

Chapter 3

DISTRIBUTION FUNCTIONS AND ORDER PARAMETERS

CLAUDIO ZANNONI

*Department of Chemistry, The University,
Risorgimento 4, 40136 Bologna, Italy*

Introduction

The most fundamental characteristic of liquid crystals, at least from a microscopic point of view, is the presence of long-range orientational order while positional order is limited or absent altogether [1]. In this Chapter we shall discuss in some detail the way to describe this ordering. We shall also introduce distribution functions and other concepts from statistical mechanics which can help us in calculating order parameters as well as other relevant averages. In the following two sections we recall some important definitions and concepts from statistical mechanics and, where necessary, provide the generalizations needed to treat anisotropic fluids. We discuss in particular the singlet and pair distributions and give equations for the relevant thermodynamic observables in terms of these distributions. In the third section we shall introduce order parameters by expanding the singlet distribution in a complete basis set. The effect of molecular and mesophase symmetry on the orientational order parameters will be examined. In the final section a general expansion of the pair distribution will be given. The coefficients in this expansion will be interpreted as correlations and their importance will be discussed.

Distributions

We start by recalling some basic definitions from statistical mechanics and by describing the notation involved. We consider a macroscopic system of N classical rigid particles with position (e.g. centre of mass) specified by a vector r and orientation defined by the three Euler angles $(\alpha\beta\gamma) \equiv \Omega$. The equilibrium configurational partition function for such a system can be written as [2]

$$\begin{aligned} Q_N &= (1/N!) \int \{d\mathbf{X}^N\} \exp[-\beta U(\{\mathbf{X}^N\})], \\ &\equiv Z_N/N! \end{aligned} \quad (1)$$

where $U(\{\mathbf{X}^N\})$ is the potential energy of the N particles and, as usual,

the β in the Boltzmann factor is $\beta \equiv (kT)^{-1}$ where k is the Boltzmann constant and T is the absolute temperature. For economy of notation we have used \mathbf{X} to indicate the six variables (\mathbf{r}, Ω) and the curly brackets to denote collectively N variables. Thus $\{\mathbf{X}^N\} \equiv (X_1, X_2, \dots, X_N)$ and, similarly, $\{d\mathbf{X}^N\} \equiv dX_1 \cdot dX_2 \dots dX_N$. Each volume element $d\mathbf{X}$ is equivalent to $d\mathbf{r}d\Omega$, where $d\mathbf{r} \equiv dr_x dr_y dr_z$ and $d\Omega \equiv d\alpha \sin\beta d\beta d\gamma$. To complete the remarks about notation we mention that in the absence of possible ambiguities we shall use only one integration sign to indicate the, possibly multiple, integration over all the variables whose volume elements appear. Integration is extended to the sample volume V for positions and to the usual domains $0 \leq \alpha \leq 2\pi$, $0 \leq \beta \leq \pi$ and $0 \leq \gamma \leq 2\pi$ for angles [3].

The probability of finding n particles out of the given N in the range $X_1 + dX_1, X_2 + dX_2, \dots, X_n + dX_n$, can be written as the n -particle distribution

$$P^{(n)}(\{\mathbf{X}^n\}) = (N! / (N-n)! Z_N) \int \{d\mathbf{X}_{n+1}^N\} \exp[-\beta U(\{\mathbf{X}^N\})], \quad (2)$$

where, with a slight extension of the previous convention, we have introduced $\{d\mathbf{X}_m^N\} \equiv dX_m dX_{m+1} \dots dX_N$. Notice that $P^{(n)}$ is not normalized to one but to the number of n -plets that can be formed by choosing n variables out of N i.e.

$$\int \{d\mathbf{X}^n\} P^{(n)}(\{\mathbf{X}^n\}) = N! / (N-n)! \quad (3)$$

Here we shall not need to concern ourselves very much with the general n -particle distribution but mainly with the one- and two-particle distributions, or, as they are often called, the singlet and the pair distributions. These can be used to define the canonical ensemble average $\langle A \rangle$ of any property depending on position and orientation of one or two particles respectively. Thus

$$\langle A(\mathbf{X}_1) \rangle = (1/N) \int d\mathbf{X}_1 A(\mathbf{X}_1) P^{(1)}(\mathbf{X}_1) \quad (4)$$

and

$$\langle A(\mathbf{X}_1, \mathbf{X}_2) \rangle = [1/N(N-1)] \int d\mathbf{X}_1 d\mathbf{X}_2 A(\mathbf{X}_1, \mathbf{X}_2) P^{(2)}(\mathbf{X}_1, \mathbf{X}_2). \quad (5)$$

The singlet distribution $P^{(1)}$ which gives the probability of finding a molecule at a particular position and orientation is

$$P^{(1)}(\mathbf{r}_1, \Omega_1) = (N/Z_N) \int \{d\mathbf{r}_2^N\} \{d\Omega_2^N\} \exp[-\beta U(\{\mathbf{r}^N, \Omega^N\})]. \quad (6)$$

Similarly the pair distribution function, giving the probability of finding simultaneously a particle in a volume $d\mathbf{r}_1 d\Omega_1$ centred at \mathbf{r}_1, Ω_1 and a second one in a volume $d\mathbf{r}_2 d\Omega_2$ centred at \mathbf{r}_2, Ω_2 is

$$P^{(2)}(\mathbf{r}_1, \Omega_1; \mathbf{r}_2, \Omega_2) = [N(N-1)/Z_N] \int \{d\mathbf{r}_3^N\} \{d\Omega_3^N\} \exp[-\beta U(\{\mathbf{r}^N, \Omega^N\})]. \quad (7)$$

Inspection of eqs. (4) and (5) shows that formal alternative definitions of $P^{(1)}$ and $P^{(2)}$ are [2]

$$p^{(1)}(\mathbf{r}_1, \Omega_1) = N \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\Omega_1 - \Omega'_1) \rangle \quad (8)$$

and

$$p^{(2)}(\mathbf{r}_1, \Omega_1; \mathbf{r}_2, \Omega_2) = N(N-1) \langle \delta(\mathbf{r}_1 - \mathbf{r}'_1) \delta(\Omega_1 - \Omega'_1) \delta(\mathbf{r}_2 - \mathbf{r}'_2) \delta(\Omega_2 - \Omega'_2) \rangle. \quad (9)$$

Similarly we have in general

$$p^{(n)}(\mathbf{X}_1, \dots, \mathbf{X}_n) = [N! / (N-n)!] \langle \delta(\mathbf{X}_1 - \mathbf{X}'_1) \dots \delta(\mathbf{X}_n - \mathbf{X}'_n) \rangle, \quad (10)$$

where $\delta(\mathbf{a}-\mathbf{b})$ is a Dirac delta function and the integration implied in the ensemble average $\langle \dots \rangle$ is over the primed variables. Eqs. (8-10) can be rewritten in a convenient way using the Fourier integral representation of the spatial delta function

$$\delta(\mathbf{r}) = (2\pi)^{-3} \int d\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (11)$$

and the representation of the angular delta function

$$\delta(\Omega - \Omega') = \sum_L [(2L+1)/8\pi^2] D_{m,n}^L(\Omega) D_{m,n}^{L*}(\Omega'), \quad (12)$$

where the functions $D_{m,n}^L(\Omega)$ are the Wigner rotation matrices[3]; we define them and give their important properties in the Appendix. The sum in eq. (12) runs over L , m and n ; we shall normally take the summations on the right hand side of an equation to run over all indices not appearing on the left hand side. Replacing the delta functions in eqs. (8-10) gives some general expansions for the probability distributions. As an example

$$p^{(1)}(\mathbf{r}_1, \Omega_1) = N \int d\mathbf{k} \sum_{Lmn} c_{Lmn}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_1) D_{m,n}^L(\Omega_1); \quad (13)$$

the coefficients

$$c_{Lmn}(\mathbf{k}) = [(2L+1)/64\pi^5] \langle \exp(-i\mathbf{k} \cdot \mathbf{r}') D_{m,n}^{L*}(\Omega') \rangle, \quad (14)$$

will be identified later with the order parameters for the system.

It is possible to give a limiting expression for the n -particle distribution valid for very low densities. In fact, when the distance between particles is very large and their reciprocal influence negligible, the probabilities of finding them in their respective volume elements become statistically independent. Therefore, in the limit that $|\mathbf{r}_i - \mathbf{r}_j| \rightarrow \infty$ for all pairs of particles i and j , the n -particle joint distribution must yield simply the product of n single particle distributions

$$p^{(n)}(\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_n) = [N! / (N-n)! N^n] p^{(1)}(\mathbf{X}_1) p^{(1)}(\mathbf{X}_2) \dots p^{(1)}(\mathbf{X}_n). \quad (15)$$

We can use this property to introduce reduced n -particle distributions or correlations, which tend to unity as the inter-particle distances tend to infinity or, in practice, when these distances become many orders of magnitude larger than typical intermolecular distances. Thus we define

$$g^{(n)}(\{\mathbf{X}^n\}) \equiv P^{(n)}(\{\mathbf{X}^n\}) / \prod_{i=1}^n P^{(1)}(\mathbf{X}_i). \quad (16)$$

The most important of this family of $g^{(n)}$ is the pair correlation function

$$g^{(2)}(\mathbf{X}_1, \mathbf{X}_2) \equiv P^{(2)}(\mathbf{X}_1, \mathbf{X}_2) / P^{(1)}(\mathbf{X}_1)P^{(1)}(\mathbf{X}_2). \quad (17)$$

For a uniform system the physical properties are invariant under translation and the interaction energy $U(\{\mathbf{X}^N\})$ depends only on relative distances. Therefore for an ordinary isotropic fluid or for a nematic, but not for a smectic, we can write

$$P^{(1)}(\mathbf{r}_1, \Omega_1) = \rho f(\Omega_1) \quad (18)$$

and

$$P^{(2)}(\mathbf{r}_1, \Omega_1; \mathbf{r}_2, \Omega_2) = \rho^2 f(\Omega_1) f(\Omega_2) g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2), \quad (19)$$

where $\rho \equiv N/V$ is the number density and $f(\Omega_1)$ is a purely orientational singlet distribution normalized to unity:

$$f(\Omega_1) = (V/Z_N) \int \{d\mathbf{X}_2^N\} \exp[-\beta U(\{\mathbf{X}^N\})], \quad (20)$$

with

$$\int d\Omega_1 f(\Omega_1) = 1.$$

For an isotropic molecular fluid we have simply

$$P^{(1)}(\mathbf{r}_1, \Omega_1) = \rho / 8\pi^2$$

and

$$P^{(2)}(\mathbf{r}_1, \Omega_1; \mathbf{r}_2, \Omega_2) = (\rho / 8\pi^2)^2 g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2). \quad (21)$$

If, moreover, the constituent particles are spherical (e.g. atoms) the pair correlation function $g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ depends on inter-particle distance alone and $g(r_{12})$ is called the radial distribution function.

