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Neutron scattering from mixtures of isotopically labelled molecules. A new method for determining the orientational distribution function in liquid crystals

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Neutron scattering from mixtures of isotopically labelled molecules

A new method for determining the orientational distribution function in liquid crystals

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Neutron scattering from a mixture of normal hydrogeneous and perdeuteriated 4-*n*-pentyloxybenzylidene-4′-*n*-heptyl quiline (5O.7) has been shown to contain a component which depends *only* on the structure and orientational distribution of the molecules. It has been used to determine the orientational order parameters $\bar{P}_n$ for $n = 2$, 4 or 6 in the smectic and nematic phases of 5O.7. These values were much less than predicted by the Maier–Saupe molecular field theory, but in qualitative agreement with a model based on biaxial intermolecular interactions. Comparison with the $\bar{P}_2$ values obtained by analysing the smearing into arcs of intermolecular interfence features, suggested that the correlation of orientation of neighbouring molecules is not very high so that the method tends to overestimate the order parameters. Other possible applications of the technique of neutron scattering from isotopically labelled mixtures are discussed.

1. Introduction

Recent years have seen considerable interest in the structure and dynamics of liquid crystals. One long term aim has been to establish a theory linking liquid-crystalline properties to molecular structure. In order to test and develop such theories, it is useful to determine the spatial and orientational distributions of the molecules and their internal conformations. Many techniques have been used to study these distributions but generally they give incomplete information. For instance X-ray diffraction can determine the repeat distances, or the wavelength of the density waves, in a liquid crystal but the shape and conformation of the molecules can only be inferred.

The non-uniform distribution of molecular orientations is the most important feature of most liquid crystal phases since it is *the* structural property which distinguishes these phases from the isotropic liquid. Several spectroscopic technqiues have been used to study this distribution but generally they can only determine the average of some function over the orientational distribution. The usual orientational order parameter, $\bar{P}_2$, is the average of the second Legendre polynomial over the distribution, $f(\beta)$, of angles, β between some long molecular axis and the director,

$$\bar{P}_n = \int_0^\pi P_n(\cos\beta) f(\beta) d\cos\beta, \qquad (1)$$

where $n = 2$. Nuclear magnetic resonance techniques [1] can determine $\bar{P}_2$ but not, in general, $f(\beta)$. Raman scattering [2] can determine $\bar{P}_2$ and $\bar{P}_4$ but not the complete

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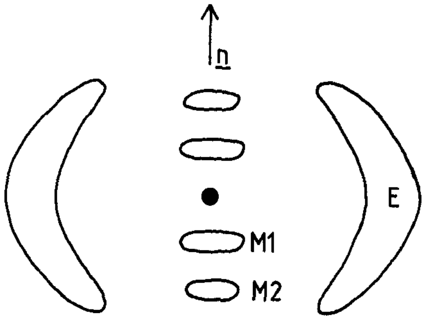


Figure 1. Schematic X-ray or neutron scattering pattern for a nematic phase in which the director has been aligned vertically.

distribution $f(\beta)$. The limitations of such spectroscopic methods arise from the fact that they only measure second (or fourth) rank tensor properties of the liquid crystal phase. Electron spin resonance techniques [3] are able to measure $\bar{P}_2$ and $\bar{P}_4$ of solute molecules in liquid-crystalline hosts. In order to obtain more detailed information of $f(\beta)$, X-ray or neutron scattering techniques must be used.

Figure 1 shows a schematic X-ray (or neutron) diffraction pattern from a nematic liquid crystal of elongated molecules. The first equatorial and meridional scattering maxima (E and M1) result from intermolecular interference while maxima at higher scattering vectors (e.g. M2) may result from predominantly intramolecular interference. Both types of feature have been exploited in attempts to measure the orientational distribution function of the molecules. X-ray diffraction techniques can easily determine the angular distribution of the equatorial maxima, but the interpretation of this distribution in terms of a distribution of molecular orientations is highly model dependent. Two extreme models can be imagined: if it is assumed that the molecules are packed within regions in which the orientations of neighbouring molecules are well correlated, but that the regions have a distribution of orientations (i.e. director fluctuations), then the degree of smearing of the equatorial E maxima into arcs will depend upon $f(\beta)$. However, if there is no correlation between the orientation of neighbouring molecules, then there will be no such smearing of the intermolecular diffraction maxima into arcs. In thermotropic nematics some orientational correlation is expected and analysis of the length of the arcs has been found a useful (but approximate) method of determining $f(\beta)$ (see [4] and references therein). It is probably best regarded as determining the angular distribution of large groups of molecules rather than that of individual molecules. The $f(\beta)$ determined in this way will be equal to or narrower than the true molecular $f(\beta)$ and the value of $\bar{P}_2$ will be higher than the correct value. It is possible that the groups of molecules are large enough to define a director and, in this case, the measured $f(\beta)$ could be regarded as a director distribution. For lyotropic discotic nematics [5] there is very little correlation between the aggregates and so this type of analysis tends to give rather high values of $\bar{P}_2$.

In order to try to determine a molecular $f(\beta)$, it is necessary to study the smearing into an arc of genuinely intramolecular scattering feature. Such features occur at high scattering vector (where intermolecular effects have died away). For such measurements neutron scattering [6, 7] from fully deuteriated materials offers some advantage over X-rays because the neutron atomic scattering factor does not decay with increasing scattering vector. Useful results have been obtained in this way but calculations have shown that in the scattering vector range which contains the most useful maxima for these experiments, the scattering also contains an excluded volume term as well as intramolecular terms and cannot be regarded as completely intramolecular. Furthermore, the method only provided ratios of order parameters because the absolute intensity of the scattering is not accurately known.

The limitations of the methods discussed here for determining the orientational distribution function of the molecules in a liquid crystal phase have lead us to explore the possibilities of a new method. In this paper we show that the true single molecule scattering can be measured by neutron scattering from a mixture of normal hydrogeneous and perdeuteriated versions of the same compound. The single molecule scattering contains information on the effective size and shape of the molecules in the mesophase and on the molecular orientational distribution function, $f(\beta)$. The diffraction patterns obtained also contain the intermolecular feature (E) and so a comparison can be made between the molecular and director distributions.

2. Theory

This method of obtaining single molecule scattering relies on the fact that the scattering lengths for neutrons of hydrogen and deuterium are different ($b_H = -3{\cdot}74 \times 10^{-15}$ m while $b_D = +6{\cdot}67 \times 10^{-15}$ m) but the two isotopes are almost identical chemically. A mixture of a normal hydrogeneous (H) and a perdeuteriated (D) version of the same molecule will therefore be strictly random in that the probability of finding a hydrogeneous molecule as nearest neighbour to any given origin molecule will only depend on the mole fraction of hydrogenous molecules, x_H, and will be independent of whether the origin molecule is H or D.

The scattering from a molecular fluid depends upon the following functions:

(i) The molecular structure factors, $\hat{m}(\mathbf{Q}, \Omega)$ which depends upon the structure of one molecule and its orientation, Ω. For a rigid molecule it may be calculated as a summation over M atoms in the molecule

$$\hat{m}(\mathbf{Q}, \Omega) = \sum_{j=1}^{M} b_j \exp(i\mathbf{Q}, \mathbf{r}_j(\Omega)),$$

where $\mathbf{Q}$ is the scattering vector and the $\mathbf{r}_j(\Omega)$s are the positions of the atoms. The orientation Ω is defined by the angle β, between the long molecular axis and the director, and α, the azimuthal angles shown in figure 2. (For completeness Ω should also define an angle of rotation about the long molecular axis. Since we have chosen to use cylindrically symmetric molecules this angle has not been included explicitly in this summary of the theory.) The molecular structure factor, $\hat{m}(\mathbf{Q}, \Omega)$, will be different for H or D versions of the same molecule because $b_H \neq b_D$. i.e. $m_H \neq m_D$.

