ON THE DESCRIPTION OF ORDERING IN LIQUID CRYSTALS

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ABSTRACT. We introduce the description of translational, orientational and internal order parameters in liquid crystals. We give a systematic approach to the identification of the relevant parameters as expansion coefficients of the singlet distribution function in a suitable basis set. The construction of approximate distributions from a limited set of order parameters using the maximum entropy principle is discussed. We treat in detail order parameters and distribution functions for three cases: rigid molecules with cylindrical or biaxial symmetry and non-rigid molecules with one internal rotor dissolved in various mesophases.

1. Introduction

The description of order in liquid crystals [1-3] started many years ago with a reasonably easy and well-defined question. How do we define the orientational order in a system of cylindrically symmetric, elongated objects that form a mesophase with overall cylindrical symmetry? An answer was provided half a century ago by Tsvetkov [4], i.e.,

$$S = < (3 \cos^2 \beta - 1)/2 >, \tag{1}$$

where β is the angle between the molecular and the mesophase symmetry axes and the angular brackets indicate a statistical average. This order parameter has the nice feature of being zero when the molecular axes are randomly distributed with respect to the laboratory axes, i.e., when the mesophase is isotropic. It also becomes one when the molecular axes are completely aligned with respect to a laboratory direction (the director). It is rather curious that fifty years later the situation looks much more complicated and the task of describing ordering in liquid crystals is much more difficult. On the one hand the number and importance of different liquid crystal types has increased enormously. There are many important smectic phases [3], discotic [5,6] and pyramidic [7,8] phases let alone lyotropics [9] and polymer liquid crystals [10]. Moreover the same liquid crystals, i.e., nematics can be produced in many more different ways, with nematogenic molecules that are not simple rods or discs [11]. Thus on the one hand it would be tempting to consider a description of ordering in terms of the arrangement of very simple building blocks (see the schemes in [11] as an example) with ellipsoids, discs, wiggly lines and to treat many systems at this semi-qualitative level.

On the other hand there is an increasing number of detailed studies on solute molecules dissolved in simple liquid crystals, nematics, say and on simple mesogenic molecules themselves where a detailed knowledge of molecular order, including biaxiality, flexibility etc. is required [12,13]. The other extreme would be that of having a complete, systematic classification and using it consistently. However, this description would be very complicated and cumbersome and

basically useless, except for a very few systems. Indeed that kind of detail is not accessible to most experimental techniques.

To reconcile the two needs, we shall try to give a systematic, albeit rather formal procedure for introducing order parameters [14-16]. However, in the next sections we shall also try to give very detailed examples for simple but important cases, like that of purely orientational order. These sections will be kept reasonably self-contained, so the next formal section can be skipped by the reader interested only in those aspects.

2. General Approach

As a starting point we consider a system of N molecules in a certain state of aggregation. For a real system the microscopic description we are looking for is a statistical one and the state of the system is represented by the information necessary to calculate all of the average properties of interest. We assume the molecules to be classical particles with position specified by a vector $\mathbf{r}$ locating a molecule fixed point with respect to the chosen laboratory frame. If the molecule is rigid we can also specify its orientation Ω. In this case the orientation of the molecule is given in terms of up to three Euler angles $\alpha\beta\gamma$ [17] or four quaternions linked by a normalisation relation [18,19]. This set of quantities defines the origin and the orientation of a coordinate frame fixed on the molecule (the molecular frame). In the special case of cylindrical symmetry only two angles are necessary to specify the molecular orientation. Notice, however, that real molecules are often neither cylindrically symmetric nor rigid, for they can have for example, flexible chains or rings that can rotate with respect to each other. We shall have, therefore, to expect that, beyond a certain level of sophistication, features such as deviation from cylindrical symmetry and flexibility will have to be taken into account [20]. If we assume that a molecule is formed of a collection of connected rigid rotors, we can specify its state by giving the position, $\mathbf{r}$, and orientation, Ω, of one rigid fragment and another set of variables, Φ specifying the orientation of the other fragments with respect to the first [16]. We shall discuss in some detail the case of molecules with one internal rotor where $\Phi = \phi$ specifies the conformational state [16,21]. For our purposes, however, the complete static information about the system is represented by its configuration i.e., by the set of positions $\mathbf{r}$, orientations Ω, and conformational variables Φ of all the particles.

The enormous number of positional and orientational coordinates specifying the various configurations is fortunately unnecessary if we are only interested in calculating average properties. Suppose, for example, that the probability for a molecule to have a certain position ($\mathbf{r} + d\mathbf{r}$), orientation ($\Omega + d\Omega$), and internal state ($\Phi + d\Phi$) i.e., $P(\mathbf{r},\Omega,\Phi)$ is known. In this case the average of any property $A(\mathbf{r},\Omega,\Phi)$ relating to a single molecule can be calculated as

$$< A > = < A(\mathbf{r},\Omega,\Phi) >, \qquad (2)$$

$$= \int d\mathbf{r}\, d\Omega\, d\Phi\ A(\mathbf{r},\Omega,\Phi)\, P(\mathbf{r},\Omega,\Phi),$$

where we use the angular brackets to indicate the statistical average. Here the volume elements $d\mathbf{r}$, $d\Omega$ are respectively $dxdydz$ and $d\alpha\sin\beta d\beta d\gamma$. The conformational variables will, of course, have to be detailed explicitly, for the one rotor case $d\Phi = d\phi$. The integrals are extended to the sample volume and to the appropriate angular volumes. The normalisation of the distribution $P(\mathbf{r},\Omega,\Phi)$, is

$$\int d\mathbf{r}\, d\Omega\, d\Phi\ P(\mathbf{r},\Omega,\Phi) = 1. \qquad (3)$$

The singlet distribution P contains therefore all of the microscopic information necessary to calculate one particle properties. In turn the structure and ordering of the system will be reflected by P

$$P(\mathbf{r},\Omega,\Phi) = < \delta(\mathbf{r} - \mathbf{r}')\, \delta(\Omega - \Omega')\, \delta(\Phi - \Phi') >, \qquad (4)$$

where $\delta(a - b)$ is a Dirac delta function and the integration implied in the ensemble average $<..>$ is over the primed variables. The Dirac function acts as a counting device, since it is different from zero only when the primed variable equals the desired value. We could visualise a realisation of this in terms of an idealised experiment or a computer simulation where we have all the positions, orientations, etc. for every particle. The distribution function is obtained by counting all of the particles that have the position-orientation-internal variable equal to the desired value in the given configuration and then averaging over the equilibrium configurations. Generalisation to distributions for n variables can be similarly given, yielding pair and in general multiplet distributions [14]. The singlet distribution can be rewritten in a convenient way using the Fourier integral representation of the positional delta function [22]

$$\delta(\mathbf{r} - \mathbf{r}') = (2\pi)^{-3} \int d\mathbf{k}\ \exp\left(i\mathbf{k}.(\mathbf{r} - \mathbf{r}')\right), \qquad (5)$$

and the expansion of the angular delta function in generalised spherical harmonics or Wigner rotation matrices $D_{mn}^{L}(\Omega)$ [17,14]

$$\delta(\Omega - \Omega') = \sum_{L=0}^{\infty} \sum_{m=-L}^{L} \sum_{n=-L}^{L} \{(2L + 1)/8\pi^2\}\, D_{mn}^{L}(\Omega)\, D_{mn}^{L*}(\Omega'). \qquad (6)$$

The functions $D_{mn}^{L}(\Omega)$, with L,m,n integers and $L \geq 0$, $-L \leq m \leq L$, $-L \leq n \leq L$, are of particular importance in the description of ordering. Their properties are briefly summarised in [14]. We also assume that there exists a suitable orthogonal basis set $\psi_{\lambda}(\Phi)$ for the internal variables as well, so that we can write one more representation of the delta function [22]

$$\int d\Phi\ \psi_{\lambda}(\Phi)\, \psi_{\lambda'}^{*}(\Phi) = k_{\lambda}\, \delta(\lambda - \lambda'), \qquad (7)$$

where k_{λ} is a normalisation constant. Thus

$$\delta(\Phi - \Phi') = \sum_{\lambda} k_{\lambda}^{-1}\, \psi_{\lambda}(\Phi)\, \psi_{\lambda}^{*}(\Phi'). \qquad (8)$$

