Liquid Crystals and Light

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Outline

- motivation: why LCs?
- light and matter
- matter governing light
- nonlinear optics
- light governing matter
- summary

I. Motivation

Motivation

- Why LCs?
  - interesting aspects:

    1. orientationally ordered

    2. responsive

Orientation

- concept not necessary, but useful
  - else have to specify position of many points

- unusual aspects:

position	orientation	
two particles **cannot** have same position	two particles **can have** same orientation	
to change from one position to another, particle **must have** linear momentum	to change from one orientation to another, particle **need not have** angular momentum	
fermion-like	boson-like	

Orientation

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  - else have to specify position of many points

- unusual aspects:

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fermion-like	boson-like	

Responsivity

- LCs respond readily to stimuli
- Why?

Goldstone's theorem:

Broken continuous symmetry → *low energy excitations*

→ *responsive*

- – nematic liquid crystals:

  director breaks continuous symmetry; system is necessarily 'SOFT'

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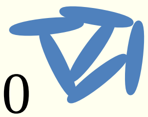
Goldstone modes ?

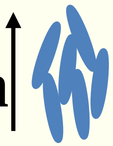
– at high T, rodlike particles are randomly oriented

$S = 0$



– below a critical temperature, they orient so that, on the average, they point in some direction $\hat{\mathbf{n}}$

$\hat{\mathbf{n}}$



– this direction is arbitrary

- (Hamiltonian is invariant under rotation $\rightarrow$ broken continuous symmetry $\rightarrow$ no external field)

– energy of changing $\hat{\mathbf{n}}$ can only depend on $\nabla\hat{\mathbf{n}}$

- no coupling of $\hat{\mathbf{n}}$ to external field

– energy of long wavelength excitations is vanishingly small

Goldstone modes ?

- the energy of deformation per volume goes as

$$\sim K(\nabla\hat{\mathbf{n}})^2 = KA_q^{\,2}q^2 = KA_q^{\,2}(\frac{2\pi}{\lambda})^2$$

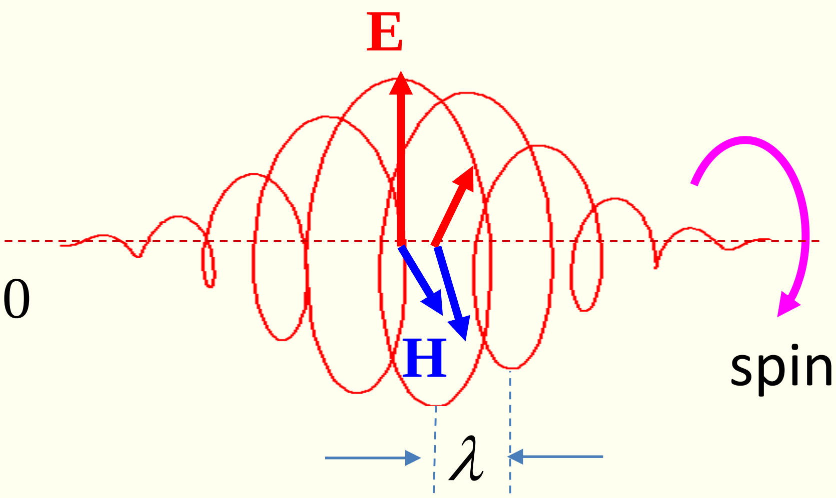
- which vanishes as $\lambda \to \infty$!

- these low-energy excitations are Goldstone modes
  - they destroy long range order in 1D (Peierls) and 2D (Hohenberg-Mermin-Wagner)
  - make 'soft' materials responsive

II. Light

- current of photons

- photons have:
  - no rest mass $m_0 = 0$
  - wavelength λ
  - frequency ν
  - energy $h\nu$
  - energy current density $\mathbf{E} \times \mathbf{H}$
  - linear momentum h / λ
  - angular momentum (spin) $\hbar$



Photons and classical fields

- classical fields are 'wavefunctions' of photons

- photon number density: $\rho_p = \frac{1}{2}\frac{\varepsilon_0 E^2}{h\nu}$, $\rho_p = \frac{1}{2}\frac{\mu_0 H^2}{h\nu}$

- photon current density: $\mathbf{J}_p = \frac{\mathbf{E}\times\mathbf{H}}{h\nu}$

- momentum conservation can explain light induced forces and torques on reflection & absorption

II. Fields and matter

Fields and matter

- coupling is via forces on charges in matter
  - electric fields create electric dipoles

$$\mathbf{P} = \frac{1}{V}\int \rho_q \mathbf{r}\, dV$$

$$\boxed{\mathbf{P} = \varepsilon_0 \alpha \mathbf{E}}$$

linear response

$$\mathbf{D} = \varepsilon_0 \varepsilon_r \mathbf{E} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (\mathbf{I} + \alpha)\mathbf{E}$$

  - magnetic fields create magnetic dipoles

$$\mathbf{M} = \frac{1}{V}\int \frac{1}{2}\mathbf{r} \times \mathbf{J}_q\, dV$$

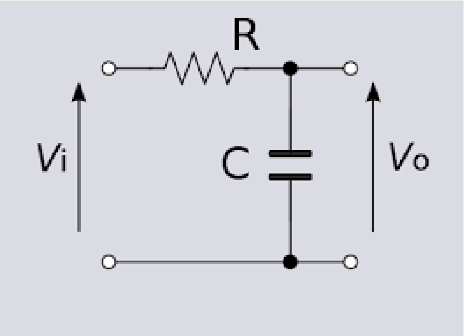
»

$$\boxed{\mathbf{M} = \chi \mathbf{H}}$$

linear response

$$\mathbf{B} = \mu_o \mu_r \mathbf{H} = \mu_0 (\mathbf{H} + \mathbf{M})$$

Linear Response



impulse response (Green's function) $g(t) = \frac{1}{RC} e^{-t/RC}\ ,\ t > 0$

- we have, in real space $v_0(t) = \int_{-\infty}^{\infty} v_i(\tau) g(\mathrm{t} - \tau)\, \mathrm{d}\tau$
- and, in Fourier space, $V_0(\omega) = G(\omega) V_i(\omega)$

- it follows that $\mathbf{D} = \varepsilon \mathbf{E}$ is valid in Fourier space

Caveat:
only if system is homogeneous
(invariant under translation)

$$\mathbf{D}(\omega, \mathbf{k}) = \varepsilon(\omega, \mathbf{k}) \mathbf{E}(\omega, \mathbf{k})$$

- key notion: response is nonlocal

Light Propagation

- The propagation of electromagnetic radiation is described by Maxwell's equations:

$$\nabla \cdot \mathbf{D} = 0$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}$$

where

$$\mathbf{D} = \varepsilon_o \varepsilon_r \mathbf{E} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$

$$\mathbf{B} = \mu_o \mu_r \mathbf{H} = \mu_0 (\mathbf{H} + \mathbf{M})$$

and there are no free charges.

The wave equation

- if the material properties do not change in time, we write

$$\nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t}$$

$$\nabla \times \mathbf{H} = \varepsilon \frac{\partial \mathbf{E}}{\partial t}$$

- where μ and ε are tensors.
- if magnetic properties are isotropic and uniform, then

$$\nabla \times \nabla \times \mathbf{E} = -\mu\varepsilon \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

- and

$$\boxed{\nabla^2 \mathbf{E} - \nabla(\nabla \cdot \mathbf{E}) = \mu\varepsilon \frac{\partial^2 \mathbf{E}}{\partial t^2}}$$ with $\nabla \cdot \varepsilon \mathbf{E} = 0$.

The wave equation

- we look for solutions of the form .

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$$

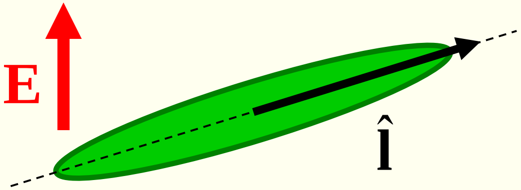
- here $\mathbf{k} = \frac{2\pi}{\lambda}\hat{\mathbf{k}}$ is the wave vector,
- the speed of the wave is $v = \frac{\omega}{k} = \frac{\omega}{2\pi}\lambda$
- the wave equation becomes an eigenvalue equation
- $$(\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{E}_0 = \mu\varepsilon v^2 \mathbf{E}_0$$ with $\mathbf{k}\cdot\varepsilon\mathbf{E}_0 = 0$

The wave equation

- we have $$(\mathbf{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{E}_0 = \mu\varepsilon v^2\mathbf{E}_0$$
- in vacuum, $$v = c = \frac{1}{\sqrt{\varepsilon_0\mu_0}}$$ $$c = \frac{\omega}{k} = \frac{\omega}{2\pi}\lambda_0$$
- in general, $$v = \frac{1}{\sqrt{\varepsilon\mu}}$$ $$v = \frac{\omega}{k} = \frac{\omega}{2\pi}\lambda$$
- refractive index: $$n = \frac{c}{v} = \sqrt{\varepsilon_r\mu_r}$$ $$\lambda = \frac{\lambda_o}{n}$$

Dielectric tensor

- in liquid crystals, the polarizability is anisotropic



$$\mathbf{p} = \alpha_{\|}(\mathbf{E}\cdot\hat{\mathbf{l}})\hat{\mathbf{l}} + \alpha_{\perp}(\mathbf{E} - (\mathbf{E}\cdot\hat{\mathbf{l}})\hat{\mathbf{l}})$$

- rearrange

$$\mathbf{p} = [(\frac{\alpha_{\|} + 2\alpha_{\perp}}{3})\mathbf{I} + \frac{2}{3}(\alpha_{\|} - \alpha_{\perp})\frac{1}{2}(3\hat{\mathbf{l}}\hat{\mathbf{l}} - \mathbf{I})]\mathbf{E}$$

- and

$$\mathbf{P} = \rho[\bar{\alpha}\mathbf{I} + \Delta\alpha Q]\mathbf{E}$$

- dielectric tensor

$$\varepsilon_r = (1 + \frac{\rho\bar{\alpha}}{\varepsilon_0})\mathbf{I} + \frac{\rho\Delta\alpha}{\varepsilon_0}\mathrm{Q}$$

$$\varepsilon = \varepsilon_{\perp}\mathbf{I} + (\varepsilon_{\|} - \varepsilon_{\perp})\hat{\mathbf{n}}\hat{\mathbf{n}} \qquad \varepsilon^{-1} = \frac{1}{\varepsilon_{\perp}}\mathbf{I} + (\frac{1}{\varepsilon_{\|}} - \frac{1}{\varepsilon_{\perp}})\hat{\mathbf{n}}\hat{\mathbf{n}}$$

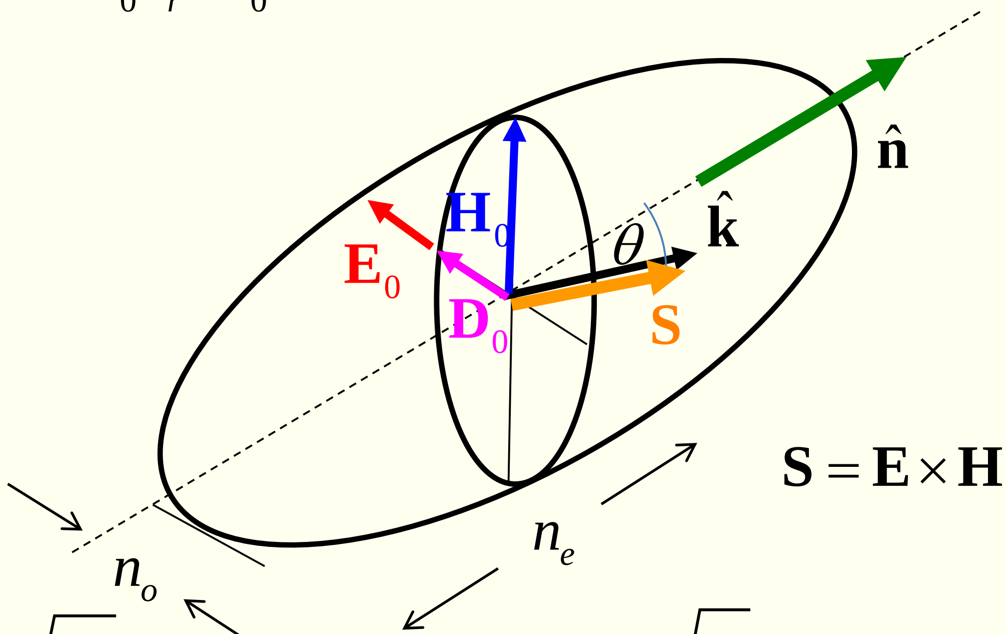
IV. Matter governing light:

Light propagation in uniaxial crystals

Solutions of the wave equation

- have $$(\mathbf{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{E}_0 = \frac{1}{n^2}\mu_r\varepsilon_r\mathbf{E}_0$$
- better to consider $$(\mathbf{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\varepsilon_r^{-1}\mathbf{D}_0 = \frac{1}{n^2}\mathbf{D}_0 \qquad (\mu_r \simeq 1)$$
- index ellipsoid: $$\mathbf{D}_0\varepsilon_r^{-1}\mathbf{D}_0 = 1$$

$$\varepsilon^{-1} \simeq \frac{1}{\varepsilon_\perp}\mathbf{I} + \left(\frac{1}{\varepsilon_\parallel} - \frac{1}{\varepsilon_\perp}\right)\hat{\mathbf{n}}\hat{\mathbf{n}}$$



$$\mathbf{S} = \mathbf{E}\times\mathbf{H}$$

Ordinary mode:

$\mathbf{E} \parallel \mathbf{D}$

$\mathbf{D},\mathbf{E} \perp \mathbf{k},\hat{\mathbf{n}}$

$n = n_o$

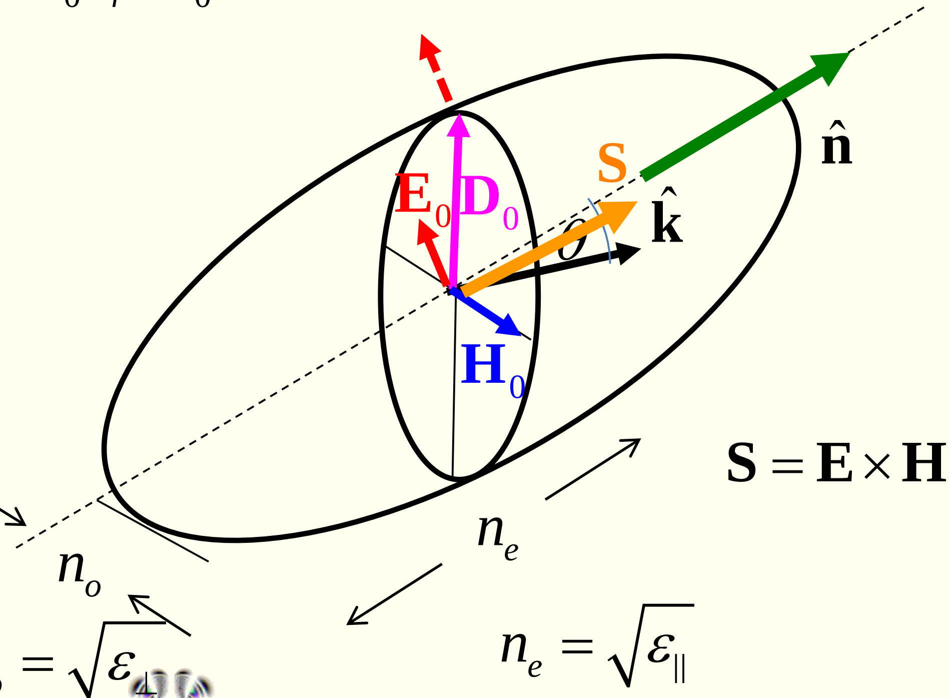
$\mathbf{S} \parallel \mathbf{k}$

$$n_o = \sqrt{\varepsilon_\perp} \qquad n_e = \sqrt{\varepsilon_\parallel}$$

Solutions of the wave equation

- have $$(\mathbf{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\mathbf{E}_0 = \frac{1}{n^2}\mu_r \varepsilon_r \mathbf{E}_0$$
- better to consider $$(\mathbf{I}-\hat{\mathbf{k}}\hat{\mathbf{k}})\varepsilon_r^{-1}\mathbf{D}_0 = \frac{1}{n^2}\mathbf{D}_0$$
- index ellipsoid: $$\mathbf{D}_0 \varepsilon_r^{-1}\mathbf{D}_0 = 1$$

$$\varepsilon^{-1} \simeq \frac{1}{\varepsilon_\perp}\mathbf{I} + \left(\frac{1}{\varepsilon_{\|}} - \frac{1}{\varepsilon_\perp}\right)\hat{\mathbf{n}}\hat{\mathbf{n}}$$



$$\mathbf{S} = \mathbf{E} \times \mathbf{H}$$

Extraordinary mode:

$$\mathbf{D},\mathbf{E} \;\perp\; \mathbf{k},\hat{\mathbf{n}}$$

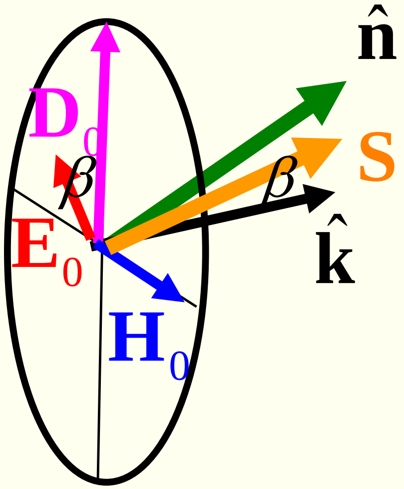
$$n = \frac{n_e n_o}{\sqrt{n_e{}^2 \cos^2\theta + n_o{}^2 \sin^2\theta}}$$

$\mathbf{S} \measuredangle \mathbf{k}$ $\qquad$ $\mathbf{D} \measuredangle \mathbf{E}$

Two propagating modes: ordinary & extraordinary

- have orthogonal polarizations
- rays travel in different directions
- describes light propagation in nematics

