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07. Liquid Crystals I

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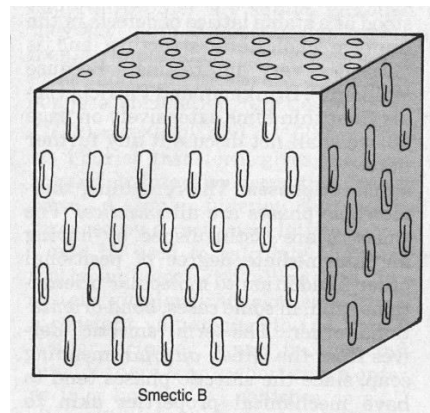
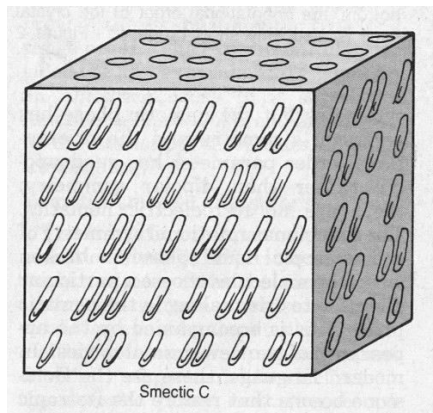
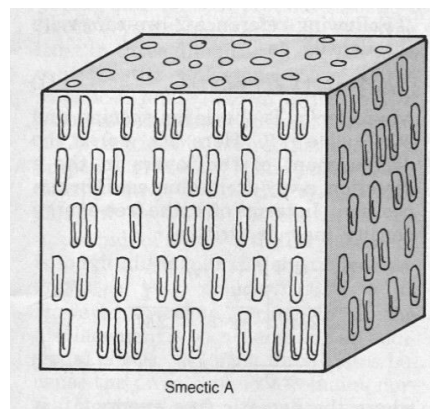
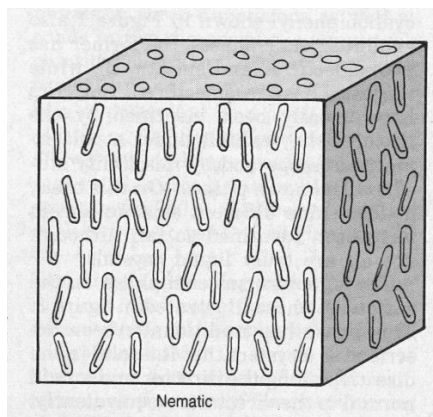
Physics of Liquid Crystals [p1n79]

Points of interests:

- Thermal equilibrium state with liquid flow attributes and some attributes of (orientational and partial translational) long-range order.
- The liquid crystalline states are not to be confused with the semi-crystalline state, a common nonequilibrium state in soft matter (e.g. polymers).
- Liquid crystal phases may reflect ordering of molecules or ordering of molecular aggregates (e.g. colloids). The particles undergoing ordering are named mesogens. some but not all mesogens are in solution.
- Typical sequence of phases of increasing order: (i) isotropic liquid, (ii) nematic liquid crystal, (iii) smectic liquid crystal, (iv) solid crystal.
- Liquid crystal phases may form out of isotropic liquids in two main modes:
 - thermotropically (driven by change in temperature),
 - lyotropically (driven by change in concentration).
- Liquid crystal ordering is stabilized by entropic effects (gaining wiggle room through alignment) and enthalpic effects (repulsive and attractive interactions between adjacent molecules).
- Each liquid crystal phase has its distinct order parameter that grows from zero continuously or discontinuously and breaks some spatial symmetry.
- Liquid crystalline ordering is susceptible to defects of three main types: (i) point defects are localized, (ii) wall defects exist along surfaces and interfaces, (iii) line defects are topological in nature.
- Disclinations are topological defects associated with orientational order and dislocations are topological defects associated with translational order.
- Polymers that are sufficiently stiff may show a propensity, in solution, to realize liquid crystal phases. One source of stiffness are helix conformations.
- The typical size of mesogens, $\sim 20\text{nm} - 50\text{nm}$ is well below the resolution limit of optical microscopes, $\sim 200\text{nm}$. However, defect structures (e.g. disclinations) can be resolved optically.
- X-ray diffraction is useful for probing molecular packing structures in liquid crystals. Soft materials tend to yield low scattering intensity. Diffraction peaks are broadened by spatial deformations of LRO.

Common Liquid Crystal Phases [tsl51]

- **Nematic:** Molecular orientational ordering. Continuous rotational symmetry about *director*.
- **Smectic A:** Nematic ordering plus density wave along symmetry axis (director).
- **Smectic C:** Smectic A ordering with broken rotational symmetry. Density wave not perpendicular to director.
- **Smectic B:** Smectic A ordering plus density wave perpendicular to director.



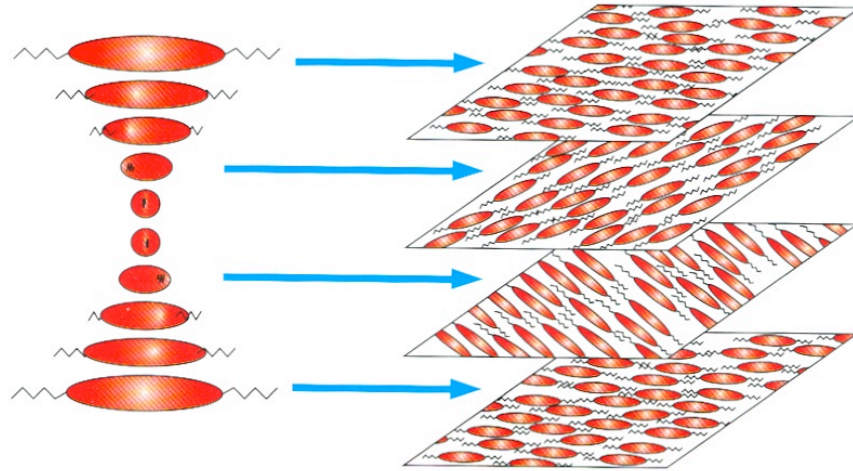
[images from Physics Today, May 1982]

Thermotropic transitions between smectic C and A are continuous. The tilt angle has a cusp singularity, $\theta(T) \sim (T_c - T)^\gamma$.