For example, for a molecule with M independent internal rotational degrees of freedom, each described by an angle of rotation ϕ_i about a certain bond

$$\delta(\Phi - \Phi') = \prod_{i=1}^{M} \delta(\phi_i - \phi_i'), \qquad (9)$$

so that for each degree of freedom an expression like

$$\delta(\phi - \phi') = \sum_{\lambda} k_{\lambda} \, \psi_{\lambda}(\phi) \, \psi_{\lambda}^{*}(\phi'), \tag{10a}$$

$$= (2\pi)^{-1} \sum_{n} \exp\{-in(\phi - \phi')\} \tag{10b}$$

with integer n holds, since for the one rotor case the basis set is just the one dimensional Fourier set $\{\exp(-in\phi)\}$ and $k_n = 2\pi$. Before becoming involved in details of the distribution functions it is worth seeing if we can make some general statements about them. Let us consider as a first example a uniform system i.e., a system that does not change under translation. For a uniform fluid the singlet probability will be independent of the position of the molecules with respect to the laboratory frame

$$P(\mathbf{r},\Omega,\Phi) = (\rho/N) \, P(\Omega,\Phi), \tag{11}$$

where $\rho \equiv N/V$ is the number density and $P(\Omega,\Phi)$ is an orientational-conformational distribution normalised to unity i.e.,

$$\int d\Omega \, d\Phi \, P(\Omega,\Phi) = 1. \tag{12}$$

For an ordinary fluid $P(\Omega,\Phi)$ cannot depend on Ω and for rigid molecules it must be a constant. For a system like this i.e., a rare gas, if we limit ourselves to one particle properties, all that can change at the liquid-gas transition is just the density. We can take as the order parameter the difference between the density of the gas and that of the liquid. This could be the case of an ordinary isotropic liquid or of a nematic, but not of a smectic or a crystal, where molecular positions are regularly arranged. The situation is, however, quite different in an anisotropic system, as we shall see in detail in the next section. Substitution of the various delta function representations gives

$$P(\mathbf{r},\Omega,\Phi) = \int d\mathbf{k} \sum_{L,m,n,\lambda} \left[\frac{(2L+1)}{64\pi^5 k_{\lambda}} \right] \left\langle \exp(-i\mathbf{k}\cdot\mathbf{r}') D_{mn}^{L*}(\Omega') \psi_{\lambda}^{*}(\Phi') \right\rangle \exp(i\mathbf{k}\cdot\mathbf{r}) D_{mn}^{L}(\Omega) \psi_{\lambda}(\Phi), \tag{13a}$$

$$\equiv \int d\mathbf{k} \sum_{L,m,n,\lambda} P_{L,m,n,\lambda}(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{r}) D_{mn}^{L}(\Omega) \psi_{\lambda}(\Phi). \tag{13b}$$

Another equivalent way of seeing this is to say that the distribution $P(\mathbf{r},\Omega,\Phi)$ is a function of the positional, orientational and internal variables. As any other well-behaved function we should be able to expand it in a basis set over these variables. Now the plane waves $\exp(i\mathbf{k}'.\mathbf{r})$, the Wigner rotation matrices $D_{mn}^{L}(\Omega)$ and the functions $\psi_{\lambda}(\Phi)$ constitute suitable orthogonal basis sets for positions, orientations and for the internal variables. The distribution can be written in general as the expansion equation (13) and the coefficients obtained using the orthogonality of the basis set. Thus

$$P_{L,m,n,\lambda}(\mathbf{k}) = \left[\frac{(2L+1)}{64\pi^5 k_{\lambda}} \right] \frac{\int d\mathbf{r} \, d\Omega \, d\Phi \, P(\mathbf{r},\Omega,\Phi) \exp(-i\mathbf{k}\cdot\mathbf{r}) D_{mn}^{L*}(\Omega) \psi_{\lambda}^{*}(\Phi)}{\int d\mathbf{r} \, d\Omega \, d\Phi \, P(\mathbf{r},\Omega,\Phi)}. \tag{14}$$

We shall call the positional-orientational-conformational order parameters the infinite set of averages of the basis functions

$$\left\langle \exp(-i\mathbf{k}\cdot\mathbf{r}') D_{mn}^{L*}(\Omega') \psi_{\lambda}^{*}(\Phi') \right\rangle. \tag{15}$$

Clearly a complete set of order parameters has an information content equivalent to that of the distribution function. A subset of these coefficients will contain some necessarily partial, but as we shall see possibly very significant information on the same distribution. When the positions are on average distributed on some regular lattice, defined by the primitive vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ the integral over $\mathbf{k}$ in equation (13) reduces to a sum [23] and we can write

$$P(\mathbf{r},\Omega,\Phi) = \sum_{k,L,m,n,\lambda} \left[\frac{(2L+1)}{8 v_0 \pi^2 k_{\lambda}} \right] \left\langle \exp(-i\mathbf{k}\cdot\mathbf{r}') D_{mn}^{L*}(\Omega') \psi_{\lambda}^{*}(\Phi') \right\rangle \exp(i\mathbf{k}\cdot\mathbf{r}) D_{mn}^{L}(\Omega) \psi_{\lambda}(\Phi), \tag{16}$$

with $\mathbf{k}$ a point in the reciprocal lattice. More explicitly

$$\mathbf{k} = 2\pi [h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3], \tag{17}$$

where h_i are integers and the reciprocal lattice vectors $\mathbf{b}_i$ are

$$\mathbf{b}_i = (\mathbf{a}_j \times \mathbf{a}_k)/v_0, \tag{18}$$

$$\mathbf{a}_i . \mathbf{b}_j = \delta_{ij}, \tag{19}$$

with i, j, k an even permutation of 1, 2, 3

$$v_0 = \mathbf{a}_1 . \mathbf{a}_2 \times \mathbf{a}_3 \tag{20}$$

is the volume of the primitive cell in the real lattice. In the special case of an orthorombic lattice, where $\mathbf{a}_1 \perp \mathbf{a}_2 \perp \mathbf{a}_3$ can be taken along x, y, z we have

$$\mathbf{k} = 2\pi \left[n_x d_x^{-1} \mathbf{x} + n_y d_y^{-1} \mathbf{y} + n_z d_z^{-1} \mathbf{z} \right], \tag{21}$$

where d_i are the lattice spacings in the three directions and n_i are integer. We shall study this important special case later on.

Equation (21) is useful to see how order parameters can be introduced in rather general situations. However, it is too complicated to carry around in the present form and in the remainder of this chapter we shall treat special cases, trying to understand their significance in detail. We shall consider first pure positional order, the orientational order in rigid molecules, then positional-orientational and internal order.

3. Purely Positional Order

Systems of spherical particles can have purely positional order when they arrange somehow on a lattice. In complex liquid crystal systems the other degrees of freedom will normally be present. However, if we wish to concentrate on regularities in the positions, we can define purely translational distributions as

$$P(\mathbf{r}) = \int d\Omega \, d\Phi \, P(\mathbf{r},\Omega,\Phi) \Big/ \int d\mathbf{r} \, d\Omega \, d\Phi \, P(\mathbf{r},\Omega,\Phi) \tag{22a}$$

$$= \sum_{k} \langle \exp(-i\,k.r') \rangle \exp(i\,k.r) \qquad (22b)$$

where

$$\langle \exp(-i\,k.r') \rangle \qquad (23)$$

are the purely translational order parameters. The case of full three dimensional order is more pertinent to molecular crystals, but liquid crystals present many systems with order in one or two dimensions. Let us now see a simple example in detail.

3.1. ONE DIMENSIONAL POSITIONAL ORDER

We consider one dimensional translational order such as that presented by the distribution of molecular positions along the director (z say) in a smectic A or a smectic C, so that $P(r)$ reduces to $P(z)$. When this ordering is perfect the positional distribution function $P(z)$ consists of a series of Dirac deltas (the so-called Dirac's comb) separated by the lattice spacing d. If the order is not perfect the peaks of the distribution will become broader (see figure 1). In the limit of no positional order (i.e., a nematic) the distribution becomes flat. For a smectic A-like system such as that in figure 1 $P(z)$ remains a periodic function of position z,

$$P(z) = P(z + d). \qquad (24)$$

Incidentally we note that strictly true order in one dimension should not exist (see, for example,
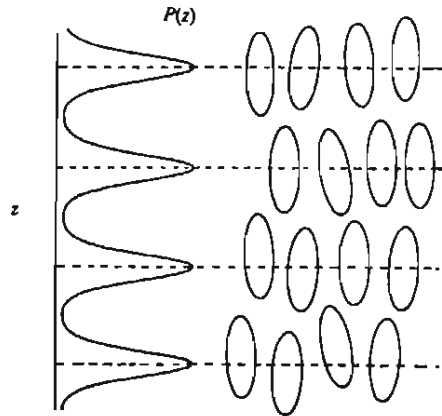

Figure 1. A system with incomplete positional ordering in one dimension; on the left we have the probability distribution $P(z)$.

[24]). Since smectics exist quite happily anyway, the contradiction has been resolved with the hypothesis, apparently confirmed experimentally by high resolution X-ray studies, that the order decreases very slowly with the layer separation [25-27]. For any practical purpose, we can certainly consider smectic A phases as periodic structures. This implies that we can limit ourselves to considering $P(z)$ with $0 \leq z \leq d$. Moreover we can expand $P(z)$, like any other periodic function, in a Fourier series, [17] i.e., we write it as a combination of sines and cosines. If the distribution

is an even one, like that for a smectic A it will suffice to consider a basis of cosines, since these and not the sines have the correct symmetry. We have therefore

$$P(z) = \sum_{n_z} p_{n_z} \cos(2\pi n_z z/d). \qquad (25)$$

The p_m coefficient can be easily obtained by multiplying both sides of this equation by $\cos(2\pi mz/d)$ and integrating to give

$$\int_0^d dz\, P(z) \cos(2\pi mz/d) = \sum_{n_z} p_{n_z} \int_0^d dz\, \cos(2\pi n_z z/d) \cos(2\pi mz/d), \qquad (26a)$$

$$= p_m d(\delta_{m0}\,\delta_{n_z 0} + \delta_{mn_z})/2, \qquad (26b)$$

where we have used the orthogonality of the cosine functions. We find, therefore,

$$p_0 = d^{-1} \int_0^d dz\, P(z) \qquad (27)$$

and

$$p_m = (2/d) \int_0^d dz\, P(z) \cos(2\pi mz/d) \qquad (28a)$$

$$= (2/d) < \cos(2\pi mz/d) > \quad ; m > 0. \qquad (28b)$$

This implies that the p_m coefficients are positional averages of the Fourier factors, by using the definition of $P(z)$. The averages

$$\tau_m = < \cos(2\pi mz/d) > \qquad (29)$$

represent our set of positional order parameters [14,27,28]. We can, in turn, write $P(z)$ as

$$P(z) = d^{-1} + (2/d) < \cos(2\pi z/d) > \cos(2\pi z/d) + ... \qquad (30a)$$

$$= d^{-1} + (2/d) \sum_{n_z} \tau_{n_z} \cos(2\pi n_z z/d). \qquad (30b)$$

The purely positional order parameters can be obtained from X-ray diffraction as described in [27,28].