It is helpful to gain greater physical understanding of the pair distribution by considering some limiting situations. For very dilute fluid systems, the density is so low that configurations with three or more particles interacting simultaneously are extremely rare and can be neglected. Therefore, in this limit,

$$g^{(2)}(\mathbf{X}_1, \mathbf{X}_2) = \exp[-\beta U(\mathbf{X}_1, \mathbf{X}_2)], \quad \rho \rightarrow 0. \quad (22)$$

In accord with the definition, eq. (17), we have for $N \gg 1$

$$\lim_{r_{12} \rightarrow \infty} g^{(2)}(\mathbf{X}_1, \mathbf{X}_2) = 1, \quad (23)$$

corresponding to no correlation at all. If the particles have a hard impenetrable core, there is clearly a vanishing probability of finding a second molecule nearer than a minimum approach distance σ from the first

one. Then

$$g^{(2)}(\mathbf{X}_1, \mathbf{X}_2) = 0, \quad r_{12} < \sigma(\Omega_1, \Omega_2). \quad (24)$$

Another limiting situation where we can sketch the behaviour of $g^{(2)}$ is that of an ideal solid. Imagine this solid composed of spherical particles exactly positioned at the lattice sites. Every particle will have z_1 nearest neighbours at a distance r_1 , z_2 at a distance r_2 and so on.

Therefore

$$\begin{aligned} g(r) &= (1/4\pi r^2 \rho) \sum_i z_i \delta(r-r_i), \\ &= (1/4\pi r^2 \rho) \lim_{\epsilon \rightarrow 0} \sum_i z_i (4\pi\epsilon)^{-1/2} \exp\{-(r-r_i)^2/4\epsilon\}, \end{aligned} \quad (25)$$

where the second equality follows from simply writing the delta function as a gaussian of vanishing width. We see that for an idealized solid $g(r)$ consists of a series of peaks corresponding to the various shells of neighbours. In a real crystal the positions will not be defined with absolute certainty due to the possibility of thermal oscillations etc. and the peaks will obviously be smeared out; e.g. they could be more or less sharp gaussians instead of delta functions. In a liquid the peaks will be even more diffuse and we could have something like the behaviour sketched in figure 1. The successive peaks in $g(r)$ can still be associated

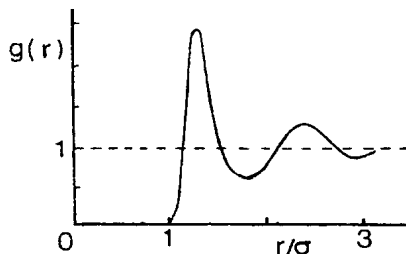


Fig. 1 *The possible behaviour of the radial distribution function in a liquid; σ is the distance of closest approach for two particles.*

with the presence of average shells of neighbours and give an indication of short-range order (structure) in a fluid. Notice the fundamental difference between $g(r)$ in a fluid and in the idealized solid. In the fluid $g(r)$ decays to one in the absence of correlations while in the solid $g(r)$ keeps oscillating even when the separation r is extremely large. In other words in a solid we have long-range positional order, which vanishes at the melting transition.

Thermodynamic Properties

The configurational partition function and the distributions introduced in the previous section provide a convenient link between microscopic or molecular properties and thermodynamic observables. In general we have for the configurational contributions to the Helmholtz free energy A , entropy S , pressure P and internal energy U the expressions [2,4],

$$A = -kT \ln Q_N, \quad (26)$$

$$S = -(\partial A / \partial T)_V, \quad (27)$$

$$P = -(\partial A / \partial V)_T, \quad (28)$$

$$\begin{aligned} U &= A + TS, \\ &= -T^2 (\partial (A/T) / \partial T)_V, \\ &= kT^2 (\partial (\ln Q_N) / \partial T)_V. \end{aligned} \quad (29)$$

Other important observables are the specific heat at constant volume C_V and the isothermal compressibility κ_T ,

$$\begin{aligned} C_V &= (\partial U / \partial T)_V = T(\partial S / \partial T)_V, \\ &= -T(\partial^2 A / \partial T^2)_V, \end{aligned} \quad (30)$$

$$\kappa_T = -(1/V)(\partial V / \partial P)_T. \quad (31)$$

Since C_V is positive eq. (30) implies that the free energy at constant volume is a downward concave function of temperature.

We recall also the Ehrenfest scheme of classifying phase transitions [4,5], which, although not of general applicability, sometimes gives a useful practical framework. According to the scheme a transition is classified as being of n th order if the first $(n-1)$ derivatives of the free energy are continuous across the phase transition while the n th shows a discontinuity. Thus in a first order transition, e.g. melting or condensation away from the critical point, there is a finite jump in the first derivative of the free energy, the entropy, and a latent heat $T\Delta S$. In a higher order transition, however, the entropy change is continuous across the transition. This idealized behaviour is sketched in figure 2. The nematic-isotropic phase transition is a first order transition with a small latent heat. For this reason it is often called a weak first order phase transition. The prediction and the location of this phase transition is central to any statistical theory of liquid crystals. A cautionary remark is thus perhaps not inappropriate here. If we look back at eq. (1), we see that the partition function Q_N is a continuous and infinitely differentiable function of inverse temperature

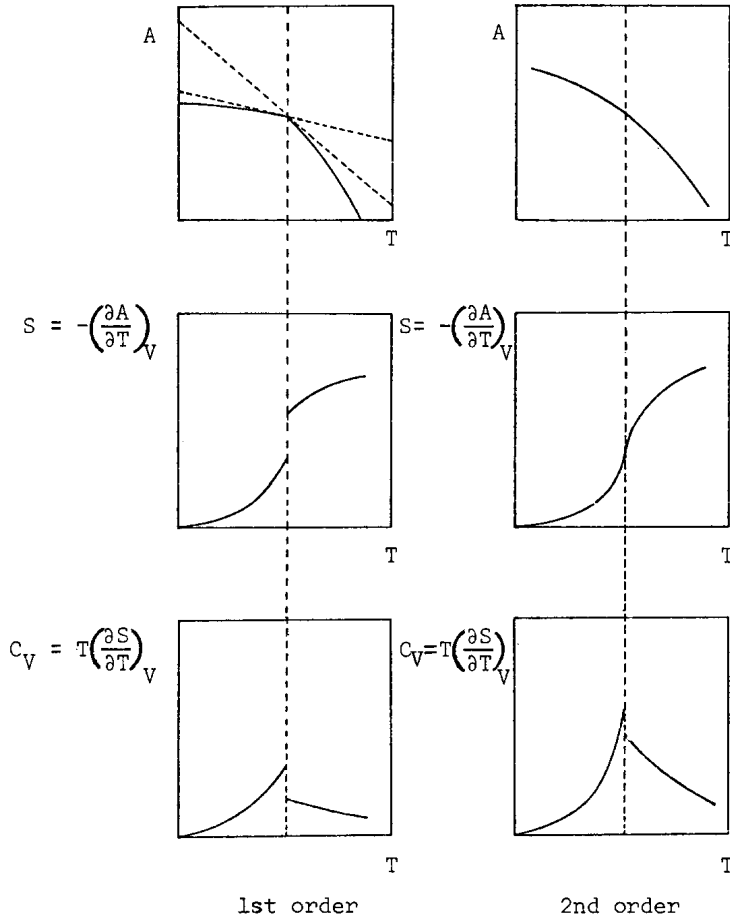


Fig. 2 A sketch of the behaviour of the free energy, A , and of its temperature derivatives at a first order and second order phase transition, according to the Ehrenfest scheme.

for any finite N . This implies that the free energy and its derivatives are also continuous and differentiable. Strictly, therefore, we cannot have a true phase transition for a system of finite size [2a]. We have to go to the so-called thermodynamic limit, that is calculate the free energy per particle and take the limit

$$a(\rho, T) = \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} A(V, T)/N, \quad \rho = \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} N/V = \text{constant.}$$

This limiting free energy can have the discontinuities which correspond to phase transitions. Another important reason for going to the thermodynamic limit, by letting N tend to infinity, while keeping the density N/V constant, is that only in this limit do the various ensembles used in statistical thermodynamics become exactly equivalent [2].

Let us now write down explicit expressions for energy, pressure and specific heat as ensemble averages using the distributions we have defined previously.

Energy

Assume that the total potential energy can be decomposed as a sum of pairwise interactions;

$$U(\{\mathbf{X}^N\}) = \sum_{1 \leq i < j \leq N} U(\mathbf{X}_i, \mathbf{X}_j). \quad (32)$$

Then the total average potential energy is

$$\begin{aligned} \langle U \rangle &= \langle U(\{\mathbf{X}^N\}) \rangle = \frac{1}{2} \int d\mathbf{X}_1 d\mathbf{X}_2 U(\mathbf{X}_1, \mathbf{X}_2) P^{(2)}(\mathbf{X}_1, \mathbf{X}_2), \\ &\equiv \frac{1}{2} \rho^2 \int d\mathbf{X}_1 d\mathbf{X}_2 U(\mathbf{X}_1, \mathbf{X}_2) G(\mathbf{X}_1, \mathbf{X}_2), \end{aligned} \quad (33)$$

for uniform fluids $U(\mathbf{X}_1, \mathbf{X}_2) = U(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ and we find

$$\begin{aligned} \langle U \rangle &= \frac{1}{2} V \rho^2 \int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 U(\mathbf{r}_{12}, \Omega_1, \Omega_2) f(\Omega_1) f(\Omega_2) g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2), \\ &\equiv \frac{1}{2} V \rho^2 \int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 U(\mathbf{r}_{12}, \Omega_1, \Omega_2) G(\mathbf{r}_{12}, \Omega_1, \Omega_2). \end{aligned} \quad (34)$$

Thus we see that for an anisotropic fluid the key quantity to be calculated is $P^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2) \equiv \rho^2 G(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ and not $g^{(2)}$ as in an ordinary isotropic fluid. The reason is, of course, that in an anisotropic fluid the orientational distribution $f(\Omega)$ is not a constant so that $g^{(2)}$ does not have a simple normalization. We have therefore introduced for convenience the reduced distribution G , which is normalized according to

$$\int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 G(\mathbf{r}_{12}, \Omega_1, \Omega_2) = V(1-N^{-1}) \quad (35)$$

and has simple properties,

$$G(\mathbf{r}_{12}, \Omega_1, \Omega_2) = f(\Omega_1) f(\Omega_2), \quad r_{12} \rightarrow \infty \quad (36)$$

and

$$G(\mathbf{r}_{12}, \Omega_1, \Omega_2) = f(\Omega_1) f(\Omega_2) \exp\{-\beta U(\mathbf{r}_{12}, \Omega_1, \Omega_2)\}, \quad \rho \rightarrow 0. \quad (37)$$

Pressure

An equation linking the pressure to the other thermodynamic variables, the so-called equation of state, can also be given an ensemble average representation by combining eqs. (26) and (28). The volume dependence of the configurational integral Q_N can be made explicit by transforming to dimensionless coordinates: $\mathbf{s}_i = \mathbf{r}_i / V^{1/3}$. We then find the virial equation

$$P = \rho kT - (1/3V) \sum \mathbf{r}_i \cdot \partial U(\{\mathbf{X}^N\}) / \partial \mathbf{r}_i. \quad (38)$$

For a pair additive potential eq. (38) can be reduced to

$$P = \rho kT - (1/6) \int d\mathbf{X}_1 \int d\mathbf{X}_2 P^{(2)}(\mathbf{X}_1, \mathbf{X}_2) \mathbf{r}_{12} \cdot \partial U(\mathbf{X}_1, \mathbf{X}_2) / \partial \mathbf{r}_{12}. \quad (39)$$

