ON THE ORIGIN OF ORDER PARAMETERS AND MEAN FIELD THEORY IN NEMATIC LIQUID CRYSTAL

Abstract

This chapter is designed to deal with the mathematical foundation needed in determining the order parameters in Nematic liquid crystal (NLC). This is important because orientational order in Nematics is construed in many different ways involving scalars, vectors and tensors. This is essentially due to different experimental methods, which primarily involve Nuclear Magnetic Resonance (NMR), Fluorescence Depolarization technique (FD),Polarized Raman effect (PR), computer simulations etc. that are employed in various levels to determine the orientational order. As a result, different techniques throw up different set of data and accordingly which the order parameters are defined. However, this convenience in data interpretation brings in fresh challenges from academic point of view, which demands correlation among various types of definitions introduced for order parameters. Based on this premise, a novel unified approach is provided purely from theoretical perspective to understand the nature of symmetry and order present in NLC.

Keywords: Angular momentum, Wigner Rotation matrix, order parameters, Mean-field theory and Nematic Liquid crystal.

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I. INTRODUCTION

Liquid Crystals (LC) are unique for many different reasons and most important among them is the long range orientational order with partial or no positional order that they exhibit over a narrow temperature range between crystals and isotropic liquid [1, 2]. This is possible mainly due to the anisotropic shape of their constituent molecules, typically denoted as mesogens [1]. Nematic Liquid Crystal (NLC), which is recognized as the most common LC phases, exhibits optical birefringence like a crystalline solid and yet shows viscous nature same as that of the liquid [3]. This special character, which is partly associated with crystals and partly with liquids, justifies the nomenclature “Liquid Crystal”, which was first suggested by G. Friedel [4].

The shape of mesogens, which are typically taken to be rod shaped, plays an important role in the determination of the orientational order in NLC [5].However, it is important to acknowledge that various other shapes, which include discs [6], boomerangs [7], bananas [8], helices [9] etc., can also produce Nematic phases. Therefore, a microscopic approach, which can capture the symmetry of different mesogens, is needed for defining a macroscopic order parameter, which must also vanish for the isotropic liquid. Based on this simple premise, order parameters of different nature such as scalars, vectors and even tensors are introduced [2]. However, a unified prescription, which involves both cartesian and spherical coordinates, may be developed [10]. This is beneficial for the following reasons: first, the definitions become coherent, which is essential for theoretical understanding, second, the technique of data interpretation also becomes efficient, which are otherwise difficult due to experimental subtleties, and finally, the results of computer simulations can be meaningfully comprehended, which are now a days important part of liquid crystal physics. Based on scientific intuitions, it is clearly evident that the basic approach in defining the orientational orders in Nematic should rest upon the fundamental understanding on rotations, angular momentum and tensor algebra. The present work is devised starting from these fundamental ideas to the gradual development of more intricate definitions involving the orientational order parameters in NLC.

II. THEORY

1. **Rotations and Angular Momentum**: In quantum mechanics, the momentum operator acts as a generator of translation for the wave function ψ(x), which can be shown as follow [11]:

   Let us first construct an operator of the form (Details in Appendix-A):

$$\hat{T} = \text{Exp}\left[-\frac{i\ell\hat{\text{p}}_x}{\hbar}\right] \tag{1}$$

   Here, in Eq. (1), $\hat{p}_x$ is the x-component of the momentum operator and $\hbar$ is the reduced Planck’s constant. The new parameter ℓ, which bears the dimension of length, is inserted just to make the exponential dimensionless. Now, operating $\hat{T}$ over the wave function $\psi(x)$, we get:

$$\hat{T}\psi(x) = \mathrm{Exp}\left[-\frac{i\ell\hat{p}_x}{\hbar}\right]\psi(x)$$
$$= \left[1 - \frac{i\ell\hat{p}_x}{\hbar} + \frac{1}{2!}\left(\frac{i\ell\hat{p}_x}{\hbar}\right)^2 - \ldots\ldots.\right]\psi(x) \qquad (2)$$

The right-hand side of Eq. (2) is obtained by expanding the exponential in Taylor series.

Now, using the expression for the momentum operator $\hat{p}_x = -i\hbar\frac{d}{dx}$, in Eq. (2), we obtain:

$$\hat{T}\psi(x) = \left[\psi(x) - \ell\frac{d\psi(x)}{dx} + \frac{1}{2!}\ell^2\frac{d^2\psi(x)}{dx^2} + \ldots\ldots\ldots\ldots\right]$$
$$= \psi(x-\ell) \qquad (3)$$

Therefore, the operator $\hat{T}$ generates a translation in the wave function $\psi(x)$ by an amount ℓ. Inspired by this simple calculation, it is highly intuitive to develop a similar operator, which can generate a rotation in the wave function $\psi(\vec{r})$. Here, we make a deliberate distinction between the wave function $\psi(x)$, which is one-dimensional in nature with $\psi(\vec{r})$, which is now a function in 3D. This is reasonable because wave function can translate in 1D but for rotation, we need a three-dimensional wave function $\psi(\vec{r})$ [12].

The rotation operator can now be defined as (Details in Appendix-A):

$$\hat{\mathcal{R}}(z,\delta\phi) = \mathrm{Exp}\left[-\frac{i\delta\phi\hat{L}_z}{\hbar}\right] \qquad (4)$$

Here, $\hat{\mathcal{R}}(z,\delta\phi)$is the rotation operator corresponding to an infinitesimal rotation by an angle $\delta\phi$ about z-axis. Moreover,$\hat{L}_z$is the z-component of the angular momentum operator. It is important to mention here that a rigorous approach in obtaining the operator in Eq. (4) is possible; however, for the present scenario, an intuitive approach suffice the job.

When this operator is applied over the wave function $\psi(\vec{r}) = \psi(r,\theta,\phi)$, we get:

$$\hat{\mathcal{R}}(z,\delta\phi)\psi(r,\theta,\phi)$$
$$= Exp\left[-\frac{i\delta\phi\hat{L}_z}{\hbar}\right]\psi(r,\theta,\phi) \qquad (5)$$

Now, using the definition of the angular momentum operator $\hat{L}_Z = -i\hbar\frac{\partial}{\partial\phi}$ [11], Eq. (5) can be greatly simplified as follow:

$$\begin{aligned}\hat{\mathcal{R}}(z,\delta\phi)\psi(r,\theta,\phi) &\\ = \left[\psi(r,\theta,\phi) - \delta\phi\frac{\partial\psi(r,\theta,\phi)}{\partial\phi} + \frac{1}{2!}(\delta\phi)^2\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2} + \ldots\ldots\ldots\ldots\right] &\\ = \psi(r,\theta,\phi-\delta\phi) & \qquad (6)\end{aligned}$$

Clearly, the rotation operator $\widehat{\mathcal{R}}(z,\delta\phi)$, which involves the z-component of the angular momentum operator $\widehat{\mathrm{L}}_z$, generates rotation of the wavefunction $\psi(r,\theta,\phi)$ by an angle $\delta\phi$.