3.2. TWO DIMENSIONAL POSITIONAL ORDER

Two dimensional positional order can be found, i.e., in certain discotic phases, where we have columns of mesogenic molecules which have ideally no positional order inside the column, while the columns themselves are arranged on a hexagonal (D_{hd}) or rectangular lattice (D_{rd}) [6]. For a D_{rd} rectangular discotic phase we should have, choosing the z axis along the columns axis that the k vector lies in the (xy) plane and

$$P(x,y) = (d_x d_y)^{-1} + (4/d_x d_y) \sum_{n_x, n_y} \langle \cos(2\pi n_x x/d_x) \cos(2\pi n_y y/d_y) \rangle \cos(2\pi n_x x/d_x) \cos(2\pi n_y y/d_y) \qquad (31)$$

with $n_x, n_y > 0$.

4. Orientational Order

When the molecule is rigid and the system uniform, so that only orientational degrees of freedom are relevant, the general distribution $P(\mathbf{r},\Omega,\Phi)$ reduces to $P(\Omega)$. More generally we can define a purely orientational distribution

$$P(\Omega) = \int d\mathbf{r}\, d\Phi\, P(\mathbf{r},\Omega,\Phi) \Big/ \int d\mathbf{r}\, d\Omega\, d\Phi\, P(\mathbf{r},\Omega,\Phi). \qquad (32)$$

For the purely orientational case equation (13) reduces to an expansion in Wigner rotation matrices [14,29]

$$P(\Omega) = \sum_{L,m,n} p_{L,m,n}\, D^{L}_{m,n}(\Omega). \qquad (33)$$

This equation can be simplified by using the symmetries of the mesophase and of the molecule, if any. We have given elsewhere some general prescriptions for doing this [14] using group theory. The procedure consists essentially in projecting onto the totally symmetric representation of the point group of the molecule and of the mesophase [30-33]. The action of the various symmetry operations has been considered as a combination of rotations and inversion, following Blum and Torruella [31]. Essentially the same method has been used by Pick and Yvinec for the distributions in molecular crystals [33]. Here we wish to discuss in detail a few simple examples, that are the most important in practical situations.

4.1. CYLINDRICAL MOLECULES IN UNIAXIAL PHASES

We shall treat the case of uniaxial mesophases (i.e., nematics, smectic A or columnar with transverse positional disorder). We shall assume the axis of this cylindrical symmetry, the director, to be along the Z laboratory axis. Thus rotating the sample about Z no observable property will change. Thus the probability for a molecule to have orientation $(\alpha\beta\gamma)$ should be the same whatever the angle α, since the angle α describes a rotation around the laboratory Z axis. Here we also make the assumption, very often made in the literature, that the molecules possess uniaxial symmetry. In this case the distribution should not depend on the angle γ which is defined as a rotation around the molecular z axis, so that

$$P(\alpha\beta\gamma) \propto P(\beta), \qquad (34)$$

with the normalisation condition

$$\int_{0}^{\pi} d\beta \sin \beta\, P(\beta) = 1. \qquad (35)$$

If the molecules are unable to distinguish head from tail we should have

$$P(\beta) = P(\pi - \beta). \qquad (36)$$

For nematics this corresponds to the experimental finding that on 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 $P(\beta)$ is to expand the distribution in a basis set of functions orthogonal when integrated over $\sin \beta\, d\beta$. Such a set is that of the Legendre polynomials [34] $P_{L}(\cos \beta)$, for which we have

$$\int_{0}^{\pi} d\beta \sin \beta\, P_{L}(\cos \beta)\, P_{N}(\cos \beta) = \{2/(2L + 1)\}\delta_{LN}. \qquad (37)$$

Clearly these functions correspond to a special subset of the Wigner rotation matrices used in the general expansion in equation (6). The explicit forms of the first few Legendre polynomials are

$$P_{0}(\cos \beta) = 1, \qquad (38a)$$

$$P_{1}(\cos \beta) = \cos \beta, \qquad (38b)$$

$$P_{2}(\cos \beta) = (3 \cos^{2} \beta - 1)/2, \qquad (38c)$$

$$P_{3}(\cos \beta) = (5 \cos^{3} \beta - 3 \cos \beta)/2, \qquad (38d)$$

$$P_{4}(\cos \beta) = (35 \cos^{4} \beta - 30 \cos^{2} \beta + 3)/8. \qquad (38e)$$

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 [34], i.e.,

$$P_{L}(\cos \beta) = (-)^{L} P_{L}(-\cos \beta). \qquad (39)$$

Thus we only need to retain even L terms when expanding the even distribution $P(\beta)$, (see equation (36)), in terms of $P_{L}(\cos \beta)$ and we can write

$$P(\beta) = \sum_{L=0}^{-} p_{L} P_{L}(\cos \beta) \quad ; L \text{ even}. \qquad (40)$$

The Jth coefficient in the expansion can be easily obtained using the orthogonality of the basis set. Multiplying both sides of equation (40) by $P_{J}(\cos \beta)$ and integrating over $\sin \beta\, d\beta$ gives

$$\int_{0}^{\pi} d\beta \sin \beta\, P(\beta)\, P_{J}(\cos \beta) = \sum_{L=0}^{-} p_{L} \int_{0}^{\pi} d\beta \sin \beta\, P_{L}(\cos \beta)\, P_{J}(\cos \beta), \qquad (41)$$

we find the coefficients in equation (40) as

$$p_{J} = \{(2J + 1)/2\} < P_{J} >, \qquad (42)$$

where

$$< P_{J} > = \int_{0}^{\pi} d\beta \sin \beta\, P_{J}(\cos \beta)\, P(\beta). \qquad (43)$$

It is apparent that the knowledge of the (infinite) set of $< P_{J} >$ completely defines the distribution and that the Legendre polynomials averages $< P_{J} >$ represent our set of orientational order parameters. We can write

$$P(\beta) = (1/2) + (5/2) < P_{2} > P_{2}(\cos \beta) + (9/2) < P_{4} > P_{4}(\cos \beta) + \dots . \qquad (44)$$

The first non-trivial term contains the second rank order parameter

$$< P_2 > = < (3 \cos^2 \beta - 1)/2 >, \qquad (45)$$

which corresponds exactly to the S order parameter introduced by Tsvetkov [4] (see equation (1)). It is worth stressing that equation (40) is exact as an infinite expansion, but that in practice it does not give a very good approximation to $P(\beta)$ when we truncate after the first few terms. For instance if we have $< P_2 > = 0.6$ the $P(\beta)$, as given by the orthogonal expansion truncated at the second rank level, is shown in figure 2 as the dashed line. We see that $P(\beta)$ constructed in this way can even become negative, which is certainly not physical when we recall that $P(\beta)$ is a probability. Notice that any property depending only on $< P_2 >$ is calculated correctly using this $P(\beta)$. However, $< P_4 >$ 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.
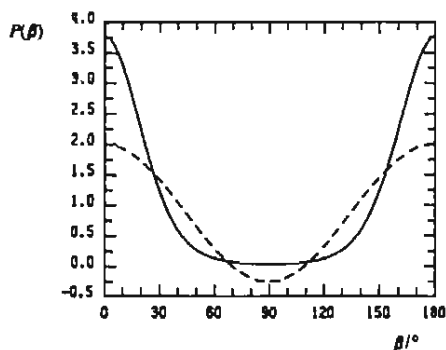
Figure 2. The orientational distribution $P(\beta)$ corresponding to $< P_2 >= 0.6$ as obtained from the orthogonal expansion truncated to second rank (dashed line) and from the maximum entropy procedure (continuous line).

4.2. MAXIMUM ENTROPY

The problem of finding the best, in the sense of least biased approximation to the whole $P(\beta)$ or in general $P(\Omega)$ starting from a knowledge of a set of order parameters $< P_L >$, say up to rank L', can be approached using information theory [35-37]. In this approach the most probable distribution is defined as that maximising the entropy associated with the usual thermodynamic-like formula

$$S(\{a_L\}) \propto - \int d\Omega \, P(\Omega, \{a_L\}) \ln P(\Omega, \{a_L\}), \qquad (46)$$

with respect to the set $\{a_L\}$. It has been shown using the standard lagrangian multiplier technique that the best distribution in this respect has the form [35-40]

$$P(\beta) = \exp\left\{\sum_{L=0}^{L'} a_L \, P_L(\cos \beta)\right\}, \qquad (47)$$

where the coefficients a_L are obtained by imposing the constraint that the $< P_L >$, $L = 0, ..., L'$ calculated from $P(\beta)$ have the known values. In particular we have the normalisation condition $< P_0 > = 1$. The information theory approach is in a way an a posteriori one. It allows the construction of an approximate full distribution from the available information but on the other hand it can make no prediction as to what the distribution will be at, say, a different temperature. In addition, the approach does not say anything as to 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 $P(\beta)$ 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 [37]. 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 [29].