- remarkable aspect of extraordinary mode:



$$\tan\beta = \frac{(n_e^{\,2} - n_o^{\,2})\sin\theta\cos\theta}{\sqrt{n_e^{\,2}\cos^2\theta + n_o^{\,2}\sin^2\theta}}$$

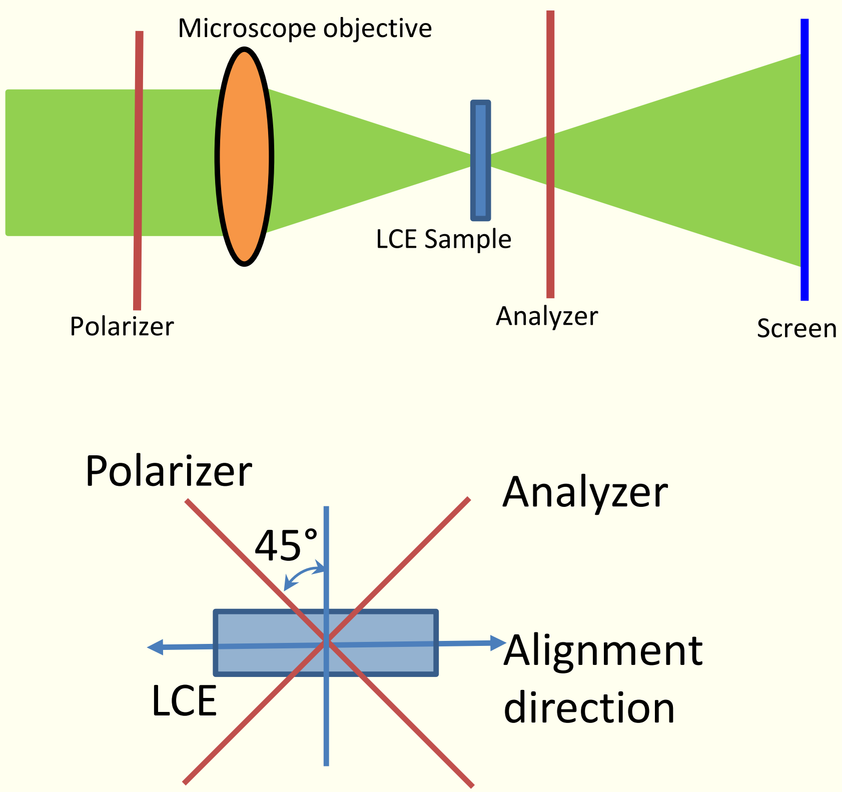
ray (energy, photons)

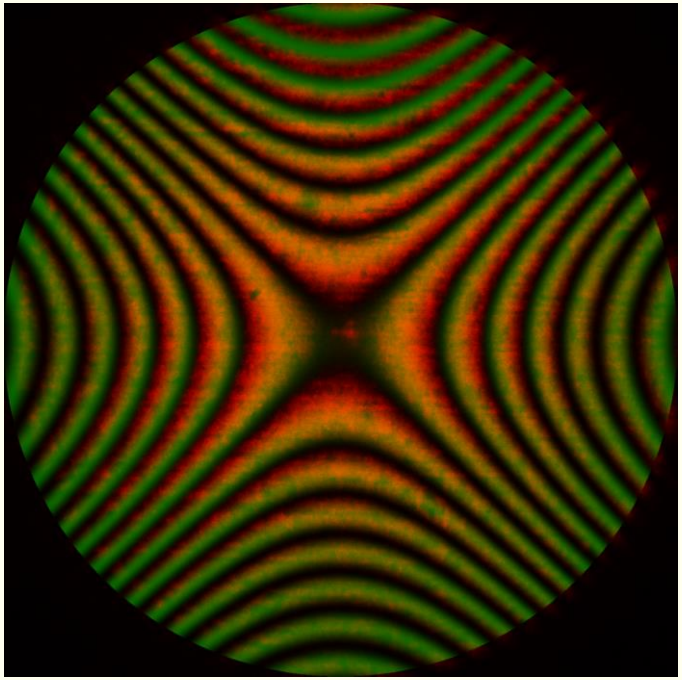
wave (phase, momentum)

- propagate in different directions !

Conoscopic pattern from nematic film

- interference between modes

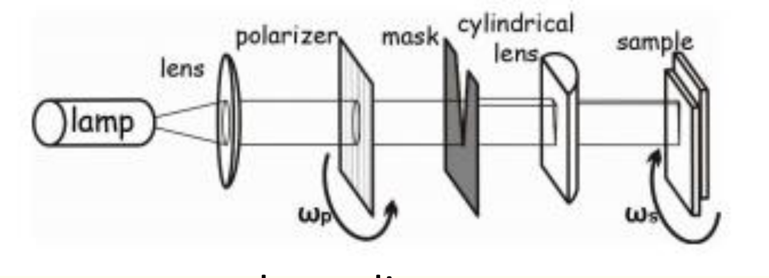




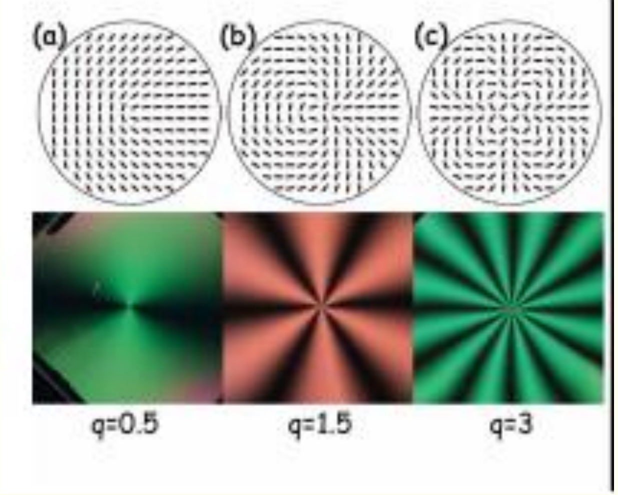
green: experiment red: theory
p.p-m. group

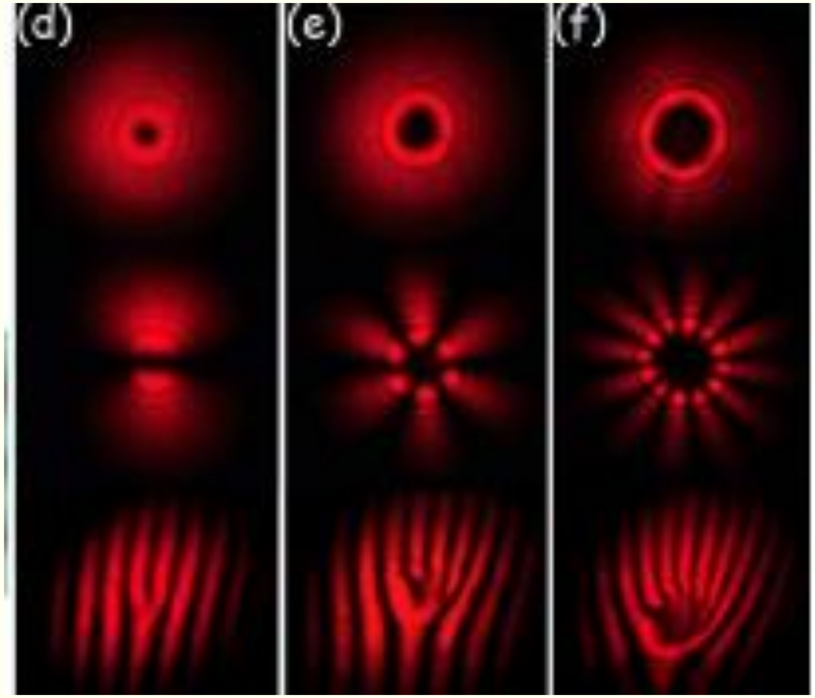
q-plates from nematic film

- spatially varying director field.



photoalignment





far field intensity pattern

- applications in quantum computing

L. Marrucci *et al.* *2011*

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IV. Matter governing light:

Chirality and optical activity

Chirality

- chirality represents broken inversion symmetry

- constituent molecules of liquid crystals may be chiral

- observable consequences:
  - optical activity (isotropic)
    - rotation of plane of polarization
  - photonic band gap with handedness (anisotropic)
    - no stable propagation for some range of frequencies

- form of $\varepsilon(\mathbf{k},\omega)$ in isotropic chiral materials?

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Optical activity (isotropic materials)

- expand $\varepsilon_{\alpha\beta}$ in $\mathbf{k}$:

$$\mathbf{D} = \varepsilon_o(\varepsilon_1\delta_{\alpha\gamma} + i\gamma\varepsilon_{\alpha\beta\gamma}k_\beta)\mathbf{E}$$

pseudo-scalar → γ; Levi-Civita → $\varepsilon_{\alpha\beta\gamma}$

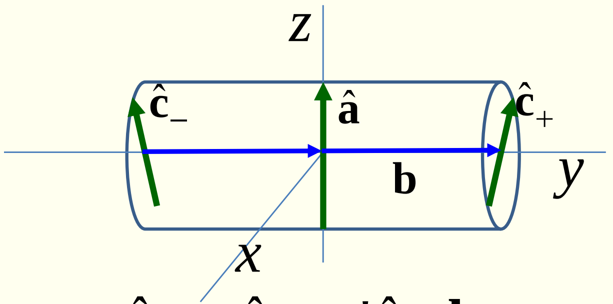
where does γ come from?

- substitute in wave equation:
  - two circularly polarized modes, opposite handedness
  - optical rotation: $\theta = \frac{1}{2}\gamma(\frac{2\pi}{\lambda_o})^2 z$

pseudoscalar $\gamma \Leftrightarrow$ optical rotation

- can write, in real space, $\mathbf{D} = \alpha\mathbf{E} + \gamma\nabla\times\mathbf{E} = \alpha\mathbf{E} - \gamma\frac{\partial\mathbf{B}}{\partial t}$

Particle shape and the pseudoscalar γ



$$\hat{\mathbf{c}}_+ = \hat{\mathbf{a}} + \gamma' \hat{\mathbf{a}} \times \mathbf{b}$$

- consider the chiral molecule/particle
  - $\hat{\mathbf{c}}_-, \hat{\mathbf{a}}, \hat{\mathbf{c}}_+$ polarizable segments
  - $\mathbf{E}$ field only at the origin
  - calculate dipole moment

$$\mathbf{p} = \alpha_0 (\mathbf{E}\cdot\hat{\mathbf{a}})(\hat{\mathbf{a}}\delta(\mathbf{r}) - \frac{\alpha_0}{4\pi\varepsilon_0 b^3}((\hat{\mathbf{a}} - \gamma'\hat{\mathbf{a}}\times\mathbf{b})\delta(\mathbf{r}+\mathbf{b}) + (\hat{\mathbf{a}} + \gamma'\hat{\mathbf{a}}\times\mathbf{b})\delta(\mathbf{r}-\mathbf{b}))$$

  - Fourier transform:

$$\mathbf{p} = \alpha_0 (\mathbf{E}\cdot\hat{\mathbf{a}})(\hat{\mathbf{a}} - \frac{\alpha_0}{2\pi\varepsilon_0 b^3}(\hat{\mathbf{a}}\cos(\mathbf{k}\cdot\mathbf{b}) - \mathrm{i}\gamma'(\hat{\mathbf{a}}\times\mathbf{b})\sin(\mathbf{k}\cdot\mathbf{b}))$$

  - small $\mathbf{k}\cdot\mathbf{b}$ and isotropic average

$$\mathbf{D} = \varepsilon_o\{(+\frac{\rho\alpha_0}{3\varepsilon_0})\delta_{\alpha\beta} + \overbrace{\mathrm{i}\gamma'\frac{\rho\alpha_0^2}{6\pi\varepsilon_0^2 b}}^{\gamma}\varepsilon_{\alpha\beta\gamma}k_\gamma)\}\mathbf{E}$$

Current Approaches

- two schools of thought:

- Landau & Lifshitz: (Casimir, Agranovich)
  – spatial dispersion, Fourier space

$$\mathbf{D}(\omega,\mathbf{k}) = \varepsilon(\omega,\mathbf{k})\mathbf{E}(\omega,\mathbf{k})$$

- Drude-Born-Fedorov:
  – non-locality, real space description

$$\mathbf{D} = \varepsilon(\mathbf{E} + \beta\nabla\times\mathbf{E})$$
$$\mathbf{B} = \mu(\mathbf{H} + \beta\nabla\times\mathbf{H})$$

- two approaches have been ~reconciled, but questions remain: (i.e. BCs for non-local interactions….)

V.M. Agranovich and V.L. Ginzburg, 'Crystal Optics and *Spatial Dispersion*..' (Springer, 1984)

Optical activity (isotropic materials)

- expand $\varepsilon_{\alpha\beta}$ in $\mathbf{k}$:

$$\mathbf{D} = \varepsilon_o(\varepsilon_1\delta_{\alpha\gamma} + i\gamma\varepsilon_{\alpha\beta\gamma}k_\beta)\mathbf{E}$$

pseudo-scalar → γ; Levi-Civita → $\varepsilon_{\alpha\beta\gamma}$

- substitute in wave equation:

where does γ come from?

  - two circularly polarized modes, opposite handedness
  - optical rotation:

$$\theta = \frac{1}{2}\gamma\left(\frac{2\pi}{\lambda_o}\right)^2 z$$

  - if $\gamma/\lambda << 1$, can ignore

pseudoscalar $\gamma \Leftrightarrow$ optical rotation

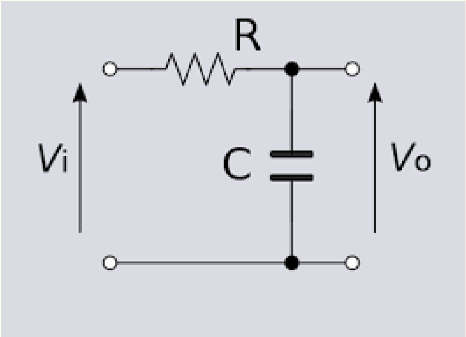
- reasonable description for homogeneous, isotropic materials

IV. Matter governing light:

Optical properties of helical cholesterics

What if material is not homogeneous ?

- inhomogeneous: not invariant under translation
  - in space: material properties vary with position
  - in time: material properties very in time



- if R, C vary in time, cannot use Green's function method

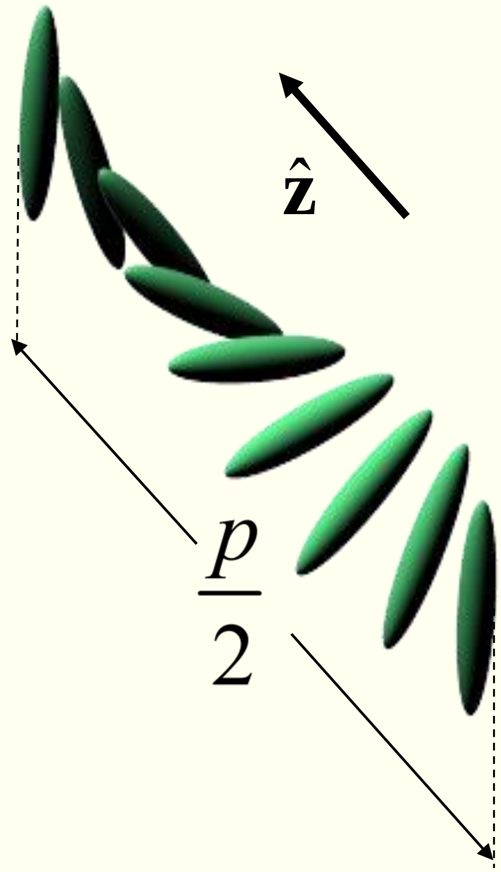
- response is not simple convolution

- strategy: determine relation between **D** and **E** and **B** and **H**
  solve PDE

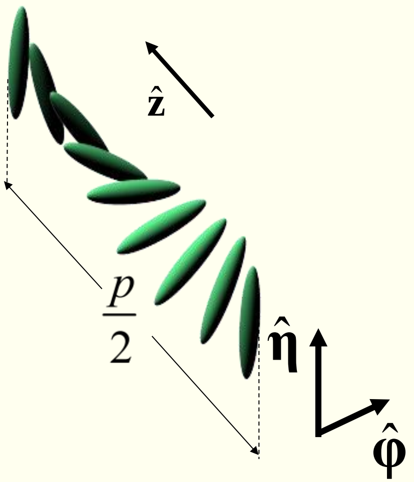
- determination of constitutive equations can be difficult

Helical cholesteric (chiral nematic) material

- chiral molecules form helical structures
  - due to symmetry; attractive and repulsive interactions
- permittivity is function of z
  - response is non-local
  - spatially inhomogeneous
- approach:
  - ignore non-locality
  - work in real space



Light propagation in helical cholesterics



- here we assume

$$\mathbf{E} = \mathbf{E}(z)e^{i(\mathrm{kz}-\omega t)}$$

- need to solve

$$\nabla^2\mathbf{E} - \nabla(\nabla\cdot\mathbf{E}) = \frac{\varepsilon_r}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}$$

- construct rotating frame

$$\hat{\boldsymbol{\eta}} = \cos qz\hat{\mathbf{x}} + \mathrm{sinqz}\,\hat{\mathbf{y}}$$

$$\hat{\boldsymbol{\varphi}} = -\sin qz\hat{\mathbf{x}} + \mathrm{cosqz}\,\hat{\mathbf{y}}$$

- in rotating frame

$$\varepsilon_r = \begin{bmatrix} \varepsilon_{\|} & 0 \\ 0 & \varepsilon_{\perp} \end{bmatrix}$$

- write field as

$$\mathbf{E}(\mathrm{z}) = E_{\|}\hat{\boldsymbol{\eta}} + E_{\perp}\hat{\boldsymbol{\varphi}}$$

Light propagation in helical cholesterics

- then

$$(-q^2 + \frac{\omega^2}{c^2}\varepsilon_{\parallel} - k^2)E_{\parallel} = 2ikqE_{\perp}$$

$$(-q^2 + \frac{\omega^2}{c^2}\varepsilon_{\perp} - k^2)E_{\perp} = -2ikqE_{\parallel}$$