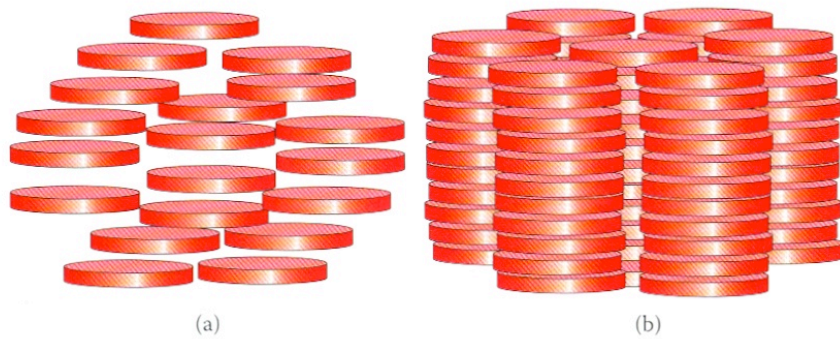
The layering in smectic phases is weak, characterized by a low-amplitude density modulation. True 1D LRO is suppressed by logarithmically diverging thermal fluctuations (Landau-Peierls instability).

- **Cholesteric:** Chiral nematic order with director rotating systematically about axis of fixed direction.

The cholesteric phase (also named chiral nematic) has a T -dependent pitch P . The director \mathbf{n} rotates 360° over this repeat distance. With T increasing, the pitch diverges at the cholesteric-nematic transition point. The T -dependent pitch is used for the design of thermochromatic devices (thermometers, sensors).



- **Discotic:** Liquid crystal order of disk-shaped molecules.
 - (a) nematic (orientational),
 - (b) hexagonal columnar (orientational and positional).



[images from Hirst 2013]

Birefringence of Nematic Phase [p1n73]

Birefringence is an optical effect characterizing anisotropic transmission of light. The refractive index depends on the polarization of light traveling through a birefringent material in a given direction.

In a nematic liquid crystal the anisotropy is caused by the orientational order of rod-like molecules. The orientational order is marked by a unit vector \mathbf{n} , named director.

The birefringence of nematics is characterized by the difference of refractive index for light polarized parallel or perpendicular to the director:

$$\Delta n \doteq n_{\parallel} - n_{\perp}.$$

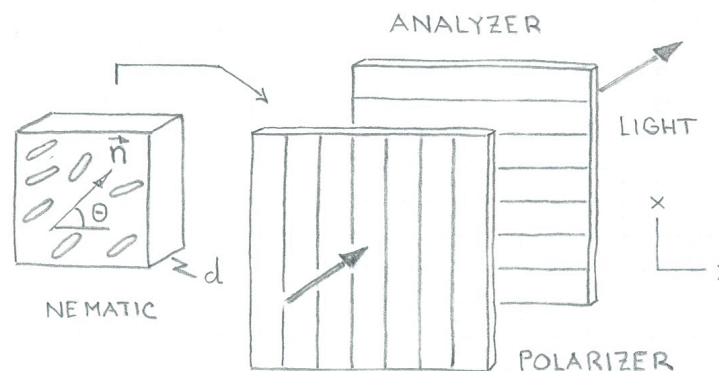
Traveling light waves of wavelength λ and one or the other linear polarization thus acquire a phase difference when traversing a nematic film of width d :

$$\Delta\phi = \frac{2\pi}{\lambda}d\Delta n.$$

Polarized optical microscopy (POM) is a powerful technique for the visualization and characterization of liquid crystal phases.

Intensity of light emerging from setup with nematic film between crossed polarizers [pex2]:

$$I \propto \sin^2(2\theta) \sin^2\left(\frac{\pi d}{\lambda}\Delta n\right).$$



[extracted from Hirst 2013]

[pex2] Nematic ordering detected via polarized optical microscopy

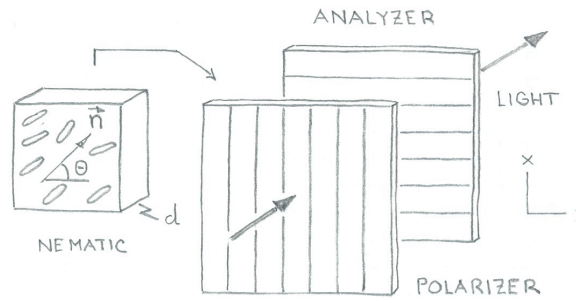
The birefringence of a nematic phase makes it detectable via polarized optical microscopy. In the simple setup sketched below consider a beam of monochromatic light of wavelength λ traveling through a slab of nematic liquid crystal with director \mathbf{n} and width d as shown. The electric field of a plane wave that has made it through the polarizer is of the form

$$\mathbf{E}_1(z, t) = A \cos(kz - \omega t) \hat{\mathbf{j}}.$$

- (a) Write the electric field vector of $\mathbf{E}_2(z, t)$ of the light wave after transmission through the slab of nematic and the electric field vector $\mathbf{E}_3(z, t)$ after the transmission through the analyzer.
 (b) Show that the intensity of the emerging light wave is of the form

$$I \propto \sin^2(2\theta) \sin^2\left(\frac{\pi d}{\lambda} \Delta n\right),$$

where $\Delta n \doteq n_{\parallel} - n_{\perp}$ is the difference of refractive index for light polarized parallel or perpendicular to the director.

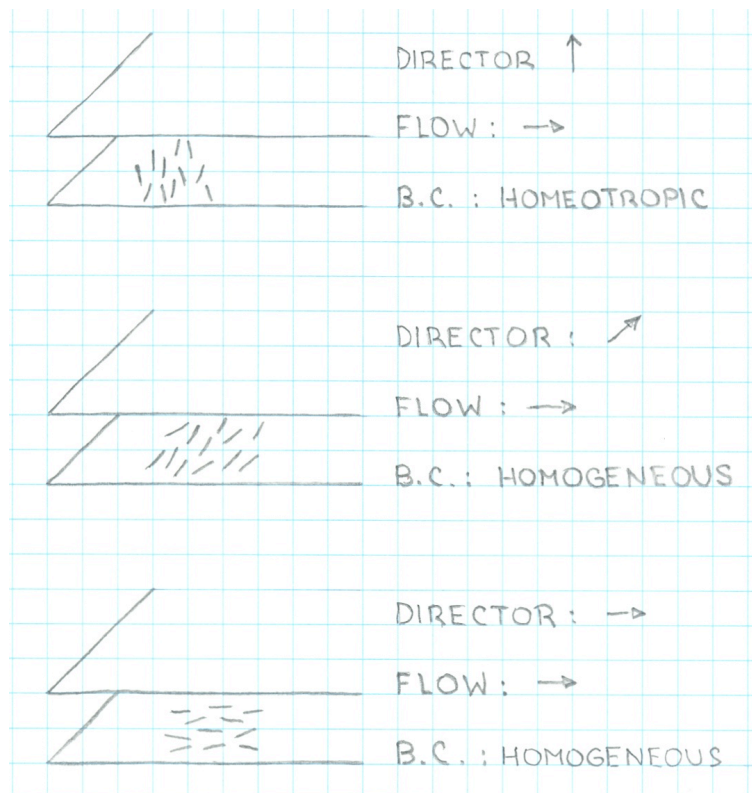


Solution:

