0$$

(which occurs when μ is isotropic).

$$s = 1 \Leftrightarrow \int_{S^2} (p \cdot n)^2 d\mu(p) = 1$$

$$\Leftrightarrow \mu = \frac{1}{2}(\delta_n + \delta_{-n})$$

(perfect ordering parallel to n).

If $Q = s(n \otimes n - \frac{1}{3}\mathbf{1})$ is uniaxial then $|Q|^2 = \frac{2s^2}{3}$, $\det Q = \frac{2s^3}{27}$.

Proposition.
Given $Q = Q^T$, $\operatorname{tr} Q = 0$, Q is uniaxial if and only if

$$|Q|^2 = 54(\det Q)^2.$$

Proof. The characteristic equation of Q is

$$\det(Q - \lambda \mathbf{1}) = \det Q - \lambda \operatorname{tr} \operatorname{cof} Q + 0\lambda^2 - \lambda^3.$$

But $2 \operatorname{tr} \operatorname{cof} Q = 2(\lambda_2\lambda_3 + \lambda_3\lambda_1 + \lambda_1\lambda_2) = (\lambda_1 + \lambda_2 + \lambda_3)^2 - (\lambda_1^2 + \lambda_2^2 + \lambda_3^2) = -|Q|^2$. Hence the characteristic equation is

$$\lambda^3 - \frac{1}{2}|Q|^2\lambda - \det Q = 0,$$

and the condition that $\lambda^3 - p\lambda + q = 0$ has two equal roots is that $p \geq 0$ and $4p^3 = 27q^2$.

Energetics

Consider a liquid crystal material filling a container $\Omega \subset \mathbf{R}^3$. We suppose that the material is incompressible, homogeneous (same material at every point) and that the temperature is constant.

At each point $x \in \Omega$ we have a corresponding measure μ_x and order parameter tensor $Q(x)$. We suppose that the material is described by a free-energy density $\psi(Q, \nabla Q)$, so that the total free energy is given by

$$I(Q) = \int_\Omega \psi(Q(x), \nabla Q(x))\, dx.$$

We write $\psi = \psi(Q, D)$, where D is a third order tensor.

The domain of ψ

For what Q, D should $\psi(Q, D)$ be defined?
Let $\mathcal{E} = \{Q \in M^{3\times 3} : Q = Q^T, \operatorname{tr} Q = 0\}$
$\mathcal{D} = \{D = (D_{ijk}) : D_{ijk} = D_{jik}, D_{kki} = 0\}$.
We suppose that $\psi : \operatorname{dom} \psi \to \mathbf{R}$, where

$$\operatorname{dom} \psi = \{(Q, D) \in \mathcal{E} \times \mathcal{D}, \lambda_i(Q) > -\frac{1}{3}\}.$$

But in order to differentiate ψ easily with respect to its arguments, it is convenient to extend ψ to all of $M^{3\times 3}\times$(3rd order tensors). To do this first set $\psi(Q, D) = \infty$ if $(Q, D) \in \mathcal{E} \times \mathcal{D}$ with some $\lambda_i(Q) \leq -\frac{1}{3}$.

Then note that

$$PA = \frac{1}{2}(A + A^T) - \frac{1}{3}(\mathrm{tr}\, A)\mathbf{1}$$

is the orthogonal projection of $M^{3\times 3}$ onto $\mathcal{E}$. So for any Q, D we can set

$$\psi(Q, D) = \psi(PQ, PD),$$

where $(PD)_{ijk} = \frac{1}{2}(D_{ijk} + D_{jik}) - \frac{1}{3}D_{llk}\delta_{ij}$.

Thus we can assume that ψ satisfies

$$\frac{\partial \psi}{\partial Q_{ij}} = \frac{\partial \psi}{\partial Q_{ji}},\ \frac{\partial \psi}{\partial Q_{ii}} = 0,$$

$$\frac{\partial \psi}{\partial D_{ijk}} = \frac{\partial \psi}{\partial D_{jik}},\ \frac{\partial \psi}{\partial D_{iik}} = 0.$$

Frame-indifference

Fix $\bar{x} \in \Omega$, Consider two observers, one using the Cartesian coordinates $x = (x_1, x_2, x_3)$ and the second using translated and rotated coordinates $z = \bar{x} + R(x - \bar{x})$, where $R \in SO(3)$. We require that both observers see the same free-energy density, that is

$$\psi(Q^*(\bar{x}), \nabla_z Q^*(\bar{x})) = \psi(Q(\bar{x}), \nabla_x Q(\bar{x})),$$

where $Q^*(\bar{x})$ is the value of Q measured by the second observer.

$$
\begin{aligned}
Q^*(\bar{x}) &= \int_{S^2} (q \otimes q - \frac{1}{3}\mathbf{1}) d\mu_{\bar{x}}(R^T q) \\
&= \int_{S^2} (Rp \otimes Rp - \frac{1}{3}\mathbf{1}) d\mu_{\bar{x}}(p) \\
&= R \int_{S^2} (p \otimes p - \frac{1}{3}\mathbf{1}) d\mu_{\bar{x}}(p) R^T.
\end{aligned}
$$

Hence $Q^*(\bar{x}) = RQ(\bar{x})R^T$, and so

$$\begin{aligned} \frac{\partial Q^*_{ij}}{\partial z_k}(\bar{x}) &= \frac{\partial}{\partial z_k}(R_{il}Q_{lm}(\bar{x})R_{jm}) \\ &= \frac{\partial}{\partial x_p}(R_{il}Q_{lm}R_{jm})\frac{\partial x_p}{\partial z_k} \\ &= R_{il}R_{jm}R_{kp}\frac{\partial Q_{lm}}{\partial x_p}. \end{aligned}$$

Thus, for every $R \in SO(3)$,

$$\psi(Q^*, D^*) = \psi(Q, D),$$

where $Q^* = RQR^T$, $D^*_{ijk} = R_{il}R_{jm}R_{kp}D_{lmp}$. Such ψ are called *hemitropic*.

Material symmetry

The requirement that

$$\psi(Q^*(\bar{x}), \nabla_z Q^*(\bar{x})) = \psi(Q(\bar{x}), \nabla_x Q(\bar{x}))$$

when $z = \bar{x} + \widehat{R}(x - \bar{x})$, where $\widehat{R} = -\mathbf{1} + 2e \otimes e$, $|e| = 1$, is a *reflection* is a condition of material symmetry satisfied by nematics, but not cholesterics, whose molecules have a chiral nature.

Since any $R \in O(3)$ can be written as $\hat{R}\tilde{R}$, where $\tilde{R} \in SO(3)$ and $\hat{R}$ is a reflection, for a nematic

$$\psi(Q^*, D^*) = \psi(Q, D)$$

where $Q^* = RQR^T$, $D^*_{ijk} = R_{il}R_{jm}R_{kp}D_{lmp}$ and $R \in O(3)$. Such ψ are called *isotropic*.

