Modeling of a Liquid Crystal Director

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1. *Vector method* (Oseen-Frank Equation)
2. *Q-tensor method* (Landau De Genne and Berreman Representation)
3. *Q-tensor method* (Dickman Representation)
4. *Fast Q-tensor method* (Gi-Dong Lee and Philip J. Bos Representation)

Oseen-Frank Equation (Vector Method)

- The axis of uniaxial symmetry being parallel to a unit vector $\vec{\mathbf{n}}$
- Consider a very small spatial region inside a macroscopic sample of nematic liquid crystal that contains a sufficiently large number of molecules.

  $\rightarrow$ long-range orientational order
- Consider the free energy associated with a distortion in the director field.
- Parallel alignment of all the local directors represents the equilibrium state, or the state of minimum free energy.

  ($\dfrac{dn_\alpha}{dx_\beta} = 0$, when distorted $\dfrac{dn_\alpha}{dx_\beta} \neq 0$)

$$f(distorted) = f_0(equilibrium) + \Delta f$$

- In general $\frac{dn_\alpha}{dx_\beta} << (\text{molecular dimension})^{-1} \Rightarrow$ slow variation

- The requirements of F_d

1.Expand in powers of the $\frac{dn_\alpha}{dx_\beta}$ around $\frac{dn_\alpha}{dn_\beta} = 0$

(director's direction = 1 -> six parameter)

2. F_d must be even in the n_α

because head and tail of a nematic director represent the same physical state (keep the degeneracy)

3.Discard term of the form

Free energy density $\vec{\nabla}\cdot\vec{U}(\vec{r})$.

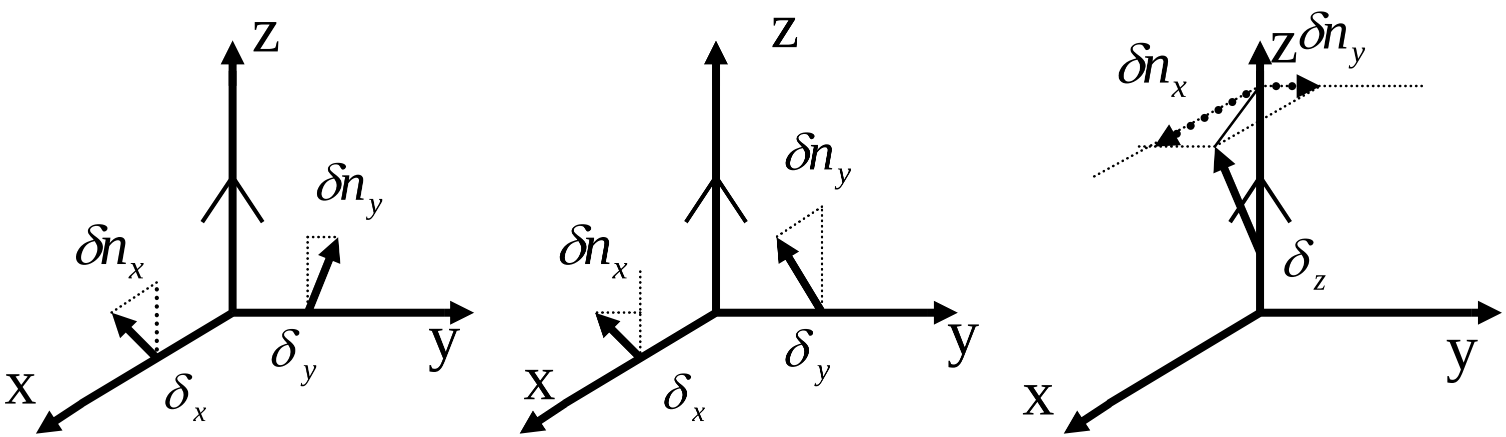
$$\vec{\nabla}\cdot\vec{U}(\vec{r})=\frac{1}{2}\{k_{11}(\vec{\nabla}\cdot\vec{n}(\vec{r}))^2+k_{22}(\vec{n}(\vec{r})\cdot\vec{\nabla}\times\vec{n}(\vec{r}))^2$$
$$+k_{33}(\vec{n}(\vec{r})\times\vec{\nabla}\times\vec{n}(\vec{r}))^2\}$$

K_{11} : splay elastic constant
K_{22} : twist elastic constant ⟶ Frank elastic constants
K_{33} : bend elastic constant

K's : units of Energy/length (dyne)
Intermolecular interaction energy ≈ 0.01 Ev
the separation between two molecules ≈ 10Å

- Geometrical observation of the deformations

If the imposed orientations are not parallel



$$s_1 = \frac{\partial n_x}{\partial x}$$

$$s_2 = \frac{\partial n_y}{\partial y}$$

$$t_1 = -\frac{\partial n_y}{\partial y}$$

$$t_2 = \frac{\partial n_x}{\partial y}$$

right handed

$$b_1 = \frac{\partial n_x}{\partial z}$$

$$b_2 = \frac{\partial n_y}{\partial z}$$

Partial derivatives in terms of n_x $\frac{\partial n_x}{\partial x}, \frac{\partial n_x}{\partial y}, \frac{\partial n_x}{\partial z}$

Partial derivatives in terms of n_y $\frac{\partial n_y}{\partial x}, \frac{\partial n_y}{\partial y}, \frac{\partial n_y}{\partial z}$