(ii) The pair distribution function, $P(\Omega_0, \Omega, \mathbf{r})$ must contain angular information and is, therefore, more complicated than (but is otherwise similar in concept to) the radial distribution function used in simple liquids. If a molecule with orientation Ω_0 is chosen as the origin, $P(\Omega_0, \Omega, \mathbf{r})$ is the conditional probability distribution of finding a molecule with orientation Ω at a vector displacement $\mathbf{r}$ from the origin.

(iii) $f(\beta_0)$ is the distribution of molecular orientations which we assume to be independent of α_0, that is there is no macroscopic biaxiality.

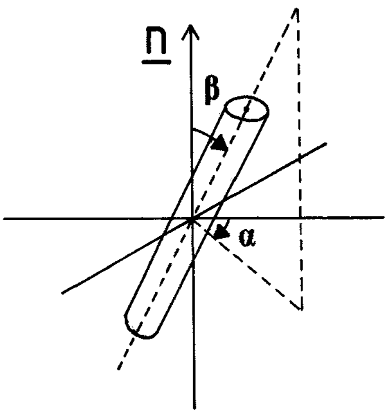


Figure 2. The molecular coordinates.

The scattered intensity from a pure liquid crystal, expressed as a differential scattering cross section $[\partial\sigma/\partial\omega]_p$ (i.e. made up of only one type of molecule) is given by the Fourier transform of P weighted by $\hat{m}(\mathbf{Q},\Omega_0)$ and the complex conjugate $\hat{m}^*(\mathbf{Q},\Omega)$, then averaged over the orientation Ω_0 of the origin molecule and the orientation of the other molecule, Ω,

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_p = \int_{\Omega_0}\int_{\Omega}\int_r f(\beta_0)P(\Omega_0,\Omega,\mathbf{r})\hat{m}(\Omega_0)\hat{m}^*(\Omega) \times \exp(i\mathbf{Q}\,.\,\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r}. \tag{2}$$

(The symbol ω, rather than the conventional Ω, denotes the solid angle for scattering to avoid confusion with the angle defining the molecular orientation.) This formula could be used to model the scattering from liquid crystals consisting of only one type of molecule. A functional form for the angular dependent pair distribution function, $P(\Omega_0,\Omega,\mathbf{r})$ would have then to be assumed. However, it is not necessary to pursue this course in order to analyse the scattering from a mixture of two differently, isotopically labelled molecules. The scattering cross section from a random mixture of H and D versions of the same compound can be shown (see the Appendix) to be

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{\text{mix}} = \int_{\Omega_0}\int_{\Omega}\int_r f(\beta_0)P(\Omega_0,\Omega,\mathbf{r})\,\overline{\hat{m}(\Omega_0)}\,\overline{\hat{m}^*(\Omega)} \times \exp(i\mathbf{Q}\cdot\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r} + x_H x_D\int_D f(\beta)|\hat{m}_H(\Omega) - \hat{m}_D(\Omega)|^2\,d\Omega, \tag{3}$$

where

$$\overline{\hat{m}(\Omega)} = x_H\hat{m}_H(\Omega) + x_D\hat{m}_D(\Omega) \tag{4}$$

and x_H, x_D are the mole fractions of hydrogeneous and deuteriated molecules. The first term in equation (3) is essentially the same as the scattering from the pure liquid crystal except that the molecular structure factor has been replaced by the weighted average for the hydrogenous and deuteriated molecules. It will, therefore, contain all of the usual diffraction features observed by X-ray or neutron scattering from pure materials. The second term is a new feature which is the diffraction of the difference between an H and a D molecule. It is incoherent scattering in the sense that there is no intermolecular interference in this term although the waves scattered from different atoms in the same molecule do interfere. For a mixture of H and D molecules, this second term can be regarded as the scattering from a single molecule consisting of atoms (each of scattering length $b_D - b_H$) at the positions normally occupied by the hydrogen atoms. This single molecule scattering is averaged over the distribution of orientations $f(\beta)$ and so, in principle, provides a means of measuring $f(\beta)$ and the effective size and shape of the molecule in the liquid crystal phase. This theory depends only on the H/D mixture being random and not on it being dilute in one component. It is possible therefore to use whatever ratio of the two components gives the strongest single molecule scattering. The idea of using strong labelling has been suggested previously for small angle scattering from polymers [8]. Section 3 describes how this scattering has been measured and analysed for one particular liquid crystal.

3. Experimental design

3.1. *Sample*

The material studied in this work was 4-*n*-pentyloxybenzylidene-4′-*n*-heptylaniline (5O.7). It was chosen mainly because a (expensive) perdeuteriated sample had been prepared for other purposes [9]. However it was known to form very good monodomains which could be retained indefinitely in the smectic G phase at room temperature. It also provided a number of different phases which could be compared

$$\text{crystal} \sim 15^\circ\text{C}\, S_G\; 38^\circ\text{C}\, S_B\; 53^\circ\text{C}\, S_C\; 56^\circ\text{C}\, S_A\; 65^\circ\text{C}\, N\; 78^\circ\text{C}\, I.$$

3.2. *Signal-to-background optimization*

In addition to the coherent nuclear scattering described in equation (2) and (3) there is a featureless background from nuclear incoherent scattering. Attaining the best single molecule signal to incoherent background is a compromise between the need to maximise the single molecule scattering (which means mole fraction of 0·5 H and 0·5 D molecules) and the need to reduce the incoherent background (which means reducing the fraction of hydrogeneous molecules). In the scattering vector region where the single molecule scattering is found, the coherent signal is given by the second term in equation (3) while the incoherent background depends upon the incoherent cross section

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_i = x_H\frac{\sigma(H)}{4\pi} + x_D\frac{\sigma(D)}{4\pi}$$
$$= \frac{1}{4\pi}[x_H(\sigma(H) - \sigma(D)) + \sigma(D)], \qquad (5)$$

where $\sigma(H)$ and $\sigma(D)$ are the incoherent neutron scattering cross sections of the two types of molecules. The signal-to-background R_{SB} is, therefore, given by

$$R_{SB} = \frac{4\pi x_H x_D[\partial\sigma/\partial\omega]_{dm}}{x_H(\sigma(H) - \sigma(D)) + \sigma(D)}, \qquad (6)$$

where

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{dm} = \int_\Omega f(\beta)|\hat{m}_H(\beta) - \hat{m}_D(\beta)|^2\, d\Omega \qquad (7)$$

is the second term in equation (3) and may be regarded as the differential scattering cross section of a difference molecule. It is, therefore, independent of composition. The optimum composition (i.e. maximum R_{SB}) is then

$$x_H = \frac{\sqrt{[\sigma(H)\sigma(D)]} - \sigma(D)}{\sigma(H) - \sigma(D)}. \tag{8}$$

For hydrogenous 5O.7 $\sigma = 2870$ b, and for 96 per cent deuteriated 5O.7 $\sigma = 278$ b, so the optimum composition is $x_H = 0{\cdot}22$. In fact the variation of R_{SB} with x_H is rather slow and $0{\cdot}1 < x_H < 0{\cdot}4$ would be satisfactory, a value of $x_H = 0{\cdot}18$ (i.e. mass fraction 0·2) was chosen for this experiment.