4.3. EXAMPLES

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

4.3.1. *Knowing $< P_2 >$ only.* To start with we suppose that only the second rank order parameter, $< P_2 >$, has been determined. The maximum entropy distribution associated with this $< P_2 >$ is

$$P(\beta) = Z_2^{-1} \exp[a_2 \, P_2(\cos \beta)], \qquad (48)$$

with the normalisation constant

$$Z_2 = \int_0^\pi d\beta \sin \beta \exp[a_2 \, P_2(\cos \beta)], \qquad (49)$$

and with a_2 determined by the condition

$$< P_2 > = Z_2^{-1} \int_0^\pi d\beta \sin \beta \, P_2(\cos \beta) \exp[a_2 \, P_2(\cos \beta)]. \qquad (50)$$

This equation can be solved for a_2 in terms of $< P_2 >$. In figure 3 we show the resulting curve for positive $< P_2 >$ as the full line. We see that for positive $< P_2 >$ 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.

A simple analytic approximation for a_2 in terms of $< P_2 >$ is obtained by expanding a_2 in a power series in $< P_2 >$ [41]

$$a_2 = 5 < P_2 > - (25/7) < P_2 >^2 + (425/49) < P_2 >^3 - (51875/3773) < P_2 >^4 + ... \qquad (51)$$

The series is, of course, divergent at $< P_2 > = 1$ but it can still be useful for order parameters realistically found in nematics. The very simple approximation

$$a_2 = 5 < P_2 > \tag{52}$$

is useful to obtain a good idea of a_2 and thus of the distribution at least up to $< P_2 > = 0.6$.
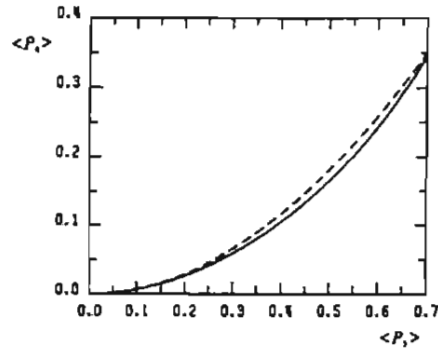

Figure 3. The fourth rank order parameter $<P_4>$ versus $<P_2>$ as obtained from the purely second rank distribution equation (48) (continuous line). We also show the approximate analytic expression $<P_4> = 5/7 <P_2>^2$ (dashed line).

Having determined a_2 we can immediately plot the distribution $P(\beta)$. For example, if we assume $< P_2 > = 0.6$, as in the previous section, we obtain the approximate maximum entropy distribution plotted as the continuous line in figure 2.

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

4.3.2. *Knowing* $< P_2 >$ *and* $< P_4 >$. We now turn to the case where both $< P_2 >$ and $< P_4 >$ have been determined. The first thing we might try is to see if the distribution in equation (48) obtained using just the information on $< P_2 >$ is consistent with the observed $< P_4 >$. Thus we would use the distribution generated by the a_2 obtained from $< P_2 >$ and calculate the fourth rank order parameter $< P_4 >$ by integration. The curve obtained is shown in figure 3 as the continuous line. A simple approximate analytic form for this relation can be obtained by expanding $< P_4 >$ in powers of a_2 and substituting into equation (51). This gives

$$< P_4 > = (5/7) < P_2 >^2 - (200/539) < P_2 >^3 + (35650/49049) < P_2 >^4 + \dots , \tag{53a}$$

$$\approx (5/7) < P_2 >^2 . \tag{53b}$$

The series contains large terms of alternating sign and is poorly convergent unless terms are properly grouped together. The very simplest approximation namely equation (53b) [41] found by retaining just the first term, is actually a good approximation up to $< P_2 > \approx 0.6$ as we see from the dashed line in figure 3. When $< P_4 >$ does not fall on the curve in figure 3 we can construct a distribution like equation (47) with $L = 0, 2, 4$. To do this we have to find a_2 and a_4 from our given $< P_2 >$ and $< P_4 >$. The first thing to observe is that the domain of the functions $a_2(< P_2 >, < P_4 >)$, $a_4(< P_2 >, < P_4 >)$ consists of the set of allowed values of $< P_2 >$ and $< P_4 >$. It is not

difficult to show, using Schwarz's inequality [34] that

$$< \cos^2 \beta >^2 \leq < \cos^4 \beta > \leq < \cos^2 \beta >. \tag{54}$$

The explicit form of $< P_2 >$ and $< P_4 >$ in equation (38), together with these inequalities yields [42]

$$(35/18) < P_2 >^2 - (5/9) < P_2 > - (7/18) \leq < P_4 > \leq (5/12) < P_2 > + (7/12). \tag{55}$$

These two inequalities define the region of space where possible values of $< P_2 >$ and $< P_4 >$ 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 coefficients a_2, a_4 can be obtained by solving the non-linear system

$$< P_2 > = Z_{24}^{-1} \int_0^\pi d\beta \sin \beta P_2(\cos \beta) \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)] \tag{56a}$$

$$< P_4 > = Z_{24}^{-1} \int_0^\pi d\beta \sin \beta P_4(\cos \beta) \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)] \tag{56b}$$

with

$$Z_{24} = \int_0^\pi d\beta \sin \beta \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]. \tag{57}$$
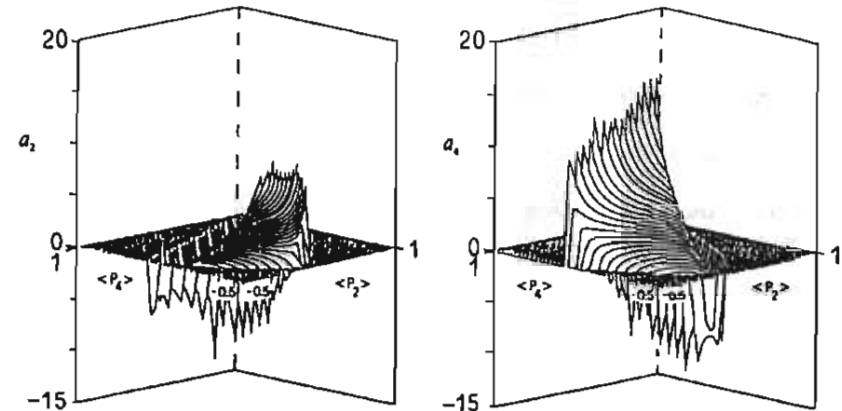

Figure 4. The coefficients a_2 and a_4 in the distribution $P(\beta) \propto \exp[a_2 P_2(\cos \beta) + a_4 P_4(\cos \beta)]$ shown as a function of $<P_2>$ and $<P_4>$ [43].

The coefficients obtained [43] are shown in figure 4. Notice that, although we expect $< P_2 >$ greater than $< P_4 >$ as it was the case in the $P_2(\cos \beta)$ distribution (see figure 3), a range of solutions exists also for $< P_4 >$ greater than $< P_2 >$. Indeed an interesting case is that of $<P_4> > <P_2>$, with the values falling on a curve like the continuous line in figure 5. This unusual behaviour has been found to be consistent with fluorescence depolarisation data of diphenyl-hexatriene in DPPC and DMPC membranes vesicles [44]. In turn the behaviour agrees with that

predicted by a model with pure $P_4(\cos \beta)$ effective potential [45], which gives a distribution

$$P(\beta) = Z_4^{-1} \exp[a_4 P_4(\cos \beta)], \tag{58}$$

where

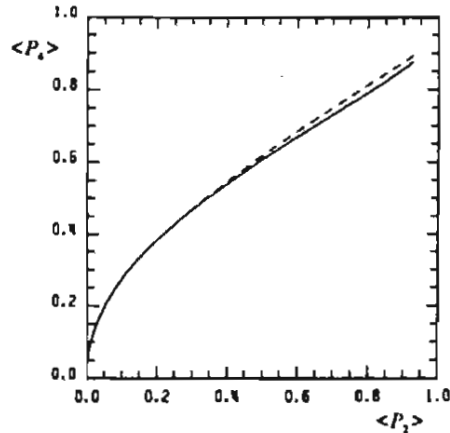$$Z_4 = \int_0^\pi d\beta \sin \beta \exp[a_4 P_4(\cos \beta)]. \tag{59}$$

Figure 5. The dependence of the fourth rank order parameter $<P_4>$ on the second rank $<P_2>$ for a purely fourth rank distribution equation (58) (continuous line). We also show the analytical approximation in equation (61) as the dashed line [29].

We wish to obtain also for this limiting case a simple approximation to the $<P_4>$ versus $<P_2>$ curve. We start by Taylor expanding the expressions for $<P_2>$ and $<P_4>$, i.e.,

$$<P_L> = Z_4^{-1} \int_0^\pi d\beta \sin \beta \, P_L(\cos \beta) \exp[a_4 P_4(\cos \beta)], \quad L = 2, 4, \tag{60}$$

with respect to a_4; reversion of the series for $<P_4>$ gives a_4 in terms of $<P_4>$. Substituting in the series expansion for $<P_2>$ we obtain $<P_2>$ in terms of $<P_4>$ and by further reversion

$$<P_4> = \frac{\sqrt{77}}{\sqrt{90}} <P_2>^{1/2} - \frac{69}{260} <P_2> + \frac{7794479}{1007760\sqrt{770}} <P_2>^{3/2} + \dots . \tag{61}$$

This simple power series in $<P_2>^{1/2}$ gives a good representation of the curve for $<P_2>$ up to 0.9. In figure 5 we show the analytical approximation to the $<P_4>$ versus $<P_2>$ curve from the truncation in equation (61) (dashed line) and the curve obtained by direct numerical integration (continuous line). Using equation (61) it is quite easy to test if a set of $<P_2>$, $<P_4>$ values has a pure $P_4(\cos \beta)$ behaviour. An example of the pure $P_4(\cos \beta)$ distribution is plotted in figure 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.
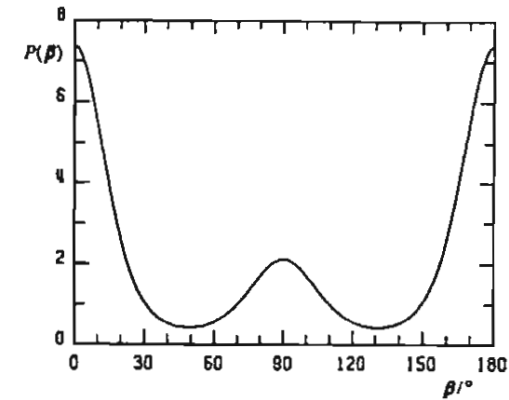
Figure 6. The angular variation of the distribution $P(\beta) \propto \exp[a_4 P_4(\cos \beta)]$ with $a_4 = 2$.

