## Mathematical Theories of Liquid Crystals

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## Course Outline

I. Fundamentals<br>II. The Maier-Saupe Theory<br>III. The Onsager Theory<br>IV. The Oseen-Frank Theory<br>V. The Landau-deGennes Theory<br>VI. The Ericksen-Leslie Theory

## Mathematical Theories of Liquid Crystals

## I. Fundamentals

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## Summary

Terminology
Order Parameters
Optical Properties
Schlieren Textures

## Terminology

Liquid crystals were discovered by Reinitzer (1888)
....it struck me that the substance, in this case, melted not into a clear transparent [liquid] but always into a cloudy, only translucent liquid, which I initially considered to be a sign of impurities ... Upon closer examination, it was then also noted that when it was heated at to higher temperatures, the clouding suddenly vanished. This remarkable phenomenon of the presence of two melting points, if one may express it thus, ...

## Mesophases

Liquid crystals are mesophases, that is, intermediate states of matter, which flow like nearly incompressible viscous fluids, and yet retain several features, especially optical, characteristic of crystals.

There are essentially two distinct ways to induce the liquid crystalline phase in a mesogenic substance:

- thermotropic, by changing its temperature;
- lypotropic, by changing its concentration.
molecular perspectives
Liquid crystals are characterised by a molecular organization intermediate between different types of order.
- nematics: No positional order (of the molecules' centre of mass), long-range orientational order (of the molecules' long axis)
- smectics: one-dimensional positional order (layering), longrange orientational order (within layers)


## molecular shape

Distinctive features of nematogenic molecules are their

- elongated shape
- head-tail symmetry

ordering cartoons



## Order Parameters

A sound theory of liquid crystals must be based on a quantitative description of the collective behaviour of molecules that makes them tend to be organized.

## Orientation Distribution

We shall consider only the orientational degrees of freedom of uniaxial molecules.

$$
\begin{gathered}
\varrho: \mathbb{S}^{2} \rightarrow \mathbb{R}^{+} \quad \text { probability density } \\
\boldsymbol{m} \in \mathbb{S}^{2} \quad \text { molecular axis } \\
\mathbb{S}^{2} \quad \text { unit sphere in } \mathbb{R}^{3} \\
\varrho(\boldsymbol{m})=\varrho(-\boldsymbol{m}) \quad \text { head-tail symmetry } \\
\varrho \text { is integrable on } \mathbb{S}^{2} \text { and it may vanish } \\
\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m}) \mathrm{d} A(\boldsymbol{m})=1
\end{gathered}
$$

If $N$ molecules constitute an ensemble,

$$
n[\mathscr{S}]:=N \int_{\mathscr{S}} \varrho(\boldsymbol{m}) \mathrm{d} A
$$

is the number of molecules expected to be oriented with $\boldsymbol{m}$ in $\mathscr{S} \in \mathbb{S}^{2}$. symmetry consequences

- Let $\mathscr{S}^{-}:=\left\{\boldsymbol{m} \in \mathbb{S}^{2}:-\boldsymbol{m} \in \mathscr{S}\right\}$. Then $n\left[\mathscr{S}^{-}\right]=n[\mathscr{S}]$
- Let $\mathbf{m}:=\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m}) \boldsymbol{m} \mathrm{d} A$ denote the first moments of $\varrho$. Then $\mathbf{m}=0$.


## second moments

The first non-vanishing moments of $\varrho$ are expressed by the second-rank tensor

$$
\mathbf{M}:=\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m}) \boldsymbol{m} \otimes \boldsymbol{m} \mathrm{d} A
$$

## properties of M

- $\operatorname{tr} \mathbf{M}=\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m}) \operatorname{tr}(\boldsymbol{m} \otimes \boldsymbol{m}) \mathrm{d} A=\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m}) \mathrm{d} A=1$
- $\mathbf{M}^{\top}=\int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m})(\boldsymbol{m} \otimes \boldsymbol{m})^{\top} \mathrm{d} A=\mathbf{M}$

M is a symmetric tensor with unit trace.

## averages

Let $\boldsymbol{e} \in \mathbb{S}^{2}$ be any given unit vector.

$$
\begin{aligned}
& \boldsymbol{e} \cdot \mathbf{M} \boldsymbol{e}= \int_{\mathbb{S}^{2}} \varrho(\boldsymbol{m})(\boldsymbol{m} \cdot \boldsymbol{e})^{2} \mathrm{~d} A=:\left\langle(\boldsymbol{m} \cdot \boldsymbol{e})^{2}\right\rangle \\
& \boldsymbol{e} \cdot \mathbf{M} \boldsymbol{e}=\left\langle\cos ^{2} \vartheta\right\rangle \in[0,1] \\
& \vartheta \quad \text { angle between } \boldsymbol{m} \text { and } \boldsymbol{e}
\end{aligned}
$$