Small variation of n_x

$$\Delta n_x = \frac{\partial n_x}{\partial x}\Delta x + \frac{\partial n_x}{\partial y}\Delta y + \frac{\partial n_x}{\partial z}\Delta z$$

$$n_x = a_1 x + a_2 y + a_3 z + O(r^2) = s_1 x + t_2 y + b_1 z + O(r^2)$$

$$\Delta n_y = \frac{\partial n_y}{\partial x}\Delta x + \frac{\partial n_y}{\partial y}\Delta y + \frac{\partial n_y}{\partial z}\Delta z$$

$$n_y = a_4 x + a_5 y + a_6 z + O(r^2) = -t_1 x + s_2 y + b_2 z + O(r^2)$$

$$\Delta n_z = \frac{\partial n_z}{\partial x}\Delta x + \frac{\partial n_z}{\partial y}\Delta y + \frac{\partial n_z}{\partial z}\Delta z$$

Δn_z ?

$$0 = \vec{\nabla} n^2 = \vec{\nabla}(n_k^2) = 2 n_k \vec{\nabla} n_k = (2 n_x \vec{\nabla} n_x + 2 n_y \vec{\nabla} n_y + 2 n_z \vec{\nabla} n_z)$$

$$\nabla n_z = 0 \quad \Rightarrow \quad \frac{\partial n_z}{\partial x}, \frac{\partial n_z}{\partial y}, \frac{\partial n_z}{\partial z} \quad \Rightarrow \quad 0$$

$$\Delta n_z = 0 \quad \Rightarrow \quad n_z = 1 + O(r^2),\ r^2 = x^2 + y^2 + z^2$$

Therefore,

$$n_x = a_1 x + a_2 y + a_3 z + O(r^2) = s_1 x + t_2 y + b_1 z + O(r^2)$$

$$n_y = a_4 x + a_5 y + a_6 z + O(r^2) = -t_1 x + s_2 y + b_2 z + O(r^2)$$

$$n_z = 1 + O(r^2)$$

Gibb's free energy

$$G = \int_V g \, dv$$

$$g = k_i a_i + \frac{1}{2} k_{ij} a_i a_j \quad (i, j = 1, \cdots, 6, \qquad k_{ij} = k_{ji})$$

g : free energy density

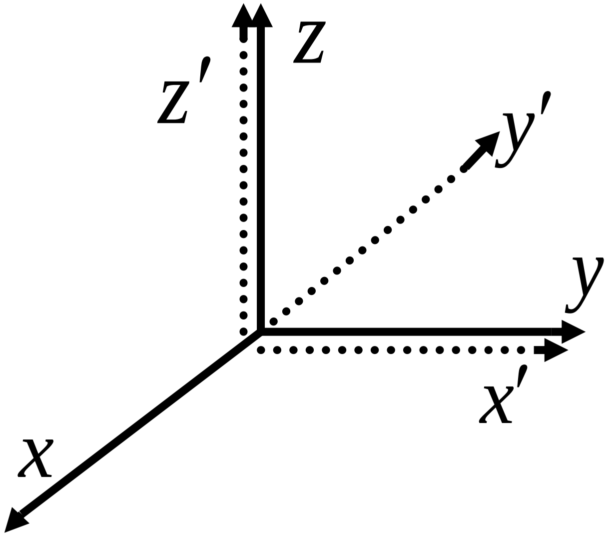
As g is invariant to arbitrary coordinate system, for a new coordinate system and the new curvature components a_i'

$$g = k_i a_i' + \frac{1}{2} k_{ij} a_i' a_j'$$

New coordinate system 1

As the choice of x-direction was arbitrary, any rotation of the coordinate system around z is permissible.

Rotation on the center of z axis



$$x' = y, \quad y' = -x, \quad z' = z$$

$$n_x = a_1 x + a_2 y + a_3 z$$

$$n_y = a_4 x + a_5 y + a_6 z$$

$$n'_x = a'_1 x' + a'_2 y' + a'_3 z'$$

$$n'_y = a'_4 x' + a'_5 y' + a'_6 z'$$

$$n_x = -n_y' \,,\;\; n_y = n_x'$$

from above,

$$a_1 x + a_2 y + a_3 z = -(a_4' x' + a_5' y' + a_6' z')$$
$$= a_5' x - a_4' y - a_6' z$$

$$a_1 = a_5' \quad , \quad a_2 = -a_4' \quad , \quad a_3 = -a_6'$$

also,

$$a_4 x + a_5 y + a_6 z = a_1' x' + a_2' y' + a_3' z'$$
$$= -a_2' x + a_1' y + a_3' z$$

$$a_4 = -a_2' \quad , \quad a_5 = a_1' \quad , \quad a_6 = a_3'$$

As $k_i a_i = k_i a_i'$

$$k_1 a_1 + k_2 a_2 + k_3 a_3 + k_4 a_4 + k_5 a_5 + k_6 a_6$$
$$= k_1 a_1' + k_2 a_2' + k_3 a_3' + k_4 a_4' + k_5 a_5' + k_6 a_6'$$
$$= k_1 a_5 - k_2 a_4 + k_3 a_3 - k_4 a_2 + k_5 a_1 - k_6 a_3$$

So $k_5 = k_1, k_2 = -k_4, k_3 = -k_6, k_4 = -k_2, k_5 = k_1, k_6 = k_3$

$$\Rightarrow k_5 = k_1, k_4 = -k_2, k_3 = k_6 = 0$$

also, $$\frac{1}{2}k_{ij}a_i a_j = \frac{1}{2}k_{ij}a'_i a'_j$$

$$\begin{array}{cccccc} a_1 & a_2 & a_3 & a_4 & a_5 & a_6 \\ a'_1 & a'_2 & a'_3 & a'_4 & a'_5 & a'_6 \\ \Downarrow & \Downarrow & \Downarrow & \Downarrow & \Downarrow & \Downarrow \\ a_5 & -a_4 & a_6 & -a_2 & a_1 & -a_3 \end{array}$$

