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Orientational distribution function in nematic liquid crystals by x-rays: Fourier method

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Abstract. The existing methods for the determination of the orientational distribution function $f(\beta)$ in the nematic liquid crystals using X-rays have been reviewed. A simple Fourier method which gives $f(\beta)$ in terms of the measured intensity is analysed. Using this distribution function, the accuracy with which the order parameters could be evaluated is discussed and the results show the elegance of the Fourier method used here.

Keywords. Orientational order; nematic; x-rays.

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1. Introduction

The orientational distribution function $f(\beta)$ relative to the director of a nematic liquid crystal can be determined by exploiting the X-ray wide angle diffuse ring corresponding to the lateral mean distance between nearest neighbour molecules. The simplest approach is that of Leadbetter group [1–3] which gives a classical formula for $I(\theta)$, the scattered intensity in a direction at an arc angle θ [see [3] for the notations] in terms of orientational distribution function [ODF] $f(\beta)$ of the rod axis as:

$$I(\theta) = \int_{\beta=\theta}^{\pi/2} \frac{f(\beta)\sin\beta\,\mathrm{d}\beta}{\cos^2\theta\sqrt{\tan^2\beta - \tan^2\theta}} \tag{1}$$

where β is the angle between the rod axis and the director.

2. Methods

A. *Calculation of ODF using equation (1)*

Equation (1) has been analytically inverted for $f(\beta)$ by Deutsch [4] and the expression for the orientational order parameter is given as

$$S = \langle p_2 \rangle = 1 - \frac{3}{2N}\int_0^{\pi/2} I(\theta)\left[\sin^2\theta + (\sin\theta\cos^2\theta)\log\left(\frac{1+\sin\theta}{\cos\theta}\right)\right]\mathrm{d}\theta \quad (2)$$

where

$$N = \int_0^{\pi/2} I(\theta)\mathrm{d}\theta. \quad (3)$$

On the basis of Maier–Saupe model, some of the earlier investigators like Kelkar and Paranjpe [5] and Haase *et al* [6] have inverted this eq. (1) numerically by using truncated Legendre polynomials or circular functions and normally the number of unknown parameters is more than eight. The corresponding expression for $I(\theta)$ used by Leadbetter [3] is

$$\begin{aligned} I(\theta) &= f_0 + \frac{2}{3}f_2\cos^2\theta + \frac{8}{15}f_4\cos^4\theta + \frac{16}{35}f_6\cos^6\theta \\ &\quad + \frac{128}{315}f_8\cos^8\theta + \frac{256}{693}f_{10}\cos^{10}\theta + \cdots \end{aligned} \quad (4)$$

and a mere fit of $I(\theta)$ in the series gives access to $f(\beta)$.

Recently Levelut and her group [7] have come up with a novel method within the frame work of Maier–Saupe model, wherein there is only one independent parameter and hence there is a direct relation between $I(\theta)$ and $f(\beta)$:

$$I(\theta) = \frac{1}{Z}\left[1 + \frac{2m}{3}\cos^2\theta + \frac{4m^2}{15}\cos^4\theta + \frac{8m^3}{105}\cos^6\theta + \frac{16m^4}{945}\cos^8\theta + \cdots\right] \quad (5)$$

where

$$Z = 4\pi\int_0^1 e^{mx^2}\,\mathrm{d}x, \quad (6)$$

is the normalisation constant.

B. *Present method*

In Fourier integrals, we have

$$I(\theta) = \int_{-\infty}^{\infty} k(\theta-\beta)f(\beta)\,\mathrm{d}\beta. \quad (7)$$

Identifying

$$k(\theta,\beta) = \frac{\sin\beta}{\cos^2\theta\sqrt{\tan^2\beta - \tan^2\theta}} \quad (8)$$