4.4. NON-CYLINDRICAL MOLECULES IN UNIAXIAL PHASES [29]

In the last section we have gone into some detail 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 treated as a rod-like or a disc-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 [17]. The probability of finding the molecule at a specific orientation, $P(\beta\gamma)$, can be expanded like any other function of the two Euler angles $\beta\gamma$, in a complete basis set of spherical harmonics. Thus we find

$$P(\beta\gamma) = \sum_{L,n} p_{L,n} D_{0n}^L(\beta\gamma), \tag{62}$$

where we have chosen the Wigner matrix notation $D_{0n}^L(\beta\gamma)$ [17]. Orthogonality of the basis set immediately permits determination of the coefficients $p_{L,n}$ which gives

$$P(\beta\gamma) = (4\pi)^{-1} \sum_{L=0}^{\infty} \sum_{n=-L}^{L} (2L + 1) < D_{0n}^{L*} > D_{0n}^L(\beta\gamma). \tag{63}$$

The set of averaged Wigner orientation matrices $< D_{0n}^L >$ allows a complete characterisation of $P(\beta\gamma)$. The generally complex quantities $< D_{0n}^L >$ are called orientational order parameters (see, for example, [15,16]). The complex conjugate of a Wigner function is $D_{-n}^{L*}(\Omega) = (-)^{-n} D_{-n-}^L(\Omega)$. Since the distribution $P(\beta\gamma)$ is real, then

$$< D_{0n}^{L*} > = (-)^n < D_{0n}^L >, \tag{64}$$

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

by Saupe [46]

$$S = \begin{pmatrix} < (3/2) \sin^2 \beta \cos^2 \gamma - \frac{1}{2} > & < \sin^2 \beta \cos \gamma \sin \gamma > & < \sin \beta \cos \beta \cos \gamma > \\ < \sin^2 \beta \cos \gamma \sin \gamma > & < (3/2) \sin^2 \beta \sin^2 \gamma - \frac{1}{2} > & < \sin \beta \cos \beta \sin \gamma > \\ < \sin \beta \cos \beta \cos \gamma > & < \sin \beta \cos \beta \sin \gamma > & < (3/2) \cos^2 \beta - \frac{1}{2} > \end{pmatrix} ; \quad (65)$$

the matrix is traceless and symmetric. Results can be easily converted from the Saupe to the Wigner rotation matrix form [14]

$$S = \begin{pmatrix} \sqrt{6}/2 \ \mathrm{Re} < D_{02}^2 > - \frac{1}{2} < D_{00}^2 > & -\sqrt{3/2} \ \mathrm{Im} < D_{02}^2 > & -\sqrt{3/2} \ \mathrm{Re} < D_{01}^2 > \\ -\sqrt{3/2} \ \mathrm{Im} < D_{02}^2 > & -\sqrt{6}/2 \ \mathrm{Re} < D_{02}^2 > - \frac{1}{2} < D_{00}^2 > & \sqrt{3/2} \ \mathrm{Im} < D_{01}^2 > \\ -\sqrt{3/2} \ \mathrm{Re} < D_{01}^2 > & \sqrt{3/2} \ \mathrm{Im} < D_{01}^2 > & < D_{00}^2 > \end{pmatrix} . \quad (66)$$

We call the ordering matrix frame the principal axis system of S, sometimes obvious by symmetry, where 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 used particularly in optical spectroscopy [47] is the set of orientation factors

$$K_{ab} = < (\mathbf{Z} \cdot \mathbf{a}) (\mathbf{Z} \cdot \mathbf{b}) >, \quad a, b = x, y, z, \quad (67)$$

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 $K_{zz} = < \cos^2 \beta >$. The K and S are simply related by

$$S_{ab} = (3 K_{ab} - \delta_{ab})/2. \quad (68)$$

The cartesian formulation can be extended to higher ranks both for the S matrices [14] and orientation factors [47] 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 [14]. 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, i.e., pyrene etc. will now be discussed in some detail.

4.5. BIAXIAL MOLECULES

First, we choose our molecular frame with axes along the three C_2 axes. Since we can turn our biaxial particle upside down without changing anything we only need to retain in equation (63) functions that are invariant for this transformation. Remembering [14,17] 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 of even rank L. The first few are

$$D_{00}^0(\beta\gamma) = 1, \quad (69a)$$

$$D_{00}^2(\beta\gamma) = P_2(\cos \beta), \quad (69b)$$

$$D_{0\pm2}^2(\beta\gamma) = \sqrt{3/8} \ \sin^2 \beta \exp(\mp i 2\gamma), \quad (69c)$$

$$D_{00}^4(\beta\gamma) = P_4(\cos \beta), \quad (69d)$$

$$D_{0\pm2}^4(\beta\gamma) = \sqrt{10} \left\{ 14 \cos^6 \frac{\beta}{2} - 14 \cos^4 \frac{\beta}{2} + 3 \cos^2 \frac{\beta}{2} \right\} \sin^2 \frac{\beta}{2} \exp(\mp i 2\gamma), \quad (69e)$$

$$D_{0\pm4}^4(\beta\gamma) = \sqrt{70} \cos^4 \frac{\beta}{2} \sin^4 \frac{\beta}{2} \exp(\mp i 4\gamma). \quad (69f)$$

Since the principal frame of the ordering matrix is determined by symmetry, at second rank level there are two relevant order parameters, $< D_{00}^2 >$, $\mathrm{Re} < D_{02}^2 >$ or, e.g., S_{zz} and $S_{xx} - S_{yy}$. While $< D_{00}^2 >$ measures the alignment of the z molecular axis with respect to the director, as we have seen for cylindrical molecules, $\mathrm{Re} < D_{02}^2 >$ 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.

4.5.1. *Maximum Entropy Distributions*. If a set of order parameters $< D_{0n}^L >$ is known, the best distribution compatible with them is, according to information theory [36]

$$P(\beta\gamma) = \exp\left[\sum_{L,n} a_{L,n} D_{0n}^L(\beta\gamma) \right], \quad (70)$$

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

$$< D_{0n}^L > = \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma \ D_{0n}^L(\beta\gamma) \exp\left[\sum_{L,n} a_{L,n} D_{0n}^L(\beta\gamma) \right], \quad (71)$$
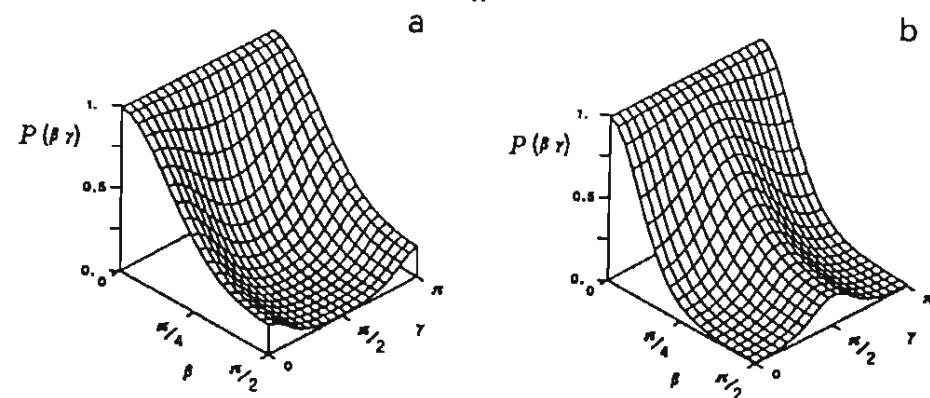
and a_{00} from the normalisation constraint $< D_{00}^0 > = 1$.

Figure 7. An example of the orientational distribution $P(\beta\gamma)$ for a biaxial molecule with $<P_2>=0.4$ and $\mathrm{Re} < D_{02}^2 >=0.1$(a) or -0.1(b) [29].

For a biaxial solute where $< D_{00}^2 >$ and $\mathrm{Re} < D_{02}^2 >$ are determined, we have simply

$$P(\beta\gamma) = \frac{\exp a[P_2(\cos\beta) + \xi\,\mathrm{Re}\,D_{02}^2(\beta\gamma)]}{\int_0^\pi d\beta\sin\beta\int_0^{2\pi}d\gamma\exp a[P_2(\cos\beta) + \xi\,\mathrm{Re}\,D_{02}^2(\beta\gamma)]}, \tag{72}$$

with $a \equiv a_{20}$, $\xi \equiv a_{22}/a_{20}$. The parameter ξ is a measure of the 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 figure 7 a few examples of distributions corresponding to biaxial objects with $< P_2 > = 0.4$ and $\mathrm{Re} < D_{02}^2 > = \pm 0.1$.