A generalization of Eq. (4) is needed for a rotation about any arbitrary direction and this can be achieved as follow:

$$\hat{\mathcal{R}}(\hat{n},\phi) = \mathrm{Exp}\left[-\frac{i\phi\hat{L}\cdot\hat{n}}{\hbar}\right] \qquad (7)$$

Here, in Eq. (7), $\hat{n}$ is taken to be any arbitrary direction about which the angular momentum operator $\hat{L}$ is now defined with the angle of rotation ϕ. Appendix A is referred for details in obtaining Eq. (7).

However, the axis-angle definition of rotation operator in Eq. (7) is not unique. There is yet another method by which rotations in quantum mechanics can be parameterized and this is called the Euler angle (α,β,γ) method [13]. These two methods, which are referred to here as the axis-angle method and the Euler angle method, are equivalent but are separately used in distinct branches of physics. For example, it is found that axis-angle definition $(\hat{n},\phi)$ is more useful for analytical calculations involved in quantum mechanics, whereas, the Euler angle(α,β,γ) method is generally used in the rotation matrices, which are found to be useful in the development of molecular level theories in physics [5]. Therefore, a formal introduction of Euler angle(α,β,γ) method is essential and it is given below:

Let us consider two set of co-ordinate systems: one is called the Laboratory co-ordinate (X, Y, Z) and the other one is denoted as the Molecular frame (x, y, z). If one starts from the Laboratory frame (X, Y, Z) and rotate about the Z-axis by an angle α, a new co-ordinate system (X',Y',Z') is reached, where $Z' \equiv Z$.

Now, a rotation by an angle β about the new Y'-axis can be implemented and yet another intermediate co-ordinate system (X'',Y'',Z'') is reached, where $Y'' \equiv Y'$. Finally, a third rotation by an angle γ can be induced about the new Z''-axis and we reach the molecular frame $(X''',Y''',Z''') \equiv (x,y,z)$. A schematic diagram exhibiting the successive rotations by angles α, β and γ, respectively, is shown in Fig. 1.

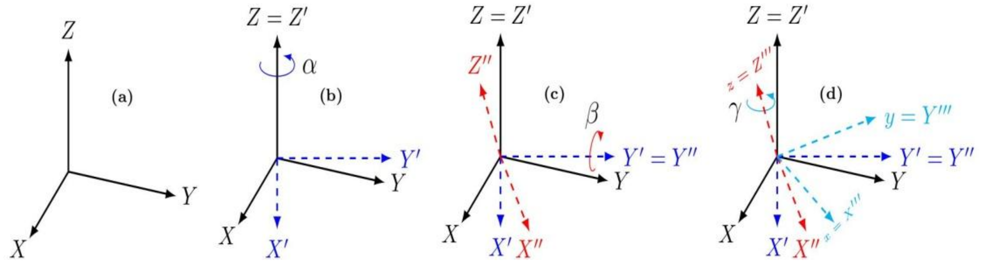

Figure 1: Scheme of Euler Rotations: (a) The Un-Rotated Laboratory Frame (X, Y, Z), (b) The Rotation Around Laboratory Z Axis is Performed by An Angle α, (c) The Intermediate Rotation About the Y' Axis is Performed by an Angle β And (d) Finally, the Molecular Frame (X,Y,Z) is Obtained by Rotating the Z'' Axis by an Angle γ.

This scheme of rotation, which is typically denoted as the (Z-Y-Z) rule of Euler angles, is not unique. There are many other choices, which are also available in literature [14]; however, for our purpose, this scheme (Z-Y-Z) is particularly convenient in defining the orientational order parameters [5, 10, 13].

In quantum mechanical terminology, these rotations about three different axes, namely (Z, Y', Z''), can be written in terms of the following operators:

$$\hat{\mathcal{R}}_Z(\alpha) = Exp\left[-\frac{i\alpha\hat{\mathcal{L}}_Z}{\hbar}\right] \tag{8}$$

$$\hat{\mathcal{R}}_{Y'}(\beta) = Exp\left[-\frac{i\beta\hat{\mathcal{L}}_{Y'}}{\hbar}\right] \tag{9}$$

$$\hat{\mathcal{R}}_{Z''}(\gamma) = Exp\left[-\frac{i\gamma\hat{\mathcal{L}}_{Z''}}{\hbar}\right] \tag{10}$$

Equations (8-10) are obtained in view of the rotation operator defined in Eq. (7). However, it is difficult to organize any molecular theory based on the operators defined in Equations (8-10). This is because they involve rotations about different intermediate axes like Y' and Z''. Therefore, it is always convenient to define these rotation operators either in the Laboratory frame (X, Y, Z) or in the Molecular frame (x, y, z). In order to achieve this goal, we proceed as follow:

Any operator in quantum mechanics obeys the following transformation rule under rotation [13]:

$$\hat{O}' = \mathcal{R}\hat{O}\mathcal{R}^{\dagger} \tag{11}$$

Here, in Eq. (11), $\hat{O}'$ is the operator in the rotated frame of reference. With this definition, the rotation operators $\hat{\mathcal{R}}_{Y'}$ and $\hat{\mathcal{R}}_{Z''}$ can be re-defined in the following form:

$$\hat{\mathcal{R}}_{Y'}(\beta) = \hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Y(\beta)\hat{\mathcal{R}}_Z^\dagger(\alpha) \tag{12}$$

Eq. (12) has been written based on the premise that the rotation operator $\hat{\mathcal{R}}_{Y'}(\beta)$ is obtained by rotating the actual rotation operator in the Laboratory frame $\hat{\mathcal{R}}_Y(\beta)$ about the Laboratory Z-axis by an angle α.

However, in order to write similar equation for $\hat{\mathcal{R}}_{Z''}$, it is to be recognized that this operation results from the successive rotations, which involve rotation of the operator $\hat{\mathcal{R}}_Z(\gamma)$, first, about the Laboratory Z-axis by an angle α and then about the intermediate axis Y' by an angle β. Therefore, $\hat{\mathcal{R}}_{Z''}(\gamma)$ should be written in the following form:

$$\hat{\mathcal{R}}_{Z''}(\gamma) = \hat{R}_{Y'}(\beta)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Z(\gamma)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{R}_{Y'}^\dagger(\beta) \tag{13}$$

Since more than one rotation is involved in the transformation Eq. (13), it is fundamentally important to note the order of operating the rotation operators on $\hat{\mathcal{R}}_Z(\gamma)$ to obtain $\widehat{\mathcal{R}}_{Z''}(\gamma)$. However, it is clearly evident that Eq. (13) is just an extension of the transformation rule already defined in Eq. (11).