3.3. *Sample container and preparation*

The sample cell and heating apparatus is shown in figure 3. Aluminium was selected for the windows since all of the diffraction features which were to be studied occur at $Q < 2{\cdot}5$ Å which is well below the Q values for the first Bragg peak from aluminium. A diameter of 5 mm for the sample container was chosen to give the best signal since the total attenuation coefficient of a mixture sample was calculated to be $\sim 0{\cdot}2\,\mathrm{mm}^{-1}$. This nicely matched the instrumental resolution as well. The sample temperature was maintained by two Thermocoax heating cables. These coils were driven in series by a single controller, but a rheostat shunt was connected across the

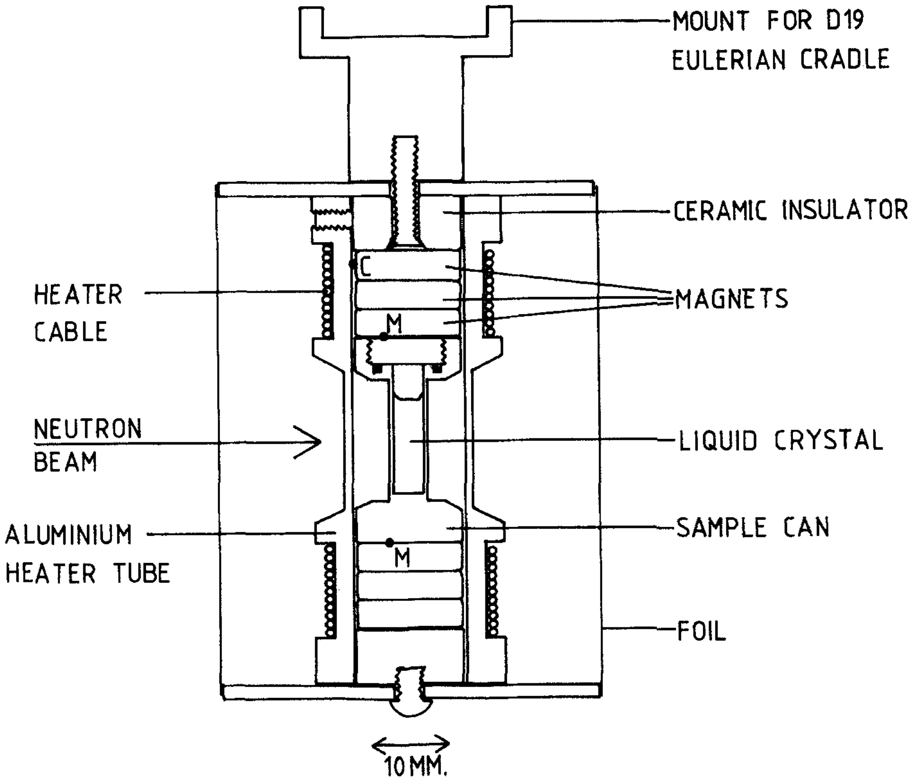


Figure 3. The cell used to contain the liquid-crystalline sample on D19. The temperature was controlled by a thermocouple at point C and monitored by two further thermocouples at points M.

upper coil so that temperature gradients across the sample could be eliminated. Six neodymium iron boron permanent magnets were used to maintain a field of 0·07 T along the axis of the sample after the initial alignment in a higher field. This first field should be sufficient to saturate the alignment of the director.

Two aligned samples were prepared in sealed aluminium cans by cooling 200 mg of material from 80°C in the isotropic phase to room temperature in an 8 T magnetic field (at the Clarendon Laboratory, Oxford). One sample was pure predeuteriated 5O.7 and the other was a mixture containinng a mass fraction of 0·2 of the hydrogenous molecule. This was maintained at 80° for 20 min in an attempt to allow complete mixing of the H and D molecules to occur. The aligned samples were transported to the Institut Laue-Langevin, Grenoble, for the neutron scattering experiment about 1 week after this alignment procedure.

3.4. *Neutron scattering geometry*

The neutron scattering instrument used for this experiment was the D19 single crystal diffractometer at the Institut Laue-Langevin, Grenoble. It has been described fully elsewhere [10] so only the features relevant to this experiment are described here. As shown in figure 4, it uses a vertically-curved, two dimensional detector which is divided into 512 × 0·125° pixels vertically and 16 × 0·25° pixels horizontally. It can be stepped through an angle γ_0 so that all of the scattering over a large two-dimensional range can be recorded. Each point on the detector surface at a given setting γ_0 is described by γ and ν, the equatorial and azimuthal angles with respect to the incident beam and the horizontal plane, of the diffracted beam striking that point. In this experiment diffraction patterns were recorded for $1{\cdot}5° \leqslant \gamma_0 \leqslant 55{\cdot}5°$. Each pattern was recorded as a series of 4° × 64° strips in γ and ν, overlapped in γ to minimize errors due to edge effects. The counts in each strip were corrected for the variation in pixel efficiency, previously determined by measuring the (incoherent) scattering from a standard vanadium sample. The stips were merged to give complete two dimensional diffraction patterns on a grid with $0° \leqslant \gamma \leqslant 58°$ and $-30° \leqslant \nu \leqslant 30°$, which could be displayed graphically or used for model fitting.

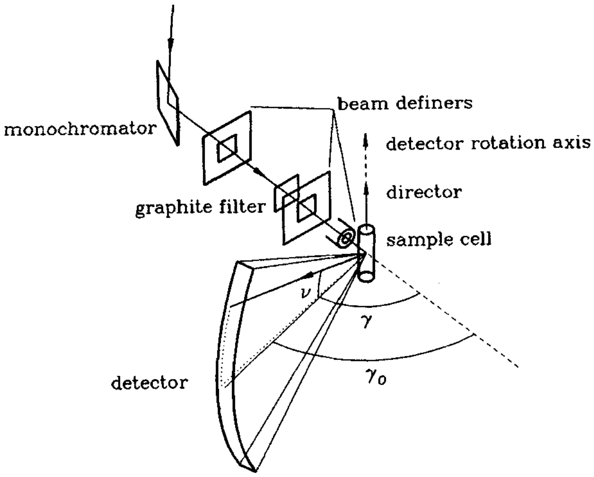


Figure 4. A schematic view of D19 diffractometer showing the angles referred to in the text.

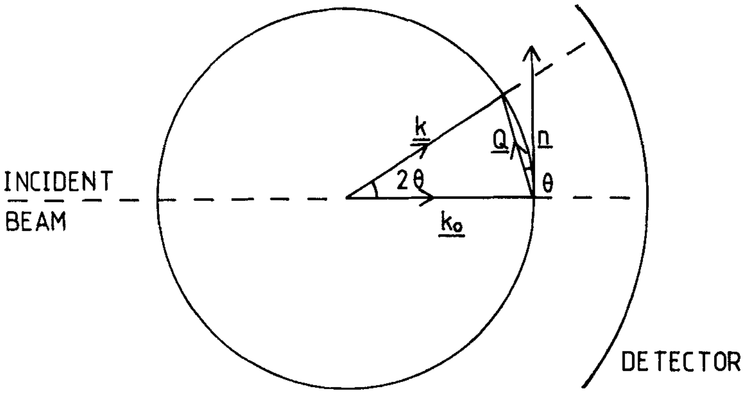


Figure 5. Vertical section of an Ewald sphere for a horizontal incident beam and a vertical director. The sphere is the locus of points in reciprocal space which can be sampled by the scattering vector, **Q** for any direction of scattered beam. Clearly **Q** cannot be parallel to **n** in this configuration and will always be at least θ from **n**.