In figure 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 $\mathrm{Re} < D_{02}^2 >$ 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

$$\mathrm{Re} < D_{02}^2 > = \sqrt{(3/8)} < \sin^2\beta\cos2\gamma >, \tag{73}$$

we see that for a rod-like molecule as the alignment increases β approaches on average more closely to zero, as will $\sin^2\beta$ and ultimately $\mathrm{Re} < D_{02}^2 >$ itself. In contrast 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.
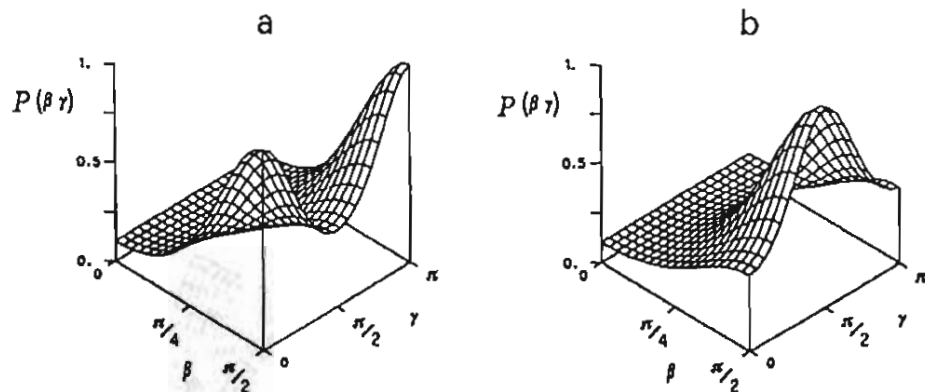

Figure 8. An example of the orientational distribution $P(\beta\gamma)$ for a biaxial molecule with $<P_2>=-0.2$ and $\mathrm{Re} < D_{02}^2 >=0.1$ (a) and -0.1 (b) [29].

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 into distributions, without offering a molecular interpretation to what is observed. However, equation (72) is formally identical to that obtained with molecular field theory, i.e., starting from a dispersion interaction [48]. 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

$$\lambda = \sqrt{(3/2)}\,(\alpha_{xx} - \alpha_{yy})/(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy}), \tag{74}$$

expressing the deviation from cylindrical symmetry of the solute polarisability α. Curves of $\mathrm{Re} < D_{02}^2 >$ versus $< D_{00}^2 >$ or equivalently of $S_{xx} - S_{yy}$ versus S_{zz} at constant ξ are often used when analysing experimental data [12]. In figure 9 we see such a family of curves. We shall now try to find some approximations for the biaxial order parameters calculated from integration over the distribution in equation (72). To do this we consider ξ fixed and expand $< P_2 >$ and $\mathrm{Re} < D_{02}^2 >$ in terms of a. Eliminating a between the last two equations and regrouping the terms we find [29]

$$\mathrm{Re} < D_{02}^2 > = < P_2 > (< P_2 > - 1)^2 \left\{ \frac{\xi}{2} + \frac{5\xi^3 - 2\xi}{28} < P_2 > \right.$$
$$\left. + \frac{25\xi^5 - 130\xi^3 + 174\xi}{196} < P_2 >^2 + ... \right\}. \tag{75}$$

We see that the performance of the simple equation (75) as the dashed lines in figure 9 is quite reasonable throughout the range and very good for $< P_2 >$ up to 0.6 - 0.7.

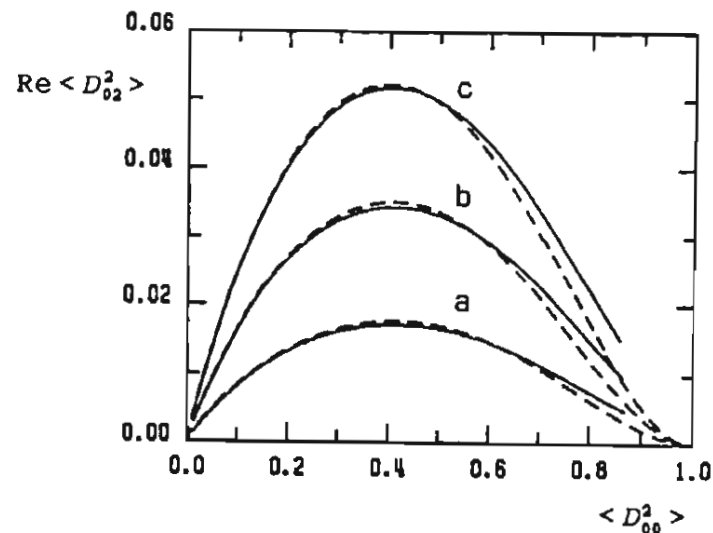Figure 9. A plot of the order parameter $\mathrm{Re} < D_{02}^2 >$ versus $< D_{00}^2 >$ for the biaxial distribution in equation (72) and for $\xi=0.2$ (a), 0.4 (b), 0.6 (c) as calculated by numerical integration (continuous lines) and from the approximate analytic expansion equation (75) (dashed lines) [29].

4.5.2. *An Example.* In [49] we have determined, through deuterium NMR, the ordering matrix for perylene dissolved in various nematic solvents. The results for the second rank order parameters in four nematics at different temperatures are shown in figure 10. The molecular coordinate system assumed has the z axis perpendicular to the perylene plane and the x axis in the direction of the peri bond. We see that the behaviour in the various solvents is different, so that order parameters are in general solute-solvent rather than just solute properties. While on the one hand this represents a source of complication, it also offers an interesting handle towards probing specific
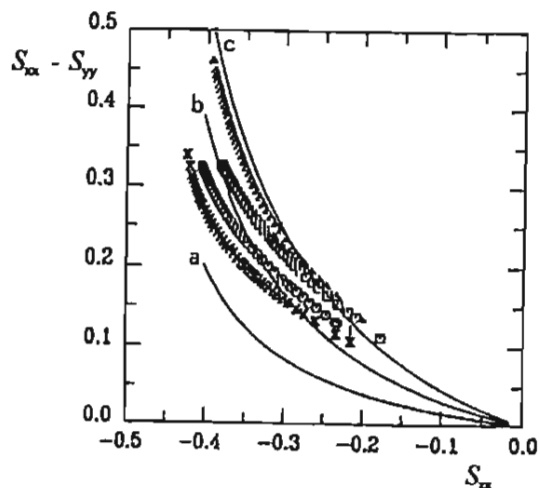
Figure 10. Plots of $(S_{xx} - S_{yy})$ against S_{zz} for perylene in the four liquid crystals: E63 (O), I52 (Δ), ZLI1167 (hourglass), ZLI2585 (□). The solid lines are theoretical predictions for the values of the molecular biaxiality parameter (cf. equation (74)) $\lambda = -0.05$ (a), -0.10 (b), -0.15 (c) [49].

interactions in the fluid phase [50]. 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 figure 11 the probability distributions for perylene in ZLI-1167 at the lowest temperature employed.
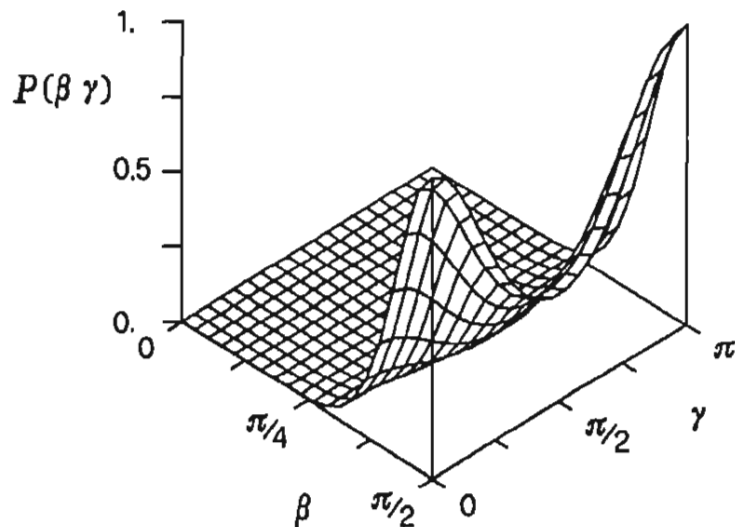

Figure 11. The probability distribution $P(\beta\gamma)$ for perylene in ZLI1167 at $<P_2> = -0.424$, $S_{xx} - S_{yy} = \sqrt{6} \, \mathrm{Re} <D_{02}^2> = 0.340$.