Anisotropic Flow Behavior of Nematics [pln83]

Miesowicz coefficients describe viscous flow between parallel plates in three distinct configurations of

- nematic director,
- flow direction,
- boundary conditions.



Maier-Saupe Theory for Nematic Ordering [p1n74]

Consider rod-like molecules with indistinguishable ends¹ at fixed concentration in solution. The nematic phase is isotropic in the plane perpendicular to the director.

The orientations of individual molecules relative to the director \mathbf{n} of nematic ordering is described by a distribution $f(\theta)$, named *orientation function*. The normalization condition under the circumstances described is

$$\mathcal{M} = 2\pi \int_0^{\pi/2} d\theta \sin \theta f(\theta) = 1. \quad (1)$$

In the isotropic liquid phase, one end of each rod is equally likely to point in any direction on a hemisphere: $f_{\text{iso}}(\theta) = 1/2\pi = \text{const.}$

The nematic order parameter,

$$\mathcal{N} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \pi \int_0^{\pi/2} d\theta \sin \theta (3 \cos^2 \theta - 1) f(\theta), \quad (2)$$

is sensitive to any deviation of $f(\theta)$ from $f_{\text{iso}}(\theta)$ that reflects an alignment tendency of the rods.

The agents of nematic ordering are, in parts, *enthalpic* and *entropic* in nature:

- attractive van der Waals forces favor alignment,
- aligned rods are more loosely packed, i.e. less constrained in positioning and motion.

The equilibrium macrostate is the state of lowest free energy, here expressed relative to the isotropic state:

$$\Delta F = \Delta H - T\Delta S. \quad (3)$$

The enthalpy change in mean-field approximation is rendered as the following function of the order parameter:

$$\Delta H = -\frac{1}{2}u\mathcal{N}^2, \quad (4)$$

where u is a measure for the coupling strength of the van der Waals attraction.

¹The molecules are assumed to be symmetric when rotated 180° perpendicular to their long axis.

The entropy reduction relative to the (most disordered) isotropic macrostate depends on the orientation function as follows:

$$\begin{aligned}\Delta S &= -k_B 2\pi \int_0^{\pi/2} d\theta \sin \theta \left[f(\theta) \ln f(\theta) - \frac{1}{2\pi} \ln \left(\frac{1}{2\pi} \right) \right] \\ &= -k_B \int_0^{\pi/2} d\theta \sin \theta [2\pi f(\theta)] \ln (2\pi f(\theta)).\end{aligned}\tag{5}$$

The Maier-Saupe theory extracts a one-parameter orientation function from the variational problem that extremizes the following functional with two Lagrange multipliers:

$$J[f] = \Delta S + \lambda_1 \mathcal{N} + \lambda_2 \mathcal{M}.\tag{6}$$

The solution of this variational problem,

$$f(\theta, b) = A(b) \exp(b \cos^2 \theta),\tag{7}$$

is worked out in [pex43] including an analytic expression for the amplitude function $A(b)$.

The Maier-Saupe theory for the thermotropic transition between an isotropic liquid and nematic phase thus expresses the scaled free energy, $\Delta \hat{F} \doteq \Delta F/k_B T$, as a function of the parameter b and the scaled coupling constant $\hat{u} \doteq u/k_B T$:

$$\Delta \hat{F}(b, \hat{u}) = -\frac{1}{2} \hat{u} [\mathcal{N}(b)]^2 - \Delta \hat{S}(b),\tag{8}$$

where $\Delta \hat{S} = \Delta S/k_B$ is a dimensionless entropy.

Plotting $\Delta \hat{F}(b, \hat{u})$ versus $\mathcal{N}(b)$ at fixed \hat{u} , as worked out in [pex44], reveals the nature of the equilibrium state: for weak coupling (or high temperature) the minimum free energy is realized for vanishing order parameter.

There exists a critical coupling strength \hat{u}_c or a transition temperature $\hat{T}_c \doteq 1/\hat{u}_c$, where the location of that minimum switches to a location at nonzero order parameter.

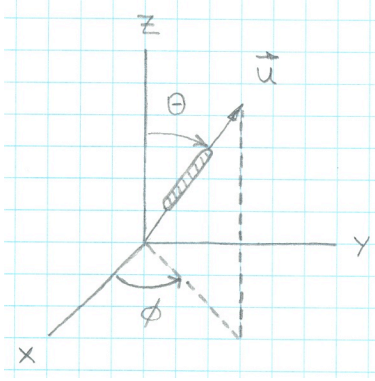
The location of the free-energy minimum determines a function $\tilde{\mathcal{N}}(\hat{T})$, which gradually decreases as \hat{T} increases from zero and then drops to zero at \hat{T}_c in a first-order phase transition. This function and the transition point are worked out quantitatively in [pex5].

[adapted from Jones 2002]

Nematic Order Parameter [pln80]

Orientation of mesogen described by unit vector,

$$\mathbf{u}^{(i)} = (u_x^{(i)}, u_y^{(i)}, u_z^{(i)}) = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i).$$



The tensor construction of the nematic order parameter must take into account that $\langle \mathbf{u}^{(i)} \rangle = 0$ in both the isotropic phase and the nematic phase. It follows that the tensor must be of second rank or higher.

Desired attributes of the 2nd-rank order-parameter tensor $\mathcal{N}_{\alpha\beta}$, $\alpha, \beta = x, y, z$:

- tensor is symmetric: $\mathcal{N}_{\alpha\beta} = \mathcal{N}_{\beta\alpha}$,
- tensor has zero trace: $\sum_{\alpha} \mathcal{N}_{\alpha\alpha} = 0$,
- $\mathcal{N}_{\alpha\beta} \equiv 0$ in isotropic phase,
- $\mathcal{N}_{\alpha\alpha} = 1$ if $\mathbf{u}^{(i)} = \hat{\mathbf{e}}_{\alpha}$ (perfect alignment).