In view of Eq. (12) and (13), the composite rotation operator now can be written as follow:

$$\begin{aligned}
&\hat{\mathcal{R}}(\alpha\beta\gamma) = \hat{\mathcal{R}}_{Z''}(\gamma)\hat{\mathcal{R}}_{Y'}(\beta)\hat{\mathcal{R}}_Z(\alpha)\\
&= \hat{R}_{Y'}(\beta)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Z(\gamma)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{R}_{Y'}^\dagger(\beta)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Y(\beta)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{\mathcal{R}}_Z(\alpha)\\
&= \hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Y(\beta)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Z(\gamma)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}^\dagger{}_Y(\beta)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Y(\beta)\hat{\mathcal{R}}_Z^\dagger(\alpha)\hat{\mathcal{R}}_Z(\alpha)\\
&= \hat{\mathcal{R}}_Z(\alpha)\hat{\mathcal{R}}_Y(\beta)\hat{\mathcal{R}}_Z(\gamma)
\end{aligned} \tag{14}$$

In deducing Eq. (14), it is assumed that the matrices representing the operators are "orthogonal" i.e.,$\hat{\mathcal{R}}_i\hat{\mathcal{R}}_i^\dagger = \hat{\mathcal{R}}_i^\dagger\hat{\mathcal{R}}_i = 1$, where $(i = X, Y, Z)$. However, the terminology "orthogonal" may be misleading, but is kept intentionally just to maintain the uniformity with Eq.(11). A closer analysis of the matrices, which are explicitly given in Equations. (15-17) and are representing the operators involved in Eq. (14), reveal that they are real. Therefore, the † sign simply implies transposition as conjugation leads to no changes.

The right-hand side of Eq. (14) is now represented only by the rotation operators defined in the Laboratory frame of reference (X, Y, Z).

Now, for the sake of completeness, the matrices representing the operators $\hat{\mathcal{R}}_Z(\alpha)$, $\hat{\mathcal{R}}_Y(\beta)$, and $\hat{\mathcal{R}}_Z(\gamma)$ in the Laboratory frame are given below [15]:

$$\hat{\mathcal{R}}_Z(\alpha) = \begin{bmatrix} cos\alpha & sin\alpha & 0 \\ -sin\alpha & cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{15}$$

$$\hat{\mathcal{R}}_Y(\beta) = \begin{bmatrix} cos\beta & 0 & -sin\beta \\ 0 & 1 & 0 \\ sin\beta & 0 & cos\beta \end{bmatrix} \tag{16}$$

$$\hat{\mathcal{R}}_Z(\gamma) = \begin{bmatrix} cos\gamma & sin\gamma & 0 \\ -sin\gamma & cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{17}$$

With the aid of Eq. (7), Eq. (14) can now be written as:

$$\hat{\mathcal{R}}(\alpha\beta\gamma) = \mathrm{Exp}\left[-\frac{i\alpha\hat{\mathcal{L}}_Z}{\hbar}\right] Exp\left[-\frac{i\beta\hat{\mathcal{L}}_Y}{\hbar}\right] Exp\left[-\frac{i\gamma\hat{\mathcal{L}}_Z}{\hbar}\right] \tag{18}$$

The primary goal is now to obtain the matrix representation of the composite operator $\hat{\mathcal{R}}(\alpha\beta\gamma)$, which involves the angular momentum operators $\hat{\mathcal{L}}_Y$ and $\hat{\mathcal{L}}_Z$. In order to achieve this, a suitable basis state needs to be identified. This can be obtained by considering the commutation relation between the operator $\widehat{\mathcal{R}}(\alpha\beta\gamma)$ and the square of the angular momentum operator $\hat{\mathcal{L}}^2$. With the Taylor series expansion of Eq. (18), it is readily observed that:

$$\left[\hat{\mathcal{R}}(\alpha\beta\gamma), \hat{\mathcal{L}}^2\right] = 0 \tag{19}$$

Therefore, Eq. (19) allows us to find the matrix representation of $\hat{\mathcal{R}}(\alpha\beta\gamma)$ in the basis state $|\ell m\rangle$, which is the simultaneous eigenstate of both $\hat{\mathcal{L}}^2$ and $\hat{\mathcal{L}}_Z$. With this suitable choice of the basis set, the matrix representation of $\hat{\mathcal{R}}(\alpha\beta\gamma)$ can now be given as:

$$\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma) = \left\langle \ell, m \middle| \hat{\mathcal{R}}(\alpha\beta\gamma) \middle| \ell, n \right\rangle \tag{20}$$

Here, in Eq. (20),$\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$ is called the Wigner rotation matrix [16] of rank ℓ, where (α,β,γ) are Euler angles, which signify the rotation from the Laboratory fixed frame (X, Y, Z) to the Molecular fixed frame (x, y, z).

2. **Properties of Wigner Rotation Matrix:** Wigner rotation matrices $\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$ play the central role in the development of molecular theories for Nematic Liquid crystal. This is because $\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$ are irreducible representation of the special orthogonal group SO(3), where, S stands for special that signifies that the determinant of the rotation matrices are 1, “O” stands for orthogonal and number 3 signify three-dimensional space. $\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$ satisfy the following properties [17, 18]:

   - The complex conjugate of $\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$ can be written as:

$$\left[\mathfrak{D}^{\ell}_{m,n}\right]^*(\alpha,\beta,\gamma) = \mathfrak{D}^{\ell}_{n,m}(-\gamma,-\beta,-\alpha) \tag{21}$$

   - The Wigner rotation matrices satisfy the following unitary relations:

$$\sum_{n=-\ell}^{n=\ell} \left[\mathfrak{D}^{\ell}_{m,n}\right]^* \mathfrak{D}^{\ell}_{\boldsymbol{m},n} = \delta_{m\boldsymbol{m}} \tag{22}$$

$$\sum_{m=-\ell}^{m=\ell} \left[\mathfrak{D}^{\ell}_{m,n}\right]^{*} \mathfrak{D}^{\ell}_{m,\boldsymbol{n}} = \delta_{n\boldsymbol{n}} \tag{23}$$

- In terms of the quantum numbers m and n, the Wigner rotation matrices can be written as:

$$\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma) = e^{-im\alpha}\left\langle \ell m \left| e^{-\frac{i\beta\hat{\mathcal{L}}_{Y}}{\hbar}} \right| \ell n \right\rangle e^{-in\gamma} = e^{-i(m\alpha+n\gamma)} d^{\ell}_{m,n}(\beta) \tag{24}$$

  Here, in Eq. (24),

$$d^{\ell}_{m,n}(\beta) = \left\langle \ell m \left| e^{-\frac{i\beta\hat{\mathcal{L}}_{Y}}{\hbar}} \right| \ell n \right\rangle \tag{25}$$

  In Eq. (25), $d^{\ell}_{m,n}(\beta)$ is termed as the reduced Wigner Rotation matrix.

- Relation with spherical harmonics and Legendre polynomials can be written as follow:

$$\mathfrak{D}^{\ell}_{m,0}(\alpha,\beta,\gamma) = \sqrt{\frac{4\pi}{2\ell+1}}\, Y^{*}_{\ell m}(\beta,\alpha) \tag{26}$$

$$\mathfrak{D}^{\ell}_{0,0}(0,\beta,0) = \mathrm{P}_{\ell}(\cos\beta) \tag{27}$$

  The meaning of Eq. (26) is the following: when a vector $\vec{r}$, which lies along the Laboratory Z-axis, is rotated through the scheme of Euler angles (α,β,γ), the rotated vector $\vec{r}'$ has the azimuthal angle β and the polar angle α.

