Liquid Crystals:

*Basics*

**Phases**

**Nematic:** parallel ordering of rodlike (or plate-like) molecules.

Order parameter: \( S \) is a second rank tensor

\[ l_2 \equiv S = \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle \]

\( \hat{n} \) = "director" \( (\hat{n} \leftrightarrow -\hat{n}) \)

Nematic ground state: \( \hat{n} \) uniform in space.

Low energy deformations: \( S \) constant, \( \hat{n}(r) \) varying.

**Smaric:** 1D periodic, 2D fluid, layers of molecules.

Sm\( A \)

Sm\( C \)

Sm\( C \) ground state: \( \hat{c} \) uniform in space; layers flat.

Low energy deformations: We will consider only flat layers, and \( c(r) \) varying. "Almost" a 2D nematic, but \( \hat{c} \leftrightarrow -\hat{c} \), for a thin film of Sm\( C \).
Molecules & source of ordering.

Nematic:

- Rod-like shape. Studies with colloidal phases which involve only repulsive excluded volume effects show that packing alone can result in a nematic. This is due to maximizing entropy, relative to the isotropic phase at the same density. (Onsager)

- Typical molecule:

  \[
  \text{Pentyl-cyano-biphenyl}
  \]

- Anisotropic molecular interactions play a role too.

Smectic:

- Cylindrical shape, as opposed to "cigar"

  \[
  \text{Smectic} \quad \Downarrow \quad \text{Smectic}
  \]

- Layers allow the best use of volume for fluctuations in plane.

Nematic-like fluctuations cost free volume (\(\downarrow\)), while good layering again maximizes entropy!

- Molecules with dissimilar parts make layers to "separate" parts. [Pentyl-cyano-biphenyl is a smectic.]

- Extreme example: Block co-polymers of incompatible components.
Nematic Elasticity (Curvature elasticity)

Expand \( \hat{\mathbf{n}}(\mathbf{r}) \) in a Taylor series, with a local coordinate system, \( \hat{\mathbf{n}}_0 = \hat{\mathbf{e}} \). Thus \( \hat{\mathbf{n}} = \hat{\mathbf{n}}_0 + \delta_{nx} \hat{\mathbf{x}} + \delta_{ny} \hat{\mathbf{y}} \), \( (\delta_{nx} = 0 \text{ since } \hat{\mathbf{n}} \text{ is a unit vector}) \)

\[
\hat{\mathbf{n}}(\mathbf{r}) = \hat{\mathbf{n}}_0 + x\left( \frac{\partial u_x}{\partial x} \hat{\mathbf{x}} + \frac{\partial u_y}{\partial y} \right) + y\left( \frac{\partial u_x}{\partial y} \hat{\mathbf{x}} + \frac{\partial u_y}{\partial y} \hat{\mathbf{y}} \right) + z\left( \frac{\partial u_x}{\partial z} \hat{\mathbf{x}} + \frac{\partial u_y}{\partial z} \hat{\mathbf{y}} \right)
\]

Construct free energy from strains: following symmetry
1) rotation about \( \hat{\mathbf{n}}_0 \)
2) reflections I and II to \( \hat{\mathbf{n}}_0 \), center of inversion (\( \hat{\mathbf{n}} \leftrightarrow -\hat{\mathbf{n}} \))
And, for bulk energy, eliminate terms of the form \( \nabla \cdot \mathbf{u} \), where \( \mathbf{u} \) is a vector field, since these can be integrated to surface terms.
This leaves only 3 terms in the free energy density:

\[
f = \frac{1}{2} K_{11} \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right)^2 + \frac{1}{2} K_{22} \left( \frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x} \right)^2 + \frac{1}{2} K_{33} \left( \frac{\partial u_x}{\partial z} + \frac{\partial u_y}{\partial z} \right)^2
\]

\[
f = \frac{1}{2} K_{11} (\hat{\mathbf{n}} \cdot \nabla \cdot \hat{\mathbf{n}})^2 + \frac{1}{2} K_{22} (\nabla \cdot \hat{\mathbf{n}})^2 + \frac{1}{2} K_{33} (\hat{\mathbf{n}} \cdot \nabla \times \hat{\mathbf{n}})^2
\]

\[
(\hat{\mathbf{n}} \cdot \nabla \cdot \hat{\mathbf{n}})^2 = \left| \hat{\mathbf{n}} \cdot (\nabla \cdot \hat{\mathbf{n}}) \right|^2 \quad \text{tension} \quad \tau^* \quad (\hat{\mathbf{n}} \times \nabla \times \hat{\mathbf{n}})^2 = \left| \mathbf{B} \right|^2 \quad \text{Bend}
\]