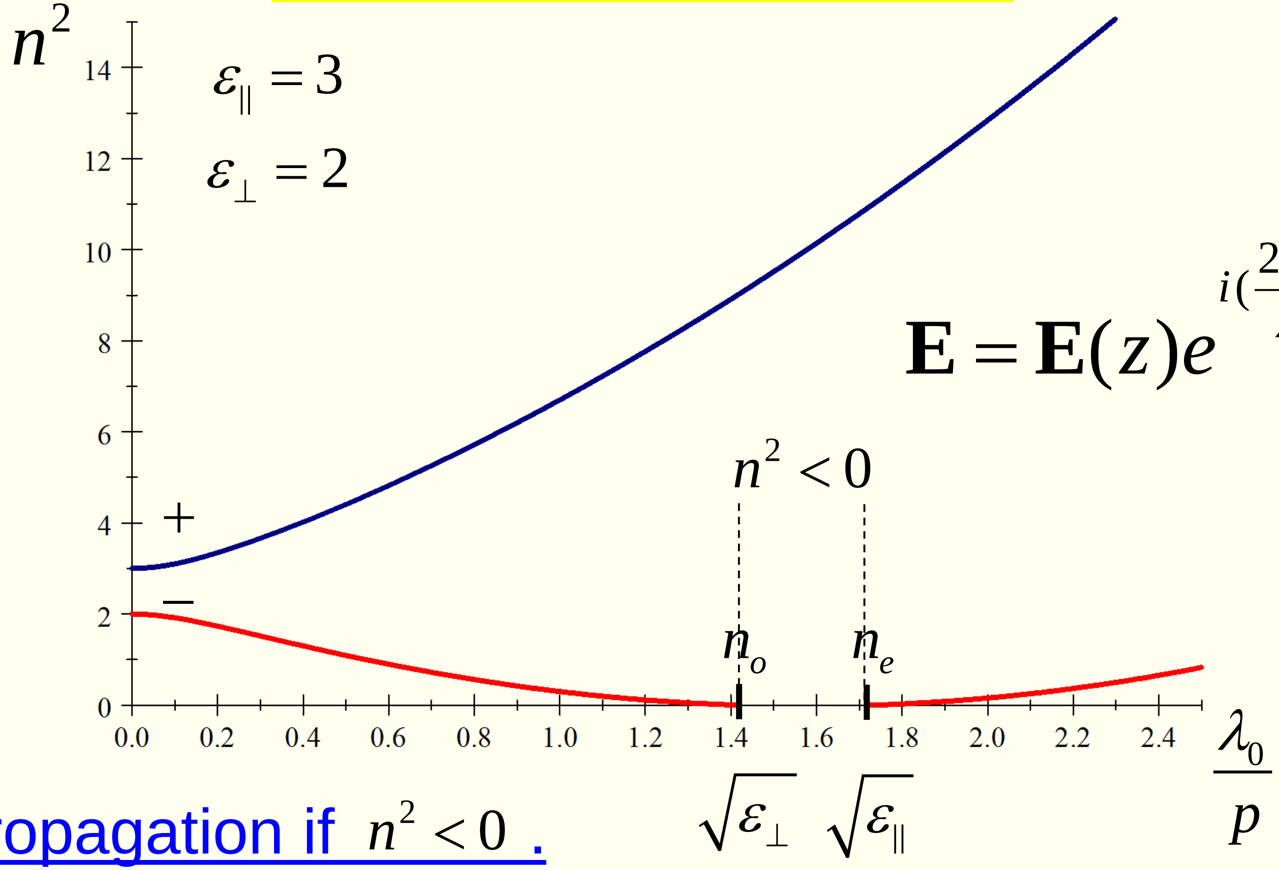
- since $q = \frac{2\pi}{p}$ and $k = \frac{2\pi n}{\lambda_0}$, we obtain

$$n^2 = \bar{\varepsilon} + (\frac{\lambda_0}{p})^2 \pm \sqrt{\delta^2 + 4\bar{\varepsilon}(\frac{\lambda_0}{p})^2}$$

- where $\bar{\varepsilon} = \frac{\varepsilon_{\parallel} + \varepsilon_{\perp}}{2}$ and $\delta = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{2}$.

Light propagation in helical cholesterics

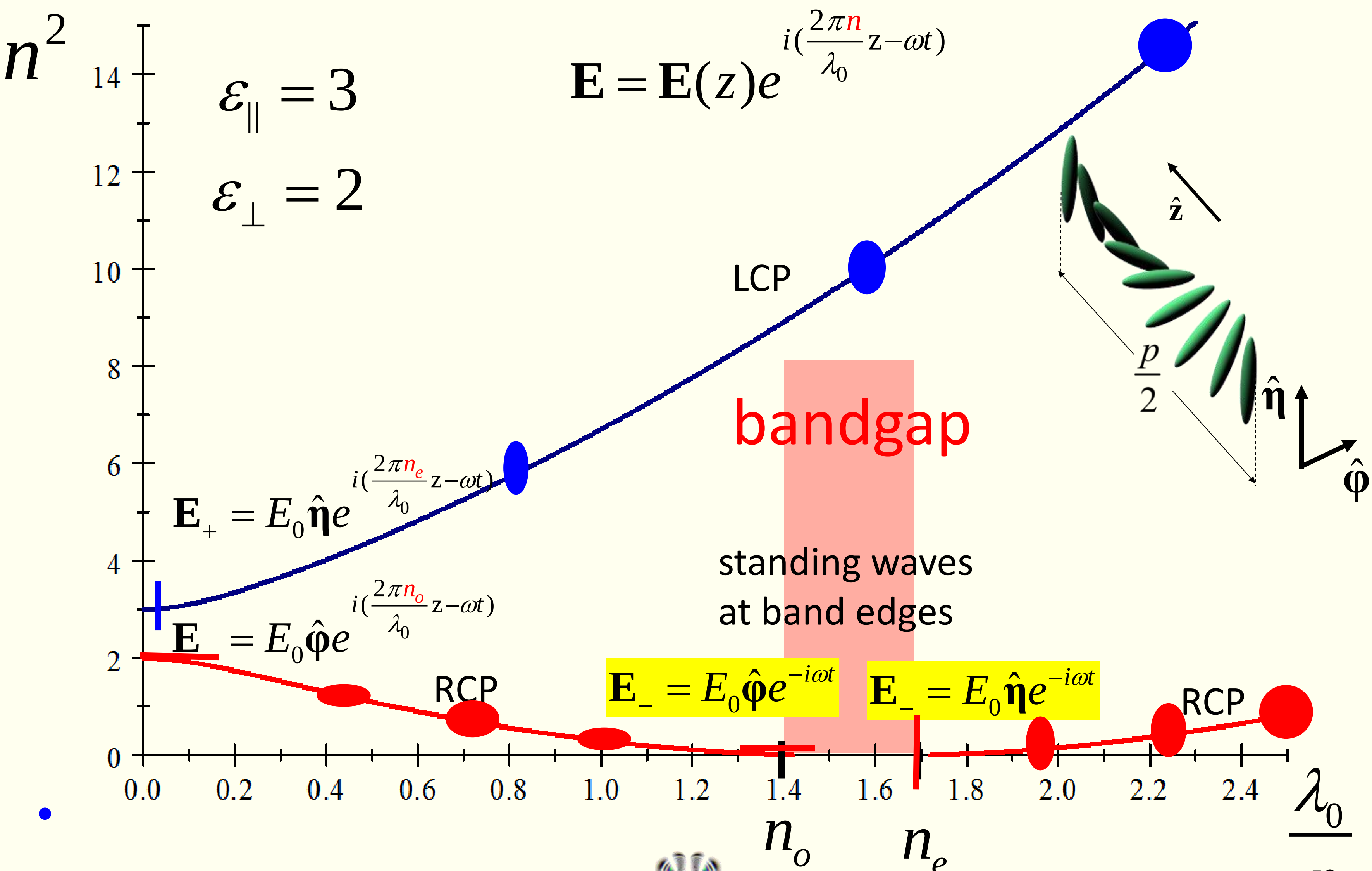
- evaluating $$n^2 = \bar{\varepsilon} + (\frac{\lambda_0}{p})^2 \pm \sqrt{\delta^2 + 4\bar{\varepsilon}(\frac{\lambda_0}{p})^2}$$



$$\mathbf{E} = \mathbf{E}(z)e^{i(\frac{2\pi n}{\lambda_0}z - \omega t)}$$

- no propagation if $n^2 < 0$.

Light propagation in helical cholesterics



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Twisted Nematic Cell

- how a TN cell works:

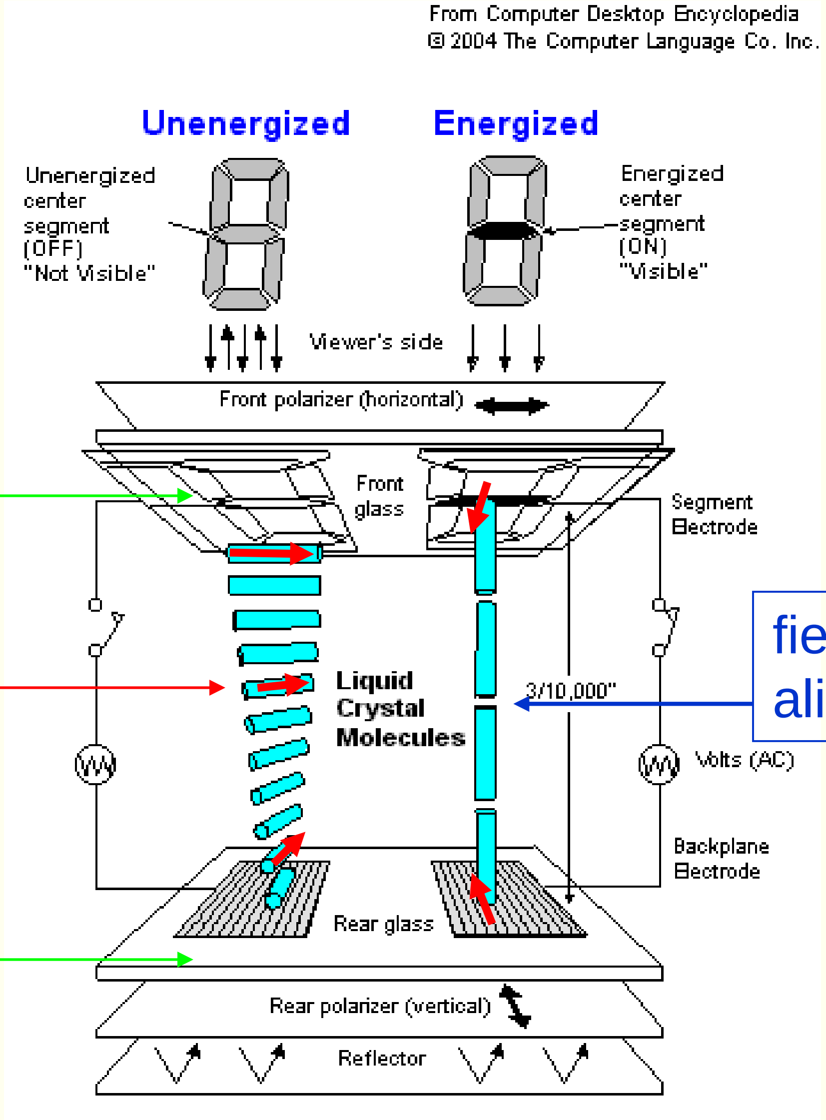
- ~cholesteric $\frac{\lambda_0}{p} << 1$

surface alignment layer

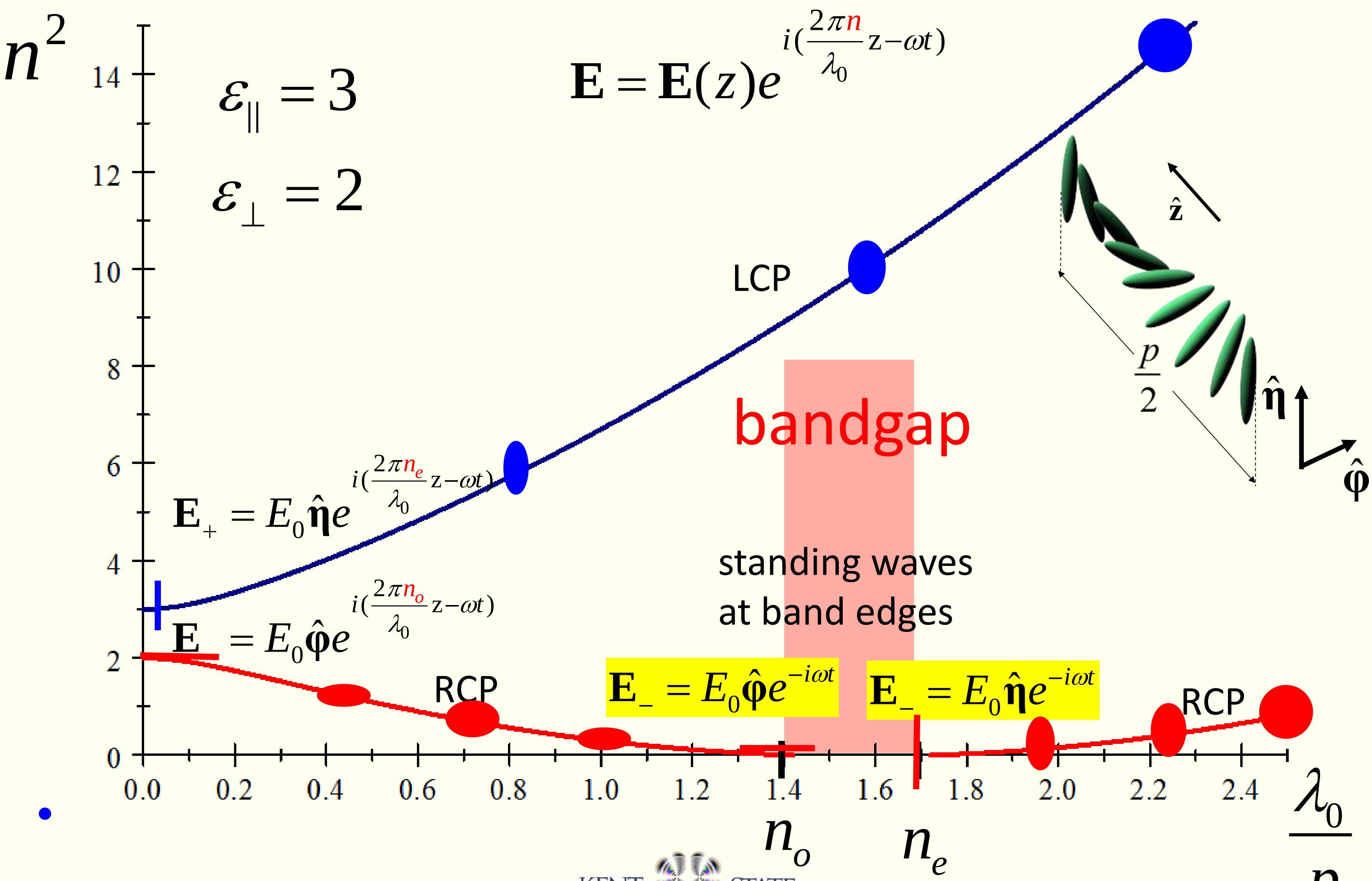
polarization of light follows director

surface alignment layer

field induced alignment



Light propagation in helical cholesterics



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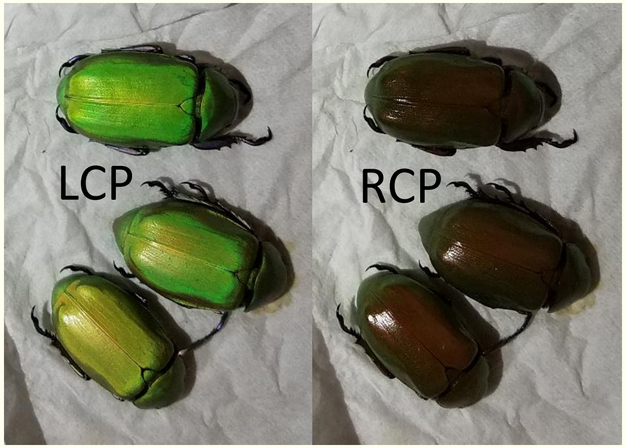
Reflection from helical cholesterics

- no propagation in the reflection band
- incident light with the ‘same handedness’ as the helical structure is reflected

Cholesteric cell with laser written image (unpolarized Illumination)



Scarab beetles: Chrysina beyeri (left- and right-circular polarized illumination)

V. Nonlinear optics

Nonlinear optics

- linear optics: $\mathbf{P} = \varepsilon_0 \alpha \mathbf{E}$
- and $\nabla^2 \mathbf{E} - \nabla(\nabla \cdot \mathbf{E}) = \mu \frac{\partial^2}{\partial t^2}(\varepsilon_0 \mathbf{E} + \mathbf{P})$

- nonlinear optics: $\mathbf{P} = \varepsilon_0(\alpha \mathbf{E} + \alpha_2 \mathbf{EE} + \alpha_3 \mathbf{EEE} + \ldots)$
- and $\nabla^2 \mathbf{E} - \nabla(\nabla \cdot \mathbf{E}) = \mu \frac{\partial^2}{\partial t^2}(\varepsilon_0 \mathbf{E} + \varepsilon_0(\alpha \mathbf{E} + \underbrace{\alpha_2 \mathbf{EE} + \alpha_3 \mathbf{EEE} + ..}_{\text{nonlinear } P})$

Nonlinear optics: basics

– consider motion of electron in an anharmonic potential $U(x)$ and a sinusoidal E field

$$U(x) = \frac{1}{2}k_1 x^2 + \frac{1}{3}k_2 x^3 + \frac{1}{4}k_3 x^4 + ..$$

– equation of motion:

$$m\frac{\partial^2 x}{\partial t^2} + k_1 x + k_2 x^2 + k_3\,\mathrm{x}^3 + ... = eE\cos\omega t$$

harmonic

$$k_1 >> k_2, k_3, ...$$

– try solution of the form

$$x = x_0 + x_1\cos\omega t + x_2\cos 2\omega t + x_3\cos 3\omega t + ...$$

– treat $x_0, x_2, x_3....$ as perturbations

Nonlinear optics: basics

– it follows that

$$x_1 \simeq \frac{(e/m)E_0}{(\omega_0^2-\omega^2)} - \frac{3k_3(e/m)^3 E_0^3}{(\omega_0^2-\omega^2)^4}$$

where e is the charge of the electron, and $\omega_0^2 = k/m$.

