

ORDER PARAMETERS AND ORIENTATIONAL DISTRIBUTIONS IN LIQUID CRYSTALS

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Oriental order parameters are introduced as expansion coefficients of the singlet orientational distribution in a suitable basis set. The construction of approximate distributions from a limited set of order parameters using the maximum entropy principles is discussed. We treat in detail order parameters and distributions for three cases: rigid molecules with cylindrical or biaxial symmetry and non rigid molecules with one internal rotor.

1. INTRODUCTION

The description of orientational order plays an important role in the investigation of anisotropic systems [1-3]. Its first objective consists in the identification of a set of parameters that can characterize the mesophase of interest in certain thermodynamic conditions. These parameters are generally called order parameters. They are supposed to change as thermodynamical variables change and to be defined so that at least some of them will become zero as we move from a lower symmetry to a higher symmetry phase. For example in thermotropic liquid crystals the relevant thermodynamic variable is temperature. As temperature increases we expect a suitably defined orientational order parameter to decrease and to become zero in the isotropic phase. It is not difficult to devise such an order parameter and indeed this was done many years ago by Zwetkoff [4] who suggested

$$S = \left\langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right\rangle . \quad (1)$$

In eq. 1 we have implicitly assumed the liquid crystal molecules to be cylindrically symmetric objects as in the typical textbook picture (see, e.g. [5]). β is the angle

between the axis of one of these objects and the preferred direction (the *director*) taken as the laboratory Z axis. It is immediate to see that S varies between one and zero as we go from a completely ordered system with all molecules parallel to the Z axis to a completely disordered, isotropic phase. The first question we may ask is if the description of the alignment offered by S is exhaustive. The answer to this is in general no. For example we could envisage various different molecular organizations leading to the same S . In one, clearly limiting, case all molecules are distributed on a cone, so that they make a constant angle $\beta = \beta_{tilt}$ with the director. In the other case we have a fraction of molecules parallel or perpendicular to the director in suitable percentage. In the third, and possibly more realistic case for nematics, we have a continuous distribution of orientations, corresponding once more to the same S . It is important to be able to distinguish between these physically different situations and thus it seems clear that additional order parameters will be necessary. One of our tasks here will be to discuss a way to systematically introduce these additional quantities. Another source of complications in describing anisotropic systems arises when we consider molecules with lower than cylindrical symmetry or, even worse, molecules with internal degrees of freedom, where the identification of relevant order parameters becomes much more complex. This will be briefly discussed in Sec. 5. As the number and variety of order parameters increase visualization becomes more difficult and extracting a picture of the molecular organization becomes accordingly harder. We shall discuss how the construction of molecular distributions compatible with a given set of order parameters according to maximum entropy principles can be of help in this visualization as well as in some data analysis cases.

Here we are mainly interested in making contact with optical spectroscopy studies such as absorption and, in another chapter in this volume, fluorescence. These studies normally concern solute molecules dissolved in the anisotropic phase in low concentration. Thus we shall be primarily concerned with single particle properties and in particular with solute order parameters. On the other hand the treatment we are going to describe will hold for order parameters relating to the liquid crystal itself.

To start with we consider that the molecules of interest are rigid. The orientation of each rigid particle can be specified in terms of the set of Euler angles $\omega \equiv (\alpha, \beta, \gamma)$ defined following Rose [6] convention. For a uniform system, like an ordinary isotropic fluid or a nematic, physical properties are invariant under translation. Thus, as long as we are interested in single particle observables, we

only need to worry about the orientational distribution $f(\alpha, \beta, \gamma)$ which expresses the probability of finding the molecule at (α, β, γ) [7]. Indeed this can be used to express any single particle orientational property $A(\alpha, \beta, \gamma)$

$$\langle A(\alpha, \beta, \gamma) \rangle = \frac{\int d\alpha \sin \beta d\beta d\gamma f(\alpha, \beta, \gamma) A(\alpha, \beta, \gamma)}{\int d\alpha \sin \beta d\beta d\gamma f(\alpha, \beta, \gamma)}, \quad (2)$$

where the angular brackets indicate an average. The distribution is of course unknown, but at least some constraints imposed upon it by symmetry can nevertheless be taken into account. For example we know that experiments, at least in a nematic and in a smectic A, are consistent with a uniaxial symmetry of the mesophase around the director [1-3]. If we choose this direction as our Z axis this means that rotating the sample about Z no observable property will change. Thus the probability for a molecule to have orientation (α, β, γ) should be the same whatever the angle α . More concisely

$$f(\alpha, \beta, \gamma) \propto f(\beta, \gamma), \quad (3)$$

with the normalization condition

$$\int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma f(\beta, \gamma) = 1. \quad (4)$$

It is clear that if the molecules have more complex structures, e.g. if they have internal degrees of freedom the treatment will need to include extra variables and will become more complicated [8]. We shall see later on one such example for rotameric molecules. For now we shall keep to the assumption of rigidity and treat in detail the case of uniaxial and biaxial particles.

2. CYLINDRICALLY SYMMETRIC MOLECULES

At this simplest level the molecules of interest are considered to possess uniaxial symmetry. If these molecules are unable to distinguish head from tail we should have

$$f(\beta) = f(\pi - \beta). \quad (5)$$

For nematics this corresponds to the experimental finding that turning the aligned sample upside down no observable property changes. The situation may be different, e.g. in monolayers, where an asymmetry exists. The first thing we can do to identify a set of parameters that we can use *in lieu* of $f(\beta)$ is to expand the

distribution in a basis set orthogonal when integrated over $\sin \beta d\beta$. Such a set of functions is that of Legendre polynomials [9] $P_L(\cos \beta)$, for which we have

$$\int_0^\pi d\beta \sin \beta P_L(\cos \beta) P_N(\cos \beta) = \frac{2}{(2L+1)} \delta_{LN}. \quad (6)$$

The explicit form of the first few Legendre polynomials is

$$P_0(\cos \beta) = 1, \quad (7.a)$$

$$P_1(\cos \beta) = \cos \beta, \quad (7.b)$$

$$P_2(\cos \beta) = \frac{3}{2} \cos^2 \beta - \frac{1}{2}, \quad (7.c)$$

$$P_3(\cos \beta) = \frac{5}{2} \cos^3 \beta - \frac{3}{2} \cos \beta, \quad (7.d)$$

$$P_4(\cos \beta) = \frac{35}{8} \cos^4 \beta - \frac{30}{8} \cos^2 \beta + \frac{5}{8}. \quad (7.e)$$

As we see from these first few examples, Legendre polynomials are even functions of $\cos \beta$ if their rank L is even and odd functions if L is odd [9]. Thus

$$P_L(\cos \beta) = (-1)^L P_L(-\cos \beta). \quad (8)$$

Since

$$\cos(\pi - \beta) = -\cos \beta, \quad (9)$$

we shall only need to retain even L terms when expanding the distribution $f(\beta)$, even in $\cos \beta$ (see eq. 5), in terms of $P_L(\cos \beta)$. Thus we can write

$$f(\beta) = \sum_{L=0}^{\infty} f_L P_L(\cos \beta) \quad ; L \text{ even}. \quad (10)$$

The J -th coefficient in the expansion can be easily obtained using the orthogonality of the basis set. Multiplying both sides of eq. 10 by $P_J(\cos \beta)$ and integrating over $\sin \beta d\beta$:

$$\int_0^\pi d\beta \sin \beta f(\beta) P_J(\cos \beta) = \sum_{L=0}^{\infty} f_L \int_0^\pi d\beta \sin \beta P_L(\cos \beta) P_J(\cos \beta), \quad (11)$$

we find the coefficients in eq. 10 as

$$f_J = \frac{(2J+1)}{2} \langle P_J \rangle, \quad (12)$$

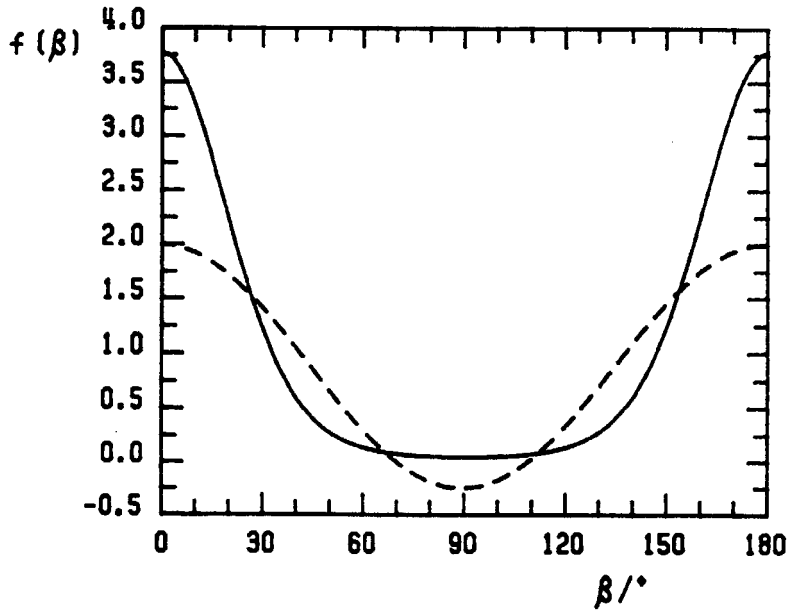


Figure 1 . The orientational distribution $f(\beta)$ corresponding to $\langle P_2 \rangle = 0.6$ as obtained from the orthogonal expansion truncated to second rank (dashed line) and from the maximum entropy procedure (continuous line).

