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Orientational order parameters in biaxial nematics: Polymorphic notation

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In this paper, a wealth of notations introduced in the past 30 years to denote second-rank orientational order parameters for biaxial nematics are compared, stressing sources of possible confusion. A unifying, intrinsic treatment of the second-rank orientational order parameters is also presented, which does not suffer from the redundancy of the Saupe matrix and is independent of the way in which rotations are parametrized.

1. Introduction

Biaxial nematics were predicted theoretically by Freiser [1] who raised the question of the existence of a biaxial nematic phase in analogy with the biaxial phase then just observed in smectic C liquid crystals by Taylor *et al.* [2]. Freiser started from the observation that the traditional picture of nematogenic molecules as elongated rods with $D_{\infty h}$ symmetry about their long axes is too simplistic, a more realistic description being that where nematogenic molecules are lath-shaped, and so have D_{2h} symmetry. Following Williams [3], who interpreted observations on the linear electro-optic effect in PAA in terms of the molecular symmetry, Freiser proposed that departure from $D_{\infty h}$ molecular symmetry could be responsible for a biaxial nematic phase, and generalized the Maier–Saupe theory to account for this effect. Before proceeding, two comments are in order. First, although lath-like molecules are a more faithful representation of nematogenic molecules than rod-like molecules, in both models molecules are conceived as *rigid*, which is a further idealization of real nematogenic molecules that are flexible. Secondly, the terms *uniaxial* and *biaxial* only indirectly refer to molecular symmetry. In fact, these terms are borrowed from the optics of anisotropic media. An optically anisotropic material is said to be *uniaxial* when there exists only one direction along which a beam of linearly polarized light can travel maintaining its state of polarization unaltered, while it is said to be *biaxial* if there are two different directions along which this property holds.

A biaxial nematic phase was first observed in a *lyotropic* mixture by Yu and Saupe [4] in 1980, ten years after the first theoretical predictions had been made. No *thermotropic* biaxial liquid crystals had been found, a possible explanation [5] being that freezing or the appearance of smectic order preempt the transition to the biaxial phase. The elusive biaxial phase in thermotropic nematics was still sought by synthesizing compounds with highly biaxial molecules. In fact, since 1986 several compounds were also claimed to exhibit a biaxial phase (see [6] for an account on this topic), but correctly detecting the fingerprint of the biaxial phase turned out to be a rather delicate issue and most of the techniques employed failed to prove unambiguously that the observed phases were indeed biaxial. By contrast, NMR spectroscopy has revealed that most liquid-crystalline compounds supposed to provide experimental evidence of biaxial phases yielded only uniaxial phases [6]. In the absence of experimental verifications, the theoretical predictions made in the 1970s could be tested by computer simulations. From the wide literature in this field, I simply quote a few papers that opened the way to simulations for biaxial liquid crystals: Luckhurst and Romano [7] performed a Monte Carlo simulation for a lattice model that generalized the Lebwohl–Lasher model to biaxial molecules; Allen [8] obtained a phase diagram for hard biaxial ellipsoids; Berardi *et al.* [9] proposed a modification of the Gay–Berne intermolecular potential tailored on biaxial particles. In the sequel, papers concerning simulations are quoted only when they contain original definitions of second-rank orientational order parameters. An updated account on computer simulations in liquid crystals has been given by Care and Cleaver [10].

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Recently, there has been a surge of interest in biaxial nematics both at the experimental and at the theoretical level. From the experimental point of view several reports appeared where thermotropic liquid crystals formed by new classes of molecules – flat molecules tied to polymer chains [11], bent-core (V-shaped) molecules [12, 13], and tetrapodes [14] – seem to produce biaxial phases. Although there are strong arguments suggesting that the observed phases are indeed biaxial – in particular, ^{2}H NMR spectroscopy was used in [12] to check biaxiality – words of caution have been used for the interpretation of the results [15, 16] since there are some debated issues concerning the origin of the observed biaxiality; see also the discussion in [17, 18].

At the theoretical level, Straley's quadrupolar model [19] has been revisited [20] and new perspectives have been disclosed since a direct transition from the isotropic to the biaxial phase along a transition line – and not only at an isolated Landau point, as in Straley's paper – has been predicted when the parameters of the model are suitably selected [21]. This renewed impetus in biaxial nematics justifies a systematic comparison of the notations employed to denote the second-rank orientational order parameters describing a biaxial phase made of rigid biaxial molecules. In fact, the number of different notations used to denote the same set of order parameters and the number of different prefactors in the definitions of order parameters is astonishingly large. The survey made in this paper identifies as many as 30 notations that differ either by the symbols chosen for a given set of order parameters or by some numerical prefactors that lead to equivalent but different sets of order parameters. This *notational polymorphism* is disturbing as it makes comparisons among results scattered in the literature quite difficult. In some sense the polymorphism of second-rank orientational order parameters is inherent to the mathematical tools employed to introduce them: Euler angles and Wigner matrices. Both tools are employed to parametrize the rotation that carries an orthonormal triad fixed in the laboratory into an orthonormal triad associated with the molecule. Two main notations have been used to denote Euler angles, the x- and the y-notation, and both entered the definition of biaxial order parameters. If the notation is not specified, an ambiguity in the sign of some order parameter occurs. Similarly, several notations on Wigner matrices have been proposed in the past (see p. 21 of [22] or Appendix F of [23]). However, while general tables of conversions exist for both Euler angles and Wigner matrices, no such systematic effort has been made to compare the proposals put forward for second-rank orientational order parameters in biaxial nematics. This is the first aim of our paper.

As mentioned above, most confusion arises when parameterizations are introduced to define second-rank orientational order parameters. Hence, it is important to find an intrinsic way to define them. One way could be the use of the Saupe – or ordering – matrix which, however, is redundant. A more concise treatment can be achieved if a set of symmetric traceless molecular tensors are orientationally averaged and then projected onto another set of symmetric, traceless macroscopic tensors. Providing such an intrinsic definition is the second aim we pursue in this paper, which is organized as follows. In Section 2 the general procedure put forward by Zannoni [24] to define orientational order parameters in liquid-crystalline phases is recalled. This general treatment can be simplified when attention is focussed only on second-rank order parameters, which are defined in a parameter-free way in Section 3 by two different approaches: the former makes use of the Saupe matrix, while the latter is based on projections upon sets of symmetric, traceless tensors. Section 4 contains a synopsis of the different notations employed to represent the set of second-rank order parameters that describe biaxial nematics. Finally, in Appendix A we recall the basic notations employed to introduce Euler angles.

2. Orientational order parameters

In this section we sketch a systematic procedure to obtain the orientational order parameters for liquid crystals that was introduced long ago by Zannoni in [24] and that employs Euler angles to parametrize a rotation. While we refer the interested reader to Appendix A for some remarks on the definition and the notations adopted for Euler angles, here we merely state that we indicate them as $(\varphi, \vartheta, \psi)$ (figure 1), following the y-notation employed, for instance, by Brink and Satchler [22] and by Rose [25].

We shall limit attention to idealized, rigid nematogenic molecules, disregarding the effects of molecular flexibility. In general, flexibility is accounted for by adding to the Euler angles a set of *torsional* angles describing the relative orientations of the rigid subunits that form a molecule (see Section D of [26]). In the following, we call a molecule *uniaxial* if it has $D_{\infty h}$ symmetry, while we call a molecule *biaxial* if it has D_{2h} symmetry. Nematic phases have been predicted and observed for molecules having lower symmetry, like C_{2v}, D_2, C_{2h}, and C_i [27, 28]. We will mention these classes of molecules in Section 3 to discuss the impact of lower molecular symmetry on the set of meaningful order parameters. Let $P^{(1)}(\boldsymbol{r}, \Omega)$ be the one-particle distribution function depending on the position $\boldsymbol{r}$ of the

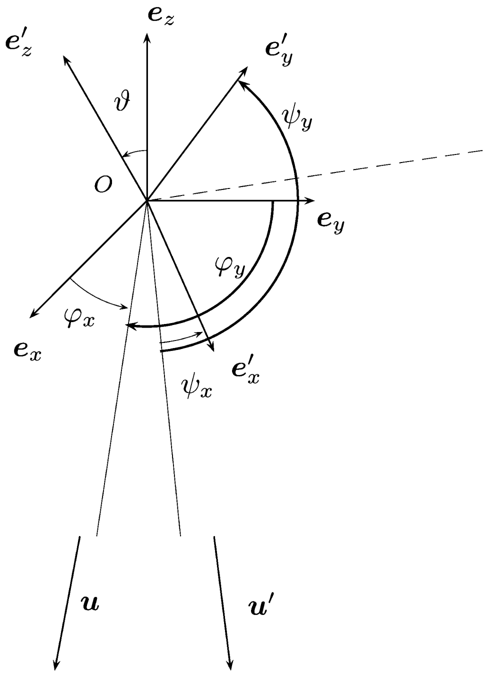

Figure 1. Sketch of the Euler angles $\{\varphi, \vartheta, \psi\}$ carrying the orthonormal frame $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ into the orthonormal frame $\{\boldsymbol{e}_x', \boldsymbol{e}_y', \boldsymbol{e}_z'\}$. Both the x-notation $\{\varphi_x, \vartheta_x, \psi_x\}$ and the y-notation $\{\varphi_y, \vartheta_y, \psi_y\}$ are shown. Here φ denotes the angle of precession, ϑ the angle of nutation, and ψ the angle of proper rotation. The first rotation is through an angle φ about $\boldsymbol{e}_z$; it maps the x-axis into the nodal line – where the $\{\boldsymbol{e}_x, \boldsymbol{e}_y\}$ and the $\{\boldsymbol{e}_x', \boldsymbol{e}_y'\}$ planes intersect – directed along the unit vector $\boldsymbol{u}$. The second rotation is about the dashed line – orthogonal to both $\boldsymbol{e}_z$ and $\boldsymbol{u}$ – through an angle ϑ. It maps $\boldsymbol{e}_z$ into $\boldsymbol{e}_z'$ and the nodal line into the line directed along $\boldsymbol{u}'$. A third rotation about $\boldsymbol{e}_z'$ through an angle ψ completes the transformation from $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ into $\{\boldsymbol{e}_x', \boldsymbol{e}_y', \boldsymbol{e}_z'\}$.