4.6. EXPERIMENTAL DETERMINATION: LINEAR DICHROISM

We consider an example of the experimental determination of second rank orientational order parameters. We shall choose the anisotropy in the optical absorption, i.e., a linear dichroism experiment [29], but the treatment is similar for other techniques. Typically an experiment consists of performing measurements of anisotropy on a suitable tensor property. In the present example the absorption of light by a solute relative to a certain electronic transition is determined by the transition moment μ [47]. If for simplicity we deal with a single transition from a state with wavefunction 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., $\mu \equiv <\psi_i | \hat{M} | \psi_j>$. In general there will be, of course, complications arising e.g., from overlapping transitions etc. with a well-defined orientation in the molecular frame. The probability of absorption of plane polarised light with a polarisation direction e does not depend directly on μ but rather is

$$P_{abs} \propto <(e \cdot \mu)^2>,$$

$$= \sum_{a,b} <e_a e_b \mu_a \mu_b>, \tag{76}$$

$$= \sum_{a,b} <E_{ab} A_{ab}>,$$

with a, $b = x$, y, z and where we have introduced the polarisation tensor [51]

$$E = e \otimes e, \tag{77}$$

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

$$A = \mu \otimes \mu. \tag{78}$$

This equation is useful because it stresses that we are really looking at a second rank tensor, not a vector. We could now measure the absorbance parallel and perpendicular to the director and try to relate it to the 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

$$A_{xx} = -\frac{1}{\sqrt{3}} A^{0,0} - \frac{1}{\sqrt{6}} A^{2,0} + \frac{1}{2}(A^{2,2} + A^{2,-2}), \tag{79a}$$

$$A_{xy} = \frac{-i}{2}(A^{2,2} - A^{2,-2}), \tag{79b}$$

$$A_{xz} = \frac{1}{2}(A^{2,-1} - A^{2,1}), \tag{79c}$$

$$A_{yy} = -\frac{1}{\sqrt{3}} A^{0,0} - \frac{1}{\sqrt{6}} A^{2,0} - \frac{1}{2}(A^{2,2} + A^{2,-2}). \tag{79d}$$

$$A_{yz} = \frac{i}{2}(A^{2,1} + A^{2,-1}), \tag{79e}$$

$$A_{ZZ} = -\frac{1}{\sqrt{3}} A^{0,0} + \sqrt{\frac{2}{3}} A^{2,0}, \tag{79f}$$

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

$$A_{LAB}^{L,m} = \sum_n D_{mn}^{L*}(\alpha\beta\gamma) A_{MOL}^{L,n}, \tag{80}$$

with 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. The averaged measurable irreducible components will be

$$< A_{LAB}^{L,m} > = \sum_n < D_{mn}^{L*}(\alpha\beta\gamma) > A_{MOL}^{L,n}. \tag{81}$$

For a uniaxial phase invariance for rotation around Z requires δ_{m0}. The measured absorption parallel to the director can be written as

$$< A_\parallel > \equiv < A_{ZZ} >_{LAB},$$

$$= a + \sqrt{(2/3)} < A_{LAB}^{2,0} >, \tag{82}$$

$$= a + \sqrt{(2/3)} \sum_m < D_{0m}^{2*} > A_{MOL}^{2,m}.$$

Quite similarly the measured perpendicular component will be

$$< A_\perp > = a - \sqrt{(1/6)} \sum_m < D_{0m}^{2*} > A_{MOL}^{2,m}. \tag{83}$$

For a biaxial molecule the experimentally measurable anisotropy of $< \mathbf{A} >$ is

$$< A_\parallel > - < A_\perp > = \sqrt{(3/2)} \left\{ A_{MOL}^{2,0} < D_{00}^2 > + 2\mathrm{Re}(A_{MOL}^{22} < D_{02}^{2*} >) \right\}. \tag{84}$$

Thus the measurement of at least two anisotropy values is required to determine both $< D_{00}^2 >$ and $< D_{02}^2 >$. Moreover the parameter of deviation from cylindrical symmetry, $< D_{02}^2 >$, only becomes measurable when the tensor $\mathbf{A}$ has an off-axis component so that $A^{22} \neq 0$. If the molecule has effective cylindrical symmetry, in the sense that the order parameters $< D_{0m}^2 > = < D_{00}^2 > \delta_{m0}$, then we have

$$< P_2 > = (< A_\parallel > - < A_\perp >) / \left[(A_{MOL})_\parallel - (A_{MOL})_\perp \right]. \tag{85}$$

We should be aware that the order parameter $< P_2 >$ measured for a molecule dissolved in a liquid crystal is clearly 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 for 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 dissolved 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 relatively small jump. Typical values for $< P_2 >$ at the nematic to isotropic transition are in the range 0.3 - 0.4. Order parameters for different liquid crystals, when plotted against the reduced temperature T/T_{NI}, with T_{NI} the nematic-isotropic transition temperature follow fairly closely a universal curve [2]. 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.

4.7. ORIENTATIONAL ORDER IN BIAXIAL PHASES

The purely orientational distribution will depend, in general, on the three Euler angles. Thus

$$P(\alpha\beta\gamma) = \sum_{Lmn} p_{Lmn} D_{mn}^L(\alpha\beta\gamma), \tag{86}$$

and the order parameters will be averages of the Wigner rotation matrices $< D_{mn}^L >$. We shall only consider the case of rigid biaxial molecules in biaxial phases, where application of the simple symmetry arguments mentioned previously shows that we can have order parameters $< D_{00}^2 >$, $\mathrm{Re} < D_{02}^2 >$, $\mathrm{Re} < D_{20}^2 >$, $\mathrm{Re} < D_{22}^2 + D_{2-2}^2 >$ in the principal axis system of the liquid crystal and of the molecule.

Experimentally we can consider once more equation (80) and the averages in equation (81). In an ideal experiment we can determine all of the components $< A_{ab} >$, with $ab = $ X, Y, Z, and then diagonalise the tensor $\mathbf{A}$ to find the liquid crystal principal axis system. In practice the measurements are more easily performed on an aligned system, where we imagine from the start to be in the principal system. In this case the surviving measurable components of a second rank tensor would be

$$< A_{XX} > = -\frac{1}{\sqrt{3}} A^{0,0} - (< D_{0,0}^2 > A_{MOL}^{2,0} + 2\mathrm{Re} < D_{02}^{2*} > A_{MOL}^{22})/\sqrt{6}$$

$$+ (\mathrm{Re} < D_{20}^{2*} > A_{MOL}^{2,0} + \mathrm{Re} < D_{22}^{2*} + D_{2-2}^{2*} > A_{MOL}^{22}) \tag{87}$$

$$< A_{YY} > = -\frac{1}{\sqrt{3}} A^{0,0} - (< D_{0,0}^2 > A_{MOL}^{2,0} + 2\mathrm{Re} < D_{02}^{2*} > A_{MOL}^{22})/\sqrt{6}$$

$$- (\mathrm{Re} < D_{20}^{2*} > A_{MOL}^{2,0} + \mathrm{Re} < D_{22}^{2*} + D_{2-2}^{2*} > A_{MOL}^{22}) \tag{88}$$

$$< A_{ZZ} > = -\frac{1}{\sqrt{3}} A^{0,0} + \sqrt{2/3} (< D_{0,0}^2 > A_{MOL}^{2,0} + 2\mathrm{Re} < D_{02}^{2*} > A_{MOL}^{22}), \tag{89}$$

for a biaxial solute dissolved in a biaxial phase formed of biaxial particles. As we see the order parameters describing the phase biaxiality i.e., $\mathrm{Re} < D_{20}^2 >$ and $\mathrm{Re} < D_{22}^2 + D_{2-2}^2 >$ cause $< A_{XX} >$ to be different from $< A_{YY} >$. Notice that the observation of phase biaxiality does not require an off-axis molecular tensor or even biaxiality in the molecular tensor (i.e., it can be obtained even when we have $A_{MOL}^{22} = 0$). Indeed phase biaxiality can often be demonstrated using a uniaxial probe. For example the deuterium NMR spectrum of deuteriated benzene is often used. The phase biaxiality can determine the quadrupolar splitting of perpendicular lines in the spectra in an X and

a Y pair, as verified experimentally in various systems [6,12,52]. In a real situation observation or not of mesophase biaxiality will, of course, depend on the relative magnitude of the terms in equation (87) - (89) and on the sensitivity of the experiment. The splitting of the perpendicular lines in an X and a Y pair will be proportional to

$$2 \,\mathrm{Re} < D_{20}^{2*} > q_{MOL}^{2,0}, \tag{90}$$

where the $q_{MOL}^{2,n}$ are spherical components of the quadrupolar tensor [12].

5. Positional-Orientational Order in Uniaxial Phases

5.1. CYLINDRICAL MOLECULES

Here we recall the description of ordering in systems with a layer structure and positional disorder inside the layer, such as a smectic A phase. We assume the phase to be uniaxial around the z laboratory axis and to be made of cylindrically symmetric particles. We also assume the centres of mass of the molecules to be distributed at random in the xy plane while they may possess some regularity (layering) along the z direction. The single particle distribution function can thus be written as $P(z, \cos \beta)$ and expanded as

$$P(z, \cos \beta) = \sum_{L=0} \sum_{n_z=0} p_{L;n_z} P_L(\cos \beta) \cos(2\pi n_z z / d), \quad L \text{ even}, \tag{91}$$

in a product basis set of Legendre polynomials for orientations and Fourier harmonics for position. We assume the distribution to be normalised as

$$\int_0^\pi d\beta \sin \beta \int_0^d dz\, P(z, \cos \beta) = 1. \tag{92}$$

Orthogonality of the basis gives at once the coefficient $p_{L;n_z}$

$$p_{L;n_z} = \{(2L + 1)/d\} \int dz\, d\beta \sin \beta\, P(z, \cos \beta)\, P_L(\cos \beta) \cos(2\pi n_z z / d), \tag{93a}$$

$$= \{(2L + 1)/d\} < P_L(\cos \beta) \cos(2\pi n_z z / d) >, \quad n_z \neq 0, \tag{93b}$$

where the angular brackets have been used to indicate an average over $P(z, \cos \beta)$. The first few terms are rather instructive, we have

$$p_{0;0} = 1/d, \tag{94a}$$

$$p_{2;0} = 5 < P_2 > /(2d), \tag{94b}$$

$$p_{0;1} = < \cos(2\pi z / d) > /d, \tag{94c}$$
$$\equiv \tau / d,$$

$$p_{2;1} = 5 < P_2(\cos \beta) \cos(2\pi z / d) > /d, \tag{94d}$$
$$= 5\sigma / d.$$

These first terms show the three kinds of order parameters present in a smectic phase. Thus,

$< P_2 >$ is the usual orientational order parameter familiar from work on nematics. By contrast $\tau = < \cos(2\pi z / d) >$ is a purely translational order parameter telling us how effectively the molecules are arranged in layers. The last type of parameter, σ, is a mixed term related to the extent of translational-orientational coupling [27-28].