## eigenvalues of M

$$
\begin{gathered}
\mu_{1}+\mu_{2}+\mu_{3}=1 \\
0 \leqq \mu_{i} \leqq 1
\end{gathered}
$$

isotropic distribution

$$
\begin{gathered}
\varrho_{0} \equiv \frac{1}{4 \pi} \\
\mathbf{M}_{0}=\int_{\mathbb{S}^{2}} \varrho_{0} \boldsymbol{m} \otimes \boldsymbol{m} \mathrm{~d} A
\end{gathered}
$$

Since $\mathbb{S}^{2}$ in invariant under rotations, for any $\mathbf{R} \in S O(3)$,

$$
\mathbf{M}_{0}=\int_{\mathbb{S}^{2}} \varrho_{0} \mathbf{R} \boldsymbol{m} \otimes \mathbf{R} \boldsymbol{m} \mathrm{~d} A=\int_{\mathbb{S}^{2}} \varrho_{0} \mathbf{R}(\boldsymbol{m} \otimes \boldsymbol{m}) \mathbf{R}^{\top} \mathrm{d} A=\mathbf{R M}_{0} \mathbf{R}^{\top}
$$

Since $\mathbf{R}^{\top} \mathbf{R}=\mathbf{R R}^{\top}=\mathbf{I}$

$$
\mathbf{M}_{0} \mathbf{R}=\mathbf{R M}_{0} \quad \text { for all } \quad \mathbf{R} \in \mathrm{SO}(3)
$$

Since $\operatorname{tr} \mathbf{M}_{0}=1$,

$$
\begin{gathered}
\mathbf{M}_{0}=\frac{1}{3} \mathbf{I} \text { and so }\left\langle\cos ^{2} \vartheta\right\rangle=\frac{1}{3} \\
\text { Order Tensor }
\end{gathered}
$$

$$
\mathrm{Q}:=\mathbf{M}-\mathbf{M}_{0} \quad \text { De Gennes (1974) }
$$

pitfall
Let $\mathrm{SO}(\boldsymbol{e}):=\{\mathbf{R} \in \mathrm{SO}(3): \mathbf{R} \boldsymbol{e}=\boldsymbol{e}\}$. Consider a probability density $\varrho$ which is axis-symmetric about $e$

$$
\varrho(\mathbf{R} \boldsymbol{m})=\varrho(\boldsymbol{m}) \quad \text { for all } \quad \mathbf{R} \in \mathrm{SO}(\boldsymbol{e})
$$

Then,

$$
\mathbf{M}=\frac{1}{2}(3 \alpha-1) \boldsymbol{e} \otimes \boldsymbol{e}+\frac{1}{2}(1-\alpha) \mathbf{I} \quad \text { where } \quad \alpha=\boldsymbol{e} \cdot \mathbf{M} \boldsymbol{e}
$$

## conical distribution

Letting $\alpha=\frac{1}{3}$, we see that $\mathbf{M}=\mathbf{M}_{0}$ also for molecules distributed uniformly about a cone with axis $e$ and semi-amplitude equal to the magic angle

$$
\begin{aligned}
& \vartheta_{0}:=\arccos \sqrt{\frac{1}{3}} \\
& \text { properties of } \mathrm{Q}
\end{aligned}
$$

- $\operatorname{tr} \mathbf{Q}=0$
- $\mathbf{Q}=\lambda_{1} \boldsymbol{n}_{1} \otimes \boldsymbol{n}_{1}+\lambda_{2} \boldsymbol{n}_{2} \otimes \boldsymbol{n}_{2}+\lambda_{3} \boldsymbol{n}_{3} \otimes \boldsymbol{n}_{3}$
- $\lambda_{1}+\lambda_{2}+\lambda_{3}=0$
- $-\frac{1}{3} \leqq \lambda_{i} \leqq \frac{2}{3}$


## scalar order parameters

Three cases may arise

- $\lambda_{1}=\lambda_{2}=\lambda_{3}=0 \quad \mathbf{Q}$ is isotropic

$$
\mathrm{Q}=0
$$

- $\lambda_{1}=\lambda_{2} \quad \lambda_{3}=-2 \lambda_{1} \quad \mathrm{Q}$ is uniaxial

$$
\mathbf{Q}=S\left(\boldsymbol{n} \otimes \boldsymbol{n}-\frac{1}{3} \mathbf{I}\right) \quad \boldsymbol{n}=\boldsymbol{n}_{3}, \quad S=-3 \lambda_{1}
$$

$S$ degree of orientation $\boldsymbol{n}$ nematic director

- $\lambda_{1} \neq \lambda_{2} \neq \lambda_{3} \quad \mathrm{Q}$ is biaxial

$$
\begin{aligned}
& \mathbf{Q}=S_{1}\left(\boldsymbol{n}_{1} \otimes \boldsymbol{n}_{1}-\frac{1}{3} \mathbf{I}\right)+S_{2}\left(\boldsymbol{n}_{2} \otimes \boldsymbol{n}_{2}-\frac{1}{3} \mathbf{I}\right) \\
& S_{1}=2 \lambda_{1}+\lambda_{2}, S_{2}=\lambda_{1}+2 \lambda_{2}
\end{aligned}
$$