molecule and on the set $\Omega \equiv (\varphi, \vartheta, \psi)$ of Euler angles describing – in the y-notation – the molecular orientation with respect to an orthonormal frame that is fixed in the laboratory. $P^{(1)}(\boldsymbol{r}, \Omega)$ is the probability of finding a molecule at position $\boldsymbol{r}$, oriented like Ω. The singlet *orientational* distribution function $f(\Omega)$ is obtained by averaging $P^{(1)}(\boldsymbol{r}, \Omega)$ over $\boldsymbol{r}$

$$f(\Omega) := \frac{1}{N}\int \mathrm{d}\boldsymbol{r}\, P^{(1)}(\boldsymbol{r}, \Omega), \tag{1}$$

where N is the number of molecules in the sample. If the system is invariant under translation, as in the case of nematic liquid crystals, then

$$f(\Omega) = \frac{1}{\varrho} P^{(1)}(\Omega),$$

where $\varrho := N/V$ is the number density and V is the volume occupied by the sample. The ensemble average $<A>_o$ of any function $A(\Omega)$ can be then written as (p. 61 of [24])

$$\langle A \rangle_o := \int f(\Omega) A(\Omega) \mathrm{d}\Omega, \tag{2}$$

where the subscript 'o' reminds us that only the orientational variables are involved in the averaging process. The invariant measure $\mathrm{d}\Omega$ is expressed in terms of Euler angles as $\mathrm{d}\Omega = \sin\vartheta \mathrm{d}\vartheta \mathrm{d}\varphi \mathrm{d}\psi$. We know from statistical mechanics (see pp. 30–31 of [29]) that averages of one-particle properties $g(\boldsymbol{r}, \Omega)$ can be expressed as

$$\langle g \rangle_{po} = \frac{1}{N}\int g(\boldsymbol{r}, \Omega) P^{(1)}(\boldsymbol{r}, \Omega) \mathrm{d}\boldsymbol{r}\, \mathrm{d}\Omega,$$

where the subscript $_{po}$ has been used to recall that averaging involves both positional and orientational variables.[1] Clearly, $<g>_{po} \equiv <g>_o$ if $g(\boldsymbol{r}, \Omega) = g(\Omega)$. If the orientational distribution function f is smooth, it can be expanded on the basis of Wigner rotation matrices $D^l_{mn}(\Omega)$ that form an orthogonal set of functions since

$$\int D^l_{mn}(\Omega) D^{l'*}_{m'n'}(\Omega) \mathrm{d}\Omega = \int_0^{2\pi} \mathrm{d}\psi \int_0^{2\pi} \mathrm{d}\varphi$$
$$\int_0^{\pi} \sin\vartheta \mathrm{d}\vartheta D^l_{mn}(\Omega) D^{l'*}_{m'n'}(\Omega) = \frac{8\pi^2}{2l+1} \delta_{ll'} \delta_{mm'} \delta_{nn'},$$

for all integer or half-integer l and for all $m, n = -l, -l+1, \ldots, l-1, l$. The asterisk * denotes complex conjugation. Thus,

$$f(\Omega) = \sum_{l=0}^{+\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} f_{lmn} D^l_{mn}(\Omega) \tag{3}$$

where the coefficients f_{lmn} can be determined by multiplying both sides of (3) by D^{l*}_{mn} and integrating on all the orientations Ω:

$$f_{lmn} = \frac{(2l+1)}{8\pi^2} \langle D^{l*}_{mn} \rangle_o. \tag{4}$$

The averages $\langle D^l_{mn} \rangle_o$ are the *orientational order parameters* of rank l. We record here the expression of D^l_{mn}:

$$D^l_{mn}(\Omega) = D^l_{mn}(\varphi, \vartheta, \psi) := \mathrm{e}^{-\mathrm{i}(m\varphi + n\psi)} d^l_{mn}(\vartheta) \tag{5}$$

where i is the imaginary unit and

$$d^l_{mn}(\vartheta) := \sum_t (-1)^t \frac{[(l+m)!(l-m)!(l+n)!(l-n)!]^{1/2}}{(l+m-t)!(l-n-t)!t!(t+n-m)!} \tag{6}$$
$$\left(\cos\frac{\vartheta}{2}\right)^{2l+m-n-2t} \left(\sin\frac{\vartheta}{2}\right)^{2t+n-m},$$

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[1] The notation used here departs from that adopted by Zannoni [24] where $\overline{(\cdot)}$ is used for $<\cdot>_o$ and $<\cdot>$ is used for $<\cdot>_{po}$.

are the *reduced* rotation matrices or small Wigner matrices (see p. 22 of [22]). In equation (6) summation is restricted to the integer values of t that make the argument of all factorials non-negative. For our development, only the reduced matrices with $l=2$ are important, that is (see p. 24 of [22])

$$\begin{aligned} d^2_{00}(\vartheta) &= \frac{1}{2}\left(3\cos^2\vartheta - 1\right), \\ d^2_{20}(\vartheta) &= d^2_{-20}(\vartheta) = d^2_{02}(\vartheta) = d^2_{0-2}(\vartheta) = \sqrt{\frac{3}{8}}\sin^2\vartheta, \\ d^2_{22}(\vartheta) &= d^2_{-2-2}(\vartheta) = \cos^4\left(\frac{\vartheta}{2}\right) = \frac{1}{4}(1+\cos\vartheta)^2, \\ d^2_{2-2}(\vartheta) &= d^2_{-22}(\vartheta) = \sin^4\left(\frac{\vartheta}{2}\right) = \frac{1}{4}(1-\cos\vartheta)^2. \end{aligned} \tag{7}$$

For any fixed value of l, there exist $(2l+1)^2$ orientational order parameters of rank l. The number of independent order parameters can be reduced, however, by resorting to the symmetry properties of both the mesophase and the molecules. In particular, if both the molecules and the mesophase are biaxial, the relevant second-rank orientational order parameters are

$$\begin{aligned} &\langle D^2_{00},\rangle \quad \mathrm{Re}\langle D^2_{02}\rangle = \mathrm{Re}\langle D^2_{0-2}\rangle, \\ &\mathrm{Re}\langle D^2_{20}\rangle = \mathrm{Re}\langle D^2_{-20}\rangle, \\ &\mathrm{Re}\left[\langle D^2_{22}\rangle + \langle D^2_{-22}\rangle\right] = \mathrm{Re}\left[\langle D^2_{2-2}\rangle + \langle D^2_{-2-2}\rangle\right] \end{aligned}$$

which, by resorting to equations (5) and (7), can be given the form

$$\begin{aligned} \langle D^2_{00}\rangle &= \langle \frac{1}{2}\left(3\cos^2\vartheta - 1\right)\rangle = \langle P_2(\cos\vartheta)\rangle, \\ \mathrm{Re}\langle D^2_{0\pm 2}\rangle &= \sqrt{\frac{3}{8}}\langle \sin^2\vartheta\cos 2\psi\rangle \\ \mathrm{Re}\langle D^2_{\pm 20}\rangle &= \sqrt{\frac{3}{8}}\langle \sin^2\vartheta\cos 2\varphi\rangle, \end{aligned}$$

and

$$\begin{aligned} &\mathrm{Re}\left[\langle D^2_{22}\rangle + \langle D^2_{-22}\rangle\right] = \\ &\langle \frac{1}{2}\left(1+\cos^2\vartheta\right)\cos 2\varphi\cos 2\psi - \cos\vartheta\sin 2\varphi\sin 2\psi\rangle, \end{aligned}$$

where P_2 denotes the second Legendre polynomial. Here and in the following, we omit the subscript 'o' since we are concerned only with orientational averages, and so no risk of confusion arises. This set of order parameters can be expressed in terms of the set of symmetry-adapted functions $\Delta^{(2)}_{m,n}$ introduced by Mulder [30]

$$\begin{aligned} \Delta^{(2)}_{0,0}(\Omega) &:= \frac{1}{2}\left(3\cos^2\vartheta - 1\right), \\ \Delta^{(2)}_{0,2}(\Omega) &:= \frac{\sqrt{3}}{2}\sin^2\vartheta\cos 2\psi, \\ \Delta^{(2)}_{2,0}(\Omega) &:= \frac{\sqrt{3}}{2}\sin^2\vartheta\cos 2\varphi, \\ \Delta^{(2)}_{2,2}(\Omega) &:= \frac{1}{2}\left(1+\cos^2\vartheta\right)\cos 2\varphi\cos 2\psi - \cos\vartheta\sin 2\varphi\sin 2\psi, \end{aligned} \tag{8}$$

that belong to the larger family of symmetry-adapted functions $\Delta^{(l)}_{m,n}$ defined as

$$\Delta^{(l)}_{m,n}(\Omega) := \left(\frac{\sqrt{2}}{2}\right)^{2+\delta_{m,0}+\delta_{n,0}} \sum\nolimits_{\sigma,\sigma'=\{-1,1\}} D^l_{\sigma m,\sigma' n}(\Omega), \tag{9}$$

with l even, $0 \leq m, n \leq l$, even or,

with l odd, $2 \leq m, n \leq l$, even.