where we have used the notation

$$\langle P_J \rangle = \int_0^\pi d\beta \sin \beta P_J(\cos \beta) f(\beta). \quad (13)$$

The knowledge of the (infinite) set of $\langle P_J \rangle$ would completely define the distribution. The Legendre polynomials averages $\langle P_J \rangle$ thus represent our set of orientational order parameters. We can write

$$f(\beta) = \frac{1}{2} + \frac{5}{2} \langle P_2 \rangle P_2(\cos \beta) + \frac{9}{2} \langle P_4 \rangle P_4(\cos \beta) + \dots \quad (14)$$

The first non trivial term contains the second rank order parameter

$$\langle P_2 \rangle = \left\langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \right\rangle, \quad (15)$$

which corresponds exactly to the S order parameter introduced by Zwetkoff [5] (see eq. 1). It is worth stressing that eq. 10 is exact as an infinite expansion, but that in practice it does not give a very good approximation to $f(\beta)$ when we truncate to the first few terms. For instance if we have $\langle P_2 \rangle = 0.6$ then $f(\beta)$, as given by the orthogonal expansion truncated at P_2 , is shown in Fig. 1 as the dashed line. We see that $f(\beta)$ constructed in this way can even become negative,

which is certainly unphysical when we think that $f(\beta)$ is a probability. Notice that any property depending only on $\langle P_2 \rangle$ is calculated correctly using this $f(\beta)$. However, $\langle P_4 \rangle$ and the higher order parameters calculated with the second rank approximation are zero, because of the orthogonality of the Legendre polynomials. Thus the orthogonal approximation is exact for terms that we have included but very bad if we want higher terms.

2.1. Exponential approximation

The problem of finding the best, in the sense of least biased approximation to the whole $f(\beta)$ or in general $f(\omega)$ starting from a knowledge of a set of order parameters $\langle P_L \rangle$, say up to rank L' , can be approached using Information Theory [10-11]. In this approach the most probable distribution is defined as that maximizing the entropy associated with the usual thermodynamic - like formula

$$S(\{a_L\}) \propto - \int d\omega f(\omega, \{a_L\}) \ln f(\omega, \{a_L\}), \quad (16)$$

with respect to the set $\{a_L\}$. It has been shown using standard Lagrange multipliers technique that the best distribution in this respect has the form [10-14]

$$f(\beta) = \exp\left\{ \sum_{L=0}^{L'} a_L P_L(\cos \beta) \right\}, \quad (17)$$

where the coefficients a_L are obtained imposing the constraint that the $\langle P_L \rangle$, $L = 0, \dots, L'$ calculated from $f(\beta)$ have the known values. In particular we have the normalization condition $\langle P_0 \rangle = 1$. The information theory approach is in a way an *a posteriori* one. It allows constructing an approximate full distribution from available information but on the other hand it can make no prediction on what the distribution will be at, say, a different temperature. The approach also does not say anything on the molecular origin of the distribution itself. It is a way of translating the experimental information into the most probable distribution compatible with the data themselves. As more and more order parameters or in general observables become available the estimate of $f(\beta)$ can be refined. The method does not rely on *a priori* assumptions and as the number of terms increases the sequence of maximum entropy approximations converges to the true one [15]. It is also important to stress that at any level of approximation the distribution obtained is positive and of exponential character. It may be worth discussing in some detail the differences between the orthogonal and the maximum entropy approximations.

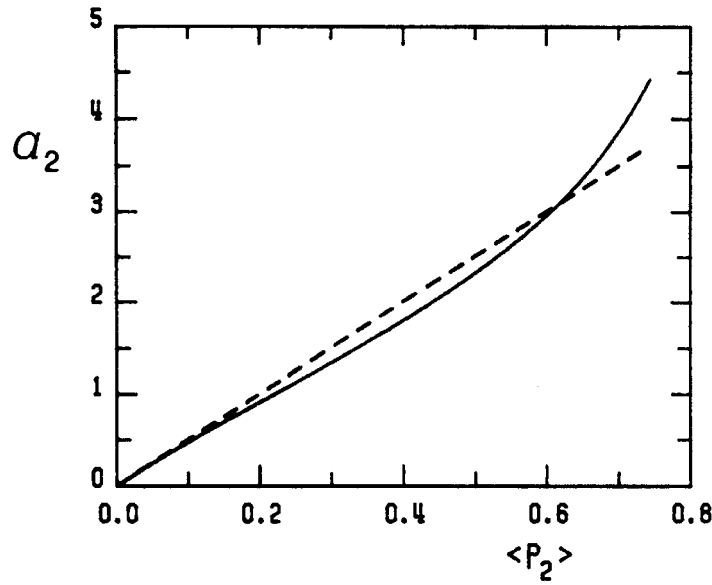


Figure 2 . The maximum entropy parameter a_2 defining the distribution in eq.18 plotted against $\langle P_2 \rangle$ (continuous line). We also show the simple analytic approximation $a_2 = 5 \langle P_2 \rangle$ as the dashed line.

2.2. Examples

We now consider briefly what inferences can be made about the molecular organization starting from a knowledge of a small number of order parameters and in particular of $\langle P_2 \rangle$, $\langle P_4 \rangle$.

2.2.1. Knowing $\langle P_2 \rangle$ only To start with we suppose that only the second rank order parameter, $\langle P_2 \rangle$, has been determined. The maximum entropy distribution associated with this $\langle P_2 \rangle$ will be

$$f(\beta) = \frac{\exp[a_2 P_2(\cos \beta)]}{\int_0^\pi d\beta \sin \beta \exp[a_2 P_2(\cos \beta)]}, \quad (18)$$

with a_2 determined by the condition

$$\langle P_2 \rangle = \frac{\int_0^\pi d\beta \sin \beta P_2(\cos \beta) \exp[a_2 P_2(\cos \beta)]}{\int_0^\pi d\beta \sin \beta \exp[a_2 P_2(\cos \beta)]}. \quad (19)$$

Eq. 19 can be solved for a_2 in terms of $\langle P_2 \rangle$. In Fig. 2 we show the resulting curve for positive $\langle P_2 \rangle$ as the full line. We see that for positive $\langle P_2 \rangle$ the distribution is peaked at $\beta = 0$, so that the majority of molecules will be parallel to the director. This is normally the case when we dissolve an elongated molecule in a nematic.

It is sometimes useful to quickly estimate a_2 from $\langle P_2 \rangle$ without having to turn to a computer. We can expand a_2 in a power series in $\langle P_2 \rangle$ obtaining [16]

$$a_2 = 5 \langle P_2 \rangle - \frac{25}{7} \langle P_2 \rangle^2 + \frac{425}{49} \langle P_2 \rangle^3 - \frac{51875}{3773} \langle P_2 \rangle^4 + \frac{1419625}{49049} \langle P_2 \rangle^5 - \dots \quad (20)$$

The series is of course divergent at $\langle P_2 \rangle = 1$ but it can still be useful for order parameters to be realistically found in nematics. In Fig. 2 we show as the dashed line the very simple approximation

$$a_2 = 5 \langle P_2 \rangle . \quad (21)$$

Eq. 21 is useful to get a good idea of a_2 and thus of the distribution at least up to $\langle P_2 \rangle = 0.6$. Having determined a_2 we can immediately plot the distribution $f(\beta)$. For example, if we assume $\langle P_2 \rangle = 0.6$, like in the previous section, we obtain the approximate distribution obtained from maximum entropy as the continuous line in Fig. 1.

We notice that a_2 becomes negative as $\langle P_2 \rangle$ changes sign and that the corresponding distribution becomes peaked at $\beta = \frac{\pi}{2}$. Physically this will normally happen when we study a disk-like molecule dissolved in a nematic, since in this case the molecular Z axis (the disk axis) is preferentially aligned perpendicular to the director.