– continuing gives

$$x = \frac{-1}{2}\frac{k_2}{k_1}x_1{}^2 + x_1\cos\omega t - \frac{k_2/m}{2(\omega_0^2-(2\omega)^2)}x_1^2\cos 2\omega t - \frac{k_3/\mathrm{m}}{(\omega_0^2-(3\omega)^2)}x_1^3\cos 3\omega t + ..$$

– the polarization is

$$P = \rho p = \rho e x$$

Nonlinear optics: basics

- having the polarization, one can write explicitly

$$
\begin{array}{rll}
P = & -\rho e \frac{1}{2}\frac{k_2}{k_1}\frac{(e/m)^2 E_o^2}{(\omega_o^2-\omega^2)^2} & \text{d.c. optical rectification} \\
& +\rho e \frac{(e/m)E_o}{(\omega_o^2-\omega^2)}\cos\omega t & \text{linear response} \\
& -\rho e \frac{3k_3}{4m}\frac{(e/m)^3 E_o^3}{(\omega_o^2-\omega^2)^4}\cos\omega t & \text{optical Kerr effect} \\
& -\rho e \frac{(k_2/m)}{2(\omega_o^2-(2\omega)^2)}\frac{(e/m)^2 E_o^2}{(\omega_o^2-\omega^2)^2}\cos 2\omega t & \text{second harmonic generation} \\
& -\rho e \frac{(k_3/m)}{(\omega_o^2-(3\omega)^2)}\frac{(e/m)^3 E_o^3}{(\omega_o^2-\omega^2)^3}\cos 3\omega t & \text{third harmonic generation}
\end{array}
$$

- note powers of E_0 .

Nonlinear optics: standard form

– in general, the susceptibilities are written as

$$P_\mu^{(3)}(\mathbf{k},\omega) = \varepsilon_0 \chi_{\mu\alpha\beta\gamma}(\mathbf{k},\omega) E_\alpha(\mathbf{k}_1,\omega_1) E_\beta(\mathbf{k}_2,\omega_2) E_\gamma(\mathbf{k}_3,\omega_3)$$

– where $\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ (momentum conservation)

– and $\omega = \omega_1 + \omega_2 + \omega_3$ (energy conservation)

$\chi^{(1)}(-\omega;\omega)$	$+\frac{\rho e}{\varepsilon_o}\frac{(e/m)}{(\omega_o^2-\omega^2)}$	linear susceptibility
$\chi^{(2)}(0;\omega,-\omega)$	$-\frac{\rho e}{\varepsilon_o}\frac{1}{2}\frac{k_2}{k_1}\frac{(e/m)^2}{(\omega_o^2-\omega^2)^2}$	optical rectification
$\chi^{(2)}(-\omega;\omega_1,\omega_2)$		sum frequency generation
$\chi^{(2)}(-\omega;\omega_1,-\omega_2)$		difference frequency generation
$\chi^{(2)}(-2\omega;\omega,\omega)$	$-\frac{\rho e}{\varepsilon_o}\frac{(k_2/m)}{2(\omega_o^2-(2\omega)^2)}\frac{(e/m)^2}{(\omega_o^2-\omega^2)^2}$	second harmonic generation
$\chi^{(3)}(-\omega;0,0,\omega)$		d.c. Kerr effect
$\chi^{(3)}(-\omega;-\omega,\omega,\omega)$	$-\frac{\rho e}{\varepsilon_o}\frac{3k_3}{4m}\frac{(e/m)^3}{(\omega_o^2-\omega^2)^4}$	optical Kerr effect
$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$	$-\frac{\rho e}{\varepsilon_o}\frac{(k_3/m)}{(\omega_o^2-(3\omega)^2)}\frac{(e/m)^3}{(\omega_o^2-\omega^2)^3}$	third harmonic generation

Nonlinear optics: liquid crystals

- two types of NLO effects:
  - nonlinear electronic response which originates in LC structure
    - LC lasers, SHG
  - linear electronic response with light induced changes in structure
    - optical Kerr effect, material response to light-induced forces and torques

V. Nonlinear Optics

Liquid crystal lasers

Mathematical origins

- Floquet's theorem:

  periodic coefficient in 2nd order ODE $\Rightarrow$

  - solution is of the form $\sim e^{i\mu z}\phi(z)$
  - allowed solutions are in divided into 'bands' (μ real)
  - *no* stable solutions between bands! (μ imag)

G. Floquet, *C. R. Acad. Sci.* Paris **91**, 880–882 (1880).

Bandgaps: examples and applications

$$-\frac{\hbar^2}{2m}\nabla^2\psi = (E - V(\mathbf{r}))\psi$$

– electronics: periodic crystal structure $\Rightarrow$

- electronic band gap materials: semiconductors, ...

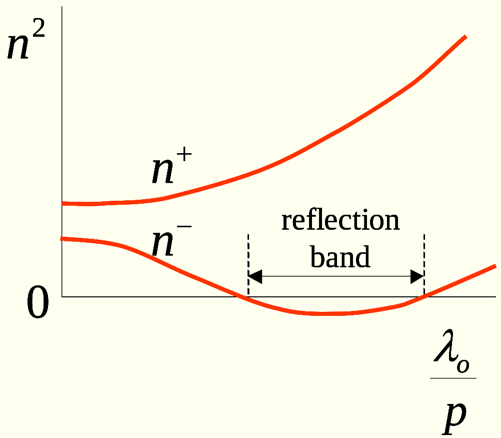
$$\nabla^2\mathbf{E} = -\omega^2\mu\varepsilon(\mathbf{r})\mathbf{E}$$

– photonics: periodic dielectric structure $\Rightarrow$

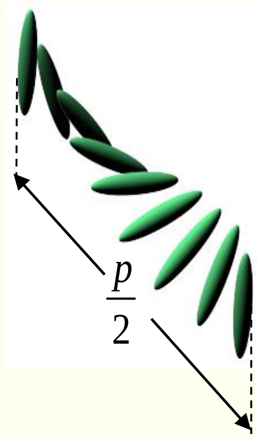
- photonic band gap materials: optical switches, lasers,..?

Helical Cholesteric

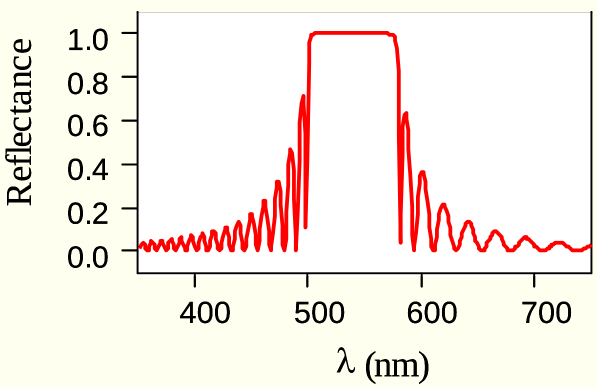
- band structure:

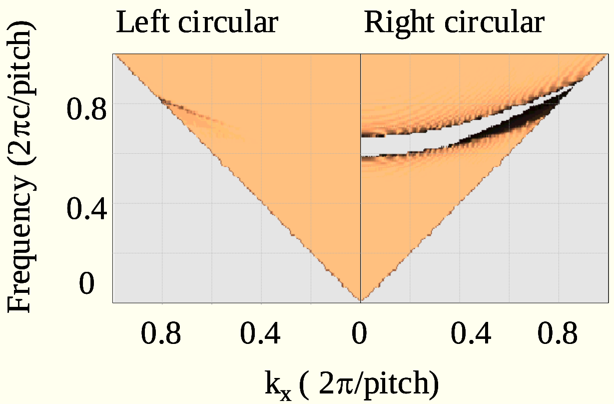


$$\mathbf{E} = e^{i\frac{2\pi n}{\lambda_o}z}\,\mathbf{E}(z)$$



- reflection band: band edges at $\lambda_- = n_o p$ and $\lambda_+ = n_e p$





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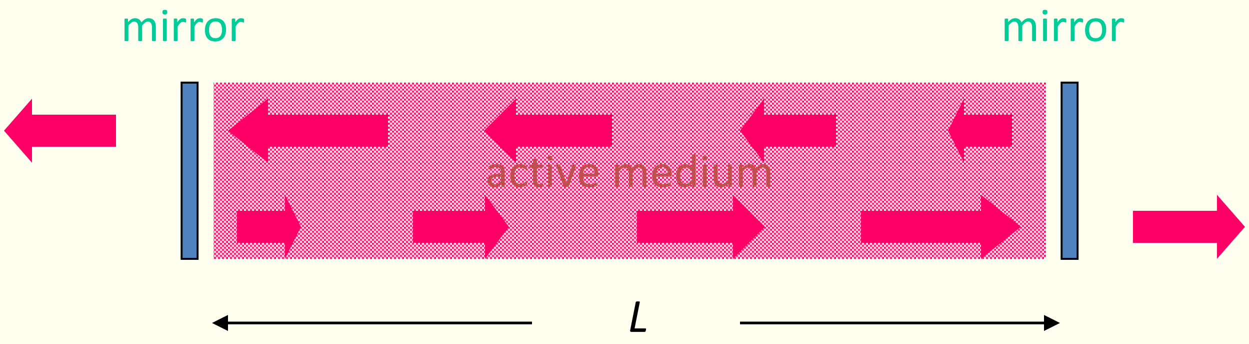
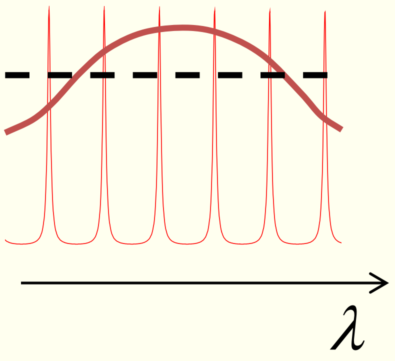
Lasing: feedback effects

- coupled waves



- coupling: $$E_{n+1} = E_n e^{(ikL-\alpha L+\gamma L)} r e^{(ikL-\alpha L+\gamma L)} r$$



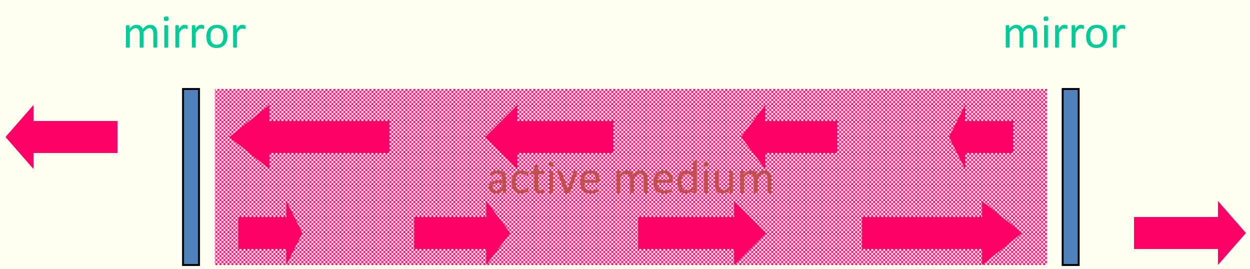
- threshold gain: $$\gamma_{th} = \alpha - \frac{1}{2L}\ln r^2$$ if $$kL = m\pi$$

- standing wave & coherent emission

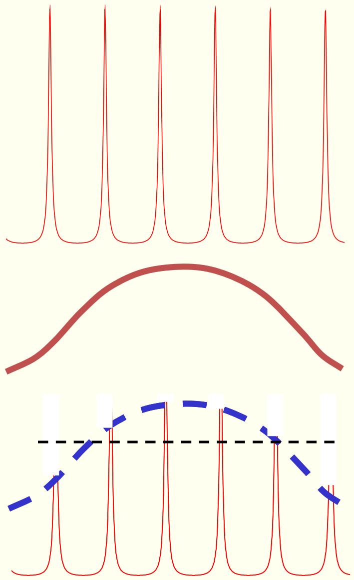
Lasing: cavity effects

- emission rate: $\gamma = \gamma_o \rho(\omega)$

Fermi's Golden Rule



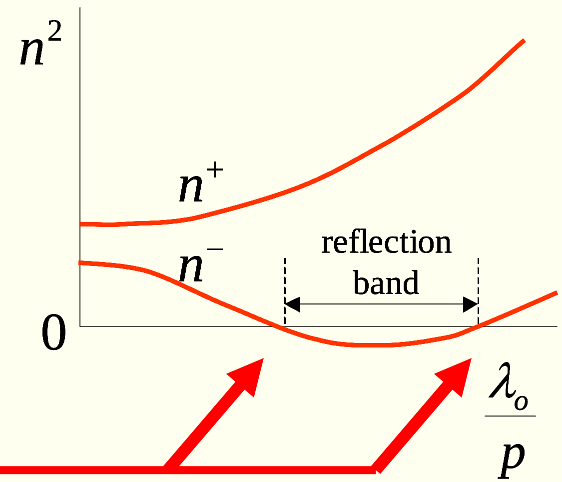
- density of states: $\rho(\omega) = \dfrac{dk}{d\omega}$
- bare emission rate: γ_o
- emission rate: $\gamma = \gamma_o \rho(\omega)$



DOS in bulk cholesterics

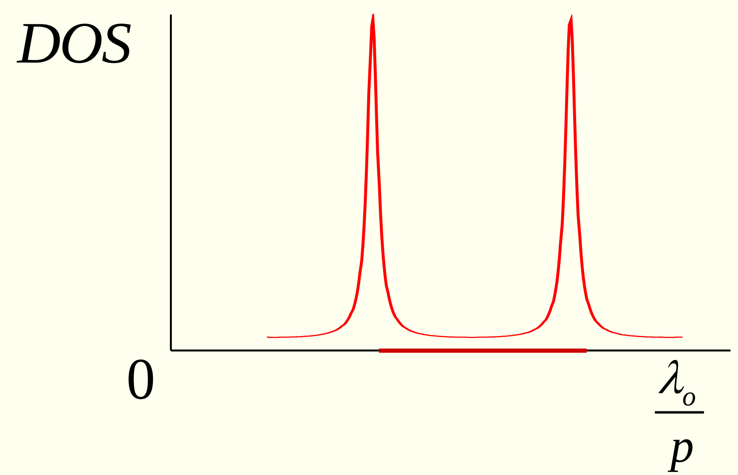
- infinite sample:

$$\rho(\omega) = \frac{dk}{d\omega} = \frac{k}{\omega} - \frac{\pi}{\omega n}\frac{dn^2}{d\lambda_o}$$



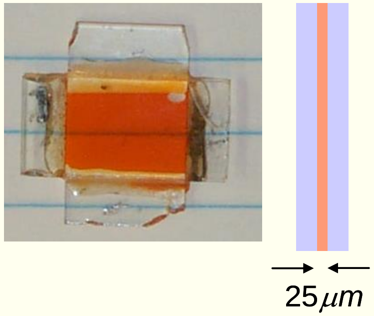
- density of states diverges

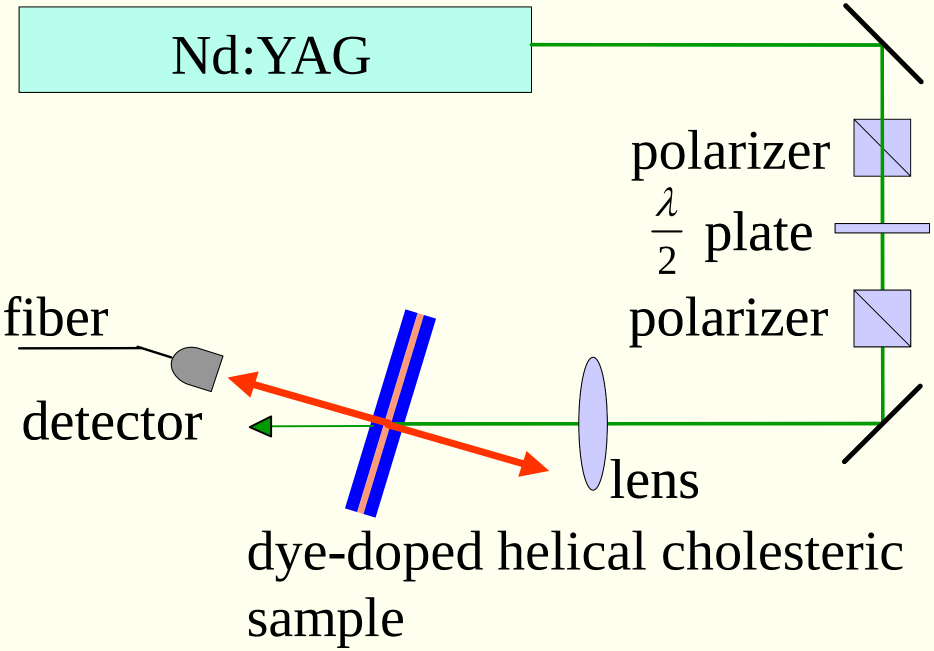
- expect ~thresholdless lasing at band edges!