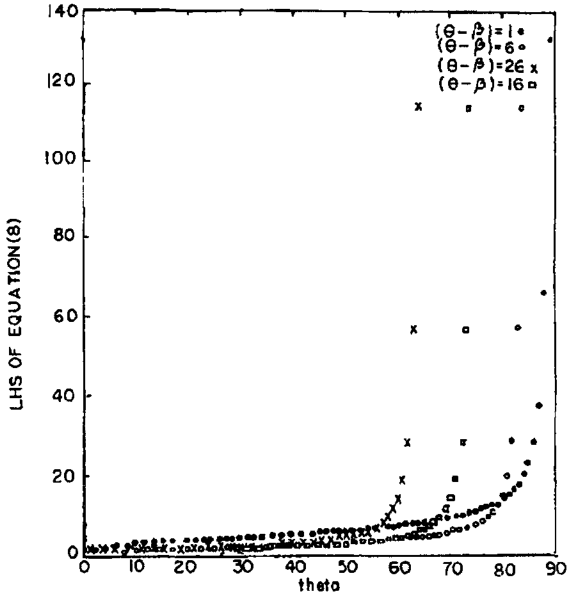

Figure 1. A graphical plot of LHS of eq. (8) versus θ at different constant values of $(\theta-\beta)$.

and $I(\theta)$ as the intensity distribution along equatorial arcs in the diffraction pattern, $f(\beta)$ is the unknown function. The kernel of the above equation is a real valued, non-symmetric and definite function. In principle, to use the Fourier transform technique to invert the eq. (7), the left hand side (LHS) of eq. (8) should be a function of $(\theta-\beta)$ and not (θ,β)[8]. In other words, a plot of LHS of eq. (8) for various values of θ, at constant $(\theta-\beta)$ should be a line parallel to the ordinate. Figure 1 shows one such graphical plot of LHS of eq. (8) vs θ at different constant values of $(\theta-\beta)$. It can be inferred from figure 1 that LHS of the eq. (8) is a function of $(\theta-\beta)$ within an error of less than 10% in the region of θ values for which the arc intensity drops to half of its maximum value. Approximating the function $k(\theta,\beta)$ as $k(\theta-\beta)$ and assuming that the required transform exists, we apply Fourier convolution theorem to obtain

$$I(\theta)=\int \mathcal{K}(\beta)\mathcal{F}(\beta)e^{-i\theta\beta}\mathrm{d}\beta \tag{9}$$

where $\mathcal{K}(\beta)$ and $\mathcal{F}(\beta)$ are the Fourier transforms of $k(\theta)$ and $f(\theta)$ respectively. Inverting eq. (9) we have

$$\mathcal{K}(\beta)\mathcal{F}(\beta)=\frac{1}{2\pi}\int_0^{\pi/2} I(\theta)e^{i\theta\beta}\mathrm{d}\beta=\frac{\mathcal{F}[I(\theta)]}{\sqrt{2\pi}} \tag{10}$$

and

$$\mathcal{F}(\beta)=\frac{1}{\sqrt{2\pi}}\frac{\mathcal{F}[I(\theta)]}{\mathcal{K}(\beta)} \tag{11}$$

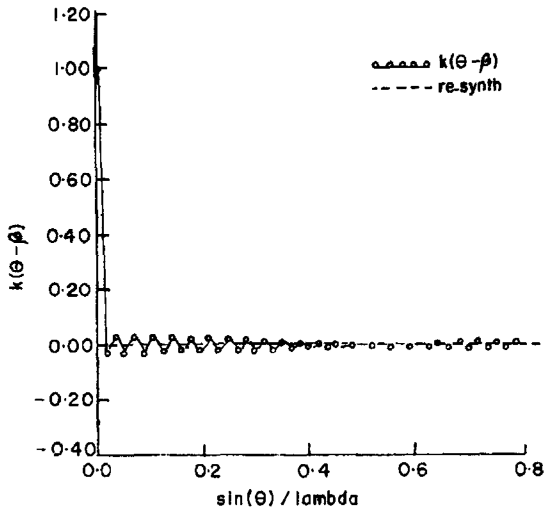

Figure 2. Variation of $k(\theta - \beta)$ vs. $\sin(\theta/\lambda)$.

Again inverting we have

$$f(\theta) = \frac{1}{2\pi} \int_0^{\pi/2} \frac{\mathcal{F}[I(\theta)]}{\mathcal{K}(\beta)} e^{-i\theta\beta} \mathrm{d}\beta \tag{12}$$

and here θ also varies from 0 to $\pi/2$. For a rigorous justification of the result when the kernel is of the form $k(\theta - \beta)$ is given in Arfken [8]. The function $k(\theta - \beta)$ as $\beta \to 0$ is given in figure 2 and the Fourier transform of such a function is obtained numerically and is given in figure 3. This function is independent of the instrument or the wavelength used for recording the X-ray diffraction pattern. Figure 3 also gives the resynthesised function $k(\theta - \beta)$ using the Fourier coefficients.

