MATHEMATICAL THEORIES OF LIQUID CRYSTALS

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Course Outline

I. Fundamentals II. The Maier-Saupe Theory III. The Onsager Theory IV. The Oseen-Frank Theory V. The Landau-deGennes Theory 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.

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

If N molecules constitute an *ensemble*,

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

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

• Let
$$\mathscr{S}^{-} := \{ \boldsymbol{m} \in \mathbb{S}^{2} : -\boldsymbol{m} \in \mathscr{S} \}$$
. Then $n[\mathscr{S}^{-}] = n[\mathscr{S}]$

• Let
$$\mathbf{m} := \int_{\mathbb{S}^2} \rho(\mathbf{m}) \mathbf{m} dA$$
 denote the *first moments* of ρ . Then $\mathbf{m} = \mathbf{0}$.

second moments

The first non-vanishing moments of ϱ 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

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

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

M is a *symmetric* tensor with *unit* trace.

averages

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

$$oldsymbol{e} \cdot \mathbf{M}oldsymbol{e} = \int_{\mathbb{S}^2} \varrho(oldsymbol{m}) (oldsymbol{m} \cdot oldsymbol{e})^2 \mathrm{d}A =: \langle (oldsymbol{m} \cdot oldsymbol{e})^2
angle$$

 $oldsymbol{e} \cdot \mathbf{M}oldsymbol{e} = \langle \cos^2 artheta
angle \in [0, 1]$
 $oldsymbol{artheta}$ angle between $oldsymbol{m}$ and $oldsymbol{e}$

eigenvalues of M

$$\mu_1 + \mu_2 + \mu_3 = 1$$
$$0 \leq \mu_i \leq 1$$

isotropic distribution

$$\varrho_0 \equiv \frac{1}{4\pi}$$
$$\mathbf{M}_0 = \int_{\mathbb{S}^2} \varrho_0 \boldsymbol{m} \otimes \boldsymbol{m} \mathrm{d}A$$

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

$$\mathbf{M}_0 = \int_{\mathbb{S}^2} \varrho_0 \mathbf{R} \boldsymbol{m} \otimes \mathbf{R} \boldsymbol{m} \mathrm{d} A = \int_{\mathbb{S}^2} \varrho_0 \mathbf{R} (\boldsymbol{m} \otimes \boldsymbol{m}) \mathbf{R}^\mathsf{T} \mathrm{d} A = \mathbf{R} \mathbf{M}_0 \mathbf{R}^\mathsf{T}$$

Since $\mathbf{R}^{\mathsf{T}}\mathbf{R} = \mathbf{R}\mathbf{R}^{\mathsf{T}} = \mathbf{I}$

$$\mathbf{M}_0 \mathbf{R} = \mathbf{R} \mathbf{M}_0$$
 for all $\mathbf{R} \in \mathsf{SO}(3)$

Since $\operatorname{tr} \mathbf{M}_0 = 1$,

$$\mathbf{M}_0 = \frac{1}{3}\mathbf{I}$$
 and so $\left\langle \cos^2 \vartheta \right\rangle = \frac{1}{3}$

Order Tensor

 $\mathbf{Q} := \mathbf{M} - \mathbf{M}_0$ DE GENNES (1974)

pitfall

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

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

Then,

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

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*

$$\vartheta_{0} := \arccos \sqrt{\frac{1}{3}}$$
properties of **Q**

• tr
$$\mathbf{Q} = 0$$

• $\mathbf{Q} = \lambda_1 \boldsymbol{n}_1 \otimes \boldsymbol{n}_1 + \lambda_2 \boldsymbol{n}_2 \otimes \boldsymbol{n}_2 + \lambda_3 \boldsymbol{n}_3 \otimes \boldsymbol{n}_3$

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

• $-\frac{1}{3} \leq \lambda_i \leq \frac{2}{3}$

scalar order parameters

Three cases may arise

• $\lambda_1 = \lambda_2 = \lambda_3 = 0$ **Q** is *isotropic*

$$\mathbf{Q} = \mathbf{0}$$

•
$$\lambda_1 = \lambda_2$$
 $\lambda_3 = -2\lambda_1$ **Q** is **uniaxial**
 $\mathbf{Q} = S\left(n \otimes n - \frac{1}{3}\mathbf{I}\right)$ $n = n_3$, $S = -3\lambda_1$