Bulk and elastic energies

We can decompose ψ as

$$\begin{aligned}\psi(Q,D) &= \psi(Q,0) + (\psi(Q,D) - \psi(Q,0)) \\ &= \psi_B(Q) + \psi_E(Q,D) \\ &= \text{bulk} + \text{elastic}\end{aligned}$$

Thus, putting $D = 0$,

$$\psi_B(RQR^T) = \psi_B(Q) \ \text{ for all } R \in SO(3),$$

which holds if and only if ψ_B is a function of the principal invariants of Q, that is, since $\operatorname{tr} Q = 0$,

$$\psi_B(Q) = \bar{\psi}_B(|Q|^2, \det Q).$$

Following de Gennes, Schophol & Sluckin PRL 59(1987), Mottram & Newton, Introduction to Q-tensor theory, we consider the example

$$\psi_B(Q,\theta) = a(\theta)\,\mathrm{tr}\,Q^2 - \frac{2b}{3}\mathrm{tr}\,Q^3 + \frac{c}{2}\mathrm{tr}\,Q^4,$$

where θ is the temperature, $b > 0, c > 0, a = \alpha(\theta - \theta^*), \alpha > 0$.

Then

$$\psi_B = a\sum_{i=1}^{3}\lambda_i^2 - \frac{2b}{3}\sum_{i=1}^{3}\lambda_i^3 + \frac{c}{2}\sum_{i=1}^{3}\lambda_i^4.$$

ψ_B attains a minimum subject to $\sum_{i=1}^{3}\lambda_i = 0$. A calculation shows that the critical points have two λ_i equal. Thus $\lambda_1 = \lambda_2 = \lambda, \lambda_3 = -2\lambda$ say, where $\lambda = 0$ or $\lambda = \lambda_\pm$, and

$$\lambda_\pm = \frac{-b \pm \sqrt{b^2 - 12ac}}{6c}.$$

Hence we find that there is a phase transformation from an isotropic fluid to a uniaxial nematic phase at the critical temperature $\theta_{\mathrm{NI}} = \theta^* + \frac{2b^2}{27ac}$. If $\theta > \theta_{\mathrm{NI}}$ then the unique minimizer of ψ_B is $Q = 0$.
If $\theta < \theta_{\mathrm{NI}}$ then the minimizers are

$$Q = s_{\mathrm{min}}(n \otimes n - \frac{1}{3}\mathbf{1}) \text{ for } n \in S^2,$$

where $s_{\mathrm{min}} = \frac{b+\sqrt{b^2-12ac}}{2c} > 0$.

Examples of isotropic functions quadratic in ∇Q :

$$I_1 = Q_{ij,j}Q_{ik,k}, \quad I_2 = Q_{ik,j}\ Q_{ij,k}$$
$$I_3 = Q_{ij,k}Q_{ij,k}, \quad I_4 = Q_{lk}Q_{ij,l}Q_{ij,k}$$

Note that

$I_1 - I_2 = (Q_{ij}Q_{ik,k})_{,j} - (Q_{ij}Q_{ik,j})_{,k}$

is a null Lagrangian.

An example of a hemitropic, but not isotropic, function is

$$I_5 = \varepsilon_{ijk}Q_{il}Q_{jl,k}.$$

For the elastic energy we take

$$\psi_E(Q, \nabla Q) = \sum_{i=1}^{4} L_i I_i,$$

where the L_i are material constants.

The constrained theory

If the L_i are small (in comparison to the steepness of the potential well about the minimum of ψ_B), it is reasonable to consider the *constrained theory* in which Q is required to be uniaxial with a constant scalar order parameter $s > 0$, so that

$$Q = s(n \otimes n - \frac{1}{3}\mathbf{1}).$$

In this theory the bulk energy is constant and so we only have to consider the elastic energy

$$I(Q) = \int_\Omega \psi_E(Q, \nabla Q)\, dx.$$

Oseen-Frank energy

Formally calculating ψ_{E} in terms of n, ∇n we obtain the Oseen-Frank energy functional

$$I(n) = \int_\Omega [K_1(\mathrm{div}\, n)^2 + K_2(n \cdot \mathrm{curl}\, n)^2 + K_3|n \times \mathrm{curl}\, n|^2$$
$$+(K_2 + K_4)(\mathrm{tr}(\nabla n)^2 - (\mathrm{div} n)^2)]\, dx,$$

where

$$K_1 = 2L_1 s^2 + L_2 s^2 + L_3 s^2 - \tfrac{2}{3} L_4 s^3,$$
$$K_2 = 2L_1 s^2 - \tfrac{2}{3} L_4 s^3,$$
$$K_3 = 2L_1 s^2 + L_2 s^2 + L_3 s^2 + \tfrac{4}{3} L_4 s^3,$$
$$K_4 = L_3 s^2.$$

Function Spaces
(part of the mathematical model)

Unconstrained theory.

We are interested in equilibrium configurations of finite energy

$$I(Q) = \int_\Omega [\psi_B(Q) + \psi_E(Q, \nabla Q)]\, dx.$$

We use the Sobolev space $W^{1,p}(\Omega; M^{3\times 3})$. Since usually we assume

$$\psi_E(Q, \nabla Q) = \sum_{i=1}^{4} L_i I_i,$$

$$I_1 = Q_{ij,j}Q_{ik,k},\ I_2 = Q_{ik,j}Q_{ij,k},$$

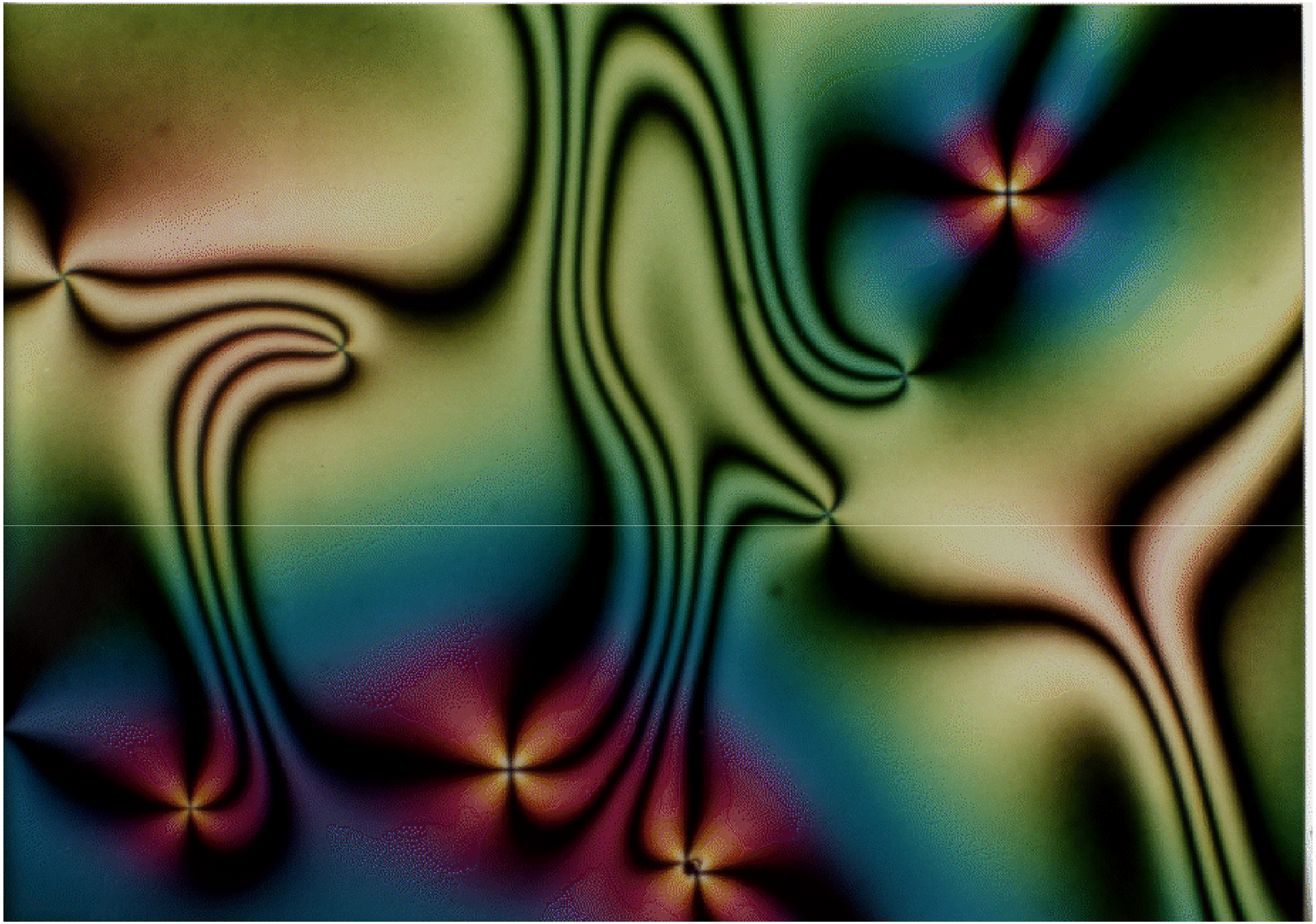
$$I_3 = Q_{ij,k}Q_{ij,k},\ I_4 = Q_{lk}Q_{ij,l}Q_{ij,k},$$

