Identification of low-symmetry phases in nematic liquid crystals

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Abstract

Mesophases of nematic liquid crystals (NLC) are traditionally identified by building a second-rank ordering tensor $\mathbb{S}$ that efficiently describes the average orientation of nematogenic molecules with respect to a fixed laboratory/reference frame. In general, both in experiments and in simulations, the symmetry group of the molecules is known *a-priori*, contrary to the symmetry group of the phase; this latter has to be determined by analysing the numerical realisation of $\mathbb{S}$, possibly affected by numerical errors. Furthermore, when a mesophase has a simple symmetric structure, as is the case of uniaxial nematics, the identification of the preferred direction is relatively an easy task. However, this task becomes less straightforward when the symmetry group of a mesophase is more complex. There is no generally accepted procedure to perform this analysis, but we have provided in a previous paper a new algorithm suited to identifying the symmetry group of the phase. We implement here such algorithm which gives a canonical representation of $\mathbb{S}$ for each of the classes that can be distinguished with a second-rank ordering tensor, and determines the nearest tensor of the assigned symmetry by group averaging.

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I. INTRODUCTION

Liquid crystals are complex fluids made of anisotropic molecules. These molecules tend to align to a common direction, and different orientational orders correspond to different mesophases. These phases are characterised by different rheological and optical properties of the material, such as viscosity coefficients and refracting index. To provide a quantitative description of the order, we resort to the orientational probability density function of the molecules. However, from the experimental and theoretical point of view, in general this function is known only through its second moments. These are then used to define the order tensor $\mathbf{Q}$, and, subsequently a second-rank ordering supertensor $\mathbb{S}$ can be built [1–4]. The matrix entries of $\mathbb{S}$ are considered to capture correctly the most important features of the mesoscopic order.

In molecular dynamics or Monte-Carlo simulations, the ordering tensor $\mathbb{S}$ is computed by averaging over all molecular orientations, in terms of the orientation of the molecular frames of reference, for all molecules, with respect to an arbitrarily chosen laboratory frame. Likewise, in experiments the entries of bS can be obtained only after choosing such reference frame. In both cases, a proper choice of the frame must be done in order to get physical information such as phase symmetry, directors and order parameters.

In a previous work [5] we have proposed a method to perform the analysis of the data leading to the identification of the optimal orientation for the laboratory reference frame, and therefore to provide a systematic procedure to determine the symmetry class (the "phase" of the system), the symmetry axes (the "directors"), and the scalar order parameters of a liquid crystal compound whose second-rank ordering tensor is obtained through experiments or simulations.

In general, experimental or numerical errors are a further source of complications and may hinder the correct identification of the phase symmetry, even in the simplest case (for instance, a uniaxial order, naively described as a state in which rod-like molecules are substantially parallel to a director $\boldsymbol{n}$). Under these assumptions, most of the entries of $\mathbb{S}$ should vanish, but the presence of errors can make all the entries generally non-zero. In addition to that, the orientation of the laboratory axes may not match that of the director, and several non-vanishing entries are obtained. In this case, it may not be immediately clear whether these non-vanishing entries reveal an intrinsic lack of uniaxial phase symmetry or are a consequence of the issues above.

In this paper we review the theory developed in [5], and provide a more systematic and practical discussion of the related algorithm.

This paper is organised as follows. Sec. II reviews the theoretical background on orientational order parameters; in particular, the spherical and Cartesian definitions of orientational ordering tensors are discussed. The specific case of *second-rank* ordering tensors is developed in Sec. III. In Secs. III B and III C we recall the notion of symmetry-class of an ordering tensor, and that it is only possible to distinguish five phase-symmetry classes at the second-rank level. A finer identification of the phase group of a non-polar liquid crystal would require higher rank ordering tensors. The following Sec. IV deals with the identification of the closest ordering tensor that belongs to a given symmetry class. To this end, we introduce the invariant projection on the linear space of ordering tensors that are fixed by a given symmetry group; subsequently, we the distance of the raw ordering tensor from one of the five symmetry classes, and provide a canonical representation of the ordering tensor in each symmetry class. After all these mathematical ingredients are established, we describe the algorithm for the determination of the effective phase in Sec. IV. Sec. V contains the description of a code in which the algorithm is implemented, and Sec. VI summarises the results.

In all sections we stick to the notation adopted in [5]; in particular, for point symmetry groups, i.e. subgroups of $\mathsf{O}(3)$, we comply with the standard Schönflies notation [6–8]. Here, we only give a few examples of these groups, and refer the reader to the references cited above for a complete discussion. The cyclic groups of order n are denoted by C_n; these groups contain only an n-fold axis of rotational symmetry. D_n contains an n-fold axis of rotational symmetry about an axis, and a 2-fold rotation about an axis perpendicular to this. D_{nh} adds to D_n a horizontal plane of symmetry (orthogonal to the n-fold axis). C_{nh} and C_{nv} have a horizontal and a vertical plane of symmetry, respectively, in addition to the n-fold axis of C_n. Finally, $D_{\infty h}$ and $C_{\infty h}$ describe the symmetry groups of a cylinder and of a cone, respectively. There are also seven exceptional groups (T, T_d, T_h, O, O_h, I, I_h), which describe the tetrahedral, octahedral and icosahedral symmetry groups.

II. ORIENTATIONAL ORDER PARAMETERS

We give here the framework of the basics of liquid crystal theory, although it might be well known to the reader this allows recalling notation and theoretical basis of our work.

For a simple mesogenic molecule, endowed with cylindrical symmetry ($D_{\infty h}$) we introduce the probability distribution $f(\boldsymbol{m})$, describing the probability that a molecule has orientation given by $\boldsymbol{m}$, being $\boldsymbol{m}$ the axis of symmetry. For non-polar molecules $f(\boldsymbol{m}) = f(-\boldsymbol{m})$, hence the first moment of the distribution vanishes; as a consequence, the second moment of the distribution is the first significant description of the order

$$\mathbf{N} = \int_{S^2} (\boldsymbol{m} \otimes \boldsymbol{m}) f(\boldsymbol{m}) \, \mathrm{d}\Omega \,,$$

where the integration is performed over the unit sphere S^2, in other words on all directions (e.g. $\mathrm{d}\Omega = \sin\beta \mathrm{d}\beta \, \mathrm{d}\alpha$, with α and β defined as the colatitude and the azimuth in a spherical frame).

The symmetric traceless order tensor $\mathbf{Q} = \mathbf{N} - \frac{1}{3}\mathbf{I}$ is used; this is identically zero in the isotropic phase. With a wise choice of the laboratory frame (i.e. $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$, with $\boldsymbol{\ell}_3$ along the *director* $\boldsymbol{n}$) the order tensor can be written as

$$\mathbf{Q} = S\left(\boldsymbol{\ell}_3 \otimes \boldsymbol{\ell}_3 - \frac{1}{3}\mathbf{I}\right) + P(\boldsymbol{\ell}_1 \otimes \boldsymbol{\ell}_1 - \boldsymbol{\ell}_2 \otimes \boldsymbol{\ell}_2) = S\left(\boldsymbol{n} \otimes \boldsymbol{n} - \frac{1}{3}\mathbf{I}\right) + P(\boldsymbol{m} \otimes \boldsymbol{m} - \boldsymbol{m}' \otimes \boldsymbol{m}') \,, \tag{II.1}$$

where $S \in [-\frac{1}{2}, 1] = \langle \frac{3}{2}\cos^2\beta - \frac{1}{2} \rangle$ is the main uniaxial order parameter, ranging in $[-\frac{1}{2}, 1]$; $P = \langle \sin^2\beta \, \cos 2\alpha \rangle$ is the biaxial order parameter, ranging in $[-1, 1]$; $\{\boldsymbol{m}, \boldsymbol{m}', \boldsymbol{n}\}$ is an orthonormal basis (the average $\langle \cdot \rangle$ is computed on the whole ensemble). If (and only if) $P \neq 0$ the phase is not purely uniaxial, but has a *biaxial* (or 'orthorhombic', or D_{2h}) phase symmetry, lower than that of the molecule.