## alternative representation

For a generic, biaxial $\mathbf{Q}$, we can also write

$$
\begin{gathered}
\mathbf{Q}=S\left(\boldsymbol{n}_{3} \otimes \boldsymbol{n}_{3}-\frac{1}{3} \mathbf{I}\right)+T\left(\boldsymbol{n}_{1} \otimes \boldsymbol{n}_{1}-\boldsymbol{n}_{2} \otimes \boldsymbol{n}_{2}\right) \\
S:=-\frac{1}{2}\left(S_{1}+S_{2}\right) \quad \text { uniaxial scalar order parameter } \\
T:=\frac{1}{2}\left(S_{1}-S_{2}\right) \quad \text { biaxial scalar order parameter } \\
\text { admissible order parameters }
\end{gathered}
$$

By requiring

$$
-\frac{1}{3} \leqq \boldsymbol{e} \cdot \mathbf{Q} \boldsymbol{e} \leqq \frac{2}{3} \quad \text { for all } \boldsymbol{e} \in \mathbb{S}^{2}
$$

we obtain

$$
-\frac{1}{2} \leqq S \leqq \quad \text { and } \quad-\frac{1}{3}(1-S) \leqq T \leqq \frac{1}{3}(1-S)
$$

order parameter interpretation
For any given $e \in \mathbb{S}^{2}$,

$$
\begin{aligned}
\boldsymbol{e} \cdot \mathbf{M} \boldsymbol{e} & =\frac{1}{3}(1-S)+S\left(\boldsymbol{n}_{3} \cdot \boldsymbol{e}\right)^{2}+T\left[\left(\boldsymbol{n}_{1} \cdot \boldsymbol{e}\right)^{2}-\left(\boldsymbol{n}_{2} \cdot \boldsymbol{e}\right)^{2}\right] \\
& =\left\langle(\boldsymbol{m} \cdot \boldsymbol{e})^{2}\right\rangle
\end{aligned}
$$

- $\boldsymbol{e}=\boldsymbol{n}_{3} \quad S=\frac{3}{2}\left[\left\langle\left(\boldsymbol{m} \cdot \boldsymbol{n}_{3}\right)^{2}\right\rangle-\frac{1}{3}\right]=\left\langle P_{2}\left(\boldsymbol{m} \cdot \boldsymbol{n}_{3}\right)\right\rangle$

$$
P_{2}(x):=\frac{1}{2}\left(3 x^{2}-1\right) \quad \text { second Legendre polynomial }
$$

- $\boldsymbol{e}=\boldsymbol{n}_{1} \& \boldsymbol{e}=\boldsymbol{n}_{2} \quad T=\frac{1}{2}\left[\left\langle\left(\boldsymbol{m} \cdot \boldsymbol{n}_{1}\right)^{2}\right\rangle-\left\langle\left(\boldsymbol{m} \cdot \boldsymbol{n}_{2}\right)^{2}\right\rangle\right]$
limiting cases
- $\boldsymbol{m} \| \boldsymbol{n}_{3} \quad S=1 \quad T=0$
- $m \perp \boldsymbol{n}_{3} \quad S=-\frac{1}{2} \quad T=0$
- $\boldsymbol{m} \| \boldsymbol{n}_{1,2} \quad S=-\frac{1}{2} \quad T= \pm \frac{1}{2}$


## order parameter conjugacies

In the general biaxial case, the eigenframe ( $\boldsymbol{n}_{1}, \boldsymbol{n}_{2}, \boldsymbol{n}_{3}$ ) of Q has no intrinsic meaning. A permutation of the $\boldsymbol{n}_{i}$ 's, with $S$ and $T$ left unchanged, delivers a Q representing the same molecular organization seen in a different frame.

Conversely, we can keep the eigenframe of $\mathbf{Q}$ fixed and permute its eigenvalues. This results in a six-fold conjugacy group generated by the elementary eigenvalue exchanges

$$
\begin{aligned}
& (S, T) \mapsto(S,-T) \\
& (S, T) \mapsto\left(\frac{3 T-S}{2}, \frac{T+S}{2}\right) \\
& (S, T) \mapsto\left(\frac{-3 T-S}{2}, \frac{T-S}{2}\right)
\end{aligned}
$$

## uniaxial lines

The loci of the $(S, T)$ plane invariant under the eigenvalue exchanges are the lines

$$
T=0 \quad T= \pm S
$$

- The union of these lines is a set invariant under all eigenvalue exchanges.
- They represent all uniaxial states of Q.
admissible triangle

aligned uniaxial $\mathrm{U}_{+}=(1,0), \mathrm{U}_{+}^{\prime}=\left(-\frac{1}{2}, \frac{1}{2}\right), \mathrm{U}_{+}^{\prime \prime}=\left(\frac{1}{2},-\frac{1}{2}\right)$
planar uniaxial $\mathrm{U}_{-}=\left(\frac{1}{4}, \frac{1}{4}\right), \mathrm{U}_{-}^{\prime}=\left(-\frac{1}{2}, 0\right), \mathrm{U}_{-}^{\prime \prime}=\left(\frac{1}{4},-\frac{1}{4}\right)$


## Optical Properties

A proper description of the optic properties of liquid crystals relies on understanding their electric and magnetic behaviour in response to applied external fields.