  In, Equations. (26) and (27), $Y_{\ell m}(\beta,\alpha)$ is the Spherical Harmonics and $P_{\ell}(cos\,\beta)$ is the Legendre Polynomial [19].

- The Wigner rotation matrices $\mathfrak{D}^{\ell}_{m,n}(\alpha,\beta,\gamma)$, satisfy the following orthogonality relation:

$$\int \mathfrak{D}^{\ell *}_{m,n}(\alpha,\beta,\gamma)\mathfrak{D}^{r*}_{p,q}(\alpha,\beta,\gamma)\, sin\,\beta\, d\alpha d\beta d\gamma = \frac{8\pi^{2}}{2\ell+1}\delta_{m,p}\delta_{n,q}\delta_{\ell,r} \tag{28}$$

3. **Symmetry and definition of order parameter in Nematic Liquid crystal:** As it is already mentioned in the introduction section, the molecules in NLC are typically taken to be rod shaped [1, 2]. Even though the actual molecules, e.g., 5CB (4-cyano-$4'$ −pentylbiphenyl) has both rigid core and a flexible part, a coarse-grained view, which is generally taken as rigid rod, becomes theoretically convenient for modelling. This is because the whole machinery of rigid body theory comes as handy tools and the mathematical foundation involving the rotation of a rigid body, which is partially laid down in the previous sections, can be effectively utilized in proposing the definition of the orientational order parameters in Nematic Liquid Crystal. A pictorial representation of such a coarse-grained view is given in Fig. 2. However, it is important to understand that flexibility of molecular shape can also be taken into account; but such a

representation unnecessarily complicates the definitions without any appreciable gain in the physical reality for an NLC.

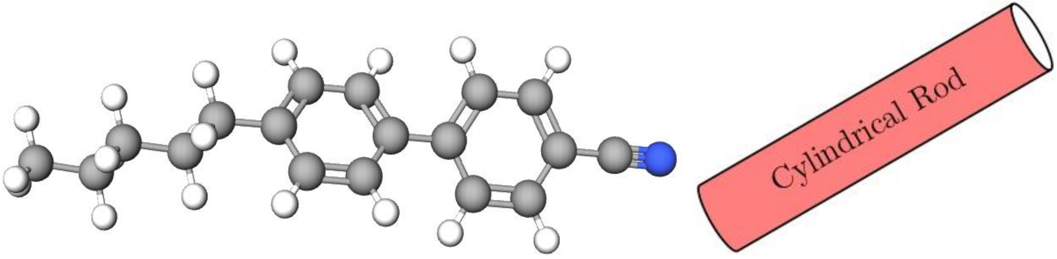

Figure 2: On the Left, the Actual Chemical Structure of 5CB is Shown. The Benzene Rings Constitute the Rigid Core and the Rest Part is the Flexible Chain. This Whole Molecule can be represented as a Rod, which is shown in the Right Side. This Type of Representation is termed as Coarse-Grained Representation.

When a compound, made of molecules such as the one shown in Fig. 2[20],is either heated from the crystalline solid or cooled down from the isotropic liquid, the nematic phase is formed. Here, the molecules, which are represented as cylindrical rods (coarse-grained view), orient on an average about a particular direction, which is equivalent both in head and tail, is generally taken as the director $\hat{n}$. This is shown in Fig. 3.

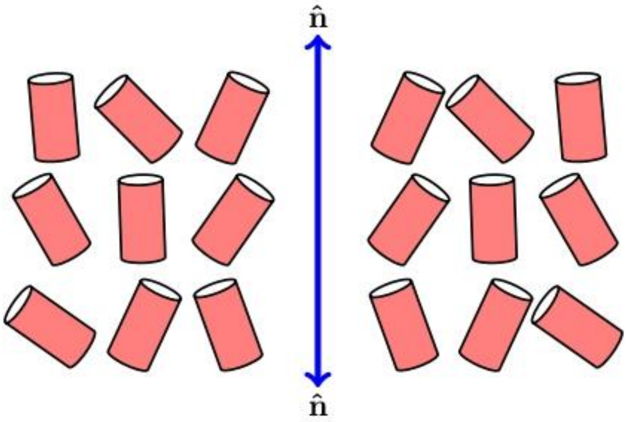

Figure 3: A Schematic Diagram Showing the nematic Phase. The Cylindrical Shapes are Molecules and the Director Exhibiting Up-Down Symmetry.

Therefore, from group theoretical point of view, the nematic phase shows cylindrical symmetry with molecules exhibiting perfect cylindrical symmetry. For such a system, Wigner rotation matrices, which are introduced in section 3, constitute a well-defined order parameter. This can be understood from the following ideas:

Let us consider $\wp_1(\vec{r},\omega)$ as the probability of finding a mesogen at position $\overrightarrow{r}$ with orientation $\omega = (\alpha, \beta, \gamma)$. This probability distribution is related with the orientational distribution function $f(\omega)$ in the following way:

$$f(\omega) = \frac{1}{N}\int d\vec{r}\,\wp_1(\vec{r},\omega) \tag{29}$$

For a Nematic phase, which possesses full translational symmetry, the single particle orientational distribution function $f(\omega)$ can be written as:

$$f(\omega) = \frac{1}{\rho} \wp_1(\omega) \tag{30}$$

Any distribution function, which is governed solely by the Euler angles(α, β, γ),can be expanded with respect to the Wigner rotation matrices [21, 22]. This can be achieved as follow:

$$f(\omega) = \sum_{\ell=0}^{+\infty} \sum_{m=-\ell}^{+\ell} \sum_{n=-\ell}^{+\ell} C_{\ell mn}\, \mathfrak{D}^{\ell}_{m,n}(\omega) \tag{31}$$

Here in Eq. (31), the unknown co-efficient $C_{\ell mn}$ plays the central role in the determination of the orientational order parameter in Nematic phase. In order to calculate $C_{\ell mn}$, we first multiply Eq. (31), on both sides by the Wigner rotation matrix $\mathfrak{D}^{\ell *}_{m,n}(\omega)$ and then integrate over the solid angle $d\omega = sin\,\beta\, d\beta d\alpha d\gamma$. This can be represented as follow:

$$\int \mathfrak{D}^{\ell *}_{m,n}(\omega)\, sin\,\beta\, d\beta d\alpha d\gamma = \sum_{\ell=0}^{+\infty} \sum_{m=-\ell}^{+\ell} \sum_{n=-\ell}^{+\ell} \int C_{\ell' m' n'}\, \mathfrak{D}^{\ell'}_{m',n'}(\omega)\, \mathfrak{D}^{\ell *}_{m,n}(\omega)\, sin\,\beta\, d\beta d\alpha d\gamma \tag{32}$$

