Boulder 2002

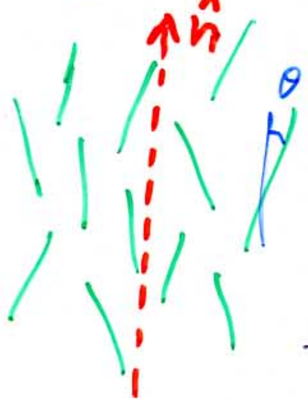
Liquid Crystals:

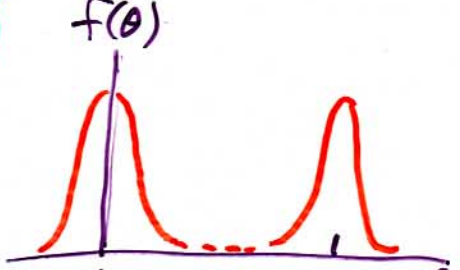
Elasticity, static equilibrium, textures

Basics

Phases

Nematic: parallel ordering of rodlike (or platelike) molecules.





Order parameter: $\underset{\approx}{Q}$ is a second rank tensor

$$|\underset{\approx}{Q}| = S = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2} \rangle$$

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

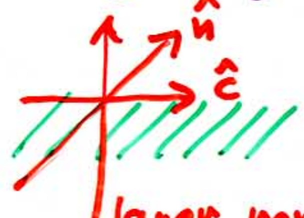
Nematic ground state: $\hat{n}$ uniform in space.

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

Smectic: 1D periodic, 2D fluid, layers of molecules.

SmA

SmC



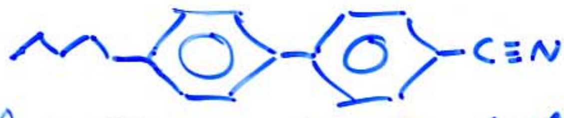
SmC ground state: $\hat{c}$ uniform in space; layers flat.

Low energy deformations: We will consider only flat layers, and $c(\vec{r})$ varying. "Almost" a 2D nematic, <u>but</u> $\hat{c} \not\leftrightarrow -\hat{c}$, for a <u>thin film</u> of SmC.

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:



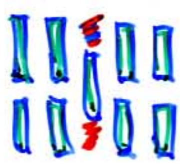
Pentyl-cyano-biphenyl

* Anisotropic molecular interactions play a role too.

Smectic: * Cylindrical shape, as opposed to "cigar".

 vs. 

↓ forms smectic ↓ no smectic



 → no tendency for layers

↳ layers allow the best use of volume for fluctuations in plane. Nematic-like fluctuations cost free volume ( ), while good layering again maximizes entropy!

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

Extreme example: Block co-polymers of incompatible components.

Nematic Elasticity (Curvature elasticity)

Expand $\hat{n}(r)$ in a Taylor series, with a local coordinate system, $\hat{n}_0 = \hat{z}$. Thus $\hat{n} = \hat{n}_0 + \delta n_x \hat{x} + \delta n_y \hat{y}$, ($\delta n_z = 0$ since $\hat{n}$ is a unit vector.)

$$\hat{n}(\vec{r}) = \hat{n}_0 + x\left(\frac{\partial n_x}{\partial x}\hat{x} + \frac{\partial n_y}{\partial x}\hat{y}\right) + y\left(\frac{\partial n_x}{\partial y}\hat{x} + \frac{\partial n_y}{\partial y}\hat{y}\right) + z\left(\frac{\partial n_x}{\partial z}\hat{x} + \frac{\partial n_y}{\partial z}\hat{y}\right)$$

Construct free energy from strains: following symmetry

1) ∞ rotation about $\hat{n}_0$
2) reflections $\perp$ and $\parallel$ to $\hat{n}_0$, center of inversion ($\hat{n} \leftrightarrow -\hat{n}$)

And, for bulk energy, eliminate terms of the form $\nabla \cdot \vec{u}$, where $\vec{u}$ is a vector field, since these can be integrated to surface terms.