## Magnetic permeability

The magnetic properties of macroscopic media are described by the fields

$$
\begin{gathered}
\boldsymbol{B} \quad \text { magnetic induction } \\
\boldsymbol{H} \quad \text { magnetic strength } \\
\boldsymbol{M} \quad \text { magnetization } \\
\boldsymbol{H}:=\frac{1}{\mu_{0}} \boldsymbol{B}-\boldsymbol{M} \\
\mu_{0}=4 \pi \times 10^{-7} \mathrm{SI} \text { magnetic permeability of free space } \\
\boldsymbol{M}=\chi \boldsymbol{H} \quad \text { linear constitutive law } \\
\chi \quad \text { magnetic susceptibility tensor }
\end{gathered}
$$

$$
\boldsymbol{B}=\mu_{0}(\underbrace{\mathbf{I}+\boldsymbol{\chi}}_{\mu_{\mathrm{rel}}}) \boldsymbol{H}
$$

$\boldsymbol{\mu}_{\text {rel }} \quad$ relative permeability tensor
molecular magnetic susceptibility
An individual molecule feels a magnetic field that differs from the applied field by the field $\boldsymbol{H}_{\text {mag }}$ produced by the molecular currents associated with the induced magnetic dipole $\boldsymbol{\mu}_{\text {mol }}$.

$$
\begin{gathered}
\boldsymbol{\mu}_{\mathrm{mol}}=\chi_{\mathrm{mol}}\left(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{mag}}\right) \\
\text { uniaxial symmetry }
\end{gathered}
$$

If the molecular response is uniaxial, symmetry dictates that

$$
\begin{gathered}
\boldsymbol{\chi}_{\mathrm{mol}}=\chi_{\|}^{(\mathrm{mol})} \boldsymbol{m} \otimes \boldsymbol{m}+\chi_{\perp}^{(\mathrm{mol})}(\mathbf{I}-\boldsymbol{m} \otimes \boldsymbol{m}) \\
\chi_{\|}^{(\mathrm{mol})} \quad \text { parallel } \text { molecular susceptibility } \\
\chi_{\perp}^{(\mathrm{mol})} \quad \text { perpendicular molecular susceptibility }
\end{gathered}
$$

## remarks

- To compute $\boldsymbol{H}_{\text {mag }}$ we need some kind of molecular model.
- $\boldsymbol{H}_{\mathrm{mag}}$ is expected to be (linearly) related to $\boldsymbol{\mu}_{\mathrm{mol}}$.
- Liquid crystal molecules are diamagnetic with small (negative) susceptibilities.
- $\boldsymbol{\mu}_{\mathrm{mol}}=\boldsymbol{\chi}_{\mathrm{mol}}\left(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{mag}}\right)$; hence, we may neglect $\boldsymbol{H}_{\mathrm{mag}}$. macroscopic susceptibility

$$
\boldsymbol{M}=\rho_{0}\left\langle\boldsymbol{\mu}_{\mathrm{mol}}\right\rangle=\boldsymbol{\chi} \boldsymbol{H} \quad \boldsymbol{\chi}=\rho_{0}\left\langle\boldsymbol{\chi}_{\mathrm{mol}}\right\rangle
$$

$\chi$ macroscopic magnetic susceptibility tensor $\rho_{0}$ molecular number density
molecular uniaxial tensor

$$
\begin{gathered}
\mathbf{q}:=\boldsymbol{m} \otimes \boldsymbol{m}-\frac{1}{3} \mathbf{I} \\
\chi_{\mathrm{mol}}=\bar{\chi}_{\mathrm{mol}} \mathbf{I}+\chi_{a}^{(\mathrm{mol})} \mathbf{q} \\
\bar{\chi}_{\mathrm{mol}}:=\frac{1}{3}\left(2 \chi_{\perp}^{(\mathrm{mol})}+\chi_{\|}^{(\mathrm{mol})}\right) \\
\text { average molecular susceptibility }
\end{gathered}
$$

$$
\chi_{a}^{(\mathrm{mol})}:=\chi_{\|}^{(\mathrm{mol})}-\chi_{\perp}^{(\mathrm{mol})}
$$

molecular susceptibility anisotropy
order tensor

$$
\chi=\rho_{0}\left\langle\chi_{\mathrm{mol}}\right\rangle=\rho_{0}\left(\bar{\chi}_{\mathrm{mol}} \mathbf{I}+\chi_{a}^{(\mathrm{mol})} \mathbf{Q}\right) \quad \mathbf{Q}=\langle\mathbf{q}\rangle
$$