These attributes are satisfied by the following construction [pex1]:¹

$$\mathcal{N}_{\alpha\beta} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \frac{1}{2} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta g(\theta, \phi) (3u_{\alpha}u_{\beta} - \delta_{\alpha\beta}),$$

where $g(\theta, \phi)$ is the orientation function characterizing the macrostate and

$$u_x = \sin \theta \cos \phi, \quad u_y = \sin \theta \sin \phi, \quad u_z = \cos \theta.$$

The order parameter $\mathcal{N}_{\alpha\beta}$ is being used in the Maier-Saupe theory [pln74] and in the Onsager theory [pln75].

¹Note the relation to Legendre polynomials: $P_0(x) = 1$, $P_1(x) = x$, $P_2(x) = \frac{1}{2}(3x^2 - 1)$, ... In the case of a ferromagnet, the order parameter (magnetization) is constructed from a first-rank tensor (vector), corresponding to the first-order Legendre polynomial.

[pex1] Attributes of nematic order parameter

Consider the nematic order parameter proposed in [pln80]:

$$\mathcal{N}_{\alpha\beta} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle = \frac{1}{2} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta g(\theta, \phi) (3u_\alpha u_\beta - \delta_{\alpha\beta}),$$

where

$$u_x = \sin \theta \cos \phi, \quad u_y = \sin \theta \sin \phi, \quad u_z = \cos \theta.$$

(a) Show that all elements of $\mathcal{N}_{\alpha\beta}$ vanish in the isotropic phase, where the orientation function is uniform:

$$g(\theta, \phi)_{\text{iso}} = \frac{1}{4\pi}.$$

(b) Show that the tensor $\mathcal{N}_{\alpha\beta}$ is diagonal if the nematic ordering is perfect and aligned with one axis, for example the x -axis:

$$g(\theta, \phi)_{\text{nem}} = \delta(\phi) \delta(\cos \theta).$$

Calculate the diagonal elements $\mathcal{N}_{\alpha\alpha}$, $\alpha = x, y, z$ for this case.

Solution:

[pex43] Maier-Saupe theory I: variational problem

The Maier-Saupe theory for the thermotropic transition between an isotropic liquid and a nematic phase as described in [pln74] arrives at the functional,

$$J[f] = \Delta S + \lambda_1 \mathcal{N} + \lambda_2 \mathcal{M},$$

with Lagrange multipliers, λ_1, λ_2 , and where

$$\Delta S = -k_B \int_0^{\pi/2} d\theta \sin \theta [2\pi f(\theta)] \ln (2\pi f(\theta)),$$
$$\mathcal{N} = \pi \int_0^{\pi/2} d\theta \sin \theta (3 \cos^2 \theta - 1) f(\theta), \quad \mathcal{M} = 2\pi \int_0^{\pi/2} d\theta \sin \theta f(\theta) = 1,$$

represent entropy, order parameter, and normalization, respectively, all expressed as integrals involving the unknown orientation function $f(\theta)$.

(a) Find the extremum of the functional $J[f]$ by variational calculus to produce the orientation function,

$$f(\theta, b) = A(b) \exp(b \cos^2 \theta),$$

and determine the amplitude $A(b)$ analytically by imposing the normalization condition $\mathcal{M} = 1$.

(b) Plot the orientation function $f(\theta, b)$ versus θ for $0 < \theta < \pi/2$ and several values of the parameter $b \geq 0$. Interpret the shape of the orientation function thus obtained in the context of nematic ordering.

[adapted from Jones 2002]

Solution:

[pex44] Maier-Saupe theory II: free energy, entropy, order parameter

This is the continuation of [pex43], where we have solved the variational problem and determined the one-parameter orientation function, $f(\theta, b) = A(b) \exp(b \cos^2 \theta)$ with an explicit expression for the amplitude $A(b)$.

(a) Use Mathematica to calculate analytic expressions for the order parameter,

$$\mathcal{N}(b) = \pi \int_0^{\pi/2} d\theta \sin \theta (3 \cos^2 \theta - 1) f(\theta, b),$$

and the entropy,

$$\Delta S(b) = -k_B \int_0^{\pi/2} d\theta \sin \theta [2\pi f(\theta, b)] \ln (2\pi f(\theta, b)).$$

(b) Use ParametricPlot of Mathematica to plot entropy $\Delta S/k_B$ versus order parameter \mathcal{N} . Interpret the shape of the curve thus obtained.

(c) From these ingredients and the enthalpy,

$$\Delta H = -\frac{1}{2} u [\mathcal{N}(b)]^2,$$

we express the scaled free energy, $\Delta \hat{F} \doteq \Delta F/k_B T$, as a function of the parameter b and the scaled coupling constant $\hat{u} \doteq u/k_B T$:

$$\Delta \hat{F}(b, \hat{u}) = -\frac{1}{2} \hat{u} [\mathcal{N}(b)]^2 - \Delta \hat{S}(b),$$

where $\Delta \hat{S} = \Delta S/k_B$ is a dimensionless entropy. Plot $\Delta \hat{F}(b, \hat{u})$ versus $\mathcal{N}(b)$ for $\hat{u} = 3, 4, \dots, 7$. Note that the thermal energy, $k_B T$, is used as energy scale for both the coupling strength and the free energy itself. For each value of \hat{u} , the order parameter \mathcal{N} settles at the value for which the free energy, $\Delta \hat{F}$, has a minimum.

[adapted from Jones 2002]

Solution:

[pex5] Maier-Saupe theory III: first-order phase transition

This is the continuation of [pex44], where we have determined an explicit, parametric expression for the scaled free energy in terms of order parameter and entropy:

$$\Delta\hat{F}(b, \hat{u}) = -\frac{1}{2}\hat{u}[\mathcal{N}(b)]^2 - \Delta\hat{S}(b),$$

where b is the parameter and $\hat{u} = 1/\hat{T}$ is a scaled coupling constant.

The location of the free-energy minimum determines a function $\bar{\mathcal{N}}(\hat{T})$, which we examine here.