2.2.2. Knowing $\langle P_2 \rangle$ and $\langle P_4 \rangle$ We now turn to the case where both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been determined. The first thing we might try is to test if the distribution eq. 18 obtained using just the information on $\langle P_2 \rangle$ is consistent with the observed $\langle P_4 \rangle$. Thus we would use the distribution generated by the a_2 gotten from $\langle P_2 \rangle$ and calculate the fourth rank order parameter $\langle P_4 \rangle$ by integration. The curve obtained is shown in Fig. 3 as the continuous line.

A simple approximate analytic form for this relation can be obtained expanding $\langle P_4 \rangle$ in powers of a_2 and substituting eq. 20 . This gives

$$\langle P_4 \rangle = \frac{5}{7} \langle P_2 \rangle^2 - \frac{200}{539} \langle P_2 \rangle^3 + \frac{35650}{49049} \langle P_2 \rangle^4 + \dots \quad (22)$$

The series contains large terms of alternating sign and is poorly convergent unless terms are properly grouped together. The very simplest approximation [16] retains just the first term, i.e.

$$\langle P_4 \rangle = \frac{5}{7} \langle P_2 \rangle^2, \quad (23)$$

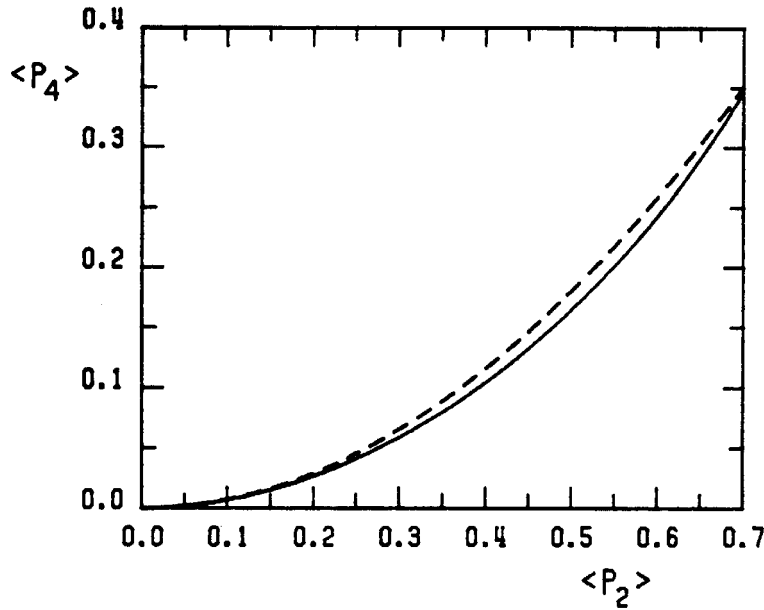


Figure 3 . The fourth rank order parameter $\langle P_4 \rangle$ vs. $\langle P_2 \rangle$ as obtained from the purely second rank distribution eq. 18 (continuous line). We also show the approximate analytic expression $\langle P_4 \rangle = \frac{5}{7} \langle P_2 \rangle^2$ (dashed line).

and is actually a good approximation up to $\langle P_2 \rangle \approx 0.6$ as we see from the dashed line in Fig. 3 . When $\langle P_4 \rangle$ does not fall on the curve in Fig. 3 we can construct a distribution like eq. 17 with $L = 0, 2, 4$. To do this we have to find a_2 and a_4 from our given $\langle P_2 \rangle$ and $\langle P_4 \rangle$. The first thing to observe is that the domain of the functions $a_2(\langle P_2 \rangle, \langle P_4 \rangle)$, $a_4(\langle P_2 \rangle, \langle P_4 \rangle)$ consists of the set of allowed values of $\langle P_2 \rangle, \langle P_4 \rangle$. It is not difficult to show, using Schwarz' s inequality [9] that

$$\langle \cos^2 \beta \rangle^2 \leq \langle \cos^4 \beta \rangle \leq \langle \cos^2 \beta \rangle . \quad (24)$$

The explicit form of P_2 and P_4 , eq. 7 , together with these inequalities yields [17]

$$\frac{35}{18} \langle P_2 \rangle^2 - \frac{5}{9} \langle P_2 \rangle - \frac{7}{18} \leq \langle P_4 \rangle \leq \frac{5}{12} \langle P_2 \rangle + \frac{7}{12} . \quad (25)$$

These two inequalities define the region of space where possible values of $\langle P_2 \rangle$, $\langle P_4 \rangle$ consistent with their respective trigonometric form should lie. It goes without saying that it makes sense to check that experimental values do fall within this area. The determination of a_2, a_4 can be carried out in general by solving the non linear system

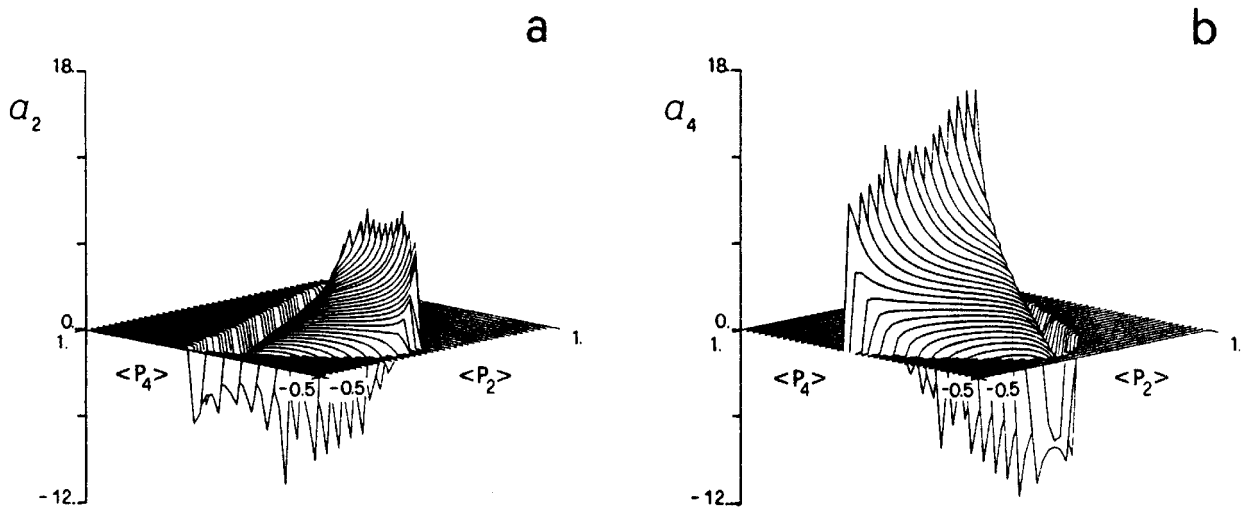


Figure 4 . The exponential coefficients a_2 (a) and a_4 (b) in the distribution $f(\beta) \propto \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]$ shown as a function of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ [18].

$$\langle P_2 \rangle = \frac{\int_0^\pi d\beta \sin \beta P_2(\cos \beta) \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]}{\int_0^\pi d\beta \sin \beta \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]}, \quad (26.a)$$

$$\langle P_4 \rangle = \frac{\int_0^\pi d\beta \sin \beta P_4(\cos \beta) \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]}{\int_0^\pi d\beta \sin \beta \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]}. \quad (26.b)$$

The results we obtain [18] are shown in Fig. 4 . Notice that, although we expect $\langle P_2 \rangle$ greater than $\langle P_4 \rangle$ as it was the case in the P_2 distribution (see Fig. 3), a range of solutions exists also for $\langle P_4 \rangle$ greater than $\langle P_2 \rangle$. Indeed an interesting case is that of $\langle P_4 \rangle > \langle P_2 \rangle$, with the values falling on a curve like the continuous one in Fig. 5 . This unusual behaviour has been found to be consistent with fluorescence depolarization data of diphenylhexatriene in DPPC and DMPC membrane vesicles [19]. In turn the behaviour agrees with that predicted by a model with pure P_4 effective potential [20], which gives a distribution

$$f(\beta) = \frac{e^{a_4 P_4(\cos \beta)}}{\int_0^\pi d\beta \sin \beta \exp[a_4 P_4(\cos \beta)]}. \quad (27)$$

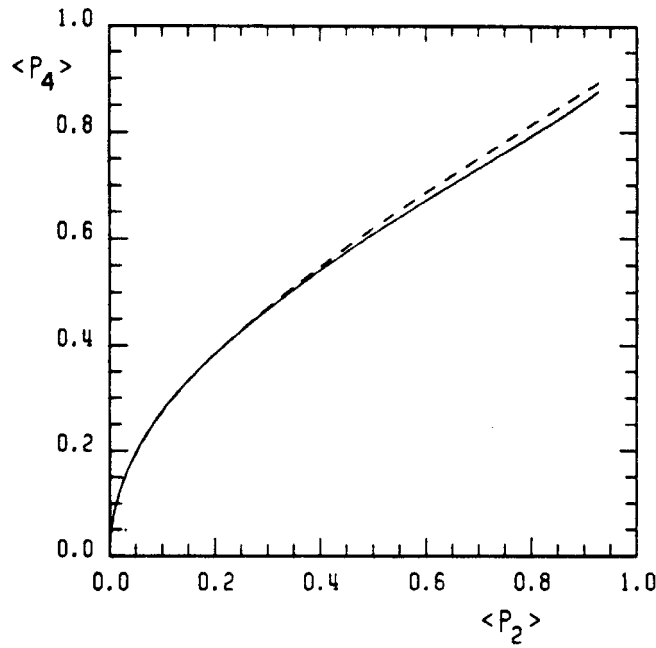


Figure 5 . The dependence of the fourth rank order parameter $\langle P_4 \rangle$ on the second rank one $\langle P_2 \rangle$ for a purely fourth rank distribution eq.27 (continuous line). We also show the analytical approximation in eq. 32 (dashed line).