## Electric permittivity

The electric properties of macroscopic media are described by the fields

$$
\begin{gathered}
\boldsymbol{E} \quad \text { electric field } \\
\boldsymbol{D} \quad \begin{array}{c}
\text { electric displacement } \\
\boldsymbol{P} \quad \text { electric polarization }
\end{array} \\
\boldsymbol{D}:=\epsilon_{0} \boldsymbol{E}+\boldsymbol{P} \\
\epsilon_{0}=8.85 \times 10^{-12} \mathrm{SI} \quad \text { electric permittivity of free space } \\
\boldsymbol{P}=\epsilon_{0} \boldsymbol{\alpha} \boldsymbol{E} \quad \text { linear constitutive law } \\
\boldsymbol{\alpha} \quad \text { electric susceptibility (polarizability) tensor } \\
\boldsymbol{D}=\epsilon_{0}(\underbrace{\mathbf{I}+\boldsymbol{\alpha}}_{\varepsilon_{\mathrm{rel}}}) \boldsymbol{E} \\
\varepsilon_{\mathrm{rel}} \quad \text { relative permittivity tensor } \\
\boldsymbol{\varepsilon}:=\epsilon_{0} \varepsilon_{\mathrm{rel}} \quad \text { dielectric tensor }
\end{gathered}
$$

## (relative) molecular polarizability

In complete analogy with the magnetic case, an individual molecule feels an electric field that differs from the applied field by the field $\boldsymbol{E}_{\text {pol }}$ produced by the displaced charges responsible for the induced electric dipole $\boldsymbol{p}_{\text {mol }}$

$$
\begin{gathered}
\boldsymbol{p}_{\mathrm{mol}}=\epsilon_{0} \boldsymbol{\alpha}_{\mathrm{mol}}\left(\boldsymbol{E}-\boldsymbol{E}_{\mathrm{pol}}\right) \\
\text { uniaxial symmetry }
\end{gathered}
$$

If the molecular response is uniaxial, symmetry dictates that

$$
\begin{aligned}
& \boldsymbol{\alpha}_{\mathrm{mol}}=\alpha_{\|}^{(\mathrm{mol})} \boldsymbol{m} \otimes \boldsymbol{m}+\alpha_{\perp}^{(\mathrm{mol})}(\mathbf{I}-\boldsymbol{m} \otimes \boldsymbol{m}) \\
& \alpha_{\|}^{(\mathrm{mol})} \quad \text { parallel molecular polarizability } \\
& \alpha_{\perp}^{(\mathrm{mol})} \quad \text { perpendicular molecular polarizability }
\end{aligned}
$$

## remarks

- We need a molecular model to compute $\boldsymbol{E}_{\text {pol }}$.
- $\boldsymbol{E}_{\mathrm{pol}}$ is expected to be (linearly) related to $\boldsymbol{p}_{\mathrm{mol}}$.
- Liquid crystal molecules are easily polarizable.
- We cannot neglect $\boldsymbol{E}_{\mathrm{pol}}$.


## molecular model

Let $\mathscr{B}$ denote the region in space occupied by an isolated, electrically neutral molecule and let $V_{\mathrm{mol}}$ be its volume.

$$
\begin{gathered}
\boldsymbol{E}_{\mathrm{pol}}=\frac{1}{V_{\mathrm{mol}}} \int_{\mathscr{B}} \boldsymbol{E}_{\text {mol }} \mathrm{d} V \\
\boldsymbol{E}_{\mathrm{mol}} \text { molecular electric field } \\
\rho_{\mathrm{e}} \text { molecular charge density generating } \boldsymbol{E}_{\mathrm{mol}}
\end{gathered}
$$

$$
\begin{gathered}
\boldsymbol{E}_{\mathrm{mol}}(\boldsymbol{x})=-\nabla \Phi(\boldsymbol{x}) \\
\Phi(\boldsymbol{x})=\frac{1}{4 \pi \epsilon_{0}} \int_{\mathscr{B}} \frac{\rho_{\mathrm{e}}\left(\boldsymbol{x}^{\prime}\right)}{\left|\boldsymbol{x}-\boldsymbol{x}^{\prime}\right|} \mathrm{d} V\left(\boldsymbol{x}^{\prime}\right) \quad \text { electrostatic potential } \\
\boldsymbol{E}_{\mathrm{pol}}=-\frac{1}{V_{\mathrm{mol}}} \int_{\mathscr{B}} \frac{1}{4 \pi \epsilon_{0}} \rho_{\mathrm{e}}\left(\boldsymbol{x}^{\prime}\right) \underbrace{\left(\int_{\partial \mathscr{B}} \frac{\boldsymbol{\nu}(\boldsymbol{x})}{\left|\boldsymbol{x}-\boldsymbol{x}^{\prime}\right|} \mathrm{d} A(\boldsymbol{x})\right)}_{\boldsymbol{F}\left(\boldsymbol{x}^{\prime}\right)} \mathrm{d} V\left(\boldsymbol{x}^{\prime}\right)
\end{gathered}
$$