- (a) Locate the transition temperature $\hat{T}_c \doteq 1/\hat{u}_c$, as the inverse coupling strength for which the location of that minimum in $\Delta\hat{F}(b, \hat{u})$ switches between $\mathcal{N} = 0$ to a nonzero value of \mathcal{N} .
- (b) Design a way to produce an accurate graphical representation of the function $\bar{\mathcal{N}}(\hat{T})$.

[adapted from Jones 2002]

Solution:

Lyotropic Transition to Nematic Phase [pln75]

Rod-shaped molecules in solution with gradually increasing concentration undergo a lyotropic transition between an isotropic liquid and a nematic liquid crystal, described here in a much simplified version of Onsager's theory.

Specifications:

- rods of length L and circular cross section with diameter D ,
- aspect ratio: L/D ,
- volume of rod: $v_r = \pi(D/2)^2L$,
- concentration of rods: $c = N/V$,
- volume fraction of rods: $\phi = v_r c$.

Configurational entropy originating from two sources of disorder.

(a) *Oriental disorder*:

- orientation function:¹ $g(\theta)$ (distribution of angles relative to director),
- entropy reduction: $\frac{\Delta S_a}{Nk_B} = -2\pi \int_0^\pi d\theta \sin \theta g(\theta) \ln (4\pi g(\theta)) \doteq -q[g(\theta)]$.

(b) *Translational disorder*:

- entropy of ideal gas: $\frac{S_{icg}}{Nk_B} = \ln (V/V_0) + f(T)$.
- entropy reduction due to exclusion volume caused by increasing numbers of rods and their partial misalignment:

$$\frac{\Delta S_b}{Nk_B} = \ln \left(\frac{V - Nb}{N} \right) = \ln \left(\frac{V}{N} \right) + \underbrace{\ln \left(1 - \frac{bN}{V} \right)}_{\simeq -bN/V} \simeq -\ln c - cb.$$

- estimate of average exclusion volume: $b = DL^2 \langle |\sin \gamma| \rangle$,
- angle between rods neighboring rods: γ ,
- averaging carried out:

$$\begin{aligned} \langle |\sin \gamma| \rangle &= \int_0^{2\pi} d\phi_1 \int_0^\pi d\theta_1 \sin \theta_1 \int_0^{2\pi} d\phi_2 \int_0^\pi d\theta_2 \sin \theta_2 \\ &\quad \times g(\theta_1)g(\theta_2) |\sin \gamma(\theta_1, \phi_1, \theta_2, \phi_2)| \doteq p[g(\theta)], \end{aligned}$$

- isotropic limit: $g(\theta) = \frac{1}{4\pi} \Rightarrow \langle |\sin \gamma| \rangle = \frac{\pi}{4}$.

¹Note the reduced molecular symmetry assumed here in comparison to [pln74].

Functional of entropy reduction:

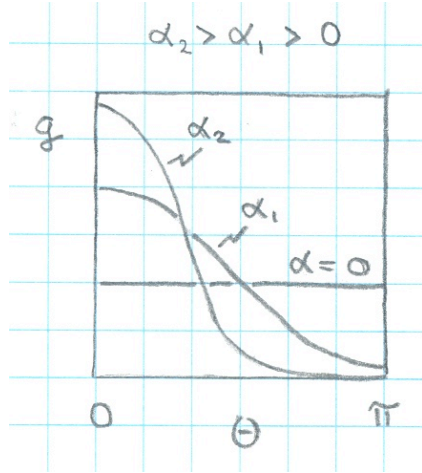
$$\frac{\Delta S}{Nk_B} = \frac{\Delta S_b}{Nk_B} + \frac{\Delta S_a}{Nk_B} = -\ln c - cDL^2 p[g(\theta)] - q[g(\theta)], \quad (1)$$

- physically relevant parameter: $x \doteq \frac{\phi L}{D} \Rightarrow cDL^2 = \frac{4x}{\pi}$,

$$\Rightarrow \frac{\Delta S}{Nk_B} = -\ln x - \frac{4x}{\pi} p[g(\theta)] - q[g(\theta)]. \quad (2)$$

Phenomenological one-parameter orientation function:

$$g(\theta, \alpha) \doteq \frac{\alpha \cosh(\alpha \cos \theta)}{4\pi \sinh \alpha} \xrightarrow{\alpha \rightarrow 0} \frac{1}{4\pi}. \quad (3)$$



Parametrized versions of order parameter and entropy reduction:

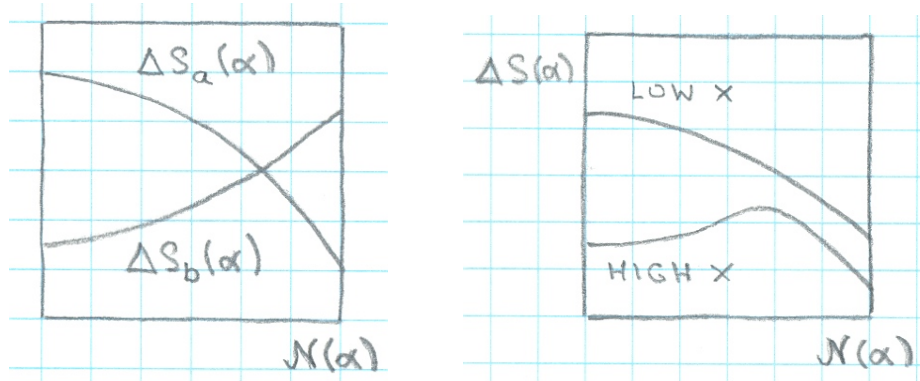
$$\mathcal{N}(\alpha) = \pi \int_0^\pi d\theta \sin \theta (3 \cos^2 \theta - 1) g(\theta, \alpha), \quad (4)$$

$$\Delta s(\alpha) \doteq \frac{\Delta S}{Nk_B} = -\ln x - \frac{4x}{\pi} p(\alpha) - q(\alpha). \quad (5)$$

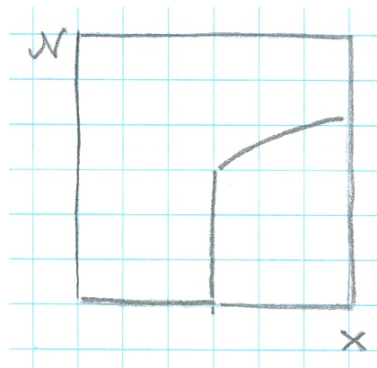
with functionals turned into functions of the parameter:

$$p(\alpha) = p[g(\theta, \alpha)], \quad q(\alpha) = q[g(\theta, \alpha)].$$

Graphical representations of entropy reduction versus order parameter:



- low x : Δs has a maximum at $\mathcal{N} = 0$,
- high x : Δs has a maximum at $\mathcal{N} \neq 0$,
- critical x : position of maximum switches from $\mathcal{N} = 0$ to $\mathcal{N} \neq 0$.