Using the orthogonality relation in Eq. (28), we get:

$$\int \mathfrak{D}^{\ell *}_{m,n}(\omega)\, sin\,\beta\, d\beta d\alpha d\gamma = \sum_{\ell=0}^{+\infty} \sum_{\mathrm{m}=-\ell}^{+\ell} \sum_{\mathrm{n}=-\ell}^{+\ell} \frac{8\pi^2}{2\ell' + 1} \mathrm{C}_{\ell' \mathrm{m'} \mathrm{n'}} \delta_{\ell,\ell'}\, \delta_{\mathrm{m,m'}} \delta_{\mathrm{n,n'}} \quad = \frac{8\pi^2}{2\ell + 1} C_{\ell mn} \tag{33}$$

Therefore, from Eq. (33), $C_{\ell mn}$ can be found as:

$$C_{\ell mn} = \frac{2\ell + 1}{8\pi^2} \langle \mathfrak{D}^{\ell *}_{m,n}(\omega) \rangle \tag{34}$$

In Eq. (34), the angular bracket signifies $\langle \mathfrak{D}^{\ell *}_{m,n}(\omega) \rangle = \int \mathfrak{D}^{\ell *}_{m,n}(\omega)\, sin\,\beta\, d\beta d\alpha d\gamma$, which is the orientational average of the Wigner rotation matrix $\mathfrak{D}^{\ell *}_{m,n}(\omega)$.

In view of Eq. (34), the orientational distribution function in Eq. (31) can now be written as:

$$f(\omega) = \sum_{\ell mn} \frac{2\ell + 1}{8\pi^2} \left\langle \mathfrak{D}^{\ell *}_{m,n}(\omega) \right\rangle \mathfrak{D}^{\ell}_{\mathrm{m,n}}(\omega) \tag{35}$$

Equation (35) is of paramount importance in liquid crystal physics and the average $\left\langle \mathfrak{D}^{\ell}_{m,n}(\omega) \right\rangle$, whose complex conjugate appears on the right-hand side of Eq. (35), is defined as the orientational order parameter. It is clearly evident from this definition that there are $(2\ell + 1)^2$ order parameters possible for a given ℓ. For example, if it is assumed that $\ell = 2$, then there are 25 possible order parameters, whereas, for $\ell = 3$, this number becomes 49, which are enormously large even for ranks as low as 2 and 3, respectively. However, it is to be recognized that these numbers reduce considerably if the symmetry of the molecules and the phase are taken into consideration. However, before embarking on the symmetry consideration, it is important to recognize the glaring problem with the convergence of the series in Eq. (35). In fact, this series never converges, which even though may create some problem in the construction of any molecular level theory, but for the time being suffice the job of predicting the order parameters successfully.

Let us first consider the case of NLC, which exhibits uniaxial symmetry. For such a phase, if the Laboratory Z-axis is taken to be the direction of director $\hat{n}$, then any rotation about this Z-axis should not change the orientational distribution function $f(\omega)$. Therefore, it enforces $m = 0$ for the Wigner rotation matrices. Moreover, from Group theoretical perspective, a uniaxial Nematic phase possesses $D_{\infty h}$ symmetry, which contains inversion as a symmetry element. That means, if the system as a whole is reflected about a certain plane containing the inversion center, the Nematic phase remains the same as before when the reflection operation was carried out. Mathematically, this simply implies that the quantum number ℓ can have only even values. Finally, the symmetry of the constituent molecules is to be taken into consideration. For most purposes, it is taken to be rigid rod, possessing the same cylindrical symmetry as that of the phase itself. It means any rotation of the molecule about the molecular z-axis will not change anything about the orientational distribution function $f(\omega)$. This symmetry operation implies that $n = 0$ for Wigner rotation matrices.

Having outlined the symmetries of a uniaxial Nematic phase consisting of cylindrically symmetric molecules, it is clearly evident that for NLC, the following order parameters are allowed:

$$\mathfrak{D}^{\ell}_{0,0}(0, \beta, 0) \tag{36}$$

Here, in Eq. (36), only even values of ℓ are permitted.
From Eq. (27), the order parameters can now be simply written as:

$$\mathfrak{D}^{\ell}_{0,0}(0, \beta, 0) = P_{\ell}(cos\, \beta) \tag{37}$$

In view of Eq. (37), the distribution function in Eq. (35) can be written as follow:

$$f(\omega) = \frac{1}{4\pi^2}\sum_{\ell}\frac{2\ell+1}{2}\langle P_\ell(cos\,\beta)\rangle P_\ell(cos\,\beta) \tag{38}$$

In deducing Eq. (38), we have used the following relation:

$$\left\langle \mathfrak{D}^{\ell*}_{0,0}(0,\beta,0)\right\rangle = \langle P^*_\ell(cos\,\beta)\rangle = \langle P_\ell(cos\,\beta)\rangle \tag{39}$$

Eq. (38) can be further modified as follow:

$$f(\beta) = \sum_{\ell}\frac{(2\ell+1)}{2}\langle P_\ell(cos\,\beta)\rangle P_\ell(cos\,\beta) \tag{40}$$

Here, we have taken $f(\omega) = \frac{f(\beta)}{4\pi^2}$, which enables us to write Eq. (40) in the form stated above.

Eq. (40) clearly shows that for Nematic, the orientational order parameters are simply the averages over the Legendre Polynomials, where the rank ℓ can take only even values.

The expressions for few Legendre polynomials are given below:

$$P_0(cos\,\beta) = 1 \tag{41}$$
$$P_1(cos\,\beta) = cos\,\beta \tag{42}$$
$$P_2(cos\,\beta) = \frac{1}{2}(3-1) \tag{43}$$
$$P_3(cos\,\beta) = \frac{1}{2}(5\,cos^3\,\beta - 3\,cos\,\beta) \tag{44}$$
$$P_4 z = \frac{1}{8}(35\,cos^4\,\beta - 30\,cos^2\,\beta + 3) \tag{45}$$
$$P_5(cos\,\beta) = \frac{1}{8}(63\,cos^5\,\beta - 70\,cos^3\,\beta + 15\,cos\,\beta) \tag{46}$$
$$P_6(cos\,\beta) = \frac{1}{48}(693\,cos^6\,\beta - 945\,cos^4\,\beta + 315\,cos^2\,\beta - 15) \tag{47}$$

Evidently, from Eqs. (41-47), the Legendre Polynomials are even for even values of ℓ and odd for the odd values of ℓ.