Splay \( \text{I/I} \) \quad \text{twist} \quad \text{Bend}
Thin films of SmC (2D system)

Only splay and bend deformations exist:

\[ f = \frac{1}{2} K_s (\nabla \cdot \hat{e})^2 + \frac{1}{2} K_b (\nabla \times \hat{e})^2 \]

[\( f \) is energy per unit area]

Notice on elastic moduli: \( K_{1i}, K_s, K_b \):

Nematic: Picture extreme curvature:

\[ \frac{\Delta \psi}{\Delta x} \approx \frac{1}{L} \]

with \( L \) = molecular length. This "disorders" the nematic \( \rightarrow \) isotropic. \( \Delta f \approx \Delta K_{NE} \approx 1 \text{kJ/m} \)

\[ \frac{1}{2} K_{1i} \left( \frac{1}{L} \right)^2 = \frac{\text{molecular interaction energy}}{L^3} \]

\[ [K_{1i}] \sim \frac{[\text{energy}]}{[L]} \sim 10^{-12} \text{ J/m} \]

SmC (2D):

\[ K_s, b \sim K_{1i} (\sin^2 \Theta) \tau \]

where \( \Theta = \) tilt angle,
\[ \tau = \text{film thickness} \]

\[ [K_{s, b}] \sim [\text{energy}] \]

Boundary Conditions

Strong Anchoring: Molecules interact at a boundary so that their orientation at the boundary is fixed.

Weak Anchoring: Elastic torques in the interior are strong enough to compete with anchoring.
Boundary Value Problems: nematic

For some volume of nematic, with specified boundary conditions the free energy in the volume is:

$$F = \int dxdydz f(\hat{n}(\vec{r}))$$.

In general, find $\hat{n}(\vec{r})$ that minimises $F$. For any particular problem, choose coordinate system, make assumptions (guesses!) about the form of solution, generate $f$, and use Calculus of Variations to minimise $F$.

**Example:** Planar structures: $\hat{n} \parallel (x, y)$ plane

$$n_x = \cos \Theta, \quad n_y = \sin \Theta, \quad n_z = 0 \quad \text{(clearly } \|n\| = 1\)$$

$$\hat{n} \cdot \hat{n} = -\sin \Theta \frac{\partial \Theta}{\partial x} + \cos \Theta \frac{\partial \Theta}{\partial y}$$

$$\hat{n} \cdot \nabla \hat{n} = -\frac{\partial \Theta}{\partial z}$$

$$\hat{n} \times \nabla \hat{n} = \hat{x} \left( \sin \Theta \cos \Theta \frac{\partial \Theta}{\partial x} + \sin^2 \Theta \frac{\partial \Theta}{\partial y} \right) + \hat{y} \left( -\cos \Theta \frac{\partial \Theta}{\partial x} - \sin \Theta \cos \Theta \frac{\partial \Theta}{\partial y} \right)$$

Assume $K_{11} = K_{22} = K$ then

$$F = \int dxdydz \left[ \frac{1}{2} K \left( \frac{\partial \Theta}{\partial x} \right)^2 + \frac{1}{2} K \left( \frac{\partial \Theta}{\partial y} \right)^2 \right] + \frac{1}{2} K_{22} \left( \frac{\partial \Theta}{\partial z} \right)^2$$

Rescale $z = \sqrt{\frac{K_{22}}{K} \frac{\partial \Theta}{\partial z}}$

$$F = \frac{1}{2} \sqrt{K K_{22}} \int dxdydz (\nabla \Theta)^2 \Rightarrow \text{Euler Lagrange eqn.:} \quad \nabla^2 \Theta = 0 \quad \text{electric field}$$
**Planar Structures**

**Twist layer (1D)**

\[ \Delta^2 \phi = 0 \Rightarrow \frac{\partial^2 \phi}{\partial z^2} = \text{const.} = \frac{\pi}{2d} \]

\[ \phi = \frac{\pi}{2} \uparrow^2 \]

\[ \theta = 0 \]

\[ \text{area} = \int_0^d 2 \pi d z \left( \frac{\pi}{2} \right)^2 = \frac{\pi^2}{8d} k_{22} \]

Curvature distributed evenly minimizes energy

**Disclinations (2D)**  Polar coordinates \((r, \phi)\)

\[ \phi = \frac{\pi}{2} \]

\[ m = \pm \frac{1}{2} \]

\[ \theta_0 = 0 \]

\[ m = \pm 1 \]

\[ \theta_0 = 0 \]

\[ m = \pm 1 \]

\[ \theta_0 = \frac{\pi}{2} \]

\[ m = -1 \]

\[ \theta_0 = 0 \]

\[ \text{Invariant in } z \]

\[ F = \int_0^\text{length} 2 \pi r d r \frac{1}{2} \kappa \left( \frac{m^2}{r} \right) = \pi K' m^2 \ln \frac{R}{\varepsilon} + E_{\text{core}} \]

*Note:* for \( m = \pm \frac{1}{2} \) need "branch cuts" for the vector field \( \hat{\mathbf{d}} \), while physically the nematic is continuous.