The set of functions (8) is denoted as $F^{(2)}_{\mu\nu}$ by Fiałkowski *et al.* [31] and by Kapanowski [32], as $E^2_{\mu\nu}$ by Kapanowski and Wietecha [33], as Q^2_{mn} by Camp and Allen [34], and as Q_{mn} by Hołyst and Poniewierski [35]. A different normalization is introduced in [36–38] where the following set of symmetry-adapted functions is employed:

$$\begin{aligned} R^2_{00} &:= \frac{3}{2}\cos^2\vartheta - \frac{1}{2} = \Delta^{(2)}_{0,0} \\ R^2_{20} &:= \sqrt{\frac{3}{8}}\sin^2\vartheta\cos 2\varphi = \frac{1}{\sqrt{2}}\Delta^{(2)}_{2,0} \\ R^2_{02} &:= \sqrt{\frac{3}{8}}\sin^2\vartheta\cos 2\psi = \frac{1}{\sqrt{2}}\Delta^{(2)}_{0,2} \\ R^2_{22} &:= \frac{1}{4}\left(1+\cos^2\vartheta\right)\cos 2\varphi\cos 2\psi - \\ &\quad \frac{1}{2}\cos\vartheta\sin 2\varphi\sin 2\psi = \frac{1}{2}\Delta^{(2)}_{2,2}. \end{aligned} \tag{10}$$

In [39], Romano makes a distinction between the parameters R^2_{mn}, which refer to the rotation from a molecule-based frame to a laboratory frame that is the eigenframe of a tensorial property of the liquid crystal, and the parameters K^2_{mn} where the laboratory-based frame is left unspecified.

Finally, we note that Mulder introduced the functions $\Delta^{(l)}_{m,n}$ of equation (9) for even values of l, while Fiałkowski *et al.* [31] realized that also odd values of l yield combinations of Wigner matrices with the required D_{2h} symmetry.

Historically, the first systematic definition of the orientational order parameter in a uniaxial phase is due to Buckingham [40] who expanded the singlet distribution function $f(\Omega)$ of a molecule in terms of the direction cosines of the preferred direction in a Cartesian frame. We do not enter into the details of this approach here; the interested reader is referred to the original paper [40] and to p. 68 of [24]. We only note that, when defined in this way, the second-rank orientational order parameters involve the Saupe ordering matrix, which we are going to introduce.

3. Second-rank orientational order parameters

Wigner matrices provide a compact formalism to deal with orientational order parameters, and for this reason they are a favourite among theoreticians. On the other hand, the derivation of order parameters in terms of the Saupe ordering matrix is a favourite among experimentalists, especially for second-rank orientational order parameters since, for instance, the outcomes of NMR experiments can be directly restated in terms of this matrix defined as (cf. p. 45 of [41])

$$\begin{aligned} S_{ij}^{\alpha\beta} &:= \frac{1}{2}\langle 3(\boldsymbol{m}_i\cdot\boldsymbol{\ell}_\alpha)(\boldsymbol{m}_j\cdot\boldsymbol{\ell}_\beta)-\delta_{ij}\delta_{\alpha\beta}\rangle \\ &= \frac{1}{2}\langle 3(\boldsymbol{m}_i\otimes\boldsymbol{m}_j)\cdot(\boldsymbol{\ell}_\alpha\otimes\boldsymbol{\ell}_\beta)-(\boldsymbol{m}_i\otimes\boldsymbol{\ell}_\alpha)\cdot(\boldsymbol{m}_j\otimes\boldsymbol{\ell}_\beta)\rangle \qquad (11) \\ &\quad \text{for } i, j, \alpha, \beta = 1, 2, 3. \end{aligned}$$

where $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$ is an orthonormal triad associated with a molecule, and $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ is an orthonomal triad defined in the laboratory. The matrix in (11) has a high redundancy since, by exploiting the symmetries of $S_{ij}^{\alpha\beta}$ and the fact that only scalar products between unit vectors enter in (11), only 25 among the 81 elements of (11) are independent [42]. Further reductions can be made when the matrix describes molecules and phases that are both biaxial. Let us assume that $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$ are chosen along the axes of molecular symmetry, with the stipulation that $\boldsymbol{m}_1$ lies along the shortest axis, and $\boldsymbol{m}_3$ lies along the longest axis. Similarly, let $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ be a lab-based frame with the unit vectors along the principal axes of a tensorial property of the liquid crystal like, for instance, the dielectric tensor $\boldsymbol{\varepsilon}$ [20]. The axes $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ can be labelled by taking $\boldsymbol{\ell}_1$ in the eigenspace associated with the smallest eigenvalue of $\boldsymbol{\varepsilon}$ and $\boldsymbol{\ell}_3$ in the eigenspace associated with the largest eigenvalue of $\boldsymbol{\varepsilon}$. If α and β are fixed, the elements of (11) with $i\neq j$ change their sign if one of the molecular vectors $\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3$ is mapped into its opposite. Since we are concerned with biaxial molecules that are clearly invariant against this change, only elements like $S_{ii}^{\alpha\beta}$ are different from zero, while the remaining elements vanish because of the symmetry of the distribution function involved in the averaging process used in equation (11). Similarly, if the phase is biaxial, the Saupe matrix computed in the frame $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ should be unaffected by mapping $\boldsymbol{\ell}_i$ into $-\boldsymbol{\ell}_i$. Elements like $S_{ii}^{\alpha\beta}$ with $\alpha\neq\beta$ change their sign under such transformation and so they have to vanish in a biaxial phase. We then conclude that only the nine *diagonal* elements $S_{ii}^{\alpha\alpha}$ can be used in the description of a biaxial phase formed by biaxial molecules. However, by definition, the following constraints must be satisfied [41, 43]

$$\sum_{\alpha=1}^{3} S_{ii}^{\alpha\alpha} = \sum_{i=1}^{3} S_{ii}^{\alpha\alpha} = 0;$$

it is not difficult to check that only *four* elements of the Saupe matrix are needed to express all the diagonal elements.

The reader will note that a *specific* tensorial property, the dielectric tensor $\boldsymbol{\varepsilon}$, has been selected to introduce and to label the axes $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$. As noted in [26] this is a major difference between uniaxial and biaxial phases consisting of biaxial molecules, since only in the former case 'the director is uniquely associated with the symmetry axis of any second rank property' (p. 71 of [26]). Labelling the axes in a particular way is a matter of convention. Besides the proposal made here, another possibility adopted in the literature is the following. Let us consider, according to [26], the magnetic susceptibility $\boldsymbol{\chi}$ of the phase as the relevant second-rank tensorial property and let (X, Y, Z) denote its principal axes. Then, the axes are labelled so that the eigenvalues χ_{XX}, χ_{YY} and χ_{ZZ} of $\boldsymbol{\chi}$ satisfy

$$|\chi_{ZZ}| > \chi_{XX} - \chi_{YY} > 0.$$

In other terms, Z is approximately an axis of symmetry for $\boldsymbol{\chi}$ while the remaining axes are labelled so that the biaxiality of $\boldsymbol{\chi}$ is positive.

Here, we propose an intrinsic way to arrive at the second-rank order parameters, that is, a way independent of any parametrization in terms of Euler angles and that, unlike the Saupe matrix, is not affected from redundancy. The approach followed here is a systematic presentation of ideas developed in the Appendix of [44], as well as in [45] and [46]. Following [47, 48], we associate to each molecule an orthonormal basis spanning the *five*-dimensional linear space of symmetric, traceless tensors

$$\begin{aligned} M_0 &:= \sqrt{\frac{3}{2}}\left[\boldsymbol{m}_3\otimes\boldsymbol{m}_3-\frac{1}{3}\boldsymbol{I}\right] \\ M_1 &:= \frac{1}{\sqrt{2}}[\boldsymbol{m}_1\otimes\boldsymbol{m}_1-\boldsymbol{m}_2\otimes\boldsymbol{m}_2] \\ M_2 &:= \frac{1}{\sqrt{2}}[\boldsymbol{m}_1\otimes\boldsymbol{m}_2+\boldsymbol{m}_2\otimes\boldsymbol{m}_1] \qquad (12) \\ M_3 &:= \frac{1}{\sqrt{2}}[\boldsymbol{m}_1\otimes\boldsymbol{m}_3+\boldsymbol{m}_3\otimes\boldsymbol{m}_1] \\ M_4 &:= \frac{1}{\sqrt{2}}[\boldsymbol{m}_2\otimes\boldsymbol{m}_3+\boldsymbol{m}_3\otimes\boldsymbol{m}_2]. \end{aligned}$$