Now, Eq. (40) can be written as:

$$\begin{aligned} f(\beta) &= \frac{1}{2} + \frac{5}{2}\langle \mathrm{P}_2(\mathrm{co\,s}\,\beta)\rangle \mathrm{P}_2(\mathrm{co\,s}\,\beta) + \frac{9}{2}\langle \mathrm{P}_4(\mathrm{co\,s}\,\beta)\rangle \mathrm{P}_4(\mathrm{co\,s}\,\beta) \\ &+ \frac{13}{2}\langle \mathrm{P}_6(\mathrm{co\,s}\,\beta)\rangle \mathrm{P}_6(\mathrm{co\,s}\,\beta) + \ldots\ldots\ldots\ldots\ldots \end{aligned} \tag{48}$$

The first non-trivial term in the expansion of Eq. (48) is, therefore:

$$\langle P_2(\,cos\ \beta)\rangle = \langle\frac{1}{2}(3cos^2\beta - 1)\rangle \tag{49}$$

The average of the second Legendre Polynomial defined in Eq. (49) is typically considered as the orientational order parameter for Nematic Liquid crystal. This was first proposed by Tsvetkov in 1942 [23] and subsequently used by Maier and Saupe for their development of the mean field theory [24].

It is important to understand the reasons behind the choice of this order parameter defined in Eq. (49). For a perfectly aligned Nematic, we can take either $\beta = 0$ or $\beta = \pi$. In either of these cases, Eq. (49) gives $\langle P_2(cos\,\beta)\rangle = 1$. Now, for an isotropic liquid, the average in Eq. (49) can be calculated as follow:

$$\langle cos^2\,\beta\rangle = \frac{\int_0^{\pi} cos^2\,\beta\, sin\,\beta\, d\beta}{\int_0^{\pi} sin\,\beta\, d\beta} = \frac{1}{3} \qquad (50)$$

With the aid of Eq. (50), the order parameter in Eq. (49) becomes $\langle P_2(cos\,\beta)\rangle = 0$. Therefore, for a partially aligned Nematic, which is typically the most ubiquitous scenario, the order parameter varies between the range 0, which is applicable for an isotropic liquid and 1, which implies perfect Nematic order.

A careful examination of Eq. (48) suggests that the order parameters in Nematic is not just restricted to $\langle P_2(cos\,\beta)\rangle$ but higher rank order parameters such as $\langle P_4(cos\,\beta)\rangle$, $\langle P_6(cos\,\beta)\rangle$ etc. are also possible choices. It must be emphasized that with the presence of higher rank Legendre Polynomials in the distribution function in Eq. (48), the orientational order of the Nematic is characterized more precisely; however, as already stated, this series never converges. In practice, it is found that the distribution of the mesogens, which are measured through various techniques, are in good agreement with the experiment if this series is truncated after $\langle P_4(cos\,\beta)\rangle$ [5, 10]. A better argument, which enables to truncate the series after $\langle P_4(cos\,\beta)\rangle$, is possible when one considers the case of potential of mean torque [25].

Finally, a flow chart showing the prescription of calculating the orientational order parameter through Wigner rotation matrices is showing Figure 4:

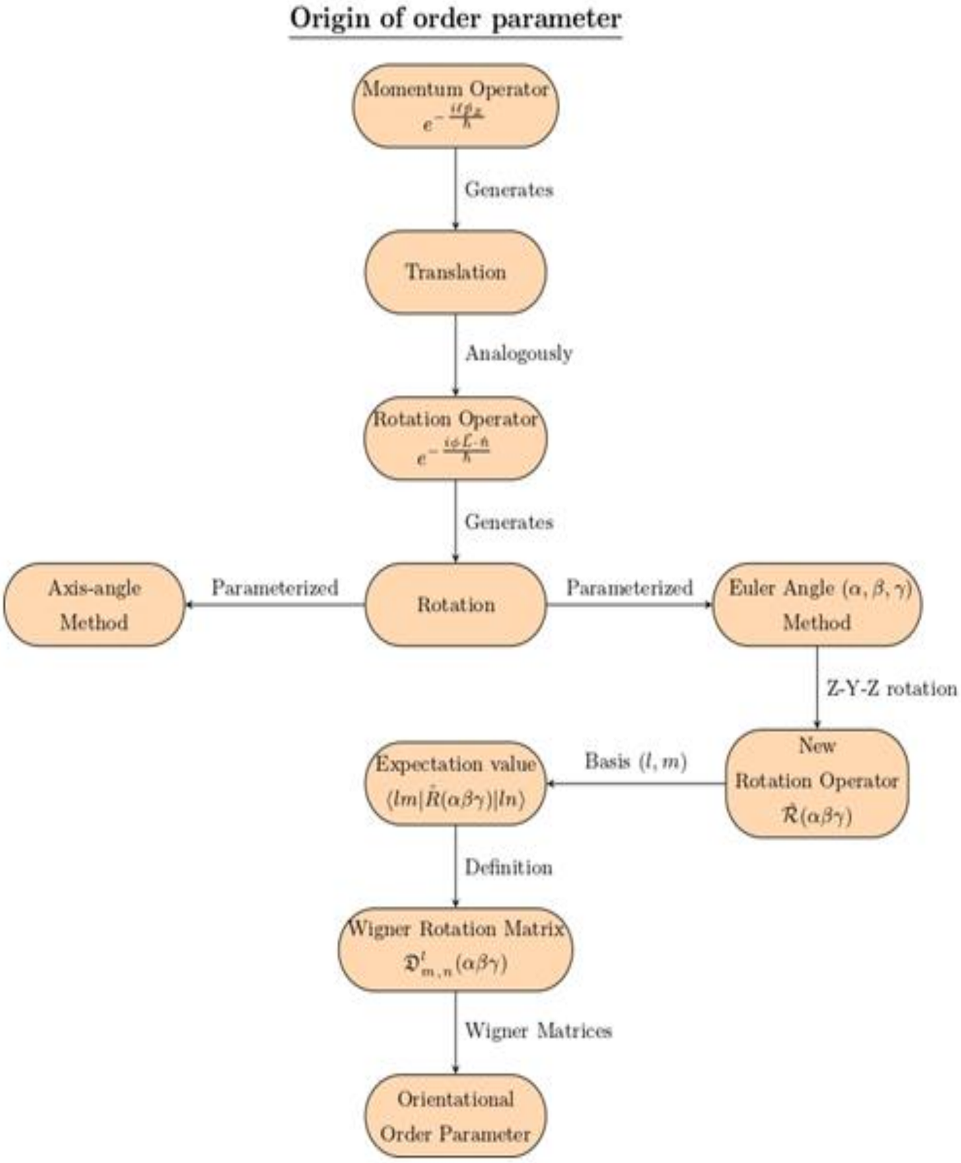

Figure 4: Flow Chart Exhibiting the Steps in Calculating the Orientational Order Parameter.

4. **The Maier-Saupe type Mean field theory for Nematic:** The Maier-Saupe (MS) molecular theory of NLC can be developed based on the discussion of order parameters, which is carried out comprehensively in section 3. The fundamental idea is to construct the mean field potential, which is felt by each individual molecule due all others present in the system. Irrespective of any repulsive forces, which may operate between the mesogens, the Maier-Saupe type potential is purely attractive in nature [26, 27].