we typically take $p = 2$.

Constrained theory.

For $1 \leq p < \infty$ the Sobolev space $W^{1,p}(\Omega, \mathbf{R}P^2)$ is the set of $Q = s(n \otimes n - \frac{1}{3}\mathbf{1})$ with weak derivative ∇Q satisfying $\int_\Omega |\nabla Q(x)|^p dx < \infty$.

Thus for the Landau - de Gennes energy density, the space of Q with finite elastic energy is $W^{1,2}(\Omega, \mathbf{R}P^2)$.



Schlieren texture of a nematic film with surface point defects (boojums).
Oleg Lavrentovich (Kent State)

Possible defects in constrained theory

$$Q = s(n \otimes n - \frac{1}{3}\mathbf{1})$$

Hedgehog $\quad n(x) = \dfrac{x}{|x|}$

$$\nabla n(x) = \tfrac{1}{|x|}(\mathbf{1} - n \otimes n)$$

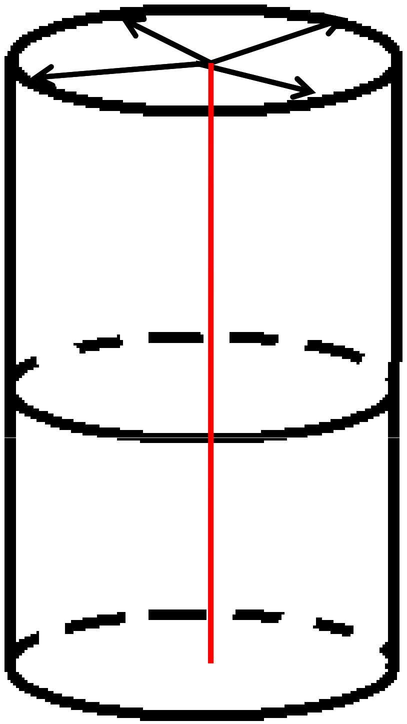
$$|\nabla n(x)|^2 = \tfrac{2}{|x|^2}$$

$$\textstyle\int_0^1 r^{2-p} dr < \infty$$

$Q, n \in W^{1,p}, \ 1 \leq p < 3$

Finite energy

Disclinations



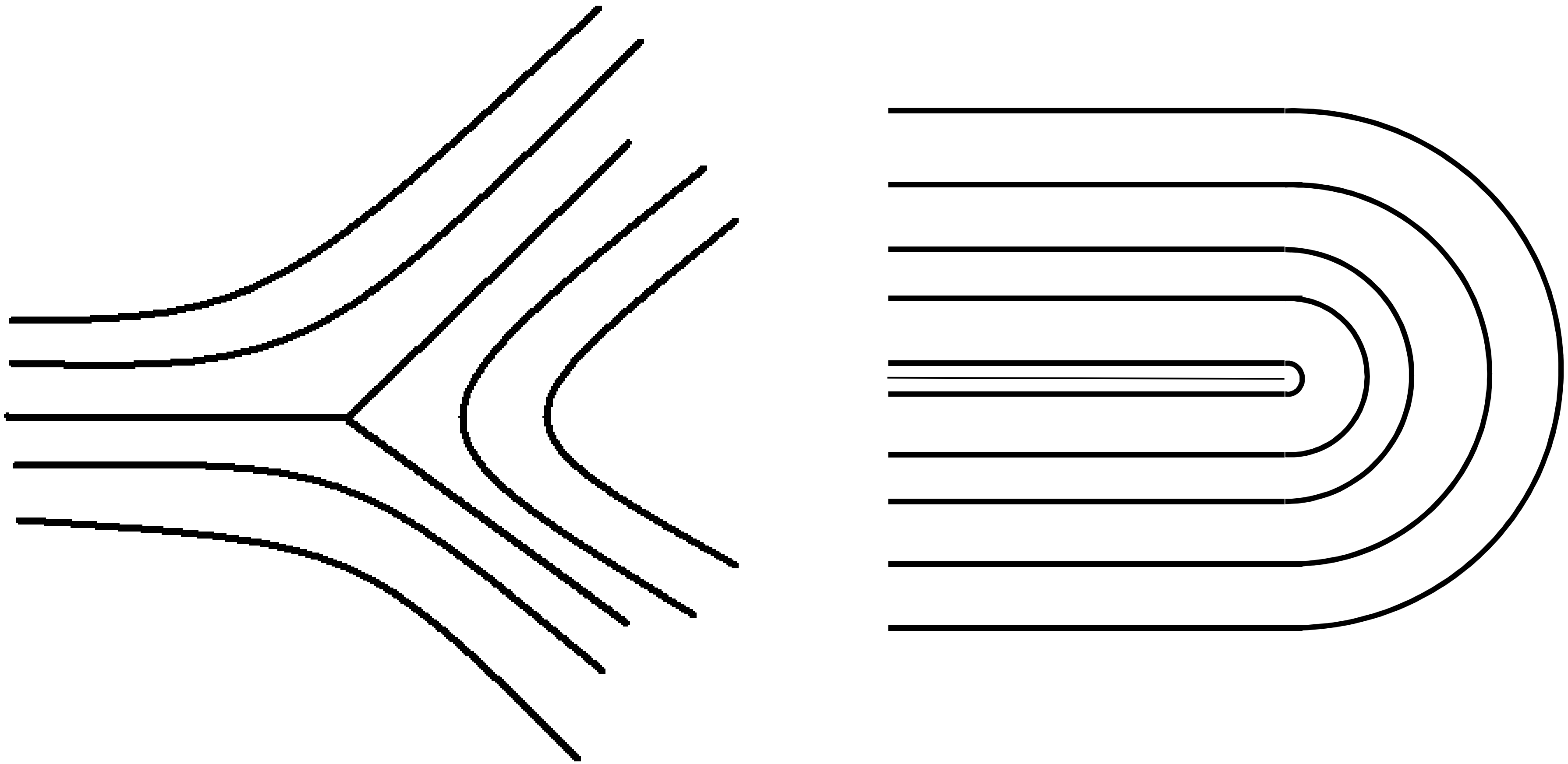
$$n(x) = (\frac{x_1}{r}, \frac{x_2}{r}, 0) \quad r = \sqrt{x_1^2 + x_2^2}$$