There are splay-bend disclinations (no twist involved).
Planar Structures

$\gamma = \frac{1}{2}$ twist disclination in a twist layer. (3D)

$\beta = -\frac{\pi}{2}$

$\beta = \frac{\pi}{2}$

$\delta = 0$

Equilibrium position midway between plates (repelled by identical "image" disclinations)

$$F_{\text{length}} = \frac{\pi K}{L} \left[ \ln \left( \frac{d}{2\pi \varepsilon} \right) + \ln \csc \left( \frac{\pi \varepsilon}{d} \right) \right]$$

$\varepsilon \ll d$

Since $\nabla^2 \theta = 0$ is linear, add any linear function $\beta$, $\gamma$, $\theta$, or a constant to the solution; energy is independent of orientation of line relative to surface directions.

Energy is localized in band of width $\frac{d}{2\pi}$ around the core. The disclination acts like an elastic "string" which shrinks to minimize its length.

- Loops shrink to vanishing under their own tension.
- Pinned lines tend to become straight.

These lines are the "threads" (nema) giving rematrix their name.
3D structures (\( \theta \) no longer planar)

* Point disclinations are possible
* Integer index (\( m=1 \)) disclinations disappear!

"escape" to the third dimension 
"hedgehog" 
"negative hedgehog"

For the cylinder of radius \( r_0 \), assume \( n_1 = \cos \theta \), \( n_2 = \sin \theta \)

\[ n_\theta = 0 = \frac{F}{\text{length}} = \pi K \int_0^{r_0} \frac{dr}{r} \left[ \cos^2 \theta - 2r \sin \theta \cos \theta \frac{d\theta}{dr} + r^2 (\frac{d\theta}{dr})^2 \right] \]

\((\kappa = K_{11} = K_{33})\) Euler Lagrange eqn: change to \( x = \ln \left( \frac{r}{r_0} \right) \)

\[ \frac{d^2 \theta}{dx^2} = -\sin \theta \cos \theta \]

Solution \( \theta = 2 \tan^{-1} \left( \frac{r}{r_0} \right) - \frac{\pi}{2} \).

\[ \frac{F}{\text{length}} = 3\pi K \text{ independent of } r_0. \text{ This is less than the disclination energy, so only for } \ln \frac{r_0}{\varepsilon} > 3. \]

**Note:** Index \( \pm \frac{1}{2} \) disclinations cannot escape.

They are topologically stabilized by their "Mobius" geometry.
Nematic Emulsions: A droplet of isotropic liquid suspended in a nematic:

Example: Normal boundary conditions at interface

Pearl chain:

= hedgehog → needs a negative hedgehog nearby to cancel long range distortions.

13. Droplets of nematic suspended in an isotropic matrix (solid or liquid): For I or II boundary conditions, need disclinations in the structure of the droplet:
Field effects

1. Anisotropy of susceptibility

Magnetic field: diamagnetic \( X \approx 10^{-6} \) negative.

\( \pi \) electrons in benzene rings are good at producing currents to oppose applied \( H \).

Therefore rings tend to align parallel to \( H \).

Electric field: Combination of electronic and dipolar effects:

Magnetic free energy density:

\[ f_m = \frac{1}{2} \alpha a H^2 \sin^2 \theta \]

\( \alpha = \alpha_{\parallel} - \alpha_{\perp} \)

Electric field - more complicated due to large polarizations.

\[ \mathbf{D} = \text{constant through layer}, \quad \mathbf{E} \neq \text{constant} \]

Dielectric free energy:

\[ f_e = \frac{1}{8\pi} \mathbf{E} \cdot \mathbf{D} = \frac{1}{8\pi} \frac{D^2}{\varepsilon_{22}} \]

\( f_e \) minimized when \( \varepsilon_{22} = \varepsilon_{\perp} \alpha^2 \theta + \varepsilon_{\parallel} \sin^2 \theta \) is max.