This can be simplified further, for a uniform fluid, to

$$P = \rho kT - (\rho^2/6) \int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 G(\mathbf{r}_{12}, \Omega_1, \Omega_2) \mathbf{r}_{12} \cdot \partial U(\mathbf{r}_{12}, \Omega_1, \Omega_2) / \partial \mathbf{r}_{12}, \quad (40)$$

which reduces, for isotropic fluids, to

$$P = \rho kT - (\rho^2/384\pi^4) \int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2) \times \mathbf{r}_{12} \cdot \partial U(\mathbf{r}_{12}, \Omega_1, \Omega_2) / \partial \mathbf{r}_{12}. \quad (41)$$

For spherically symmetric particles and isotropic intermolecular interactions we recover the familiar expression

$$P = \rho kT - (2\pi\rho^2/3) \int d\mathbf{r}_{12} g(r_{12}) r_{12}^3 \partial U(r_{12}) / \partial r_{12}. \quad (42)$$

Eqs. (38-42) hold, of course, for any potential that is a continuous differentiable function of positions. However, their validity can be shown to extend also to the important hard-core potentials. Consider, as a simple example, the hard-sphere potential

$$U(r_{12}) = \begin{cases} 0 & \text{when } r_{12} \geq \sigma \\ \infty & \text{when } r_{12} < \sigma. \end{cases}$$

Eq. (42) can be rewritten as [2b]

$$P/kT = \rho + (2\pi\rho^2/3) \int_0^\infty dr r^3 y(r) dH(r-\sigma)/dr, \quad (43)$$

where $y(r) \equiv g(r) \exp\{\beta U(r)\}$ is assumed to be an everywhere continuous function of r and $H(r-\sigma) \equiv \exp\{-\beta U(r)\}$. Integration can now be easily performed noticing that $H(r-\sigma)$ is a unit step function. The derivative of a unit step function is a delta function so we have at once

$$P/kT = \rho + (2\pi\rho^2\sigma^3/3) y(\sigma), \quad (44)$$

where $y(\sigma)$ is $\lim_{\epsilon \rightarrow \sigma^+} g(\sigma+\epsilon)$.

This equation is particularly important in computer simulations, where the pair distribution at the contact point $y(\sigma)$ can be calculated numerically [6,7]. Eq. (38) can be generalized to systems composed of hard anisotropic particles [7], at least in principle.

Specific Heat

Some manipulation of eq. (30) shows that the specific heat can be written as

$$C_V = (\langle U^2 \rangle - \langle U \rangle^2) / kT^2, \quad (45)$$

$$= \frac{1}{2} \rho^2 \int dX_1 dX_2 U(X_1, X_2) \partial G(X_1, X_2) / \partial T, \quad (46)$$

for temperature independent intermolecular potentials. Eq. (45) shows that C_V is a positive quantity determined essentially by the fluctuations in the internal energy.

Compressibility

Consider a macroscopic subvolume V_A of the total volume V and the mean square fluctuation in the number of particles N_A occupying it. Clearly

$$\langle N_A \rangle = \int_{V_A} dX_1 P^{(1)}(X_1) \quad (47)$$

and

$$\langle N_A(N_A - 1) \rangle = \int_{V_A} dX_1 dX_2 P^{(2)}(X_1, X_2). \quad (48)$$

Therefore

$$\langle N_A^2 \rangle - \langle N_A \rangle^2 = \langle N_A \rangle + \int_{V_A} dX_1 dX_2 [P^{(2)}(X_1, X_2) - P^{(1)}(X_1)P^{(1)}(X_2)] \quad (49)$$

and, remembering [2] that κ_T can also be written as $\kappa_T = (V/kT) \langle \Delta N^2 \rangle / \langle N \rangle^2$,

$$\kappa_T = (1/kT) \left\{ (1/\rho) + (1/\rho^2 V_A) \int_{V_A} dX_1 dX_2 [P^{(2)}(X_1, X_2) - P^{(1)}(X_1)P^{(1)}(X_2)] \right\}. \quad (50)$$

For a uniform fluid this reduces to

$$\kappa_T = (1/kT) \left\{ (1/\rho) + \int_{V_A} d\mathbf{r} d\Omega_1 d\Omega_2 [G(\mathbf{r}, \Omega_1, \Omega_2) - f(\Omega_1)f(\Omega_2)] \right\} \quad (51)$$

and for an isotropic fluid to the equation given by Steele [8],

$$\kappa_T = (1/kT) \left\{ (1/\rho) + (1/64\pi^2) \int d\mathbf{r} d\Omega_1 d\Omega_2 [g^{(2)}(\mathbf{r}, \Omega_1, \Omega_2) - 1] \right\}. \quad (52)$$

Near a phase transition, where the compressibility diverges it follows from eqs. (50-52) that the area under the correlation G must also diverge. In other words, the range of the correlations, the correlation length, has to diverge.

Order Parameters

When studying phase transformations it is often useful to define an order parameter, that is a quantity which changes value on going from one phase to the other and can therefore be used to monitor the transition. In many instances there is a simple practical choice for this order parameter, such as the magnetization in a magnetic system [5], or the anisotropy in some tensor property for a nematic-isotropic transition [1,9]. From a molecular point of view, however, we should describe the passage from one phase to another in terms of the modifications that this produces in the distribution functions. It is natural, therefore, to in-

introduce in a general way order parameters as expansion coefficients of, say, the singlet distribution in a suitable basis set. Thus, if the distribution depends on positions and orientations, we will have positional, orientational and mixed positional-orientational order parameters [1b]. These parameters will, of course, alter with the variable producing the phase change, and, if properly chosen, will vanish when the transition to the more symmetric phase takes place. The most characteristic and, perhaps, the most important order parameters for liquid crystal phases are the orientational ones. These define the distribution function $f(\Omega)$,

$$f(\Omega) = (1/N) \int d\mathbf{r} P^{(1)}(\mathbf{r}, \Omega), \quad (53)$$

which, of course, for a translationally invariant fluid such as a nematic, reduces to

$$f(\Omega) = P^{(1)}(\Omega)/\rho.$$

The ensemble average of any single-particle orientational function $A(\Omega)$ can be written in terms of $f(\Omega)$ as

$$\bar{A} = \int d\Omega f(\Omega) A(\Omega). \quad (54)$$

We use an upper bar instead of the usual angular brackets to indicate this purely orientational average. Any well behaved function of the three Euler angles $f(\Omega)$ can be expanded in a Wigner series [3], that is in a basis of Wigner rotation matrices;

$$f(\Omega) = \sum_{Lmn} f_{Lmn} D_{m,n}^L(\Omega). \quad (55)$$

Multiplying both sides of eq. (55) by D_{mn}^{L*} and integrating over the angles we find

$$f_{Lmn} = [(2L+1)/8\pi^2] \overline{D_{m,n}^{L*}}, \quad (56)$$

because of the orthogonality of the Wigner rotation matrices and the definition in eq. (54). The averages $\overline{D_{m,n}^L}$, which completely define $f(\Omega)$, are just the orientational order parameters. We give the explicit expressions for the rotation matrices of rank $L = 0, 1, 2, 4$ in the Appendix. There can be up to $(2L+1)^2$ order parameters of rank L although this number can be drastically reduced by exploiting the symmetry properties of the mesophase and of its constituent particles. For example in a uniaxial phase the singlet distribution must be invariant under rotation about the director i.e. the axis of symmetry. If this is chosen to be z , it follows that m must be zero in the average $\overline{D_{m,n}^L}$. In addition if a uniaxial mesophase has a symmetry plane perpendicular to the director

($D_{\infty h}$ symmetry) then only terms with even L can appear in eq. (55). To simplify further one has to investigate the symmetry of the molecules forming the mesophase. Let us consider the simplest case of all, which arises when the molecules are cylindrically symmetric. In this limit rotation about the molecular symmetry axis should not modify the distribution $f(\Omega)$, which implies $n = 0$ in eq. (55). In other words for a cylindrically symmetric mesophase composed of cylindrically symmetric particles the singlet orientational distribution has to depend only on the angle β between the director and the molecular symmetry axis. Accordingly we have $f(\beta) = f(\Omega)/4\pi^2$, where

$$f(\beta) = \sum_L D_{0,0}^L(\beta), \quad L \text{ even}, \quad (57)$$

and

$$\int d\beta \sin\beta f(\beta) = 1.$$

In this important but, strictly, unrealistic case the expansion coefficients are $f_L = [(2L+1)/2] \bar{P}_L$ and the order parameters are just averages of the even Legendre polynomials. Obviously a knowledge of $f(\Omega)$ implies that all the order parameters can be calculated. *Vice versa* a knowledge of \bar{P}_2, \bar{P}_4 etc. gives us progressively more information on the singlet distribution function and allows a test of the various theoretical models put forward for nematics or other liquid crystals.

We cannot say very much about the rate of convergence of expansion (57). However, since the number of zeros in the Legendre polynomials increases with their rank we expect the \bar{P}_L to decrease if the distribution $f(\Omega)$ is peaked at $\beta=0$ and monotonically non-increasing. If this is the case we expect the expansion coefficients f_L to decrease with L at low order. As the order increases, the convergence will get worse as all the \bar{P}_L tend to their limit $\bar{P}_L = 1$ (L even) for complete order. We do not expect convergence to be very rapid in the region of intermediate order: $\bar{P}_2 \sim 0.4 \div 0.6$. Thus, unless we have a technique able to yield directly $f(\beta)$ [10] or, in general, $f(\Omega)$ the determination of order parameters of rank as high as possible is a problem of great importance. We do not want to discuss the problems connected with the practical measurement of the order parameters here, since these are treated in detail in other Chapters. However, we think it worthwhile to examine briefly how the order parameters $\bar{D}_{m,n}^L$ can be related to measurable quantities.

Let us consider, as an example, the determination of a second rank tensor property during a time sufficiently long to allow observation of statically averaged quantities. If $F^{(L,m)}$ are the irreducible spherical components of the tensor F , as defined in the Appendix and if F is symm-

etric, then its only non-zero components will be those of rank $L=0$ and $L=2$. Let us consider the anisotropic, $L=2$, component. The tensor \mathbf{F} is measured in a laboratory frame and its components can be related to the molecule fixed components $F^{(2,m)}$ by

$$F^{(2,n)} = \sum D_{n,m}^{2*}(\Omega) F^{(2,m)}.$$

Taking an ensemble average we have, for a uniaxial mesophase,

$$\begin{aligned} \overline{F^{(2,n)}} &= \overline{F^{(2,0)}} \delta_{n0}, \\ &= \overline{\sum D_{0,m}^{2*}} F^{(2,m)}, \end{aligned} \quad (58)$$

where we have taken the laboratory z axis to be parallel to the director. If the molecule has cylindrical symmetry, in the sense that $\overline{D_{0,m}^2} = \overline{D_{0,0}^2} \delta_{m0}$, then we have

$$\begin{aligned} \bar{P}_2 &\equiv \frac{\overline{D_{0,0}^2}}{F^{(2,0)}} \\ &= \overline{F^{(2,0)}} / F^{(2,0)}. \end{aligned} \quad (59)$$

Thus, the orientational order parameter \bar{P}_2 can be obtained in practice from the measured anisotropy in $\bar{\mathbf{F}}$.