$$|\nabla n(x)|^2 = \frac{1}{r^2}$$

$$n, Q \in W^{1,p} \Leftrightarrow 1 \leq p < 2$$

infinite energy for quadratic models

Index one half singularities



$$Q \notin W^{1,2}$$

Existence of minimizers in the constrained theory

Immediate in $W^{1,2}(\Omega, \mathbf{R}P^2)$, for a variety of boundary conditions, under suitable inequalities on the L_i, since ψ_E is then convex in ∇Q and coercive and the uniaxiality contraint is weakly closed.

The equilibrium equations (JB/Majumdar)

Let Q be a minimizer of

$$I(Q) = \int_\Omega \psi_E(Q, \nabla Q)\, dx$$

subject to $Q \in K = \{s(n \otimes n - \frac{1}{3}\mathbf{1}) : n \in S^2\}$. Considering a variation

$$Q_\varepsilon = s\left(\frac{[n + \varepsilon a \wedge n] \otimes [n + \varepsilon a \wedge n]}{|n + \varepsilon a \wedge n|^2} - \frac{1}{3}\mathbf{1}\right),$$

with a smooth and of compact support, we get the weak form of the equilibrium equations

$$ZQ = QZ,$$

where $Z_{ij} = \frac{\partial \psi_E}{\partial Q_{ij}} - \frac{\partial}{\partial x_k}\frac{\partial \psi_E}{\partial D_{ijk}}$ (ψ_E symmetrized).

Can we orient the director? (JB/Zarnescu)

We say that $Q = Q(x)$ is *orientable* if we can write

$$Q(x) = s(n(x) \otimes n(x) - \frac{1}{3}\mathbf{1}),$$

where $n \in W^{1,p}(\Omega, S^2)$.
This means that for each x we can make a choice of the unit vector $n(x) = \pm\tilde{n}(x) \in S^2$ so that $n(\cdot)$ has some reasonable regularity, sufficient to have a well-defined gradient ∇n (in topological jargon such a choice is called a *lifting*).

Relating the Q and n descriptions

Proposition

Let $Q = s(n \otimes n - \frac{1}{3}\mathbf{1})$, s a nonzero constant, $|n| = 1$ a.e., belong to $W^{1,p}(\Omega; \mathbf{R}P^2)$ for some p, $1 \leq p < \infty$. If n is continuous along almost every line parallel to the coordinate axes, then $n \in W^{1,p}(\Omega, S^2)$ (in particular n is orientable), and

$$n_{i,k} = Q_{ij,k} n_j.$$

Theorem 1

An orientable Q has exactly two orientations.

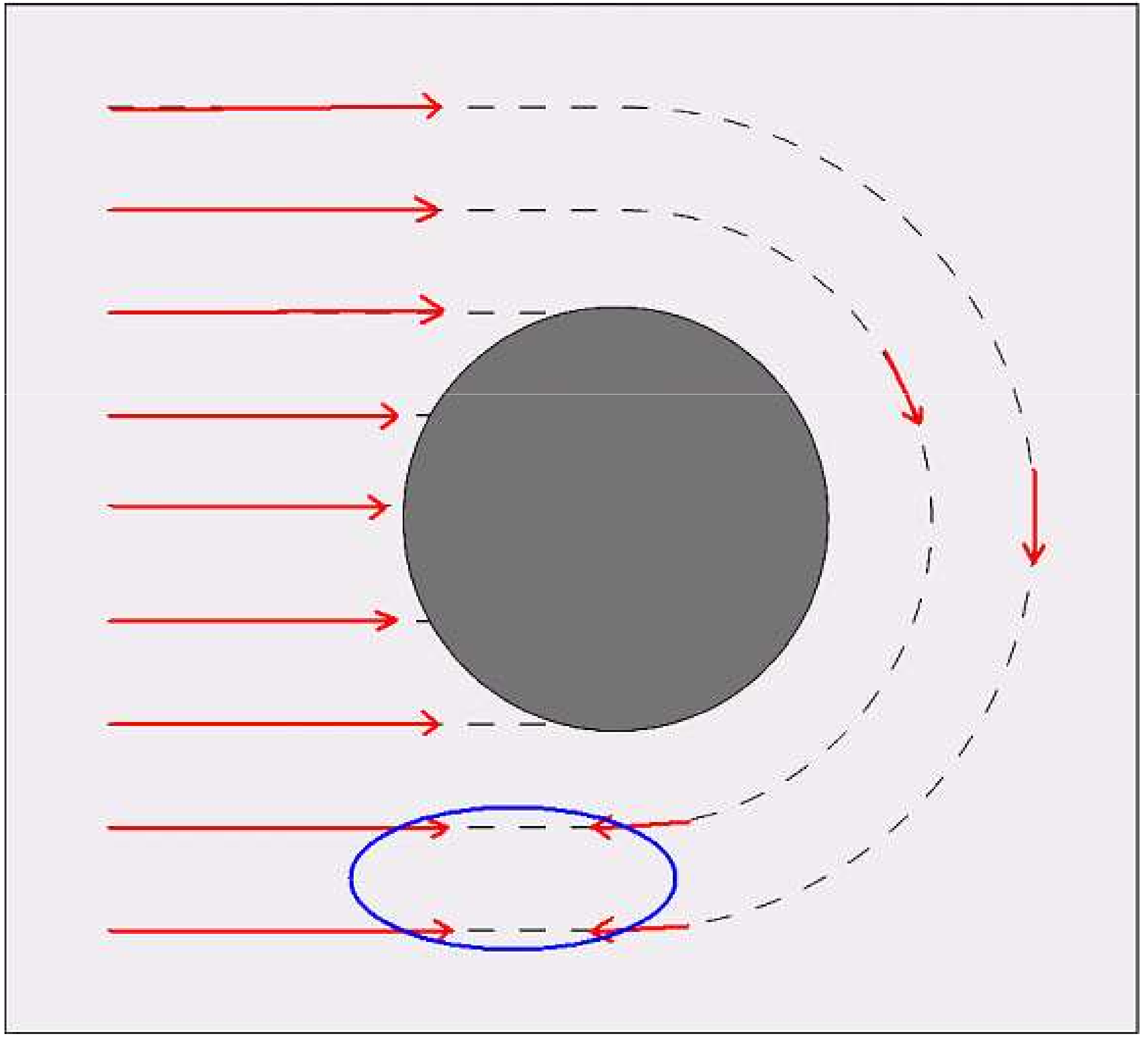
Proof

Suppose that n and τn both generate Q and belong to $W^{1,1}(\Omega, S^2)$, where $\tau^2(x) = 1$ a.e.. For a.e. x_2, x_3, both $n(x)$ and $\tau(x)n(x)$ are absolutely continuous in x_1. Hence