For pentyl-cyano-biphenyl, \( \varepsilon_{\perp} - \varepsilon_{\parallel} \approx 12 \), so \( \mathbf{E} \parallel \mathbf{D} \)

* Generally in a finite sample surface alignment and field alignment can compete. At low fields surface wins. At high fields field wins, depending on sample dimensions.
Calculus of variations and Linear Stability Analysis

Example: Fredericks transition in splay-bend geometry

\[ F \left( \frac{\partial}{\partial \theta} \right) = \int_0^d dx \left[ \left( \frac{1}{2} K_1 \cos^2 \theta + \frac{1}{2} K_3 \sin^2 \theta \right) \left( \frac{\partial \theta}{\partial x} \right)^2 - \frac{1}{2} K_2 H^2 \sin^2 \theta \right] \]

\[ = \int_0^d dx \left[ A(\theta) \left( \frac{\partial \theta}{\partial x} \right)^2 + C(\theta) \right] \]

Calculation of variations: find \( \theta(x) \) which minimizes this free energy. For the solution \( \theta_0(x) \), if we add any small perturbing function \( \theta(x) \) to \( \theta_0(x) \), to first order in \( \theta \), \( F \) will not change \( \delta F = 0 \) and to second order in \( \theta \), \( F \) will increase \( \delta F > 0 \). This proves that "locally" in function space, \( \theta_0(x) \) minimizes \( F \).

To carry out this process, set \( \theta = \theta_0 + \phi \) and expand the integrand to second order in \( \phi \), integrating by parts to convert factors of \( \frac{\partial^2 \theta}{\partial x^2} \) to \( \phi \), as necessary.

Note: \( \phi \) must respect the boundary conditions on \( \theta \).
\[
\frac{E}{\text{area}} = \int_0^d \left[ (A(\theta) + A'(\theta) \phi + \frac{1}{2} A''(\theta) \phi^2) \left(\frac{d\theta}{dx}\right)^2 + 2 \frac{d\theta}{dx} \frac{d\phi}{dx} + \frac{d\phi}{dx}^2 \right]
+ C(\theta) + C'(\theta) \phi + \frac{1}{2} C''(\theta) \phi^2 \right]
\]

\[
= \frac{E(\theta_0)}{\text{area}} + \int_0^d \left[ 2A(\theta) \frac{d\theta}{dx} \frac{d\phi}{dx} + A'(\theta) \frac{d\theta}{dx}^2 \phi + C'(\theta) \phi \right]
+ \int_0^d \left[ \frac{1}{2} A''(\theta) \frac{d\phi}{dx}^2 \phi^2 + A(\theta) \frac{d\theta}{dx}^2 + 2A'(\theta) \frac{d\theta}{dx} \frac{d\phi}{dx} \phi + \frac{1}{2} C''(\theta) \phi^2 \right]
\]

\[
= \frac{E(\theta_0)}{\text{area}} + \int_0^d \left[ -2 \frac{d}{dx} \left( A(\theta) \frac{d\theta}{dx} \right) + A'(\theta) \frac{d\theta}{dx}^2 + C'(\theta) \right] \phi
\]

To guarantee that this integral is 0 for any \( \phi \), the factor \([\ldots]\) must be 0. This is the Euler-Lagrange equation:

\[-2 A(\theta) \frac{d^2\theta}{dx^2} - A'(\theta) \frac{d\theta}{dx}^2 + C'(\theta) = 0\]

Because \( x \) does not appear in the integrand, a first integral of this equation is:

\[\frac{d\theta}{dx} = \pm \left[ \frac{C(\theta) + \phi}{A(\theta)} \right]^{1/2}\]

where \( \phi \) is a constant of integration.

For second order term: integration by parts:

\[A(\theta) \frac{d\theta}{dx} \frac{d\phi}{dx} \rightarrow -\left[ \frac{d}{dx} \left( A(\theta) \frac{d\theta}{dx} \right) \right] \phi \]

\[2 A'(\theta) \frac{d\theta}{dx} \frac{d\phi}{dx} \phi \rightarrow -A''(\theta) \frac{d\theta}{dx}^2 \phi^2 - A'(\theta) \frac{d^2\theta}{dx^2} \phi^2\]
Second order term:

$$\frac{\delta E}{\delta \phi} = \int_0^L \left[ \frac{\delta L}{\delta \phi} \right] \, dx,$$
where

$$L = -\frac{d}{dx} \left( A(x) \frac{d\phi}{dx} \right) + V(x)$$

and

$$V(x) = -\frac{1}{2} A''(x) \left( \frac{d\phi}{dx} \right)^2 - A'(x) \frac{d^2\phi}{dx^2} + \frac{1}{2} C''(x)$$

this should remind you of

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x),$$
except that we have

$$\frac{d}{dx} \left( g(x) \frac{d\phi}{dx} \right).$$
The important thing is that

$$L$$
is a "Hermitian," or "self-adjoint," or "symmetric" operator:

