LIQUID CRYSTALS

Introduction

- LC mesophases
- LCs in the bulk and in confined geometries
- optical properties of LCs
- fluctuations and light scattering
- applications of LCs
AGGREGATION STATES OF MATTER

Example: H₂O molecule

Solid phase (crystal) → Heating → Liquid phase (cooling)
THERMOTROPIC LIQUID CRYSTALS

Solid phase (crystal)  Liquid crystalline phase  Liquid phase

Rod-like molecules (calamatic LCs)
example: alkyl-cyanobiphenyls

Disc-shape molecules (discotic LCs)
example: triphenylene derivatives

Texture of the LC phase observed by polarization optical microscopy

Synthetic materials
LIOTROPIC LIQUID CRYSTALS

decreasing concentration

increasing concentration

Solid phase (crystal)  Liquid phase

Liquid crystalline phase

Examples: soaps, lipids, viruses, DNA...

Natural materials

Molecular solutions

100 nm

TM virus
POLYMER LIQUID CRYSTALS

main chain polymer LCs

Examples:
Kevlar (du Pont), solutions of biopolymers

side chain polymer LCs

Kevlar
GENERAL PROPERTIES OF LC-MESOPHASES

1) They flow and form surface level (similar to liquids)

2) They exhibit anisotropic material properties (similar to crystals)

Example: optical birefringence

3) In some cases they can transmit mechanical stress (similar to crystals)

Example: bend strain
THERMOTROPIC LIQUID CRYSTAL PHASES

of achiral molecules

Parameters describing the liquid crystalline phase:

- Orientational order
- Positional order
- Bond orientational order

nematic phase (N)

smectic A phase (SmA)

smectic C phase (SmC)

columnar phase (2D lattice)
NEMATIC LC PHASE – theoretical description

Basic thermodynamic argument for the I-N phase transition:
Although orientational alignment of the molecules results in the loss of the entropy $S$, this loss is compensated by a decrease of the interaction energy $U$ (because van der Waals attractive forces are increased, molecular packing is optimized, ...)

$$F = U - TS$$

Microscopic description: $f(\theta)$ angular distribution function

$$f(\theta)d\Omega = \text{fraction of the molecules pointing into a solid angle } \Omega$$

**Head to tail invariance of the nematic phase requires** $f(\theta) = f(\pi - \theta)$!!

**Nematic order parameter**

$$S_N = \langle (3\cos^2 \theta - 1)/2 \rangle = \frac{1}{2} \int \left( (3 \cos^2 \theta - 1) f(\theta) d\Omega \right)$$

*Isotropic phase: $S_N = 0$, totally aligned N phase $S_N = 1$. *

Maier-Saupe theory: $U = -u S_N^2$, $S = -k \int f(\theta)(\ln f(\theta)) d\Omega$

$n=director$

$$\Delta F_{I-N} = -u S_N^2 + kT \left[ \int f(\theta)(\ln f(\theta)) d\Omega \right] + \ln 4\pi$$
$S_N$ can be measured via anisotropy of the material properties.

example: *diamagnetic susceptibility*

$$\chi_z = n(\eta_{||} \langle \cos^2 \theta \rangle + \eta_{\perp} \langle \sin^2 \theta \rangle) = n(\bar{\eta} + (2/3)\eta_a S_N)$$

$$S_N = (\chi_z - \chi_x)/(n\eta_a)$$

$$\chi_x = \chi_y = n(\bar{\eta} - (1/3)\eta_a S_N)$$

where molecular parameters

$$\bar{\eta} = (\eta_{||} + 2\eta_{\perp})/3, \quad \eta_a = (\eta_{||} - \eta_{\perp}), \quad n = N/V$$

should be known from other measurements.
Nematic phase can transmit forces in cases in which the corresponding deformation perturbs the long-range orientational order.

For example: shear stress will produce usual viscous liquid flow, while splay, twist and bend deformations will produce elastic response.