[adapted from Jones 2002]

Multicritical NAC Point [pln81]

The transition between nematic and smectic A (or C) can be continuous or discontinuous. The order parameter describes amplitude and direction of a density wave perpendicular to the emerging layers

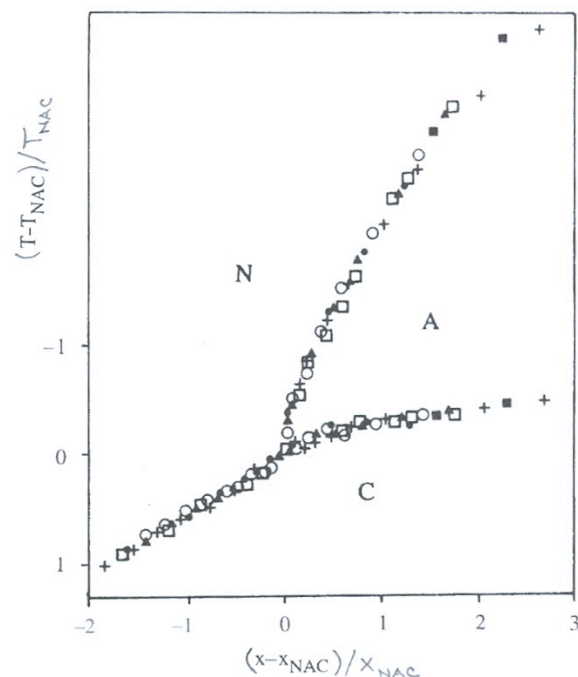
The transition between smectic A and smectic C is continuous. The order parameter describes the tilt angle between mesogens and the normal to the layers.

There exist mesogens that undergo continuous transitions between nematic and either smectic A or smectic C and between smectic A and smectic C.

In a diagram of concentration x versus temperature T , the transitions of each type are located on a line segment. The three line segments of critical points are joined in the multicritical NAC point.

The coordinates of the NAC point define natural units for x and T . These units facilitate graphical representations of features of universality as are common in critical phenomena.

The graph below shows critical-point data near the NAC point for five different mixtures of mesogens.



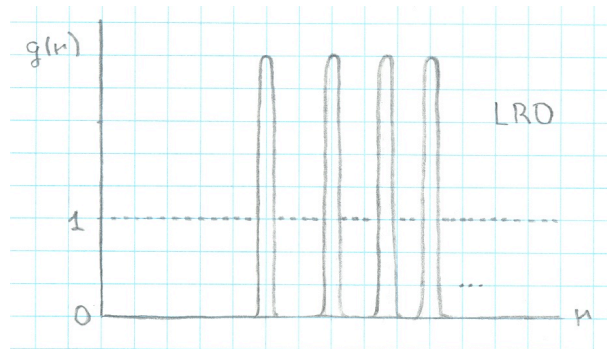
[image from Hamley 2007]

Stages of Positional Ordering [pln82]

The signature quantity here is $g(r)$, the radial distribution function (RDF). It is, in some measure, the probability for finding another mesogen at radius r from any given mesogen.

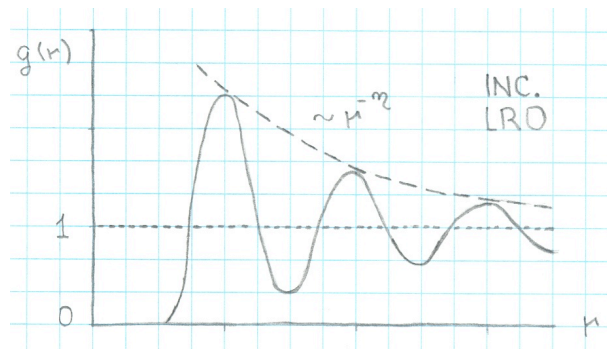
Strong positional ordering:

True long-range order is realized in hard and soft crystal phases including some versions of smectic B. The RDF is strongly peaked at discrete radii that reflect the given lattice structure. Thermal fluctuations cause a mild broadening of the peaks.



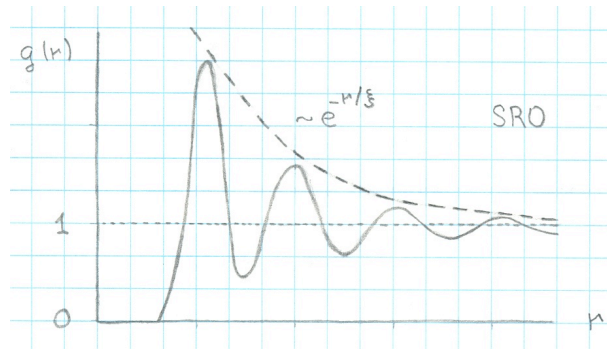
Intermediate positional ordering:

Incipient long-range order is realized across layers of smectic A and smectic C phases. The peaks in the RDF are now significantly broader. The heights of successive peaks decrease with increasing radius according to a power law, $\sim r^{-\eta}$, with a T -dependent exponent η .



Weak positional ordering:

Short-range order is realized in isotropic liquids and nematic liquid crystals. The heights of successive peaks now decrease exponentially with increasing radius, $\sim e^{-r/\xi}$, with a T -dependent correlation length ξ .



[adapted from Hamley 2007]

Distorted nematic ordering: splay, twist, bend [ps116]

Orientational ordering in nematic phase characterized by director \mathbf{n} .

Nematic liquid crystal responds to shear stress with viscous flow. Director field remains largely uniform.

Deformations $\mathbf{n}(\mathbf{r})$ from uniformity can be imposed by boundary conditions.

Depending on the forces between liquid crystal molecules and container surfaces we have a

- homeotropic boundary condition (\mathbf{n} perpendicular to the surface),
- homogeneous boundary conditions (\mathbf{n} parallel to the surface).