Liquid crystal DFB lasers

- Experimental setup:





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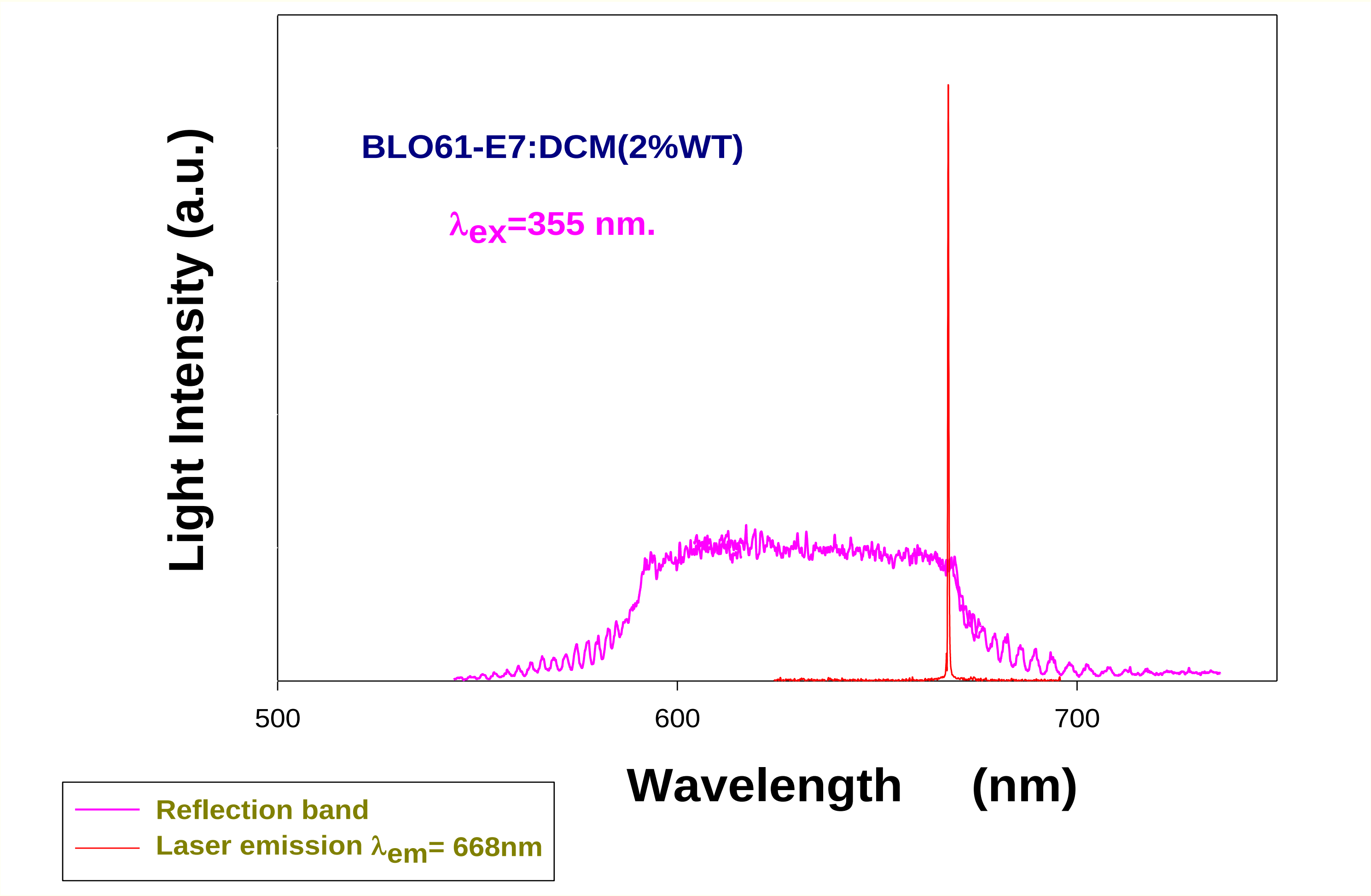
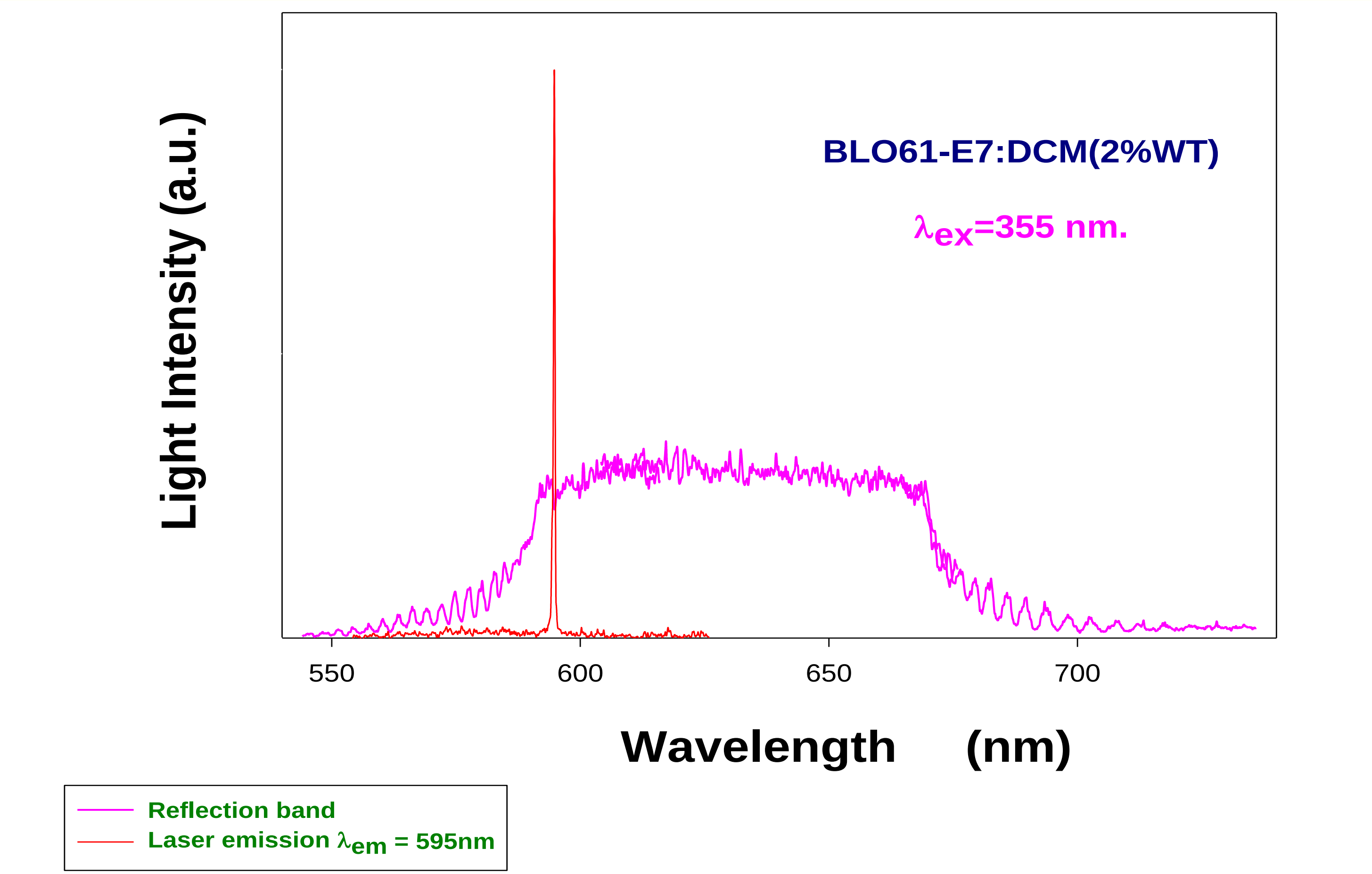
Lasing at the low energy band edge

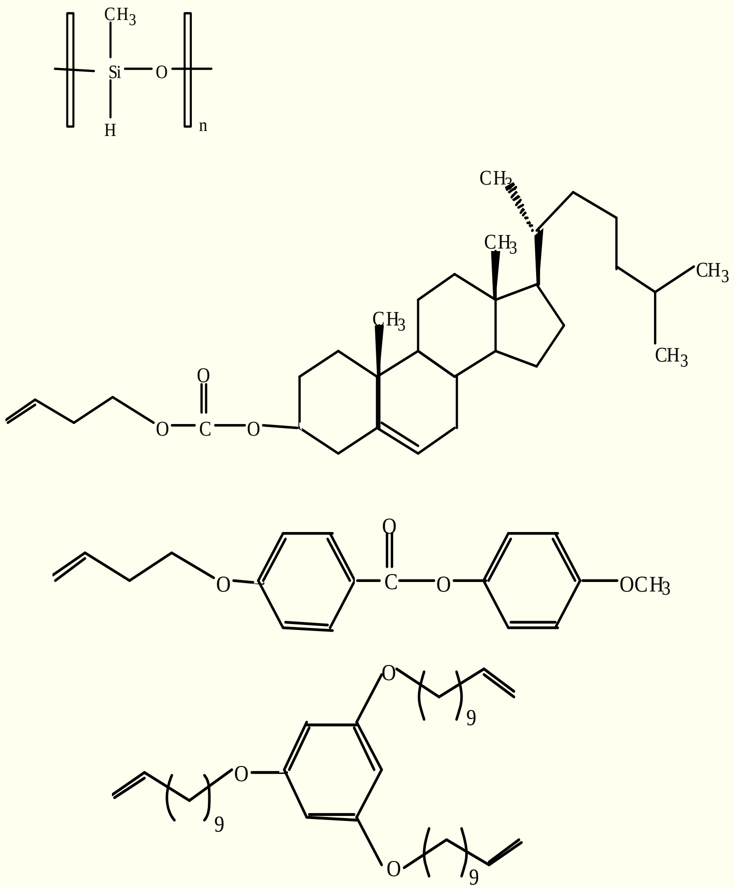


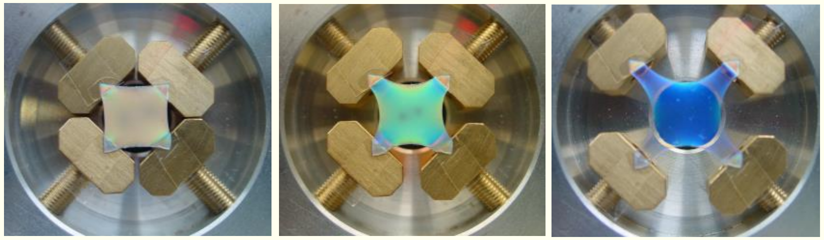
Lasing at the high energy band edge



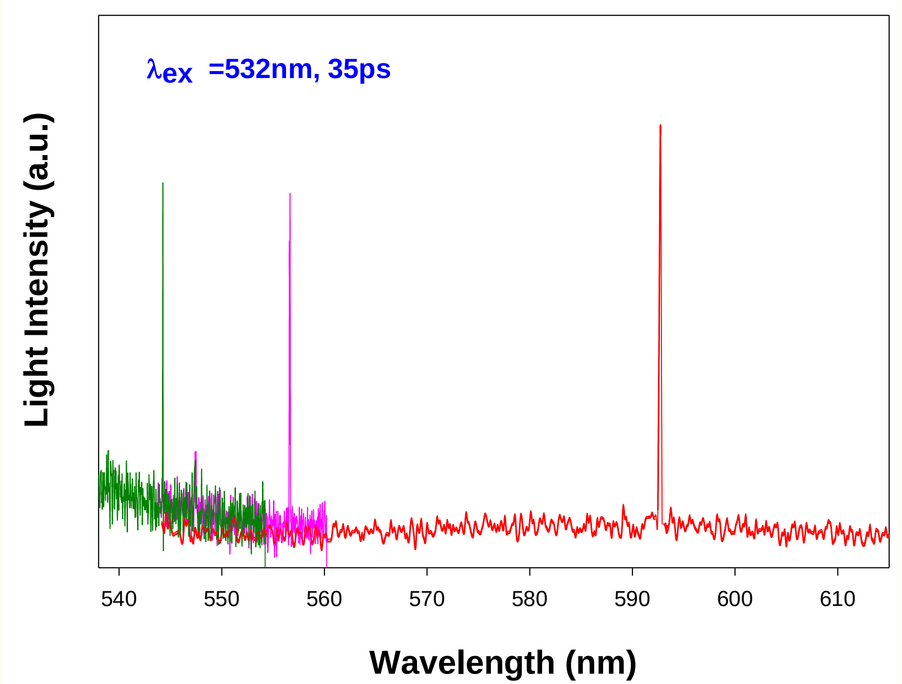
B. Taheri, A.F. Munoz, P. Palffy-Muhoray, R. Twieg, *Mol.Cryst. Liq. Cryst.* . **358,** 73, 2001

Mechanically tunable cholesteric elastomer laser



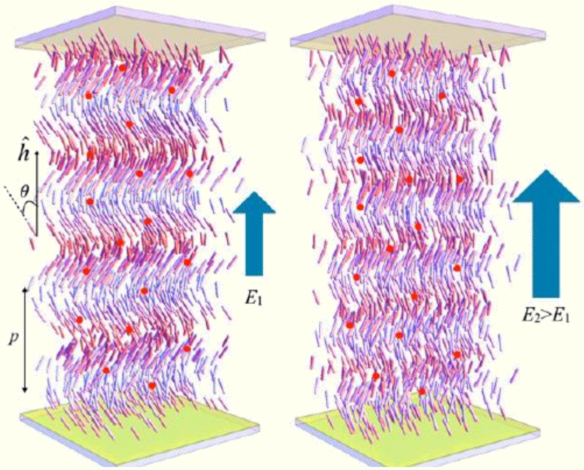


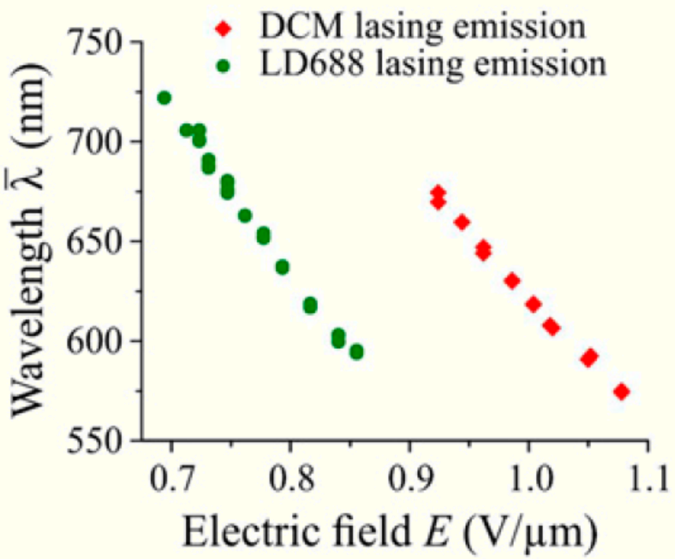
tunable rubber laser!

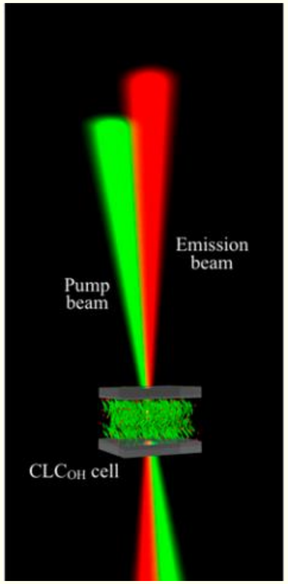


H. Finkelmann, S-T. Kim, A. Munoz, P. Palffy-Muhoray and B. Taheri, *Adv. Mat.* **13**, 1069 (2001)

Electrically tunable heliconical cholesteric laser







– increasing E-field decreases pitch

J. Xiang, F. Minkowski, D.A. Paterson, J.M.D. Storey, C.T. Imrie, O.D. Lavrentovich, P. P-M, PNAS **113,** 12925 (2016)

V. Nonlinear Optics

Second Harmonic Generation

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Second harmonic generation by LCs

- $U(x)$ seen by electron cannot be even; need $k_2 \neq 0$
- inversion symmetry must be broken:
  - DC electric field $\mathbf{E}$
    - electric field induced second harmonic: EFISH
  - surface normal $\hat{\mathbf{N}}$
    - surface second harmonic generation
  - more generally $\nabla \cdot \varepsilon$
    - variety of ways

Second harmonic generation

- in liquid crystals, $\varepsilon = \varepsilon_{\perp}\mathbf{I} + (\varepsilon_{\parallel} - \varepsilon_{\perp})\hat{\mathbf{n}}\hat{\mathbf{n}}$, and
  - splay $\hat{\mathbf{n}}(\nabla \cdot \hat{\mathbf{n}})$
  - bend $\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}})$

flexo-electricity

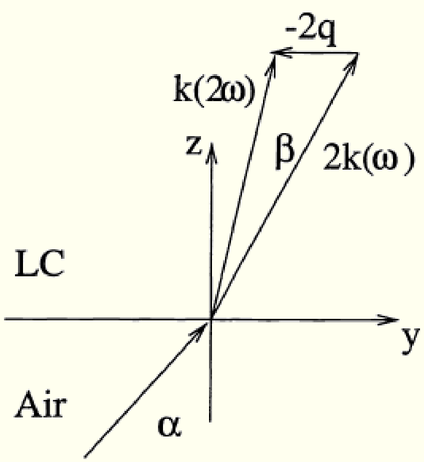
  - order parameter gradients $\nabla \cdot Q$

order-electricity

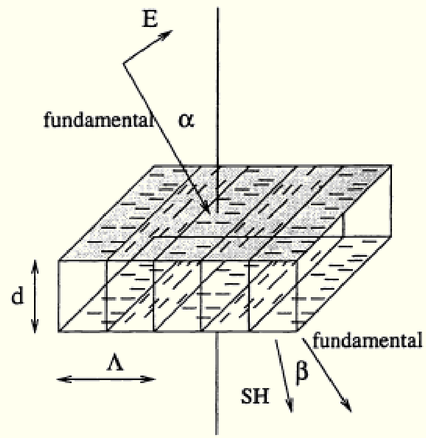
- break the symmetry.
- SHG can probe director field/order parameter structure