We wish to obtain also for this limiting case a simple approximation to the $\langle P_4 \rangle$ vs. $\langle P_2 \rangle$ curve. We start by Taylor expanding the expressions for $\langle P_2 \rangle$ and $\langle P_4 \rangle$, i.e.

$$\langle P_L \rangle = \frac{\int_0^\pi d\beta \sin \beta P_L(\cos \beta) e^{a_4 P_4(\cos \beta)}}{\int_0^\pi d\beta \sin \beta e^{a_4 P_4(\cos \beta)}}, \quad L = 2, 4, \quad (28)$$

with respect to a_4 . This provides the first few terms as

$$\langle P_2 \rangle = \frac{10a_4^2}{693} + \frac{10a_4^3}{3003} + \frac{1010a_4^4}{26189163} - \frac{83990a_4^5}{909431523} + \dots, \quad (29)$$

$$\langle P_4 \rangle = \frac{a_4}{9} + \frac{9a_4^2}{1001} - \frac{1367a_4^3}{1378377} + \frac{457a_4^4}{2909907} + \frac{119776729a_4^5}{5426577897741} + \dots, \quad (30)$$

Reversion of the series for $\langle P_4 \rangle$ gives a_4 in terms of $\langle P_4 \rangle$

$$a_4 = 9 \langle P_4 \rangle - \frac{6561 \langle P_4 \rangle^2}{1001} + \frac{273458673 \langle P_4 \rangle^3}{17034017} + \dots \quad (31)$$

Then we get $\langle P_2 \rangle$ in terms of $\langle P_4 \rangle$ and by further reversion

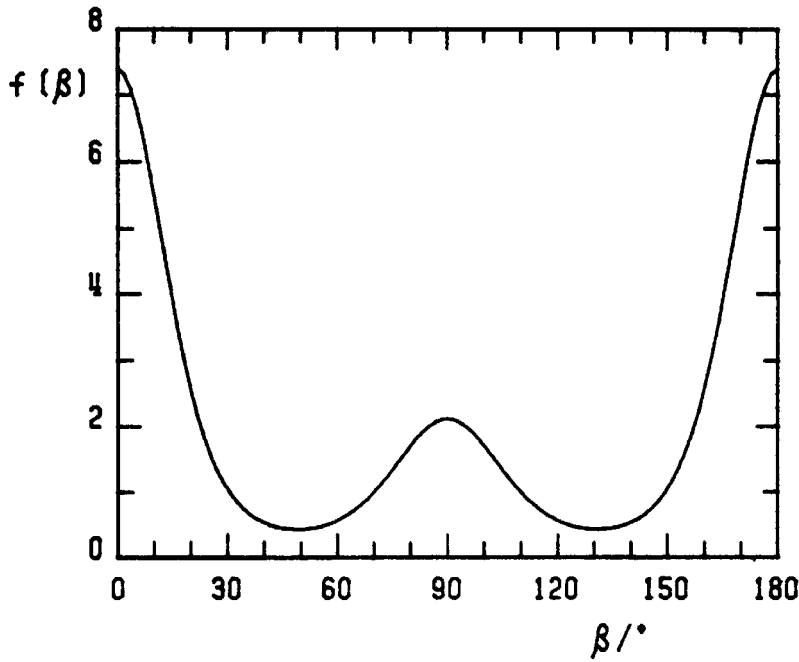


Figure 6 . The angular variation of the distribution $f(\beta) \propto \exp[a_4 P_4(\cos \beta)]$ with $a_4 = 2$.

$$\langle P_4 \rangle = \sqrt{\frac{77}{90}} \langle P_2 \rangle^{\frac{1}{2}} - \frac{69}{260} \langle P_2 \rangle + \frac{7794479}{1007760\sqrt{770}} \langle P_2 \rangle^{\frac{3}{2}} + \dots \quad (32)$$

This simple power series in $\sqrt{\langle P_2 \rangle}$ gives a good representation of the curve for $\langle P_2 \rangle$ up to 0.9. In Fig.5 we show the analytical approximation to the $\langle P_4 \rangle$ vs. $\langle P_2 \rangle$ curve from the truncation in eq.32 (dashed line) and the curve obtained by direct numerical integration (continuous line). Using eq. 32 it is quite easy to test if a set of $\langle P_2 \rangle$, $\langle P_4 \rangle$ values has a pure P_4 behaviour. An example of pure P_4 distribution is plotted in Fig. 6 . Notice that the probability shows a maximum not only for molecules parallel to the director, but also a smaller one for molecules perpendicular to it.

3. NON-CYLINDRICAL MOLECULES

3.1. Identification of order parameters

In the last Section we have gone into some details in treating cylindrically symmetric objects. This will now allow us to skip some explicit steps, since the logic here is the same, even though the algebra is somewhat more complicated. To

start with we notice that when the rigid molecule of interest, which we still assume to be dissolved in a uniaxial phase, cannot be assimilated to a rod like or a disk like particle, we need an extra angle in defining its orientation. Thus if β , is the angle between the Z axis of the particle and the director, the extra angle, γ is an angle of rotation around the molecular Z direction [6]. The probability of finding the molecule at a specific orientation, $f(\beta, \gamma)$, can be expanded like any other function of the two Euler angles β, γ , in a complete basis set of spherical harmonics. Thus we get

$$f(\beta, \gamma) = \sum_{L,n} f_{L,n} D_{0n}^L(\beta, \gamma), \quad (33)$$

where we have chosen the Wigner matrix notation $D_{0n}^L(\beta, \gamma)$ [6]. Orthogonality of the basis set immediately permits identifying the coefficients $f_{L,n}$ and obtaining

$$f(\beta, \gamma) = \frac{1}{4\pi} \sum_{L=0}^{\infty} \sum_{n=-L}^L (2L+1) \langle D_{0,n}^{L*} \rangle D_{0n}^L(\beta, \gamma) \quad (34)$$

The set of averaged Wigner orientation matrices $\langle D_{0n}^L \rangle$ allows a complete characterization of $f(\beta, \gamma)$. The generally complex quantities $\langle D_{0n}^L \rangle$ are called orientational order parameters [see, e.g. 8, 21]. The complex conjugate of a Wigner function is $D_{mn}^{L*}(\omega) = (-)^{m-n} D_{-m-n}^L(\omega)$. Since the distribution $f(\beta, \gamma)$ is real, then

$$\langle D_{0n}^{L*} \rangle = (-)^n \langle D_{0n}^L \rangle, \quad (35)$$

and the number of independent quantities is correspondingly reduced. At second rank level, $L = 2$, there are at most five independent order parameters $\langle D_{0n}^2 \rangle$. The five order parameters could also be chosen as the independent components of the cartesian ordering matrix \mathbf{S} first introduced by Saupe [22]

$$\mathbf{S} = \begin{pmatrix} \langle \frac{3}{2} \sin^2 \beta \cos^2 \gamma - \frac{1}{2} \rangle & \langle \sin^2 \beta \cos \gamma \sin \gamma \rangle & \langle \sin \beta \cos \beta \cos \gamma \rangle \\ \langle \sin^2 \beta \cos \gamma \sin \gamma \rangle & \langle \frac{3}{2} \sin^2 \beta \sin^2 \gamma - \frac{1}{2} \rangle & \langle \sin \beta \cos \beta \sin \gamma \rangle \\ \langle \sin \beta \cos \beta \cos \gamma \rangle & \langle \sin \beta \cos \beta \sin \gamma \rangle & \langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \rangle \end{pmatrix}. \quad (36)$$

The matrix is traceless and symmetric. Results can be easily converted from the Saupe to the Wigner rotation matrix form [7]

$$S_{xx} - S_{yy} = \sqrt{6} \operatorname{Re} \langle D_{02}^2 \rangle, \quad (37.a)$$

$$S_{xy} = -\sqrt{\frac{3}{2}} \text{Im} \langle D_{02}^2 \rangle, \quad (37.b)$$

$$S_{xz} = -\sqrt{\frac{3}{2}} \text{Re} \langle D_{01}^2 \rangle, \quad (37.c)$$

$$S_{yz} = \sqrt{\frac{3}{2}} \text{Im} \langle D_{01}^2 \rangle, \quad (37.d)$$

$$S_{zz} = \langle D_{00}^2 \rangle. \quad (37.e)$$

We call ordering matrix frame the principal axis system of \mathbf{S} , possibly obvious by symmetry, where \mathbf{S} is diagonal.