Similarly, we introduce five symmetric, traceless tensors $\{\boldsymbol{L}_0, \ldots, \boldsymbol{L}_4\}$ defined in terms of $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$. Let Sym_{0m} be the five-dimensional vector space of symmetric, traceless, molecular tensors and Sym_{0L} its laboratory-based counterpart. We define a linear mapping $\mathbb{S}$: $\mathrm{Sym}_{0m} \mapsto \mathrm{Sym}_{0L}$ as

$$\mathbb{S}(\boldsymbol{M}) := \langle \boldsymbol{M} \rangle.$$

Clearly, the mapping $\mathbb{S}$ is a fourth-rank tensor and, by fixing orthonormal bases $\{\boldsymbol{M}_0, \ldots, \boldsymbol{M}_4\}$ and $\{\boldsymbol{L}_0, \ldots, \boldsymbol{L}_4\}$ in Sym_{0m} and Sym_{0L}, 25 components $\mathbb{S}_{i\alpha}$ are needed to specify the action of $\mathbb{S}$. In $\mathbb{S}_{i\alpha}$, i is a molecular index, while α is a laboratory index and we can write

$$\mathbb{S}(\boldsymbol{M}_i) = \sum_{\alpha=0}^{4} \mathbb{S}_{i\alpha} \boldsymbol{L}_\alpha.$$

Since the tensors $\{\boldsymbol{L}_0, \ldots, \boldsymbol{L}_4\}$ are orthonormal with respect to the standard scalar product

$$\boldsymbol{T} \cdot \boldsymbol{L} := \mathrm{tr}\, \boldsymbol{T}^{\mathrm{T}} \boldsymbol{L}$$

between second-rank tensors $\boldsymbol{T}$ and $\boldsymbol{L}$, by exploiting the definitions (11) and (12) we can readily find the relation between the coefficients $\mathbb{S}_{i\alpha}$ and the entries of the Saupe ordering matrix (11):

$$\mathbb{S}_{00} = S_{33}^{33}, \quad \mathbb{S}_{01} = \frac{1}{\sqrt{3}}\left(S_{33}^{11} - S_{33}^{22}\right), \quad \mathbb{S}_{02} = \frac{2}{\sqrt{3}} S_{33}^{12}, \quad \mathbb{S}_{03} = \frac{2}{\sqrt{3}} S_{33}^{13}, \quad \mathbb{S}_{04} = \frac{2}{\sqrt{3}} S_{33}^{23}$$

$$\mathbb{S}_{10} = \frac{1}{\sqrt{3}}\left(S_{11}^{33} - S_{22}^{33}\right), \quad \mathbb{S}_{11} = \frac{\left(S_{11}^{11} - S_{11}^{22} - S_{22}^{11} - S_{22}^{22}\right)}{3}, \quad \mathbb{S}_{12} = \frac{2}{3}\left(S_{11}^{12} - S_{22}^{12}\right),$$

$$\mathbb{S}_{13} = \frac{2}{3}\left(S_{11}^{13} - S_{22}^{13}\right), \quad \mathbb{S}_{14} = \frac{2}{3}\left(S_{11}^{23} - S_{22}^{23}\right)$$

$$\mathbb{S}_{20} = \frac{2}{\sqrt{3}} S_{12}^{33}, \quad \mathbb{S}_{21} = \frac{2}{3}\left(S_{12}^{11} - S_{12}^{22}\right), \quad \mathbb{S}_{22} = \frac{2}{3}\left(S_{12}^{12} + S_{12}^{21}\right),$$

$$\mathbb{S}_{23} = \frac{2}{3}\left(S_{12}^{13} + S_{12}^{31}\right), \quad \mathbb{S}_{24} = \frac{2}{3}\left(S_{12}^{23} + S_{12}^{32}\right)$$

$$\mathbb{S}_{30} = \frac{2}{\sqrt{3}} S_{13}^{33}, \quad \mathbb{S}_{31} = \frac{2}{3}\left(S_{13}^{11} - S_{13}^{22}\right), \quad \mathbb{S}_{32} = \frac{2}{3}\left(S_{13}^{12} + S_{13}^{21}\right),$$

$$\mathbb{S}_{33} = \frac{2}{3}\left(S_{13}^{13} + S_{13}^{31}\right), \quad \mathbb{S}_{34} = \frac{2}{3}\left(S_{13}^{23} + S_{13}^{32}\right)$$

$$\mathbb{S}_{40} = \frac{2}{\sqrt{3}} S_{23}^{33}, \quad \mathbb{S}_{41} = \frac{2}{3}\left(S_{23}^{11} - S_{23}^{22}\right), \quad \mathbb{S}_{42} = \frac{2}{3}\left(S_{23}^{12} + S_{23}^{21}\right),$$

$$\mathbb{S}_{43} = \frac{2}{3}\left(S_{23}^{13} + S_{23}^{31}\right), \quad \mathbb{S}_{44} = \frac{2}{3}\left(S_{23}^{23} + S_{23}^{32}\right).$$

We stress that only $\boldsymbol{M}_0$, $\boldsymbol{M}_1$, $\boldsymbol{L}_0$, and $\boldsymbol{L}_1$ do not change their sign if one vector of either the molecular or the laboratory frame is mapped into its opposite. Hence, the averages of $\boldsymbol{M}_i$, with i=2, 3, 4 vanish identically for an assembly of biaxial molecules with symmetry group D_{2h}. The same is true for V-shaped molecules with symmetry group C_{2v} [27] but it is false for molecules with lower symmetry. For instance, for molecules with point group C_{2h}, $<\boldsymbol{M}_2>$ can be different from $\boldsymbol{0}$, if $\boldsymbol{m}_3$ coincides with the normal to the plane of symmetry of the molecule. Further lack of symmetry could lead to a non-zero average also for $\boldsymbol{M}_3$ and $\boldsymbol{M}_4$. Hereafter, we restrict attention to mesogens endowed with point group D_{2h} or C_{2v}. The coefficients of the expansion of $<\boldsymbol{M}_0>$ and $<\boldsymbol{M}_1>$ along $\boldsymbol{L}_2$, $\boldsymbol{L}_3$, and $\boldsymbol{L}_4$ cannot serve as order parameters for a biaxial phase, as they change sign when one of the unit vectors $\boldsymbol{\ell}_i$ is mapped into its opposite. Hence, the biaxial symmetry of the phase makes it possible to use as scalar order parameters the four coefficients $S \equiv \mathbb{S}_{00}$, $P \equiv \mathbb{S}_{01}$, $M \equiv \mathbb{S}_{10}$, and $F \equiv \mathbb{S}_{11}$ that satisfy

$$\begin{cases} \langle \boldsymbol{M}_0 \rangle = S\boldsymbol{L}_0 + P\boldsymbol{L}_1 \\ \langle \boldsymbol{M}_1 \rangle = U\boldsymbol{L}_0 + F\boldsymbol{L}_1; \end{cases} \tag{13}$$

in other words, we see that biaxial symmetry makes it possible to diagonalize simultaneously $<\boldsymbol{M}_0>$ and $<\boldsymbol{M}_1>$. By definition, we have

$$S := \langle \boldsymbol{M}_0 \cdot \boldsymbol{L}_0 \rangle = \frac{3}{2}\left\langle (\boldsymbol{\ell}_3 \cdot \boldsymbol{m}_3)^2 - \frac{1}{3} \right\rangle, \tag{14}$$

$$U := \langle \boldsymbol{M}_1 \cdot \boldsymbol{L}_0 \rangle = \frac{\sqrt{3}}{2}\left\langle (\boldsymbol{m}_1 \cdot \boldsymbol{\ell}_3)^2 - (\boldsymbol{m}_2 \cdot \boldsymbol{\ell}_3)^2 \right\rangle, \tag{15}$$

$$P := \langle \boldsymbol{M}_0 \cdot \boldsymbol{L}_1 \rangle = \frac{\sqrt{3}}{2}\left\langle (\boldsymbol{m}_3 \cdot \boldsymbol{\ell}_1)^2 - (\boldsymbol{m}_3 \cdot \boldsymbol{\ell}_2)^2 \right\rangle, \tag{16}$$

and

$$\begin{aligned} F :&= \langle \boldsymbol{M}_1 \cdot \boldsymbol{L}_1 \rangle = \\ &\frac{1}{2}\left\langle (\boldsymbol{m}_1 \cdot \boldsymbol{\ell}_1)^2 - (\boldsymbol{m}_1 \cdot \boldsymbol{\ell}_2)^2 - (\boldsymbol{m}_2 \cdot \boldsymbol{\ell}_1)^2 + (\boldsymbol{m}_2 \cdot \boldsymbol{\ell}_2)^2 \right\rangle, \end{aligned} \tag{17}$$

which directly follows from (12). The parameters defined in equations (14)–(17) can be expressed in terms of the Saupe matrix as

$$\begin{cases} S = S_{33}^{33} \quad U = \dfrac{1}{\sqrt{3}}\left(S_{11}^{33} - S_{22}^{33}\right) \\ P = \dfrac{1}{\sqrt{3}}\left(S_{33}^{11} - S_{33}^{22}\right) \quad F = \dfrac{1}{3}\left(S_{11}^{11} - S_{11}^{22} - S_{22}^{11} + S_{22}^{22}\right). \end{cases}$$