Second harmonic generation

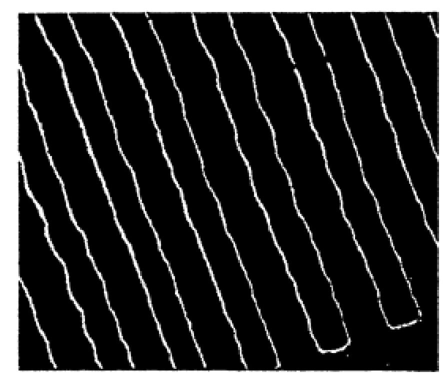
- periodic director field



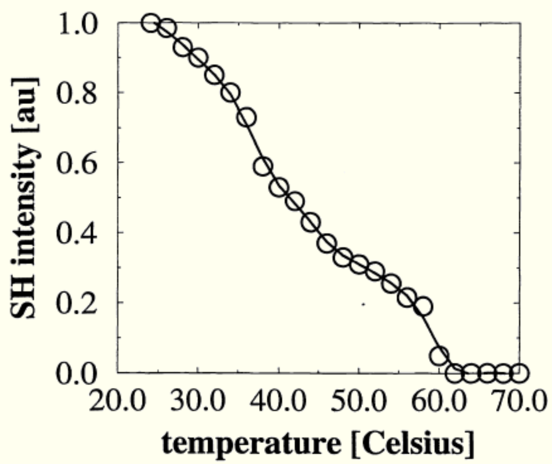
phase matching condition
probes structure



E7, optically buffed
40 μm thick,
25 μm strips



micrograph of sample

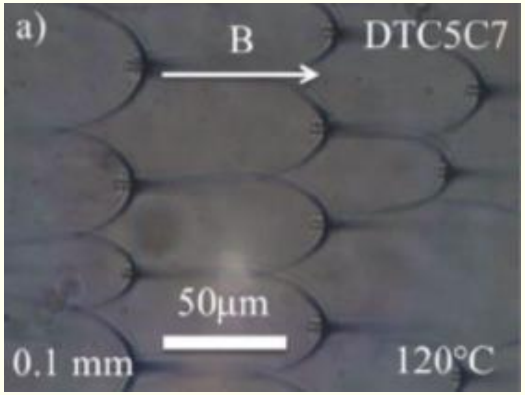


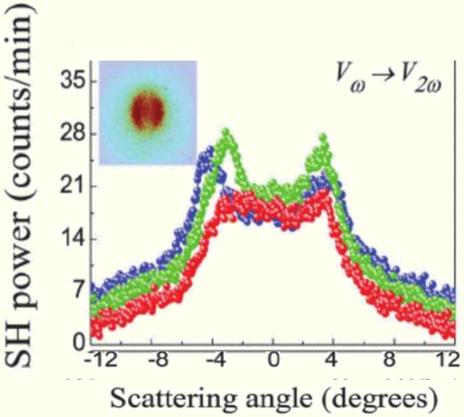
- SHG can probe order parameter field gradients

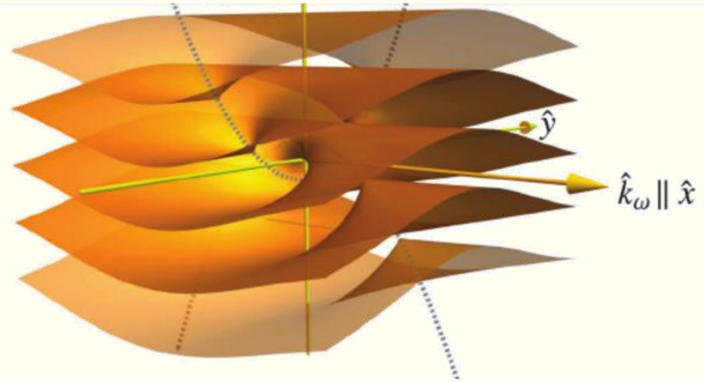
K.M. Hsia, T. Kosa and P.P-M, *SPIE* Vol. **3015**, 32 (1997)

Second harmonic generation

- parabolic focal conic defects in nematic twist-bend phase







- SHG can unravel details of defect structure

S. A. Pardaev, S. M. Shamid, M. G. Tamba,.C. Welch, G. H. Mehl, J. T. Gleeson, D. W. Allender, J. V. Selinger, B. Ellman, A. Jakli, S. Sprunt. *Soft Matter*, **12,** 4472 (2016)

VI. Light governing matter

Light induced forces and torques

- Minkowski stress tensor:

$$T = \mathbf{ED} + \mathbf{HB} - \frac{1}{2}(\mathbf{E}\cdot\mathbf{D} + \mathbf{H}\cdot\mathbf{B})\mathbf{I}$$

  - force:

$$\mathbf{F} = \int T \cdot d\mathbf{A}$$

  - torque density:

$$\boldsymbol{\tau} = \frac{3}{4\pi}\int (\hat{\mathbf{r}} \times T \cdot \hat{\mathbf{r}}) d^2\hat{\mathbf{r}}$$

- Einstein-Laub torque density:

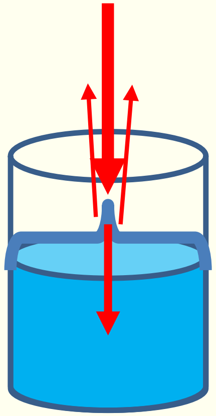
$$\boldsymbol{\tau} = \mathbf{D}\times\mathbf{E} + \mathbf{B}\times\mathbf{H}$$

VI. Light governing matter:

Light induced forces

Light induced forces

- light exerts outward force on liquid surface



  - reflected light pushes down $P_r = -\frac{I}{h\nu} R \frac{2h}{\lambda_0}$
  - reflection coeff. $R = \frac{(n-1)^2}{(n+1)^2}$
  - transmitted light pushes up $P_t = \frac{I}{h\nu}(1-R)(\frac{nh}{\lambda_0} - \frac{h}{\lambda_0})$
  - net pressure $P = 2\frac{I}{c}(n-1)$

- effect small; similar for water and nematics $H \approx 10nm.$

N.G.C. Astrath, L.C. Malacarne, M.L. Baesso, G.V.B. Lukasievicz, S.E. Bialkowski, *Nature Communications* **5**, 4363 (2014)

Ashkin, A. & Dziedzic, J. M. Radiation pressure on a free liquid surface. Phys. Rev. Lett. 30, 139–142 (1973).

VI. Light governing matter:

Light induced torques

Optical Freedericksz transition

- Freedericksz transition:
  - configurational transition in nematic cell due to $\mathbf{E}$ or $\mathbf{H}$ field

  - threshold field: $E_c = \dfrac{\pi}{d}\sqrt{\dfrac{K_1}{\varepsilon_0 \Delta\varepsilon}}$
  - net torque on plates is zero.

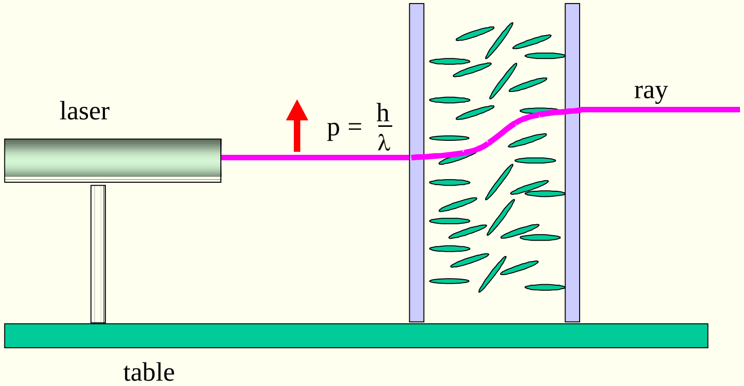
- Question: can light create such a transition?

V. K. Freedericksz and V. Zolina, Trans. Faraday Soc. **29**, 919 (1933).

B.Ya. Zel'dovich, N.F. Pilipetskii, A.V. Sukhov, N.V. Tabiryan, *Pis'ma Eksp. Teor. Fiz.* **31**, 287 (1980)

Optical Freedericksz transition

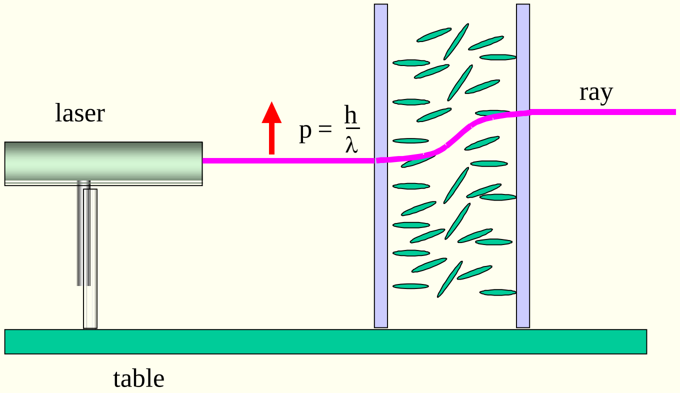
- polarized light can cause transition if intensity is above threshold



- interesting to consider momentum transport

B.Ya. Zel’dovich, N.F. Pilipetskii, A.V. Sukhov, N.V. Tabiryan, *Pis’ma Eksp. Teor. Fiz.* **31**, 287 (1980)

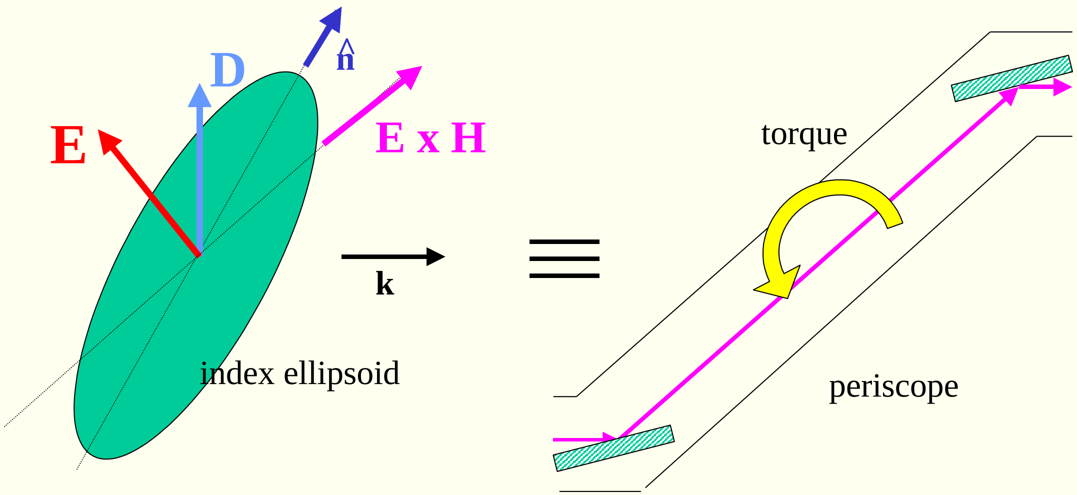
Light induced torques in nematics



$$\boldsymbol{\tau}^{opt} = \mathbf{D} \times \mathbf{E}$$

$$\boldsymbol{\tau}^{opt} + \boldsymbol{\tau}^{el} = 0$$

angular momentum transfer:



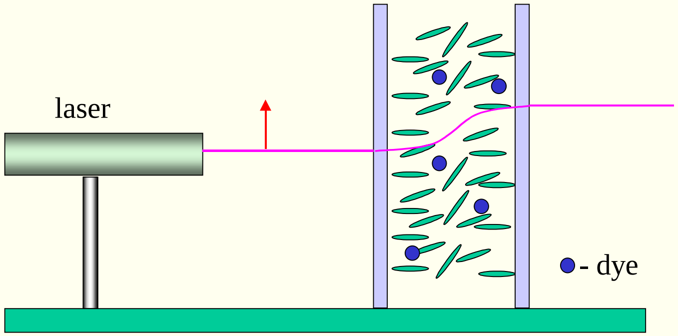
torque results from change in extrinsic angular momentum of light.

Optical Freedericksz transition in nematics is well understood.

Optical torque on nematic+dye: Janossy effect

addition of 1% of anthroquinone dye

$\Rightarrow$ reduction of threshold intensity[1] by ~$\times$100!



without dye: $\tau_{vol}^{el} + \tau_{vol}^{opt} = 0$

with dye: $\tau_{vol}^{el} + \frac{1}{100}\tau_{el}^{opt} + ?? = 0$

Torque on nematic causing elastic deformation
CANNOT come from light! Source of torque?? (A. Saupe)

1, I. Janossy, A.DD. Lloyd and B.S. Wherret, *Mol. Cryst.Liq. Cryst*. **179**, 1, 1990.
I. Janossy, *Phys. Rev. E* **49**, 2957, 1994.

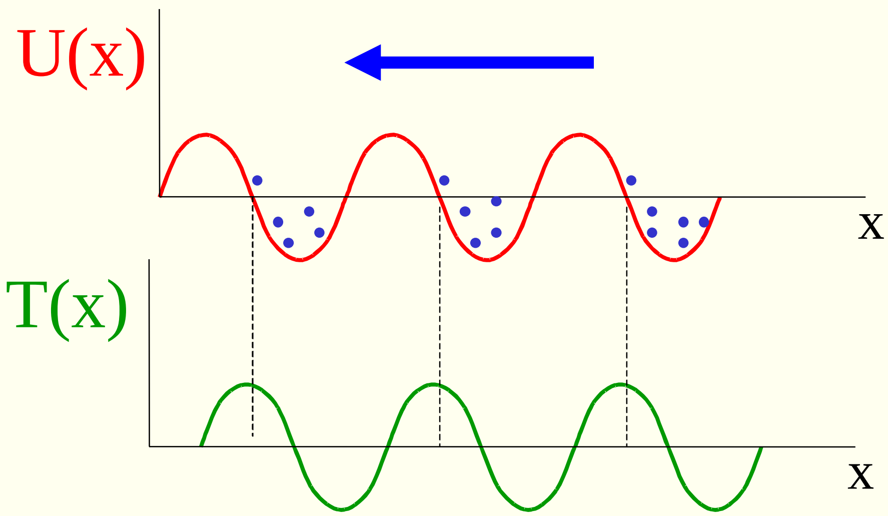
the Puzzle:

- light causes the director to reorient, against a restoring elastic torque, essentially without the transfer of angular momentum.

- light causes rotation without exerting a torque!

diversion

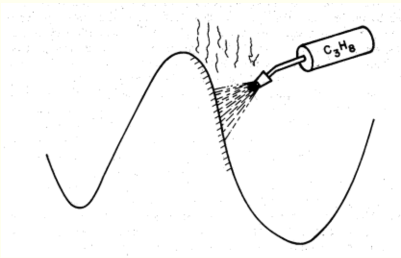
Landauer's Blowtorch*:



particles in periodic potential & temperature field

particles near sides with negative slope are more likely to be excited & diffuse over barrier

∴ net current flows to the left!

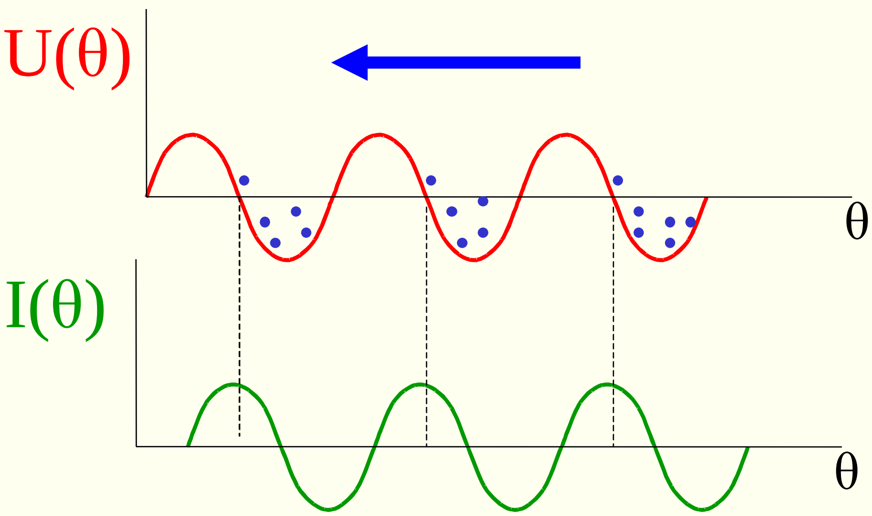


⇒ heat source drives current without transfer of momentum.

* R. Landauer, *J. Stat. Phys*. **53**, 233 (1988)

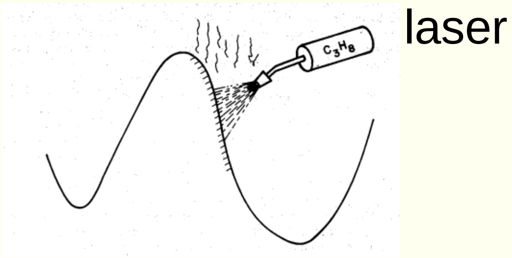
diversion

Landauer's Blowtorch*



dye in nematic potential
& temperature field

particles near sides with negative slope are more likely to be excited & diffuse over barrier

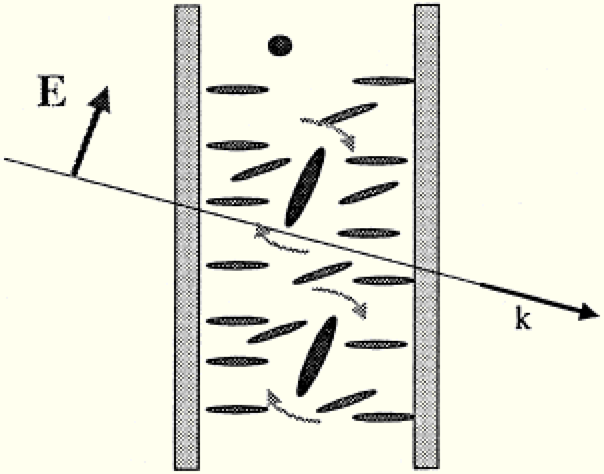


∴ net current flows to the left!

⇒ laser drives orientational current without transfer of momentum.