A similar analysis can obviously be given for a tensor of higher rank. However, while it is relatively easy to determine \bar{P}_2 from the anisotropy of some second rank tensor \mathbf{F} (e.g. the dipolar coupling between two nuclei) it is much more difficult to find a tensor quantity of higher rank which can be measured directly. One is then forced to resort to somewhat indirect methods. For example the fourth rank order parameter \bar{P}_4 can be extracted from measurements of the mean square value of a second rank quantity [11,12]. In the limit of cylindrical symmetry, we have, in fact,

$$\overline{(F^{(2,0)})^2} = \{(1/5) + (2/7)\bar{P}_2 + (18/35)\bar{P}_4\} (F^{(2,0)})^2. \quad (60)$$

In the Raman scattering technique described by Pershan [11], in Chapter 17 the molecular quantity \mathbf{F} is the differential polarizability tensor for a certain localized Raman mode.

Information about all the parameters is contained, in principle, in the single molecule coherent contribution $(d\sigma/d\Omega)_s^{\text{coh}}$ to the cross section for neutrons scattered by a monodomain nematic [13,14]. In fact, assuming that the nematogenic molecules are rigid, we have

$$(d\sigma/d\Omega)_s^{\text{coh}} = \sum_{i,j} a_i a_j \overline{\exp(i\mathbf{Q} \cdot \mathbf{r}_{ij})}, \quad (61)$$

where \mathbf{Q} is the scattering vector, \mathbf{r}_{ij} the vector joining nuclei i and j , which have bound coherent scattering lengths a_i and a_j respectively.

Rayleigh expansion of the exponential gives

$$\overline{\exp(i\mathbf{Q}\cdot\mathbf{r}_{ij})} = \sum (i)^L (2L+1) j_L(Qr_{ij}) \overline{D_{0,0}^L(Q-r_{ij})}, \quad (62)$$

where we use the notation $D_{m,n}^L(B-A)$ to indicate a rotation from A to B; e.g. here, from \mathbf{r}_{ij} to \mathbf{Q} . $j_L(Qr_{ij})$ is a spherical Bessel function of rank L. Using the properties of the Wigner rotation matrices we can write

$$\begin{aligned} \overline{D_{0,0}^L(Q-r_{ij})} &= \overline{\sum D_{m,0}^L(r_{ij}-L) D_{m,0}^{L*}(Q-L)}, \\ &= \overline{\sum D_{m,n}^L(M-L) D_{n,0}^L(r_{ij}-M) D_{m,0}^{L*}(Q-L)}, \end{aligned} \quad (63)$$

where $D_{m,n}^L(M-L)$ indicates a rotation from a laboratory to a molecule fixed frame. For a uniaxial mesophase and cylindrically symmetric molecules we have $\overline{D_{m,n}^L} = \bar{P}_L \delta_{m0} \delta_{n0}$ if the laboratory z axis is along the director and the molecular z axis is parallel to the axis of cylindrical symmetry. Substitution in eq. (62) gives eventually the desired expression for the cross section in terms of the order parameters

$$(d\sigma/d\Omega)_s^{\text{coh}} = \sum \{a_i a_j (i)^L (2L+1) j_L(Qr_{ij}) \overline{D_{0,0}^L(Q-L)} \overline{D_{0,0}^L(r_{ij}-M)} \bar{P}_L\}. \quad (64)$$

Molecular Symmetry and Mesophase Symmetry

As we have seen in the previous section the general expansion of the singlet orientational distribution $f(\Omega)$ can be simplified when the mesophase and its constituent molecules are both cylindrically symmetric. In general, however, the exploitation of the symmetry of the molecule and the phase is not quite so intuitive. Thus we wish to introduce a formal procedure for determining the independent order parameters. Admittedly, we have not yet defined what we mean by the symmetry of a phase. This problem was recently discussed by Goshen *et al.* [15]. They noticed that Landau's original suggestion [2c] of defining the symmetry of a fluid as that of the singlet distribution $P^{(1)}(\mathbf{r})$ and that of nematics by the symmetry of $P^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is inadequate, but they did not propose an alternative definition. However, following our approach it seems clear that Landau's definition only needs generalization to the case of anisotropic particles. We shall therefore define the symmetry group of a phase as the group of transformations of the laboratory system that leave the singlet distribution $P^{(1)}(\mathbf{r}, \Omega)$ as well as the higher ones invariant. Similarly, we can define an effective symmetry for the molecule in terms of the group of molecular transformations leaving the singlet distribution unchanged.

The same considerations hold, of course, for the purely orientational

distribution $f(\Omega)$ which is of primary concern to us. In group theoretical language [16] we would say that $f(\Omega)$ belongs to the totally symmetric representation of the group of the molecule and of the mesophase. Therefore one way of applying symmetry is to project the distribution onto the totally symmetric representation of these groups [8,16-18]. We shall actually use this method in a later section to simplify the pair distribution. Another way, strictly related to the previous one, which we find convenient for the simplification of order parameters depends on their definition;

$$\overline{D_{m,n}^L} = \int d\Omega f(\Omega) D_{m,n}^L(\Omega). \quad (65)$$

Now a symmetry transformation O does not alter $\int d\Omega$ and also leaves $f(\Omega)$ invariant. It then follows that the action of O on the order parameters depends solely on its effect on the Wigner rotation matrices. Since these are just a representation of the rotation $D(\alpha\beta\gamma)$ in an angular momentum basis $|Lm\rangle$;

$$D_{m,n}^L(\alpha\beta\gamma) \equiv \langle Lm | D(\alpha\beta\gamma) | Ln \rangle,$$

it follows that to investigate the effect of a molecular symmetry operation O_M we need to determine the matrix elements

$$\langle Lm | \overbrace{O_M D(\Omega)} | Ln \rangle.$$

Similarly, the application of a laboratory transformation such as a symmetry operation of the mesophase O_L yields

$$\langle Lm | O_L D(\Omega) | Ln \rangle.$$

Every symmetry operation for the molecule or for the phase gives a relation that the order parameters have to satisfy, that is

$$\overline{D_{m,n}^L} = \overline{\langle Lm | \overbrace{O_M D(\Omega)} | Ln \rangle}, \quad (66)$$

for the molecule and

$$\overline{D_{m,n}^L} = \overline{\langle Lm | O_L D(\Omega) | Ln \rangle}, \quad (67)$$

for the phase. Any point operation can be written as a certain combination of rotations and inversion. Let us consider therefore each of these at a time. Thus suppose that the symmetry operation of the mesophase O_L is a rotation; then it will transform the original laboratory frame L into another frame L' and give

$$\begin{aligned} \langle Lm | O_L D(M-L) | Ln \rangle &= \langle Lm | D(L-L') D(M-L) | Ln \rangle, \\ &= \sum_q D_{m,q}^L(L-L') D_{q,n}^L(M-L), \end{aligned} \quad (68)$$

where for greater clarity we have written the rotation from the laboratory to the molecular frame as $D(M-L)$ instead of $D(\Omega)$. Quite analogously, if the molecule has a rotation O_M amongst its symmetry operations, we find

$$\begin{aligned} \langle Lm | O_M D(M-L) | Ln \rangle &= \langle Lm | D(M-L) D(M'-M) | Ln \rangle, \\ &= \sum_q D_{m,q}^L(M-L) D_{q,n}^L(M'-M). \end{aligned} \quad (69)$$

Notice that successive rotations D are applied in reverse order, that is from left to right (cf. the Appendix, eq. A8). If a symmetry operation O contains the inversion operation, I , it is clear that to investigate its effect we also need the matrix elements $\langle Lm | I | Ln \rangle$. These are obtained by remembering [16a] that $I | Lm \rangle = (-)^L | Lm \rangle$. Therefore [17]

$$\langle Lm | I | Ln \rangle = (-)^L \delta_{mn}. \quad (70)$$

The inversion and rotation operations commute:

$$\begin{aligned} \langle Lm | ID | Ln \rangle &= \sum_q \langle Lm | I | Lq \rangle \langle Lq | D | Ln \rangle, \\ &= (-)^L D_{m,n}^L, \\ &= \langle Lm | DI | Ln \rangle. \end{aligned}$$

Therefore, for our purposes, the inversion has the same effect in either a laboratory or a molecular frame.

Let us illustrate the previous arguments with a simple example. Suppose that the mesophase has a plane of symmetry perpendicular to the z axis, that is $O_L = \sigma_h = \sigma(xy)$. Since we can write [16] $\sigma(xy) = ID(\pi 00)$ we find

$$\begin{aligned} \langle Lm | \sigma(xy)_L D | Ln \rangle &= \sum_q \langle Lm | I | Lq \rangle \langle Lq | D(\pi 00) | Lp \rangle \langle Lp | D | Ln \rangle, \\ &= (-)^L \delta_{mq} \exp(-iq\pi) \delta_{qp} D_{p,n}^L, \\ &= (-)^{L+m} D_{m,n}^L. \end{aligned}$$

A symmetry plane $\sigma(xy)$ in the molecule would give instead

$$\langle Lm | \sigma(xy)_M D | Ln \rangle = (-)^{L+n} D_{m,n}^L.$$

Proceeding in a similar way we obtain the results reported in Table 1 for the effect of various molecular symmetry operations on the Wigner functions. The effect of mesophase symmetries can also be easily obtained from Table 1 remembering that the order of operations is changed so that for example, the first subscript, m , in $D_{m,n}^L$ is changed instead of n .

Table 1 Effect of various molecular symmetry operations O_M on the Wigner rotation matrices. The notation for the symmetry operators [16e] is as follows. I stands for the inversion; $\sigma(xy)$ for a symmetry plane perpendicular to z ; σ_ϕ for a plane making an angle ϕ with (zx) . A rotation of $2\pi/k$ about z is written as $C_k(z)$ and a continuous rotation of γ about z as $C_\gamma(z)$. A rotation of π about an axis perpendicular to z and making an angle ϕ with x is indicated by $C_2(\phi)$. S_k stands for a k -fold rotoreflection axis.

Operator O_M	$\langle Lm O_M D Ln \rangle$
$I = S_2$	$(-)^L D_{m,n}^L$
$\sigma(xy)$	$(-)^{L+n} D_{m,n}^L$
$\sigma(xz)$	$(-)^n D_{m,-n}^L$
$\sigma(yz)$	$D_{m,-n}^L$
σ_ϕ	$(-)^n \exp(-i2n\phi) D_{m,-n}^L$
$C_2(z)$	$(-)^n D_{m,n}^L$
$C_k(z)$	$\exp(-in2\pi/k) D_{m,n}^L$
$C_\gamma(z)$	$\exp(-in\gamma) D_{m,n}^L$
$C_2(x)$	$(-)^L D_{m,-n}^L$
$C_k(x)$	$(-)^{L-n} \exp(-in2\pi/k) D_{m,-n}^L$
$C_\gamma(x)$	$(-)^{L-n} \exp(-in\gamma) D_{m,-n}^L$
$C_2(y)$	$(-)^{L-n} D_{m,-n}^L$
$C_\beta(y)$	$\sum_q D_{m,q}^L d_{q,n}^L(\beta)$
$C_2(\phi)$	$(-)^L \exp(-i2n\phi) D_{m,-n}^L$
S_k	$(-)^{L+n} \exp(-in2\pi/k) D_{m,n}^L$

Having studied the effect of symmetry transformations on the Wigner rotation matrices it remains to substitute eqs.(66) and (67) to obtain the corresponding symmetries of the order parameters. Thus, in the example we have just seen, a $\sigma(xy)$ plane in the laboratory gives

$$\overline{D}_{m,n}^L = (-)^{L+m} \overline{D}_{m,n}^L,$$

while a $\sigma(xy)$ operation in the molecule yields

$$\overline{D}_{m,n}^L = (-)^{L+n} \overline{D}_{m,n}^L.$$

In general an additional symmetry for the order parameters follows immediately from the reality of $f(\Omega)$ and the relation $D_{m,n}^{L*} = (1)^{m-n} D_{-m,-n}^L$ for the Wigner functions. Thus

$$\overline{D}_{m,n}^{L*} = (-)^{m-n} \overline{D}_{-m,-n}^L. \quad (71)$$

The symmetry relations just determined allow us to find the relevant order parameters for molecules and phases of various symmetry. As an example we give in Table 2 the surviving order parameters of second and fourth rank for a uniaxial phase and various molecular symmetries. Finally, it is perhaps worth mentioning that the relations we have found only tell us about the order parameters that can be different from zero. Thus they indicate which order parameters we can try to measure but, of course, do not say anything about their magnitudes. Indeed it may well turn out that molecules of low symmetry exhibit order parameters consistent, within experimental error, with some higher symmetry.