S degree of orientation n nematic director

• $\lambda_1 \neq \lambda_2 \neq \lambda_3$ **Q** is *biaxial*

$$\mathbf{Q} = \mathbf{S_1} \left(\mathbf{n}_1 \otimes \mathbf{n}_1 - \frac{1}{3} \mathbf{I} \right) + \mathbf{S_2} \left(\mathbf{n}_2 \otimes \mathbf{n}_2 - \frac{1}{3} \mathbf{I} \right)$$

 $S_1 = 2\lambda_1 + \lambda_2, \ S_2 = \lambda_1 + 2\lambda_2$

alternative representation

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

$$\mathbf{Q} = S\left(\boldsymbol{n}_3 \otimes \boldsymbol{n}_3 - \frac{1}{3}\mathbf{I}\right) + T(\boldsymbol{n}_1 \otimes \boldsymbol{n}_1 - \boldsymbol{n}_2 \otimes \boldsymbol{n}_2)$$

 $S := -\frac{1}{2} (S_1 + S_2)$ uniaxial scalar order parameter $T := \frac{1}{2} (S_1 - S_2)$ biaxial scalar order parameter

admissible order parameters

By requiring

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

we obtain

$$-\frac{1}{2} \le S \le 1$$
 and $-\frac{1}{3}(1-S) \le T \le \frac{1}{3}(1-S)$

order parameter interpretation

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

$$\boldsymbol{e} \cdot \mathbf{M}\boldsymbol{e} = \frac{1}{3}(1-S) + S(\boldsymbol{n}_3 \cdot \boldsymbol{e})^2 + T[(\boldsymbol{n}_1 \cdot \boldsymbol{e})^2 - (\boldsymbol{n}_2 \cdot \boldsymbol{e})^2]$$
$$= \left\langle (\boldsymbol{m} \cdot \boldsymbol{e})^2 \right\rangle$$

•
$$e = n_3$$
 $S = \frac{3}{2} \left[\left\langle (\boldsymbol{m} \cdot \boldsymbol{n}_3)^2 \right\rangle - \frac{1}{3} \right] = \left\langle P_2(\boldsymbol{m} \cdot \boldsymbol{n}_3) \right\rangle$
 $P_2(\boldsymbol{x}) := \frac{1}{2} (3\boldsymbol{x}^2 - 1)$ second Legendre polynomial
• $e = \boldsymbol{n}_1 \& \boldsymbol{e} = \boldsymbol{n}_2$ $T = \frac{1}{2} \left[\left\langle (\boldsymbol{m} \cdot \boldsymbol{n}_1)^2 \right\rangle - \left\langle (\boldsymbol{m} \cdot \boldsymbol{n}_2)^2 \right\rangle \right]$
limiting cases

- $m \parallel n_3$ S = 1 T = 0
- $m \perp n_3$ $S = -\frac{1}{2}$ T = 0
- $m \parallel n_{1,2}$ $S = -\frac{1}{2}$ $T = \pm \frac{1}{2}$

order parameter conjugacies

In the general **biaxial** case, the eigenframe (n_1, n_2, n_3) of **Q** has no intrinsic meaning. A **permutation** of the 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*

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

uniaxial lines

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

$$T = 0 \qquad T = \pm S$$

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

admissible triangle



aligned uniaxial $U_{+} = (1,0), U'_{+} = \left(-\frac{1}{2}, \frac{1}{2}\right), U''_{+} = \left(\frac{1}{2}, -\frac{1}{2}\right)$ *planar uniaxial* $U_{-} = \left(\frac{1}{4}, \frac{1}{4}\right), U'_{-} = \left(-\frac{1}{2}, 0\right), U''_{-} = \left(\frac{1}{4}, -\frac{1}{4}\right)$