With little more labour, it is possible to express all diagonal elements $S_{ii}^{\alpha\alpha}$ of the Saupe matrix in terms of the parameters S, U, P, and F as [46]

$$\begin{array}{ll} S_{33}^{33} = S & S_{33}^{22} = \frac{1}{2}\left(-S - \sqrt{3}P\right) \\ S_{33}^{11} = \frac{1}{2}\left(-S + \sqrt{3}P\right) & S_{22}^{33} = \frac{1}{2}\left(-S - \sqrt{3}U\right) \\ S_{22}^{22} = \frac{1}{4}\left(S + \sqrt{3}P + \sqrt{3}U + 3F\right) & S_{22}^{11} = \frac{1}{4}\left(S - \sqrt{3}P + \sqrt{3}U - 3F\right) \\ S_{11}^{33} = \frac{1}{2}\left(-S + \sqrt{3}U\right) & S_{11}^{22} = \frac{1}{4}\left(S + \sqrt{3}P - \sqrt{3}U - 3F\right) \\ S_{11}^{11} = \frac{1}{4}\left(S - \sqrt{3}P - \sqrt{3}U + 3F\right). & \end{array} \tag{18}$$

If the molecules are uniaxial, there is no way to distinguish $\boldsymbol{m}_1$ from $\boldsymbol{m}_2$, and so U and F vanish identically. If the phase is uniaxial too, only $\boldsymbol{\ell}_3$ plays a distinguished rôle in the laboratory frame and so S is the unique surviving order parameter. If we consider biaxial molecules in a uniaxial phase, U is different from zero. On the other hand, if the phase is biaxial P enters the scene also when the molecules are uniaxial. Finally, the order parameter F is different from zero when both the molecules and the phase are biaxial. The notation adopted here for order parameters needs some explanation. The choice of S is a homage to tradition. Then I used P for the order parameter that measures *Phase biaxiality* in the presence of uniaxial molecules. The parameter U measures molecular biaxiality in a uniaxial phase and so can be considered as a *Uniaxial parameter*. Finally, F is different from 0 when biaxiality is *Fully* displayed, both at the molecular and at the phase level. The normalizing factors adopted here clearly depend on the definition (13). As a result, we cannot guarantee that, for instance, the upper bound on all the order parameters is 1 when there is perfect order. This latter criterion led, for instance, Straley in his definition (see p. 1882 of [19]).

Since labelling the molecular and the laboratory axes as we did is purely conventional, in the spirit of [49] we can study the action on the traceless tensors $\boldsymbol{M}_0, \ldots, \boldsymbol{M}_4$ and $\boldsymbol{L}_0, \ldots, \boldsymbol{L}_4$ of the permutation operators τ_i, (i=1, 2, 3) that keep the i-th unit vector in either $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$ or $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ fixed and exchange the remaining two unit vectors. It is readily verified that

$$\tau_1(\boldsymbol{M}_0)=\sqrt{\frac{3}{2}}\left[\boldsymbol{m}_2\otimes\boldsymbol{m}_2-\frac{1}{3}I\right]=-\frac{1}{2}\boldsymbol{M}_0-\frac{\sqrt{3}}{2}\boldsymbol{M}_1,$$

$$\tau_1(\boldsymbol{M}_1)=\sqrt{\frac{1}{2}}[\boldsymbol{m}_1\otimes\boldsymbol{m}_1-\boldsymbol{m}_3\otimes\boldsymbol{m}_3]=-\frac{\sqrt{3}}{2}\boldsymbol{M}_0+\frac{1}{2}\boldsymbol{M}_1,$$

$$\tau_1(\boldsymbol{M}_2)=\boldsymbol{M}_3,\ \tau_1(\boldsymbol{M}_3)=M_2,\ \tau_1(\boldsymbol{M}_4)=\boldsymbol{M}_4,$$

$$\tau_2(\boldsymbol{M}_0)=-\frac{1}{2}\boldsymbol{M}_0+\frac{\sqrt{3}}{2}\boldsymbol{M}_1,\ \tau_2(\boldsymbol{M}_1)=\frac{\sqrt{3}}{2}\boldsymbol{M}_0+\frac{1}{2}\boldsymbol{M}_1,$$

$$\tau_2(\boldsymbol{M}_2)=\boldsymbol{M}_4,\ \tau_2(\boldsymbol{M}_3)=\boldsymbol{M}_3,\ \tau_2(\boldsymbol{M}_4)=\boldsymbol{M}_2,$$

and

$$\tau_3(\boldsymbol{M}_0)=\boldsymbol{M}_0,\quad \tau_3(\boldsymbol{M}_1)=-\boldsymbol{M}_1\quad \tau_3(\boldsymbol{M}_2)=\boldsymbol{M}_2,$$
$$\tau_3(\boldsymbol{M}_3)=\boldsymbol{M}_4,\quad \tau_3(\boldsymbol{M}_4)=\boldsymbol{M}_3.$$

It is interesting to note that the permutation operators τ_i decompose the space of symmetric, traceless tensors into the direct sum of the linear subspaces spanned by $\{\boldsymbol{M}_0, \boldsymbol{M}_1\}$ and by $\{\boldsymbol{M}_2, \boldsymbol{M}_3, \boldsymbol{M}_4\}$. Since a similar decomposition also holds in the laboratory frame $\{\boldsymbol{L}_0, \ldots, \boldsymbol{L}_4\}$, we conclude that the description of a biaxial phase is unaffected by axes relabelling, since it only requires combinations of $\{\boldsymbol{M}_0, \boldsymbol{M}_1\}$ and $\{\boldsymbol{L}_0, \boldsymbol{L}_1\}$. Axes relabelling simply shuffles the set of order parameters (S, U, P, F) into some equivalent, though often less transparent, set. For instance, the action of τ_3 on both the molecular and the laboratory frames maps (S, U, P, F) into (S, $-U$, $-P$, F); it is precisely this mapping that makes it possible to compare Straley's order parameters – defined by use of the x-notation for Euler angles – with those defined using the y-notation (see also [50] and [51]). For a less trivial example, we record here that the action of τ_1 on both frames maps

$$S\mapsto\tfrac{1}{4}\left(S+\sqrt{3}P+\sqrt{3}U+3F\right),\quad U\mapsto\tfrac{1}{4}\left(\sqrt{3}S+3P-U-\sqrt{3}F\right),$$
$$P\mapsto\tfrac{1}{4}\left(\sqrt{3}S-P+\sqrt{3}U-3F\right),\quad F\mapsto\tfrac{1}{4}\left(3S-\sqrt{3}P-\sqrt{3}U+F\right).$$

Finally, the order parameters S, U, P, F range in the following intervals [52]

$$\begin{aligned}&S\in\left[-\tfrac{1}{2},1\right], && U\in\left[-\tfrac{1}{\sqrt{3}}(1-S),\ \tfrac{1}{\sqrt{3}}(1-S)\right],\\ &P\in\left[-\tfrac{1}{\sqrt{3}}(1-S),\ \tfrac{1}{\sqrt{3}}(1-S)\right] && F\in[F_m, F^M],\end{aligned}\tag{19}$$

where

$$F_m:=-\frac{1}{3}\min\left\{2+S+\sqrt{3}(P+U),\ 2+S+\sqrt{3}(U-P)\right\}$$

and

$$F^M:=\frac{1}{3}\min\left\{2+S+\sqrt{3}(U-P),\ 2+S+\sqrt{3}(P-U)\right\}.$$

In particular, the bounds for F obtained in [52] improve the earlier limitation $F\in[-1, 1]$ found in [20].

Until now, we did not parametrize the rotation mapping the director frame $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$ into the molecular frame $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$. Let φ, ϑ, and ψ be the Euler angles associated to this rotation (see figure 1), defined according to the y-notation. Then we have (see p. 607 of [53])

$$\begin{aligned}\boldsymbol{m}_1&=(\cos\vartheta\cos\varphi\cos\psi-\sin\varphi\sin\psi)\boldsymbol{\ell}_1\\&\quad+(\cos\vartheta\sin\varphi\cos\psi+\cos\varphi\sin\psi)\boldsymbol{\ell}_2-\sin\vartheta\cos\psi\boldsymbol{\ell}_3,\\ \boldsymbol{m}_2&=-(\cos\vartheta\cos\varphi\sin\psi+\sin\varphi\cos\psi)\boldsymbol{\ell}_1+\\&\quad(\cos\varphi\cos\psi-\cos\vartheta\sin\varphi\sin\psi)\boldsymbol{\ell}_2+\sin\vartheta\sin\psi\boldsymbol{\ell}_3,\end{aligned}$$

and

$$\boldsymbol{m}_3=\sin\vartheta\cos\varphi\boldsymbol{\ell}_1+\sin\vartheta\sin\varphi\boldsymbol{\ell}_2+\cos\vartheta\boldsymbol{\ell}_3$$

from which it follows that

$$\begin{cases}S=\dfrac{1}{2}\left\langle\left(3\cos^2\vartheta-1\right)\right\rangle=\left\langle D^2_{0,\,0}\right\rangle\\[2mm] U=\dfrac{\sqrt{3}}{2}\left\langle\sin^2\vartheta\cos 2\psi\right\rangle=\sqrt{2}\,\mathrm{Re}\left\langle D^2_{0\pm2}\right\rangle\\[2mm] P=\dfrac{\sqrt{3}}{2}\left\langle\sin^2\vartheta\cos 2\varphi\right\rangle=\sqrt{2}\,\mathrm{Re}\left\langle D^2_{\pm20}\right\rangle\\[2mm] F=\left\langle\dfrac{1}{2}\left(1+\cos^2\vartheta\right)\cos 2\varphi\cos 2\psi-\cos\vartheta\sin 2\varphi\sin 2\psi\right\rangle\\ \quad=\mathrm{Re}\left[\left\langle D^2_{22}\right\rangle+\left\langle D^2_{-22}\right\rangle\right].\end{cases}\tag{20}$$

4. Notations for second-rank order parameters

This section contains a table of conversion for a wealth of notations employed in the literature to denote the second-rank order parameters defined in Section 3. Any row contains the notations employed to denote the order parameters S, U, P, and F defined through equations (14)–(17) and (20). The first row corresponds to the most recent, the last row to less recent notation. I consider two notations as different when either two order parameters differ at least by a constant multiple, or when different symbols are employed for the same set of order parameters. An empty cell mean that the corresponding order parameter is not defined by the authors. This happens when attention is confined to either uniaxial particles in a biaxial phase or biaxial particles in a uniaxial phase.