It should be stressed that other equivalent formulations can be given to the problem of describing orientational order. A set of second rank ordering constants particularly used in optical spectroscopy [23] is the set of orientation factors

$$K_{a,b} = \langle (\mathbf{Z} \cdot \mathbf{a})(\mathbf{Z} \cdot \mathbf{b}) \rangle, \quad a, b = x, y, z, \quad (38)$$

where \mathbf{a} , \mathbf{b} are unit vectors that can be parallel to the x , y or z molecular axes and \mathbf{Z} is along the director. For instance $K_{x,x} = \langle \cos^2 \beta \rangle$. The \mathbf{K} and \mathbf{S} are simply related

$$S_{a,b} = \frac{3}{2} K_{a,b} - \frac{1}{2} \delta_{a,b}. \quad (39)$$

The cartesian formulation can be extended to higher ranks both for the \mathbf{S} matrices [7] and orientation factors [23] although it becomes progressively more complicated than the spherical one as the rank increases. Whatever the formalism used the relevant order parameters for molecules of a certain point group can be listed. A fairly general treatment of the allowed order parameters for various molecular symmetries has been given elsewhere [7]. In practice, in a great number of practical cases, the assumption is made that the molecules of interest are biaxial particles. This case, which includes many molecules of interest in optical studies, e.g. perylene, pyrene etc. will now be discussed in some detail.

3.2. Biaxial molecules

We wish to list the explicit trigonometric form of the first few relevant Wigner rotation matrices in the description of biaxial objects. First we choose our molecular frame axis along the three C_2 axes. Since we can turn our biaxial particle upside down without changing anything we only need to retain in eq. 34 functions that are invariant for this transformation. Remembering [6, 7] that the spherical harmonics

$D_{0n}^L(\beta, \gamma)$ are multiplied by $(-)^L$ under the same operation, we see that we only need to expand in Wigner rotation matrices with even rank L . The first few are

$$D_{00}^0(\beta, \gamma) = 1, \quad (40.a)$$

$$D_{00}^2(\beta, \gamma) = P_2(\cos \beta), \quad (40.b)$$

$$D_{0\pm 2}^2(\beta, \gamma) = \sqrt{\frac{3}{8}} \sin^2 \beta e^{\mp i 2 \gamma}, \quad (40.c)$$

$$D_{00}^4(\beta, \gamma) = P_4(\cos \beta), \quad (40.d)$$

$$D_{0\pm 2}^4(\beta, \gamma) = \sqrt{10} \left\{ 14 \cos^6 \frac{\beta}{2} - 14 \cos^4 \frac{\beta}{2} + 3 \cos^2 \frac{\beta}{2} \right\} \sin^2 \frac{\beta}{2} e^{\mp i 2 \gamma}, \quad (40.e)$$

$$D_{0\pm 4}^4(\beta, \gamma) = \sqrt{70} \cos^4 \frac{\beta}{2} \sin^4 \frac{\beta}{2} e^{\mp i 4 \gamma} \quad (40.f)$$

Since the principal frame of the ordering matrix is determined by symmetry, at second rank level there are two relevant order parameters, $\langle D_{00}^2 \rangle$, $Re \langle D_{02}^2 \rangle$ or, e.g. S_{zz} , $S_{xx} - S_{yy}$. While $\langle D_{00}^2 \rangle$ measures the alignment of the z molecular axis with respect to the director, as we have seen for cylindrical molecules, $Re \langle D_{02}^2 \rangle$ is a biaxiality parameter. It provides the difference in ordering of the x and y axes for the molecule in that liquid crystal solvent and at the given thermodynamic conditions. A perhaps more immediate interpretation can be obtained by constructing approximate molecular distributions consistent with a given set of order parameters.

3.3. Maximum Entropy Distributions

If a set of order parameters $\langle D_{0n}^L \rangle$ is known, the best distribution compatible with them is, according to Information Theory [11]

$$f(\beta, \gamma) = \exp \sum_{L,n} a_{L,n} D_{0n}^L(\beta, \gamma), \quad (41)$$

where the coefficients $a_{L,n}$ are obtained solving the non linear system of consistency constraints

$$\langle D_{0n}^L \rangle = \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma D_{0n}^L(\beta, \gamma) \exp \sum_{L,n} a_{L,n} D_{0n}^L(\beta, \gamma), \quad (42)$$

and $a_{0,0}$ from the normalization constraint $\langle D_{00}^0 \rangle = 1$. For a biaxial solute where $\langle D_{00}^2 \rangle$ and $Re \langle D_{02}^2 \rangle$ are determined, we have simply

$$f(\beta, \gamma) = \frac{\exp a [P_2(\cos \beta) + \xi Re D_{02}^2(\beta, \gamma)]}{\int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma \exp a [P_2(\cos \beta) + \xi Re D_{02}^2(\beta, \gamma)]}, \quad (43)$$

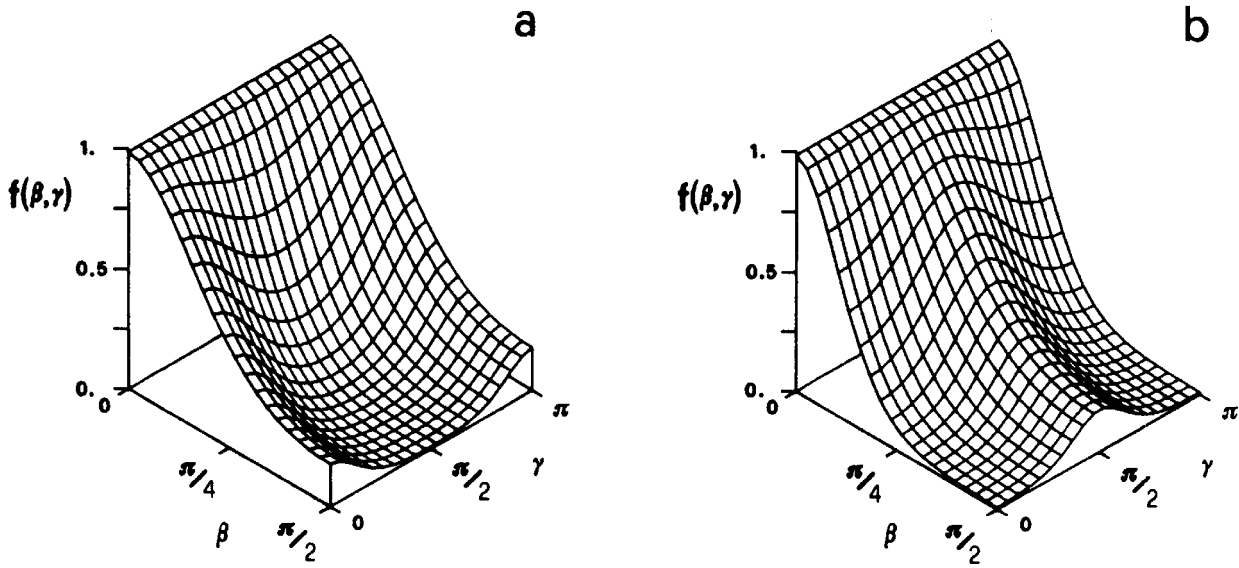


Figure 7 . An example of orientational distribution $f(\beta, \gamma)$ for a biaxial molecule with $\langle P_2 \rangle = 0.4$ and $Re \langle D_{02}^2 \rangle = 0.1(a)$ or $-0.1(b)$.

with $a \equiv a_{2,0}$, $\xi \equiv a_{2,2}/a_{2,0}$. The parameter ξ is a measure of deviation from cylindrical symmetry, since it is zero for the special case of uniaxial molecules. To illustrate the interplay between order parameters and distributions, we show in Fig. 7 a few examples of distributions corresponding to elongated biaxial objects with $\langle P_2 \rangle = 0.4$ and $Re \langle D_{02}^2 \rangle = \pm 0.1$.