This leaves only 3 terms in the free energy density:

$$f = \frac{1}{2}K_{11}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2 + \frac{1}{2}K_{22}\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)^2 + \frac{1}{2}K_{33}\left(\frac{\partial n_x}{\partial z}^2 + \frac{\partial n_y}{\partial z}^2\right)$$

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

$(\vec{S})^2 = |\hat{n}(\nabla\cdot n)|^2$ torsion "t" $(\hat{n}\times\nabla\times\hat{n})^2 = |\vec{B}|^2$

Splay \|// twist Bend

Thin films of Sm C (2D system)

Only splay and bend deformations exist:

$$f = \frac{1}{2} K_S (\nabla \cdot \hat{c})^2 + \frac{1}{2} K_B (\nabla \times \hat{c})_\perp^2 \quad \left[\begin{array}{c} f \text{ is energy} \\ \text{per unit area} \end{array} \right]$$

Notes on elastic moduli K_{ii}, K_S, K_B:

Nematic: Picture extreme curvature:

$\frac{\partial n_x}{\partial x} \sim \frac{1}{\ell}$ with ℓ = molecular length. This "disorders" the nematic $\rightarrow$ isotropic. $\Delta f \sim \Delta H_{NI} \sim 1\,\mathrm{kC/mol}$

$$\frac{1}{2} K_{ii} \left(\frac{1}{\ell}\right)^2 = \frac{\text{molecular interaction energy}}{\ell^3}$$

$$[K_{ii}] \sim \frac{[\text{energy}]}{[\ell]} \sim 10^{-12}\ \mathrm{J/m}.$$

Sm C (2D):

$K_{S,B} \sim K_{ii} (\sin^2\theta) t$ where θ = tilt angle, t = 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:

$$F = \int dx\,dy\,dz\ f(\hat{n}(\vec{r})).$$

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

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

$n_x = \cos\theta,\ n_y = \sin\theta\quad n_z = 0\quad$ (clearly $|n| = 1$)

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

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

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

Assume $K_{11} = K_{33} = K$ then

$$F = \int dx\,dy\,dz\left[\frac{1}{2}K\left(\left(\frac{\partial\theta}{\partial x}\right)^2 + \left(\frac{\partial\theta}{\partial y}\right)^2\right) + \frac{1}{2}K_{22}\left(\frac{\partial\theta}{\partial z}\right)^2\right]$$

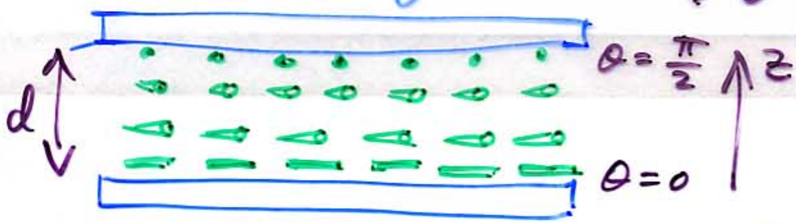
rescale $z = \sqrt{\frac{K_{22}}{K}}\,\xi$

$$F = \frac{1}{2}\sqrt{K K_{22}}\int dx\,dy\,d\xi\,(\nabla\theta)^2 \rightarrow$$

Euler Lagrange eqn.: $\nabla^2\theta = 0$ electrostatics!

Planar Structures

twist layer (1D)



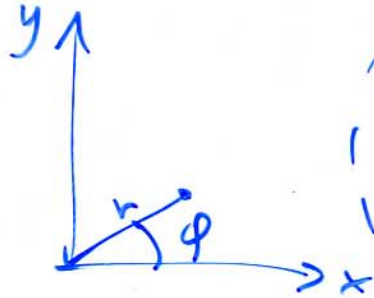
$$\nabla^2\theta = 0 \Rightarrow \frac{\partial\theta}{\partial z} = \text{const.} = \frac{\pi}{2d}$$

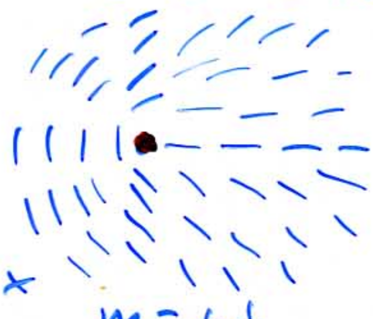
$$\frac{F}{\text{area}} = \int_0^d dz\, \tfrac{1}{2} K_{22}\left(\frac{\pi}{2d}\right)^2 = \frac{\pi^2}{8d} K_{22}$$