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

- **B** magnetic induction
- **H** magnetic strength
 - M magnetization

$$oldsymbol{H}:=rac{1}{\mu_0}oldsymbol{B}-oldsymbol{M}$$

 $\mu_0 = 4\pi \times 10^{-7} \, \text{SI}$ magnetic permeability of free space $M = \chi H$ linear *constitutive* law χ magnetic susceptibility *tensor*

$$oldsymbol{B} = \mu_0(\underbrace{\mathbf{I}+oldsymbol{\chi}}_{oldsymbol{\mu_{rel}}})oldsymbol{H}$$

 $\mu_{\rm rel}$ relative permeability tensor

molecular magnetic susceptibility

An individual molecule feels a magnetic field that differs from the applied field by the field H_{mag} produced by the molecular currents associated with the induced magnetic dipole μ_{mol} .

$$oldsymbol{\mu_{\mathrm{mol}}} = oldsymbol{\chi_{\mathrm{mol}}}(oldsymbol{H} - oldsymbol{H_{\mathrm{mag}}})$$

uniaxial symmetry

If the molecular response is uniaxial, symmetry dictates that

$$\boldsymbol{\chi}_{\mathrm{mol}} = \chi_{\parallel}^{(\mathrm{mol})} \boldsymbol{m} \otimes \boldsymbol{m} + \chi_{\perp}^{(\mathrm{mol})} (\mathbf{I} - \boldsymbol{m} \otimes \boldsymbol{m})$$

 $\begin{array}{ll} \chi_{\parallel}^{(\rm mol)} & {\rm parallel} \; \textit{molecular} \; {\rm susceptibility} \\ \chi_{\perp}^{(\rm mol)} & {\rm perpendicular} \; \textit{molecular} \; {\rm susceptibility} \end{array}$

remarks

- To compute H_{mag} we need some kind of molecular model.
- H_{mag} is expected to be (linearly) related to μ_{mol} .
- Liquid crystal molecules are *diamagnetic* with *small* (negative) susceptibilities.
- $\mu_{\text{mol}} = \chi_{\text{mol}}(H H_{\text{mag}})$; hence, we may *neglect* H_{mag} .

macroscopic susceptibility

$$oldsymbol{M} =
ho_0 \left< oldsymbol{\mu_{
m mol}}
ight> = oldsymbol{\chi} oldsymbol{H} \qquad oldsymbol{\chi} =
ho_0 \left< oldsymbol{\chi_{
m mol}}
ight>$$

 χ macroscopic magnetic susceptibility tensor ρ_0 molecular number density

molecular uniaxial tensor

$$egin{aligned} \mathbf{q} &:= m{m} \otimes m{m} - rac{1}{3} \mathbf{I} \ \mathbf{\chi}_{ ext{mol}} &= \overline{\chi}_{ ext{mol}} \mathbf{I} + \chi_a^{(ext{mol})} \mathbf{q} \end{aligned}$$

$$\overline{\chi}_{\text{mol}} := \frac{1}{3} (2\chi_{\perp}^{(\text{mol})} + \chi_{\parallel}^{(\text{mol})})$$

average molecular susceptibility

 $\chi_a^{(\text{mol})} := \chi_{\parallel}^{(\text{mol})} - \chi_{\perp}^{(\text{mol})}$ molecular susceptibility anisotropy

order tensor

$$\boldsymbol{\chi} = \rho_0 \langle \boldsymbol{\chi}_{\text{mol}} \rangle = \rho_0 (\overline{\chi}_{\text{mol}} \mathbf{I} + \chi_a^{(\text{mol})} \mathbf{Q}) \qquad \mathbf{Q} = \langle \mathbf{q} \rangle$$

Electric permittivity

The electric properties of macroscopic media are described by the fields

- **E** electric field
- **D** electric displacement
- **P** electric polarization

$\boldsymbol{D} := \epsilon_0 \boldsymbol{E} + \boldsymbol{P}$

 $\epsilon_0 = 8.85 \times 10^{-12} \,\mathrm{SI}$ electric permittivity of free space $P = \epsilon_0 \alpha E$ linear *constitutive* law α electric susceptibility (polarizability) *tensor*

$$D = \epsilon_0(\underbrace{\mathbf{I} + \boldsymbol{lpha}})E$$

 $oldsymbol{arepsilon}_{\mathrm{rel}}$

 $\boldsymbol{\varepsilon}_{rel}$ relative permittivity tensor $\boldsymbol{\varepsilon} := \epsilon_0 \boldsymbol{\varepsilon}_{rel}$ dielectric tensor