In Fig. 8 we show a similar distribution for plate - like biaxial particles. In this case the particle has a greater probability of having the z axis perpendicular to the director, with the plate plane tending to be aligned parallel to the director. The sign of the order parameter tells us which of the two axes in the plane is most aligned.

It is interesting to notice that biaxiality effects are somewhat magnified for oblate molecules. If we remember that

$$Re \langle D_{02}^2 \rangle = \sqrt{\frac{3}{8}} \langle \sin^2 \beta \cos 2\gamma \rangle, \quad (44)$$

we see that for a rod like molecule as the alignment increases β is on average more and more approaching zero and the same will do $\sin^2 \beta$ and ultimately $Re \langle D_{02}^2 \rangle$ itself. On the contrary for an oblate like molecule, β in a similar situation approaches $\frac{\pi}{2}$ and $\sin^2 \beta$ approaches 1, thus allowing the γ dependence to emerge.

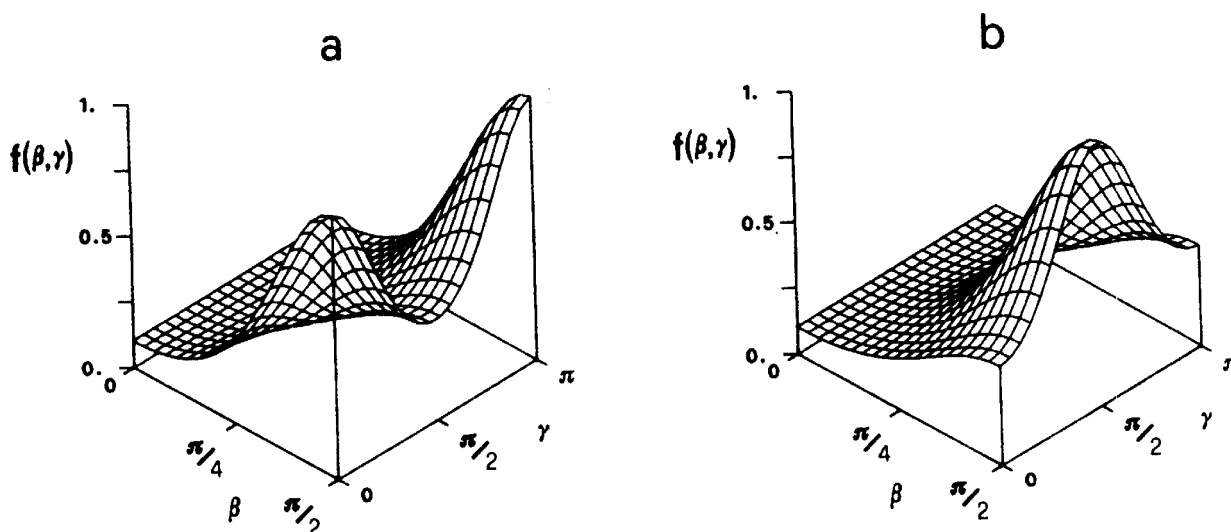


Figure 8 . An example of orientational distribution $f(\beta, \gamma)$ for a biaxial molecule with $\langle P_2 \rangle = -0.2$ and $Re \langle D_{02}^2 \rangle = 0.1$ (a) and -0.1 (b).

Notice that here we have no means of knowing if ξ is a molecular property or not. The maximum entropy formalism just converts order parameters in distributions, without offering a molecular interpretation to what is observed. However, eq. 44 is formally identical to that obtained with Mean Field Theory, e.g. starting from a dispersion interaction [24]. In that case, the parameters a , ξ do indeed have a molecular interpretation. For dispersion forces $\xi = 2\lambda$, where λ is a molecular constant

$$\lambda = \sqrt{\frac{3}{2}} \frac{\alpha_{xx} - \alpha_{yy}}{2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}} \quad (45)$$

expressing the deviation from cylindrical symmetry of the solute polarizability α . Curves of $Re \langle D_{02}^2 \rangle$ vs. $\langle D_{00}^2 \rangle$ or equivalently of $S_{xx} - S_{yy}$ vs. S_{zz} at constant ξ are often used when analyzing experimental data [25]. In Fig. 9 we see such a family of curves.

We shall now try to find some approximations for the biaxial order parameters calculated for integration over the distribution in eq. 43 . To do this we consider ξ fixed and start with an expansion in terms of a . The first few terms are

$$\langle P_2 \rangle = \frac{1}{5}a - \frac{(\xi^2 - 2)}{70}a^2 - \frac{(\xi^2 + 2)}{350}a^3 + \frac{3\xi^3 + 2\xi}{1925}a^4 + \dots, \quad (46)$$

$$Re \langle D_{02}^2 \rangle = \frac{\xi}{10}a - \frac{\xi}{35}a^2 - \frac{(\xi^3 + 2\xi)}{700}a^3 + \frac{3\xi^4 + 12\xi^2 - 20}{7700}a^4 + \dots \quad (47)$$

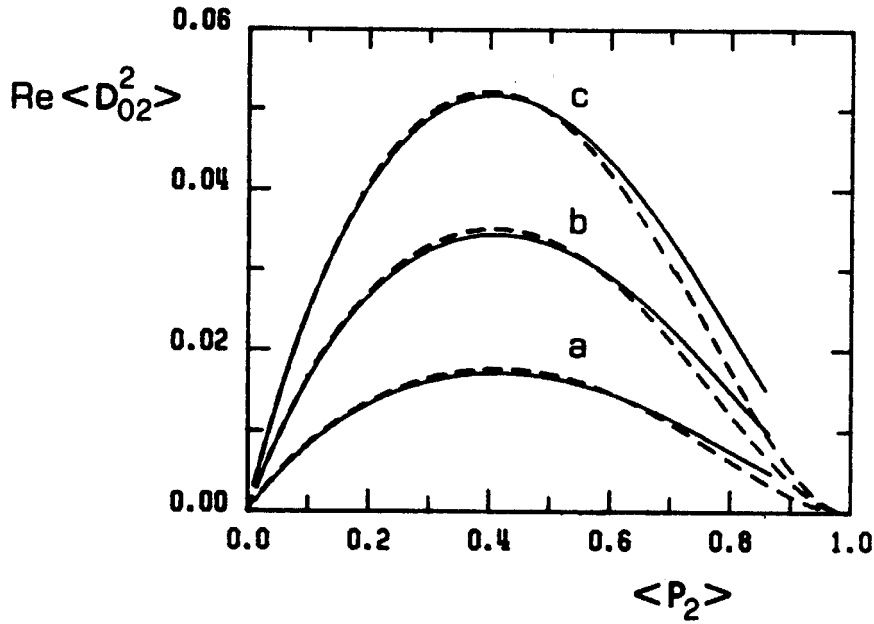


Figure 9 . A plot of the order parameter $Re \langle D_{02}^2 \rangle$ vs. $\langle P_2 \rangle$ for the biaxial distribution in eq.43 and for $\xi = 0.2$ (a), 0.4 (b), 0.6 (c) as calculated by numerical integration (continuous lines) and from the approximate analytic expansion eq.48 (dashed lines).

Eliminating a between the last two equations and regrouping we find

$$Re \langle D_{02}^2 \rangle = \langle P_2 \rangle (\langle P_2 \rangle - 1)^2 \left\{ \frac{\xi}{2} + \frac{5\xi^3 - 2\xi}{28} \langle P_2 \rangle + \frac{25\xi^5 - 130\xi^3 + 174\xi}{196} \langle P_2 \rangle^2 + \dots \right\} \quad (48)$$

We see that the performance of the simple eq. 48 as the dashed lines in Fig. 9 is quite reasonable throughout the range and very good for order parameter $\langle P_2 \rangle$ up to 0.6 – 0.7.

3.4. An example

In [26] we have determined through NMR the order parameters for pyridine in various nematic solvents and in particular in the commercial 4-cyano-4'-alkyl bicyclohexane mixture ZLI-1167 (Merck) and in 4-ethoxybenzylidene-4'-n-butylaniline (EBBA). The results for the second rank order parameters in the two solvents at different temperatures are shown in Fig. 10. The molecular coordinate system assumed has the z axis perpendicular to the pyridine plane and the y axis going through the positions of the nitrogen and of the para-hydrogen.