Curvature distributed evenly minimizes energy

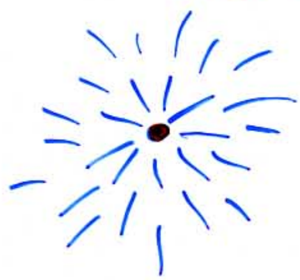
Disclinations (2D)

Polar coordinates (r, φ); $\theta = (\pm) m\varphi + \theta_0$



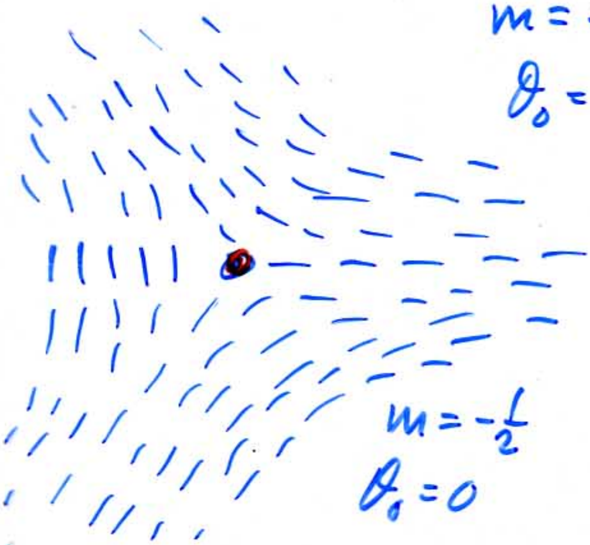


$m = +\frac{1}{2}$
$\theta_0 = 0$

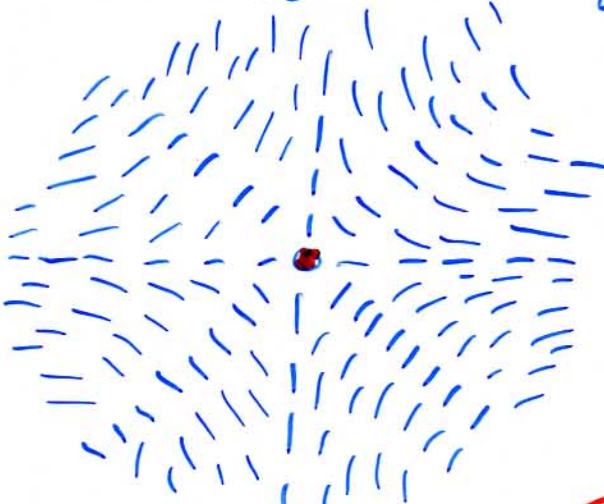


$m = +1$
$\theta_0 = 0$

$m = +1$
$\theta_0 = \frac{\pi}{2}$



$m = -\frac{1}{2}$
$\theta_0 = 0$



$m = -1$
$\theta_0 = 0$

[Invariant in z]

$$\frac{F}{\text{length}} = \int_\epsilon^R 2\pi r\, dr\, \frac{1}{2} K \left(\frac{m}{r}\right)^2 = \pi K m^2 \ln \frac{R}{\epsilon} + E_{core}$$

cutoff distance

"core" size

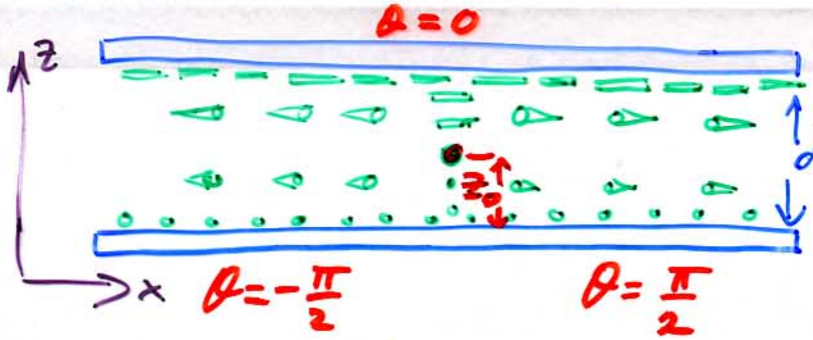
<u>Note</u>: for $m = \pm\frac{1}{2}$ need "branch cuts" for the vector field $\hat{n}$, while <u>physically</u> the nematic is continuous.

These are <u>splay-bend</u> disclinations (no twist involved.)