An incident wavelength of 2·42° Å was chosen, obtained by reflection from the 002 planes of a graphite monochromator. For this arrangement the wavelength resolution, $\Delta\lambda/\lambda$ was about 4 per cent. The $\lambda/2$ contribution to the diffraction pattern was reduced to less than 0·3 per cent by a graphite filter. The choice of a longer wavelength would have moved the single molecule scattering away from the beam stop making it cleaner, but would also have increased to an unacceptable level the inaccessible arc along β. The curvature of the Ewald sphere means that an arc of length 2θ around $\beta = 0$ is inaccessible with the director vertical as shown in figure 5. The scattering vector could have been scanned along the director by tilting the sample, but this would have added greatly to the time taken and risked loss of sample alignment due to flow in the cell.

4. Results and discussion

4.1. *Experimental results*

Neutron scattering measurements were made on the H/D mixture starting in the S_C phase. Figure 6 shows contour plots of some examples of scattering from this mixture in the same order that the data were obtained during the experiment. Figure 7 shows the scattering from the pure D component. The scattering from an empty cell was found to be negligible. It can be seen that in addition to the usual diffraction features, a new component to the scattering can be seen in the data from the H/D mixture. This is the single molecule scattering which is not present in the scattering from the pure sample. The intensity of the single molecule component was disappointingly weak in the initial S_G data but increased gradually in the subsequent runs. Apparently the mixing of the two components during the sample preparation was not complete but since each data set took 20 hours to acquire, mutual diffusion ensured complete mixing by the end of run 6. For future experiments the H and D samples will be mixed in solution and evaporated down to avoid this problem. X-ray diffraction studies of 50·7 have indicated that in this smectic phase the molecules are well aligned with the original aligning magnetic field (in the tilted phase it is the layers not the molecules that tilt). Since the molecules are rod shaped we expect the single molecule scattering to have the form of a disc in reciprocal space. This is entirely

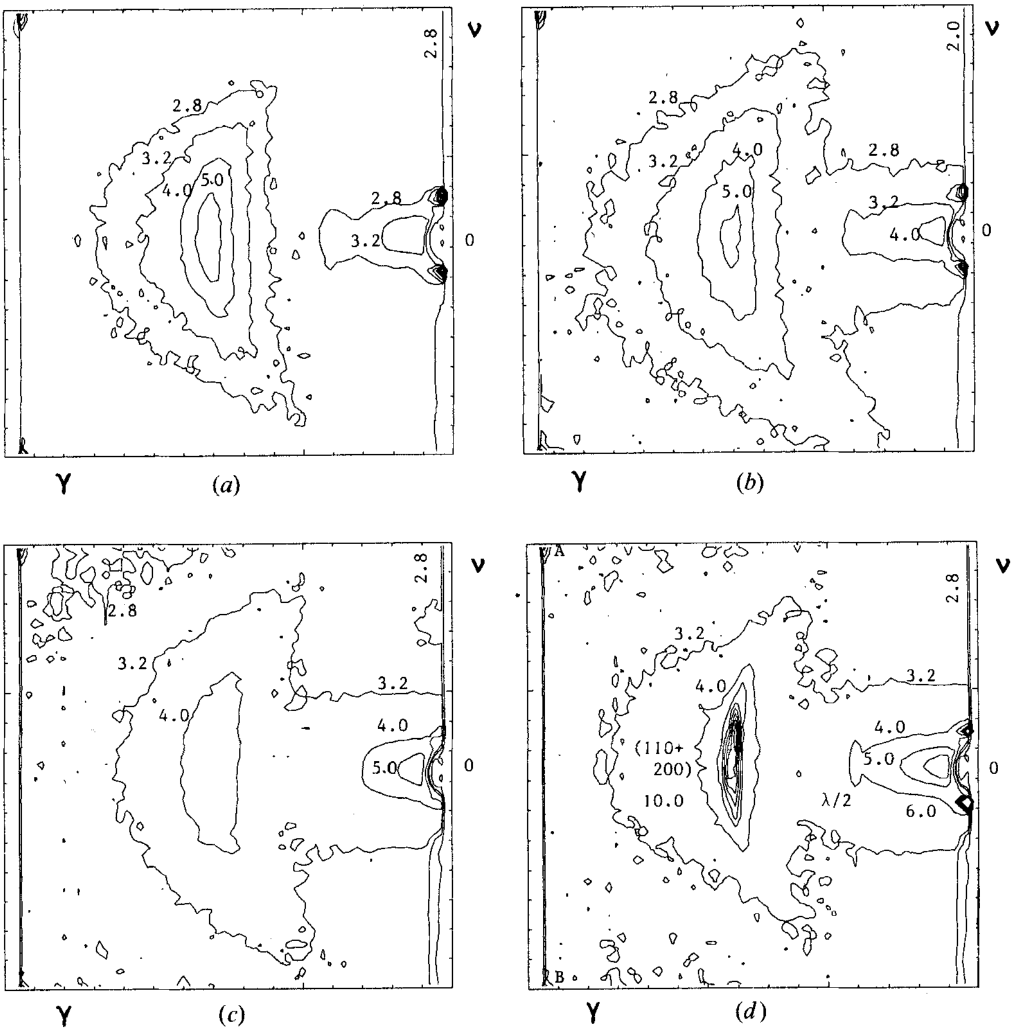
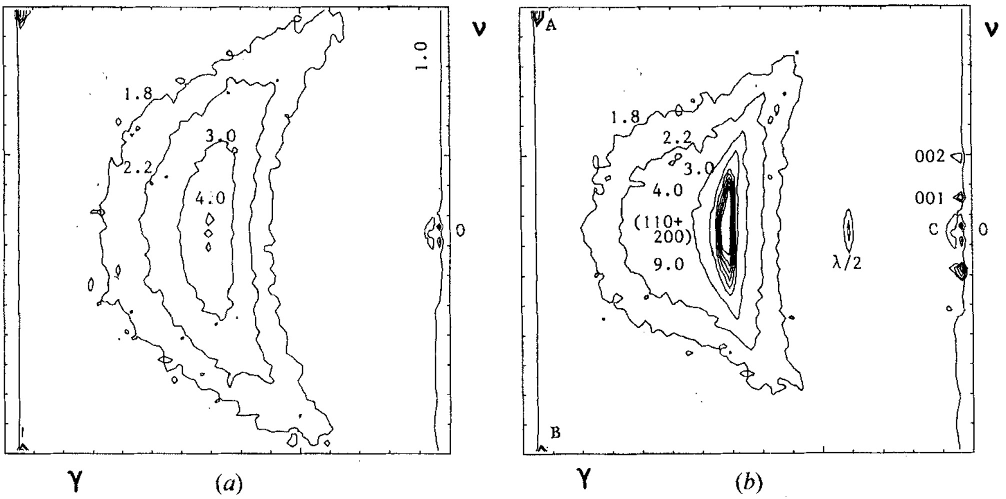


Figure 6. Contour plots of the neutron scattering from the H/D mixture of 5O.7 in (a) S_C, (b) S_A, (c) N at 66°C and (d) S_B phases. The horizontal range is $0° \leqslant \gamma \leqslant 60°$ and the vertical range is $-30° < \nu < 30°$. The normal diffraction features are marked for the S_B phase including a small amount of contamination from $\lambda/2$ neutrons. The single molecule scattering is the horizontal band near the origin. The contours are labelled in thousands of counts.

consistent with the band of scattering spread out from the origin. This band is the observed result when the disc in reciprocal space is cut by the Ewald sphere. The single molecule scattering from a nematic mixture (see e.g. figure 8 (a)) is smeared about the origin because the molecules are no longer well aligned with the field and in the isotropic phase (see figure 8 (b)) this scattering has become isotropic.