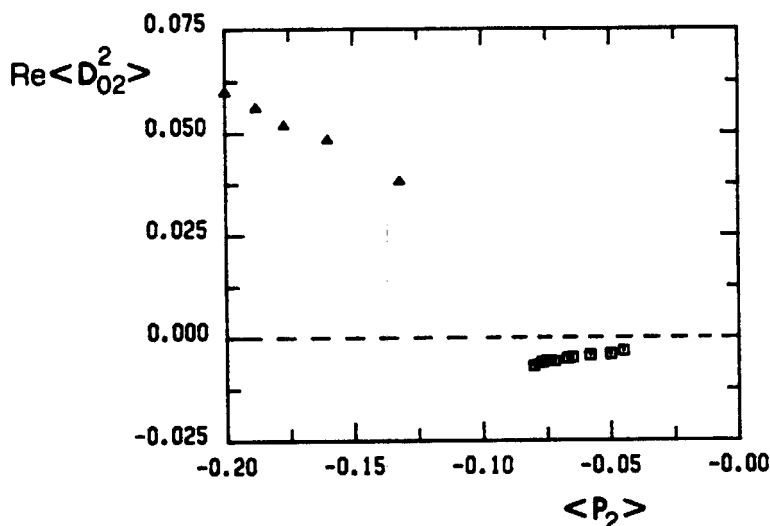


Figure 10 . The second rank order parameters $\text{Re} \langle D_{02}^2 \rangle \equiv (S_{xx} - S_{yy})/\sqrt{6}$ vs. $\langle P_2 \rangle$ for pyridine dissolved in the nematics EBBA (squares) and ZLI-1167 (triangles) [26] .

We see that the behaviour in the two solvents is quite different, so that order parameters are in general solute - solvent rather than just solute properties. While on one hand this represents a source of complication, it also offers an interesting handle toward probing specific interactions in the fluid phase [26]. The construction of distributions corresponding to these different situations can help in making sense of what the most probable orientation is. As an example we show in Fig.11 the probability distributions for pyridine in ZLI-1167 at the lowest temperature employed. A similar plot for pyridine in EBBA hardly shows a dependence on the angle γ because of the small biaxiality values (cf. Fig.10).

4. EXPERIMENTAL DETERMINATION: LINEAR DICHOISM

All what we know about ordering has eventually to be obtained experimentally. Typically an experiment consists in performing measurements of anisotropy on a suitable tensor property. For example the absorption of light by a solute relative to a certain electronic transition is determined by the transition moment μ [23]. If we assume for simplicity to deal with a single transition from a state with wave function ψ_i to a state ψ_j ; then the transition dipole moment is the matrix element between these two states of the electric dipole operator \hat{M} , i.e. $\mu \equiv \langle \psi_i | \hat{M} | \psi_j \rangle$. In general there will be of course complications arising e.g. from overlapping transitions etc. However, for our purposes here the transition moment can be considered as a vector

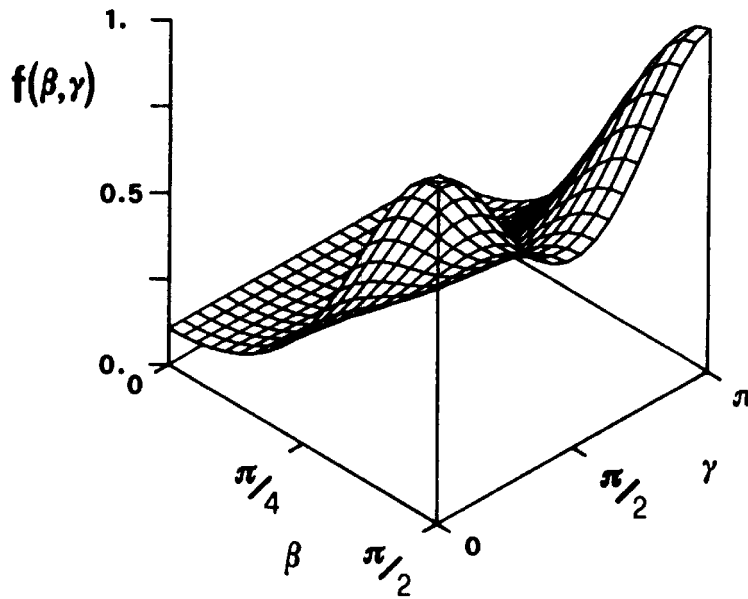


Figure 11 . The probability distribution $f(\beta, \gamma)$ for pyridine in ZLI-1167 at $\langle P_2 \rangle = -0.207$, $Re \langle D_{02}^2 \rangle = 0.0624$.

with a well defined orientation in the molecular frame. The probability of absorption of plane polarized light with a polarization direction \mathbf{e} does not depend directly on μ but rather is

$$\begin{aligned}
 P_{abs} &\propto \langle (\mathbf{e} \cdot \boldsymbol{\mu})^2 \rangle, \\
 &= \sum_{a,b} \langle e_a e_b \mu_a \mu_b \rangle, \\
 &= \langle \mathbf{E} : \mathbf{A} \rangle,
 \end{aligned} \tag{49}$$

where we have introduced the polarization tensor [27]

$$\mathbf{E} = \mathbf{e} \otimes \mathbf{e}, \tag{50}$$

containing all the experiment geometrical information and the absorption transition tensor containing the molecular information

$$\mathbf{A} = \boldsymbol{\mu} \otimes \boldsymbol{\mu}. \tag{51}$$

Eq.51 is useful because it stresses that we are really looking at a second rank tensor,

not at a vector. The contraction operation $\mathbf{E} : \mathbf{A}$ is defined as

$$\mathbf{E} : \mathbf{A} = \sum_{a,b} E_{a,b} A_{a,b}. \quad (52)$$

We could now measure absorbance parallel and perpendicular to the director and try to relate it to order parameters. It is convenient to do this using spherical, rather than cartesian tensors. In practice for second rank symmetric cartesian tensors this can be done explicitly :

$$A_{X,X} = -\frac{1}{\sqrt{3}} A^{0,0} - \frac{1}{\sqrt{6}} A^{2,0} + \frac{1}{2} (A^{2,2} + A^{2,-2}), \quad (53.a)$$

$$A_{X,Y} = \frac{-i}{2} (A^{2,2} - A^{2,-2}), \quad (53.b)$$

$$A_{X,Z} = \frac{1}{2} (A^{2,-1} - A^{2,1}), \quad (53.c)$$

$$A_{Y,Y} = -\frac{1}{\sqrt{3}} A^{0,0} - \frac{1}{\sqrt{6}} A^{2,0} - \frac{1}{2} (A^{2,2} + A^{2,-2}), \quad (53.d)$$

$$A_{Y,Z} = \frac{i}{2} (A^{2,1} + A^{2,-1}), \quad (53.e)$$

$$A_{Z,Z} = -\frac{1}{\sqrt{3}} A^{0,0} + \sqrt{\frac{2}{3}} A^{2,0}, \quad (53.f)$$

where the so called irreducible components $A^{L,m}$ of rank L and component m have, under rotation, the simple transformation properties

$$A_{LAB}^{L,m} = \sum_n D_{mn}^{L*}(\alpha\beta\gamma) A_{MOL}^{L,n}, \quad (54)$$

with the LAB and MOL subscripts referring to the laboratory and rotated frame. In particular the term $A^{0,0} = -a/\sqrt{3}$, where a is the trace of \mathbf{A} , is a scalar. Using this formalism the measured absorption parallel to the director can be written as

$$\begin{aligned} \langle A_{\parallel} \rangle &\equiv \langle A_{ZZ} \rangle_{LAB}, \\ &= \frac{a}{3} + \sqrt{\frac{2}{3}} \langle A_{LAB}^{2,0} \rangle, \\ &= \frac{a}{3} + \sqrt{\frac{2}{3}} \sum_m \langle D_{0m}^{2*} \rangle A_{MOL}^{2,m}. \end{aligned} \quad (55)$$

Quite similarly the measured perpendicular component will be

$$\langle A_{\perp} \rangle = \frac{a}{3} - \sqrt{\frac{1}{6}} \sum_m \langle D_{0m}^{2*} \rangle A_{MOL}^{2,m}. \quad (56)$$

For a biaxial molecule the experimentally measurable anisotropy of $\langle A \rangle$ is

$$\langle A_{\parallel} \rangle - \langle A_{\perp} \rangle = \sqrt{\frac{3}{2}} \{ A_{MOL}^{2,0} \langle D_{00}^2 \rangle + 2 \operatorname{Re}(A_{MOL}^{2,2} \langle D_{02}^{2*} \rangle) \} \quad (57)$$

Thus the measurement of at least two anisotropy values is required to determine both $\langle D_{00}^2 \rangle$ and $\langle D_{02}^2 \rangle$. Moreover the parameter of deviation from cylindrical symmetry, $\langle D_{02}^2 \rangle$, only becomes measurable when the tensor A has an off axis component so that $A^{2,2} \neq 0$. If the molecule has effective cylindrical symmetry, in the sense that $\langle D_{0n}^2 \rangle = \langle D_{00}^2 \rangle \delta_{n0}$, then we have

$$\langle P_2 \rangle = \frac{\langle A_{\parallel} \rangle - \langle A_{\perp} \rangle}{(A_{MOL})_{\parallel} - (A_{MOL})_{\perp}} \quad (58)$$

We should be aware of the fact that the order parameter $\langle P_2 \rangle$ measured for a molecule dissolved in a liquid crystal is not the same as that of the pure liquid crystal, since solute - solvent terms in the anisotropic potential acting on the molecule are different from the solvent - solvent ones. This also means that except special cases where the solute is very similar to the solvent, probe techniques give information on the behaviour of solutes in anisotropic phases and thus only indirectly report on the phase itself. While this has been perceived as a limitation of these class of measurements, there is instead a lot of scope for learning about the behaviour of interesting classes of molecules in liquid crystals.