Elastic energy density of distortion (continuum theory):

\[
F_d = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_3 ((\hat{n} \times \nabla \times \hat{n})^2
\]

Frank elastic constants: \(K_i \sim 10^{-12} \text{ N}\)
EFFECT OF INTERFACE INTERACTIONS

Nematic phase between two planar surfaces.

Surface forces generally induce bulk alignment in some preferential direction (easy axis).

\[ F_{\text{surface}} = f_0 + B \sin^2 \Phi \]

\( \Phi = \text{angle between } \hat{n} \text{ and the easy axis} \)

Rapini-Papoular approximation

*Surface anchoring energy coefficients: \( B_\theta \geq B_\varphi \sim 10^{-5} \text{ N/m} \)*

Nematic phase confined to spherical droplets.

\[ F = F_{\text{surface}} + F_d = \text{MIN} \]

Approximation of infinitely strong anchoring (\( B = \infty \)) is often reasonable.
STANDARD TECHNIQUE TO ACHIEVE PLANAR SURFACE ANCHORING

Polymer surface is melted due to applied force and melted polymer molecules align in the direction of the rubbing.
Anisotropic interaction between the polymer substrate and the rod-shape liquid crystal molecules induces orientational ordering of the LC layer.

Nematic LC texture in a cell without and with the alignment layer.
Due to head-tail invariance of the molecular arrangement, the nematic phase has no spontaneous macroscopic electric polarization \( P \) and magnetization \( M \). External electric and magnetic fields produce induced polarization/magnetization \( (P=\varepsilon_0\chi_e E, M=\chi_m H) \).

For dielectric polarization local field corrections are quite important!!

\[
P_z = \varepsilon_o n(\alpha+\frac{2}{3}\alpha_a S_N) f h E_z = \varepsilon_o (\varepsilon || - 1) E_z
\]
\[
P_x = \varepsilon_o n(\alpha-\frac{1}{3}\alpha_a S_N) f h E_x = \varepsilon_o (\varepsilon \perp - 1) E_x
\]

Dielectric tensor in case of \( z \parallel \hat{n} \): \( \varepsilon = \begin{pmatrix}
\varepsilon \perp, 0, 0 \\
0 , \varepsilon \perp, 0 \\
0 , 0 , \varepsilon ||
\end{pmatrix}
\)

in general: \( \varepsilon = \varepsilon \perp 1 + \varepsilon_a (\hat{n} \otimes \hat{n}) \), where \( \varepsilon_a = (\varepsilon || - \varepsilon \perp) \) is dielectric anisotropy.

\[
D = \varepsilon_o (\varepsilon \perp E + \varepsilon_a (\hat{n} \cdot E) \hat{n})
\]
Temperature dependence of the dielectric constant and the DSC response of the liquid crystal 5CB.
**FREEDERICKSZ EFFECT**

Electrostatic free energy density: 

\[ F_e = -\frac{1}{2} ED = -\frac{1}{2} \varepsilon_0 \varepsilon_\perp E^2 - \frac{1}{2} \varepsilon_0 \varepsilon_a (\hat{n}E)^2 \]

For \( \varepsilon_a > 0 \) electric field tends to align the LC director \( \hat{n} \) along the field direction. In confined geometries this tendency is opposed by surface anchoring. Competition results in the threshold behaviour. *Example: nematic cell with planar anchoring:*

![Diagram](image)

Reorientation: \( \hat{n} = n_0 + \delta n(z) \), \( n_0 = e_x \), \( \delta n \parallel e_z \), approximation: \( \delta n(z) = (\delta n) \sin(\pi z/d) \)

Total free energy density: 

\[ F_t = F_e + F_d = \frac{1}{2} K_1 \left( \frac{\partial \delta n(z)}{\partial z} \right)^2 - \frac{1}{2} \varepsilon_0 \varepsilon_a E^2 (\delta n(z))^2 - C \]

\[ \int_0^d F_t dz = (\delta n)^2 \left[ \left( \frac{K_1 \pi^2}{4d} \right) - \left( \frac{\varepsilon_0 \varepsilon_a E^2 d}{4} \right) \right] < 0 \]

\[ \Rightarrow \quad E_{th} = \frac{\pi}{d} \sqrt{\frac{K_1}{\varepsilon_0 \varepsilon_a}} \]

*critical field ~ 1V/\mu m*
THERMOTROPIC LIQUID CRYSTAL PHASES
of chiral molecules

Via intramolecular interactions chirality is transmitted from the microscopic to the macroscopic scale.