Looking at table 1, it turns out that two different symbols $<\cdot>$ and $\cdot$ have been adopted to denote one and the same orientational average, defined according to equation (2).[2] In table 1, I put a $\pm$ in front of the order parameters corresponding to P or U whenever the authors do not specify whether they use the x- or the y-notation for Euler angles. As mentioned above, such discrepancies can be absorbed by different labelling of the vectors $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$ or $\{\boldsymbol{\ell}_1, \boldsymbol{\ell}_2, \boldsymbol{\ell}_3\}$.

Table 1 does not contain notations employed, for instance, in [1, 75–77]. At variance with most papers in the literature, these authors did not express a symmetric, traceless tensor in terms of either $\{\boldsymbol{M}_i\}$ or $\{\boldsymbol{L}_i\}$, and so only *two* order parameters were employed that mix the sources of biaxiality. To compare this approach with that described in Section 3, we now rephrase Freiser's procedure [1, 75] in the language of Section 3.

The molecular axes $\{\boldsymbol{m}_1, \boldsymbol{m}_2, \boldsymbol{m}_3\}$ associated to a reference molecule are placed along the principal axes of a symmetric, traceless, second rank tensor $\boldsymbol{Q}$, called the *quasi-quadrupole* tensor, in terms of which the effective interaction energy w_{ij} between the i-th (reference) molecule and the j-th molecule is written as $w_{ij} = -\boldsymbol{Q}\cdot\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^{\mathrm{T}}$, where $\boldsymbol{R}$ is the orthogonal tensor associated with the rotation carrying the axes of the i-th into those of the j-th molecule. The tensor $\boldsymbol{Q}$ is then written as

$$Q = \left(2q - \sqrt{\frac{2}{3}}Q\right)\boldsymbol{m}_1\otimes\boldsymbol{m}_1 - \left(2q + \sqrt{\frac{2}{3}}Q\right)\boldsymbol{m}_2\otimes\boldsymbol{m}_2$$

$$+ 2\sqrt{\frac{2}{3}}Q\boldsymbol{m}_3\otimes\boldsymbol{m}_3 = 2\left(Q\boldsymbol{M}_0 + \sqrt{2}q\boldsymbol{M}_1\right),$$

where Q and q are the *spherical* components of the tensor $\boldsymbol{Q}$ (see, e.g. Appendix B of [78]). To obtain the order parameters $\bar{Q}_0$ and $\bar{Q}_2$, the orientational average $<\boldsymbol{Q}>$ of $\boldsymbol{Q}$ is then projected along $\boldsymbol{L}_0$ and $\boldsymbol{L}_1$, arriving at

$$Q_0 = 2\left(QS + \sqrt{2}qU\right) \quad Q_2 = 2\left(QP + \sqrt{2}qF\right)$$

from which we see that $\bar{Q}_0$ is a *uniaxial* parameter which is proportional to S when the molecules are uniaxial, while $\bar{Q}_2$ measures phase biaxiality.[3] As noted before, the order parameters S, U, P, and F are mixed in this description. They could be formally singled out by setting $\boldsymbol{q}_u := 2Q\boldsymbol{M}_0$ and $\boldsymbol{q}_b := 2\sqrt{2}q\boldsymbol{M}_1$ from which we arrive at

$$S = \frac{\langle \boldsymbol{q}_u\cdot\boldsymbol{L}_0\rangle}{2Q}, \quad U = \frac{\langle \boldsymbol{q}_b\cdot\boldsymbol{L}_0\rangle}{2q\sqrt{2}},$$

$$P = \frac{\langle \boldsymbol{q}_u\cdot\boldsymbol{L}_1\rangle}{2Q}, \quad \text{and} \quad F = \frac{\langle \boldsymbol{q}_b\cdot\boldsymbol{L}_1\rangle}{2q\sqrt{2}}.$$

Remler and Haymet [76] followed the same avenue as Freiser [1, 75] using a slightly different notation, since they introduce a *degree of biaxiality* $r := q/Q$ and define the order parameters A_0 and A_2 as

$$A_0 = 2\left(S + r\sqrt{2}U\right) \quad \text{and} \quad A_2 = 2\left(\frac{1}{r}P + \sqrt{2}F\right).$$

A common feature of these approach is the use of Wigner matrices. A slightly different procedure that avoids them was employed by Boccara *et al.* [77]. Here, a molecular tensor $\boldsymbol{q}$ is written as

$$\boldsymbol{q} = q\left(-\sqrt{6}\boldsymbol{M}_0 + \varepsilon\sqrt{2}\boldsymbol{M}_1\right)$$

and two order parameters a and b are introduced such that

$$\langle\boldsymbol{q}\rangle = q\left(-a\sqrt{6}\boldsymbol{L}_0 + b\sqrt{2}\boldsymbol{L}_1\right),$$

from which, by resorting to equations (14)–(17), we

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[2] Precisely, Collings *et al.* [71, 72] consider $<\cdot>$ as a *time* average, instead of an *ensemble* average, since NMR measurements involve precisely time averages. The two averages are conceptually quite different from one another and an ergodic hypothesis should be invoked – and proved – to be sure that they produce the same results. Mettout [27] claims that his averages coincide with those employed in [71], and excludes the factor $5\pi^2/16$ from orientational averages. Here, we consider both $<\cdot>$ and $\overline{(\cdot)}$ as equivalent notations for ensemble averages.

[3] Precisely, the parameters $\bar{Q}_0$ and $\bar{Q}_2$ defined here are proportional to that introduced by Freiser, who did not use the normalizing factors in $\boldsymbol{L}_0$ and $\boldsymbol{L}_1$. A similar remark holds for the order parameters A_0 and A_2 introduced by Remler and Haymet [76].

Table 1. The second-rank order parameters S, U, P, and F introduced in equations (14)–(17) and (20) are expressed in terms of notations employed in the past three decades. Notations are arranged in order of appearance, from most recent (top) to less recent (bottom). An empty cell occurs when the corresponding order parameter is not defined.