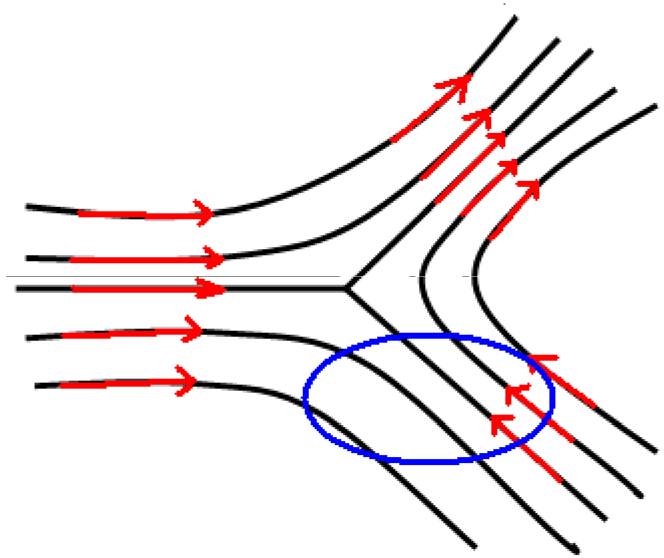
$$\tau(x)n(x) \cdot n(x) = \tau(x)$$

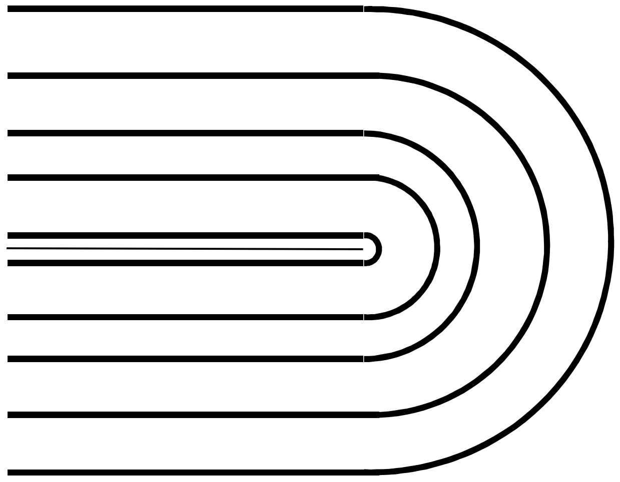
is continuous in x_1. Hence $\tau_{,1}$ exists and is zero. Similarly $\tau_{,2}, \tau_{,3}$ exist and are zero. Thus $\tau \in W^{1,\infty}$ and $\nabla\tau = 0$ a.e. in Ω. Hence $\tau = 1$ a.e. or $\tau = -1$ a.e..

A smooth nonorientable director field in a non simply connected region.



The index one half singularities are non-orientable



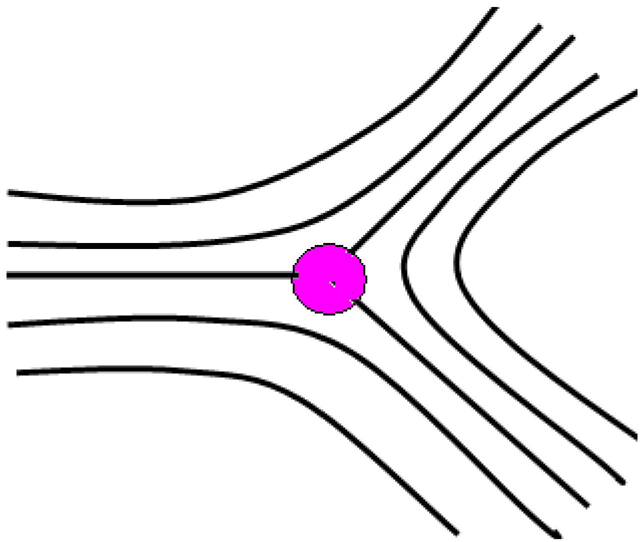


Theorem 2

If Ω is simply-connected and $Q \in W^{1,p}$, $p \geq 2$, then Q is orientable.

(See also a recent topologically more general lifting result of Bethuel and Chiron for maps u:Ω→N.)

Thus in a simply-connected region the uniaxial de Gennes and Oseen-Frank theories are equivalent.



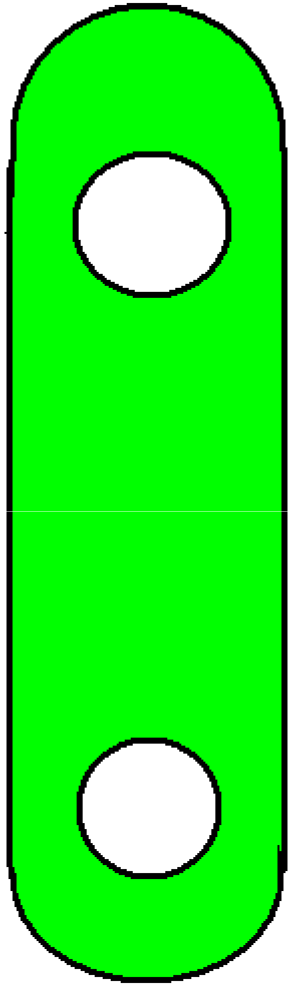
Another consequence is that it is impossible to modify this Q-tensor field in a core around the singular line so that it has finite Landau-de Gennes energy.

Ingredients of Proof of Theorem 2

- Lifting possible if Q is smooth and Ω simply-connected
- Pakzad-Rivière theorem (2003) implies that if $\partial\Omega$ is smooth, then there is a sequence of smooth $Q^{(j)}$ converging weakly to Q in $W^{1,2}$
- We can approximate a simply-connected domain with boundary of class C by ones that are simply-connected with smooth boundary
- The Proposition implies that orientability is preserved under weak convergence