Chiral nematic phase (N*), known also as cholesteric phase (Ch)
Spontaneously twisted

Chiral smectic A phase (SmA*)
Similar to achiral SmA, but exhibits optical activity

Chiral smectic C phase (SmC*)
Tilted and spontaneously twisted (exhibits ferroelectricity)
Example: LC phases of DNA in aqueous solutions

spherulite of the cholesteric phase
\[ c > 10 \text{ wt \%} \]

segment of DNA

hexagonal LC phase
OPTICAL PROPERTIES
optical properties of the nematic phase

\[ \varepsilon = \varepsilon_\perp \mathbf{1} + \varepsilon_a (\mathbf{n} \otimes \mathbf{n}), \quad \varepsilon_a = (\varepsilon_\parallel - \varepsilon_\perp) = n S_N (\alpha_\parallel - \alpha_\perp) f h \]

Dielectric tensor at optical frequencies (~10^{15} Hz), refractive index \( n = (\varepsilon)^{1/2} \)

LC phases have very large birefringence: \( n_\parallel - n_\perp = \Delta n \sim 0.2 \)

Optical axis is parallel to the nematic director \( \hat{n} \).

\[ \mathbf{E}(r,t) = A s_E e^{i k r - i \omega t} \]

\[ k = (\omega/c) n \]

Ordinary beam: \( n_o = n_\perp \)

Extraordinary beam:

\[ \frac{1}{n_e^2} = \frac{\sin^2 \theta}{n_\parallel^2} + \frac{\cos^2 \theta}{n_\perp^2} \]
**OPTICAL BIREFRINGENCE**

Nematic liquid crystals are strongly birefringent “liquids”!!!

\[(n_e - n_o) \propto S_N\]

Phase retardation between ordinary and extraordinary ray in \(d=4\lambda\) thick LC layer is \(2\pi!!!\)

Phase retardation can be mediated by relatively low external voltages (Freedericksz effect).

Liquid crystal have large electrooptic response!!!
COLORFULL NEMATIC TEXTURES observed between crossed polarizers

Phase retardation between ordinary and extraordinary ray

\[ \Phi = \frac{2\pi(\Delta n)d}{\lambda} \]

depends on local orientation of the director field \( \hat{n}(r) \)

Optical polarization microscopy:

Transmittance \( T = T(\Phi) \)
Spatial periodicity (pitch $p$) of the director field $n(r)$ is typically in the range of optical wavelengths.

$$\hat{n}(z) = (\cos(qz), \sin(qz), 0)$$

$q = 2\pi/p$

Dielectric tensor in x,y plane:

$$\varepsilon = \varepsilon_\perp \mathbf{1} + \varepsilon_a (\hat{n} \otimes \hat{n}) =$$

$$\begin{bmatrix}
a + b\cos(2qz), & b\sin(2qz) \\
b\sin(2qz), & a - b\cos(2qz)
\end{bmatrix}$$

$$a = (\varepsilon_\parallel + \varepsilon_\perp) / 2, \ b = (\varepsilon_\parallel - \varepsilon_\perp) / 2$$

Spiralling index ellipsoid.

(Analytical solutions of WE for $k||z$ and $d=\infty$

$I\!m K$ means strong selective reflection for $\lambda \sim p$.

Cholesteric LCs are natural 1D photonic band-gap media !!
SELECTIVE REFLECTION and MAUGUIN LIMIT

- For $\lambda \approx p$ circularly polarized beam which matches the chirality of the structure is totally reflected. The width of the reflection (forbidden) band $\Delta \lambda \approx \Delta n \cdot p$.