C. *Procedure to obtain ODF*

Using the intensity distribution along the equatorial arc, $I(\theta)$ is deconvoluted employing eq. (11) and Fourier coefficients of the function $k(\theta - \beta), \beta \to 0$. These corrected coefficients are inverted again by using eq. (12) to obtain $f(\theta)$ or $f(\beta)$, the orientational distribution function (ODF). Then the orientational order parameter is given by

$$\langle p_2 \rangle = \frac{\int_0^{\pi/2} p_2(\cos\theta) f(\beta) \sin\beta \mathrm{d}\beta}{\int_0^{\pi/2} f(\beta) \sin\beta \mathrm{d}\beta}. \tag{13}$$

For deconvolution and integration we have used simple Fortran routines available in 'numerical recipes' [9].

3. Results and discussion

For testing this procedure we have used the profiles given in Davidson *et al* [7] and for

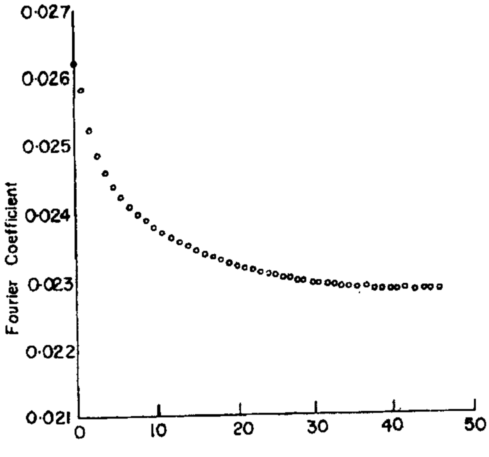

Figure 3. Fourier transform of figure 2.

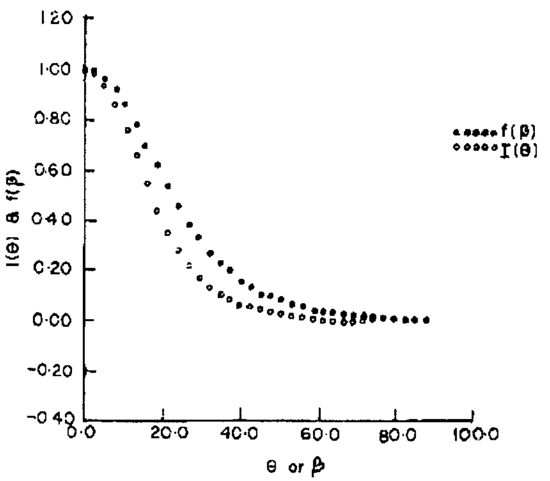

Figure 4. Intensity of diffused arc for various θ values along with $f(\beta)$ for various β values.

comparison, we have written programmes (FTN77) to calculate orientational order employing Deutsch [4], Leadbetter [3] and Davidson *et al* [7] methods also. The results obtained are given in table 1. It is evident from table 1, that orientational order obtained from present method is in close agreement with Deutsch method and these values lie inbetween the values computed from the other two methods. The various profiles reported by Levelut group [7] essentially lead to the same conclusion. The present method gives the whole distribution function $f(\beta)$ and hence it is possible to compute higher moments like $\langle p_4 \rangle$ using

$$\langle p_L \rangle = \frac{\int_0^{\pi/2} p_L(\cos\theta) f(\beta) \sin\beta \mathrm{d}\beta}{\int_0^{\pi/2} f(\beta) \sin\beta \mathrm{d}\beta}. \tag{14}$$

Table 1. Orientational order parameter obtained by different methods using X-ray diffused profile along the arc.