This paper	S	U	P	F
Bates & Luckhurst [42]	S^2_{00}	$\frac{1}{\sqrt{3}}S^2_{02}$	$\frac{1}{\sqrt{3}}S^2_{20}$	$\frac{1}{3}S^2_{22}$
Mettout [27]	$\frac{16\pi^2}{5}\eta_0$	$\frac{16\pi^2}{5}\eta_2$	$\frac{16\pi^2}{5}\eta'_0$	$\frac{16\pi^2}{5}\eta'_2$
Aver'yanov [54]	S	$\frac{1}{\sqrt{3}}G$		
Romano [43]	R_{20}		$2\sqrt{2}R_{22}$	
Sonnet *et al.* [20]	S	$\frac{1}{\sqrt{3}}S'$	$\sqrt{3}T$	T'
Low [55]	S		$-\frac{2}{\sqrt{3}}\xi$	
Zhang *et al.* [56]	$<P_2(\cos\beta)>$	$\sqrt{2}\langle B(\beta, \gamma)\rangle$		
Singh [57]	$\bar{P}_2$	$\bar{\eta}_2$	$\bar{\mu}_2$	$\bar{\tau}_2$
Dunmur & Toriyama [58]	S	$\frac{1}{\sqrt{3}}D$	$\frac{1}{\sqrt{3}}P$	$\frac{C}{3}$
Teixeira *et al.* [59]	s_1	$\frac{\sqrt{3}}{2}s_3$	$\frac{\sqrt{3}}{2}s_2$	s_4
Kröger, Sellers [60]	S_2		$\frac{\sqrt{3}}{2}b$	
Sarman [61]	$Q^{(2)}_{00}$	$\sqrt{2}Q^{(2)}_{0,2}$	$\sqrt{2}Q^{(2)}_{2,0}$	$Q^{(2)}_{2,2}$
Biscarini *et al.* [36]	$\langle R^2_{00}\rangle$	$\langle\sqrt{2}R^2_{02}\rangle$	$\langle\sqrt{2}R^2_{20}\rangle$	$\langle 2R^2_{22}\rangle$
Osipov & Pikin [45, 62]	S	$\frac{1}{\sqrt{3}}S'$	$\sqrt{3}\Delta Q$	D
Singh *et al.* [63]	$\bar{P}$	$\bar{\eta}$	$\bar{\mu}$	$\bar{\tau}$
Chen [64]	S_2		$\frac{1}{\sqrt{3}}\Delta S$	
Tjipto-Margo & Evans [65]	$<F_1>$	$\frac{\sqrt{3}}{2}\langle F_2\rangle$	$\frac{\sqrt{3}}{2}\langle F_3\rangle$	$<F_4>$
Yim, Gilson [66]	S_{33}	$\frac{1}{\sqrt{3}}(S_{11}-S_{22})$		
Hołyst & Poniewierski [35]	$<Q_{00}>$	$<Q_{02}>$	$<Q_{20}>$	$<Q_{22}>$
Baalss [51]	a_1	$\frac{1}{\sqrt{3}}(a_1+2a_2)$	$\sqrt{3}b_1$	$2b_2-b_1$
Mulder [30]	$\psi_{2,00}$	$\psi_{2,02}$	$\psi_{2,20}$	$\psi_{2,22}$
Bergersen *et al.* [67], [50]	Q	$\frac{1}{\sqrt{3}}D$	$\frac{1}{\sqrt{3}}P$	$\frac{1}{3}C$
Dunmur *et al.* [68]	$\frac{Q}{S_0}$		$\frac{P}{\sqrt{3}S_0}$	
Stroobants & Lekkerkerker [69]	S		$\frac{\sqrt{3}}{2}\Delta$	
Goldfarb *et al.* [70]	C_{00}	$\sqrt{2}C_{\overline{02}}$	$\sqrt{2}C_{\overline{20}}$	$4C_{\overline{22}}$
Collings *et al.* [71]	S_1	$\pm\frac{\sqrt{3}}{2}S_2$	$\pm\frac{\sqrt{3}}{2}S_4$	S_5
Photinos *et al.* [72]	$S_{0,0}$	$\pm\frac{2}{\sqrt{3}}S_{0,2}$	$\pm\frac{2}{\sqrt{3}}S_{2,0}$	$2S_{2,2}$
Luckhurst *et al.* [5]	$\overline{d^{(2)}_{0,0}}$	$\sqrt{2}\overline{d^{(2)}_{0,2}\cos 2\gamma}$		
Straley [19]	S	$-\frac{\sqrt{3}}{2}U$	$-\frac{\sqrt{3}}{2}T$	V
Priest & Lubensky [73]	S	$\frac{1}{\sqrt{3}}\eta'$	$\frac{\sqrt{3}}{2}\Delta$	2η
Alben *et al.* [74]	$\bar{S}$	$-\frac{1}{\sqrt{3}}\overline{D}$		

arrive at

$$a = S - \varepsilon\frac{U}{\sqrt{3}} \quad \text{and} \quad b = \varepsilon F - \sqrt{3}P,$$

so that a is the only non-vanishing parameter in a uniaxial phase.

The order parameters employed in [77] are closely related to that introduced by Alben [79], who defined a molecular tensor

$$\boldsymbol{Q}_m := \boldsymbol{n}\otimes\boldsymbol{n} - \boldsymbol{m}\otimes\boldsymbol{m},$$

where $\boldsymbol{n}$ is a unit vector along the longest axis of the molecule, and $\boldsymbol{m}$ is a unit vector normal to the molecule, conceived as a rectangular plate; in our notation

$$\boldsymbol{Q}_m = \boldsymbol{m}_3\otimes\boldsymbol{m}_3 - \boldsymbol{m}_1\otimes\boldsymbol{m}_1 = \sqrt{\frac{3}{2}}\boldsymbol{M}_0 - \frac{1}{\sqrt{2}}\boldsymbol{M}_1.$$

The tensor $\boldsymbol{Q}_m$ is then averaged to obtain a tensor $\boldsymbol{Q}_{av}$, which is then expressed in terms of polar coordinates in the parameter space. Using the procedure of Section 3, we can obtain two order parameters defined as

$$\boldsymbol{Q}_{av}\cdot\boldsymbol{L}_0 = \langle\boldsymbol{Q}_m\rangle\cdot\boldsymbol{L}_0 = \sqrt{\frac{3}{2}}\left(S - \frac{1}{\sqrt{3}}U\right)$$

and

$$\boldsymbol{Q}_{av}\cdot\boldsymbol{L}_1 = \langle\boldsymbol{Q}_m\rangle\cdot\boldsymbol{L}_1 = \sqrt{\frac{3}{2}}\left(P - \frac{1}{\sqrt{3}}F\right).$$

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References

[1] M.J. Freiser. *Phys. Rev. Lett.*, **24**, 1041 (1970).
[2] T.R. Taylor, J.L. Fergason, S.L. Arora. *Phys. Rev. Lett.*, **24**, 359 (1970).
[3] R. Williams. *J. Chem. Phys.*, **50**, 1324 (1969).
[4] L.J. Yu, A. Saupe. *Phys. Rev. Lett.*, **45**, 1000 (1980).
[5] G.R. Luckhurst, C. Zannoni, P.L. Nordio, U. Segre. *Mol. Phys.*, **30**, 1345 (1975).
[6] G.R. Luckhurst. *Thin Solid Films*, **393**, 40 (2001).
[7] G.R. Luckhurst, S. Romano. *Mol. Phys.*, **40**, 129 (1980).
[8] M.P. Allen. *Liq. Cryst.*, **8**, 499 (1990).
[9] R. Berardi, C. Fava, C. Zannoni. *Chem. Phys. Lett.*, **236**, 462 (1995).
[10] C.M. Care, D.J. Cleaver. *Rep. Progr. Phys.*, **68**, 2665 (2005).
[11] K. Severing, K. Saalwächter. *Phys. Rev. Lett.*, **92**, 125501 (2004).
[12] L.A. Madsen, T.J. Dingemans, M. Nakata, E.T. Samulski. *Phys. Rev. Lett.*, **92**, 145505 (2004).
[13] B.R. Acharya, A. Primak, S. Kumar. *Phys. Rev. Lett.*, **92**, 145506 (2004).
[14] K. Merkel, A. Kocot, J.K. Vij, R. Korlacki, G.H. Mehl, T. Meyer. *Phys. Rev. Lett.*, **93**, 237801 (2004).
[15] G.R. Luckhurst. *Nature*, **430**, 413 (2004).
[16] G.R. Luckhurst. *Angew. Chem. Int. Ed.*, **44**, 2834 (2005).
[17] Y. Galerne. *Phys. Rev. Lett.*, **96**, 219803 (2006).
[18] L.A. Madsen, T.J. Dingemans, M. Nakata, E.T. Samulski. *Phys. Rev. Lett.*, **96**, 219804 (2006).
[19] J.P. Straley. *Phys. Rev. A*, **10**, 1881 (1974).
[20] A.M. Sonnet, E.G. Virga, G.E. Durand. *Phys. Rev. E*, **67**, 061701 (2003).
[21] F. Bisi, E.G. Virga, E.C. Jr. Gartland, G. De Matteis, A.M. Sonnet, G.E. Durand. *Phys. Rev. E*, **73**, 051709 (2006).
[22] D.M. Brink, G.R. Satchler. *Angular Momentum*. Oxford University Press, Oxford (1962).
[23] J.-M. Normand. *A Lie Group: Rotations in Quantum Mechanics*. North-Holland, Amsterdam (1980).
[24] C. Zannoni. In *The Molecular Physics of Liquid Crystals*, G.R. Luckhurst, G.W. Gray (Eds), pp. 51–83, Academic Press, London (1979).
[25] M.E. Rose. *Elementary Theory of Angular Momentum*. Dover, New York (1995).
[26] G.R. Luckhurst. In *Physical Properties of Liquid Crystals: Nematics*, D. Dunmur, A. Fukuda, G.R. Luckhurst (Eds), pp. 57–88, Institution of Engineering and Technology, London (2001).
[27] B. Mettout. *Phys. Rev. E*, **72**, 031706 (2005).
[28] B. Mettout, P. Tolédano, H. Takezoe, J. Watanabe. *Phys. Rev. E*, **66**, 031701 (2002).
[29] V.I. Kalikmanov. *Statistical Physics of Fluids*. Springer, Berlin (2001).
[30] B. Mulder. *Phys. Rev. A*, **39**, 360 (1989).
[31] M. Fiałkowski, A. Kapanowski, K. Sokalski. *Mol. Cryst. Liq. Cryst.*, **265**, 371 (1995).
[32] A. Kapanowski. *Phys. Rev. E*, **55**, 7090 (1997).
[33] A. Kapanowski, T. Wietecha. *Phys. Rev. E*, **71**, 021710 (2005).
[34] P.J. Camp, M.P. Allen. *J. Chem. Phys.*, **106**, 6681 (1997).
[35] R. Hołyst, A. Poniewierski. *Mol. Phys.*, **89**, 193 (1990).
[36] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, C. Zannoni. *Phys. Rev. Lett.*, **75**, 1803 (1995).
[37] C. Chiccoli, P. Pasini, F. Semeria, C. Zannoni. *Int. J. Mod. Phys. C*, **10**, 469 (1999). We note in passing that R^2_{22} was misprinted in this paper since $\sin 2\psi$ is missing in the last term.
[38] R. Berardi, C. Zannoni. *J. Chem. Phys.*, **113**, 5971 (2000).
[39] S. Romano. *Physica A*, **337**, 505 (2004).
[40] A.D. Buckingham. *Disc. Faraday Soc.*, **43**, 205 (1967).
[41] P.G. de Gennes, J. Prost. *The Physics of Liquid Crystals* 2nd edn, Clarendon Press, Oxford (1993).
[42] M. Bates, G.L. Luckhurst. *Phys. Rev. E*, **72**, 051702 (2005).
[43] S. Romano. *Physica A*, **322**, 432 (2003).