$\rho_{\mathrm{e}}$ molecular charge density
$\nu$ outer unit normal to $\partial \mathscr{B}$
shape depolarization factor
Objectivity demands that

$$
\boldsymbol{F}\left(\boldsymbol{x}^{\prime}\right)=\lambda_{\mathscr{B}} \boldsymbol{x}^{\prime}
$$

Scaling invariance demands that $\lambda_{\mathscr{B}}$ be a dimensionless function of the orientation of $\boldsymbol{x}^{\prime}$ relative to a frame fixed in $\mathscr{B}$.

$$
\begin{gathered}
\boldsymbol{E}_{\mathrm{pol}}=-\frac{1}{V_{\mathrm{mol}}} \frac{1}{4 \pi \epsilon_{0}} \int_{\mathscr{B}} \lambda_{\mathscr{B}} \underbrace{\rho_{\mathrm{e}}\left(\boldsymbol{x}^{\prime}\right) \boldsymbol{x}^{\prime}}_{\text {moment }} \mathrm{d} V\left(\boldsymbol{x}^{\prime}\right) \\
\text { simplest case }
\end{gathered}
$$

For $\mathscr{B}$ a ball of radius $a$,

$$
\begin{gathered}
\lambda_{\mathscr{B}}=\frac{4 \pi}{3} \quad \boldsymbol{E}_{\mathrm{pol}}=-\frac{1}{4 \pi \epsilon_{0} a^{3}} \boldsymbol{p}_{\mathrm{mol}} \\
\boldsymbol{p}_{\mathrm{mol}}=\epsilon_{0}\left(\mathbf{I}-\frac{1}{4 \pi a^{3}} \boldsymbol{\alpha}_{\mathrm{mol}}\right)^{-1} \boldsymbol{\alpha}_{\mathrm{mol}} \boldsymbol{E} \\
\text { macroscopic polarization }
\end{gathered}
$$

$$
\begin{aligned}
\boldsymbol{P} & =\rho_{0}\left\langle\boldsymbol{p}_{\mathrm{mol}}\right\rangle=\epsilon_{0} \boldsymbol{\alpha} \boldsymbol{E} \\
\boldsymbol{\alpha} & =\left(\frac{\rho_{0} \alpha_{\|}^{(\mathrm{mol})}}{1-\frac{\alpha_{\|}^{(\mathrm{mol})}}{4 \pi a^{3}}}\right)\langle\boldsymbol{m} \otimes \boldsymbol{m}\rangle+\left(\frac{\rho_{0} \alpha_{\perp}^{(\mathrm{mol})}}{1-\frac{\alpha_{\perp}^{(\mathrm{mol})}}{4 \pi a^{3}}}\right)\langle\mathbf{I}-\boldsymbol{m} \otimes \boldsymbol{m}\rangle
\end{aligned}
$$

Clausius-Mossotti anisotropic relation

$$
\begin{array}{r}
\varepsilon_{\mathrm{rel}}=\bar{\varepsilon} \mathbf{I}+\varepsilon_{a} \mathbf{Q} \quad \mathbf{Q}=\langle\mathbf{q}\rangle \\
\bar{\varepsilon}:=\frac{1}{3}\left(2 \varepsilon_{\perp}+\varepsilon_{\|}\right) \quad \varepsilon_{a}:=\varepsilon_{\|}-\varepsilon_{\perp} \\
\varepsilon_{\|}:=1+\frac{\rho_{0} \alpha_{\|}^{(\mathrm{mol})}}{1-\alpha_{\|}^{(\mathrm{mol})} / 4 \pi a^{3}} \quad \varepsilon_{\perp}:=1+\frac{\rho_{0} \alpha_{\perp}^{(\mathrm{mol})}}{1-\alpha_{\perp}^{(\mathrm{mol})} / 4 \pi a^{3}} \\
\\
\text { URANO \& INOUE (1977) }
\end{array}
$$

## Maxwell Equations

The fields $\boldsymbol{E}, \boldsymbol{B}$ and their derived counterparts $\boldsymbol{D}, \boldsymbol{H}$, possibly depending on time $t$, obey the equations

$$
\begin{aligned}
& \operatorname{div} \boldsymbol{D}=\rho_{\mathrm{f}} \\
& \operatorname{div} \boldsymbol{B}=0 \\
& \operatorname{curl} \boldsymbol{E}=-\frac{\partial \boldsymbol{B}}{\partial t} \\
& \operatorname{curl} \boldsymbol{H}=\boldsymbol{J}+\frac{\partial \boldsymbol{D}}{\partial t} \\
& \rho_{\mathrm{f}} \quad \text { density of free charges } \\
& J \text { current density }
\end{aligned}
$$