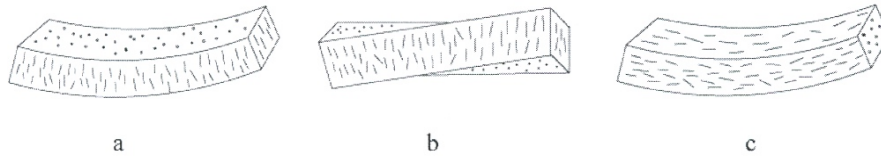
Boundary induced deformations $\mathbf{n}(\mathbf{r})$ represent elastic response.

Three fundamental types of deformations produce different contributions to the distortion Helmholtz free energy:

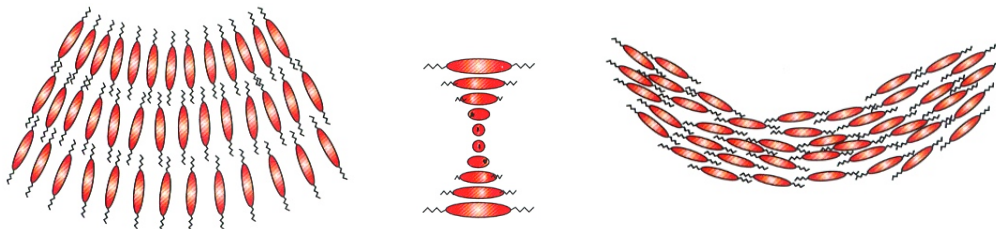
(a) splay: $\nabla \cdot \mathbf{n} \neq 0$, $\Delta A_1 = \frac{1}{2}K_1(\nabla \cdot \mathbf{n})^2$,

(b) twist: $\nabla \times \mathbf{n} \parallel \mathbf{n}$, $\Delta A_2 = \frac{1}{2}K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2$,

(c) bend: $\nabla \times \mathbf{n} \perp \mathbf{n}$, $\Delta A_3 = \frac{1}{2}K_3[\mathbf{n} \times (\nabla \times \mathbf{n})]^2$.



[image from Andrienko 2006]

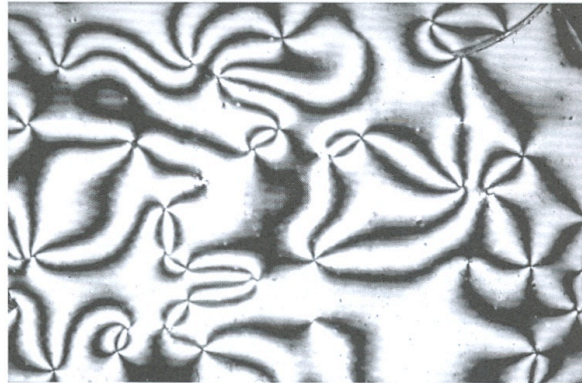


[image from Hirst 2013]

Disclinations in nematic phase [ps117]

Disclinations are topological line defects in the orientational ordering. At a disclination the director field $\mathbf{n}(\mathbf{r})$ is discontinuous.

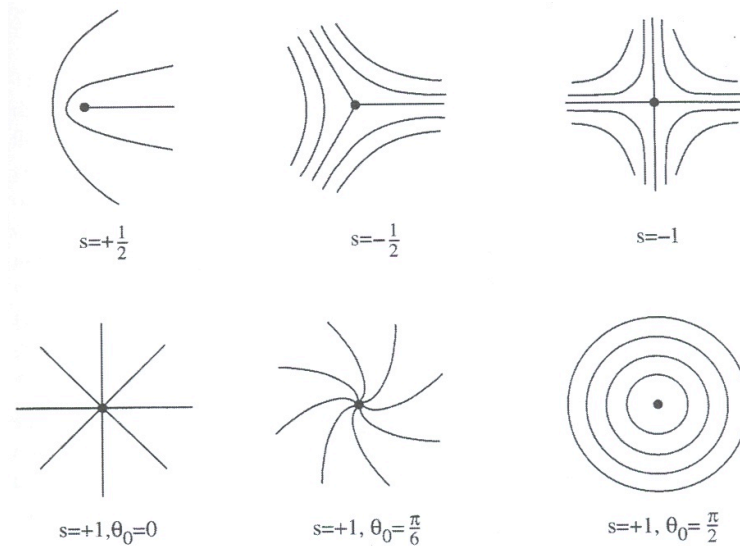
Polarizing optical microscopy yields images of characteristic *Schlieren* textures with identifiable surface ends of disclinations.



Consider two-dimensional director field in a plane perpendicular to a disclination line. The disclination line cuts through the plane at the origin of the coordinate system.

$$\mathbf{n}(\mathbf{r}) = \cos(\theta(\mathbf{r}))\hat{\mathbf{i}} + \sin(\theta(\mathbf{r}))\hat{\mathbf{j}}, \quad \mathbf{r} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}},$$

$$\theta(\mathbf{r}) = s \arctan\left(\frac{y}{x}\right) + \theta_0.$$



[images from Hamley 2007]

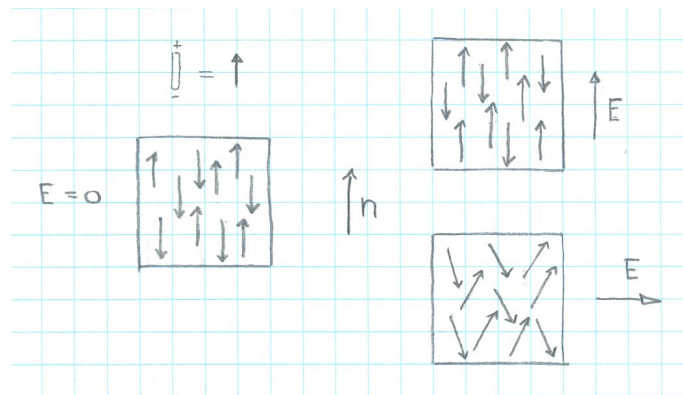
Response of Nematic to Electric Field [pln76]

Consider rod-like molecules with a permanent electric dipole moment in a nematic liquid crystal phase.

$\mathbf{E} = 0$: In the absence of an external electric field, no ferroelectric ordering is observed. The average electric dipole moment vanishes even though the nematic order parameter is nonzero. Individual molecules tend to align in one direction (director \mathbf{n})¹ but the projection of the dipole moment \mathbf{p} is equally likely to have a positive or a negative projection onto the director: $\langle \mathbf{p} \cdot \mathbf{n} \rangle = 0$.

