ANALYSIS OF THE 2-DIMENSIONAL SCATTERING DISTRIBUTION FROM: - POORLY ORDERED (LIQUID) CRYSTALS, ON A SMALL ANGLE SCATTERING - A LAMINAR (TEXTURED) SAMPLE, ON A 4 CIRCLE DIFFRACTOMETER SPECTROMETER

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ANALYSIS OF THE 2-DIMENSIONAL SCATTERING DISTRIBUTION FROM:
- POORLY ORDERED (LIQUID) CRYSTALS, ON A SMALL ANGLE SCATTERING
- A LAMINAR (TEXTURED) SAMPLE, ON A 4 CIRCLE DIFFRACTOMETER
SPECTROMETER

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Abstract - When samples are ill-ordered, few scattering peaks may be observed, still fewer can be resolved. A simulation of the peak shapes is then essential. Two examples are given; one concerns the low angle neutron scattering by a polymer liquid crystal; the other one deals with the neutron scattering by laminated polyacetylene on a 4 circle diffractometer.

Recently two physical problems for which the data are 2d pictures required new programming. In one case we started to use the small angle neutron scattering spectrometer PAXY at the Orphée reactor for low angle scattering from liquid crystals. On the 2d pictures so obtained Bragg or diffuse peaks can be observed; there arises again a problem of peak shape characterisation: position, intensity, width, type (gaussian, lorentzian...). In the other case we got from D19 at the ILL a mass of data representing the neutron scattering from polyacetylene. Only one Debye-Sherrer ring was resolved: for a detailed data analysis we needed a model to account for the observed ring shape. This model includes the calculation of a profile fitting method.

Our aim was to describe the details of the shape of the few observed peaks, rather than list the integrated intensity of a great number of well defined Bragg spots as in classical 4 circle diffractometry.

On Figure 1 are examples of the images of neutron scattering obtained at low angle on the PAXY spectrometer. The sample was a comb type polymer liquid crystal [1]. A magnetic field along x axis pulls the mesomorphic cores parallel to itself, moreover these organize in smectic layers orthogonal to x axis: the [100] Bragg peak is clearly seen. One notices also diffuse peaks at h = 1/2 and h = 2 on each side of the horizontal x axis. For the understanding of the structure it is important to determine the position, the shape and the width of these peaks.

For instance, the h = 1/2 line means that there is some tendency of the molecules to build bilayers. The fact that these spots are displaced from the alignment axis (x) means that there is some oscillation (pseudoperiodicity) of a part of the sample, which appears to be the polymer chain itself.

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Fig. 1. Low angle scattering from a polymer liquid crystal in the smectic state. Image obtained on the 128 × 128 gas multidetector part of the PAXY small angle neutron spectrometer. The picture has been normalized for cell efficiency and the background subtracted. The cross marks the point hit by the main beam (origin of the axes). The aligning magnetic field is parallel to the horizontal x axis. The y axis is vertical. In Fig. 1a the polymer chain was deuterated. One can see the [1,0,0] Bragg peak and four diffuse spots. For Fig. 1b only half the polymer chains were deuterated; besides the same features, one notices strong forward scattering near the origin.

On Figure 2 are shown various treatments of the data of picture 1a. In order to extract quantitative information, the interactive program PXY was written. Besides the basic data treatment (normalisation, background subtraction) it allows to draw a histogram of the picture, in order to choose a mask (right part of Fig. 2a, 2b). The intensity of the points inside the masked area are added along one or the other direction, and thereafter displayed on a drawing in the middle of the picture. Then one may choose among several functions (gaussian, lorentzian...) to fit one or several peaks. The initial and final parameters are shown on the bottom left corner of the picture, together with the $\chi^2$ value and size parameters converted to reciprocal space lengths. The fitted functions are 1 or 2 dimensional, to the individual measured points. On Fig. 2b is shown such a treatment for the [100] Bragg peak: the fitting to a gaussian gives the position and width. Meanwhile, which part of the width is due to the resolution and which part has a physical meaning (lack of long range order) remains unknown.