In a non-conductive, neutral dielectric

$$
\rho_{\mathrm{f}}=0 \quad \boldsymbol{J}=\mathbf{0}
$$

## constitutive assumptions

To describe light propagation

- we neglect magnetization effects

$$
\boldsymbol{M}=\mathbf{0} \quad \boldsymbol{B}=\mu_{0} \boldsymbol{H}
$$

- we consider monochromatic waves

$$
\begin{gathered}
\boldsymbol{E}(\boldsymbol{x}, t)=\boldsymbol{E}_{0} \mathrm{e}^{i(\boldsymbol{k} \cdot \boldsymbol{x}-\omega t)} \quad \boldsymbol{H}(\boldsymbol{x}, t)=\boldsymbol{H}_{0} \mathrm{e}^{i(\boldsymbol{k} \cdot \boldsymbol{x}-\omega t)} \\
\boldsymbol{k} \quad \text { wave vector } k=\frac{2 \pi}{\lambda}=\frac{\omega}{v} \\
\lambda \text { wavelength } \\
\omega \quad \text { wave (angular) frequency } \\
v \text { phase velocity }
\end{gathered}
$$

- we write

$$
\boldsymbol{D}=\boldsymbol{\varepsilon} \boldsymbol{E}=\underbrace{\boldsymbol{\varepsilon} \boldsymbol{E}_{0}}_{\boldsymbol{D}_{0}} \mathrm{e}^{i(\boldsymbol{k} \cdot \boldsymbol{x}-\omega t)}
$$

## reduced equations

$$
\begin{aligned}
\nabla \boldsymbol{E}=i \boldsymbol{E} \otimes \boldsymbol{k} & \frac{\partial \boldsymbol{H}}{\partial t}=-i \omega \boldsymbol{H} \\
\boldsymbol{k} \cdot \boldsymbol{D} & =0 \\
\boldsymbol{k} \cdot \mu_{0} \boldsymbol{H} & =0 \\
\boldsymbol{k} \times \boldsymbol{H} & =-\omega \boldsymbol{D} \\
\boldsymbol{k} \times \boldsymbol{E} & =\omega \mu_{0} \boldsymbol{H}
\end{aligned}
$$

- The first three equations ensure that $\boldsymbol{k}, \boldsymbol{H}$, and $\boldsymbol{D}$ are mutually orthogonal vectors.
- Combining the last two equations,

$$
k^{2} \boldsymbol{E}-(\boldsymbol{k} \cdot \boldsymbol{E}) \boldsymbol{k}=\mu_{0} \omega^{2} \boldsymbol{D}
$$

## Fresnel Equation



$$
S:=\boldsymbol{E} \times \boldsymbol{H} \quad \text { Pointing vector }
$$

Compatibility with the constitutive assumption on $D$ requires that

$$
k^{2} \boldsymbol{E}-(\boldsymbol{k} \cdot \boldsymbol{E}) \boldsymbol{k}=\mu_{0} \epsilon_{0} \omega^{2} \varepsilon_{\mathrm{rel}} \boldsymbol{E}
$$

$$
\left(N^{2} \mathbf{I}-\boldsymbol{N} \otimes \boldsymbol{N}-\varepsilon_{\mathrm{rel}}\right) \boldsymbol{E}=\mathbf{0} \quad \boldsymbol{N}:=\frac{1}{\omega \sqrt{\mu_{0} \epsilon_{0}}} \boldsymbol{k}
$$

$N$ refractive vector
$N=c / v \quad$ refractive index $c=1 / \sqrt{\mu_{0} \epsilon_{0}} \quad$ speed of light in a vacuum

## solubility condition

$$
\operatorname{det}\left(N^{2} \mathbf{I}-\boldsymbol{N} \otimes \boldsymbol{N}-\boldsymbol{\varepsilon}_{\mathrm{rel}}\right)=0
$$

If $\varepsilon_{\mathrm{rel}}$ is uniaxial (implying that also Q is so)

$$
\begin{gathered}
\boldsymbol{\varepsilon}_{\mathrm{rel}}=\varepsilon_{\perp} \mathbf{I}+\varepsilon_{a} \boldsymbol{n} \otimes \boldsymbol{n} \quad \varepsilon_{a}=\varepsilon_{\|}-\varepsilon_{\perp} \\
\operatorname{det}[\left(N^{2}-\varepsilon_{\perp}\right) \mathbf{I}-\underbrace{\left(\boldsymbol{N} \otimes \boldsymbol{N}+\varepsilon_{a} \boldsymbol{n} \otimes \boldsymbol{n}\right)}_{\operatorname{det}(\cdot)=0}]=0
\end{gathered}
$$

$$
\left(N^{2}-\varepsilon_{\perp}\right)\left(\varepsilon_{\|} \varepsilon_{\perp}-\varepsilon_{\|} N_{\|}^{2}-\varepsilon_{\perp} N_{\perp}^{2}\right)=0
$$

ordinary wave
$n_{o}:=\sqrt{\varepsilon_{\perp}} \quad$ ordinary refractive index
the ordinary wave propagates in all directions with the same velocity refractive index ellipsoid

$$
\frac{N_{\|}^{2}}{\varepsilon_{\perp}}+\frac{N_{\perp}^{2}}{\varepsilon_{\|}}=1
$$