   There is a rigorous mathematical calculation [28], which leads to the formulation of such a potential. However, such an extensive calculation may be dropped and based purely on the orientational order present in Nematic, the potential can be developed. First, it is to be recognized that the potential is dependent purely on angular orientation of the molecule [24]. Moreover, such a potential should vanish in the isotropic phase. Therefore, this potential should be proportional to the order parameter $\langle P_2(co\,s\,\beta)\rangle$ i.e.

$$V(cos\,\beta) \propto \langle P_2(co\,s\,\beta)\rangle \tag{51}$$

This proportionality in Eq. (51) ensures that the mean field potential vanishes in the isotropic phase.

Further, for a perfect Nematic, the molecules are supposed to be aligned parallel to each other, which should yield the thermodynamically stable equilibrium condition with minimum energy configuration. Based on this simple supposition, the potential should also be proportional to the following term:

$$V(cos\,\beta) \propto \frac{1}{2}(3\,cos^2\,\beta - 1) \tag{52}$$

Combining Eqs. (51) and (52), the overall potential energy can now be written as:

$$V(co\,s\,\beta) = -JP_2(co\,s\,\beta)\langle P_2(co\,s\,\beta)\rangle \tag{53}$$

Here, in Eq. (53), J is called the strength of the Maier-Saupe potential.
Now, the single particle orientational distribution function is related with the potential in Eq. (53) in the following way:

$$f(\beta) = \frac{1}{Z}\,\mathrm{Exp}\left[-\frac{V(cos\,\beta)}{K_B T}\right] \tag{54}$$

Where, in Eq. (54), Z is the normalization constant, which is given by:

$$Z = \int_0^{\pi} \mathrm{Exp}\left[-\frac{V(cos\,\beta)}{K_B T}\right] sin\,\beta\, d\beta \tag{55}$$

With the definition of the orientational distribution function in Eq. (54), the order parameter is now defined as:

$$S = \langle P_2(cos\,\beta)\rangle = \int_0^{\pi} P_2(cos\,\beta) f(\beta)\, sin\,\beta\, d\beta \tag{56}$$

Equation (56) is a self-consistent equation, which can be solved numerically and the plot is given in Fig. 5. However, it is to be recognized that the definition in Eq. (56) may seem at first glance to be adhoc in nature but a careful construction of the Helmholtz free energy, which when minimized for a stable equilibrium state,can automatically lead us to Eq. (56). This is also achieved in our theory and exhibited later when the Helmholtz free energy of the entire system is calculated. Moreover, the scalar order parameter S, which is defined in Eq. (56), is typically taken as the orientational average of the second Legendre polynomial. For other order parameters, which involve fourth, sixth, eighth (etc.) order Legendre polynomials, the prescription is to average the corresponding Legendre Polynomial over the orientational distribution function $f(\beta)$.

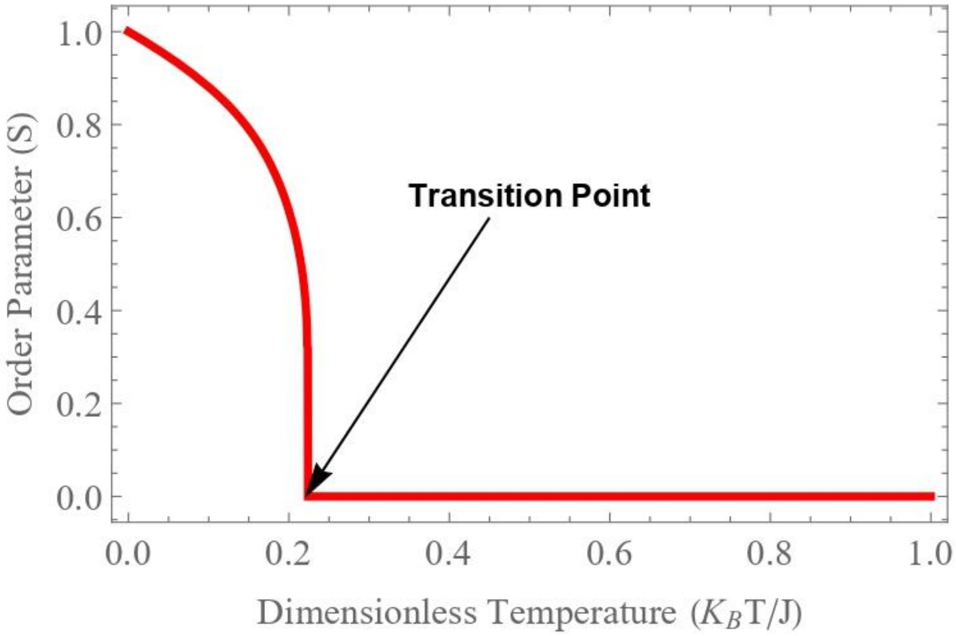

Figure 5: Variation of the Order Parameter S with the Dimensionless Temperature $\frac{K_B T}{J}$.

Figure 5, shows the variation of the scalar order parameter S with respect to the dimensionless temperature $\tau = \frac{K_B T}{J}$. Evidently, as temperature is decreased, at a certain value $\tau = 0.22$, which is found numerically from the curve in Fig. 5, the order parameter S suddenly jumps. This is the point of transition between the isotropic and the Nematic phase. Therefore, the potential, which was constructed purely based on physical arguments without any rigorous calculation in Eq. (53),though completely attractive in nature, successfully captures the subtleties of a transition between isotropic and Nematic phase.

The Helmholtz free energy of the system can now be written as:

$$F = U - TS_{\text{entropy}} \tag{57}$$

Here, U is the mean field energy of the system, and it can be calculated as the average of the potential energy $\langle V(co\,s\,\beta)\rangle$. Moreover, $S_{entropy}$ stands for the entropic contribution to the free energy. The symbol $S_{entropy}$ is utilized purposefully in Eq. (57) just to make it distinct from the scalar order parameter, which is also universally symbolized as S.

In view of Eq. (53), the mean field energy U can be calculated as follow:

$$U = \frac{1}{2}N\langle V(cos\,\beta)\rangle = \frac{1}{2}N\langle -JP_2(cos\,\beta)\langle P_2(cos\,\beta)\rangle\rangle = -\frac{1}{2}NJ\langle P_2(cos\,\beta)\rangle^2 \tag{58}$$

Here, in Eq. (58), N is the number of molecules present in the system and a factor of $\frac{1}{2}$ is inserted just to avoid double counting of each individual molecule.

Now, the entropy of the system can be calculated as follow:

$$S_{entropy} = -NK_B\langle lnf(\beta)\rangle \tag{59}$$

With the aid of Eq. (54), which specifies the expression for the single particle orientational distribution function $f(\beta)$, Eq. (59) can be written as:

$$S_{entropy} = -\frac{NJ}{T}\langle P_2(cos\,\beta)\rangle^2 + NK_B ln\int_0^{\pi} \text{Exp}\left[\frac{J}{K_BT}P_2(cos\,\beta)\langle P_2(cos\,\beta)\rangle\right] sin\,\beta\, d\beta \tag{60}$$

Therefore, the free energy in Eq. (57) now becomes:

$$F = \frac{1}{2}NJ\langle P_2(cos\,\beta)\rangle^2 - NK_BT\, ln\int_0^{\pi} \text{Exp}\left[\frac{J}{K_BT}P_2(cos\,\beta)\langle P_2(cos\,\beta)\rangle\right] sin\,\beta\, d\beta \tag{61}$$

This free energy in Eq.(61) is plotted in Fig. 6.