therefore, $$k_{ij}a_i a_j = k_{ij}a'_i a'_j = a'_i k_{ij} a'_j$$

$$= (a'_1 \quad a'_2 \quad a'_3 \quad a'_4 \quad a'_5 \quad a'_6)\begin{vmatrix} k_{11} & k_{12} & k_{13} & k_{14} & k_{15} & k_{16} \\ k_{21} & k_{22} & k_{23} & k_{24} & k_{25} & k_{26} \\ k_{31} & k_{32} & k_{33} & k_{34} & k_{35} & k_{36} \\ k_{41} & k_{42} & k_{43} & k_{44} & k_{45} & k_{46} \\ k_{51} & k_{52} & k_{53} & k_{54} & k_{55} & k_{56} \\ k_{61} & k_{62} & k_{63} & k_{64} & k_{65} & k_{66} \end{vmatrix}\begin{vmatrix} a'_1 \\ a'_2 \\ a'_3 \\ a'_4 \\ a'_5 \\ a'_6 \end{vmatrix}$$

$$= (a_5 \quad -a_4 \quad a_6 \quad -a_2 \quad a_1 \quad -a_3)\begin{bmatrix} k_{11} & k_{12} & k_{13} & k_{14} & k_{15} & k_{16} \\ k_{21} & k_{22} & k_{23} & k_{24} & k_{25} & k_{26} \\ k_{31} & k_{32} & k_{33} & k_{34} & k_{35} & k_{36} \\ k_{41} & k_{42} & k_{43} & k_{44} & k_{45} & k_{46} \\ k_{51} & k_{52} & k_{53} & k_{54} & k_{55} & k_{56} \\ k_{61} & k_{62} & k_{63} & k_{64} & k_{65} & k_{66} \end{bmatrix}\begin{bmatrix} a_5 \\ -a_4 \\ a_6 \\ -a_2 \\ a_1 \\ -a_3 \end{bmatrix}$$

$$= (a_1 \quad -a_2 \quad -a_3 \quad -a_4 \quad a_5 \quad a_6)\begin{bmatrix} k_{55} & -k_{54} & -k_{56} & -k_{52} & k_{51} & k_{53} \\ -k_{45} & k_{44} & k_{46} & k_{42} & -k_{41} & -k_{43} \\ -k_{65} & k_{64} & k_{66} & k_{62} & -k_{61} & -k_{63} \\ -k_{25} & k_{24} & k_{26} & k_{22} & -k_{21} & -k_{23} \\ k_{15} & -k_{14} & -k_{16} & -k_{12} & k_{11} & k_{13} \\ k_{35} & -k_{34} & -k_{36} & -k_{32} & k_{31} & k_{33} \end{bmatrix}\begin{bmatrix} a_1 \\ -a_2 \\ -a_3 \\ -a_4 \\ a_5 \\ a_6 \end{bmatrix}$$

$$=\begin{pmatrix} a_1 & a_2 & a_3 & a_4 & a_5 & a_6 \end{pmatrix}\begin{vmatrix} k_{55} & -k_{54} & -k_{56} & -k_{52} & k_{51} & k_{53} \\ -k_{45} & k_{44} & k_{46} & k_{42} & -k_{41} & -k_{43} \\ -k_{65} & k_{64} & k_{66} & k_{62} & -k_{61} & -k_{63} \\ -k_{25} & k_{24} & k_{26} & k_{22} & -k_{21} & -k_{23} \\ k_{15} & -k_{14} & -k_{16} & -k_{12} & k_{11} & k_{13} \\ k_{35} & -k_{34} & -k_{36} & -k_{32} & k_{31} & k_{33} \end{vmatrix}\begin{vmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{vmatrix}$$

therefore,

$$\left.\begin{array}{l} k_{11} = k_{55}, k_{22} = k_{44} \\ k_{33} = k_{66}, k_{12} = -k_{54} \\ k_{13} = -k_{56}, k_{14} = -k_{52} \\ k_{16} = k_{53}, k_{23} = k_{46}, k_{46} = -k_{23} \end{array}\right)$$

$$\Rightarrow k_{46} = 0, k_{35} = -k_{61} = k_{53}$$

and

$$\left.\begin{array}{l} k_{25} = -k_{41}, k_{26} = -k_{43}, k_{34} = k_{62} \\ k_{46} = k_{64} = k_{23} = k_{32} = 0 \\ k_{35} = k_{61} = k_{16} = k_{53} = 0 \end{array}\right)$$

$$\Rightarrow k_{26} = k_{43} = k_{62} = k_{34} = 0$$

$$k_{36} = -k_{63}$$

$$\Rightarrow k_{36} = k_{63} = 0$$

$$k_{56} = k_{13} = -k_{56}$$

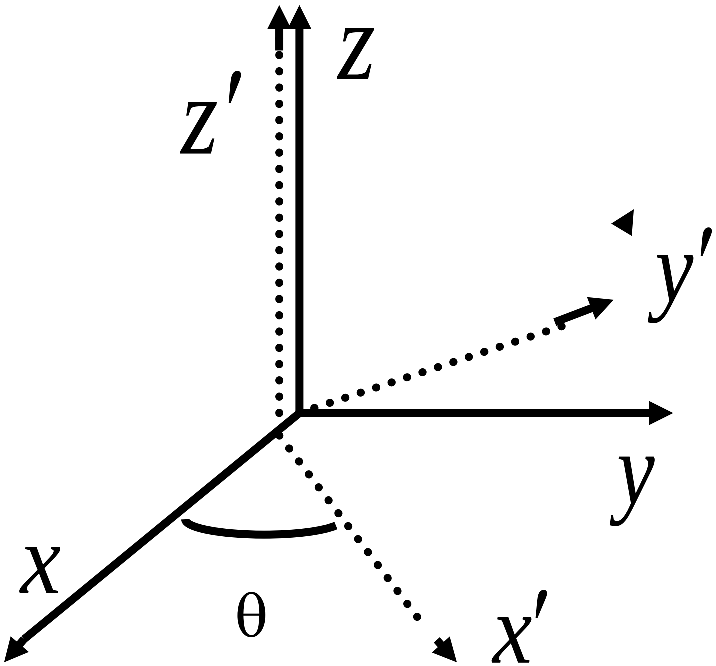
$$\Rightarrow k_{56} = k_{13} = k_{65} = k_{31} = 0$$