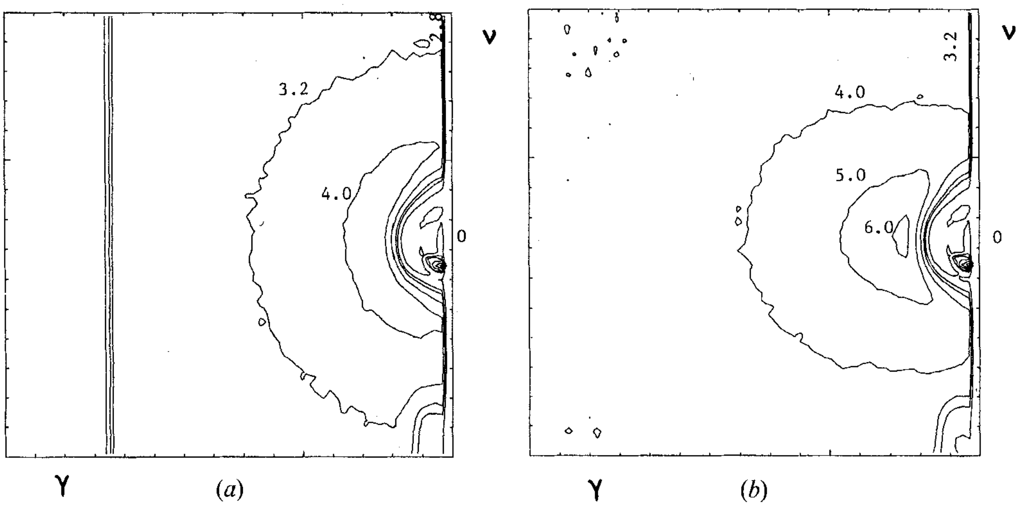
4.2. *Analysis of single molecule scattering*

In principle the orientational distribution function $f(\beta)$ of the molecules could be obtained directly from the variation of the single molecule scattering around a circle



(*a*) (*b*)

Figure 7. Contour plots of neutron scattering from pure deuteriated 5O.7 in (*a*) N and (*b*) S_B phases. The angular ranges are the same as in figure 6. Note that there is no single molecule scattering.



(*a*) (*b*)

Figure 8. Contour plots of neutron scattering from the H/D mixture of 5O.7 in (*a*) the nematic at 74°C and (*b*) the isotropic phase. The horizontal range is $0° \leqslant \gamma < 24°$ and the vertical range is $-12° \leqslant \nu < 12°$.

of constant scattering angle 2θ (see figure 5). There are a number of disadvantages to this approach. (i) The curvature of the Ewald sphere means that $f(\beta)$ is not sampled for low β (i.e. $\beta < \theta$). (ii) The measured intensity variation as a function of azimuthal angle ϕ would have to be corrected for the effect of the molecular structure factor unless the molecules were very long [$L \gg (2\pi/Q)$]. A correction is therefore required for the effective size of the molecule in the liquid crystal phase. (iii) The $f(\beta)$ obtained would be very sensitive to the level at which it was decided to separate the single molecule signal from the flat incoherent background. For these reasons it was decided to analyse the data by model fitting rather than direct determination of

$f(\beta)$. The following model was adopted:

(i) The difference molecule comprising only atoms at the H/D positions was assumed to be rod shaped with a half-length L and a radius R

$$\begin{aligned}|\Delta\hat{m}(Q,A)|^2 &= H_\mathrm{m}|F_\mathrm{m}(\mathbf{Q})|^2,\\ &= H_\mathrm{m}\left[\frac{2J_1(QR\sin A)}{QR\sin A}\right]^2\left[\frac{\sin(QL\cos A)}{QL\cos A}\right]^2,\end{aligned} \tag{9}$$

where A is the angle between the long molecular axis and the scattering vector, $\mathbf{Q}$ and $|F_\mathrm{m}(\mathbf{Q})|^2$ is the molecular form factor. If β_Q is the angle between the scattering vector and the (vertical) director, $\bar{\mathbf{n}}$, and α is the difference between the azimuthal angle of the molecules and that of $\mathbf{Q}$, then

$$\cos A = \sin\beta\sin\beta_Q\cos\alpha + \cos\beta\cos\beta_Q. \tag{10}$$

H_m is the intensity of the single molecule scattering at $Q = 0$ since $|F_\mathrm{m}(\mathbf{Q})|^2$ tends to unity at zero Q. A more realistic assumption might have been to sum over the actual H/D atoms in assumed molecular structures. However this would have required a detailed knowledge of the molecular conformations in the liquid crystal phase. Since we only see the strong central peak of $|F_\mathrm{m}|^2$ the assumption of rods is not expected to introduce a serious error. Our approach has been to treat R as a disposable parameter but to check that its value is in reasonable agreement with an average radius of the molecule (i.e. $1 < R/\text{Å} < 2{\cdot}5$) and to fix L at a reasonable value.

(ii) We have followed two different approaches to modelling the distribution of molecular axes, $f(\beta)$. The first is to assume the Maier–Saupe [11] molecular field potential

$$f(\beta) = \frac{1}{Z}\exp(\mathrm{m}\cos^2\beta), \tag{11}$$

where Z is a normalization constant; the orientational order parameters $\bar{P}_n$ may be calculated using equation (1). The second approach is to assume a more general distribution which is a series of Legendre polynomials:

$$f(\beta) = 1 + a_2P_2(\cos\beta) + a_4P_4(\cos\beta) + a_6P_6(\cos\beta) + \dots \tag{12}$$

In this case the number of terms in the series may be increased until satisfactory agreement with the data is achieved. The order parameters are given by equation (1) or the formula

$$\bar{P}_n = \frac{a_n}{2n+1}. \tag{13}$$

(iii) The model single molecule intensity was calculated by averaging $\Delta\hat{m}$ over $f(\beta)$ numerically

$$I(\mathbf{Q}) = \int_\Omega f(\beta)|\Delta\hat{m}(Q,A)|^2\,d\Omega, \tag{14}$$

where

$$d\Omega = d\alpha d(\cos\beta).$$

(iv) A flat (i.e. **Q** independent) background, B, was then added to $I(\mathbf{Q})$ to represent the incoherent scattering. The scattered intensity was measured on an arbitrary scale so the actual values of H and B are not significant. However their ratio should in theory be given by the ratio of the coherent single molecule to incoherent neutron scattering cross sections at $Q = 0$. The coherent scattering cross section of a difference molecule at $Q = 0$ depends only on the number of atoms in the different molecule and the scattering lengths of H and D

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{dm},\,Q=0} = n_{\mathrm{H}}^2(b_{\mathrm{D}} - b_{\mathrm{H}})^2,$$

where n_{H} is the number of hydrogen positions in a molecule (i.e. 35). The incoherent scattering cross section is given by equations (5) so the ratio as Q tends to zero is

$$\left[\frac{H_{\mathrm{m}}}{B}\right]_{\mathrm{theory}} = \frac{[\partial\sigma/\partial\omega]_{\mathrm{dm},\,Q=0}}{[\delta\sigma/\delta\omega]_{\mathrm{i}}} = \frac{4\pi n_{\mathrm{H}}^2(b_{\mathrm{D}} - b_{\mathrm{H}})^2 x_{\mathrm{H}} x_{\mathrm{D}}}{x_{\mathrm{H}}(\sigma(\mathrm{H}) - \sigma(\mathrm{D})) + \sigma(\mathrm{D})}.$$

For the H/D mixture of 50.7 used in this work, a ratio of $(H_{\mathrm{m}}/B)_{\mathrm{theory}} = 3{\cdot}3$ was expected once complete mixing had taken place.