Ordering Matrix

An alternative definition for order parameters in uniaxial phases can be obtained by expanding the singlet orientational distribution $f(\Omega)$ in terms of the direction cosines l_α ($\alpha = x, y, z$) of the director with respect to a molecule fixed frame [19]. Thus

$$f(\Omega) = (1/8\pi^2) \{1 + 5 \sum_{\alpha,\beta} S_{\alpha\beta} l_\alpha l_\beta + 9 \sum_{\alpha,\beta,\gamma,\delta} S_{\alpha\beta\gamma\delta} l_\alpha l_\beta l_\gamma l_\delta + \dots\}, \quad (72)$$

where

$$S_{\alpha\beta} = (3\overline{l_\alpha l_\beta} - \delta_{\alpha\beta})/2 \quad (73)$$

is called the Saupe ordering matrix and

$$S_{\alpha\beta\gamma\delta} = [35\overline{l_\alpha l_\beta l_\gamma l_\delta} - 5(\overline{l_\alpha l_\beta} \delta_{\gamma\delta} + \overline{l_\alpha l_\gamma} \delta_{\beta\delta} + \overline{l_\alpha l_\delta} \delta_{\beta\gamma} + \overline{l_\beta l_\gamma} \delta_{\alpha\delta} + \overline{l_\beta l_\delta} \delta_{\alpha\gamma} + \overline{l_\gamma l_\delta} \delta_{\alpha\beta}) + (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma})]/8. \quad (74)$$

In general, expansions in Wigner matrices are more convenient for theoretical manipulations in view of their simple transformation properties. However the ordering matrix is used almost universally, as for example in nuclear magnetic resonance, so we give in Table 3 the relation between $S_{\alpha\beta}$ and $D_{0,n}^2$. Notice that from eq. (73) it follows at once that the second rank S matrix is traceless

$$\sum_{\alpha} S_{\alpha\alpha} = 0.$$

Table 2. Independent orientational order parameters of second and fourth rank for uniaxial phases and molecules of various symmetry. n_2 and n_4 indicate the number of independent real quantities to be determined. Schönflies notation is used for the point group symbols.

Molecular point group	n_2	$\overline{D}_{0,n}^2$	n_4	$\overline{D}_{0,n}^4$
C_1, C_i	5	$\overline{D}_{0,0}^2, \overline{D}_{0,1}^2, \overline{D}_{0,2}^2$	9	$\overline{D}_{0,0}^4, \overline{D}_{0,1}^4, \overline{D}_{0,2}^4, \overline{D}_{0,3}^4, \overline{D}_{0,4}^4$
C_S, C_2, C_{2h}	3	$\overline{D}_{0,0}^2, \overline{D}_{0,2}^2$	5	$\overline{D}_{0,0}^4, \overline{D}_{0,2}^4, \overline{D}_{0,4}^4$
C_{2v}, D_2, D_{2h}	2	$\overline{D}_{0,0}^2, \overline{D}_{0,2}^2 = \overline{D}_{0,2}^{2*}$	3	$\overline{D}_{0,0}^4, \overline{D}_{0,2}^4 = \overline{D}_{0,2}^{4*}, \overline{D}_{0,4}^4 = \overline{D}_{0,4}^{4*}$
C_3, S_6	1	$\overline{D}_{0,0}^2$	3	$\overline{D}_{0,0}^4, \overline{D}_{0,3}^4$
C_4, C_{4h}, S_4	1	$\overline{D}_{0,0}^2$	3	$\overline{D}_{0,0}^4, \overline{D}_{0,4}^4$
C_{3v}, D_3, D_{3d}	1	$\overline{D}_{0,0}^2$	2	$\overline{D}_{0,0}^4, \overline{D}_{0,3}^4 = \overline{D}_{0,3}^{4*}$
$C_{4v}, D_{2d}, D_{4h}, D_4$	1	$\overline{D}_{0,0}^2$	2	$\overline{D}_{0,0}^4, \overline{D}_{0,4}^4 = \overline{D}_{0,4}^{4*}$
C_5, C_{5h}, C_{5v}	1	$\overline{D}_{0,0}^2$	1	$\overline{D}_{0,0}^4$
$D_{4d}, D_5, D_{5h}, D_{5d}$	1	$\overline{D}_{0,0}^2$	1	$\overline{D}_{0,0}^4$
$C_{3h}, C_6, C_{6h}, C_{6v}$	1	$\overline{D}_{0,0}^2$	1	$\overline{D}_{0,0}^4$
$D_{3h}, D_6, D_{6h}, D_{6d}$	1	$\overline{D}_{0,0}^2$	1	$\overline{D}_{0,0}^4$
$C_\infty, C_{\infty v}, C_{\infty h}, D_{\infty h}$	1	$\overline{D}_{0,0}^2$	1	$\overline{D}_{0,0}^4$
T, T_h, T_d, O, O_h	0		1	$\overline{D}_{0,0}^4$
Y, Y_h, K, K_h	0		0	

Table 3 *The relation between Saupe's ordering matrix elements $S_{\alpha\beta}$ and the order parameters $D_{0,n}^2$*

$$\begin{aligned}
 S_{zz} &= \overline{D_{0,0}^2} \\
 S_{xx} - S_{yy} &= (6)^{\frac{1}{2}} \operatorname{Re} \overline{D_{0,2}^2} = (3/2)^{\frac{1}{2}} (\overline{D_{0,2}^2} + \overline{D_{0,-2}^2}) \\
 S_{xy} &= -(3/2)^{\frac{1}{2}} \operatorname{Im} \overline{D_{0,2}^2} = i (3/8)^{\frac{1}{2}} (\overline{D_{0,-2}^2} - \overline{D_{0,2}^2}) \\
 S_{xz} &= -(3/2)^{\frac{1}{2}} \operatorname{Re} \overline{D_{0,1}^2} = (3/8)^{\frac{1}{2}} (\overline{D_{0,-1}^2} - \overline{D_{0,1}^2}) \\
 S_{yz} &= (3/2)^{\frac{1}{2}} \operatorname{Im} \overline{D_{0,1}^2} = i (3/8)^{\frac{1}{2}} (\overline{D_{0,1}^2} + \overline{D_{0,-1}^2})
 \end{aligned}$$

Smectics

In a system with some translational order the distribution functions depend on position as well as orientation. We consider here the singlet distribution $P^{(1)}(\mathbf{r}, \Omega)$ for such systems and introduce order parameters for smectic phases. We shall assume, for simplicity, that the system is contained in a large cubic box of edge λ . Then the functions $\psi_{\mathbf{k}} = \lambda^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r})$, where the lattice vector \mathbf{k} has components $k_{\alpha} = 0, \pm 2\pi/\lambda, \pm 4\pi/\lambda, \dots, \pm n2\pi/\lambda$, $\alpha = x, y, z$, constitute a suitable orthonormal set and we can write

$$P^{(1)}(\mathbf{r}, \Omega) = \sum P_{Lmn}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) D_{m,n}^L(\Omega), \quad (75)$$

with

$$P_{Lmn}(\mathbf{k}) = \{(2L+1)/8\pi^2 V\} \int_V d\mathbf{r} d\Omega P^{(1)}(\mathbf{r}, \Omega) \exp(-i\mathbf{k} \cdot \mathbf{r}) D_{m,n}^{L*}(\Omega), \quad (76)$$

because of the orthogonality condition

$$(1/\lambda^3) \int_V d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) \exp(-i\mathbf{k}' \cdot \mathbf{r}) = \delta(\mathbf{k} - \mathbf{k}'). \quad (77)$$

Eq. (75) is a very general expression which holds in principle for crystals, smectics and nematics as special cases. Thus for a monoatomic lattice, $L = m = n = 0$, we have the Fourier expansion [2c]

$$P^{(1)}(\mathbf{r}, \Omega) = \sum P_{000}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (78)$$

where \mathbf{k} is a vector in reciprocal space and the spatial integrations in eq. (76) can be limited to the repeat unit. For a uniform nematic or an isotropic liquid eq. (75) becomes

$$P^{(1)}(\mathbf{r}, \Omega) = \sum P_{Lmn}(0) D_{m,n}^L(\Omega). \quad (79)$$

Here the container size is assumed to be large, in the sense that $\lambda \rightarrow \infty$, so that finite size effects are negligible and we can only have $\mathbf{k}=0$.

For a smectic phase with positional order in one dimension only (e.g. a smectic A or C phase) we can restrict the series (75) to

$$P^{(1)}(z, \Omega) = \sum P_{Lmn}(k) \exp(ikz) D_{m,n}^L(\Omega), \quad (80)$$

where $k \equiv k_z$ and z is parallel to the layer normal. The expansion can be simplified by using the symmetry of the molecule and the mesophase. For example in a smectic A, with uniaxial symmetry about z ,

$$P^{(1)}(z, \Omega) = \sum P_{L0n}(k) \exp(ikz) D_{0,n}^L(\Omega). \quad (81)$$

Now suppose that the phase also has a symmetry plane $\sigma(xy)$, perpendicular to the z direction; then

$$P_{L0n}(k) = (-)^L P_{L0n}(-k).$$

Consequently, for $k=0$, this implies that L has to be even. If L is even because of molecular symmetry then $P_{L0n}(k) = P_{L0n}(-k)$ and eq. (81) can be reduced to

$$P^{(1)}(z, \Omega) = \sum_{M=0}^{\infty} \sum (2-\delta_{M0}) P_{L0n}(2\pi M/d) \cos(2\pi Mz/d) D_{0,n}^L(\Omega), \quad (82)$$

where d is the average interlayer spacing and the notation $|k| = (2\pi M/d)$ has been introduced. Of course, for cylindrically symmetric ($D_{\infty h}$) molecules, this reduces to the expression given by Wojtowicz [1b],

$$P(z, \cos\beta) = \sum_{\substack{M=0 \\ L=0}}^{\infty} P_{L;M} \cos(2\pi Mz/d) P_L(\cos\beta), \quad L \text{ even}, \quad (83)$$

which we normalize so that

$$\int_0^d dz \int_0^\pi d\beta \sin\beta P(z, \cos\beta) = N. \quad (84)$$

Then

$$P_{L;M} = (2L+1) \langle \cos(2\pi Mz/d) P_L(\cos\beta) \rangle / 2d, \quad (85)$$

$$P_{0;0} = N/d, \quad (86)$$

$$P_{0;M} = \langle \cos(2\pi Mz/d) \rangle / 2d, \quad (87)$$

$$P_{L;0} = (2L+1) \langle P_L \rangle / 2d, \quad (88)$$

where

$$\langle A \rangle = \int_0^d dz \int_0^\pi d\beta \sin\beta P(z, \cos\beta) A(z, \cos\beta) / N \quad (89)$$

and the coefficients $P_{L;M}$ represent the order parameters for the system. In particular the terms $P_{0;M}$ and $P_{L;0}$ give the positional and orientational order respectively.