therefore,

$$k_{ij} = \begin{vmatrix} k_{11} & k_{12} & k_{13} & k_{14} & k_{15} & k_{16} \\ k_{21} & k_{22} & k_{23} & k_{24} & k_{25} & k_{26} \\ k_{31} & k_{32} & k_{33} & k_{34} & k_{35} & k_{36} \\ k_{41} & k_{42} & k_{43} & k_{44} & k_{45} & k_{46} \\ k_{51} & k_{52} & k_{53} & k_{54} & k_{55} & k_{56} \\ k_{61} & k_{62} & k_{63} & k_{64} & k_{65} & k_{66} \end{vmatrix} = \begin{vmatrix} k_{11} & k_{12} & 0 & k_{14} & k_{15} & 0 \\ k_{12} & k_{22} & 0 & k_{24} & -k_{14} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ k_{14} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ k_{15} & -k_{14} & 0 & -k_{12} & k_{11} & k_{56} \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{vmatrix}$$

$k_{11}, k_{12}, k_{14}, k_{15}, k_{22}, k_{24}, k_{33}$: 7 coefficients

New coordinate system 2



$$x' = x\cos\theta + y\sin\theta$$

$$y' = -x\sin\theta + y\cos\theta$$

$$\begin{cases} n_x = a_1 x + a_2 y + a_3 z \\ n_y = a_4 x + a_5 y + a_6 z \end{cases}$$

$$\begin{cases} n'_x = a'_1 x' + a'_2 y' + a'_3 z' \\ n'_y = a'_4 x' + a'_5 y' + a'_6 z' \end{cases}$$

$$\theta = 45°$$

$$\begin{pmatrix} n'_x \\ n'_y \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} n_x \\ n_y \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} n_x + n_y \\ -n_x + n_y \end{pmatrix}$$

$$n_x' = \frac{1}{\sqrt{2}}(n_x + n_y), \quad n_y' = \frac{1}{\sqrt{2}}(-n_x + n_y)$$

$$n_x' = \frac{1}{\sqrt{2}}(n_x + n_y) = \frac{1}{\sqrt{2}}[(a_1 + a_4)x + (a_2 + a_5)y + (a_3 + a_6)z]$$

$$n_x' = a_1'x' + a_2'y' + a_3'z' = a_1'\frac{1}{\sqrt{2}}(x + y) + a_2'\frac{1}{\sqrt{2}}(-x + y) + a_3'z'$$

$$= \frac{1}{\sqrt{2}}x(a_1' - a_2') + \frac{1}{\sqrt{2}}y(a_1' + a_2') + a_3'z$$

$$a_1 + a_4 = a_1' - a_2', \quad a_2 + a_5 = a_1' + a_2', \quad \frac{1}{\sqrt{2}}(a_3 + a_6) = a_3'$$

$$n_y' = \frac{1}{\sqrt{2}}(-n_x + n_y) = \frac{1}{\sqrt{2}}[(a_4 - a_1)x + (a_5 - a_2)y + (a_6 - a_3)z]$$

$$n_y' = a_4' \frac{1}{\sqrt{2}}(x + y) + a_5' \frac{1}{\sqrt{2}}(-x + y) + a_6' z'$$

$$= \frac{1}{\sqrt{2}} x(a_4' - a_5') + \frac{1}{\sqrt{2}} y(a_4' + a_5') + a_6' z$$

$$a_4 - a_1 = a_4' - a_5', \quad a_5 - a_2 = a_4' + a_5', \quad a_6' = \frac{1}{\sqrt{2}}(a_6 - a_3)$$

$$a_1 + a_4 = a_1' - a_2', \quad a_2 + a_5 = a_1' + a_2', \quad \frac{1}{\sqrt{2}}(a_3 + a_6) = a_3'$$

$$a_4 - a_1 = a_4' - a_5', \quad a_5 - a_2 = a_4' + a_5', \quad a_6' = \frac{1}{\sqrt{2}}(a_6 - a_3)$$

→ Relationship btn. two coordinates

$$a_1' = \frac{a_1 + a_2 + a_4 + a_5}{2}, \quad a_2' = \frac{-a_1 + a_2 - a_4 + a_5}{2}$$

$$a_3' = \frac{1}{\sqrt{2}}(a_3 + a_6), \quad a_4' = \frac{-a_1 - a_2 + a_4 + a_5}{2}$$

$$a_5' = \frac{a_1 - a_2 - a_4 + a_5}{2}, \quad a_6' = \frac{1}{\sqrt{2}}(a_6 - a_3)$$

again

$$k_{ij}a_ia_j = k_{ij}a'_ia'_j$$

$$\begin{pmatrix} a_1 & a_2 & a_3 & a_4 & a_5 & a_6 \end{pmatrix} \begin{vmatrix} k_{11} & k_{12} & 0 & k_{14} & k_{15} & 0 \\ k_{21} & k_{22} & 0 & k_{24} & -k_{14} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ k_{14} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ k_{15} & -k_{14} & 0 & -k_{12} & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{vmatrix} \begin{vmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ a_5 \\ a_6 \end{vmatrix}$$