Planar Structures

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

(Invariant in y)



Solve by conformal mapping

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

* $$\frac{F}{\text{length}} = \frac{\pi K}{4}\left[\ln\left(\frac{d}{2\pi\epsilon}\right) + \ln\csc\left(\frac{\pi z_0}{d}\right)\right] \quad \epsilon \ll d$$

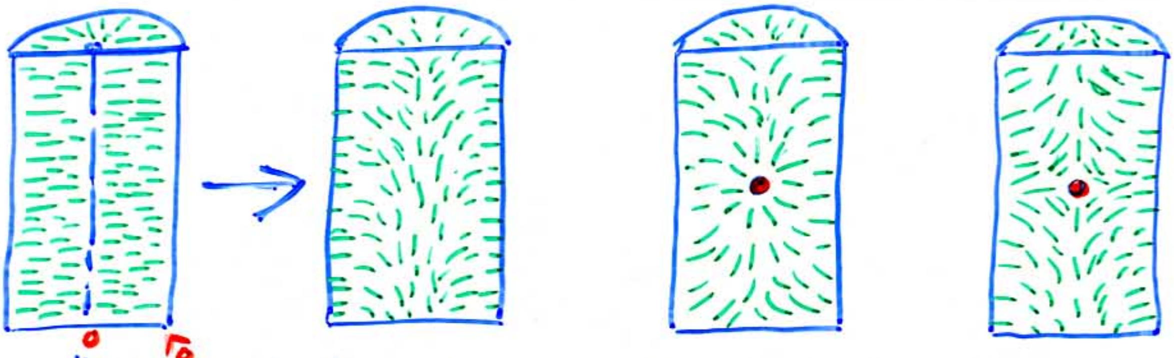
* Since $\nabla^2\theta=0$ is linear, add any linear fcn of z, or a constant to the solution; energy is independent of orientation of line relative to surface directions.

* 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 nematics their name.

3D structures ($\hat{n}$ no longer planar)

* point disclinations are possible
* Integer index ($m=1$) disclination disappear!



"escape" to the third dimension

"hedgehog"

"negative hedgehog"

For the cylinder of radius r_0, assume $n_r = \cos\theta$, $n_z = \sin\theta$

$n_\varphi = 0$:

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

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

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

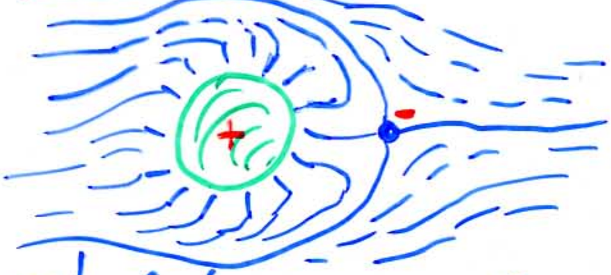
Solution $\theta = 2\tan^{-1}\left(\frac{r_0}{r}\right) - \frac{\pi}{2}$.

$\frac{F}{\text{length}} = 3\pi K$ independent of r_0. This is less than the disclination energy, surely for $\ln\frac{r_0}{\epsilon} > 3$.

Note: Index $\pm\frac{1}{2}$ disclinations cannot escape. They are topologically stabilized by their "Mobius" geometry.

Nematic emulsions: A. droplets of isotropic liquid suspended in a nematic:

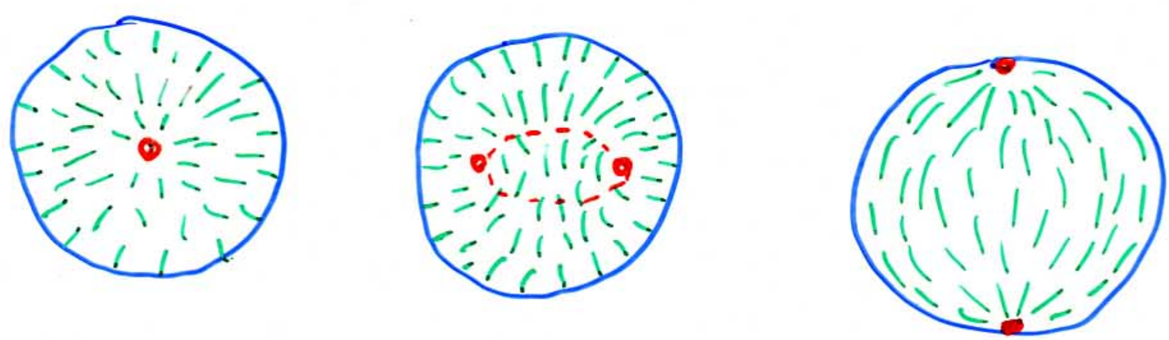
Example: normal boundary conditions at interface