If the reference lab frame is poorly chosen, the matrix representation

$$Q_{ij} = \boldsymbol{\ell}_i \cdot \mathbf{Q}\boldsymbol{\ell}_j, \quad i, j = 1, 2, 3$$

of the tensor $\mathbf{Q}$ can can have off-diagonal entries even when it describes a uniaxial phase.

In a generic uniaxial phase, the order parameter does not attain its maximum value, as molecules are slightly dispersed, and their main axes are randomly distributed in a region close to $\boldsymbol{n}$. When $P \neq 0$, this dispersion is not uniform (basically, main direction of molecules are scattered in an elliptical cone of axis $\boldsymbol{n}$).

Conversely, molecules endowed with a D_{2h} symmetry, characterised by 3 main axes instead of one, can assemble in a phase with higher $D_{\infty h}$ (uniaxial) symmetry whenever only one of the main axes is aligned along a preferred direction; on the contrary, such molecules can assemble in a phase with the same D_{2h} (biaxial) symmetry when also the other two axes tend to align to two orthogonal directions, respectively. Details of the description in the laboratory frame can be found in several references (see [9–11]).

In general, when no symmetry for the molecule or the phase can be assumed *a-priori*, the orientational distribution of a set of molecules should be described by a space-dependent probability density function $f(\boldsymbol{x}, \mathbf{R})$. Here $\boldsymbol{x}$ is the position of the a molecule in the set, and $\mathbf{R} \in \mathsf{SO}(3)$ is the rotation of a right orthonormal frame set in the molecule (namely the unit vectors $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ defining main axes of the molecule), with respect to the laboratory frame of reference, i.e. the orthonormal set $(\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3)$. We drop the dependence on $\boldsymbol{x}$, as we are intested in the orientational properties of the molecules, and assume a continuous dependence of f on $\mathbf{R}$. In other words, $f \colon \mathsf{SO}(3) \to \mathbb{R}^+$ is a continuous function from the group of proper rotations to the non-negative real numbers ($\int_{\mathsf{SO}(3)} f = 1$). Several equivalent description can be given of the rotation matrix $\mathbf{R}$ that describes the orientation of the molecule with respect to the laboratory axes. We define matrix $\mathbf{R}$ as the rotation that brings each unit vector $\boldsymbol{\ell}_i$ into coincidence with the corresponding molecular unit vector $\boldsymbol{m}_i$: $\mathbf{R}\boldsymbol{\ell}_i = \boldsymbol{m}_i$, $i = 1, \ldots, 3$, and the matrix entries of $\mathbf{R}$ are given by $R_{ij} = \boldsymbol{\ell}_i \cdot \mathbf{R}\boldsymbol{\ell}_j = \boldsymbol{\ell}_i \cdot \boldsymbol{m}_j$, $i, j = 1, \ldots, 3$.

Group representation theory (more precisely, Peter-Weyl theorem, see for instance [12, 13]) ensures the matrix entries of all the irreducible representations of the rotation group $\mathsf{SO}(3)$ form a complete orthonormal set for the continuous functions $f \colon \mathsf{SO}(3) \to \mathbb{R}$. Traditionally, this irreducible decomposition is based on the properties of the spherical harmonic functions.

However, also traceless symmetric tensors can be used to form a basis for the irreducible representations of $\mathsf{SO}(3)$ [14, 15] (also known as *harmonic tensor decomposition* [16]). In this case Peter-Weyl theorem can be used to show that a purely Cartesian complete system for the continuous functions in $\mathsf{SO}(3)$ can be formed with the entries $\sqrt{2j+1}\, D^{(j)}_{pm}(\mathbf{R})$; this system is orthonormal with respect to its *normalised invariant (or Haar) measure*. Functions $D^{(j)}_{pm}(\mathbf{R})$ can also be obtained as suitable linear combinations of Wigner rotation matrices, so that the resulting representation is real. We recall that the so-called Wigner rotation matrices are defined as:

$$\mathscr{D}^{(j)}_{lk}(\alpha,\beta,\gamma) := e^{-i(l\alpha+k\gamma)} d^{(j)}_{lk}(\beta), \qquad j = 0, 1, 2, \dots \tag{II.2}$$

where i is the imaginary unit, $\{\alpha,\beta,\gamma\}$ are the Euler angles parameterising a particular element $\mathbf{R} \in \mathsf{SO}(3)$ defined according to the y-convention (see, e.g. pp. 50-52 of [17]), and we have introduced the shorthand for the reduced Wigner function

$$d^{(j)}_{lk}(\beta) := \sum_{t=t_m}^{t_M} (-1)^t \frac{[(j+l)!(j-l)!(j+k)!(j-k)!]^{1/2}}{(j+l-t)!(j-k-t)!t!(t+k-l)!} (\cos\frac{\beta}{2})^{2j+l-k-2t} (\sin\frac{\beta}{2})^{2t+k-l}\,, \quad k, l \in [-j, j]; \tag{II.3}$$

here the summation is restricted to the integers t that make the factorials well defined, namely

$$\begin{aligned} &t_m \le t \le t_M\,, \\ &t_m := \max\{0, l-k\}\,, \\ &t_M := \min\{j+l, j-k\}\,. \end{aligned}$$

The Fourier expansion of the probability distribution function is

$$f(\mathbf{R}) = \sum_{j=0}^{+\infty} (2j+1) \sum_{p,m=0}^{2j} f^{(j)}_{pm} D^{(j)}_{pm}(\mathbf{R}), \tag{II.4}$$

and the coefficients are readily obtained from the integrals

$$f^{(j)}_{pm} = \int_{\mathsf{SO}(3)} D^{(j)}_{pm}(\mathbf{R}) f(\mathbf{R})\, \mathrm{d}\mu(\mathbf{R})\,. \tag{II.5}$$

(in terms of α,β,γ, the measure $\mathrm{d}\mu$ is explicitly given by $\mathrm{d}\mu = \frac{1}{8\pi^2}\sin\beta \mathrm{d}\beta\ \mathrm{d}\alpha\ \mathrm{d}\gamma$).