$$= \begin{pmatrix} \frac{a_1 + a_2 + a_4 + a_5}{2} \\ \frac{-a_1 + a_2 - a_4 + a_5}{2} \\ \frac{a_3 + a_6}{\sqrt{2}} \\ \frac{-a_1 - a_2 + a_4 + a_5}{2} \\ \frac{a_1 - a_2 - a_4 + a_5}{2} \\ \frac{a_6 - a_3}{\sqrt{2}} \end{pmatrix}^T \begin{vmatrix} k_{11} & k_{12} & 0 & k_{14} & k_{15} & 0 \\ k_{21} & k_{22} & 0 & k_{24} & -k_{14} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ k_{14} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ k_{15} & -k_{14} & 0 & -k_{12} & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{vmatrix} \begin{pmatrix} \frac{a_1 + a_2 + a_4 + a_5}{2} \\ \frac{-a_1 + a_2 - a_4 + a_5}{2} \\ \frac{a_3 + a_6}{\sqrt{2}} \\ \frac{-a_1 - a_2 + a_4 + a_5}{2} \\ \frac{a_1 - a_2 - a_4 + a_5}{2} \\ \frac{a_6 - a_3}{\sqrt{2}} \end{pmatrix}$$

$$a_1 a_1 \Rightarrow$$

$$k_{11} = \frac{1}{4}(k_{11} - k_{12} - k_{14} + k_{15} + k_{22} + k_{24} + k_{14} - k_{14} + k_{24} + k_{22} + k_{12} + k_{15} + k_{14} + k_{12} + k_{11})$$

$$k_{11} = k_{15} + k_{22} + k_{24} \quad \Leftrightarrow \quad k_{15} = k_{11} - k_{22} - k_{24}$$

$$a_2 a_1 \Rightarrow$$

$$k_{12} + k_{12} = \frac{k_{11}}{4} \times 2 - \frac{k_{12}}{4} + \frac{k_{12}}{4} - \frac{k_{14}}{4} \times 2 + \frac{k_{15}}{4} - \frac{k_{15}}{4} - \frac{k_{22}}{4} \times 2 - \frac{k_{14}}{4} \times 2 - \frac{k_{14}}{4} \times 2 + \frac{k_{22}}{4} \times 2 - \frac{k_{14}}{4} \times 2 - \frac{k_{11}}{4} \times 2$$

$$k_{12} = -k_{14} = -k_{45} = k_{25}$$

So,

$$k_{ij} = \begin{pmatrix} k_{11} & k_{12} & 0 & -k_{12} & (k_{11}-k_{22}-k_{24}) & 0 \\ k_{12} & k_{22} & 0 & k_{24} & k_{12} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ -k_{12} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ (k_{11}-k_{22}-k_{24}) & k_{12} & 0 & -k_{12} & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{pmatrix}$$

$k_{11}, k_{12}, k_{22}, k_{24}, k_{33}$: five coefficien t

Gibb's free energy density *g*

$$g = k_i a_i + \frac{1}{2} k_{ij} a_i a_j = g_1 + g_2$$

$$g_1 = k_i a_i = k_1 a_1 + k_2 a_2 - k_2 a_4 + k_1 a_5$$

$$= k_1 (a_1 + a_5) + k_2 (a_2 - a_4) = k_1 (s_1 + s_2) + k_2 (t_1 + t_2)$$

$$g_2 = \frac{1}{2} k_{ij} a_i a_j$$

$$= \frac{1}{2} [k_{11} a_1 a_1 + k_{12} a_1 a_2 - k_{12} a_1 a_4 + (k_{11} - k_{22} - k_{24}) a_1 a_5 + k_{12} a_2 a_1$$

$$+ k_{22} a_2 a_2 + k_{24} a_2 a_4 + k_{12} a_2 a_5 + k_{33} a_3 a_3 - k_{12} a_4 a_1 + k_{24} a_4 a_2$$

$$+ k_{22} a_4 a_4 - k_{12} a_4 a_5 + (k_{11} - k_{22} - k_{24}) a_5 a_1 + k_{12} a_5 a_2 - k_{12} a_5 a_4$$

$$+ k_{11} a_5 a_5 + k_{33} a_6 a_6]$$

$$= \frac{1}{2}[k_{11}a_1^2 + k_{22}a_2^2 + k_{33}a_3^2 + k_{44}a_4^2 + k_{55}a_5^2 + k_{66}a_6^2 + 2k_{12}a_1a_2 - 2k_{12}a_1a_4 + 2k_{11}a_1a_5 - 2k_{22}a_1a_5$$

$$-2k_{24}a_1a_5 + 2k_{24}a_2a_4 + 2k_{12}a_2a_5 - 2k_{12}a_4a_5]$$

$$= \frac{1}{2}[k_{11}s_1^2 + k_{22}t_2^2 + k_{33}b_1^2 + k_{22}t_1^2 + k_{11}s_2^2 + k_{33}b_2^2 + 2k_{12}s_1t_2 + 2k_{12}s_1t_1 + 2k_{11}s_1s_2 - 2k_{22}s_1s_2$$

$$-2k_{24}s_1s_2 - 2k_{25}t_2t_1 + 2k_{12}t_2s_2 + 2k_{12}t_1s_2]$$

$$= \frac{1}{2}[k_{11}(s_1 + s_2)^2 + k_{22}(t_1 + t_2)^2 - 2k_{22}t_1t_2 + k_{33}(b_1^2 + b_2^2) + 2k_{12}(s_1 + s_2)(t_1 + t_2) - 2k_{22}s_1s_2$$

$$-2k_{24}s_1s_2 - 2k_{24}t_2t_1 - 2k_{22}(s_1s_2 + t_1t_2) - 2k_{24}(s_1s_2 + t_1t_2)]$$

$$= \frac{1}{2}k_{11}(s_1 + s_2)^2 + \frac{1}{2}k_{22}(t_1 + t_2)^2 + \frac{1}{2}k_{33}(b_1^2 + b_2^2) + k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1s_2 + t_1t_2)$$