After much trial and error the following method was employed when fitting the data. It was found to be essential that the flat background, B, was fixed at the lowest point in the data. In the scattering from H/D mixtures this was found to be the points A and B shown in figure 6 (*d*). Inspection of the scattering data from pure D material confirmed that the incoherent background was flat and that its value in the region where the single molecule scattering occurred (C in figure 7 (*b*)) was the same as in the corners (points A and B). It was found that the background was strongly correlated with other parameters (e.g. the radius R, and the Maier–Saupe parameter, m) so any attempt to let it refine during the fitting produced unreliable results. It was also found necessary to fix the length of the molecules. A value of 27 Å was chosen since that is consistent with the length of fully extended molecules and the smectic layer spacing. Small variations (± 3 Å) of this value did not influence the results significantly. The remaining parameters (i.e. the molecular radius R, the maximum height of the single molecule scattering H_{m} and the parameters controlling $f(\beta)$) were allowed to refine during the fitting process. Although the fitting involved refining several parameters, it was quite stable because there was little correlations between the parameters once the background was fixed. For the Legendre polynomial series it was found that terms up to $a_{10}P_{10}(\cos\beta)$ could be included in the series, and that including or omitting high order terms had not influence on the coefficients, a_n, of lower terms. A typical fit is shown in figure 9 and the results are given in terms or order parameters in table 1. Figure 10 shows the distribution $f(\beta)$ reconstructed from the order parameters using equations (12) and (13). The results of the fits for the Maier–Saupe distribution are listed in table 2. In this case, the ratio $\bar{P}_2/\bar{P}_4$ is fixed by the assumption of a Maier–Saupe distribution, but the values of $\bar{P}_4$ are still given for comparison with the Legendre series results. The sum of squares of the deviation between the model and data (SSQ) show that the Legendre series give a marginally better fit to the data except for the $\mathrm{S_B}$ phase where more terms in the series are probably needed.

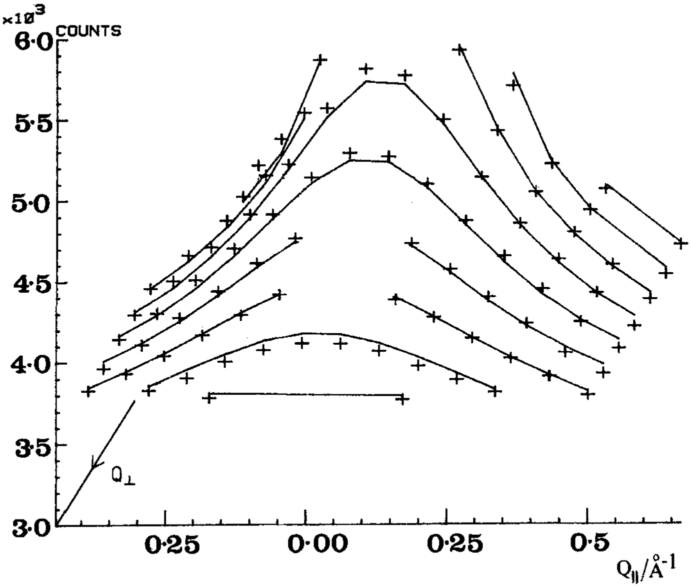


Figure 9. A three-dimensional plot of a typical model fit (lines) to the single molecule scattering (points) from the nematic phase at 74°C. The abscissae are the components of **Q** parallel and perpendicular to the director.

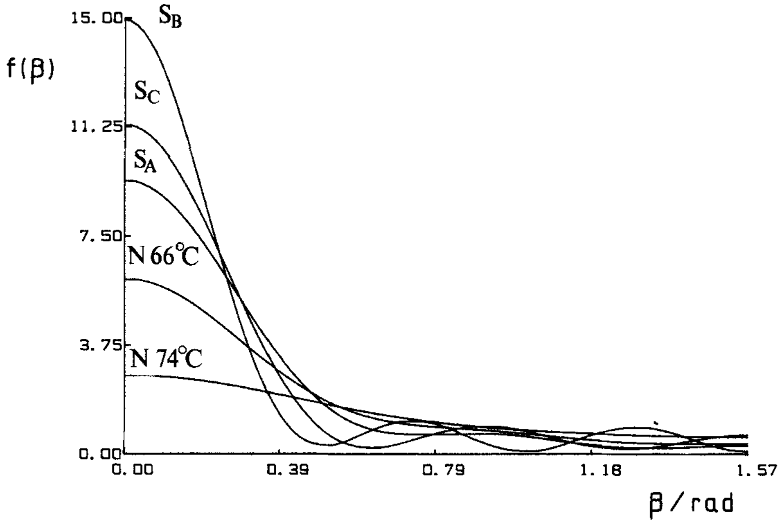


Figure 10. Orientational distribution functions reconstructed from results in table 1.

4.3. *Discussion of single molecule results*

It can be seen from tables 1 and 2 that the height of the single molecule scattering H_m increased dramatically during the course of the experiment. The ratio (H_m/B) increased from about 1 and levelled off at a value of 3·3 which is the theoretical value. We believe therefore that complete mixing had occurred by run 7. The fact that the flat background level also increased slightly from run to run suggests that there may be a small contribution from single molecule scattering at the point at which the background was estimated. (We have repeated the analysis of the data from the results

Table 1. Results from the Legendre series fits.

Run No.	$\frac{T}{^\circ\mathrm{C}}$	Phase	$\frac{B}{10^3\ \mathrm{counts}}$	$\frac{H_m}{10^3\ \mathrm{counts}}$	$\frac{R}{\mathrm{Å}}$	$\bar{P}_2$	$\bar{P}_4$	$\bar{P}_6$	$\bar{P}_8$	$\frac{\mathrm{SSQ}}{10^6}$
1	27	S_G	2·2							
2	40	S_B	2·3	2·5						
3	58	S_C	2·4	3·9	2·0	0·45 ± 0·02	0·31 ± 0·03	0·22 ± 0·04	0·14 ± 0·06	0·28
4	58	S_A	2·6	4·7	1·3	0·52 ± 0·02	0·28 ± 0·02	0·16 ± 0·03	0·06 ± 0·05	0·31
5	66	N	2·9	8·0	1·5	0·40 ± 0·01	0·16 ± 0·01	0·08 ± 0·02	<0·06	0·78
6	40	S_B	2·9	10·3	1·7	0·43 ± 0·01	0·33 ± 0·02	0·24 ± 0·03	0·16 ± 0·04	1·04
7	74	N	3·0	10·1	1·4	0·22 ± 0·01	0·05 ± 0·01	<0·03	–	0·26
8	80	I	3·0	10·1	1·5	0·0 ± 0·01				0·38

Table 2. Results from the Maier–Saupe fits (N.B. the $\bar{P}_2$ ratio $\bar{P}_4$ is fixed by the model).