To solve such a problem requires a good calculation of the resolution function. This latter can be calculated easily in the frame of the gaussian approximation. Since Cagliotti et al. [2] many authors have applied this approximation to a variety of cases [2,3,4,5,6,7,8]. For instance, programs based on it are routinely and successfully applied to the analysis of the data obtained on 3 axis spectrometers. This approximation tells that considering a neutron with given missets in length $dk/k$ and direction $\varepsilon$ from the mean wave-vector we assume that its probability:

- to pass through a collimator with divergence $\alpha$ is $\alpha \exp - 1/2(\varepsilon/\alpha)^2$

- to be reflected by a crystal monochromator at Bragg angle $\theta_M$, with mosaicity $\eta_M$ is $\exp - 1/2 \left( \frac{2 \tan \theta_M + \varepsilon}{\eta_M} \right)^2$
Fig. 2. Examples of data treatment with the PXY program. The image concerned is the one displayed on Fig. 1a.

Fig. 2a: Fitting of a section of 2 diffuse spots with two different lorentzians.

Fig. 2b: Fitting of a section of the Bragg peak to a gaussian.
Fig. 3. The [100] and [100] peaks of a polymer liquid crystal observed on the PAXY multidetector centered on and perpendicular to the main beam. Notice the asymmetry on Fig. 3a.
On Fig. 3b the continuous line shows the intensity calculated through the PXY program: the calculation uses the resolution function appropriate to the case of monochromatization with a velocity selector. There is no adjustable parameter other than background and a scale factor.
- to be transmitted by a helical velocity selector with helicity angle $\theta_s$, and slit divergence $\alpha_s$ is $\exp -\frac{1}{2} \left( \frac{\theta - \varepsilon_{ih}}{\alpha_s} \right)^2$

Then the overall probability may be expressed as an exponential: its exponent is a quadratic function of the five missets:

$$P = \exp -\frac{1}{2} V_R R \bar{V}_R$$

$$V_R = \left( \frac{dk}{k}, \varepsilon_{ih}, \varepsilon_{iv}, \varepsilon_{fh}, \varepsilon_{fv} \right)$$

where the subscripts $i$ and $f$ stands for initial and final and $h$ and $v$ stand for horizontal and vertical.

The elements of the $5 \times 5$ $R$ matrix may be found in the appendix.

The case of a Bragg reflection in the usual (horizontal) scattering plane is very easily handled since:
- it allows separate integration over the vertical angular missets
- the Dirac function property concerning integration reduces the number of variables by one.
- an analytical solution is then tractable.

The calculated peak width is (on the horizontal axis):

$$\Delta = \frac{1}{r_{33}} + \frac{4 \tan^2 \theta_B}{r_{22} - 4 \tan \theta_B r_{12} + r_{11}} \frac{r_{11} r_{22} - r_{12}^2}{r_{11} r_{22} - r_{12}^2}$$

where the $r_{ij}$ are the elements of the resolution matrix $R$ and $\theta_B$ is the Bragg angle.

As an application of this we show the picture 3. The multidetector already used for Fig. 1, is now centered perpendicular to the direct beam, monochromatised by a velocity selector. The same Bragg peak appears on both sides of the beam catcher as the [100] and [100] Bragg peaks. Clearly the width and height differ. This fact is puzzling if one considers that everything is symmetric in the experimental set up. However one has to remember of the helicity of the velocity selector: $dk/k$ and $\varepsilon_{ih}$ in the neutron packet must be coupled.

The above formula for $\Delta$ for the case of crystal monochromator can be applied as well in the case of a velocity selector as can be seen on Figure 3b. The full line is calculated with no adjustable parameter except scale and background level [4].

If one wants to describe a Bragg peak out of the horizontal plane, or a Debye-Sherrer ring one needs a calculation of the resolution function at any point of the Ewald sphere. This was indeed necessary to treat the data obtained on D19A from the diffraction of laminated polyacetylene (Fig.4).