Pearl chains:

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

B. Droplets of nematic suspended in an isotropic matrix (solid or liquid): For $\perp$ or $\parallel$ boundary conditions, need disclinations in the structure of the droplet:



Field effects

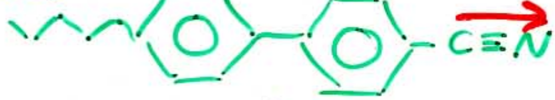
① Anisotropy of susceptibility

Magnetic field: <u>diamagnetic</u> $\chi \sim 10^{-6}$ & negative.

π electrons in benzene rings are good at producing currents to <u>oppose</u> applied H.

Therefore rings tend to align <u>parallel</u> to H.

Electric field: Combination of <u>electronic</u> and <u>dipolar</u> effects:



large dipole dominates response: $\hat{n} \parallel E$.

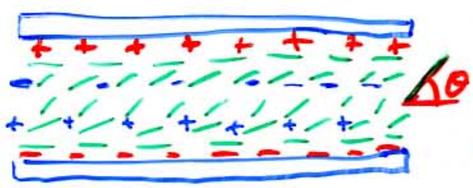
Magnetic free energy density:

$$f_H = \frac{1}{2}\chi_a H^2 \sin^2\theta$$

$$\chi_a = \chi_\parallel - \chi_\perp$$

Electric field – more complicated due to large polarizations.

$\vec{D}, \vec{E}$ ↓ z



± free charges – source of D field

± polarization charges – contribute to E field

$\vec{D}$ = constant through layer. $\vec{E}$ <u>not</u> constant.

Dielectric free energy: $f_E = \frac{1}{8\pi}\vec{E}\cdot\vec{D} = \frac{1}{8\pi}\frac{D^2}{\epsilon_{zz}}$

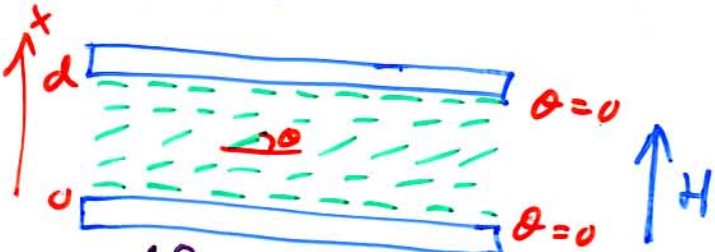
f_E minimized when $\epsilon_{zz} = \epsilon_\perp \cos^2\theta + \epsilon_\parallel \sin^2\theta$ is max.

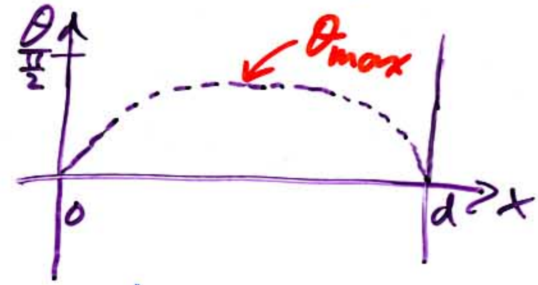
For pentyl-cyano-biphenyl, $\epsilon_\parallel - \epsilon_\perp \sim 12$, so $\hat{n} \parallel \vec{D}$

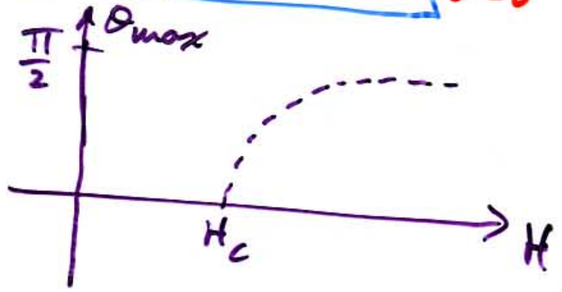
* Generally in a <u>finite</u> sample surface alignment and field alignment can compete. At low fields surface wins. At high field field wins, depending on sample dimensions.

Calculus of variations and Linear Stability Analysis.