Introducin g $s_0 = -\frac{k_1}{k_{11}}, \; t_0 = -\frac{k_2}{k_{22}}, \quad g' = g + \frac{1}{2}k_{11}s_0^2 + \frac{1}{2}k_{22}t_0^2$

$$g' = -k_{11}s_0(s_1 + s_2) - k_{22}t_0(t_1 + t_2) + \frac{1}{2}k_{11}s_0^2 + \frac{1}{2}k_{22}t_0^2$$

$$+\frac{1}{2}k_{11}(s_1 + s_2)^2 + \frac{1}{2}k_{22}(t_1 + t_2)^2 + \frac{1}{2}k_{33}(b_1^2 + b_2^2)$$

$$+k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1 s_2 + t_1 t_2)$$

$$= \frac{1}{2}k_{11}(s_1 + s_2 - s_0)^2 + \frac{1}{2}k_{22}(t_1 + t_2 - t_0)^2 + \frac{1}{2}k_{33}(b_1^2 + b_2^2)$$

$$+k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1 s_2 + t_1 t_2)$$

$$= \frac{1}{2}k_{11}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} - s_0\right)^2 + \frac{1}{2}k_{22}\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x} - t_0\right)^2$$

$$+\frac{1}{2}k_{33}\left(\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right) + k_{12}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)$$

$$-(k_{22} + k_{24})\left(\frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y} - \frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}\right)$$

$$\frac{\partial n_x}{\partial x}+\frac{\partial n_y}{\partial y}\Rightarrow \boxed{\vec{\nabla}\cdot\vec{n}\ \ splay}$$

$$\frac{\partial n_x}{\partial y}-\frac{\partial n_y}{\partial x}\Rightarrow (n_x=0)(\frac{\partial n_z}{\partial y}-\frac{\partial n_y}{\partial z})+(n_y=0)(\frac{\partial n_x}{\partial z}-\frac{\partial n_z}{\partial x})+(n_z=1)(\frac{\partial n_y}{\partial x}-\frac{\partial n_x}{\partial y})$$

$$\Rightarrow \boxed{-\vec{n}\cdot\vec{\nabla}\times\vec{n}\quad \text{twists}}$$

$$(\frac{\partial n_x}{\partial z})^2+(\frac{\partial n_y}{\partial z})^2\Rightarrow[(\vec{n}\cdot\vec{\nabla})\vec{n}]^2=[(n_x\frac{\partial}{\partial x}+n_y\frac{\partial}{\partial y}+n_z\frac{\partial}{\partial z})\vec{n}]^2=[n_z\frac{\partial}{\partial z}\vec{n}]^2$$

$$=(\frac{\partial n_x}{\partial z})^2+(\frac{\partial n_y}{\partial z})^2\Leftarrow \boxed{[\vec{\mathrm{n}}\times(\vec{\nabla}\times\vec{\mathrm{n}})]^2\ \ bend}$$

$$(\frac{\partial n_x}{\partial x}+\frac{\partial n_y}{\partial y})(\frac{\partial n_x}{\partial y}-\frac{\partial n_y}{\partial x})\Rightarrow \boxed{(\vec{\nabla}\cdot\vec{\mathrm{n}})(-\vec{n}\cdot\vec{\nabla}\times\vec{n})}$$

$$\frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y}-\frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}\Rightarrow \boxed{(\vec{\nabla}\cdot\vec{n})^2+(\vec{\nabla}\times\vec{n})^2-\vec{\nabla}\vec{n}:\vec{\nabla}\vec{n}}\longrightarrow$$

where,

$$\vec{\nabla}\vec{n}:\vec{\nabla}\vec{n} \Rightarrow [(\vec{a}_x \frac{\partial}{\partial x} + \vec{a}_y \frac{\partial}{\partial y} + \vec{a}_z \frac{\partial}{\partial z})(\vec{a}_x n_x + \vec{a}_y n_y + \vec{a}_z n_z)]^2$$

$$= [\vec{a}_x\vec{a}_x \frac{\partial n_x}{\partial x} + \vec{a}_x\vec{a}_y \frac{\partial n_y}{\partial x} + \vec{a}_x\vec{a}_z \frac{\partial n_z}{\partial x} + \vec{a}_y\vec{a}_x \frac{\partial n_x}{\partial x} + \vec{a}_y\vec{a}_y \frac{\partial n_y}{\partial x}$$

$$+ \vec{a}_y\vec{a}_z \frac{\partial n_z}{\partial x} + \vec{a}_z\vec{a}_x \frac{\partial n_x}{\partial x} + \vec{a}_z\vec{a}_y \frac{\partial n_y}{\partial x} + \vec{a}_z\vec{a}_z \frac{\partial n_z}{\partial x}]^2$$

$$= \left(\frac{\partial n_x}{\partial x}\right)^2 + \left(\frac{\partial n_y}{\partial x}\right)^2 + \left(\frac{\partial n_z}{\partial x}\right)^2 + \left(\frac{\partial n_x}{\partial y}\right)^2 + \left(\frac{\partial n_y}{\partial y}\right)^2$$

$$+ \left(\frac{\partial n_z}{\partial y}\right)^2 + \left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2 + \left(\frac{\partial n_z}{\partial z}\right)^2$$

so,

$$(\vec{\nabla}\cdot\vec{n})^2+(\vec{\nabla}\times\vec{n})^2-\vec{\nabla}\vec{n}:\vec{\nabla}\vec{n}$$

$$=\left(\frac{\partial n_x}{\partial x}+\frac{\partial n_y}{\partial y}+\frac{\partial n_z}{\partial z}\right)^2+\left(\frac{\partial n_z}{\partial y}-\frac{\partial n_y}{\partial z}\right)^2$$