(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 $E_{\rm pol}$ produced by the displaced charges responsible for the induced electric dipole $p_{\rm mol}$

 $m{p}_{
m mol} = \epsilon_0 m{lpha}_{
m mol} (m{E} - m{E}_{
m pol})$

uniaxial symmetry

If the molecular response is uniaxial, symmetry dictates that

$$\boldsymbol{lpha}_{\mathrm{mol}} = lpha_{\parallel}^{\mathrm{(mol)}} \boldsymbol{m} \otimes \boldsymbol{m} + lpha_{\perp}^{\mathrm{(mol)}} (\mathbf{I} - \boldsymbol{m} \otimes \boldsymbol{m})$$

 $\alpha_{\parallel}^{(mol)}$ parallel *molecular* polarizability $\alpha_{\perp}^{(mol)}$ perpendicular *molecular* polarizability

remarks

- We need a molecular model to compute E_{pol} .
- E_{pol} is expected to be (linearly) related to p_{mol} .
- Liquid crystal molecules are *easily* polarizable.
- We *cannot* neglect E_{pol} .

molecular model

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

$$\boldsymbol{E}_{\mathrm{pol}} = rac{1}{V_{\mathrm{mol}}} \int_{\mathscr{B}} \boldsymbol{E}_{\mathrm{mol}} \mathrm{d}V$$

 $E_{
m mol}$ molecular electric field $ho_{
m e}$ molecular charge density generating $E_{
m mol}$

$$E_{\text{mol}}(\boldsymbol{x}) = -\nabla \Phi(\boldsymbol{x})$$

$$\Phi(\boldsymbol{x}) = \frac{1}{4\pi\epsilon_0} \int_{\mathscr{B}} \frac{\rho_{\text{e}}(\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|} dV(\boldsymbol{x}') \quad \text{electrostatic potential}$$

$$E_{\text{pol}} = -\frac{1}{V_{\text{mol}}} \int_{\mathscr{B}} \frac{1}{4\pi\epsilon_0} \rho_{\text{e}}(\boldsymbol{x}') \underbrace{\left(\int_{\partial\mathscr{B}} \frac{\boldsymbol{\nu}(\boldsymbol{x})}{|\boldsymbol{x}-\boldsymbol{x}'|} dA(\boldsymbol{x})\right)}_{F(\boldsymbol{x}')} dV(\boldsymbol{x}')$$

 $\rho_{\rm e}$ molecular charge density

 $\boldsymbol{\nu}$ outer unit normal to $\partial \mathscr{B}$

shape depolarization factor

Objectivity demands that

$$oldsymbol{F}(oldsymbol{x}') = \lambda_{\mathscr{B}}oldsymbol{x}'$$

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

$$\boldsymbol{E}_{\text{pol}} = -\frac{1}{V_{\text{mol}}} \frac{1}{4\pi\epsilon_0} \int_{\mathscr{B}} \lambda_{\mathscr{B}} \underbrace{\rho_{\text{e}}(\boldsymbol{x}')\boldsymbol{x}'}_{\text{moment}} \mathrm{d}V(\boldsymbol{x}')$$

simplest case

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

$$\lambda_{\mathscr{B}} = \frac{4\pi}{3} \qquad \boldsymbol{E}_{\text{pol}} = -\frac{1}{4\pi\epsilon_0 a^3} \boldsymbol{p}_{\text{mol}}$$
$$\boldsymbol{p}_{\text{mol}} = \epsilon_0 \left(\mathbf{I} - \frac{1}{4\pi a^3} \boldsymbol{\alpha}_{\text{mol}} \right)^{-1} \boldsymbol{\alpha}_{\text{mol}} \boldsymbol{E}$$

macroscopic polarization

$$\begin{split} \boldsymbol{P} &= \rho_0 \left\langle \boldsymbol{p}_{\mathrm{mol}} \right\rangle = \epsilon_0 \boldsymbol{\alpha} \boldsymbol{E} \\ \boldsymbol{\alpha} &= \left(\frac{\rho_0 \alpha_{\parallel}^{(\mathrm{mol})}}{1 - \frac{\alpha_{\parallel}^{(\mathrm{mol})}}{4\pi a^3}} \right) \left\langle \boldsymbol{m} \otimes \boldsymbol{m} \right\rangle + \left(\frac{\rho_0 \alpha_{\perp}^{(\mathrm{mol})}}{1 - \frac{\alpha_{\perp}^{(\mathrm{mol})}}{4\pi a^3}} \right) \left\langle \mathbf{I} - \boldsymbol{m} \otimes \boldsymbol{m} \right\rangle \end{split}$$