Order parameters are often used to study phase transitions; these are quantities which change their value on going from one phase to the other, and that can therefore be used to monitor the transition. From a molecular point of view, however, we should describe the passage from one phase to another in terms of the modifications that this produces in the distribution function. Therefore, identifying the order parameters with the expansion coefficients (II.5) is the standard assumption (see Refs. [1–4, 18, 19])

III. SECOND-RANK ORDER PARAMETERS

In the expansion of Eq. (II.4), the $j = 0$ term represents the isotropic distribution, and the $j = 1$ terms vanishes for symmetry reasons. Therefore, the first non trivial information about the molecular order is provided by the $j = 2$ terms, which then acquire a particular important part in the theory. As a consequence, a stadard simplification is to truncate the expansion of the probability distribution function at the second rank level, although higher rank terms sometimes can be included. Generally speaking, this is done only in particular cases (i.e. uniaxial molecules), where simplifying assumptions or the symmetry of the problem restrict the number of independent order parameters and the complexity of their calculation. Surely, it is not an easy task the interpretation of the physical meaning of the $j = 2$ order parameters, when no particular symmetry is imposed [20–22].

Accordingly, in [5] we considered the *second-rank order parameters*, i.e. $j = 2$, and here we stick to that choice. The invariant space V_2 of the irreducible representation is then the space of symmetric and traceless second-rank tensors on the three dimensional real space $\mathbb{E}^3_O \simeq \mathbb{R}^3$; thence $\dim V_2 = 5$. Let $L(V_2)$ be the space of the linear maps $L\colon V_2 \to V_2$.

Given the general definition of Cartesian ordering tensor (II.5), we define define the second-rank ordering tensor (or order parameter tensor) as the linear map $\mathbb{S} \in L(V_2)$, such that [23, 24]

$$\mathbb{S}(\mathbf{T}) = \int_{\mathsf{SO}(3)} D^{(2)}(\mathbf{R})\mathbf{T}\, f(\mathbf{R})\ \mathrm{d}\mu(\mathbf{R}) := \langle D^{(2)}(\mathbf{R})\mathbf{T}\rangle, \tag{III.1}$$

where the $(j = 2)$-irreducible representation matrix $D^{(2)}(\mathbf{R})$ acts explicitly by conjugation as follows:

$$D^{(2)}(\mathbf{R})\mathbf{T} = \mathbf{R}\mathbf{T}\mathbf{R}^{\mathrm{T}}. \tag{III.2}$$

Under an abstract mathematical perspective it is not necessary to distinguish between isomorphic spaces. However, it is convenient for the sake of the presentation to distinguish between the linear space V_2^{M}, generated by the orthonormal frame $(\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3)$ which describes the orientation of a generic molecule and V_2^{L}, with basis obtained from the laboratory frame of reference $(\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3)$. We follow [5, 25–27], and associate an orthonormal basis to a generic molecule; such a basis spans the five-dimensional linear space of traceless symmetric tensors V_2^{M}, and is given by

$$\mathbf{M}_0 = \sqrt{\frac{3}{2}}\left(\boldsymbol{m}_3 \otimes \boldsymbol{m}_3 - \frac{1}{3}\mathbf{I}\right), \qquad \mathbf{M}_1 = \frac{1}{\sqrt{2}}\left(\boldsymbol{m}_1 \otimes \boldsymbol{m}_1 - \boldsymbol{m}_2 \otimes \boldsymbol{m}_2\right), \tag{III.3a}$$

$$\mathbf{M}_2 = \frac{1}{\sqrt{2}}\left(\boldsymbol{m}_1 \otimes \boldsymbol{m}_2 + \boldsymbol{m}_2 \otimes \boldsymbol{m}_1\right), \qquad \mathbf{M}_3 = \frac{1}{\sqrt{2}}\left(\boldsymbol{m}_2 \otimes \boldsymbol{m}_3 + \boldsymbol{m}_3 \otimes \boldsymbol{m}_2\right), \tag{III.3b}$$

$$\mathbf{M}_4 = \frac{1}{\sqrt{2}}\left(\boldsymbol{m}_1 \otimes \boldsymbol{m}_3 + \boldsymbol{m}_3 \otimes \boldsymbol{m}_1\right). \tag{III.3c}$$

Tensors $\{\mathbf{M}_0, \mathbf{M}_1, \ldots, \mathbf{M}_4\}$ are orthonormal with respect to the standard scalar product in the tensor space, i.e. $\mathbf{A} \cdot \mathbf{B} = \mathrm{tr}(\mathbf{A}^{\mathrm{T}}\mathbf{B})$.

Similarly, we define the basis of five symmetric, traceless tensors $\mathbf{L}_0, \ldots, \mathbf{L}_4$ in terms of $\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3$ that are used as laboratory frame of reference. The matrix $D^{(2)}(\mathbf{R})$ is an irreducible representation of the rotation $\mathbf{R}$ in the 5-dimensional space of symmetric traceless tensors. Specifically, it describes how the "molecular axis" $\mathbf{M}_i$ of a given molecule is rotated with respect the laboratory axis:

$$D^{(2)}(\mathbf{R})\mathbf{L}_i = \mathbf{M}_i, \qquad i = 0, \ldots, 4, \tag{III.4}$$

to be compared with the similar expression $\mathbf{R}\boldsymbol{\ell}_i = \boldsymbol{m}_i \, (i = 1, \ldots, 3)$ in the three-dimensional space.

Hence, the Cartesian components of the ordering tensor $\mathbb{S} \in L(V_2)$ are defined as

$$S_{ij} = \mathbf{L}_i \cdot \mathbb{S}(\mathbf{L}_j) = \mathbf{L}_i \cdot \langle \mathbf{M}_j \rangle, \qquad i, j = 0, \ldots, 4, \tag{III.5}$$

with the usual notation for the ensemble average. The components (III.5) give the averaged molecular direction $\mathbf{M}_j$ with respect to the laboratory axis $\mathbf{L}_i$. In general there are 25 independent entries (as expected).

In simulations, the orientational probability density $f(\mathbf{R})$ is reconstructed by keeping track of the orientations of a large number N of sample molecules. Thus, the ensemble average in (III.5) is approximated by the sample mean of $\mathbf{M}_j$, and the components S_{ij} are calculated as

$$S_{ij} = \frac{1}{N} \sum_{n=1}^{N} \mathbf{L}_i \cdot \mathbf{M}_j^{(n)}, \qquad i, j = 0, \ldots, 4, \tag{III.6}$$

where the index n runs over all the molecules in the simulation.

For a system of uniaxial molecules with long axis $\boldsymbol{m}_3$, all the averages of the molecular orientational tensors $\mathbf{M}_j$ with $j \neq 0$ vanish. The average of $\mathbf{M}_0$ yields the five components $(i = 0, 1, \ldots, 4)$

$$S_{i,0} = \sqrt{\frac{3}{2}}\, \mathbf{L}_i \cdot \langle \boldsymbol{m}_3 \otimes \boldsymbol{m}_3 - \tfrac{1}{3}\mathbf{I} \rangle, \tag{III.7}$$

equivalent to the standard de Gennes $\mathbf{Q}$ tensor or Saupe ordering matrix [4, 28], as given in Eq. (II.1).