Example: Frederiks transition in splay-bend geometry







boundary condition:
$\theta(0) = \theta(d) = 0$

$$\frac{F}{\text{area}} = \int_0^d dx\Big[\underbrace{\left(\tfrac{1}{2}K_{11}\cos^2\theta + \tfrac{1}{2}K_{33}\sin^2\theta\right)}_{A(\theta)}\left(\frac{d\theta}{dx}\right)^2 \underbrace{- \tfrac{1}{2}\chi_a H^2 \sin^2\theta}_{C(\theta)}\Big]$$

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

<u>Calculus of variations</u>: find $\theta(x)$ which minimizes this free energy. For the solution $\theta_0(x)$, if we add any any small perturbing function $\varphi(x)$ to $\theta_0(x)$, to first order in φ, F will not change ($\delta F_1 = 0$) and to second order in φ, F will <u>increase</u> ($\delta F_2 > 0$). This proves that "locally" in function space, $\theta_0(x)$ minimizes F.

To carry out this process, set $\theta = \theta_0 + \varphi$ and expand the integrand to second order in φ, integrating by parts to convert factors of $\frac{d\varphi}{dx}$ to φ, as necessary.

<u>Note</u>: φ must respect the boundary conditions on θ.

$$\frac{F}{\text{area}} = \int_0^d dx\left[\left(A(\theta_0)+A'(\theta_0)\varphi+\tfrac12 A''(\theta_0)\varphi^2\right)\left(\left(\frac{d\theta_0}{dx}\right)^2+2\frac{d\theta_0}{dx}\frac{d\varphi}{dx}+\left(\frac{d\varphi}{dx}\right)^2\right) + C(\theta_0)+C'(\theta_0)\varphi+\tfrac12 C''(\theta_0)\varphi^2\right]$$

first order

$$= \frac{F}{\text{area}}(\theta_0) + \int_0^d dx\left[2A(\theta_0)\frac{d\theta_0}{dx}\frac{d\varphi}{dx} + A'(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2\varphi + C'(\theta_0)\varphi\right]$$

$$+ \int_0^d dx\left[\tfrac12 A''(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2\varphi^2 + A(\theta_0)\left(\frac{d\varphi}{dx}\right)^2 + 2A'(\theta_0)\frac{d\theta_0}{dx}\frac{d\varphi}{dx}\varphi + \tfrac12 C''(\theta_0)\varphi^2\right]$$

second order

$$= \frac{F(\theta_0)}{\text{area}} + \underbrace{\int_0^d dx\left[-2\frac{d}{dx}\left(A(\theta_0)\frac{d\theta_0}{dx}\right) + A'(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2 + C'(\theta_0)\right]\varphi}$$

To guarantee that this integral is 0 for any φ, the factor [- - - -] must be 0. This is the Euler Lagrange equation:

$$-2A(\theta_0)\frac{d^2\theta_0}{dx^2} - A'(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2 + C'(\theta_0) = 0$$

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

$$\frac{d\theta_0}{dx} = \pm\left[\frac{C(\theta_0)+Q}{A(\theta_0)}\right]^{1/2}$$

where Q is a constant of integration.

For second order term: integration by parts:

$$A(\theta_0)\left(\frac{d\varphi}{dx}\right)^2 \longrightarrow -\left[\frac{d}{dx}\left(A(\theta_0)\frac{d\varphi}{dx}\right)\right]\varphi$$

$$2A'(\theta_0)\frac{d\theta_0}{dx}\frac{d\varphi}{dx}\varphi \longrightarrow -A''(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2\varphi^2 - A'(\theta_0)\frac{d^2\theta_0}{dx^2}\varphi^2$$

Second order term:

$$\frac{\delta F_2}{\text{area}} = \int_0^d dx \left[\phi \mathcal{L} \phi \right], \text{ where } \mathcal{L} = -\frac{d}{dx}\left(A(\theta_0)\frac{d}{dx}\right) + V(x)$$

and $V(x) = -\frac{1}{2}A''(\theta_0)\left(\frac{d\theta_0}{dx}\right)^2 - A'(\theta_0)\frac{d^2\theta_0}{dx^2} + \frac{1}{2}C''(\theta_0)$

this should remind you of $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$, except that we have $-\frac{d}{dx}\left(g(x)\frac{d}{dx}\right)$. The important thing is that $\mathcal{L}$ is a "Hermitian", or "self-adjoint", or "symmetric" operator:

[For 2 functions ϕ_1 and ϕ_2 obeying the correct boundary conditions:
$$\int_0^d dx\, \phi_1 \mathcal{L} \phi_2 = \int_0^d dx\, \phi_2 \mathcal{L} \phi_1$$
]

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

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

Now, from what you learned in QM, or following the general discussion of the "Sturm Liouville Problem" (see Morse & Feshbach) the operator $\mathcal{L}$ 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 ϕ_i has an eigenvalue C_i.