Clausius-Mossotti anisotropic relation

$$\varepsilon_{\rm rel} = \overline{\varepsilon} \mathbf{I} + \varepsilon_a \mathbf{Q} \qquad \mathbf{Q} = \langle \mathbf{q} \rangle$$
$$\overline{\varepsilon} := \frac{1}{3} (2\varepsilon_{\perp} + \varepsilon_{\parallel}) \qquad \varepsilon_a := \varepsilon_{\parallel} - \varepsilon_{\perp}$$
$$\varepsilon_{\parallel} := 1 + \frac{\rho_0 \alpha_{\parallel}^{\rm (mol)}}{1 - \alpha_{\parallel}^{\rm (mol)} / 4\pi a^3} \qquad \varepsilon_{\perp} := 1 + \frac{\rho_0 \alpha_{\perp}^{\rm (mol)}}{1 - \alpha_{\perp}^{\rm (mol)} / 4\pi a^3}$$

URANO & INOUE (1977)

Maxwell Equations

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

- div $D = \rho_{\rm f}$ div B = 0curl $E = -\frac{\partial B}{\partial t}$ curl $H = J + \frac{\partial D}{\partial t}$
- $\begin{array}{cc} \rho_{\rm f} & {\rm density \ of \ free \ charges} \\ {\color{black} {\color{black} J}} & {\rm current \ density} \end{array}$

In a non-conductive, *neutral* dielectric

$$\rho_{\rm f} = 0 \qquad \boldsymbol{J} = \boldsymbol{0}$$

constitutive assumptions

To describe light propagation

• we neglect magnetization effects

$$oldsymbol{M} = oldsymbol{0} \qquad oldsymbol{B} = \mu_0 oldsymbol{H}$$

• we consider monochromatic waves

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

$$D = \varepsilon E = \underbrace{\varepsilon E_0}_{D_0} e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)}$$

reduced equations

$$abla E = i E \otimes k$$
 $rac{\partial H}{\partial t} = -i\omega H$
 $k \cdot D = 0$
 $k \cdot \mu_0 H = 0$
 $k \times H = -\omega D$
 $k \times E = \omega \mu_0 H$

- The first three equations ensure that *k*, *H*, and *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



 $S := E \times H$ Pointing vector

Compatibility with the constitutive assumption on D requires that

$$k^2 \boldsymbol{E} - (\boldsymbol{k} \cdot \boldsymbol{E}) \boldsymbol{k} = \mu_0 \epsilon_0 \omega^2 \boldsymbol{\varepsilon}_{\mathrm{rel}} \boldsymbol{E}$$

$$(N^2 \mathbf{I} - \mathbf{N} \otimes \mathbf{N} - \boldsymbol{\varepsilon}_{\mathrm{rel}}) \mathbf{E} = \mathbf{0} \qquad \mathbf{N} := \frac{1}{\omega \sqrt{\mu_0 \epsilon_0}} \mathbf{k}$$