A. Change of basis and group action

The components S_{ij} are modified under a change of the laboratory or molecular frames of reference. In the former case, let $\boldsymbol{\ell}_i' = \mathbf{A}_P \boldsymbol{\ell}_i$ be the unit vectors along the primed axes, obtained from the original *laboratory axes* after a (proper or improper) rotation $\mathbf{A}_P$. A molecule, whose orientation was described by the rotation $\mathbf{R}$ with respect to $(\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3)$, now is oriented as $\mathbf{R}\mathbf{A}_P^{\mathrm{T}}$ with respect to the primed frame

$$\mathbf{R}\boldsymbol{\ell}_i = \boldsymbol{m}_i = \mathbf{R}'\boldsymbol{\ell}_i' = \mathbf{R}'\mathbf{A}_P\boldsymbol{\ell}_i \qquad \Rightarrow \qquad \mathbf{R}' = \mathbf{R}\mathbf{A}_P^{\mathrm{T}}.$$

In the five-dimensional space V_2, this yields a rotation bringing the new frame $\{\mathbf{L}_i'\}$ into coincidence with the molecular frame $\{\mathbf{M}_i\}$:

$$D^{(2)}(\mathbf{R}\mathbf{A}_P^{\mathrm{T}}) = D^{(2)}(\mathbf{R}) D^{(2)}(\mathbf{A}_P)^{\mathrm{T}}, \qquad D^{(2)}(\mathbf{R}\mathbf{A}_P^{\mathrm{T}})\mathbf{L}_i' = \mathbf{M}_i. \tag{III.8}$$

The components of the ordering tensor in the new basis become

$$S_{ij}' = \mathbf{L}_i' \cdot \langle \mathbf{M}_j \rangle = \sum_{k=0}^{4} D_{ik}^{(2)}(\mathbf{A}_P^{\mathrm{T}}) S_{kj}, \tag{III.9}$$

where $D_{ik}^{(2)}(\mathbf{A}_P^{\mathrm{T}}) = \mathbf{L}_k \cdot D^{(2)}(\mathbf{A}_P)\mathbf{L}_i$. However, only the relative orientation of the molecular frame with respect to the laboratory frame is important, therefore a rigid rotation of *all* the molecules is equivalent to an inverse rotation of the laboratory frame. It is easy to check that the ordering tensor is the same in the two cases.

By contrast, we can interpret a rotation $\mathbf{A}_M$ of the molecular frame as an orthogonal transformation of the molecular axes *before* the orientational displacement of the molecule, $\mathbf{R}$, has taken place; in this case, the total rotation mapping the laboratory axes in the new molecular axes is $\mathbf{R}\mathbf{A}_M$, so that the components of the ordering tensor are:

$$S_{ij}' = \mathbf{L}_i \cdot \langle D^{(2)}(\mathbf{R}\mathbf{A}_M) \rangle \mathbf{L}_j = \sum_{k=0}^{4} S_{ik} D_{kj}^{(2)}(\mathbf{A}_M)\,. \tag{III.10}$$

When both laboratory and molecular transformations are allowed, combining (III.9) and (III.10) yields

$$S_{ij}' = \sum_{h,k=0}^{4} D_{ih}^{(2)}(\mathbf{A}_P^{\mathrm{T}}) S_{hk} D_{kj}^{(2)}(\mathbf{A}_M)\,. \tag{III.11}$$

B. Molecular and phase symmetry

The symmetries of our physical system (either of the molecules or of the phase, or both) are mirrored by the symmetries of the corresponding orientational probability density $f(\mathbf{R})$. However, $\mathbb{S}$ is actually an average quantity obtained by computing the second moments of $f(\mathbf{R})$, therefore some information can be lost, and systems having different physical symmetries may be described by ordering tensors of the same symmetry. In principle, higher orders in the expansion of $f(\mathbf{R})$ could allow distinguishing such degenerate cases. It is important to know what classes of symmetry can be distinguished by truncating the expansion at second-order. We refer to [5] for more details.

According to Eq. (III.11), we define the *second-rank molecular symmetry group* as the set of all elements in $\mathsf{O}(3)$ that fix $\mathbb{S}$ under right multiplication

$$G_M(\mathbb{S}) = \{\mathbf{A}_M \in \mathsf{O}(3) : \ \mathbb{S}\, D^{(2)}(\mathbf{A}_M) = \mathbb{S}\}, \tag{III.12}$$

and similarly for the second-rank phase symmetry group, where the multiplication appears on the left

$$G_P(\mathbb{S}) = \{\mathbf{A}_P \in \mathsf{O}(3) : \ D^{(2)}(\mathbf{A}_P)\, \mathbb{S} = \mathbb{S}\}. \tag{III.13}$$

We also refer to these subgroups as the right and left stabiliser subgroup for $\mathbb{S}$.

In general, we can define a *second-rank symmetry group* or *stabiliser subgroup* as the subgroup of $\mathsf{O}(3) \times \mathsf{O}(3)$ that collects all the orthogonal transformations, both in the phase and in the molecule, that leave $\mathbb{S}$ invariant. Mathematically speaking, this is the direct product of G_P and G_M: $G(\mathbb{S}) = G_P(\mathbb{S}) \times G_M(\mathbb{S})$.

We need to introduce a relation based on the idea that different materials, which can be rotated so that their symmetry groups become identical, are ‘equivalent’, e.g. two uniaxial nematic liquid crystals in which the director has different orientation for the two compounds.

In general, if two ordering tensors $\mathbb{S}_1$ and $\mathbb{S}_2$ are related by a rotation of the axes, they represent the same material phase, and hence are equivalent; in detail we say that the two ordering tensors belong to the same (second-rank) *symmetry class* (and therefore are equivalent) when their stabiliser subgroups are conjugate. More precisely, we write $\mathbb{S}_1 \sim \mathbb{S}_2$ if and only if there exist two rotations $\mathbf{R}_P, \mathbf{R}_M \in \mathsf{SO}(3)$ such that

$$D^{(2)}(\mathbf{R}_P) G_P(\mathbb{S}_1) D^{(2)}(\mathbf{R}_P)^{\mathrm{T}} = G_P(\mathbb{S}_2) \quad \text{and} \quad D^{(2)}(\mathbf{R}_M) G_M(\mathbb{S}_1) D^{(2)}(\mathbf{R}_M)^{\mathrm{T}} = G_M(\mathbb{S}_2). \tag{III.14}$$

Finally, we note that the symmetry of the ordering tensor may not be shared by the physical system, i.e., by the probability density. It is important to find those symmetries of the physical system that collapse into the same stabiliser at the second-rank level. We say that G_1 and G_2 are *second-rank indistinguishable* if whenever $\mathbb{S}_1 \in L(V_2)$ is fixed by G_1 and $\mathbb{S}_2 \in L(V_2)$ is fixed by G_2 then $\mathbb{S}_1$, $\mathbb{S}_2$ have conjugate stabilizers ($\mathbb{S}_1 \sim \mathbb{S}_2$).

C. Symmetry classes of second-rank ordering tensors

In our case, the determination of the symmetry classes for second-rank ordering tensors takes advantage from the presence of *irreducible second-rank* tensors; furthermore, the action of molecular and phase symmetry can be studied separately, as any symmetry group G we consider is the direct product $G_P \times G_M$, i.e. phase and molecule group symmetries ('left' and 'right' actions in Eq. III.11).

Several authors have performed similar classifications based on the number of non-vanishing independent order parameters for each group [2–4, 29]. However, in our view, this classification of the symmetry classes is a direct consequence of standard theorems in group theory. We resume here main results, necessary to the comprehension of the method we implement.