For 2 functions \( \phi_1 \) and \( \phi_2 \) obeying the correct boundary conditions:

$$\int_0^L \phi_1 L \phi_2 = \int_0^L \phi_2 L \phi_1,$$

this is clearly true for \( V(x) \) in \( L \). Now check the derivative part by integrating by parts: (twice)

$$\int_0^L \phi_1 \frac{d}{dx} \left( g(x) \frac{d\phi_2}{dx} \right) = -\int_0^L g(x) \frac{d\phi_1}{dx} \frac{d\phi_2}{dx} + \int_0^L \phi_2 \frac{d}{dx} \left( g(x) \frac{d\phi_1}{dx} \right)$$

Now, from what you learned in GM, or following the general discussion of the "Sturm-Liouville Problem" (see Morse & Feshbach) the operator \( L \) has an infinite set of eigenfunctions which form a complete orthogonal set of functions for constructing all suitable functions satisfying the boundary conditions on the integral.

Each eigenfunction \( \phi_i \) has an eigenvalue \( C_i \).
Moreover, there is a lowest eigenvalue \( \lambda_i \) and its eigenfunction \( \phi_i \) has no nodes in the domain \( 0 < x < 1 \), if \( g(x) > 0 \) in that domain.

Now, expand on that function \( \phi \) in the eigenfunction \( \Phi \): \( \phi = \sum a_i \phi_i \), and assume \( \phi_i \) are normalized so that \( \int_0^1 \phi_i^2 = 1 \).

Then \( \frac{\delta F}{\delta \phi} = \int_0^1 \phi \frac{d}{dx} \phi L \phi = \sum a_i^2 \lambda_i \).

If \( \lambda_i > 0 \) this is positive. If \( \lambda_i < 0 \), then \( \phi \) clearly lowers the free energy and \( \phi \) is not a minimizing function.

**Linear Stability Analysis:** For a given free energy integral and solution \( \phi_0 \), determine \( \lambda \) and find its lowest eigenvalue. If it is negative the solution is unstable.

* For more general boundary conditions it still works.
* Often the most use is for testing the trivial initial state of a system as some external force is applied. In our problem, let \( \phi_0(x) \equiv 0 \) and gradually increase the magnetic field.
For \( \theta_0(x) \equiv 0 \), \( A(\theta) = \frac{1}{2} K_{11} \cos^2 \theta_0 + \frac{1}{2} K_{33} \sin^2 \theta_0 = \frac{1}{2} K_{11} \)

\[ V(\theta) = \frac{1}{2} c''(\theta(x)) = -\frac{1}{2} K_a H^2 \cos 2\theta_0 = -\frac{1}{2} K_a H^2 \]

\[ L = -\frac{1}{2} K_{11} \frac{d^2}{dx^2} - \frac{1}{2} K_a H^2 \]

The eigenfunctions of \( L \) are \( \Phi_n = \sin \frac{n \pi x}{d} \), and eigenvalues:

\[ C_n = \frac{1}{2} K_{11} \left( \frac{n \pi}{d} \right)^2 - \frac{1}{2} K_a H^2 \]

To find the critical value of the magnetic field for the instability, set \( C_1 = 0 \):

\[ K_{11} \left( \frac{n \pi}{d} \right)^2 - K_a H_c^2 = 0 \]

\[ H_c = \frac{\pi}{d} \sqrt{\frac{K_{11}}{K_a}}. \]

Note: If you try some arbitrary function (not \( \sin \frac{n \pi x}{d} \)) you will get a higher \( H_c \). For instance, try \( \theta = A \frac{x}{d} (1 - \frac{x}{d}) \), which seems reasonable. Calculate \( F \) and \( w \) for this function. Finding \( H_c = \frac{10}{d} \sqrt{\frac{K_{11}}{K_a}} \), slightly too large.

For \( H > H_c \) need to solve the F.L. equation. Simplify for now: \( K_{11} = K_{33} = K \):

\[ -2 \left( \frac{1}{2} K \right) \frac{d^2 \theta}{dx^2} - \frac{1}{2} K_a H^2 (2 \sin \theta \cos \theta) = 0 \]

\[ \frac{d^2 \theta}{dx^2} + \frac{1}{\xi_H^2} \sin \theta \cos \theta = 0 \]

\[ \xi_H = \frac{1}{H} \sqrt{\frac{K}{K_a}} \]

Solution are elliptic integrals. Note: \( \xi_H = \frac{L}{H} \)

High field: \( \frac{\pi}{2} \)

boundary layers of thickness \( \xi_H \)