5.2. NON-CYLINDRICAL MOLECULES

We now consider a rigid non-cylindrically symmetric molecule in a system with a layer structure and positional disorder inside the layer, such as a smectic A or a smectic C phase. The probability of finding the molecule at a specific position-orientation, $P(z, \beta\gamma)$, can be expanded as we have seen earlier in a complete basis set of spherical harmonics. Thus generalising equation (62) we find

$$P(z, \beta\gamma) = \sum_{L n_z n_z} p_{L n_z n_z} \cos\{2\pi n_z z / d\} D_{0n}^L(\beta\gamma). \tag{95}$$

The orthogonality of the basis set immediately gives the coefficients $p_{L n_z n_z}$; we can thus write the distribution as

$$P(z, \beta\gamma) = \frac{1}{4\pi d} + \frac{1}{2\pi} \sum_{n_z} \sum_{L=0} \sum_{n=-L}^{L} \frac{2L + 1}{d} < \cos(\frac{2\pi n_z z}{d}) D_{0n}^{L*} >$$
$$\times \cos(\frac{2\pi n_z z}{d}) D_{0n}^L(\beta\gamma), \quad n_z \neq 0. \tag{96}$$

The set of positional-orientational order parameters $< \cos(\frac{2\pi n_z z}{d}) D_{0n}^{L*} >$ allows a complete characterisation of $P(z, \beta\gamma)$.

5.3. COLUMNAR PHASES

The positional-orientational distribution for a non-cylindrically symmetric molecule in a columnar phase with some positional order of the columns in the (xy) plane, i.e., a D_{rd} rectangular discotic phase, with the column axes parallel to z, will be

$$P(xy; \beta\gamma) = \frac{1}{4\pi d_x d_y} + \frac{1}{2\pi} \sum_{n_x n_y} \sum_{L n} \frac{2L + 1}{d_x d_y} \left\langle \cos(\frac{2\pi n_x}{d_x} x) \cos(\frac{2\pi n_y}{d_y} y) D_{0n}^{L*}(\beta\gamma) \right\rangle$$
$$\times \cos(\frac{2\pi n_x}{d_x} x) \cos(\frac{2\pi n_y}{d_y} y) D_{0n}^L(\beta\gamma), \tag{97}$$

when $n_x, n_y \neq 0$ and

$$\int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\gamma \int_0^{d_x} dx \int_0^{d_y} dy\, P(xy; \beta\gamma) = 1. \tag{98}$$

The positional-orientational order parameters

$$p_{L;n_x n_y} \propto \left\langle \cos(\frac{2\pi n_x}{d_x}x) \cos(\frac{2\pi n_y}{d_y}y) D_{0m}^{L*}(\beta \gamma) \right\rangle, \tag{99}$$

express any regularity in the two dimensional arrangement of the columns and the coupling to the molecular orientation. If the mesophase is formed of disc-like particles we can reduce the distribution to

$$P(xy;\beta) = \frac{1}{2d_x d_y} + 2\sum_{n_x n_y}\sum_{L}\frac{2L+1}{d_x d_y}\left\langle \cos(\frac{2\pi n_x}{d_x}x)\cos(\frac{2\pi n_y}{d_y}y)P_L(\cos \beta)\right\rangle$$
$$\times \cos(\frac{2\pi n_x}{d_x}x)\cos(\frac{2\pi n_y}{d_y}y)P_L(\cos \beta), \tag{100}$$

with

$$\int_0^\pi d\beta \sin \beta \int_0^{d_x} dx \int_0^{d_y} dy\, P(xy;\beta) = 1. \tag{101}$$

6. Rotameric Molecules

We now wish to mention briefly how the present treatment of order parameters can be applied to molecules with internal degrees of freedom [16,21,53]. This is an important problem because most molecules of practical interest [54,55] including molecules forming liquid crystals possess some internal flexibility. The problem has received attention by various authors (see, for example, [12,16,20,56]). 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 shape. We shall give a specific example, that of a molecule with one degree of internal rotation [21]. The molecule we have in mind is made up of two rigid fragments, i.e., two rings. We place a molecular frame M_1 on one of the fragments and we introduce an angle ϕ giving the orientation of one ring with respect to the other. In a non-uniform system, i.e., if the molecule is dissolved in a smectic A solvent, the state of the molecule is a positional-orientational-conformational one. We can define this state r,Ω,ϕ by giving the position r and the orientation $\Omega \equiv (M_1 - L)$ of frame M_1 with respect to the laboratory frame together with the internal angle ϕ. Accordingly we write the probability of finding the molecule in a certain positional-orientational-conformational state in terms of 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., $P(r,\Omega,\phi)$. This one particle distribution is then expanded in a composite Wigner-Fourier basis set. If the molecule is in a uniaxial smectic A phase

$$P(z;\beta \gamma;\phi) = \frac{1}{8\pi^2 d}$$
$$+ \frac{1}{4\pi^2 d}\sum_{L;n_z;q}(2L+1)p_{0m;n_z;q}^L D_{0m}^{L*}(\beta \gamma)\cos(\frac{2\pi n_z z}{d})\exp(-iq\phi), \tag{102}$$

with

$$p_{0m;n_z;q}^L = < D_{0m}^L(\beta \gamma)\exp(iq\phi)\cos(\frac{2\pi n_z z}{d}) >, \tag{103}$$

as the positional-orientational-conformational order parameters. We have, even in this simple system [16], numerous types of order parameters, i.e.,

Purely orientational

$$p_{0m;0;0}^L = < D_{0m}^L(M_1 - L) >. \tag{104}$$

We have used the notation (B - A) to indicate the rotation from A to B, i.e., 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 and the position.

Purely internal

$$p_{00;q;0}^0 = < \exp(iq\phi) >; q = 0, \pm 1, \pm 2, \dots . \tag{105}$$

These parameters describe the ordering of the second part of the molecule with respect to the first irrespective of the overall orientation and position. They are quite important since they can be considered expansion coefficients of the rotameric distribution $P(\phi)$ in the fluid obtained by integrating equation (102) over $\beta\gamma;z$.

$$P(\phi) = \frac{\int dz\,d\beta \sin \beta\,d\gamma\, P(z;\beta \gamma;\phi)}{\int dz\,d\phi\,d\beta \sin \beta\,d\gamma\, P(z;\beta \gamma;\phi)}. \tag{106}$$

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

$$< D_{0m}^L(\beta \gamma)\exp(iq\phi) >. \tag{107}$$

These parameters result when both L and q are different from zero in equation (103). 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. We also have, of course, the other combinations, purely positional, positional-orientational and the following interesting ones.

Positional-conformational order parameter

$$p_{00;q;n_z}^0 = < \exp(iq\phi)\cos(2\pi n_z z/d) >. \tag{108}$$

These parameters should describe the coupling between the internal degrees of freedom, and the position in a smectic phase. For example, they could describe situations where the conformation of the molecule changes as the molecule itself is displaced from the average layer position.

For a molecule dissolved in a uniform uniaxial phase, such as a nematic we have the simpler orientational-internal distribution

$$P(\beta\gamma;\phi) = (1/8\pi^2) \sum_{L,n,q} (2L + 1) p^L_{0n,q} D^{L^*}_{0n}(\beta\gamma) \exp(-iq\phi),\qquad(109)$$

where in general $q = 0, \pm1, \pm2, \ldots$ and we have retained the notation used in [16]. The angle ϕ, with $0 \le \phi \le 2\pi$ is the dihedral rotation angle around the inter-fragments vector connecting the two parts of the molecule. The orthogonality of the basis functions immediately yields the expansion coefficients as

$$p^L_{0n,q} = <D^L_{0n}(\beta\gamma)\exp(iq\phi)>,\qquad(110)$$

where the angular brackets denote a conformational-orientational average over the distribution $P(\beta\gamma;\phi)$.

The maximum entropy method outlined in section 4.5.1 can be generalised 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 $p^L_{0n,q}$, this distribution will be of the form

$$P(\beta\gamma;\phi) = \exp\left[\sum_{n,q} a_{n,q} D^{2^*}_{0n}(\beta\gamma)\exp(iq\phi)\right],\qquad(111)$$

where the coefficients $a_{n,q}$ are obtained by minimising the squared difference between the measured quantities and those obtained by integrating this equation. The formalism has been applied to an analysis of the proton NMR spectrum of 3-phenyl-thiophene in two nematic phases: PCH and Phase IV [21] and to 4,4'dichlorobiphenyl in the nematic solvent 152 [21]. 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 internal distribution. In figure 12 we show the results obtained for the purely internal distribution $P(\phi)$ giving the probability of finding one of the two rings of 4,4'dichlorobiphenyl with respect to the other.
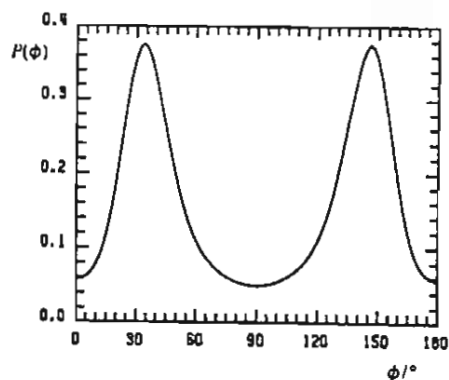

Figure 12. The probability distribution for finding an inter-ring angle ϕ for 4,4' dichlorobiphenyl dissolved in nematic 152 [53].

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CHAPTER 2