First of all, Hermann-Herman's theorem shows that, for second-rank ordering tensors, if $\mathbb{S}$ is invariant with respect to the cyclic group C_n of n-fold rotations about a fixed axis and $n > 2$, then it is C_∞-invariant relative to this axis (i.e., it is C_m-invariant for all $m \geq n$). In addition, a standard classification theorem in Group Theory [13, 16, 30] tells us that every closed subgroup of $\mathsf{SO}(3)$ is isomorphic to exactly one of the following groups ($n \geq 2$): C_1, C_n, D_n, T, O, I, C_∞, $C_{\infty v}$, $\mathsf{SO}(3)$. In view of these results, for $j = 2$ all point groups can be collected in five classes, which greatly simplifies the classification of phase or molecular symmetries. In [5] we show that there are exactly five (phase or molecular) symmetry-classes of the second-rank ordering tensor: *Isotropic, Uniaxial, Orthorhombic, Monoclinic and Triclinic.* The corresponding stabiliser subgroups for $\mathbb{S}$ are, in order: $\mathsf{O}(3)$, $D_{\infty h}$, D_{2h}, C_{2h} and C_i. This result is summarised in Table I

The last column Table I collects all of the equivalent second-rank ordering tensors, i.e. all second-rank-indistinguishable symmetries. Furthermore, since all entries of $\mathbb{S}$ vanish in the isotropic class, there are only $4 \times 4 + 1 = 17$ possible different combinations of molecular and

	Class	Stabiliser for $\mathbb{S}$	Equivalent symmetries
$\mathscr{C}_0$	Isotropic	$\mathsf{O}(3)$	$T, T_h, T_d, O, O_h, I, I_h, \mathsf{SO}(3), \mathsf{O}(3)$
	$\uparrow$		
$\mathscr{C}_1$	Uniaxial	$D_{\infty h}$	$C_n, C_{nh}, C_{nv}, D_n, D_{nh}\ (n \geq 3), S_n\ (n \geq 4), D_{nd}\ (n \geq 2)$
	$\uparrow$		
$\mathscr{C}_2$	Orthorhombic	D_{2h}	C_{2v}, D_2, D_{2h}
	$\uparrow$		
$\mathscr{C}_3$	Monoclinic	C_{2h}	C_2, C_s, C_{2h}
	$\uparrow$		
$\mathscr{C}_4$	Triclinic	C_i	C_1, C_i

TABLE I: Synopsis table describing the five symmetry classes of the second-rank ordering tensor, in increasing degree of symmetry (from bottom to top). In the second column we report the corresponding stabiliser subgroup of each class (cf. Section III B), i.e. the most representative subgroup. In the third column, all the equivalent subgroups pertaining to each class are reported; for each row, all these symmetries cannot be distuinguished at second-rank level.

phase symmetries that can be distinguished at the level of second-rank order parameters. The details of proofs can be found in [5].

IV. IDENTIFICATION OF THE NEAREST SYMMETRIC ORDERING TENSOR

If $G_M, G_P \subset \mathsf{O}(3)$ represent the real symmetry of the material, the order parameter $\mathbb{S}$ must be invariant under the action of $G_P \times G_M$. However, in practice, $\mathbb{S}$ will not be fixed exactly by any non-trivial group, due to measurements errors or non perfect symmetry of the real system. Therefore, our problem can be stated as follows: given a 5×5 ordering tensor $\mathbb{S}$, obtained experimentally, and given two subgroups G_M, G_P, find the ordering tensor $\mathbb{S}^{\mathrm{sym}}$ which is $(G_P \times G_M)$–invariant and is closest to $\mathbb{S}$; in doing this, we need to discuss how to find $\mathbb{S}^{\mathrm{sym}}$ and what is the meaning of "closest to $\mathbb{S}$".

Let us define the fixed point subspace $L(V_2)^G$ as the space of the tensors $\mathbb{S}$ that are fixed under G:

$$L(V_2)^G = \{\mathbb{S} \in L(V_2) : g\mathbb{S} = \mathbb{S}, \forall g \in G\}. \qquad \text{(IV.1)}$$

The invariant projection onto $L(V_2)^{G_P \times G_M}$ can be easily obtained by averaging over the group

$$\mathbb{S}^{\rm sym} = \frac{1}{|G_P||G_M|} \sum_{\mathbf{A}_P \in G_P} \sum_{\mathbf{A}_M \in G_M} D^{(2)}(\mathbf{A}_P)\, \mathbb{S}\, D^{(2)}(\mathbf{A}_M), \tag{IV.2}$$

where $|G_P|$ and $|G_M|$ are the orders of the two (finite) groups. The right term in Eq. (IV.2) is clearly invariant by construction, and produces an *orthogonal projection*, with respect to the standard Frobenius inner product, i.e. the natural extension to $L(V_2)$ of the scalar product between tensors. Hence, the distance of $\mathbb{S}^{\rm sym}$ from the original $\mathbb{S}$ is minimal and can be easily computed. In fact, Frobenius norm $\|\mathbb{S}^{\perp}\|$ is a suitable candidate for the "distance from the G-invariant subspace". We point out that such distance is properly defined as its calculation does not depend on the particular matrix representation of $\mathbb{S}$, i.e. on the choice of the molecular and laboratory axes. Furthermore, by orthogonality we readily obtain the following expression for the distance

$$\mathrm{d}(\mathbb{S}, L(V_2)^{G_P \times G_M}) = \|\mathbb{S}^{\perp}\| = \sqrt{\ \|\mathbb{S}\|^2 - \|\mathbb{S}^{\rm sym}\|^2}. \tag{IV.3}$$

The matrix representation of the ordering tensor $\mathbb{S}$ assumes a particularly simple form when the molecule and the laboratory axes are chosen in accordance with the molecular and phase symmetry, respectively. Table II shows explicitly a "canonical" form for the ordering tensor, obtained by using the projection (IV.2), when the z-axis is assumed to be the main axis of symmetry, and the basis tensors $\mathbf{M}_i$ and $\mathbf{L}_j$ are chosen accordingly; we recall that $S_{ij} = \mathbf{L}_i \cdot \langle \mathbf{M}_j \rangle$, and $\langle \mathbf{M}_j \rangle$ is the average computed on all molecules of the ensemble. In particular, Table II displays all entries that must vanish, when a certain molecular/phase symmetry class is considered. The total number of non-vanishing entries in each matrix corresponds to the number of independent (second-rank) order parameters necessary to describe the orientational order of molecules of the given symmetry in a given phase. The same results can be obtained by direct computation using the invariance of each matrix entry by symmetry transformations (cf. the calculations at the end of [27] relative to a nematic biaxial liquid crystal, where $S_{ij} = \langle \mathbf{M}_i \rangle \cdot \mathbf{L}_j$).