Orientalional Order Parameters for More Complex Phases

A group theoretical classification of all the possible ordered phases has been given by Goshen *et al.* [15]. Here, however, we do not want to give all the possible order parameters for every phase; instead we begin by making some general remarks, and then say something about the smectic C phase. Firstly we point out that phases possessing translational order should be given a space group like classification [15]. Thus the symmetrization of the distribution functions and of the order parameters should be done by applying all the operations of the relevant space group. This can be rather involved. Notice, however, that the purely orientational order parameters, which define the distribution $f(\Omega)$, (cf. eq. 53) can be classified simply according to the point group for the system. This is, of course, because the purely orientational order parameters are invariant under translation; they correspond to $k=0$ in expansion (75). Thus to find out the orientational parameters for a phase of a given crystallographic point group we can use exactly the same arguments as before. Consider an ideal smectic C for example. This phase is a tilted version of the smectic A phase, where the director or major optic axis make an angle θ , known as the tilt angle, with the layer normal. The point group of this model is then C_{2h} , with Z parallel to the layer and Y parallel to the layer normal; here we use X, Y, Z for the laboratory frame. According to Table 1 the symmetry operations of C_{2h} give

$$\overline{D_{m,n}^L} = (-)^m \overline{D_{m,n}^L} = (-)^{L+m} \overline{D_{m,n}^L}; \quad (90)$$

thus L and m have to be even. For second rank the possible order parameters should then be

$$\overline{D_{0,n}^2} ; \overline{D_{2,n}^2} = (-)^n \overline{D_{-2,n}^{2*}}. \quad (91)$$

Notice that, even if the particles constituting the phase have cylindrical symmetry, we still have two independent order parameters, corresponding to the biaxiality of the phase. This is perhaps more transparent in cartesian coordinates. Let us define an ordering matrix Q

$$Q_{\alpha\beta} = (3\overline{\ell_\alpha \ell_\beta} - \delta_{\alpha\beta})/2 \quad (92)$$

formally identical to the Saupe ordering matrix. However, here it is the phase that is not cylindrically symmetric instead of the particles, and so we take ℓ_α to be the direction cosines for a molecule in the laboratory frame. Now, from the assumed symmetry of the smectic C it is clear that

$$\mathbf{Q} = \begin{pmatrix} Q_{XX} & Q_{XY} & 0 \\ Q_{XY} & Q_{YY} & 0 \\ 0 & 0 & Q_{ZZ} \end{pmatrix}. \quad (93)$$

This can be diagonalized by a rotation of θ about Z , provided $\tan 2\theta = 2Q_{XY}/(Q_{XX}-Q_{YY})$. The angle θ is just the tilt angle, which represents the orientation of the director in the (XY) plane. The diagonalized form of \mathbf{Q} is

$$\mathbf{Q} = \begin{pmatrix} -\frac{1}{2}Q_{ZZ} + \xi & 0 & 0 \\ 0 & -\frac{1}{2}Q_{ZZ} - \xi & 0 \\ 0 & 0 & Q_{ZZ} \end{pmatrix},$$

where $\xi = \frac{1}{2}\{(Q_{XX}-Q_{YY})^2 + 4Q_{XY}^2\}^{\frac{1}{2}}$ is a biaxiality parameter.

Pair Distribution

In the previous section we have seen how symmetry can be used to limit the number of order parameters and hence the possible form of the singlet distribution function. Similar arguments can be applied to the pair distribution $G(X_1, X_2)$ or, rather, $G(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ since we shall confine our attention to translationally invariant liquid crystals and so ignore the smectic phases. We use the methods developed by Steele [8], Jepsen and Friedman [18] and Blum and Torruella [17] for ordinary fluids. Let us start by noticing that $G(\mathbf{r}_{12}, \Omega_1, \Omega_2)$ when written in a laboratory frame has to depend on the intermolecular separation r_{12} as well as the orientations Ω_1, Ω_2 of molecules 1 and 2, together with the orientation of the intermolecular vector Ω_r . Therefore we can write down immediately

$$G(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \sum G_{L_1 L_2}^{m_1 m_2 m; n_1 n_2}(\mathbf{r}_{12}) D_{m_1, n_1}^{L_1}(\Omega_1) D_{m_2, n_2}^{L_2}(\Omega_2) D_{m, o}^L(\Omega_r), \quad (94)$$

where this distribution should be invariant under the symmetry operations of the molecules and of the phase. Moreover permutation of identical molecules should leave G unaltered. We can therefore symmetry adapt G so that it transforms according to the totally symmetric representation of the group of transformations just mentioned. Projection onto the totally symmetric representation of a group can be achieved [8,16] by application of a projection operator P

$$P = (1/n_s) \sum_{s=1}^{n_s} O_s, \quad (95)$$

for a group of n_s transformations O_s . For a continuous group eq. (95) becomes

$$P = (1/\int ds) \int ds O_s \quad (96)$$

with an obvious change of notation.

It is clear that application of P to eq. (94) again requires investigating the effect of the operations O_s on the Wigner functions. Since we have already examined the effect of rotations and reflections the only new effect we have to study is that of permuting 1 and 2. This is rather easy, since, apart from exchanging subscripts, the permutation transforms r_{12} in $r_{21} = -r_{12}$ and then $D_{m,o}^L(r-L)$ into $(-)^L D_{m,o}^L(r-L)$. Thus, for identical molecules, we obtain the condition

$$G_{L_1 L_2 L}^{m_1 m_2 m; n_1 n_2}(r) = (-)^L G_{L_2 L_1 L}^{m_2 m_1 m; n_2 n_1}(r). \quad (97)$$

Consider a rotationally invariant fluid, such as a nematic above its clearing point or an unoriented nematic. In this case the phase symmetry is that of the full rotation group and the projector P is simply $(1/8\pi^2) \int d\Omega D(\Omega)$. Application of P gives

$$G(r_{12}, \Omega_1, \Omega_2) = \int G_{L_1 L_2 L}^{m_1 m_2 m; n_1 n_2} D_{q_1 n_1}^{L_1}(\Omega_1) D_{q_2, n_2}^{L_2}(\Omega_2) D_{q, o}^L(\Omega_r) \\ \times \int d\Omega D_{m_1, q_1}^{L_1} D_{m_2, q_2}^{L_2} D_{m, q}^L / 8\pi^2. \quad (98)$$

Use of the result for the integral of three rotation matrices [20] (cf. eq. A6) yields the most general form for the rotationally invariant distribution G as

$$G(r_{12}, \Omega_1, \Omega_2) = \int G_{L_1 L_2 L}^{q_1 q_2; n_1 n_2}(r_{12}) D_{q_1, n_1}^{L_1}(\Omega_1) D_{q_2, n_2}^{L_2}(\Omega_2) D_{-q_1 - q_2, o}^L(\Omega_r), \quad (99)$$

where

$$G_{L_1 L_2 L}^{q_1 q_2; n_1 n_2}(r_{12}) = \{(-)^{m - q_1 - q_2} / (2L+1)\} C(L_1 L_2 L; m_1 m_2) C(L_1 L_2 L; q_1 q_2) \delta_{m_1 + m_2, -m} \\ \times G_{L_1 L_2 L}^{m_1 m_2 m; n_1 n_2}(r_{12}) \quad (100)$$

and $C(abc; de)$ are Clebsch-Gordan coefficients [3]. Notice that the requirement of rotational invariance has severely limited the form of eq. (94); in fact the Clebsch-Gordan coefficients cause the ranks L_1, L_2, L to satisfy the triangular condition; $|L_1 - L_2| \leq L \leq L_1 + L_2$.

Let us now make the further assumption that the intermolecular vector is spherically distributed so that rotating r_{12} does not change G . A projection similar to the previous one gives $\delta_{L,0} \delta_{q_1, -q_2}$ in eq. (99). Since $C(L_1 L_2 0; q-q) = (-)^{L_1 - q} (2L_1 + 1)^{-\frac{1}{2}} \delta_{L_1 L_2}$, we find

$$G(r_{12}, \Omega_1, \Omega_2) = \sum (-)^q G_L^{n_1 n_2}(r_{12}) D_{q, n_1}^L(\Omega_1) D_{-q, n_2}^L(\Omega_2) (2L+1)/64\pi^4, \quad (101)$$

where

$$G_L^{n_1 n_2}(r_{12}) = \sum (-)^{m_1} G_{LLO}^{m_1 -m_1 0; n_1 n_2} (8\pi^2/2L+1)^2 \quad (102)$$

and we have removed unnecessary subscripts. Eq. (101) can be written in a more transparent form by using the property

$$D_{q, n_1}^L(\Omega_1) = D_{n_1, q}^{L*}(-\Omega_1), = (-)^{n_1 - q} D_{-n_1, -q}^L(-\Omega_1)$$

and the closure of the Wigner functions eq. (A8). Thus we find

$$G(r_{12}, \Omega_1, \Omega_2) = \sum (-)^{n_1} \{(2L+1)/64\pi^4\} G_L^{n_1 n_2}(r_{12}) D_{-n_1, n_2}^L(\Omega_{12}), \quad (103)$$

where Ω_{12} is the angle of rotation from molecule 1 to molecule 2. This shows that for a rotationally invariant fluid the reduced pair distribution $G(r_{12}, \Omega_1, \Omega_2)$, which does not depend on the orientation of the intermolecular vector must be a function of relative orientations only. The same conclusion obviously applies to $G(r_{12}, \Omega_1, \Omega_2)$ for any fluid where the distribution of intermolecular vectors is spherically symmetric. For such a situation, if the molecules are cylindrically symmetric, $n_1 = n_2 = 0$ and

$$G(r_{12}, \Omega_1, \Omega_2) = G(r_{12}, \Omega_{12}), = \sum \{(2L+1)/64\pi^4\} G_L^{00}(r_{12}) D_{0,0}^L(\Omega_{12}). \quad (104)$$

This simple equation has some important features. First of all because it is fully rotationally invariant it can be used to describe the onset of orientational order at an isotropic-nematic transition in the absence of external fields. Remember in fact that when we have introduced order parameters from the singlet distribution we have, more or less, assumed implicitly the existence of an aligned mesophase with a uniform director. This, in turn, implies the existence of an external field to break the full rotational symmetry of the mesophase above the isotropic transition. While this is perfectly legitimate it would be more satisfactory to be able to discuss how long-range ordering is set up in a system for which the nematic phase had been formed in the absence of a field. It is physically intuitive that to do this we have to resort to the pair distribution since this can tell us about the extent of orientational correlations without having to resort to a laboratory principal axis system.