$$+\left(\frac{\partial n_x}{\partial z}-\frac{\partial n_z}{\partial x}\right)^2+\left(\frac{\partial n_y}{\partial x}-\frac{\partial n_x}{\partial y}\right)^2-\left(\frac{\partial n_x}{\partial x}\right)^2-\left(\frac{\partial n_y}{\partial x}\right)^2$$

$$-\left(\frac{\partial n_z}{\partial x}\right)^2-\left(\frac{\partial n_x}{\partial y}\right)^2-\left(\frac{\partial n_y}{\partial y}\right)^2-\left(\frac{\partial n_z}{\partial y}\right)^2-\left(\frac{\partial n_x}{\partial z}\right)^2-\left(\frac{\partial n_y}{\partial z}\right)^2-\left(\frac{\partial n_z}{\partial z}\right)^2$$

$$=2\frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y}+2\frac{\partial n_y}{\partial y}\frac{\partial n_z}{\partial z}+2\frac{\partial n_x}{\partial x}\frac{\partial n_z}{\partial z}-2\frac{\partial n_z}{\partial y}\frac{\partial n_y}{\partial z}-2\frac{\partial n_x}{\partial z}\frac{\partial n_z}{\partial x}-2\frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}$$

$$=\frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y}-\frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}$$

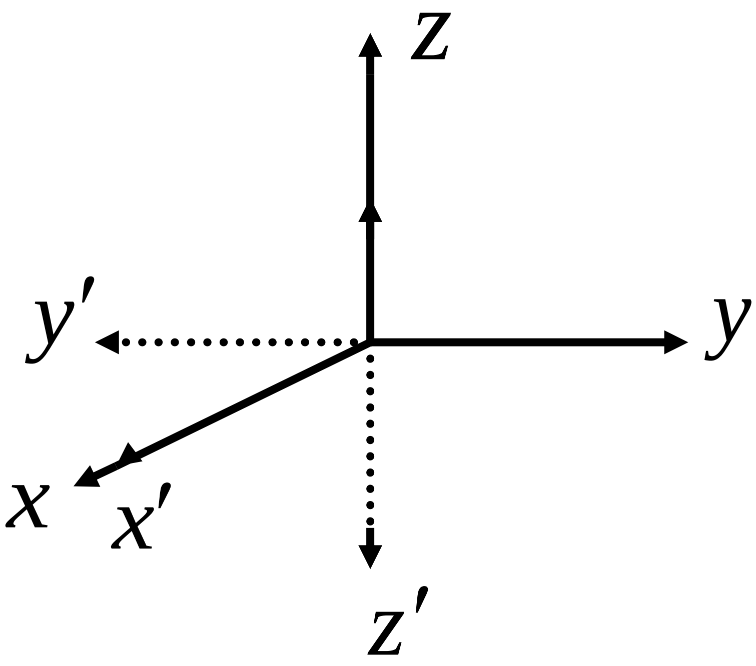
- Gibb's free energy density *g'*

$$g' = \frac{1}{2}k_{11}(\vec{\nabla}\cdot\vec{n}-s_0)^2+\frac{1}{2}k_{22}(\vec{n}\cdot\vec{\nabla}\times\vec{n}+t_0)^2$$

$$+\ \frac{1}{2}k_{33}[(\vec{n}\cdot\vec{\nabla})\vec{n}]^2+k_{12}(\vec{\nabla}\cdot\vec{n})(-\vec{n}\cdot\vec{\nabla}\times\vec{n})$$

$$-\ \frac{1}{2}(k_{22}+k_{24})[(\vec{\nabla}\cdot\vec{n})^2+(\vec{\nabla}\times\vec{n})^2-\vec{\nabla}\,\vec{n}:\vec{\nabla}\,\vec{n}]$$

Assumption for non-polar system



1. *the molecular are essentially non-polar with respect to the preferential oriented axis*

2. *The molecular are polar. But they are distributed equal likelihood in both direction*

then permissible transformation is

$$\vec{n}' = -\vec{n}, \qquad x' = x, \qquad y' = -y, \qquad z' = -z$$

$$n_x = a_1 x + a_2 y + a_3 z \leftrightarrow n'_{x'} = a'_1 x' + a'_2 y' + a'_3 z'$$

$$n_y = a_4 x + a_5 y + a_6 z \leftrightarrow n'_{y'} = a'_4 x' + a'_5 y' + a'_6 z'$$

one sign change due to director orientation

$$n'_{x'} = -n_x$$

$$a'_1 x' + a'_2 y' + a'_3 z' = a'_1 x - a'_2 y - a'_3 z = -a_1 x - a_2 y - a_3 z$$

$$a'_1 = -a_1, a'_2 = a_2, a'_3 = a_3$$

double sign change due to coordinate and director orientation

$$n'_{y'} = n_y$$

$$a'_4 x' + a'_5 y' + a'_6 z' = a'_4 x - a'_5 y - a'_6 z = a_4 x + a_5 y + a_6 z$$

$$a'_4 = a_4, a'_5 = -a_5, a'_6 = -a_6$$

So, $$n'_{x'} = -a_1 x' + a_2 y' + a_3 z' + O(r^2)$$
$$n'_{y'} = a_4 x' - a_5 y' - a_6 z' + O(r^2)$$