As anticipated, we immediately read from Eq. (III.7) that

$$S_{00} = \mathbf{L}_0 \cdot \langle \mathbf{M}_0 \rangle = \boldsymbol{\ell}_3 \cdot \left(\frac{3}{2} \left\langle \boldsymbol{m}_3 \otimes \boldsymbol{m}_3 - \frac{1}{3}\mathbf{I} \right\rangle \right) \boldsymbol{\ell}_3 = \frac{1}{2} \left\langle 3(\boldsymbol{\ell}_3 \cdot \boldsymbol{m}_3)^2 - 1 \right\rangle = S, \tag{IV.4}$$

where S is the standard uniaxial ($D_{\infty h}$) order parameter (degree of orientation). This is due to the fact that $\boldsymbol{m}_3$ is the main rotation axis of the molecule, and we have chosen the

Phase Mol.	Triclinic	Monoclinic	Orthorhomb.	Uniaxial
Triclinic	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & S_{03} & S_{04} \\ S_{10} & S_{11} & S_{12} & S_{13} & S_{14} \\ S_{20} & S_{21} & S_{22} & S_{23} & S_{24} \\ S_{30} & S_{31} & S_{32} & S_{33} & S_{34} \\ S_{40} & S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & S_{03} & S_{04} \\ S_{10} & S_{11} & S_{12} & S_{13} & S_{14} \\ S_{20} & S_{21} & S_{22} & S_{23} & S_{24} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & S_{03} & S_{04} \\ S_{10} & S_{11} & S_{12} & S_{13} & S_{14} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & S_{03} & S_{04} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$
Monoclinic	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & \cdot & \cdot \\ S_{10} & S_{11} & S_{12} & \cdot & \cdot \\ S_{20} & S_{21} & S_{22} & \cdot & \cdot \\ S_{30} & S_{31} & S_{32} & \cdot & \cdot \\ S_{40} & S_{41} & S_{42} & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & \cdot & \cdot \\ S_{10} & S_{11} & S_{12} & \cdot & \cdot \\ S_{20} & S_{21} & S_{22} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & \cdot & \cdot \\ S_{10} & S_{11} & S_{12} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & S_{02} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$
Orthorhombic	$\begin{pmatrix} S_{00} & S_{01} & \cdot & \cdot & \cdot \\ S_{10} & S_{11} & \cdot & \cdot & \cdot \\ S_{20} & S_{21} & \cdot & \cdot & \cdot \\ S_{30} & S_{31} & \cdot & \cdot & \cdot \\ S_{40} & S_{41} & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & \cdot & \cdot & \cdot \\ S_{10} & S_{11} & \cdot & \cdot & \cdot \\ S_{20} & S_{21} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & \cdot & \cdot & \cdot \\ S_{10} & S_{11} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & S_{01} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$
Uniaxial	$\begin{pmatrix} S_{00} & \cdot & \cdot & \cdot & \cdot \\ S_{10} & \cdot & \cdot & \cdot & \cdot \\ S_{20} & \cdot & \cdot & \cdot & \cdot \\ S_{30} & \cdot & \cdot & \cdot & \cdot \\ S_{40} & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & \cdot & \cdot & \cdot & \cdot \\ S_{10} & \cdot & \cdot & \cdot & \cdot \\ S_{20} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & \cdot & \cdot & \cdot & \cdot \\ S_{10} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} S_{00} & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}$

TABLE II: Canonical forms of $\mathbb{S}^{\mathrm{sym}}$ obtained by the projection of a generic ordering tensor $\mathbb{S}$ using Eq.(IV.2). The basis tensors $\mathbf{M}_i$ and $\mathbf{L}_j$, as given in (III.3), are adapted to the molecular and phase symmetries, where the z-axis is the main axis of symmetry. For the sake of readability, dots stand for vanishing entries. The isotropic class is omitted since the entries of the corresponding ordering tensors all vanish.

laboratory axis $\boldsymbol{\ell}_3$ along the uniaxial symmetry axis of the phase (see Sec. II). Likewise, we can see that, when the frames of reference are adapted to the molecular and phase symmetries of the system, S_{10} corresponds to the degree of phase biaxiality P, whilst S_{01} and S_{11} are the two additional nematic biaxial (D_{2h}) order parameters, usually written as D and C (see [27] for notations).

However, not all of the axes are uniquely defined by the group operations; contrary to common understanding, the matrix entries of $\mathbb{S}$ are not suitable candidates for the order parameters, but rather the ordering tensor $\mathbb{S}$ as a whole should be considered as the correct descriptor of the molecular order in a low symmetry system. In other words, the position of vanishing entries in S_{ij} allows identifying the phase symmetry class (and, in principle, the molecular symmetry class, if this is not known), but the matrix entries of $\mathbb{S}$ surely depend on the orientation of the axes. In general, a different choice of the $x-$ and $y-$axes could lead to different values for the matrix entries and the canonical form of the matrix $\mathbb{S}$ is thus not uniquely defined. By contrast, the *structure* of the matrix as given in Table II, and in particular the position of the vanishing entries of $\mathbb{S}$, are not affected by such a change of basis. This suggests that the order parameters should not be identified with the matrix entries, but rather with the *invariants* of $\mathbb{S}$. However, it is important to observe that the molecular and phase symmetries are uniquely identified once we recognise the structure of the canonical form, independently of the definition of the order parameters.

To evaluate the distance of $\mathbb{S}$ from a given fixed point subspace, we choose any group in the corresponding class and describe its elements concretely by assigning the orthogonal transformations and assuming the rotation axes. However, the rotation axes are not in general known (and are indeed part of the solution). Therefore, we calculate the distance with respect to all of the possible directions of the symmetry axes, and define the distance from the symmetry class as the minimum amongst the distances.

To do this, we define the *coefficient of discrepancy* [31] as the minimum relative distance of $\mathbb{S}$ (cf. Eq. (IV.3)) from a symmetry class

$$c(p,m) = \min\left\{\frac{d(\mathbb{S}, L(V_2)^{G})}{\|\mathbb{S}\|}\ :\ G = G_P \times G_M \in \mathcal{C}_{(p,m)}\right\}. \tag{IV.5}$$

However, in simulations the molecular symmetry is known, say G_M, therefore we need to minimise only with respect the phase groups; in this case, the coefficient of discrepancy depends only on the phase-index:

$$c(p) = \min\left\{\frac{d(\mathbb{S}, L(V_2)^{G\times G_M})}{\|\mathbb{S}\|}\ :\ G = G_P \in \mathcal{C}_p\right\}. \tag{IV.6}$$

In [5] we proposed an algorithm that is resumed schematically as follows (a MATLAB encoding of the algorithm is discussed in next section, and reported in Appendix A).

(1) If $\|\mathbb{S}\| = 0$, then the phase is isotropic.

(2) If $\|\mathbb{S}\| \neq 0$, then we **loop over** the phase symmetry classes for $\boldsymbol{p = 1, 2, 3}$ (there is no need to minimise in the trivial class $\mathcal{C}_4$).

(2.1) **Selection of the lowest order group in $\mathcal{C}_p$.** Select an abstract group G_P in the chosen class; this is reasonably the one with lowest order.

(2.2) **Minimisation step.** The distance (IV.3) depends on the concrete realisation of G_P, i.e. on the direction of the symmetry axes, via the averaging procedure IV.2. Therefore we need to minimise the distance (IV.3) with respect to all possible directions of the rotation axes allowed by the specific abstract group.

(3) **Selection step.** Clearly, the correct symmetry class is not simply that of the lowest distance. For instance, any ordering tensor $\mathbb{S}$ has a vanishing distance with respect to the triclinic class (absence of symmetry). As a second example, since the lattice of the stabiliser subgroups is composed by a single chain, a uniaxial ordering tensor has zero distance also from all the previous classes in the chain, i.e. orthorhombic, monoclinic and triclinic.