Let us interpret the coefficients $G_L^{00}(r_{12})$ in expansion (104). From the definition of $G(r_{12}, \Omega_{12})$ and the orthogonality of the Legendre poly-

nomials we find

$$\begin{aligned}
 G_L(r_{12}) &= \int d\Omega_1 d\Omega_2 G(r_{12}, \Omega_{12}) D_{0,0}^L(\Omega_{12}), \\
 &= \overline{P_L\{\cos\beta_{12}(r_{12})\}} G_0^{00}(r_{12}), \\
 &\equiv G_L^{00}(r_{12}) G_0^{00}(r_{12}). \tag{105}
 \end{aligned}$$

Thus $G_L(r_{12})$ is an L th rank angular correlation. For $L=0$,

$$G_0^{00}(r_{12}) = \int d\Omega_1 d\Omega_2 G(r_{12}, \Omega_{12}),$$

is simply the centre of mass pair distribution. Any $G_L(r_{12})$ with $L \neq 0$, say $G_2(r_{12})$, expresses the correlation in orientation between a molecule at the origin and another, distance r_{12} from it; we have, of course $G_L(0) = 1$. For short interparticle separations *e.g.* when r_{12} is the average nearest neighbour distance, $G_2(r_{12})$ can be taken to define the short-range order. For large separations $G_2(r_{12})$ is a measure of the long-range order. In this limit the pair distribution $G(r_{12}, \Omega_2, \Omega_2)$ reduces to the product of two singlet orientational distribution functions $f(\Omega_1)f(\Omega_2)$ (cf. eq. 36) and, similarly, the symmetrized distribution $PG(r_{12}, \Omega_1, \Omega_2)$ tends to the symmetrized product $P\{f(\Omega_1)f(\Omega_2)\}$. For a rotationally invariant phase we have

$$P\{f(\Omega_1)f(\Omega_2)\} = \sum \{(2L+1)/64\pi^4\} \overline{D_{n_1, n_2}^L(\Omega_{12})} D_{n_1, n_2}^L(\Omega_{12}), \tag{106}$$

with $n_1 = n_2 = 0$ for uniaxial molecules. Thus we find

$$G_L(r_{12}) = \overline{D_{q,0}^{L*}(\Omega_1)} \overline{D_{q,0}^L(\Omega_2)}, \tag{107}$$

for large r_{12} . Now, if r_{12} is a separation much larger than any molecular distance but small compared to the coherence length of the director we obtain

$$\begin{aligned}
 G_L(r_{12}) &= \overline{D_{0,0}^L(\Omega_1)} \overline{D_{0,0}^L(\Omega_2)} \\
 &= \overline{P}_L^2, \tag{108}
 \end{aligned}$$

for large r_{12} when we assume local uniaxial symmetry. Thus we expect the behaviour of, say, $G_2(r_{12})$ to change dramatically at the nematic-isotropic transition. Above the clearing point in fact $G_2(r_{12})$ should decay to zero with distance while in the nematic phase it should tend to the square of the order parameter. This trend is apparent in our computer simulations [21] described in Chapter 9 of the Maier-Saupe-Lasher[22]

lattice model, where we find that in the ordered phase $G_2(r_{12})$ decays to a plateau value of \overline{P}_2^{-2} after a relatively short distance corresponding to a few shells of neighbours.

Let us add a few cautionary words, however, on what we mean by the large distance limit in eq. (107). We have mentioned before that the separation r_{12} although large compared to molecular distances, should be small compared to the coherence length of the director. This is, of course, because in an unoriented nematic and for truly macroscopic separations r_{12} the director will have to arrange itself to preserve the spherical symmetry of the phase. Thus for distances greater than some coherence length the correlation will be apparently lost. In the same way there is no net macroscopic order in an unoriented nematic while there is a long-range order given by the plateau of $G_2(r_{12})$.

Another advantage of introducing the pair correlation coefficients $G_L(r_{12})$ is that they can be used to describe the pretransitional effects associated with the onset of ordering in the isotropic phase when approaching the nematic transition. In this connection it is useful to define a coefficient G_L by

$$\begin{aligned} G_L &\equiv \int dr_{12} r_{12}^2 G_L(r_{12}), \\ &= \int dr_{12} r_{12}^2 d\Omega_1 d\Omega_2 G(r_{12}, \Omega_{12}) P_L\{\cos\beta_{12}(r_{12})\}, \end{aligned}$$

as the area under the correlation $r^2 G_L(r)$. They can be used to describe experiments in the pretransitional region such as the optical birefringence induced by a strong electric field (Kerr effect).

Nematics and Cholesterics

To examine briefly some differences between nematics and cholesterics, let us go back to the expansion (101) for a rotationally invariant phase. If the fluid is also centrosymmetric the pair distribution has to be invariant under inversion. Therefore we have for such a system that $(L_1 + L_2 + L)$ has to be even in eq. (101). The same is not true if the fluid is formed by optically active molecules. Thus for cholesterics we have that $(L_1 + L_2 + L)$ can be odd as well. The presence of these odd terms indicates that the probability of finding two molecules at a given orientation can depend also on the sign of the angle of the second molecule with respect to the first. In other words the presence of odd terms means that the characteristic twist of cholesterics can be obtained. This aspect is described in greater detail in Chapter 5.

Acknowledgement

It is a pleasure to thank Professor G.R. Luckhurst for many stimulating and valuable discussions. This work was supported in part by Laboratorio C.N.R. (Ozzano E.).

Appendix

Irreducible tensors and Wigner rotation matrices

A tensor of rank n is a quantity that transforms under rotation as the n th direct power of a vector. The 3^n dimensional representation of the rotation group realized in this way can be decomposed into a set of irreducible representations $D^{(L)}$ each of dimension $(2L+1)$. If we describe the rotations in terms of Euler angles $(\alpha\beta\gamma)$ (cf. Chapter 17) then the matrix elements of the irreducible representation in a basis where J^2 , J_z (*i.e.* the angular momentum and its projection) are diagonal, are [3]

$$D_{m,n}^L(\alpha\beta\gamma) = \langle Lm | e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} | Ln \rangle. \quad (A1)$$

The matrix elements $D_{m,n}^L(\alpha\beta\gamma)$ are called Wigner rotation matrices, Wigner functions or generalized spherical harmonics. Combinations of ordinary tensor components transforming according to the representation $D^{(L)}$ are called irreducible tensor components of rank L and denoted by $T^{(L,m)}$, *e.g.*

$$T^{(L,m)'} = \sum_n D_{n,m}^L(\Omega) T^{(L,n)}. \quad (A2)$$

Equation (A2) illustrates the main reason for the usefulness of irreducible tensors in problems involving rotations *i.e.* that their transformation properties are very simple. The set of $(2L+1)$ components, $T^{(L)}$, is called an irreducible tensor of rank L . The Euler angles Ω in eq. (A2) determine the rotations which carry the original (unprimed) coordinate system into the rotated (primed) one. We follow the convention of Rose [3] for the Euler angles. From eq. (A1) it is apparent that we can express $D_{m,n}^L(\alpha\beta\gamma)$ as

$$D_{m,n}^L(\alpha\beta\gamma) = e^{-im\alpha} d_{m,n}^L(\beta) e^{-in\gamma}, \quad (A3)$$

where the real quantities,

$$d_{m,n}^L(\beta) \equiv \langle Lm | e^{-i\beta J_y} | Ln \rangle, \quad (A4)$$

are called reduced or small Wigner matrices.

The functions $D_{m,n}^L(\alpha\beta\gamma)$ constitute a complete orthogonal set spanning the space of the angles α, β, γ . Some of their properties, which we fre-

quently use, are:

Orthogonality

$$\int d\alpha \sin\beta d\beta d\gamma D_{m,n}^{L*}(\alpha\beta\gamma) D_{m',n'}^{L'}(\alpha\beta\gamma) = \{8\pi^2/(2L+1)\} \delta_{m,m'} \delta_{n,n'} \delta_{L,L'} \quad (A5)$$

Integral of three Wigner rotation matrices

$$\begin{aligned} & \int d\alpha \sin\beta d\beta d\gamma D_{m'',n''}^{L''*}(\alpha\beta\gamma) D_{m',n'}^{L'}(\alpha\beta\gamma) D_{m,n}^L(\alpha\beta\gamma) \\ & = \{8\pi^2/(2L''+1)\} \delta_{m+m',m''} \delta_{n+n',n''} C(LL'L'';mm') C(LL'L'';nn'), \end{aligned} \quad (A6)$$

where $C(abc;de)$ is a Clebsch-Gordan coefficient [3]. An equivalent expression can be obtained in terms of 3-j symbols [20] remembering that

$$C(abc;de) = (-)^{a-b-f} \delta_{d+e+f,0} (2c+1)^{\frac{1}{2}} \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}. \quad (A7)$$

Closure

$$\sum_n D_{m,n}^L(\alpha_1\beta_1\gamma_1) D_{n,m'}^L(\alpha_2\beta_2\gamma_2) = D_{m,m'}^L(\alpha\beta\gamma), \quad (A8)$$

where $(\alpha\beta\gamma)$ is the resultant of $(\alpha_1\beta_1\gamma_1)$ then $(\alpha_2\beta_2\gamma_2)$.

Symmetry

$$D_{m,n}^{L*}(\alpha\beta\gamma) = (-)^{m-n} D_{-m,-n}^L(\alpha\beta\gamma) = D_{n,m}^L(-\gamma-\beta-\alpha). \quad (A9)$$

Products

$$D_{m',n'}^{L'} D_{m'',n''}^{L''} = \sum_{L=|L'-L''|}^{L'+L''} C(L'L''L;m'm'') C(L'L''L;n'n'') D_{m'+m'',n'+n''}^L \quad (A10)$$

Special cases

$$D_{m,0}^L(\alpha\beta 0) = \{4\pi/(2L+1)\}^{\frac{1}{2}} Y_{L,m}^*(\beta\alpha), \quad (A11)$$

$$D_{0,0}^L(0\beta 0) = d_{0,0}^L(\beta) = P_L(\cos\beta),$$

where $Y_{L,m}$ is a spherical harmonic and P_L a Legendre polynomial.

We now give the explicit expressions for the Wigner rotation matrices (and implicitly the order parameters) of rank $L = 0,1,2,4$. From eq.(A3) we see that what we really need are expressions for the small matrices $d_{m,n}^L(\beta)$. Some partial tabulations can be found in the literature [20]. In general however the $d_{m,n}^L$ can be obtained from the Wigner formula [3]

$$d_{m,n}^L(\beta) = \sum_{\chi} C_{qp}^{Lmn} \cos^q(\beta/2) \sin^p(\beta/2), \quad (\text{A12})$$

where

$$q \equiv 2L + m - n - 2\chi,$$

$$p \equiv n - m + 2\chi,$$

$$C_{qp}^{Lmn} \equiv (-)^{\chi} \frac{\{(L+m)!(L-m)!(L+n)!(L-n)!\}^{\frac{1}{2}}}{(L-n-\chi)!(L+m-\chi)!(\chi+n-m)!\chi!}$$

and the sum is over the values of the integer χ for which the factorial arguments are greater or equal to zero. The number of $d_{m,n}^L$ of a given rank L to be calculated with this rather unwieldy formula is, in principle $(2L+1)^2$. This very high number of $d_{m,n}^L$ for even moderately high L can be drastically reduced if symmetry relations are taken into account;

$$d_{m,n}^L(\beta) = (-)^{m-n} d_{-m,-n}^L(\beta), \quad (\text{A13})$$

$$= (-)^{m-n} d_{n,m}^L(\beta). \quad (\text{A14})$$

Another helpful relation apparently never used in this context is

$$d_{m,n}^L(\beta) = (-)^{L+m} d_{m,-n}^L(\pi-\beta). \quad (\text{A15})$$

We shall find this rather advantageous since it gives

$$d_{m,-n}^L(\beta) = (-)^{L+m} \sum_{qp} C_{qp}^{Lmn} \sin^q(\beta/2) \cos^p(\beta/2), \quad (\text{A16})$$

because $\cos(\pi/2-\beta/2) = \sin(\beta/2)$ and $\sin(\pi/2-\beta/2) = \cos(\beta/2)$. Eq. (A16) shows the important fact that if the $d_{m,n}^L(\beta)$ are written as a combination of $\cos(\beta/2)$ and $\sin(\beta/2)$ powers then $d_{m,-n}^L$ is obtained by simply exchanging $\sin(\beta/2)$ and $\cos(\beta/2)$ and multiplying the resulting expression by $(-)^{L+m}$. As an example, from

$$d_{1,1}^4 = c^2(c^6 - 15c^4s^2 + 30c^2s^4 - 10s^6),$$

we have at once

$$d_{1,-1}^4 = -s^2(s^6 - 15s^4c^2 + 30s^2c^4 - 10c^6),$$

where $c \equiv \cos(\beta/2)$ and $s \equiv \sin(\beta/2)$. Applications of (A13-A15) allow the number of $d_{m,n}^L$ to be calculated to be reduced from $(2L+1)^2$ to $(L+1)(L+2)/2$; thus for $L=4$ only 15 elements are needed instead of 81.