* R. Landauer, *J. Stat. Phys*. **53**, 233 (1988)

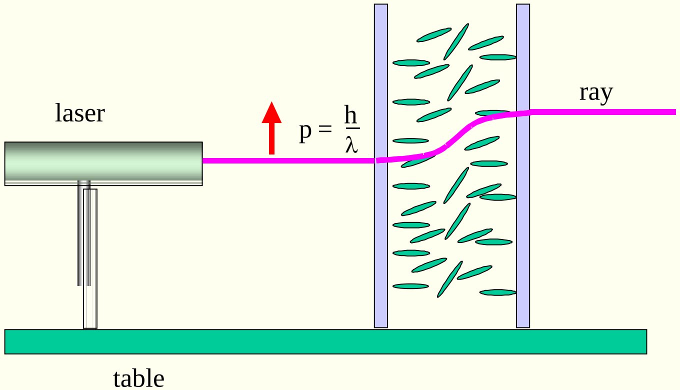
Orientational ratchet



- dye & nematic ⇒ molecular motor
- dye is rotor in field of nematic
- torque on nematic is proportional to orientational dye current
- shear carries angular momentum to cell walls
- large optical nonlinearity
- light provides energy *but not momentum* to drive molecular motor

T. Kosa, Weinan E and P. Palffy-Muhoray, *Int. J. Eng. Sci*. **38**, 1077 2000
M. Kreuzer, L, Marrucci and D. Paparo, *J.Nonlin.Opt.Phys.* **9**, 157, 2000.

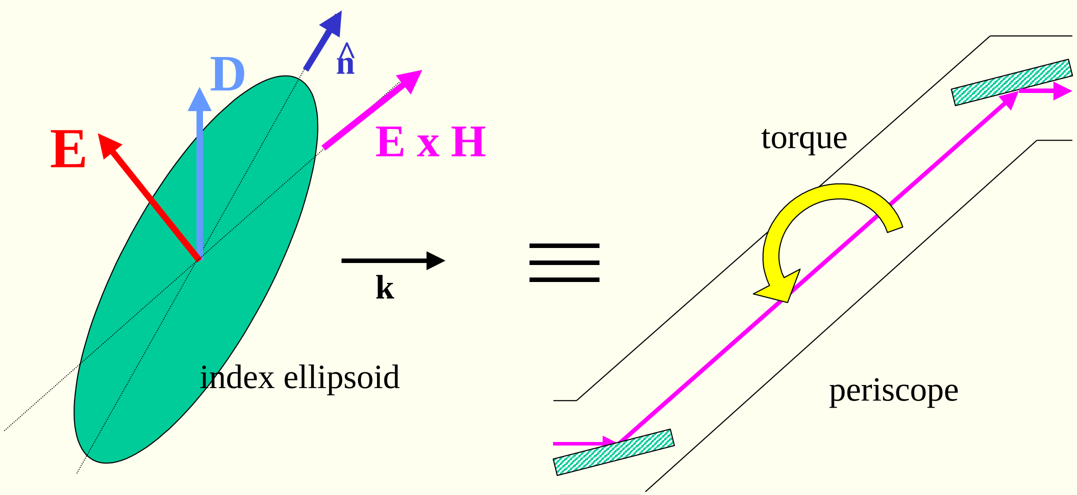
Light induced torques in nematics



$$\boldsymbol{\tau}^{opt} = \mathbf{D} \times \mathbf{E}$$

$$\boldsymbol{\tau}^{opt} + \boldsymbol{\tau}^{el} = 0$$

angular momentum transfer:



torque results from change in extrinsic angular momentum of light.

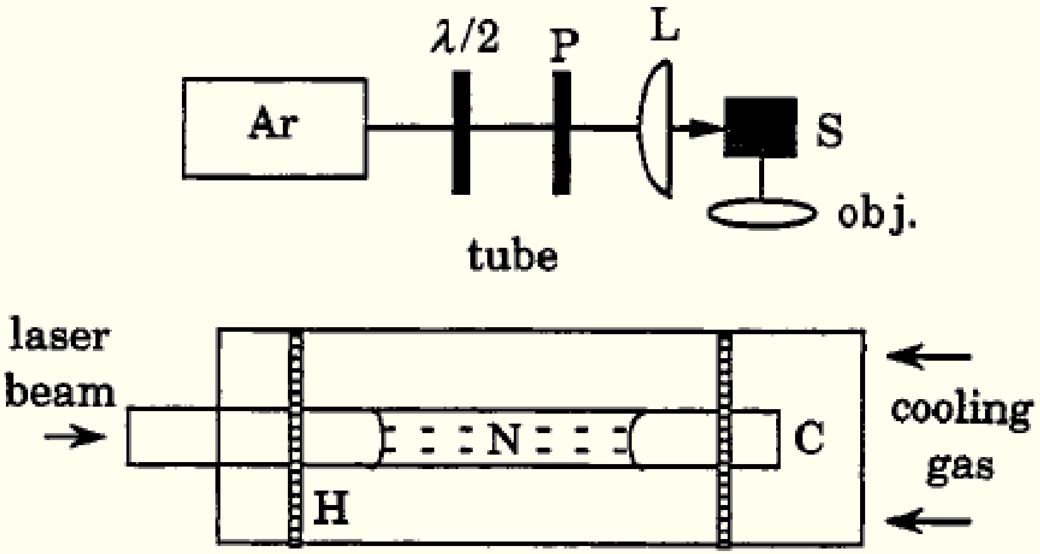
Optical Freedericksz transition in nematics is well understood.

VI. Light governing matter

Nonlinear propagation

Nonlinear propagation of light

- simple & beautiful experiment:

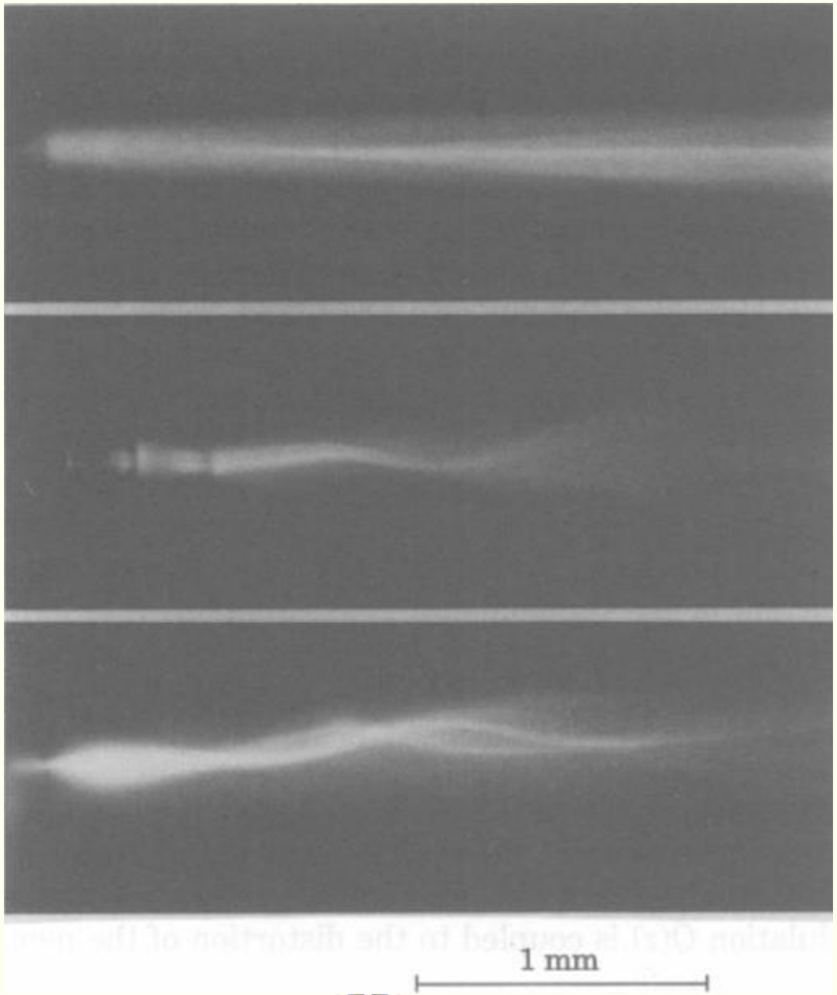


  - polarized light traverses a capillary with nematic
    - alignment is parallel to walls

E. Braun, L. P. Faucheu, A . Libchaber, D. W. McLaughlin, D. J. Muraki, M. J. Shelley, *Europhys. Lett.* **23, 239 (1993)**

Nonlinear propagation of light

- observe filamentation and undulation of self-focused laser beams

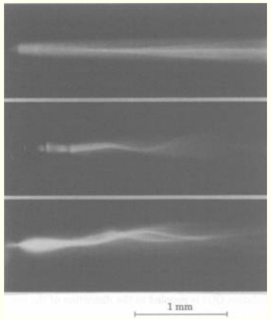


$0.84 kW / cm^2$

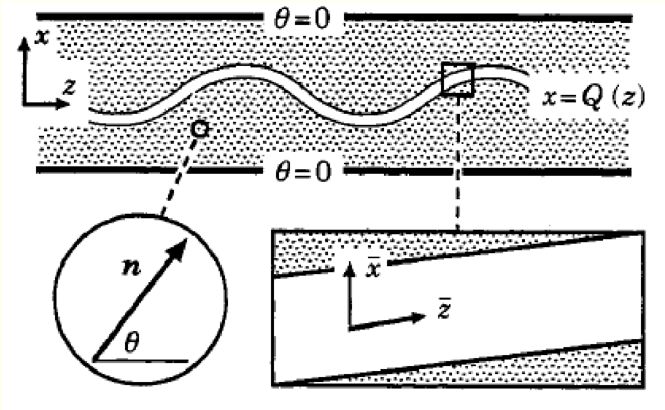
$1.87 kW / cm^2$

$3.36 kW / cm^2$

Nonlinear propagation of light



- simple model
  - inner equation: models filamented structure
  - outer problem: describes large-scale beam-nematic interaction



- describes self-focusing, self-trapping of light and beam undulation

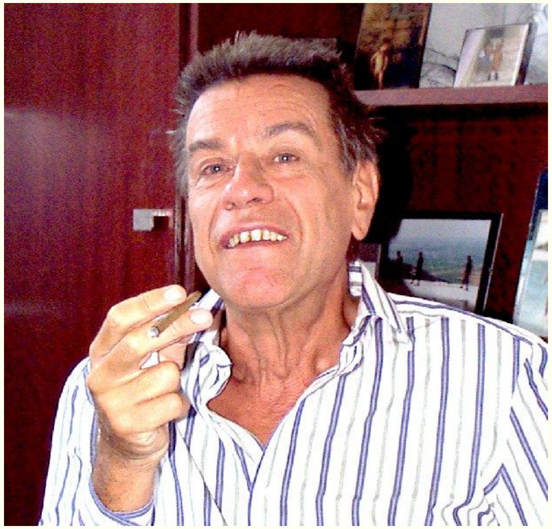
VI. Light governing matter

Solid liquid crystals and Light driven motors

KENT STATE
Liquid Crystal Institute

Liquid Crystal Elastomers

- anisotropic rubbers
  with combined features of



P.G. de Gennes, 1932-2007

LIQUID CRYSTALS

&

ELASTIC SOLIDS

H. Finkelmann

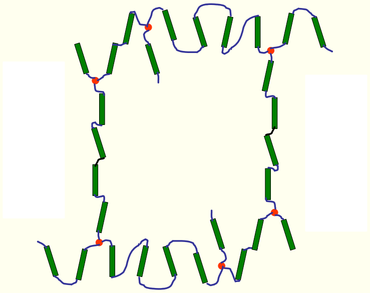
proposed by de Gennes

produced by Finkelmann

P.G. de Gennes, *C.R. Seances Acad.Sci.***218**, 725 (1975)

H. Finkelmann, H.J. Kock, G. Rehage, *Makromol. Chem.*, Rapid Commun. **2**, 317 (1981)

Liquid Crystal Elastomer



- free energy density*:

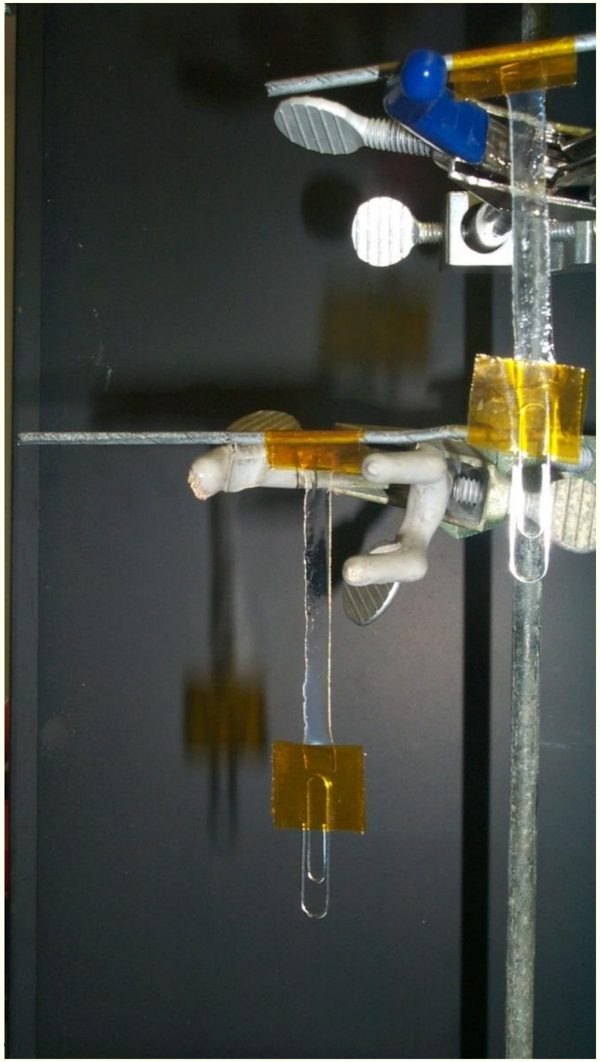
$$\mathcal{F} = \frac{1}{2} A\mathbf{Q}^2 + .. - \frac{1}{2}\Delta\varepsilon'\mathbf{QEE} - \gamma\mathbf{Qe} + \frac{1}{2}Y\mathbf{e}^2 - \boldsymbol{\sigma}^{ext}\mathbf{e}$$

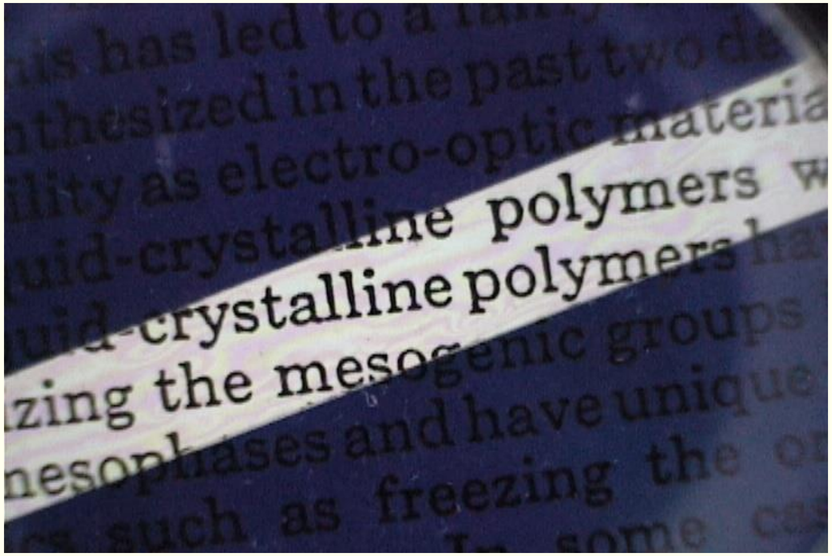
- sum of free energies of liquid crystal + elastic solid, *plus* new coupling term $\mathbf{Qe}$

- effect of strain on LC order is same as external field
- effect of LC order on strain is same as external stress

*P.G. de Gennes, *C.R. Seances Acad.Sci.* **218**, 725 (1975)

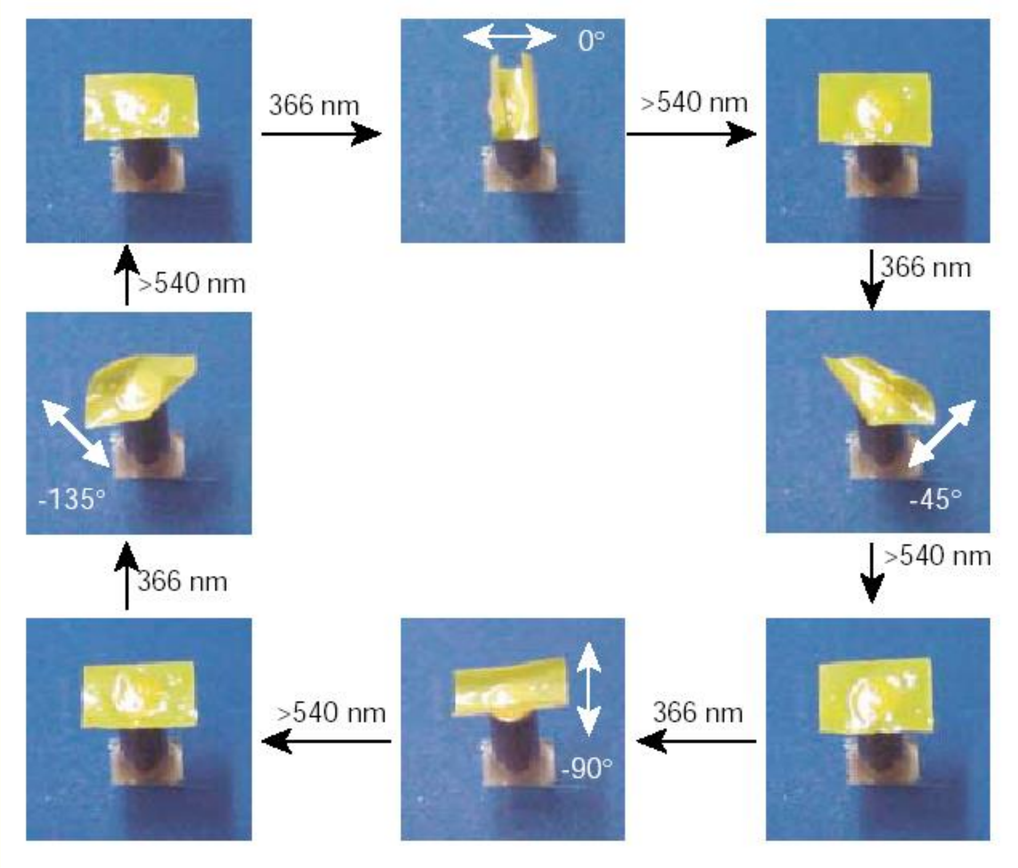
Appearance of nematic LCE samples





birefringent sample between crossed polarizers

Experimental Results (Ikeda et al.)