extraordinary wave

$$
\begin{array}{r}
N(\theta)=\frac{N_{\|}:=N(\theta) \cos \theta \quad N_{\perp}:=N(\theta) \sin \theta}{\sqrt{n_{e}^{2} \cos ^{2} \theta+n_{o}^{2} \sin ^{2} \theta}} \quad N(\theta)=\frac{c}{v(\theta)} \\
n_{e}:=\sqrt{\varepsilon_{\|}} \quad \text { extraordinary refractive index }
\end{array}
$$

optically negative medium $n_{o}>n_{e}$

optic axis
The extraordinary refractive ellipsoid and the ordinary refractive sphere touch in two points aligned with $\boldsymbol{n}$. Ordinary and extraordinary waves are indistinguishable when traveling along $\boldsymbol{n}$.
optically positive medium $n_{o}<n_{e}$

polarization of the ordinary wave

$$
\begin{gathered}
\quad\left(\boldsymbol{N} \otimes \boldsymbol{N}+\varepsilon_{a} \boldsymbol{n} \otimes \boldsymbol{n}\right) \boldsymbol{E}=\mathbf{0} \\
\boldsymbol{E}\left\|\boldsymbol{n} \times \boldsymbol{N} \quad \boldsymbol{D}=\varepsilon_{\perp} \boldsymbol{E} \quad \boldsymbol{S}\right\| \boldsymbol{k} \\
E_{\|}=0 \quad D_{\|}=0 \quad \frac{S_{\|}}{S_{\perp}}=\frac{N_{\|}}{N_{\perp}}
\end{gathered}
$$

polarization of the extraordinary wave

$$
\begin{gathered}
\left(N_{\|}^{2}+N_{\perp}^{2}-\varepsilon_{\perp}\right) \boldsymbol{E}-(\boldsymbol{N} \cdot \boldsymbol{E}) \boldsymbol{N}-\varepsilon_{a}(\boldsymbol{n} \cdot \boldsymbol{E}) \boldsymbol{n}=\mathbf{0} \\
\frac{E_{\|}}{E_{\perp}}=-\frac{\varepsilon_{\perp} N_{\perp}}{\varepsilon_{\|} N_{\|}} \quad \frac{S_{\|}}{S_{\perp}}=\frac{\varepsilon_{\|} N_{\|}}{\varepsilon_{\perp} N_{\perp}}
\end{gathered}
$$

## graphical representation

- ordinary wave: $\boldsymbol{E} \perp \boldsymbol{n}$
- extraordinary wave: $\boldsymbol{E}$ lies in the plane $(\boldsymbol{n}, \boldsymbol{k})$



## Schlieren Textures

Consider a nematic texture in a slab of thickness $d$ between crossed polarizers. The optic axis $\boldsymbol{n}$ lies in the $(x, y)$ plane and is independent of $z$.

$\beta(x, y)$ angle between $\boldsymbol{n}$ and the incoming polarization

$$
\begin{gathered}
E_{o}=E_{\perp}=A_{0} \sin \beta \cos \left(\frac{2 \pi z}{\lambda_{0}} n_{o}-\omega t\right) \quad \text { ordinary wave } \\
E_{e}=E_{\|}=A_{0} \cos \beta \cos \left(\frac{2 \pi z}{\lambda_{0}} n_{e}-\omega t\right) \quad \text { extraordinary wave } \\
A_{0} \text { amplitude of the incoming wave } \\
I_{0}=A_{0}^{2} \quad \text { intensity of the incoming wave } \\
\lambda_{0}:=\frac{\omega}{c} \quad \text { wavelength in free space } \\
\text { phase shift }
\end{gathered}
$$

$$
\Delta \varphi=\frac{2 \pi d}{\lambda_{0}}\left(n_{e}-n_{o}\right)
$$

analyzer transmitted wave

$$
\begin{aligned}
E^{(\mathrm{a})}=E_{o}^{(\mathrm{a})}+E_{e}^{(\mathrm{a})} & =A_{0} \cos \beta \sin \beta \cos \left(\frac{2 \pi d}{\lambda_{0}} n_{o}-\omega t\right) \\
& -A_{0} \sin \beta \cos \beta \cos \left(\frac{2 \pi d}{\lambda_{0}} n_{e}-\omega t\right)
\end{aligned}
$$

$$
E^{(\mathrm{a})}=-A \cos (\Delta \varphi-\omega t)
$$

## transmitted intensity

$$
I:=A^{2}=I_{0} \sin ^{2} 2 \beta \sin ^{2}\left(\frac{\pi d}{\lambda_{0}}\left(n_{e}-n_{o}\right)\right)
$$

- extinction branches $I=0$ for $\beta=0, \frac{\pi}{2}$
- colorful patterns $I$ depends on $\lambda_{0}$




## two optic axes

If Q is biaxial then the eigenvalues of $\varepsilon_{\mathrm{rel}}$ are all different from one another.


$$
\varepsilon_{x}<\varepsilon_{y}<\varepsilon_{z}
$$

The refractive surface has four symmetric self-intersection that define two axes with a single refractive index.

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