In principle, when $\mathbb{S}$ is free from numerical errors, we should choose the class with the highest symmetry and vanishing coefficient of discrepancy. However, in practice we will choose the highest symmetry compatible with a coefficient of discrepancy (IV.6) not exceeding the experimental error (or simulation error).

V. MINIMISATION CODE

We have written a plain MATLAB code, which is reported in Appendix A.

The code is a script that loads from a `.mat` file a matrix `bR` containing the rotation matrices of a set of `Nmol` molecules; the size of `bR` is $3 \times 3 \times$ `Nmol`.

A global matrix `bL` contains the matrices describing the basis of tensors (cf. Eqs. (III.3)). The ordering tensor $\mathbb{S}$ is then obtained by averaging on the ensemble of molecules the 25 entries obtained after Eqs. (III.2,III.5).

For each of the relevant symmetry classes, a minimisation is performed by using MATLAB `fminsearch` command for a function that computes the discrepancy coefficient $c(p)$ IV.6; the minimum $c(p)$ obtained is then displayed together with the Euler angles of the rotation for the miminum and the ordering tensor $\mathbb{S}$ in the rotated frame. For the uniaxial ($D_{\infty h}$) class, the equivalent cyclic group C_3 is used, i.e. the identity and the rotations of $\pm\frac{2\pi}{3}$ about $z-$axis; for biaxial (D_{2h}) class, it is enough to use group D_2, i.e. the identity and the rotations of π about the vertical axis and two mutually othogonally axes in the plane; for monoclinc (C_{2h}) class, the equivalent group C_2 is used, i.e. the identity and the rotation of π about vertical axis. Details of how the point groups are realised can be found in [8].

We have tested our code on a set of data obtained by a Monte-Carlo simulation on a lattice of $N = 1024$ molecules, and we interpret those data as a uniaxial phase, having order parameter $S = 0.97$, with a director tilted of an angle $\beta = 47^\circ.16$ with respect to the unit vector $\boldsymbol{\ell}_3$ of the laboratory frame ($z-$axis).

This is in good agreement with the outcome of the interpretation given in the simulation with the traditional conversion of the quaternion describing the reference frame of the director, obtained by the simultaneous diagonalisation of the three Cartesian order matrices; this analysis yielded $\beta = 47^\circ.625$ (R. Berardi, Department of Industrial Chemistry "Toso Montanari" University of Bologna Viale Risorgimento 4 I-40136 Bologna, Italy, personal communication).

VI. CONCLUSIONS

We implement a method proposed in [5], which is capable of providing the canonical form of an ordering tensors $\mathbb{S}$ ('supertensor'). This canonical representation readily yields the order parameters, i.e. the scalar quantities that are usually adopted to describe the order in a liquid crystal compound. The laboratory axes of the canonical form are interpreted as "directors" and provide the directions of the symmetry axes, if there are any. As we have shown, there are only five possible phase symmetry-classes, when the orientational probability density function is truncated at the second-rank level. This is a standard approximation in many theoretical studies of uniaxial and biaxial liquid crystals.

The method we propose is simple enough to be applicable to the analysis of real situations. We have written a MATLAB code implementing the algorithm proposed in [5] and reported here. We have tested our code with data obtained in a lattice Monte-Carlo simulation, and our outcome is in agreement with results traditionally obtained within the simulation, with traditional analysis of data.

However, our method is more general and has many advantages over the traditional approaches. The distinguishing features are summarised as follows:

1. Any laboratory frame of reference is suited to the analysis, there is no need to know *a-priori* the directors, as these are determined by the algorithm.

2. The phase is not found by analysing the order parameters (which, being related to the

ordering tensor entries are not uniquely defined in low-symmetry systems) but it is identified by calculating the minimum distance from a symmetry class. In this respect, it is possible to determine the phase by looking at a single number, even when it is not clear which are the important order parameters for that phase (see for instance the discussion in [4, 20] for the C_{2h} phase).

3. Our method provides a general route to the identification of the phase also in the more complex low-symmetry cases. Specifically it could be, equally well, applied to the analysis of liquid crystal compounds composed of monoclinic (C_{2h}) molecules, where there is no efficient traditional method to assess the phases.

4. In principle the approach presented in this paper, based on the second-rank ordering tensor, could be easily extended to include higher-rank ordering tensors. This would allow further distinguishing amongst the phase groups belonging to the same class. The same mathematical ideas and tools we have put forward could be applied to this more general case, only at the cost of more involved notations. To keep the exposition simple, we have not explored this possibility in the paper. Furthermore, the second-rank case is the most relevant from a physical perspective, since most tensorial properties that can be measured in liquid crystals are second-rank, and these properties have been used widely in the scientific literature. For these reasons we have analysed and encoded the algorithm only in the case of a second-rank ordering tensor.

An intriguing application of our algorithm would be the analysis of a thermotropic nematic biaxial (D_{2h}) phase in a liquid crystal compound made of D_{2h} molecules (or less symmetric molecules). In fact, despite intense study and a number of positive reports (see [32–35]), many current observations remain controversial [36, 37]. However, in order to apply our method it is necessary to determine experimentally the entire Saupe ordering matrix, which, to date, is still a challenging task in direct experiments (contrary to simulations). To the best of our knowledge, most of the experimental studies concentrate on a limited number of biaxiality parameters, and in general the full Saupe ordering-matrix is not measured or reported. Hence, the full experimental data that would allow us to use our algorithm to determine a biaxial phase unambiguously seem not to be easily available.

Acknowledgements

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Appendix A: Appendix: MATLAB code