Run No.	$\frac{T}{^\circ\mathrm{C}}$	Phase	$\frac{B}{10^3\ \mathrm{counts}}$	$\frac{H_m}{10^3\ \mathrm{counts}}$	$\frac{R}{\mathrm{Å}}$	$\bar{P}_2$	$\bar{P}_4$	$\frac{\mathrm{SSQ}}{10^6}$
1	27	S_G	2·2					
2	40	S_B	2·3					
3	53	S_C	2·4	3·9	2·1 ± 0·2	0·50 ± 0·02	0·17 ± 0·02	0·53
4	58	S_A	2·6	4·7	1·4	0·55 ± 0·01	0·20 ± 0·01	0·45
5	66	N	2·9	8·1	1·5	0·41 ± 0·01	0·11 ± 0·02	0·39
6	40	S_B	2·9	10·3	1·9	0·49 ± 0·02	0·16 ± 0·01	0·36
7	74	N	3·0	10·1	1·5	0·22 ± 0·01	0·03 ± 0·01	0·26
8	80	I	3·0	10·1	1·6	0·0 ± 0·01	0·0 ± 0·01	0·38

with the background fixed at $2\cdot2 \times 10^3$ counts (i.e. the background level in the S_G phase). The order parameters were lower but the fit was not satisfactory and the radius R became too small to be physically reasonable.)

The values of the molecular radius, R, are of the correct order for a 5O.7 molecule but they are highly dependent on the background. This is because the value of R controls the rate of decay of the single molecule scattering as $|Q|$ increases. Fortunately R is not strongly correlated with the orientational order parameters, P_n.

Tables 1 and 2 show that the values of $\bar{P}_2$ obtained by fitting the two distribution functions are very similar. In the nemaic and smectic A phases, the Legendre series fit gave rather higher values of $\bar{P}_4$ than the Maier–Saupe fit. Figure 10 shows the orientational distributions $f(\beta)$ reconstructed from the values of $\bar{P}_n$s. However, figure 11 shows that both methods of analysing the data gave values of $\bar{P}_2$, $\bar{P}_4$ and $\bar{P}_6$ very much less than the Maier–Saupe theory predicts for a given reduced temperature in the nematic phase. One way of predicting theoretically such low order parameters is to assume some biaxiality of the molecular interactions. The values of $\bar{P}_n$ are reasonably consistent with those calculated from such a model [12]. A biaxiality order parameter, $\overline{D_{0,2}(2)} \sim 0\cdot045$ gives good agreement with this data. The order parameters in the S_C phase are lower than in the S_A phase which suggests that in this sample it is the molecules and not the layers which tilt with respect to the axis of the sample cell. More surprising are the results for the crystal S_B phase which also give a rather low $\bar{P}_2$.

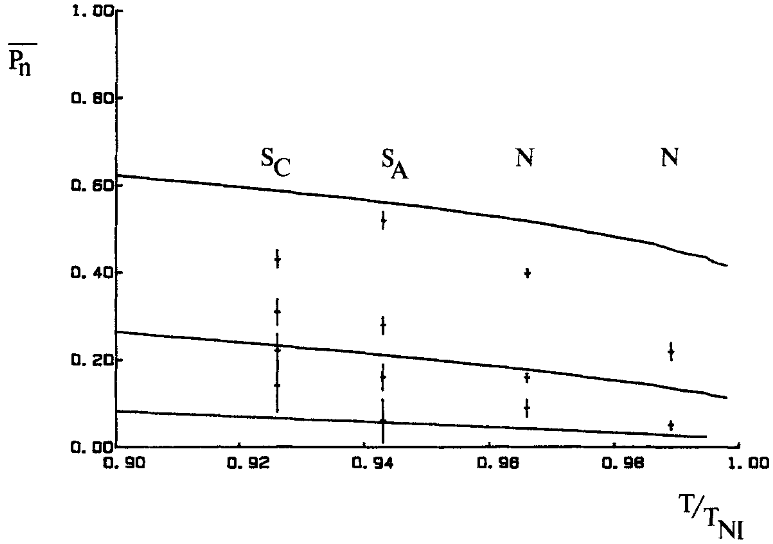


Figure 11. Order parameters $\bar{P}_n$ predicted by the Maier–Saupe theory with the values obtained from the Legendre series fits superimposed as points. In the nematic phase the $\bar{P}_2$ values obtained from the fits of the Maier–Saupe distribution can be superimposed on those from the Legendre series.

It is satisfying to note that $\bar{P}_2 = 0$ was obtained in the isotropic liquid phase. This confirms that no serious systematic errors were introduced by neutron absorption or self-shielding effects. Inspection of the contour plots confirms that the single molecule scattering from the S_B phase (run 6) is not much less smeared than the nematic phase (run 7). Furthermore the 001 peaks in the S_B phase are not confined to spots on the meridional axis but are smeared into arcs extending ~ 20° from the axis. This suggests that on cooling from the nematic phase in the rather weak (0·07 T) magnetic field an imperfectly aligned S_B phase was formed.

4.4. *Intermolecular interference*

The diffuse equatorial scattering should be smeared into an arc to the same extent as the single molecule scattering if the orientation of the molecules is highly correlated over a local region. The size of such a well correlated region would have to be greater than the lateral correlation length $\xi_\perp$. This is derived from the radial width of the equatorial scattering maxima ($\Delta Q \sim 0{\cdot}2\,\text{Å}^{-1}$ HWHM in the S_A and N phases of 5O.7) and gives $\xi_\perp \sim 5\,\text{Å}$. The smearing of the equatorial peak into arcs has been analysed in a similar way to the single molecule scattering except that a lorentzian form has been added for the interference peak

$$I_{\text{INT}}(Q) = \int_\Omega f(\beta) H_I \mathscr{L}(Q \sin A,\, P,\, W) \frac{\sin^2(QL\cos A)}{(QL\cos A)^2}\, d\Omega,$$

where

$$\mathscr{L}(Q, P, W) = \frac{1}{1 + ((Q - P)/W)^2},$$

H_I is the maximum height of the interference peak, P is its position (i.e. $\sim 1{\cdot}5\,\text{Å}^{-1}$) and W is its radial half width (i.e. $\sim 0{\cdot}2\,\text{Å}^{-1}$). This expression was then fitted to the scattering data along one arc of $1{\cdot}3 < |Q|/\text{Å}^{-1} < 1{\cdot}6$ using the Maier–Saupe dis-

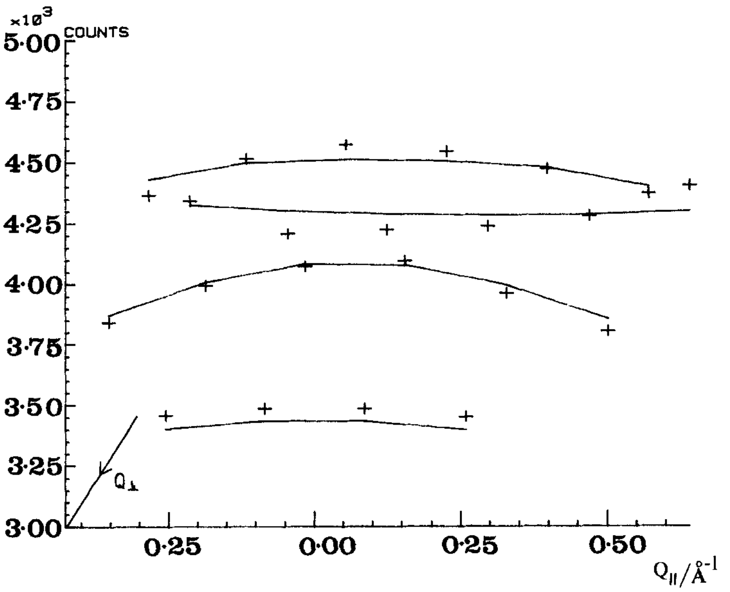


Figure 12. A three-dimensional plot of a typical model fit to the interference peak from the nematic phase at 74°C.