 $m{N}$ refractive vector N = c/v refractive index $m{c} = 1/\sqrt{\mu_0\epsilon_0}$ speed of light in a vacuum

solubility condition

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

If $\boldsymbol{\varepsilon}_{rel}$ is *uniaxial* (implying that also **Q** is so)

$$\varepsilon_{\rm rel} = \varepsilon_{\perp} \mathbf{I} + \varepsilon_a \mathbf{n} \otimes \mathbf{n} \qquad \varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp}$$
$$\det[(N^2 - \varepsilon_{\perp})\mathbf{I} - \underbrace{(\mathbf{N} \otimes \mathbf{N} + \varepsilon_a \mathbf{n} \otimes \mathbf{n})}_{\det(\cdot) = 0}] = 0$$

$$(N^2 - \varepsilon_{\perp})(\varepsilon_{\parallel}\varepsilon_{\perp} - \varepsilon_{\parallel}N_{\parallel}^2 - \varepsilon_{\perp}N_{\perp}^2) = 0$$

ordinary wave

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

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

extraordinary wave

$$\begin{split} N_{\parallel} &:= N(\theta) \cos \theta \qquad N_{\perp} := N(\theta) \sin \theta \\ N(\theta) &= \frac{n_o n_e}{\sqrt{n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta}} \qquad N(\theta) = \frac{c}{v(\theta)} \\ n_e &:= \sqrt{\varepsilon_{\parallel}} \quad \text{extraordinary refractive index} \end{split}$$

optically negative medium $n_o > n_e$



optic axis

The extraordinary refractive ellipsoid and the ordinary refractive sphere touch in two points aligned with n. Ordinary and extraordinary waves are indistinguishable when traveling along n.

optically positive medium $n_o < n_e$



polarization of the ordinary wave

$$egin{aligned} &ig(oldsymbol{N}\otimesoldsymbol{N}+arepsilon_aoldsymbol{n}\otimesoldsymbol{n}ig)oldsymbol{E}=oldsymbol{0}\ &oldsymbol{E}=oldsymbol{0}\ &oldsymbol{E}=oldsymbol{N}\ &oldsymbol{N}\ &oldsymbol{E}=oldsymbol{N}\ &oldsymbol{E}=oldsymbol{N}\ &oldsymbol{E}=oldsymbol{N}\ &oldsymbol{N}\ &oldsymbol{N}$$

polarization of the extraordinary wave

$$\begin{pmatrix} N_{\parallel}^2 + N_{\perp}^2 - \varepsilon_{\perp} \end{pmatrix} \boldsymbol{E} - (\boldsymbol{N} \cdot \boldsymbol{E}) \boldsymbol{N} - \varepsilon_a (\boldsymbol{n} \cdot \boldsymbol{E}) \boldsymbol{n} = \boldsymbol{0} \\ \frac{E_{\parallel}}{E_{\perp}} = -\frac{\varepsilon_{\perp} N_{\perp}}{\varepsilon_{\parallel} N_{\parallel}} \quad \frac{S_{\parallel}}{S_{\perp}} = \frac{\varepsilon_{\parallel} N_{\parallel}}{\varepsilon_{\perp} N_{\perp}}$$

graphical representation

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



Schlieren Textures

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



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

$$\begin{split} E_o &= E_{\perp} = A_0 \sin \beta \cos \left(\frac{2\pi z}{\lambda_0} n_o - \omega t \right) \quad \text{ordinary wave} \\ E_e &= E_{\parallel} = A_0 \cos \beta \cos \left(\frac{2\pi z}{\lambda_0} n_e - \omega t \right) \quad \text{extraordinary wave} \\ A_0 \quad \text{amplitude of the incoming wave} \\ I_0 &= A_0^2 \quad \text{intensity of the incoming wave} \\ \lambda_0 &:= \frac{\omega}{c} \quad \text{wavelength in free space} \end{split}$$

phase shift

$$\Delta \varphi = \frac{2\pi d}{\lambda_0} (n_e - n_o)$$

analyzer transmitted wave

$$E^{(a)} = E_o^{(a)} + E_e^{(a)} = A_0 \cos\beta\sin\beta\cos\left(\frac{2\pi d}{\lambda_0}n_o - \omega t\right)$$
$$-A_0 \sin\beta\cos\beta\cos\left(\frac{2\pi d}{\lambda_0}n_e - \omega t\right)$$

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

transmitted intensity

$$I := A^2 = I_0 \sin^2 2\beta \sin^2 \left(\frac{\pi d}{\lambda_0} (n_e - n_o)\right)$$

- extinction branches I = 0 for $\beta = 0, \frac{\pi}{2}$
- colorful patterns I depends on λ_0





two optic axes

If **Q** is *biaxial* then the eigenvalues of ε_{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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