- For $\lambda \ll p$ the polarization plane of the linearly polarized light is rotated synchronously with the spontaneous twist of the structure \textit{(Mauguin limit)}. The material acts as a strongly optically active medium.
LIGHT SCATTERING
LIGHT SCATTERING IN THE NEMATIC PHASE

One of the most profound optical manifestations of the thermal fluctuations.

\[ n(r) = n_0(r) + \delta n(r) \rightarrow \delta n(r) = \sum \delta n(q) e^{iqr} \]

Fluctuations of the director field \( n(r) \) produce increase of the elastic energy \( F_d \)

\[ F_d = \frac{V}{2} \sum_q \left[ |\delta n_1(q)|^2 (K_1 q_\perp^2 + K_3 q_\parallel^2) + |\delta n_2(q)|^2 (K_2 q_\perp^2 + K_3 q_\parallel^2) \right] \]

Overdamped relaxation:

\[ \frac{dF_d}{dn_i} = -\gamma_i \frac{\partial n_i}{\partial t}, \quad i=1,2 \]

\[ \delta n(q,t) = \delta n(q,0) e^{-t/\tau} \]

Relaxation rate: \( (1/\tau) \approx (K/\gamma) q^2 \)

\[ 10^{-6} \text{ to } 1 \text{ s} \quad 10^{-5} \text{ cm}^2/\text{s} \]
Photon correlation spectroscopy (known as PCS or DLS): probing range $10^{-9} - 10^3$ s

Largest scattering cross section for $\delta n(q = q_s)$.

\[
g^{(2)}(t) = \frac{<I(t')I(t'+t)>}{<I>^2} = 1 + \alpha \cdot (g^{(1)}(t))^2
\]

\[
g^{(1)}(t) = \frac{<E_s(t')E_s(t'+t)>}{<E_s(t')><E_s(t'+t)>} \propto \sum_l C_l e^{-t/\tau_l} S_l
\]

DLS provides information on $\tau$ of different fluctuation modes $\delta n(q,t)$. This gives the values of $(K_i/\gamma)$ for different types of deformations.
LIGHT SCATTERING
FROM CONFINED LC STRUCTURES

A) Spherical LC droplets of radius R

\[ q_{\text{min}} \approx \frac{\pi}{R}, \quad (1/\tau)_{\text{min}} \approx \frac{K}{\gamma}R^{-2} \]

B) Thin LC film of thickness D \( \sim \lambda \).

\[ q_{\text{min}} \approx \frac{\pi}{D}, \quad (1/\tau)_{\text{min}} \approx \frac{K}{\gamma}D^{-2} \]

DLS gives information on cavity size (R or D) and surface anchoring coefficient B.
APPLICATIONS OF LIQUID CRYSTALS

Most important commercial products based on LCs are LCDs.

Present top LCD:
WUXGA (wide ultra extended graphics array) 1920 x 1200 pixels.

Other applications:
• optical switching devices,
• optical filters,
• temperature and stress sensors,
• special paints and colorants,
• cosmetics,
• etc.
Liquid Crystal Display (LCD) PRINCIPLE

(A) Polarized output light

Electrodes

Unpolarized Light

Polariser

Analyser

No output light

(B) Voltage ON

Electrodes

Unpolarized Light

Polariser

Analyser

No output light

Picture element is white  Picture element is black
FROM PICTURE ELEMENT to THE DISPLAY

Segment-type display

Active matrix display

composition of TFT LCD

colours

colours (RGB)

backlight

polariser

liquid crystal material

common electrode

segment electrode

TFT

Gate Line

Drain Bus

Top Glass

Bottom Glass

semiconductor platform
Switchable windows are made from polymer dispersed liquid crystals (PDLC).

**voltage off**

**voltage on**

- Strong light scattering: "milky" appearance
- Transparent
OTHER APPLICATIONS

Car paint from chiral LCs.

Temperature sensor from cholesteric LCs

LCs in ART:
Art-painting made by use of the polysiloxane LC paint.
left: in reflected light
right: in transmitted light