2D examples and results for non simply-connected regions

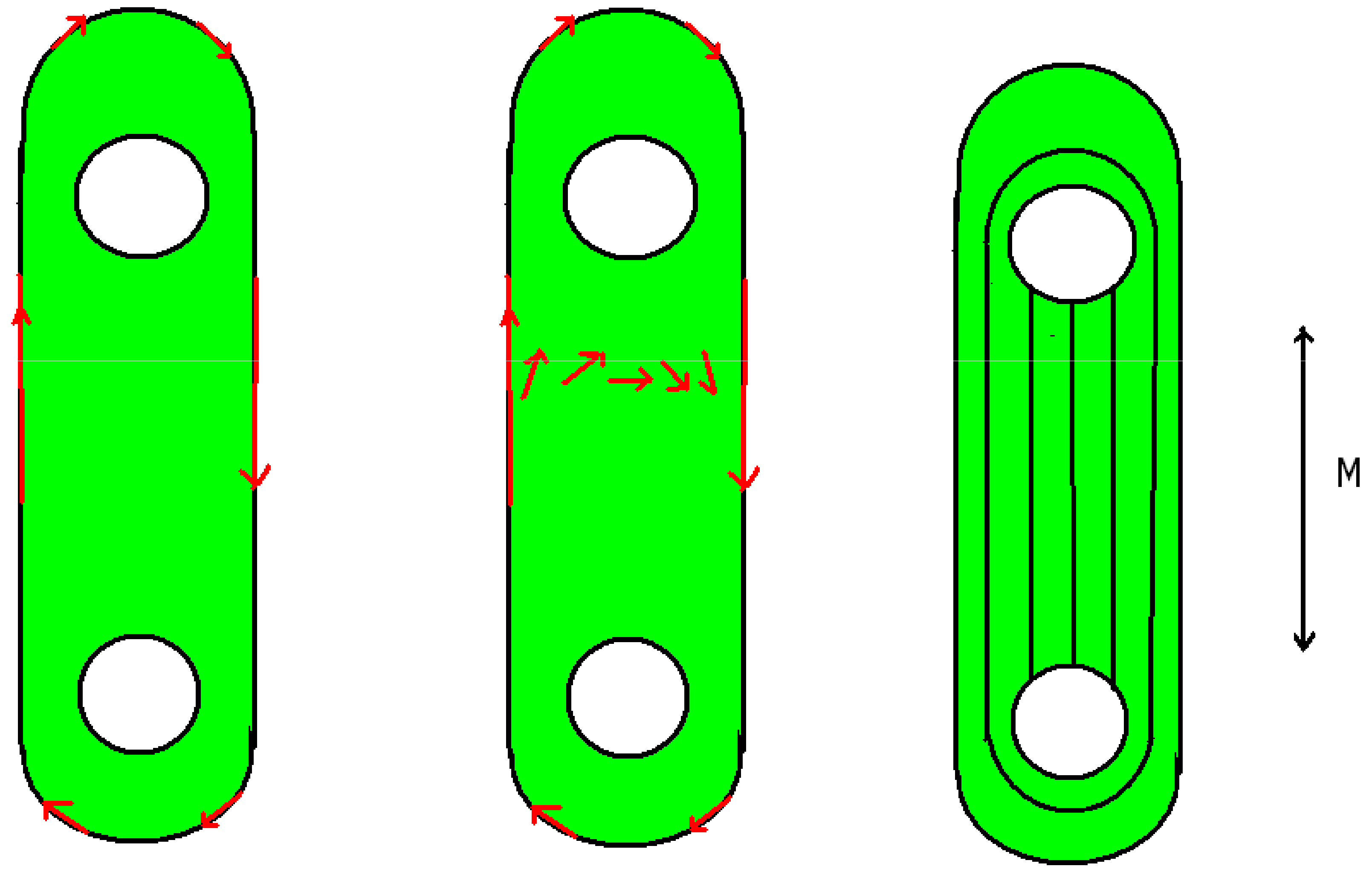
For a 2D domain with smooth boundary and a finite number of holes, $Q \in W^{1,2}$ is orientable if and only if Q is orientable on $\partial\Omega$.

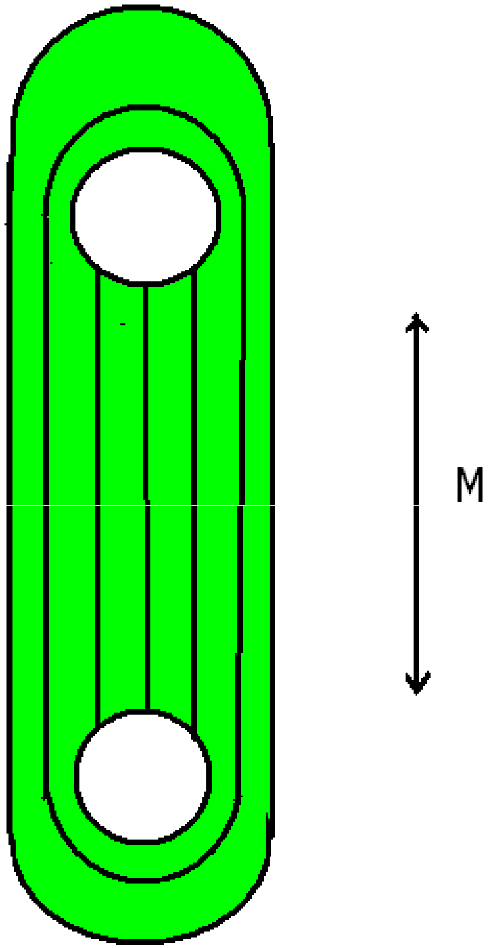


Tangent boundary conditions on outer boundary. No (free) boundary conditions on inner circles.

$$I(Q) = \int_\Omega |\nabla Q|^2 dx$$

$$I(n) = 2s^2 \int_\Omega |\nabla n|^2 dx$$


M



For M large enough the minimum energy configuration is unoriented, even though there is a minimizer among oriented maps.

If the boundary conditions correspond to the Q-field shown, then there is no orientable Q that satisfies them.

The Onsager model
(joint work with Apala Majumdar)

In the Onsager model the probability measure μ is assumed to be continuous with density $\rho = \rho(p)$, and the bulk free-energy at temperature $\theta > 0$ has the form

$$I_\theta(\rho) = U(\rho) - \theta\eta(\rho),$$

where the entropy is given by

$$\eta(\rho) = -\int_{S^2} \rho(p) \ln \rho(p)\, dp.$$

With the Maier-Saupe molecular interaction, the internal energy is given by

$$U(\rho) \;=\; \kappa\int_{S^2}\int_{S^2}[\tfrac{1}{3}-(p\cdot q)^2]\rho(p)\rho(q)\,dp\,dq$$

where $\kappa>0$ is a coupling constant.

Denoting by

$$Q(\rho)=\int_{S^2}(p\otimes p-\frac{1}{3}\mathbf{1})\rho(p)\,dp$$

the corresponding Q-tensor, we have that

$$\begin{aligned}|Q(\rho)|^2 \;&=\; \int_{S^2}\int_{S^2}(p\otimes p-\frac{1}{3}\mathbf{1})\cdot(q\otimes q-\frac{1}{3}\mathbf{1})\rho(p)\rho(q)dp\,dq\\ &=\; \int_{S^2}\int_{S^2}[(p\cdot q)^2-\frac{1}{3}]\rho(p)\rho(q)\,dp\,dq.\end{aligned}$$

Hence $U(\rho) = -\kappa|Q(\rho)|^2$ and

$$I_\theta(\rho) = \theta \int_{S^2} \rho(p) \ln \rho(p)\, dp - \kappa|Q(\rho)|^2.$$

Given Q we define

$$\begin{aligned} \psi_B(Q,\theta) &= \inf_{\{\rho : Q(\rho) = Q\}} I_\theta(\rho) \\ &= \theta \inf_{\{\rho : Q(\rho) = Q\}} \int_{S^2} \rho \ln \rho\, dp - \kappa|Q|^2 \end{aligned}$$

(cf. Katriel, J., Kventsel, G. F., Luckhurst, G. R. and Sluckin, T. J.(1986))

Let

$$J(\rho) = \int_{S^2} \rho(p) \ln \rho(p)\, dp.$$

Given Q with $Q = Q^T, \operatorname{tr} Q = 0$ and satisfying $\lambda_i(Q) > -1/3$ we seek to minimize J on the set of admissible ρ

$$\mathcal{A}_Q = \{\rho \in L^1(S^2) : \rho \geq 0, \int_{S^2} \rho\, dp = 1, Q(\rho) = Q\}.$$

Lemma. $\mathcal{A}_Q$ is nonempty.