using $k_i a_i = k_i a'_i$

$$k_i a_i = -k_1 a_1 + k_2 a_2 + k_3 a_3 + k_4 a_4 - k_5 a_5 - k_6 a_6$$

$$k_1 a_1 = -k_1 a_1, k_5 a_5 = -k_5 a_5, k_6 a_6 = -k_6 a_6$$

$$k_1 = k_5 = k_6 = 0 \quad \Leftrightarrow k_i = (0,\ k_2,\ 0,\ -k_2,\ 0,\ 0)$$

$$\frac{1}{2} k_{ij} a_i a_j = \frac{1}{2} k_{ij} a'_i a'_j$$

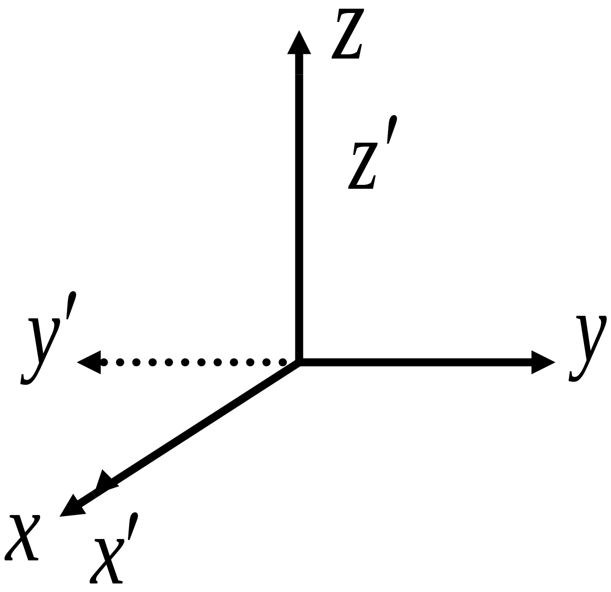
$$\Rightarrow k_{12} = k_{13} = k_{14} = k_{25} = k_{26} = k_{35} = k_{36} = k_{45} = k_{46} = 0$$

therefore,

$$k_{ij} = \begin{bmatrix} k_{11} & 0 & 0 & 0 & (k_{11}-k_{22}-k_{24}) & 0 \\ 0 & k_{22} & 0 & k_{24} & 0 & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ 0 & k_{24} & 0 & k_{22} & 0 & 0 \\ (k_{11}-k_{22}-k_{24}) & 0 & 0 & 0 & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{bmatrix}$$

In the non-polar, k_1 and k_{13} are 0

Assumption for non-enantiomophy system



There is a further element of arbitrariness in our insistence on right-handed coordinates, unless the molecules are enantiomorphic , or enantiomorphically arranged.

Empirically , it appears that enantiomorphy does not occur in liquid crystals unless the moleculars are themselves distinquishable from their mirror images, and that it also vanishes in racemic mixtures.

In the absence of enantiomorphy, then permissible transformation is

$$x' = x \,,\; y' = -y \,,\; z' = z$$

$$n'_x = a'_1 x' + a'_2 y' + a'_3 z' = a_1 x + a_2 y + a_3 z = a'_1 x - a'_2 y + a'_3 z$$

$$\Rightarrow a'_1 = a_1, a'_2 = -a_2, a'_3 = a_3$$

$$n'_y = a'_4 x' + a'_5 y' + a'_6 z', n'_y = -n_y$$

$$a_4 x + a_5 y + a_6 z = -a'_4 x' - a'_5 y' - a'_6 z' = -a'_4 x + a'_5 y - a'_6 z$$

$$\Rightarrow a_4 = -a'_4, a_5 = a'_5, a_6 = -a'_6$$

$$k_i a_i = k_i a'_i = k_1 a_1 - k_2 a_2 + k_3 a_3 - k_4 a_4 + k_5 a_5 - k_6 a_6$$

$$\Rightarrow k_2 = k_4 = k_6 = 0$$

Nematic State

→ Nonpolar and non-enantiomorphic

$k_1 = 0, k_2 = 0 \quad : s_0 = 0, t_0 = 0$

$k_{12} = 0$

⟶ k_{11} , k_{22} , k_{33} , k_{24}

$$g' = \frac{1}{2}k_{11}\left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}\right)^2 + \frac{1}{2}k_{22}\left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x}\right)^2 + \frac{1}{2}k_{33}\left[\left(\frac{\partial n_x}{\partial z}\right)^2 + \left(\frac{\partial n_y}{\partial z}\right)^2\right]$$

$$-(k_{22} + k_{24})\left(\frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y} - \frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}\right)$$

$$= \frac{1}{2}k_{11}(\vec{\nabla}\cdot\vec{n})^2 + \frac{1}{2}k_{22}(\vec{n}\cdot\vec{\nabla}\times\vec{n})^2 + \frac{1}{2}k_{33}(\vec{n}\times\vec{\nabla}\times\vec{n})^2$$

$$-\frac{1}{2}(k_{22}+k_{24})[(\vec{\nabla}\cdot\vec{n})^2 + (\vec{\nabla}\times\vec{n})^2 - \vec{\nabla}\,\vec{n} : \vec{\nabla}\,\vec{n}]$$

$$(\vec{\nabla}\times\vec{n})^2 = (\vec{n}\cdot\vec{\nabla}\times\vec{n})^2 + (\vec{n}\times\vec{\nabla}\times\vec{n})^2$$

$$\vec{\nabla}\,\vec{n} : \vec{\nabla}\,\vec{n} = (\frac{\partial n_x}{\partial x})^2 + (\frac{\partial n_y}{\partial x})^2 + (\frac{\partial n_z}{\partial x})^2 + (\frac{\partial n_x}{\partial y})^2$$

$$+ (\frac{\partial n_y}{\partial y})^2 + (\frac{\partial n_z}{\partial y})^2 + (\frac{\partial n_x}{\partial z})^2 + (\frac{\partial n_y}{\partial z})^2 + (\frac{\partial n_z}{\partial z})^2$$

$$= (\vec{n}\times\vec{\nabla}\times\vec{n})^2$$

$$\boxed{g' = \frac{1}{2}k_{11}(\vec{\nabla}\cdot\vec{n})^2 + \frac{1}{2}k_{22}(\vec{n}\cdot\vec{\nabla}\times\vec{n})^2 + \frac{1}{2}k_{33}(\vec{n}\times\vec{\nabla}\times\vec{n})^2}$$