Moreover There is a lowest eigenvalue C_1 and its eigenfunction ϕ_1 has no nodes in the domain $0<x<d$, if $g(x)>0$ in that domain.

Now, expand our test function ϕ in the eigenfunctions of $\mathcal{L}$: $\phi = \sum a_i \phi_i$, and assume ϕ_i are normalized so that $\int_0^d dx\, \phi_i^2 = 1$.

Then $$\frac{\delta F_2}{\text{area}} = \int_0^d dx\, \phi\, \mathcal{L}\phi = \sum a_i^2 C_i$$

If $C_1>0$ this is positive. If $C_1<0$, then ϕ_1 clearly lowers the free energy and θ_0 is not a minimizing function.

Linear Stability Analysis: For a given free energy integral and solution θ_0, determine $\mathcal{L}$ 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, set $\theta_0(x)\equiv 0$ and gradually increase the magnetic field:

For $\theta_0(x) \equiv 0$, $A(\theta_0) = \frac{1}{2}K_{11}\cos^2\theta_0 + \frac{1}{2}K_{33}\sin^2\theta_0 = \frac{1}{2}K_{11}$

$$V(x) = \frac{1}{2}C''(\theta_0(x)) = -\frac{1}{2}\chi_a H^2 \cos 2\theta_0 = -\frac{1}{2}\chi_a H^2$$

$$\mathcal{L} = -\frac{1}{2}K_{11}\frac{d^2}{dx^2} - \frac{1}{2}\chi_a H^2$$

The eigenfunctions of $\mathcal{L}$ are $\varphi_n = \sin\frac{n\pi x}{d}$, and eigenvalues

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

To find the critical value of the magnetic field for the instability, set $C_1 = 0$: $K_{11}\left(\frac{\pi}{d}\right)^2 - \chi_a H_c^2 = 0$

$$H_c = \frac{\pi}{d}\sqrt{\frac{K_{11}}{\chi_a}}.$$

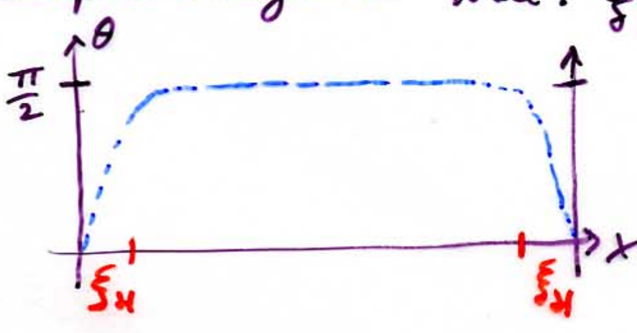
__Note__: If you try some arbitrary function (__not__ $\sin\frac{\pi x}{d}$) you will get a __higher__ H_c. For instance: try $\theta = A\frac{x}{d}\left(1-\frac{x}{d}\right)$, which seems reasonable. Calculate $\frac{F}{\text{area}}$ for this function, finding $H_c = \frac{\sqrt{10}}{d}\sqrt{\frac{K_{11}}{\chi_a}}$, slightly too large.

__For $H > H_c$__ Need to solve the E.L. equation. Simplify for now: $K_{11} = K_{33} = K$: $-2\left(\frac{1}{2}K\right)\frac{d^2\theta}{dx^2} - \frac{1}{2}\chi_a H^2(2\sin\theta\cos\theta) = 0$

$$\frac{d^2\theta}{dx^2} + \frac{1}{\xi_H^2}\sin\theta\cos\theta = 0, \quad \xi_H = \frac{1}{H}\sqrt{\frac{K}{\chi_a}}$$

Solution are elliptic integrals. Note: $\xi_{H_c} = \frac{d}{\pi}$

__High field__:



boundary layers of thickness ξ_H