$\mathbf{E} \neq 0$: The presence of an external electric field produces a dielectric response in the form of an electric polarization \mathbf{P} (average dipole moment). The dielectric response is anisotropic:²

- $\mathbf{E} \parallel \mathbf{n} \Rightarrow \mathbf{P} = (\epsilon_{\parallel} - 1)\epsilon_0\mathbf{E}$ (flip response),
- $\mathbf{E} \perp \mathbf{n} \Rightarrow \mathbf{P} = (\epsilon_{\perp} - 1)\epsilon_0\mathbf{E}$ (tilt response).



Displacement vector: $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$:

$$\mathbf{D} = \epsilon_{\parallel}\epsilon_0(\mathbf{n} \cdot \mathbf{E})\mathbf{n} + \epsilon_{\perp}\epsilon_0[\mathbf{E} - (\mathbf{n} \cdot \mathbf{E})\mathbf{n}] = \epsilon_{\perp}\epsilon_0\mathbf{E} + (\epsilon_{\parallel} - \epsilon_{\perp})\epsilon_0(\mathbf{n} \cdot \mathbf{E})\mathbf{n},$$

- $\mathbf{E} \parallel \mathbf{n} \Rightarrow \mathbf{D} = \epsilon_{\parallel}\epsilon_0\mathbf{E}$,
- $\mathbf{E} \perp \mathbf{n} \Rightarrow \mathbf{D} = \epsilon_{\perp}\epsilon_0\mathbf{E}$.

Reduction in electric energy density due to polarization (with $\chi \doteq \epsilon - 1$):

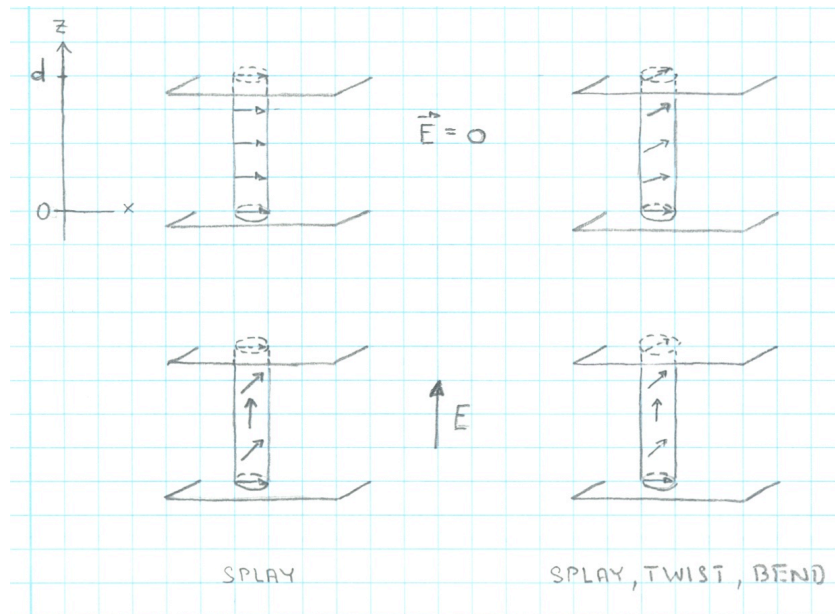
$$\Delta u = -\frac{1}{2}\chi_{\perp}\epsilon_0 E^2 - \frac{1}{2}(\chi_{\parallel} - \chi_{\perp})\epsilon_0(\mathbf{E} \cdot \mathbf{n})^2.$$

¹Most often the director \mathbf{n} is selected by boundary effects.

²In general, $\epsilon_{\parallel} > \epsilon_{\perp}$ is realized.

Fréedericksz Transition in LCD [p1n77]

Consider a thin film of nematic sandwiched (at width d) by parallel plates and homogeneous boundary conditions with parallel alignment (left) or perpendicular alignment (right) realized. An electric field \mathbf{E} perpendicular to the plane of the field is being switched on and off.



Parallel alignment:

Director field: $\mathbf{n}(z) = n_0 \hat{\mathbf{e}}_x + \delta n(z) \hat{\mathbf{e}}_z$.

Boundary conditions: $\delta n(0) = \delta n(d) = 0$.

Ansatz: $\delta n(z) = A \sin\left(\frac{\pi z}{d}\right)$.

Change in energy density has two contributions:

- elastic splay energy,
- electric potential energy.

$$\begin{aligned} \Delta u(z) &= \frac{1}{2} K_1 \left(\frac{d\delta n}{dz} \right)^2 - \frac{1}{2} \underbrace{(\epsilon_{\parallel} - \epsilon_{\perp})}_x \epsilon_0 E^2 (\delta n)^2 \\ &= \frac{1}{2} K_1 A^2 \left(\frac{\pi}{d} \right)^2 \cos^2 \left(\frac{\pi z}{d} \right) - \frac{1}{2} \chi \epsilon_0 E^2 A^2 \sin^2 \left(\frac{\pi z}{d} \right). \end{aligned}$$

$$\Delta U(E) \doteq \int_0^d dz \Delta u(z) = \frac{1}{2} K_1 A^2 \left(\frac{\pi}{d} \right)^2 \frac{d}{2} - \frac{1}{2} \chi \epsilon_0 E^2 A^2 \frac{d}{2}.$$

$$\Delta U(E_c) = 0 \quad \Rightarrow \quad E_c = \frac{\pi}{d} \sqrt{\frac{K_1}{\chi \epsilon_0}}.$$

Perpendicular alignment:

Director field has three components: $\mathbf{n}(z) = n_x(z)\hat{\mathbf{e}}_x + n_y(z)\hat{\mathbf{e}}_y + n_z(z)\hat{\mathbf{e}}_z$.

Boundary conditions: $\mathbf{n}(0) = n_0\hat{\mathbf{e}}_x$, $\mathbf{n}(d) = n_0\hat{\mathbf{e}}_y$.

Elastic energy now involves splay, twist, and bend.

$$\text{Transition field: } E_c = \frac{\pi}{d} \sqrt{\frac{K_1 + (K_3 - 2K_2)/4}{\chi \epsilon_0}}.$$

Magnetic nematics:

For rod-like molecules with a magnetic dipole moment, which can be induced or permanent, the electric potential-energy density is to be replaced by the magnetic potential-energy density,

$$\Delta u(z) = -\frac{1}{2} \chi H^2 (\delta n)^2,$$

where χ is the magnetic susceptibility and H the external magnetic field.

[adapted from Jones 2002]