Table 3. Results from fits to the equatorial interference peaks.

Run No.	$\frac{T}{^\circ\mathrm{C}}$	Phase	$\frac{B}{10^3\ \mathrm{counts}}$	$\bar{P}_2$	$(P_2)_{\mathrm{SM}}/(\bar{P}_2)_{\mathrm{I}}$
1	58	$\mathrm{S_A}$	2·6	0·72 ± 0·04	0·74
5	66	N	2·9	0·56 ± 0·06	0·73
7	74	N	3·0	0·26 ± 0·06	0·81

tribution for $f(\beta)$. A typical fit is shown in figure 12 and the results are given in table 3. The values of $\bar{P}_2$ are higher than those given by the single molecule scattering. This suggests that correlation of orientation over a local region is not absent, but neither is it perfect.

The effect of long range director fluctuation on the observation of an orientational order parameter has been discussed in detail by Warner [13]. He suggests that the observed orientational order parameter, Δ (his notation) is

$$\Delta = \langle P_2 \rangle_{\hat{n}} S_0,$$

where $\langle P_2 \rangle_{\hat{n}}$ is an order parameter for long range director fluctuations and S_0 is the local order parameter which should be calculated by a molecular field theory. We can identify the $\bar{P}_2$ derived from the single molecule scattering with Δ. As explained in §2, $\bar{P}_2$ derived from the equatorial arcs may be approximately $\langle P_2 \rangle_{\hat{n}}$. Using these rules gives an order parameter, S_0, in the region of 0·74 to 0·81 which is much higher than molecular field theories predict, but does not seem unreasonable as a description of the degree of parallelness of neighbouring molecules.

5. Conclusions

We have demonstrated a new method for studying the orientation and possibly the conformation of molecules in fluid phases by neutron scattering from a mixture of hydrogenous and deuteriated versions of the same molecule. In the nematic phase, the orientational order parameters, $\bar{P}_2$ and $\bar{P}_4$, have been found to be much less than predicted by the Maier–Saupe theory but are in better agreement with a theory involving biaxial intermolecular interactions. Comparison of the order parameters derived from the angular distribution of scattered intensity in the single molecule signal and the equatorial interference peaks suggests that local packing of the molecules can be described by an order parameter, $S_0 \sim 0{\cdot}8$.

In the future, a more detailed comparison between nuclear magnetic resonance and results from this neutron scattering technique may be expected to yield more detailed information on the conformation of molecules in the nematic phase. This could be obtained by selective isotopic labelling of different parts of the molecule (e.g. the rigid core and/or the flexible chain(s)). Nuclear magnetic resonance values of $\bar{P}_2$ for different regions of the molecule could be used to confirm the values of $\bar{P}_2$ from the single molecule scattering and hence lend weight to the other order parameters obtained. It would also be necessary to use a more accurate molecular form factor, $|F_{\mathrm{m}}|^2$, and include different conformations rather than assume rigid rods. We believe that the method has considerable potential for studies of molecules in liquids and liquid crystals.

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Appendix

We have given a formula for the differential scattering cross section of a pure liquid crystal in terms of the distribution of molecular orientations $f(\beta_0)$, the conditional probability $P(\Omega_0, \Omega, \mathbf{r})$ and the molecular structure factor $\hat{m}(\mathbf{Q}, \Omega)$,

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{p}} = \int f(\beta_0)P(\Omega_0,\Omega,\mathbf{r})\hat{m}(\mathbf{Q},\Omega_0)\hat{m}(\mathbf{Q},\Omega)\exp(i\mathbf{Q}\cdot\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r}.$$

Taking a molecule with orientation Ω_0 as the origin, $P(\Omega_0,\Omega,\mathbf{r})$ is the probability of finding any molecule (including itself) with orientation Ω at displacement $\mathbf{r}$ from it. If we now define $P_{\mathrm{D}}(\Omega_0,\Omega,\mathbf{r})$ as the probability of finding a *different* molecule at $\mathbf{r}$ (i.e.

$$P(\Omega_0,\Omega,\mathbf{r}) = \delta(\mathbf{r}) + P_{\mathrm{D}}(\Omega_0,\Omega,\mathbf{r}),$$

the cross section explicitly contains a delta function at the origin

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{p}} = \int f(\beta_0)[\delta(\mathbf{r}) + P_{\mathrm{D}}(\Omega_0,\Omega,\mathbf{r})]\hat{m}(\mathbf{Q},\Omega_0)\hat{m}^*(\mathbf{Q},\Omega)\exp(i\mathbf{Q},\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r}.$$

Now we consider a mixture of two molecules with different structure factors ($\hat{m}_1$ and $\hat{m}_2$). There will be four different combinations of the type of molecule at the origin and at $\mathbf{r}$. If the mixture is random we obtain

$$\begin{aligned}\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{m}} = \int & f(\beta_0)[x_1(\delta(\mathbf{r}) + x_1P_{\mathrm{D}})\hat{m}_1(\Omega_0)\hat{m}_1^*(\Omega) + x_1x_2P_{\mathrm{D}}\hat{m}_1(\Omega_0)\hat{m}_2^*(\Omega)\\ & + x_2x_1P_{\mathrm{D}}\hat{m}_2(\Omega_0)\hat{m}_1^*(\Omega) + x_2(\delta(\mathbf{r}) + x_2P_{\mathrm{D}})\hat{m}_2(\Omega_0)\hat{m}_2^*(\Omega)]\\ & \times \exp(i\mathbf{Q}\cdot\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r},\end{aligned}$$

where for brevity we have dropped some of the arguments. The mole fractions of molecules of type 1 and type 2 are denoted by x_1 and x_2 respectively and $P_{\mathrm{D}}(\Omega_0,\Omega,\mathbf{r})$ does *not* depend on the type of molecule at the origin or at $\mathbf{r}$. Regrouping the terms in this equation gives a delta function term containing the difference in the structure factors and a term containing their mean

$$\begin{aligned}\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{m}} = \int & f(\beta_0)[\delta(\mathbf{r})x_1x_2(\hat{m}_1(\Omega_0) - \hat{m}_2(\Omega_0))(\hat{m}_1^*(\Omega) - \hat{m}_2^*(\Omega))\\ & + (\delta(\mathbf{r}) + P_{\mathrm{D}})(x_1\hat{m}_1(\Omega_0) + x_2\hat{m}_2(\Omega_0))(x_1\hat{m}_1^*(\Omega) + x_2\hat{m}_2^*(\Omega))]\\ & \times \exp(i\mathbf{Q}\cdot\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r}.\end{aligned}$$

Since when $\mathbf{r} = 0$, the origin molecule and the one at $\mathbf{r}$ must be the same so Ω is equal to Ω_0 in the first term after integration over the delta function. Substituting for P_{D} in the second gives the final expression

$$\left[\frac{\partial\sigma}{\partial\omega}\right]_{\mathrm{m}} = \int f(\beta)x_1x_2|\hat{m}_1(\Omega) - \hat{m}_2(\Omega)|^2\,d\Omega$$
$$+ \int f(\beta_0)P(\Omega_0,\Omega,\mathbf{r})\overline{\hat{m}(\Omega_0)}\;\overline{\hat{m}^*(\Omega)}\exp(i\cdot\mathbf{Q}\cdot\mathbf{r})\,d\Omega_0\,d\Omega\,d\mathbf{r},$$

where

$$\bar{\hat{m}} = x_1\hat{m}_1 + x_2\hat{m}_2.$$

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