We report here the MATLAB code for a script that perform the search for phase in a set of data stored in a `.mat` file.

```
% MATLAB script phaseDetermination.m
% Oct-Nov 2018 - F. Bisi & S. Turzi
clear
global bL
% lab frame tensors L0 ... L4 are inmatrix bL(i,j,k)
% bL is a global matrix
bL = zeros (3, 3, 5);
bL (:,:,1) = [-1/sqrt(6), 0, 0; 0, -1/sqrt(6), 0; 0, 0, sqrt(2/3)]; % L0
cc = 1/sqrt(2);
bL (:,:,2) = [cc, 0, 0; 0, -cc, 0; 0, 0, 0];    % L1
bL (:,:,3) = [0, cc, 0; cc, 0, 0; 0, 0, 0];     % L2
bL (:,:,4) = [0, 0, 0; 0, 0, cc; 0, cc, 0];     % L3
bL (:,:,5) = [0, 0, cc; 0, 0, 0; cc, 0, 0];     % L4


% ***********************************************
%        DATA ACQUISITION AND ELABORATION
% ***********************************************

load('test.mat');
[nrw,  ncl,  Nmol] = size(bR);

Ddue = zeros(5,5,Nmol);
```

```
for k = 1:Nmol
    Ddue(:,:,k) = rho(bR(:,:,k));
end

bS = mean(Ddue,3); % S ordering tensor obtained by averaging on
                   % the ensemble of molecules

% ***********************************************
%               SEARCH FOR MINIMUM
% ***********************************************

for class = 1:3
    f = @(x) DiscrepacyC(bS,x,class);
    options = optimset('TolX',10^(-8));
    EulerBest = fminsearch(f,[pi/3,pi/6,pi/4],options);

    a = EulerBest(1); b = EulerBest(2); c = EulerBest(3);
    cbest = f([a,b,c]);
    % class 1: D_{\infty h}
    % class 2: D_{2h}
    % class 3: C_{2h}
    disp(['class = ',num2str(class),' >>> ']);
    output = ['best: c = ',num2str(cbest),' alpha = ',num2str(180*a/pi),...
        ' beta = ',num2str(180*b/pi),' gamma = ',num2str(180*c/pi)];
    disp(output);

   % ***********************************************
   %             SYMMETRY AXES DETERMINATION
   % ***********************************************

   % rotation to get the orientation of symmetry axes
```

```
   %       (bQ*bl_k = bn_k)
   bQ2 = rho(QyEuler(a,b,c));
   bSp = bQ2'*bS       % print new order-tensor

end

% ****************************************************************
%                        FUNCTIONS
% ****************************************************************

function D2 = rho(bRmol)
% from rotation matrix to irrep in V_2 (5-dim)

global bL

D2 = zeros(5,5);

for i = 1:5
    for j = 1:5
        D2(i,j) = trace(bL(:,:,i)*bRmol(:,:)*bL(:,:,j)*bRmol(:,:)');
        % Eq. III.2 (3.2):  D^2(R) T = R T R^transp
        % matrices are real
    end
end
end

function Q = rotvect2matrix( n, alpha )
%   computes the rotation matrix in terms of
%   rotation alpha about axis n
%       nx := sin(theta)*cos(phi)
%       ny := sin(theta)*sin(phi)
%       nz := cos(theta)
```

```
%
%   (wrapper)
%   uses QRnalpha( phi, theta, alpha )



% we need a unit vector
if norm(n,2) < 1e-8
    warning('Input n must be a nonvanishing vector')
    return
end

n = n/norm(n,2);

theta = acos(n(3));
phi   = atan2(n(2),n(1));

Q = QRnalpha( phi, theta, alpha );
end

function Q = QRnalpha( phi, theta, alpha )
%   computes the rotation matrix in terms of
%   rotation alpha about axis n
%       nx := sin(theta)*cos(phi)
%       ny := sin(theta)*sin(phi)
%       nz := cos(theta)

Q(1,1) = cos(alpha) + (1-cos(alpha))*sin(theta)^2*cos(phi)^2;
Q(1,2) = -sin(alpha)*cos(theta) + ...
    (1-cos(alpha))*sin(theta)^2*cos(phi)*sin(phi);
Q(1,3) = sin(alpha)*sin(theta)*sin(phi) + ...
    (1-cos(alpha))*sin(theta)*cos(phi)*cos(theta);
Q(2,1) = sin(alpha)*cos(theta) + ...
```

```
    (1-cos(alpha))*sin(theta)^2*cos(phi)*sin(phi);
Q(2,2) = cos(alpha)+(1-cos(alpha))*sin(theta)^2*sin(phi)^2;
Q(2,3) = -sin(alpha)*sin(theta)*cos(phi) + ...
    (1-cos(alpha))*sin(theta)*sin(phi)*cos(theta);
Q(3,1) = -sin(alpha)*sin(theta)*sin(phi) + ...
    (1-cos(alpha))*sin(theta)*cos(phi)*cos(theta);
Q(3,2) = sin(alpha)*sin(theta)*cos(phi) + ...
    (1-cos(alpha))*sin(theta)*sin(phi)*cos(theta);
Q(3,3) = cos(alpha) + (1-cos(alpha))*cos(theta)^2;
end

function Q = QyEuler( alpha, beta, gmm )
%   computes the rotation matrix in terms of the Euler angles
%   (alpha, beta, gamma) defined in the y-notation convention
%   ACTIVE CONVENTION: this is the rotation to be applied
%   to OBJECTS; the fixed reference frame is the same

%   1st column
Q(1,1) =  cos(alpha)*cos(beta)*cos(gmm) - sin(alpha)*sin(gmm);
Q(2,1) =  sin(alpha)*cos(beta)*cos(gmm) + cos(alpha)*sin(gmm);
Q(3,1) = -sin(beta)*cos(gmm);
%   2n column
Q(1,2) = -cos(alpha)*cos(beta)*sin(gmm) - sin(alpha)*cos(gmm);
Q(2,2) = -sin(alpha)*cos(beta)*sin(gmm) + cos(alpha)*cos(gmm);
Q(3,2) =  sin(beta)*sin(gmm);
%   3rd column
Q(1,3) =  cos(alpha)*sin(beta);
Q(2,3) =  sin(alpha)*sin(beta);
Q(3,3) =  cos(beta);
end

function bSsym = ReynoldsDinf(bS,bn)
```

```
% Reynolds projector in uniaxial class, symmetry axis: bn
% according to table in figure 1, D_{\infty h} is equivalent
% to C_3 for second-rank rep. (j=2)

G0 = rotvect2matrix(bn,0);      % E (identity)
G1 = rotvect2matrix(bn,2*pi/3); % C_3 (+rotation of 2pi/3 about bn)
G2 = rotvect2matrix(bn,4*pi/3); % C_3 (-rotation of 2pi/3 about bn)

rhoG0 = rho(G0);
rhoG1 = rho(G1);
rhoG2 = rho(G2);

bSsym = (rhoG0 + rhoG1 + rhoG2)*bS/3;

end

function bSsym = ReynoldsD2(bS,bn,bn2)
% Reynolds projector in biaxial (orthorhombic) class
% according to table in figure 1, D_{2 h} is equivalent
% to D_2 for second-rank rep. (j=2)

G0 = rotvect2matrix(bn,0);      % E (identity)
G1 = rotvect2matrix(bn,pi);     % C_2 (+rotation of pi about bn)
G2 = rotvect2matrix(bn2,pi);    % C_2^1 (+rotation of pi about bn2)
G3 = G2*G1;                     % C_2^(12) (+rotation of pi about 3rd axis)
                                % C_2^(12)=C_2 * C_2^1
rhoG0 = rho(G0);
rhoG1 = rho(G1);
rhoG2 = rho(G2);
rhoG3 = rho(G3);

bSsym = (rhoG0 + rhoG1 + rhoG2 + rhoG3)*bS/4;
```

```
end


function bSsym = ReynoldsC2(bS,bn)
% Reynolds projector in classe C2h
% according to table in figure 1, D_{\infty h} is equivalent
% to C_2 for second-rank rep. (j=2)

G0 = rotvect2matrix(bn,0);      % E (identity)
G1 = rotvect2matrix(bn,pi);     % C_2 (+rotation of pi about bn)

rhoG0 = rho(G0);
rhoG1 = rho(G1);

bSsym = (rhoG0 + rhoG1)*bS/2;

end

function cd = DiscrepacyC(bS,angles,class)

    a = angles(1);
    b = angles(2);
    c = angles(3);

    bn = [cos(a)*sin(b), sin(a)*sin(b), cos(b)];
    bn2 = [cos(a)*cos(b)*cos(c) - sin(a)*sin(c), ...
           cos(b)*cos(c)*sin(a) + cos(a)*sin(c), ...
           -cos(c)*sin(b)];

    if class == 1
        bSsym = ReynoldsDinf(bS,bn);
    elseif class == 2
```

```
        bSsym = ReynoldsD2(bS,bn,bn2);
    elseif class == 3
        bSsym = ReynoldsC2(bS,bn);
    end

    cd = 1 - sqrt(trace(bSsym*bSsym')/trace(bS*bS'));

end
```

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