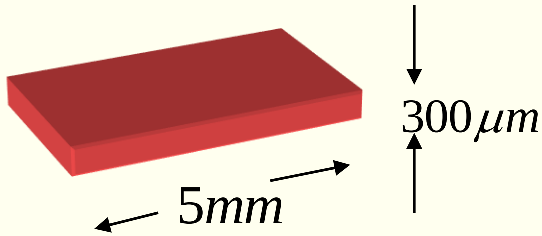
LC + diacrylate network
+ functionalized
azo-chromophore

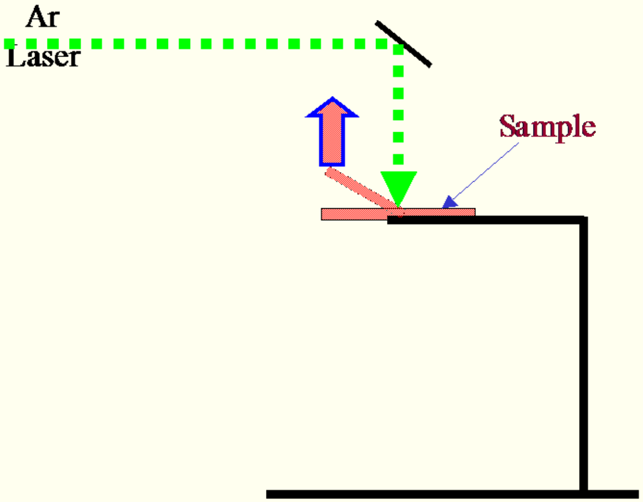
timescale: 10 s

Yanlei Yu, Makoto Nakano, Tomiki Ikeda, *Nature* **425**, 125 (2003)

Photoinduced Bending

sample: nematic elastomer EC4OCH3
+ 0.1% dissolved
Disperse Orange 1 azo dye



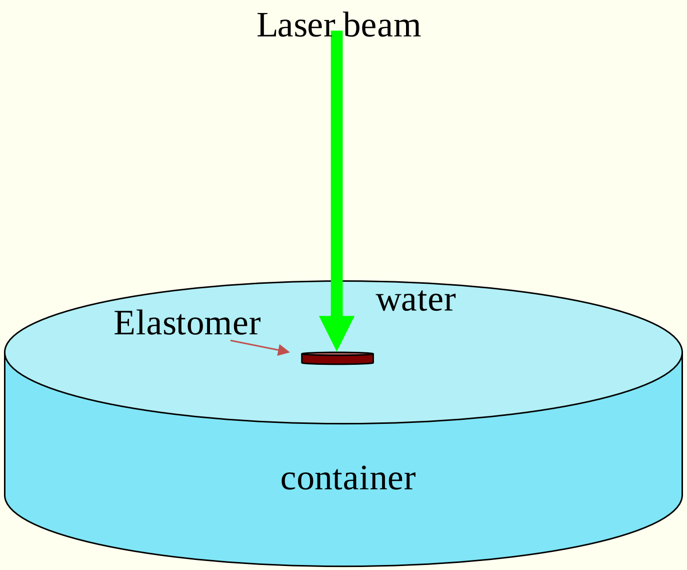


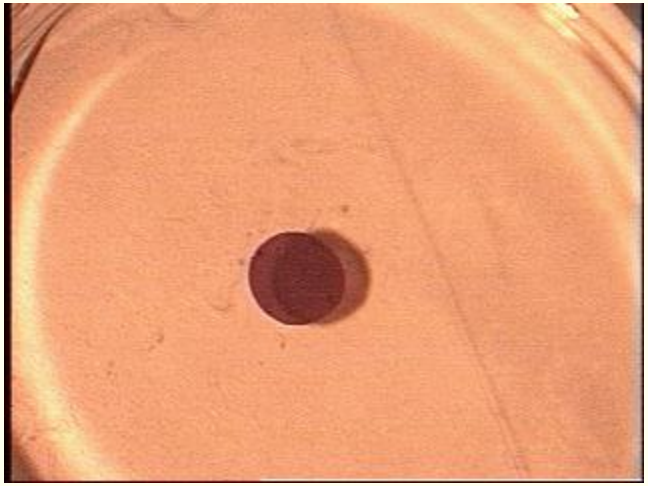
Response time: 70ms

M. Chamacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nature Mat.* **3**, 307, (2004)

Swimming away from the light

- floating nematic LCE sample illuminated from above





M. Chamacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nature Mat.* **3**, 307, (2004)

Rotary motor: light driven

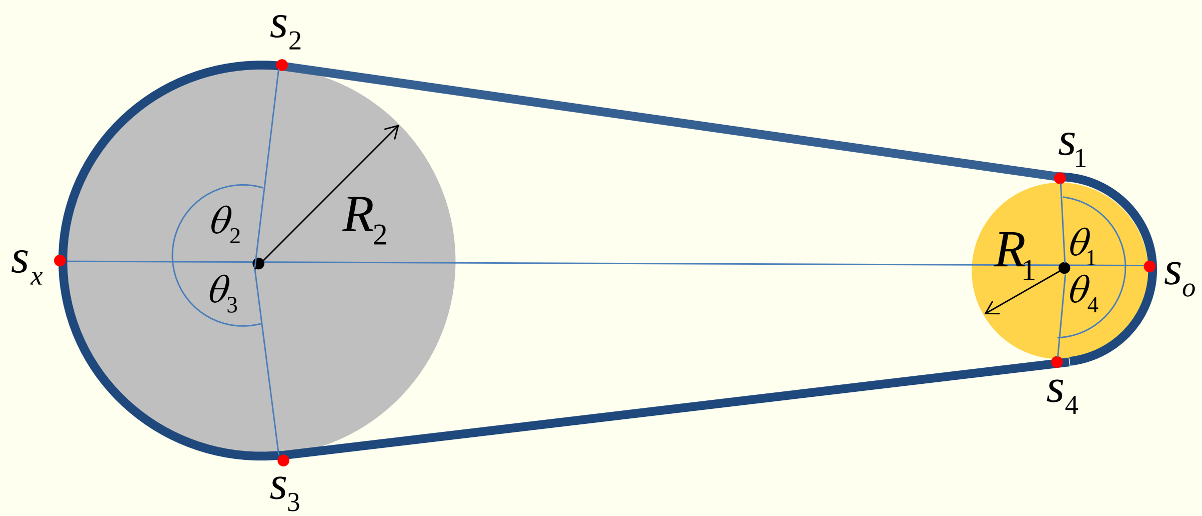
M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. Barrett, T. Ikeda, *Angew. Chem.* **47**, 4986 (2008)

Rotary motor: light driven

key aspect: light changes degree of orientational order Q

M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. Barrett, T. Ikeda,
Angew. Chem. **47**, 4986 (2008)

Model



– bend energy density: $$\mathcal{E}_b / l = \frac{1}{2} EI \frac{1}{R^2} = \frac{c}{R^2}$$

stiffness fn. of position

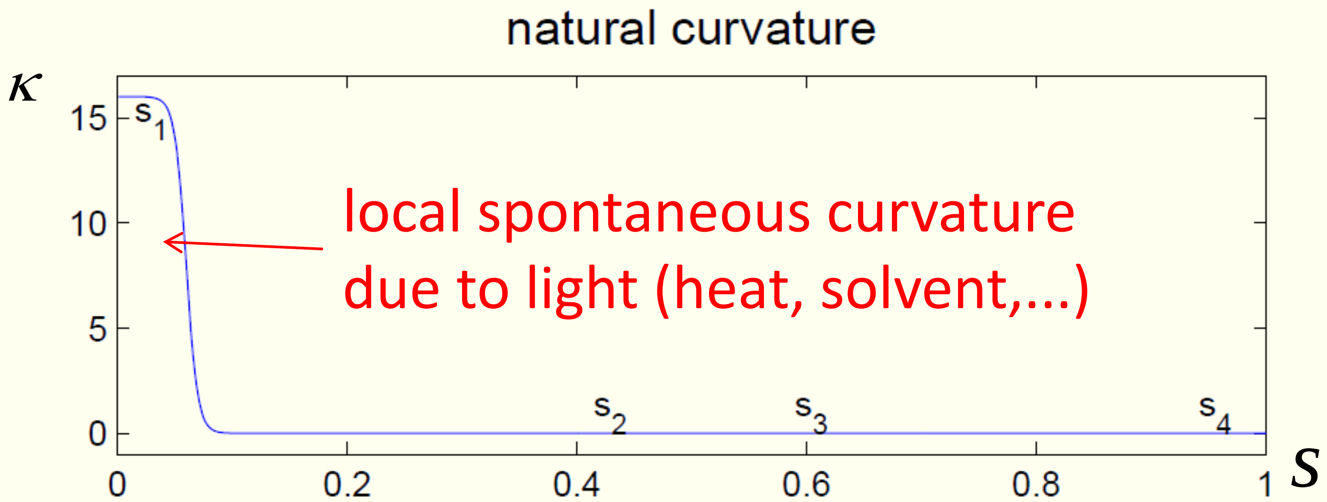
natural curvature fn. of position

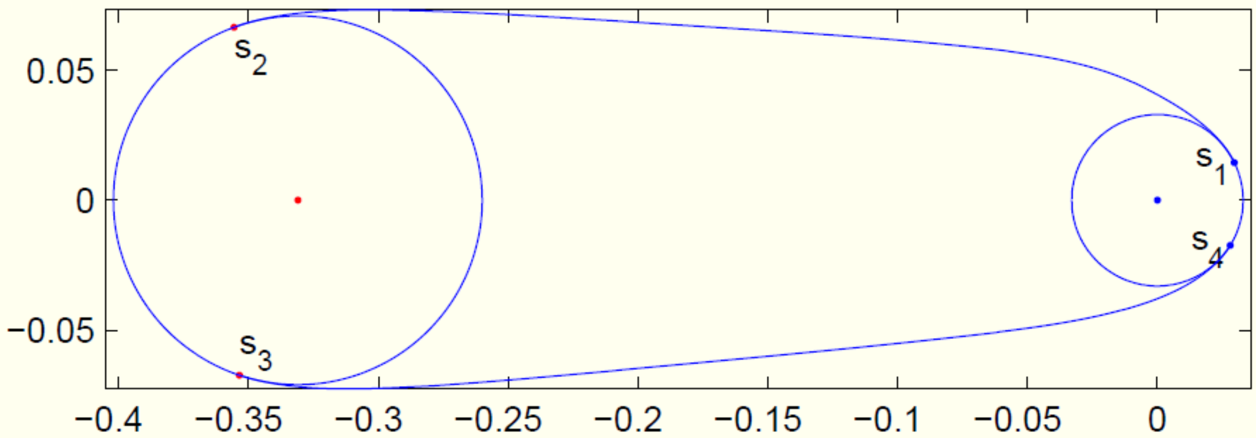
$$\mathcal{E} = \int_{s_o}^{s_1} c(\frac{1}{R_1} - \kappa)^2 ds + \int_{s_1}^{s_2} c(\frac{\partial^2 \mathbf{R}}{\partial s^2} - \kappa(\frac{\partial \mathbf{R}}{\partial s} \times \hat{\mathbf{z}}))^2 ds +$$

$$\int_{s_2}^{s_3} c(\frac{1}{R_2} - \kappa)^2 ds + \int_{s_3}^{s_4} c(\frac{\partial^2 \mathbf{R}}{\partial s^2} - \kappa(\frac{\partial \mathbf{R}}{\partial s} \times \hat{\mathbf{z}})^2 ds + \int_{s_4}^{s_o} c(\frac{1}{R_1} - \kappa)^2 ds,$$

+constraints

Numerical solution: energy minimization

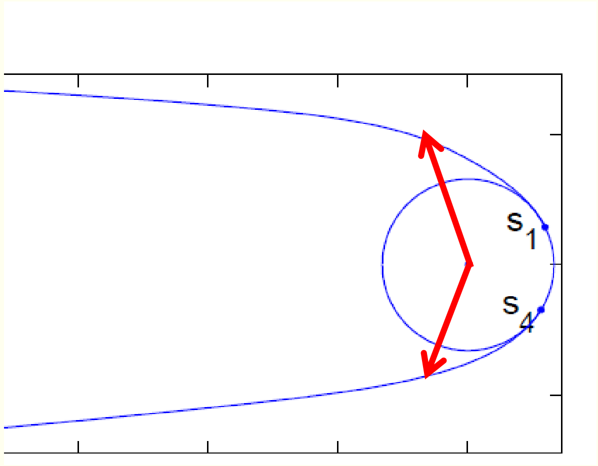




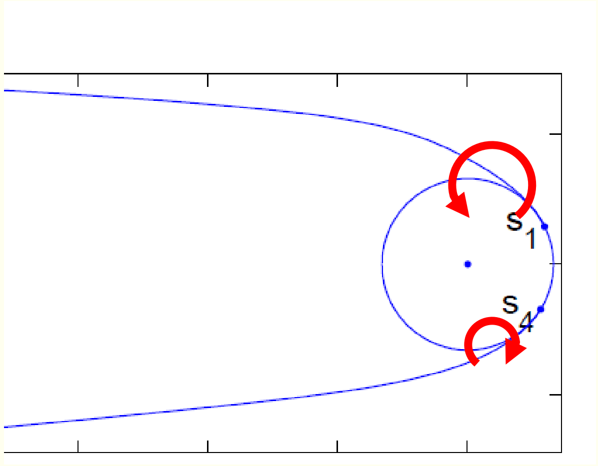
X. Zheng, P.P-M. unpublished

How does rotation come about?

- away from the small wheel,
  - longer lever arm on one side

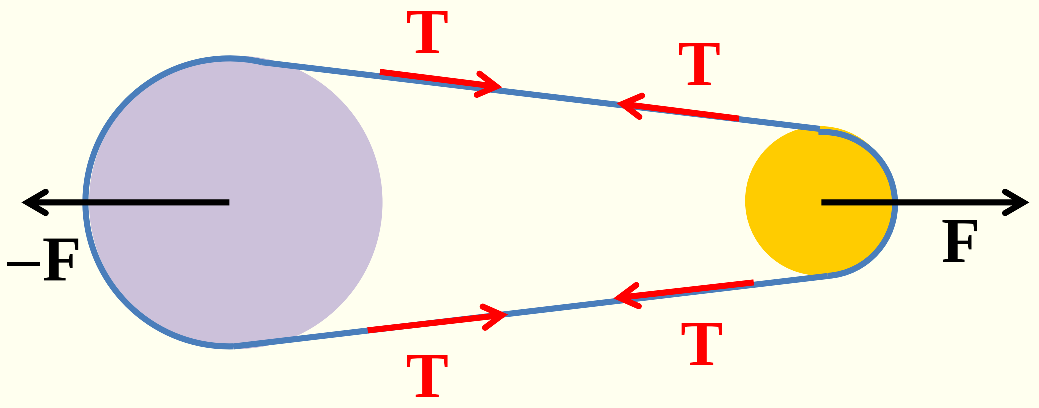


- near small wheel
  - greater point torque on one side
    - curvature is the same, but have spontaneous curvature on one side



Angular momentum current

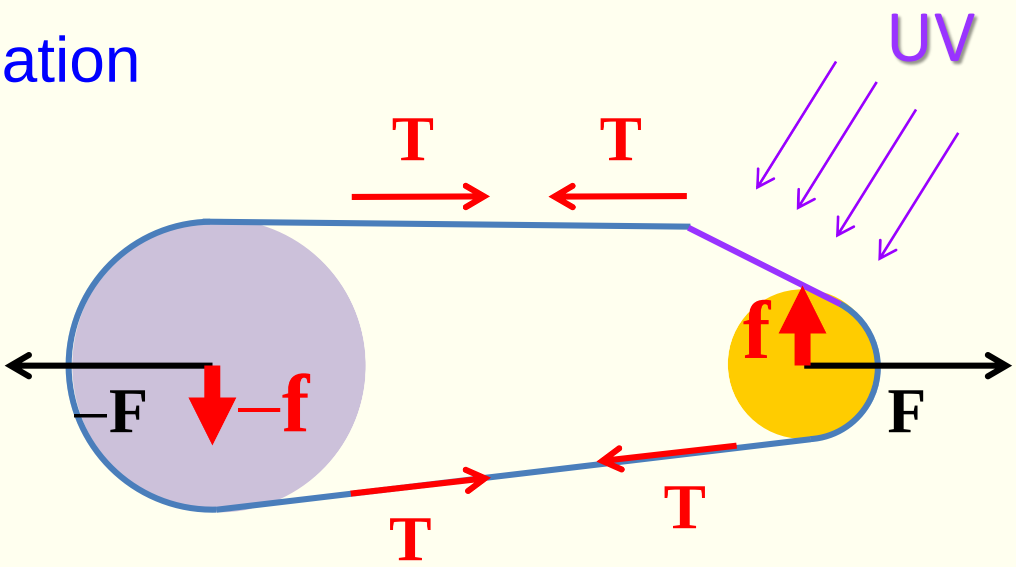
- before irradiation



  – **F** and **F** are forces provided by supports

Angular momentum current

- on UV irradiation



  - F, -F, f and -f are forces provided by supports
  - angular momentum flows in from outside to start

- light provides energy *but not momentum* to drive macroscopic motor

VI
Summary

Summary

- LCs are SOFT
  - director deformations are Goldstone modes
- LC anisotropy can guide light
- controlling director field enables light control
  - LCDs, tunable lenses, gratings, etc.
- material response is non-local
  - chirality

Summary

- periodic structures are photonic bandgaps
  - cholesteric lasers, mirrors, polarizers
- NLO response is HUGE due to coupling to soft modes
  - $10^6 - 10^{10}$ times conventional materials (but slow)
- mechanisms via momentum or energy transfer

The softness and anisotropy of liquid crystals enriches light matter interactions.