The order parameters change with temperature and jump to zero at the nematic - isotropic transition. This phase transition is a weak first order one and accordingly the order parameters present a small jump. Typical values for $\langle P_2 \rangle$ at the nematic to isotropic transition are in the range 0.3-0.4. Order parameters for different liquid crystals, when plotted against reduced temperature T/T_{NI} , with T_{NI} the nematic - isotropic transition temperature follow fairly closely a universal curve [3]. It is quite clear that in view of this and of the pronounced temperature dependence it is advisable to compare order parameters for different molecules at the same reduced temperature.

5. ROTAMERIC MOLECULES

We now wish to briefly mention how the present treatment of order parameters can be generalized to molecules with internal degrees of freedom [8]. This is an important problem because most molecules of practical interest [28, 29] including molecules forming liquid crystals possess some internal flexibility. The problem

has received attention by various authors [see e.g. 30- 31]. Here we shall only consider one mechanism for internal flexibility, i.e. internal rotation, since this often represents the most important mechanism to large changes in molecular structure. Moreover, instead of giving a fairly general treatment, as we have proposed elsewhere [8], we shall give a specific example, that of a molecule with one degree of internal rotation [32]. The molecule we have in mind is made up of two rigid fragments, e.g. two rings. The first thing we should worry about is the description of the state of the particle of interest. Indeed the set of three Euler angles ω we have used until now is only sufficient to specify the state of a rigid fragment, e.g. it can describe the orientation of a suitably defined molecular frame. When the molecule has additional degrees of internal freedom more variables have to be introduced. For a two ring molecule an angle ϕ giving the orientation of one ring with respect to the other could do. Thus we can define an orientational - conformational state ω, ϕ by choosing a molecular frame M_1 on one molecular fragment and giving its orientation $\omega \equiv (M_1 - L)$ with respect to the laboratory frame and then giving the angle ϕ that the second ring makes with the first one. We write the probability of finding the molecule in a certain orientational - conformational state as the probability of finding the first fragment at orientation ω with respect to the laboratory director frame and the second fragment at an angle ϕ from the first, i.e. $f(\omega, \phi)$. This one particle distribution is then expanded in a composite Wigner - Fourier basis set. We have for a molecule dissolved in a uniaxial phase, where $\omega = (\beta, \gamma)$,

$$f(\beta, \gamma, \phi) = \frac{1}{8\pi^2} \sum_{L, n, q} (2L + 1) f_{0nq}^L D_{0n}^{L*}(\beta, \gamma) \exp(-iq\phi), \quad (59)$$

where in general $q = 0, \pm 1, \pm 2, \dots$ and we have kept the notation used in [8]. The angle ϕ , with $0 \leq \phi \leq 2\pi$, is the dihedral rotation angle around the inter - fragment vector connecting the two parts of the molecule. The orthogonality of the basis functions immediately yields the expansion coefficients as

$$f_{0nq}^L = \langle D_{0n}^L(\beta, \gamma) \exp(iq\phi) \rangle, \quad (60)$$

where the angular brackets denote a conformational - orientational average over the distribution $f(\beta, \gamma, \phi)$. As we have seen in the previous sections the singlet distribution expansion coefficients are related to the order parameters for the system. We have, as discussed in [8], three types of order parameters, i.e.

purely orientational

$$f_{0n0}^L = \langle D_{0n}^L(M_1 - L) \rangle \quad (61)$$

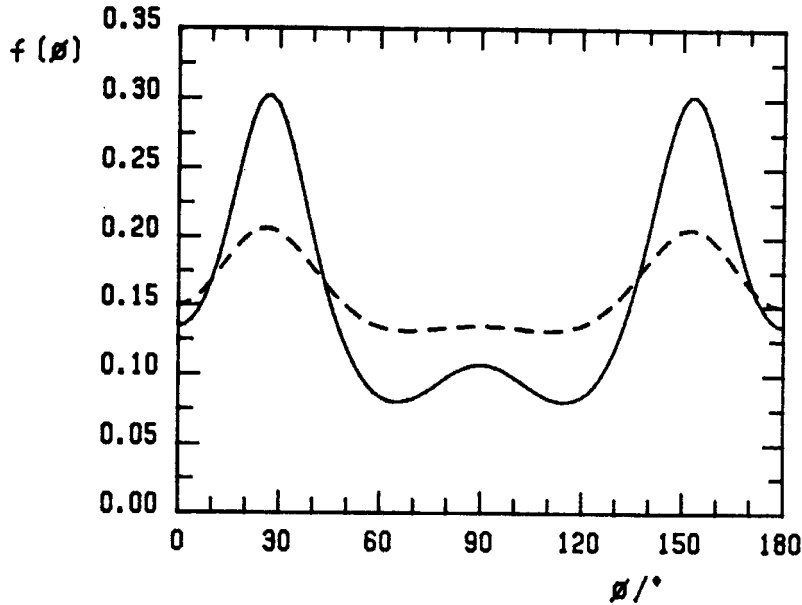


Figure 12 . The distribution probability of finding the thiophene ring at an angle ϕ from the phenyl as determined for 3-phenylthiophene in the nematics PCH (continuous line) and Phase IV (dashed line)[32] .

We have used the notation $(B - A)$ to indicate the rotation from A to B , e.g. here $(M_1 - L) \equiv \omega$. This type of expansion coefficient is essentially an ordinary orientational order parameter for the molecular frame. It gives the average orientation of the reference fragment of the molecule with respect to the director frame, whatever the conformation.

purely internal

$$f_{00q}^0 = \langle \exp(iq\phi) \rangle; q = 0, \pm 1, \pm 2, \dots \quad (62)$$

These parameters describe the ordering of the second part of the molecule with respect to the first one irrespective of the overall orientation. They are quite important since they can be considered expansion coefficients of the rotameric distribution $f(\phi)$ in the fluid obtained by integrating eq.59 over β, γ .

$$f(\phi) = \frac{\int d\beta \sin \beta d\gamma f(\beta, \gamma, \phi)}{\int d\phi d\beta \sin \beta d\gamma f(\beta, \gamma, \phi)} \quad (63)$$

The internal order parameters can be different from zero even in the isotropic phase if there is some preferential orientation of the second fragment around the internal axis.

Mixed internal - external order parameters These parameters arise when both L and q are different from zero in eq.60 . They describe coupling between internal and external degrees of freedom. A particular subset of these parameters allows the recovery of purely orientational order parameters for the second sub-unit. The maximum entropy method outlined earlier on can be generalized to yield the best distribution compatible with a given set of order parameters. For instance if an experiment determines a set of second rank order parameters f_{0nq}^L , this distribution will be of the form

$$f(\beta, \gamma, \phi) = \exp\left\{ \sum_{n,q} a_{n,q} D_{0n}^{2*}(\beta, \gamma) \exp(iq\phi) \right\}, \quad (64)$$

where the coefficients $a_{n,q}$ are obtained by minimizing the squared difference between the measured quantities and those obtained by integrating eq.64. The formalism has been recently applied to an analysis of the proton NMR spectrum of 3 - phenyl - thiophene in two nematic phases: PCH and Phase IV [32] . Using a maximum entropy approach we have obtained from the experimental proton dipolar couplings purely orientational order parameters for the two rings as well as an approximate rotamer distribution. In Fig. 12 we show the results obtained for the purely internal distribution $f(\phi)$ giving the probability of finding the thiophene at a certain angle with respect to the phenyl ring. We see that the distribution changes in the two nematics, showing a solvent effect. We think that the study of order parameters for flexible molecules promises to be an important field in the investigation of environment effects on conformations.

6. ACKNOWLEDGMENTS

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