If $k_i$, $k_f$ are the initial and final neutron wave-vector, define:

- $\beta$: the scattering angle $(k_i,k_f)$
- $\gamma$: the "longitude"
- $\nu$: the "latitude"
- $\mu$: the dihedral angle of the plane $k_i,k_f$ to the horizontal plane (usually $\mu = 0$)

The calculation of the flux falling into a given cell $\gamma$, $\nu$ is the convolution product of the spectrometer resolution function (after Cagliotti) with the scattering function. In the frame of the usual gaussian approximation the resolution function is a gaussian over $\beta$. Thence, once the convolution is made, the sensitive factor
Fig. 4. The scattering from transpolyacetylene on D19. All the "snapshots" taken for one sample setting have been combined in order to build an image of a part of the Ewald sphere versus the angular coordinates \( \gamma \) (the longitude) and \( \nu \) (the latitude).

On the right side the image is shown with \( \gamma \) along the horizontal axis.
On the left side the image was rotated by 90°. \( \nu \) is along the horizontal axis.
Here the alignment axis of the sample was /// oblique.

Describing the variation of the intensity scattered by a set of planes \( h, k, \ell \) over the reciprocal space is:

\[
\exp \left( -\frac{1}{2} \left( \frac{\beta - 2 \theta_{h\ell k}}{\Delta_{h\ell k}} \right) \right)
\]

(As a consequence of the finite size of the neutron wave-packet the scattering occurs not only along a line \( \beta = 2\theta_{h\ell k} \) but over a wide area of the reciprocal space).

In the classical (all horizontal) scattering case \( \Delta_{h\ell k} \) is independent of the cell and a trinome versus \( \tan \theta_{h\ell k} \). Once \( \mu \) is no more zero the formula for \( \Delta_{h\ell k} \) must include \( \mu \) dependence: it remains a constant only along constant \( \mu \) lines over the Ewald sphere.

\[
\Delta_{h\ell k} = \frac{1}{r_{33}} + \frac{4 \tan^2 \theta_{h\ell k} r_{22} - 4 \tan \theta_{h\ell k} \cdot r_{12} \cos \mu + r_{11} \cos^2 \mu}{r_{11} r_{22} - r_{12}^2} + \frac{\sin^2 \mu}{r_{44}}
\]

The variation of this width over the concerned area of the Ewald sphere is shown for two Bragg peaks on Fig. 5.

A program PCDX has been built in order to make a simulation of the scattered intensity of Fig. 4. Besides the usual factors (Lorentz factor...) it calculates the structure factors, the positions of the rings and makes a convolution of the resolution function with a Lorentzian scattering function. It includes also a model to take care of the ring modulation due to the texture. The fitting of the physical parameters is still in progress. Hence results shall not be discussed nor presented here.

Of the two programs here described, PXI allows a fast fitting of one or two dimensional functions to peaks with any shape observed on a multidetector. This program can also take care of Bragg peaks or gaussian diffuse spots. It is currently
being developed in order to accommodate Lorentzian or other shapes for the diffuse spots. The second one, PCDX, is more suited to the description of modulated Debye-Sherrer rings, as can be observed, for instance, from spectra gathered on D19.

The experiment on PAXY was made together with B. Carvalho, J.P. Cotton, P. Keller, M. Lambert and F. Moussa from LLB. The work on D19 was a cooperation with G. Mc Intyre, R. Stansfield from ILL and L. Rosta from KFKI.

I am pleased to acknowledge how many points concerning the resolution handling were cleared by discussions with B. Hennion.

Fig.5. Mapping of the width of the Debye-Sherrer rings as calculated from the resolution function for two [h,k,2] Bragg angles. Fig.5a. [0,2,1] ; Fig.5b. [0,0,2].
APPENDIX

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<th>crystal monochromator</th>
<th>velocity selector</th>
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<td>( (\theta_s/\alpha_s)^2 )</td>
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REFERENCES