Sample	Leadbetter [1] $\langle P_2 \rangle$	Levelut [7] $\langle P_2 \rangle$	Deutsch [4] $\langle P_2 \rangle$	Present method $\langle P_2 \rangle$	Stand. Dev. in %
4 O.4	0.75	0.65	0.71	0.70	1.1
T = 48°C (nematic)					
TBEA	0.78	0.73	0.75	0.75	0.7
T = 176°C (nematic)					
30% phasmidic +70% TBDA	0.82	0.78	0.79	0.78	0.8
T = 180°C (nematic)					
Poly. PE10	0.77	0.71	0.74	0.74	0.5
T = 123°C (nematic)					
$PMAOCH_3$	0.78	0.73	0.75	0.75	0.7
T = 63°C (nematic)					
$PMAOC_4H_9$	0.70	0.52	0.63	0.62	3.2
T = 115°C (nematic)					
$PMAOC_4H_9$	0.72	0.55	0.65	0.64	1.3
T = 101°C (SmA)					
$PMAOC_4H_9$	0.85	0.86	0.83	0.83	0.6
T = 80°C (SmA)					
$PMAOC_4H_9$	0.86	0.88	0.84	0.84	0.7
T = 25°C (SmA glass)					
4 O.8	0.68	0.43	0.59	0.57	2.7
T = 78°C (nematic)					
4 O.8	0.71	0.53	0.63	0.62	1.8
T = 74°C (nematic)					
4 O.8	0.76	0.66	0.71	0.71	0.9
T = 66°C (nematic)					
4 O.8	0.84	0.85	0.82	0.82	0.73
T = 56°C (SmA)					

Compound 4 O.4 (N-(4-n-butyl oxybenzylidine)-4-n-butylaniline)
Compound 4 O.8 (N-(4-n-butyl oxybenzylidene)-4-n-octylaniline)

In figure 4 we have reproduced the experimental intensity profile along with resynthesised ODF using eq. (12) to highlight the fact that these two are not the same as suggested by Vainshtein [10].

We have also estimated the error introduced by calculating $I(\theta)$ from eq. (1), using $f(\beta)$ obtained from eq. (12) and then comparing with the experimental normalized $I(\theta)$ profile. Figures 5 (a) and (b) give the comparison for two nematic samples, $Polym.PE10$ and $PMAOC_4H_9$ respectively. Such being the case, the approximations (ie., (i) assuming the lower limit of the integral to be zero and (ii) convolutions of the functions which are in the integrand of eq. (1)) made in this paper with regard to the integral in eq. (1), induce a negligibly small percentage of error in the calculations of orientational order parameters.

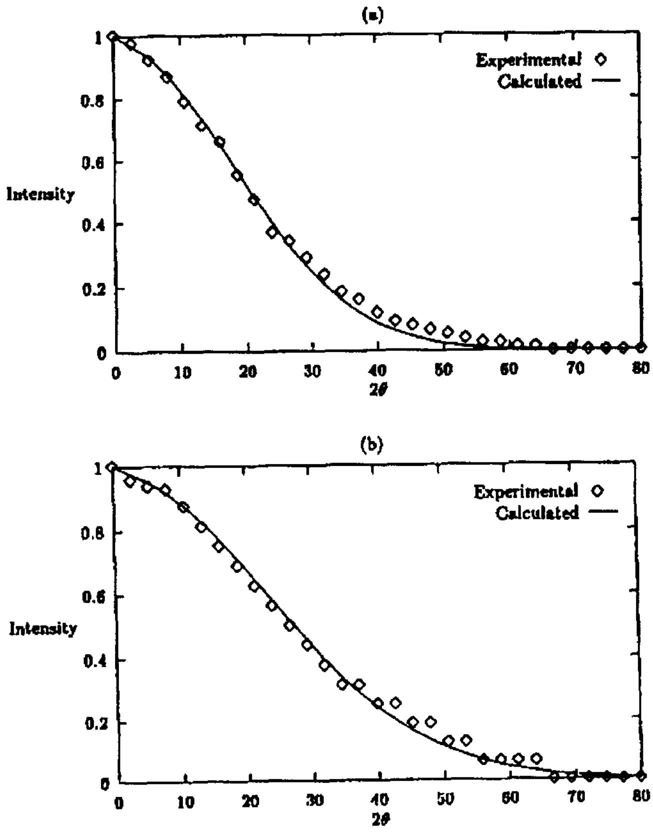

Figure 5. A comparison of experimental and calculated intensity values for two different nematic samples (**a**) $Polym.PE10$ and (**b**) $PMAOC_4H_9$.

4. Conclusion

The present method proposed here is a simple and straightforward way of obtaining orientational distribution function which involves only three steps:

(i) Fourier transform of the given arc intensity (standard routines are available for this purpose)

(ii) Fourier transform of LHS of eq. (8) when $\beta \to 0$ (or one can use the data given in figure 3)

(iii) Fourier transform of ratio of (i) and (ii). Fourier coefficients which will give the distribution function.

From these data higher moments of this function can be computed and also can be easily incorporated in standard X-ray analysis softwares. It is also useful procedure for finding the ODF in the case of polymer fibres.

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