(Remark: this is not true if we allow some $\lambda_i = -1/3$.)

Proof. A singular measure μ satisfying the constraints is

$$\mu = \frac{1}{2}\sum_{i=1}^{3}(\lambda_i + \frac{1}{3})(\delta_{e_i} + \delta_{-e_i}),$$

and a $\rho \in \mathcal{A}_Q$ can be obtained by approximating this.

For $\varepsilon > 0$ sufficiently small and $i = 1, 2, 3$ let

$$\varphi_i^\varepsilon = \begin{cases} 0 & \text{if } |p \cdot e_i| < 1 - \varepsilon \\ \frac{1}{4\pi\varepsilon} & \text{if } |p \cdot e_i| \geq 1 - \varepsilon \end{cases}$$

Then

$$\rho(p) = \frac{1}{(1 - \frac{1}{2}\varepsilon)(1 - \varepsilon)} \sum_{i=1}^{3} [\lambda_i + \frac{1}{3} - \frac{\varepsilon}{2} + \frac{\varepsilon^2}{6}] \varphi_{e_i}^\varepsilon(p)$$

works. $\square$

Theorem. J attains a minimum at a unique $\rho_Q \in \mathcal{A}_Q$.

Proof. By the direct method, using the facts that $\rho \ln \rho$ is strictly convex and grows super-linearly in ρ, while $\mathcal{A}_Q$ is sequentially weakly closed in $L^1(S^2)$. $\square$

Let $f(Q) = J(\rho_Q) = \inf_{\rho \in \mathcal{A}_Q} J(\rho)$, so that

$$\psi_B(Q, \theta) = \theta f(Q) - \kappa |Q|^2.$$

Theorem

f is strictly convex in Q and

$$\lim_{\lambda_{\min}(Q)\to -\frac{1}{3}+} f(Q) = \infty.$$

Proof

The strict convexity of f follows from that of $\rho \ln \rho$. Suppose that $\lambda_{\min}(Q^{(j)}) \to -\frac{1}{3}$ but $f(Q^{(j)})$ remains bounded. Then

$$Q^{(j)} e^{(j)} \cdot e^{(j)} + \frac{1}{3}|e^{(j)}|^2 = \int_{S^2} \rho_{Q^{(j)}}(p)(p \cdot e^{(j)})^2 dp \to 0,$$

where $e^{(j)}$ is the eigenvector of $Q^{(j)}$ corresponding to $\lambda_{\min}(Q^{(j)})$.

But we can assume that $\rho_{Q^{(j)}} \rightharpoonup \rho$ in $L^1(S^2)$, where $\int_{S^2} \rho(p)\,dp = 1$ and that $e^{(j)} \to e$, $|e| = 1$. Passing to the limit we deduce that

$$\int_{S^2} \rho(p)(p \cdot e)^2 dp = 0.$$

But this means that $\rho(p) = 0$ except when $p \cdot e = 0$, contradicting $\int_{S^2} \rho(p)\,dp = 1$. $\square$

The Euler-Lagrange equation for J

Theorem. Let $Q = \operatorname{diag}(\lambda_1, \lambda_2, \lambda_3)$. Then

$$\rho_Q(p) = \frac{\exp(\mu_1 p_1^2 + \mu_2 p_2^2 + \mu_3 p_3^2)}{Z(\mu_1, \mu_2, \mu_3)},$$

where

$$Z(\mu_1, \mu_2, \mu_3) = \int_{S^2} \exp(\mu_1 p_1^2 + \mu_2 p_2^2 + \mu_3 p_3^2)\, dp.$$

The μ_i solve the equations

$$\frac{\partial \ln Z}{\partial \mu_i} = \lambda_i + \frac{1}{3}, \quad i = 1, 2, 3,$$

and are unique up to adding a constant to each μ_i.

Proof. We need to show that ρ_Q satisfies the Euler-Lagrange equation. There is a small difficulty due to the constraint $\rho \geq 0$. For $\tau > 0$ let $S_\tau = \{p \in S^2 : \rho_Q(p) > \tau\}$, and let $z \in L^\infty(S^2)$ be zero outside S_τ and such that

$$\int_{S_\tau} (p \otimes p - \frac{1}{3}\mathbf{1}) z(p)\, dp = 0, \quad \int_{S_\tau} z(p)\, dp = 0.$$

Then $\rho_\varepsilon := \rho_Q + \varepsilon z \in \mathcal{A}_Q$ for all $\varepsilon > 0$ sufficiently small. Hence

$$\frac{d}{d\varepsilon} J(\rho_\varepsilon)|_{\varepsilon=0} = \int_{S_\tau} [1 + \ln \rho_Q] z(p)\, dp = 0.$$

So by Hahn-Banach

$$1 + \ln \rho_Q = \sum_{i,j=1}^{3} C_{ij}[p_i p_j - \frac{1}{3}] + C$$

for constants $C_{ij}(\tau)$, $C(\tau)$. Since S_τ increases as τ decreases the constants are independent of τ, and hence

$$\rho_Q(p) = A \exp\left(\sum_{i,j=1}^{3} C_{ij} p_i p_j\right) \text{ if } \rho_Q(p) > 0.$$

Suppose for contradiction that

$$E = \{p \in S^2 : \rho_Q(p) = 0\}$$

is such that $\mathcal{H}^2(E) > 0$. There exists $z \in L^\infty(S^2)$ such that

$$\int_{\{\rho_Q>0\}} (p \otimes p - \frac{1}{3}\mathbf{1}) z(p)\, dp = 0, \int_{\{\rho_Q>0\}} z(p)\, dp = 4\pi$$

(this is possible since $1 = \sum_{i,j=1}^3 (D_{ij}(p_i p_j - \frac{1}{3}\delta_{ij})$ is impossible for constants D_{ij}). Define for $\varepsilon > 0$ sufficiently small

$$\rho_\varepsilon = \rho_Q + \varepsilon - \varepsilon z.$$

Then $\rho_\varepsilon \in \mathcal{A}_Q$, since $\int_{S^2}(p \otimes p - \frac{1}{3}\mathbf{1})\,dp = 0$.
Hence, since ρ_Q is the unique minimizer,

$$\int_E \varepsilon \ln \varepsilon + \int_{\{\rho_Q>0\}} [(\rho_Q + \varepsilon - \varepsilon z) \ln(\rho_Q + \varepsilon - \varepsilon z) - \rho_Q \ln \rho_Q]\,dp > 0.$$

This is impossible since the second integral is of order ε.
Hence we have proved that

$$\rho_Q(p) = A \exp(\sum_{i,j=1}^{3} C_{ij} p_i p_j), \text{a.e. } p \in S^2.$$

Lemma. Let $R^T Q R = Q$ for some $R \in O(3)$. Then $\rho_Q(Rp) = \rho_Q(p)$ for all $p \in S^2$.