[44] L. Longa, P. Grzybowski, S. Romano, E.G. Virga. *Phys. Rev. E*, **71**, 051714 (2005).

[45] M.A. Osipov, S.A. Pikin. *J. Phys. II*, **5**, 1223 (1995).

[46] D.W. Allender, M.A. Lee. *Mol. Cryst. Liq. Cryst.*, **110**, 331 (1984).

[47] P. Kaiser, W. Wiese, S. Hess. *J. Non-Equilib. Thermodyn.*, **17**, 153 (1992).

[48] A.M. Sonnet, A. Kilian, S. Hess. *Phys. Rev. E*, **52**, 718 (1995).

[49] G. De Matteis, S. Romano, E.G. Virga. *Phys. Rev. E*, **72**, 041706 (2005).

[50] P. Palffy-Muhoray, G.L. Hoatson. *Phys. Rev. A*, **44**, 5052 (1991).

[51] D. Baalss. *Z. Naturforsch. A*, **45**, 7 (1990).

[52] F. Bisi, G. De Matteis, E.G. Virga. *Continuum Mech. Thermodyn.* Published online. DOI 10.1007/s00161-007-0041-1. (2007).

[53] H. Goldstein. *Classical Mechanics* 2nd edn, Addison-Wesley, Reading, Mass (1980).

[54] E.M. Aver'yanov. *Phys. Solid State*, **45**, 990 (2003).

[55] R.J. Low. *Eur. J. Phys.*, **23**, 111 (2002).

[56] Z.-D. Zhang, D.-X. Zhang, Y.-B. Sun. *Chinese Phys. Lett.*, **17**, 749 (2000).

[57] S. Singh. *Phys. Rep.*, **324**, 107 (2000).

[58] D. Dunmur, K. Toriyama. In *Physical Properties of Liquid Crystals*, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 87–101, Wiley-VHC, Weinheim, Germany (1999).

[59] P.I.C. Teixeira, A.J. Masters, B.M. Mulder. *Mol. Cryst. Liq. Cryst.*, **323**, 167 (1998).

[60] M. Kröger, S. Sellers. *Phys. Rev. E*, **56**, 1804 (1997).

[61] S. Sarman. *J. Chem. Phys.*, **104**, 342 (1996).

[62] M.A. Osipov. In *Physical Properties of Liquid Crystals*, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 40–71, Wiley-VHC, Weinheim, Germany (1999).

[63] Y. Singh, K. Rajesh, V.J. Menon, S. Singh. *Phys. Rev. E*, **49**, 501 (1994).

[64] Z.Y. Chen. *Phys. Rev. E*, **47**, 3765 (1993).

[65] B. Tjipto-Margo, G.T. Evans. *J. Chem. Phys.*, **94**, 4546 (1991).

[66] C.T. Yim, D.F.R. Gilson. *J. Phys. Chem.*, **95**, 980 (1991).

[67] B. Bergersen, P. Pallfy-Muhoray, D.A. Dunmur. *Liq. Cryst.*, **3**, 347 (1988).

[68] D.A. Dunmur, K. Szumilin, T.F. Waterworth. *Mol. Cryst. Liq. Cryst.*, **149**, 385 (1987).

[69] A. Stroobants, H.N.W. Lekkerkerker. *J. Phys. Chem.*, **88**, 3669 (1984).

[70] D. Goldfarb, R. Poupko, Z. Luz, H. Zimmermann. *J. Chem. Phys.*, **79**, 4035 (1983).

[71] P. Collings, D.J. Photinos, P.J. Bos, P. Ukleja, J.W. Doane. *Phys. Rev. Lett.*, **42**, 996 (1979).

[72] D.J. Photinos, P.J. Bos, J.W. Doane. *Phys. Rev. A*, **22**, 2203 (1979).

[73] R.G. Priest, T.C. Lubensky. *Phys. Rev. A*, **9**, 893 (1974). There is a misprint in equation (6) of this paper since the second-rank order parameter η reads as $\eta = \langle \frac{1}{4}(1+\cos^2\vartheta)\cos 2\varphi \cos 2\psi \rangle$, instead of $\eta = \langle \frac{1}{4}(1+\cos^2\vartheta)\cos 2\varphi \cos 2\psi - \frac{1}{2}\cos\vartheta \cos 2\psi \cos 2\varphi \rangle$, as can be obtained from equation (5) of this paper.

[74] R. Alben, J.R. McColl, C.S. Shih. *Solid State Commun.*, **11**, 1081 (1972).

[75] M.J. Freiser. *Mol. Cryst. Liq. Cryst.*, **14**, 165–182 (1971).

[76] D.K. Remler, A.D.J. Haymet. *J. Phys. Chem.*, **90**, 5246 (1986).

[77] N. Boccara, R. Mejdani, L. De Seze. *J. Phys. (France)*, **38**, 149 (1977).

[78] A.J. Stone. *The Theory of Intermolecular Forces*. Clarendon Press, Oxford (1996).

[79] R. Alben. *Phys. Rev. Lett.*, **30**, 778 (1973).

[80] E. Leimanis. *The General Problem of the Motion of Coupled Rigid Bodies about a Fixed Point*. Springer, New York (1965).

[81] S.L. Altmann. *Rotations, Quaternions, and Double Groups*. Oxford University Press, Oxford (1986).

[82] H. Goldstein. *Classical Mechanics*. Addison-Wesley, Reading, Mass. (1950).

Appendix A

Euler angles

Euler angles are a popular way to parametrize rotations. As noted by Goldstein [53], some degree of arbitrariness is unavoidably hidden in their definition since 'the sequence of rotations used to define the final orientation of the coordinate system is to some extent arbitrary. The initial rotation could be taken about any of the three Cartesian axes. In the subsequent two rotations, the only limitation is that no two successive rotations can be about the same axis' (p. 147 of [53]). As a result, twelve different notations could in principle exist. The most used notations are the x-notation employed by Goldstein himself in [53] and the y-notation employed by Brink and Satchler [22] and by Rose [25]. These notations differ in the choice of the axis about which the second rotation is performed: while in the x-notation this is performed about the nodal line which coincides with the intermediate x-axis, in the y-notation the second rotation is performed about the intermediate y-axis. Different symbols for the same set of Euler angles also exist. Goldstein uses $\varphi \in [0, 2\pi]$ for the *angle of precession*, $\vartheta \in [0, \pi]$ for the angle of *nutation*, and $\psi \in [0, 2\pi]$ for the angle of *proper rotation* (see figure 1). However φ and ψ are often interchanged[4] (see Leimanis's monograph [80], where the x-notation is adopted). Books oriented to quantum mechanics systematically avoid use of ψ as an Euler angle, since ψ is universally used for wavefunctions. In fact, Brink and Satchler [22] and Rose [25] use the set (α,

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[4] In this respect, a discrepancy exists between figure 2 and table 1 of [58]. In fact, in figure 2 of [58] and in the matrix $a_{\alpha\beta}$ of equation (3) on p. 88 of [58], φ denotes the proper rotation and ψ is the angle of precession. On the other hand, the angle of proper rotation is denoted by ψ in table 1 on p. 95 of [58], otherwise it would not be possible to define the order parameter P, since the angle of proper rotation is meaningless for uniaxial molecules in a biaxial phase (see Section 3).

β, γ) where α is the angle of precession, β the angle of nutation, and γ the angle of proper notation.

To pass from the x- to the y-notation, the following equivalence should be used ([53], p. 606):

$$\varphi_x = \varphi_y + \frac{\pi}{2}, \quad \psi_x = \psi_y - \frac{\pi}{2} \tag{21}$$

where φ_x and ψ_x are the angle of precession and of proper rotation, respectively, in the x-notation, while φ_y and ψ_y are their counterparts in the y-notation. It should also be noted that, instead of performing rotations about moving axes – like in [53], figure 3 on p. 50 of [25], and figure 2 on p. 20 of [22] – both Rose and Brink and Satchler note that the same effect can be obtained by performing three rotations about *fixed* axes, provided that the angles are reversed. That is, in the y-notation, first a rotation about the *original* z-axis through an angle γ, then a rotation about the *original* y-axis through an angle β followed by a rotation through an angle α about the *original* z-axis (see also [81]).

Most authors concerned with biaxial liquid crystals adopt the y-notation, but there are notable exceptions. In particular, Straley's paper [19] clearly uses the x-notation, as he refers to p. 107 of Goldstein's 1950 edition [82] where this notation is discussed. It is also clear from Straley's choice of the order parameters for the uniaxial phase (Section IV of [19]) that ψ is the angle of pure rotation. The x-notation is also used by Palffy-Muhoray and Hoatson [50] and by Baals [51]. It is worth noting that this fact has sometimes been overlooked by authors using the y-notation, when they compare their order parameters with Straley's; see [65] and [67].