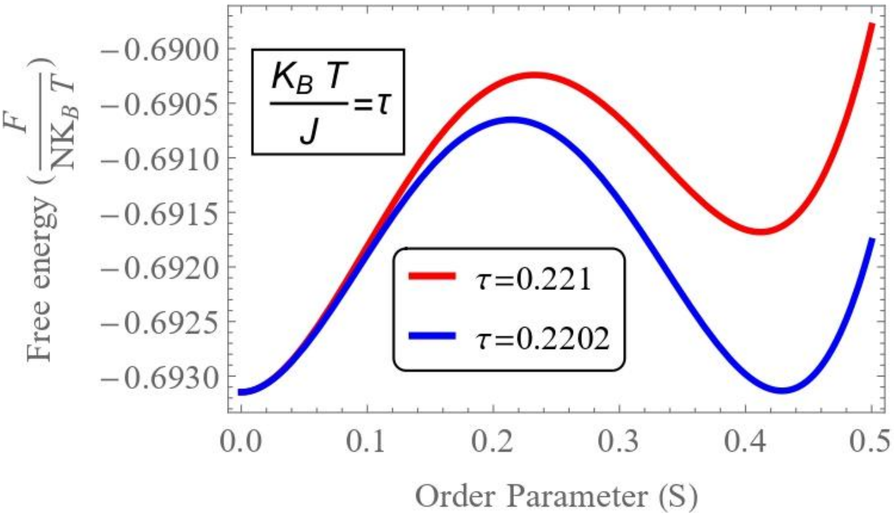

Figure 6: Variation of Free Energy $\left(\frac{F}{NK_BT}\right)$ with the Order Parameter (S) for Different Values of the Dimensionless Temperature τ.

It is clearly evident that for the temperature $\tau = 0.221$, where, the dimensionless temperature τ is defined as $\tau = \frac{K_BT}{J}$, the curve shows two distinct minima. The minimum, which is obtained at S=0, corresponds to the stable isotropic phase and the second one, which is even though correspond to $S \neq 0$, can only be attributed to the metastable Nematic phase. However, the situation is quite different when $\tau = 0.2202$, in this case, we obtain two stable minima, signifying the onset of a first-order phase transition between isotropic liquid and the Nematic phase. Further lowering of temperature makes the Nematic phase stable, whereas, the isotropic phase becomes metastable.

The scalar order parameter S, which is defined in Eq. (56), now can be obtained by minimizing Eq. (61) with respect to $S = \langle P_2(\cos\beta)\rangle$. We, therefore, readily obtain:

$$\langle P_2(\cos\beta)\rangle = \frac{\int_0^{\pi} P_2(\cos\beta)\mathrm{Exp}\left[\frac{J}{K_B T} P_2(\cos\beta)\langle P_2(\cos\beta)\rangle\right]\sin\beta\, d\beta}{\int_0^{\pi} \mathrm{Exp}\left[\frac{J}{K_B T} P_2(\cos\beta)\langle P_2(\cos\beta)\rangle\right]\sin\beta\, d\beta} \qquad (62)$$

Equation (62) is exactly equivalent to Eq. (56). However, this time, the order parameter is obtained by minimizing the Helmholtz free energy in Eq. (61). This derivation becomes necessary for the consistency in approach of developing molecular type mean field theory.

III. CONCLUSION

A gradual development of the molecular theory of liquid crystal is presented. It is shown that starting from the preliminary ideas of rotations and angular momentum, the idea of Wigner rotation matrices can be developed. These matrices act as the basis set for the space spanned by the Euler angles. From this conceptual idea, the single particle orientational distribution function has been expanded in series of Wigner rotation matrices. With the aid of orthogonality relation, the distribution function is then craftly utilized to obtain the averages of these matrices, which are defined as the orientational order parameters.

For the Nematic liquid crystal, symmetry arguments considerably decrease the number of order parameters possible and it is found that only the even rank Legendre Polynomials act as the order parameters. Then, finally we considered the case of a mean field theory, known as the Maier-Saupe theory. In this theory, a self-consistent equation for the order parameter is obtained and it is shown that it vanishes in the isotropic phase.

Therefore, simple ideas such as rotations, angular momentum play crucial role in developing the fundamental ideas related with the physics of liquid crystals. This short approach, which is devoid of any theoretical rigor, is remarkably helpful in developing novel theories for liquid crystals.

Appendix-A

Calculation of the axis-angle rotation operator $\widehat{\mathcal{R}}(\hat{n}, \phi)$:

In Quantum Mechanics, the rotation operator is determined from the infinitesimal unitary operator, which takes the following form [13]:

$$\hat{J} = \hat{I} - i\hat{G}\epsilon \qquad (A1)$$

In Equation (A1), $\hat{I}$ is the unit operator and $\hat{G}$ stands for some Hermitian operator. Moreover, ϵ signify the conjugate "displacement" corresponding to the Hermitian operator $\hat{G}$. For example, in case of generating one dimensional translation, we can choose:

$$\hat{G} = \frac{\hat{p}_x}{\hbar} \quad \text{and} \quad d\epsilon = dx \qquad (A2)$$

Here, in Equation (A2), it is clearly evident that the momentum operator is the generator of translation. Though it is not yet explicit, but Eq. (A2) is the infinitesimal analogue of Eq. (1), which generates finite translation of amount ℓ.

Similarly, any time evolution of infinitesimal amount dt, the appropriate choices are:

$$\hat{G} = \frac{\hat{H}}{\hbar} \text{ and } \epsilon = dt \qquad (A3)$$

Clearly, the Hamiltonian operator $\hat{H}$ acts as the generator of time evolution. Therefore, for the generation of rotation, the following choices are appropriate:

$$\hat{G} = \frac{\hat{\mathcal{L}}_n}{\hbar} \text{ and } \epsilon = d\phi \qquad (A4)$$

Here, $\hat{\mathcal{L}}_n$ is the angular momentum operator along n-direction and $d\phi$ defines the amount of infinitesimal rotation.

Therefore, the infinitesimal unitary operator now becomes:

$$\hat{J} = \hat{I} - i\hat{G}\epsilon = 1 - i\frac{\hat{\mathcal{L}}_n}{\hbar}d\phi \qquad (A5)$$

On the basis of the infinitesimal rotation operator $\hat{J}$, the finite rotation operator is now given by:

$$\hat{\mathcal{R}}(\hat{n}, \phi) = \lim_{N\to\infty}\left[1 - i\frac{\hat{\mathcal{L}}_n}{\hbar}\left(\frac{\phi}{N}\right)\right]^N = \text{Exp}\left[-\frac{i\hat{\mathcal{L}}_n}{\hbar}\phi\right] \qquad (A6)$$

Equation (A6) is exactly the same as Eq. (7).

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