Proof.

$$\int_{S^2} (p \otimes p - \frac{1}{3}\mathbf{1}) \rho_Q(Rp)\, dp$$

$$= \int_{S^2} (R^T q \otimes R^T q - \frac{1}{3}\mathbf{1}) \rho_Q(q)\, dq$$

$$= R^T Q R = Q,$$

and ρ_Q is unique. $\square$

Applying the lemma with $Re_i = -e_i$, $Re_j = e_j$ for $j \neq i$, we deduce that for $Q = \mathrm{diag}\,(\lambda_1, \lambda_2, \lambda_3)$,

$$\rho_Q(p) = \frac{\exp(\mu_1 p_1^2 + \mu_2 p_2^2 + \mu_3 p_3^2)}{Z(\mu_1, \mu_2, \mu_3)},$$

where

$$Z(\mu_1, \mu_2, \mu_3) = \int_{S^2} \exp(\mu_1 p_1^2 + \mu_2 p_2^2 + \mu_3 p_3^2)\, dp,$$

as claimed.

Finally

$$\begin{aligned} \frac{\partial \ln Z}{\partial \mu_i} &= Z^{-1} \int_{S^2} p_i^2 \exp(\sum_{j=1}^{3} \mu_j p_j^2)\, dp \\ &= \lambda_i + \frac{1}{3}, \end{aligned}$$

and the uniqueness of the μ_i up to adding a constant to each follows from the uniqueness of ρ_Q. $\square$

Hence the bulk free energy has the form

$$\psi_B(Q,\theta) = \theta \sum_{i=1}^{3} \mu_i(\lambda_i + \frac{1}{3}) - \theta \ln Z - \kappa \sum_{i=1}^{3} \lambda_i^2.$$

Consequences

1. Logarithmic divergence of ψ_B as $\min \lambda_i(Q) \to -\frac{1}{3}$.

2. All critical points of ψ_B are uniaxial.

3. Phase transition predicted from isotropic to uniaxial nematic phase just as in the quartic model.

4. Minimizers ρ^* of $I_\theta(\rho)$ correspond to minimizers over Q of $\psi_B(Q, \theta)$. These ρ^* were calculated and shown to be uniaxial by Fatkullin and Slastikov (2005).

5. Using a maximum principle we can show that minimizers of

$$I(Q) = \int_\Omega [\psi_B(Q) + K|\nabla Q|^2]\, dx,$$

subject to $Q(x) = Q_0(x)$ for $x \in \partial\Omega$, where $K > 0$ and $Q_0(\cdot)$ is sufficiently smooth with $\lambda_{\text{min}}(Q_0(x)) > -\frac{1}{3}$, satisfy

$$\lambda_{\text{min}}(Q(x)) > -\frac{1}{3} + \varepsilon,$$

for some $\varepsilon > 0$.

(Compare nonlinear elasticity, for which the energy is $I(y) = \int_\Omega W(\nabla y(x))\, dx$, with $W(A) \to \infty$ for $\det A \to 0+$.)

Existence for full Q-tensor theory

We have to minimize

$$I(Q) = \int_\Omega [\psi_B(Q) + \psi_E(Q, \nabla Q)]\, dx$$

subject to suitable boundary conditions.

Suppose we take $\psi_B : \mathcal{E} \to \mathbf{R}$ to be continuous, $\mathcal{E} = \{Q \in M^{3\times 3} : Q = Q^T, \mathrm{tr}\, Q = 0\}$, (e.g. of the quartic form considered previously) and

$$\psi_E(Q, \nabla Q) = \sum_{i=1}^{4} L_i I_i,$$

which is the simplest form that reduces to Oseen-Frank in the constrained case. Then ...

Proposition. For any boundary conditions, if $L_4 \neq 0$ then

$$I(Q) = \int_\Omega [\psi_B(Q) + \sum_{i=1}^{4} L_i I_i]\, dx$$

is unbounded below.

Proof. Choose any Q satisfying the boundary conditions, and multiply it by a smooth function $\varphi(x)$ which equals one in a neighbourhood of $\partial\Omega$ and is zero in some ball $B \subset \Omega$, which we can take to be $B(0,1)$. We will alter Q in B so that

$$J(Q) = \int_B [\psi_B(Q) + \sum_{i=1}^{4} L_i I_i] \, dx$$

is unbounded below subject to $Q|_{\partial B} = 0$.

Choose

$$Q(x) = \theta(r)\left[\frac{x}{|x|} \otimes \frac{x}{|x|} - \frac{1}{3}\mathbf{1}\right], \ \theta(1) = 0,$$

where $r = |x|$. Then

$$|\nabla Q|^2 = \frac{2}{3}\theta'^2 + \frac{4}{r^2}\theta^2,$$

and

$$I_4 = Q_{kl}Q_{ij,k}Q_{ij,l} = \frac{4}{9}\theta(\theta'^2 - \frac{3}{r^2}\theta^2).$$

Hence

$$J(Q) \leq 4\pi \int_0^1 r^2 \left[\psi_B(Q) + C\left(\frac{2}{3}\theta'^2 + \frac{4}{r^2}\theta^2\right) + L_4 \frac{4}{9}\theta\left(\theta'^2 - \frac{3}{r^2}\theta^2\right)\right] dr,$$

where C is a constant.

Provided θ is bounded, all the terms are bounded except

$$4\pi \int_0^1 r^2 \left(\frac{2}{3}C + \frac{4}{9}L_4\theta\right)\theta'^2 \, dr.$$

Choose

$$\theta(r) = \begin{cases} \theta_0(2 + \sin kr) & 0 < r < \frac{1}{2} \\ 2\theta_0(2 + \sin \frac{k}{2})(1 - r) & \frac{1}{2} < r < 1 \end{cases}$$

The integrand is then bounded on $(\frac{1}{2}, 1)$ and we need to look at

$$4\pi \int_0^{\frac{1}{2}} r^2 \left(\frac{2}{3}C + \frac{4}{9}L_4\theta_0(2 + \sin kr) \right) \theta_0^2 k^2 \cos^2 kr \, dr,$$

which tends to $-\infty$ if $L_4\theta_0$ is sufficiently negative. $\square$

$$I_1 = Q_{ij,j}Q_{ik,k}, \quad I_2 = Q_{ik,j}\ Q_{ij,k}$$
$$I_3 = Q_{ij,k}Q_{ij,k}, \quad I_4 = Q_{lk}Q_{ij,l}Q_{ij,k}$$

But if $\psi_B(Q) \to \infty$ when $\lambda_{\text{min}}(Q) \to -1/3$ the difficult term I_4 can be absorbed into I_3, since

$$\frac{2}{3}I_3 \geq I_4 \geq -\frac{1}{3}I_3$$

and the existence of a minimizer follows under appropriate conditions on the L_i, even when $L_4 \neq 0$.

In fact using the results when $L_4 = 0$ of Davis & Gartland (1998) we find that a minimizer exists when

$$\tilde{L}_3 > 0, -\tilde{L}_3 < L_2 < 2\tilde{L}_3, -\frac{3}{5}\tilde{L}_3 - \frac{1}{10}L_2 < L_1,$$

where

$$\tilde{L}_3 = \begin{cases} L_3 - \frac{1}{3}L_4 & \text{if } L_4 \geq 0 \\ L_3 + \frac{2}{3}L_4 & \text{if } L_4 < 0 \end{cases}.$$

The end