In Table A1 we give explicit expressions for the most important cases $L=0,1,2,4$.

Table A1 *Explicit expressions for the small Wigner matrices $d_{m,n}^L(\beta)$; $L=0, 1, 2, 4$. Here $c \equiv \cos(\beta/2)$ and $s \equiv \sin(\beta/2)$.*

$$L = 0$$

$$d_{0,0}^0 = 1$$

$$L = 1$$

$$d_{1,1}^1 = d_{-1,-1}^1 = c^2$$

$$d_{1,0}^1 = d_{-1,0}^1 = -d_{0,1}^1 = d_{0,-1}^1 = -\sqrt{2}sc$$

$$d_{1,-1}^1 = d_{-1,1}^1 = s^2$$

$$d_{0,0}^1 = -1 + 2c^2$$

$$L = 2$$

$$d_{2,2}^2 = d_{-2,-2}^2 = c^4$$

$$d_{2,1}^2 = -d_{-2,-1}^2 = -d_{1,2}^2 = d_{-1,-2}^2 = -2c^3s$$

$$d_{2,0}^2 = d_{-2,0}^2 = d_{0,2}^2 = d_{0,-2}^2 = \sqrt{6}c^2 - \sqrt{6}c^4$$

$$d_{2,-1}^2 = -d_{-2,1}^2 = -d_{-1,2}^2 = d_{1,-2}^2 = -2s^3c$$

$$d_{2,-2}^2 = d_{-2,2}^2 = s^4$$

$$d_{1,1}^2 = d_{-1,-1}^2 = -3c^2 + 4c^4$$

$$d_{1,0}^2 = -d_{-1,0}^2 = -d_{0,1}^2 = d_{0,-1}^2 = \sqrt{6}cs - 2\sqrt{6}c^3s$$

$$d_{1,-1}^2 = d_{-1,1}^2 = 3s^2 - 4s^4$$

$$d_{0,0}^2 = 1 - 6c^2 + 6c^4$$

$$L = 4$$

$$d_{4,4}^4 = d_{-4,-4}^4 = c^8$$

(Table A1
continued)

$$\begin{aligned}
d_{4,3}^4 &= -d_{-4,-3}^4 = -d_{3,4}^4 = d_{-3,-4}^4 = -2\sqrt{2} c^7 s \\
d_{4,2}^4 &= d_{-4,-2}^4 = d_{2,4}^4 = d_{-2,-4}^4 = 2\sqrt{7} c^6 s^2 \\
d_{4,1}^4 &= -d_{-4,-1}^4 = -d_{1,4}^4 = d_{-1,-4}^4 = -2\sqrt{14} c^5 s^3 \\
d_{4,0}^4 &= d_{-4,0}^4 = d_{0,4}^4 = d_{0,-4}^4 = \sqrt{70} c^4 s^4 \\
d_{4,-1}^4 &= -d_{-4,1}^4 = -d_{-1,4}^4 = d_{1,-4}^4 = -2\sqrt{14} c^3 s^5 \\
d_{4,-2}^4 &= d_{-4,2}^4 = d_{-2,4}^4 = d_{2,-4}^4 = 2\sqrt{7} c^2 s^6 \\
d_{4,-3}^4 &= -d_{-4,3}^4 = -d_{3,-4}^4 = d_{-3,4}^4 = -2\sqrt{2} c s^7 \\
d_{4,-4}^4 &= d_{-4,4}^4 = s^8 \\
d_{3,3}^4 &= d_{-3,-3}^4 = c^6 (c^2 - 7 s^2) \\
d_{3,2}^4 &= -d_{-3,-2}^4 = -d_{2,3}^4 = d_{-2,-3}^4 = -\sqrt{14} c^5 s (c^2 - 3s^2) \\
d_{3,1}^4 &= d_{-3,-1}^4 = d_{1,3}^4 = d_{-1,-3}^4 = \sqrt{7} c^4 s^2 (3c^2 - 5s^2) \\
d_{3,0}^4 &= -d_{-3,0}^4 = -d_{0,3}^4 = d_{0,-3}^4 = -2\sqrt{35} c^3 s^3 (c^2 - s^2) \\
d_{3,-1}^4 &= d_{-3,1}^4 = d_{-1,3}^4 = d_{1,-3}^4 = \sqrt{7} c^2 s^4 (5c^2 - 3s^2) \\
d_{3,-2}^4 &= -d_{-3,2}^4 = -d_{2,3}^4 = d_{2,-3}^4 = -\sqrt{14} c s^5 (3c^2 - s^2) \\
d_{3,-3}^4 &= d_{-3,3}^4 = s^6 (7 c^2 - s^2) \\
d_{2,2}^4 &= d_{-2,-2}^4 = c^4 (c^4 - 12c^2 s^2 + 15s^4) \\
d_{2,1}^4 &= -d_{-2,-1}^4 = -d_{1,2}^4 = d_{-1,-2}^4 = -\sqrt{2} c^3 s (3 c^4 - 15 c^2 s^2 + 10 s^4) \\
d_{2,0}^4 &= d_{-2,0}^4 = d_{0,2}^4 = d_{0,-2}^4 = \sqrt{10} c^2 s^2 (3 c^4 - 8c^2 s^2 + 3 s^4) \\
d_{2,-1}^4 &= -d_{-2,1}^4 = -d_{-1,2}^4 = d_{1,-2}^4 = -\sqrt{2} c s^3 (10 c^4 - 15 c^2 s^2 + 3 s^4) \\
d_{2,-2}^4 &= d_{-2,2}^4 = s^4 (15 c^4 - 12 c^2 s^2 + s^4) \\
d_{1,1}^4 &= d_{-1,-1}^4 = c^2 (c^6 - 15 c^4 s^2 + 30 c^2 s^4 - 10 s^6) \\
d_{1,0}^4 &= -d_{-1,0}^4 = -d_{0,1}^4 = d_{0,-1}^4 = -2\sqrt{5} c s (c^6 - 6c^4 s^2 + 6 c^2 s^4 - s^6) \\
d_{1,-1}^4 &= d_{-1,1}^4 = s^2 (10 c^6 - 30 c^4 s^2 + 15 c^2 s^4 - s^6) \\
d_{0,0}^4 &= c^8 - 16 c^6 s^2 + 36 c^4 s^4 - 16 c^2 s^6 + s^8
\end{aligned}$$

References

- 1a. see e.g. P.G. de Gennes, *The Physics of Liquid Crystals*, Oxford U.P., (1974).
- 1b. E.B. Priestley, P.J. Wojtowicz and P. Sheng (Eds), *Introduction to Liquid Crystals*, Plenum Press, (1975).
- 1c. G.W. Gray and P. A. Winsor (Eds), *Liquid Crystals and Plastic Crystals*, Ellis Horwood, (1974).
- 2a. R. Balescu, *Equilibrium and Non-equilibrium Statistical Mechanics*, Wiley, (1975).
- 2b. J.P. Hansen and I.R. McDonald, *Theory of Simple Fluids*, Academic Press, (1976).
- 2c. L. Landau and E.M. Lifshitz, *Statistical Physics*, 2nd Edn, Pergamon Press, (1969).
3. M.E. Rose, *Elementary Theory of Angular Momentum*, Wiley, (1957).
4. A.B. Pippard, *Elements of Classical Thermodynamics*, Cambridge U.P., (1966).
5. H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford U.P., (1971).
6. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953).
7. J. Viellard-Baron, *J. Chem. Phys.* **56**, 4729 (1972); *Mol. Phys.* **28**, 809 (1974).
8. W.A. Steele, *J. Chem. Phys.* **39**, 3197 (1963).
9. A. Saupe, *Angew Chem. Int. Ed.* **7**, 97 (1968).
10. G.R. Luckhurst, Chapter 7 of Ref. 1c.
11. E.D. Priestley and P.S. Pershan, *Mol. Cryst. Liq. Cryst.* **23**, 369 (1973); S. Jen, N.A. Clark, P.S. Pershan and E.B. Priestley, *Phys. Rev. Letts*, **26**, 1552 (1973).
12. G.R. Luckhurst and A. Sanson, *Mol. Phys.* **24**, 1297 (1972); **28**, 809 (1974); G.R. Luckhurst, M. Setaka and C. Zannoni, *Mol. Phys.* **28**, 49 (1974); G.R. Luckhurst and R.N. Yeates, *J. Chem. Soc. Faraday II*, **72**, 996 (1976).
13. P.G. de Gennes, *C.R. Acad. Sci. Paris, Sér B274*, 142 (1972).
14. R. Pynn, *J. Phys. Chem. Solids*, **34**, 735 (1973); *Acta Cryst.* **A31**, 323 (1975); M. Kohli, K. Otnes, R. Pynn and T. Riste, *Z. Physik B24*, 147 (1976).
15. S. Goshen, D. Mukamel and S. Shrikman, *Mol. Cryst. Liq. Cryst.* **31**, 171 (1975).
- 16a. L. Landau and E.M. Lifshitz, *Quantum Mechanics*, Pergamon Press, (1966).
- 16b. M. Lax, *Symmetry Principles in Solid State and Molecular Physics*, Wiley, (1974).
- 16c. P.W. Atkins, M.S. Child and C.S.G. Phillips, *Tables for Group Theory*, Oxford U.P., (1970).
17. L. Blum and A.J. Torruella, *J. Chem. Phys.* **56**, 303 (1972).
18. D.W. Jepsen and H.L. Friedman, *J. Chem. Phys.* **38**, 846 (1963).
19. A.D. Buckingham, *Disc. Faraday Soc.*, **43**, 205 (1967).
20. D.M. Brink and G.R. Satchler, *Angular Momentum*, Clarendon Press, (1968).
21. C. Zannoni, to be published.
22. G. Lasher, *Phys. Rev.* **A5**, 1350 (1972); P.A. Lebwohl and G. Lasher, *Phys. Rev.* **A6**, 426 (1972).