X-ray Diffraction-Line Broadening Analysis: Paracrystalline Method

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Abstract
Line-profile simulation and matching on the basis of a paracrystalline one-dimensional Hosemann model provides a promising approach to the analysis of line broadening. Results of analysis using X-ray wide-angle data of polymers and metallic samples are compared with Warren-Averbach multiple-order and single-order methods. Various column-length-distribution functions are also used for better agreement with the experimental profiles.

1. Introduction
X-ray diffraction of polymers/metals is a nondestructive method that gives real information about materials, like the crystal size in polycrystalline aggregates, their deformation, preferred orientation and structural defects. These properties are essential as they have considerable influence on technological properties of materials like superconducting materials (Balzar, Ledbetter & Bonefacica, 1994; Balzar, 1993), fibres (Lee, Barton & Schultz, 1995) and metals (Van Berkum, Delhez, de Keijser & Mittermeijer, 1995) annealed at high temperatures. Obtaining this information at present is highly subjective in nature. It is interesting to note that Mittemeijer and his group (Van Berkum et al., 1995) have suggested matching of the simulated line profile with the experimental profile on the basis of a strain-field model where they assume the broadening is order-independent.

In this paper, we report a method based on the one-dimensional paracrystalline model of Hosemann & Bagchi (1962) and Vainshtein (1966) that can uniquely determine the parameters like crystal size and lattice distortion (strain) from a given hkl reflection. With a brief introduction to the theory (Mark, 1988; Somashekar & Gopalkrishneurs, 1993), we develop a statistical procedure for determining the parameters. Such a point paracrystalline model approach has been used earlier by Blackwell, Cageao & Biswasa (1987) to account for X-ray diffraction patterns in liquid-crystalline polymers. At this point, no attempt has been made to include other scattering effects.

2. Theory: paracrystalline probability statistics
The probability that two lattice points, somewhere in the infinite one-dimensional paracrystal, are separated by a distance x is governed in polymers by the weak van der Waals and hydrogen-bond interaction (Schultz, 1974). The actual form of the interaction is very complex and it is not completely understood. Generally, the range of separations of nearest neighbours can be large compared to that of the covalently bonded atoms in the chains themselves. There is also a cut-off at small distances owing to the steep rise in the energy curves. The main properties of the nearest-neighbour separation, $P_1(x)$, are deduced from the features of a statistical structure as

$$\int_0^\infty P_1(x) \, dx = 1$$

$$\langle x \rangle = \int_0^\infty x P_1(x) \, dx = d$$

$$g^2 = \frac{1}{\langle x \rangle^2} \int_0^\infty \left( |x - \langle x \rangle| \right)^2 P_1(x) \, dx.$$  \hspace{1cm} (1)

The last equation in (1) gives a dimensionless quantity known as the paracrystallinity, $g^2$, where $g$ is the lattice distortion or strain. $d$ is the lattice constant of the crystal.

In real materials, $P_1(x)$ is also asymmetric around the mean value owing to the shape of the interaction curve. Hosemann & Bagchi (1962) have shown, however, that in most cases the asymmetry is not an important factor and that a Gaussian approximation to $P_1(x)$ is sufficient, i.e.

$$P(x) = \left[ \frac{1}{w(2\pi)^{1/2}} \right] \exp \left[ -\frac{1}{2} (x - d)^2 / w^2 \right].$$ \hspace{1cm} (2)

Equation (1) is satisfied by such an approximation and also gives the paracrystallinity as

$$g^2 = \left( \frac{w}{d} \right)^2,$$ \hspace{1cm} (3)

where $w$ is the standard deviation of $P_1(x)$. Real materials consist of a large number of finite scattering units rather than an infinite lattice. The finite autocorrelation function can be obtained by considering the electron density of finite scatterers. This finite electron density is written in terms of the infinite lattice electron density and a shape amplitude $S(x)$, i.e.

$$e_{\text{finite}}(x_1 + x_2) = e_{\infty}(x_1 + x_2)S(x_1).$$ \hspace{1cm} (4)
and this is shown in Fig. 1. To a first approximation, \( S(x_1) \) is expressed as a rectangular function of size \( D \) and unit height by

\[
S(x_1) = \begin{cases} 
1; & 0 \leq x_1 \leq D; \\
0; & 0 > x_1 > D.
\end{cases}
\]  

(5)

Equation (4) includes a separate variable \( x_2 \) that enables the origins of the shape amplitude and infinite lattice electron density to be shifted with respect to one another. This allows different regions of the infinite lattice to be positioned within the shape amplitude. The large number of scattering units can, therefore, contain different portions of the infinite lattice to be positioned within the shape amplitude. The large number of scattering units can, therefore, contain different portions of the infinite lattice and will ensure that all possible scatter positions will be present. Then, the autocorrelation function for a finite lattice is given by

\[
Q_{\text{finite}}(x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\pi(x_1 + x_2)(x + x_1 + x_2)} \\
\times S(x_1)S(x_2) \, dx_1 \, dx_2.
\]  

(6)

A contribution to the \( x_2 \) integral will occur only when there are scatterers positioned at \( x_1 + x_2 \) and \( x + x_1 + x_2 \). The probability of finding points separated by \( x \) in the lattice as a whole is that of the lattice point probability function \( P(x) \). The value of \( x_1 \) is not important for this integration since \( x_2 \) varies from \(-\infty\) to \( \infty \). Simplifying the above equation, we get

\[
Q_{\text{finite}}(x) = Q_\infty(x) \int_{-\infty}^{\infty} S(x_1)S(x + x_1) \, dx_1.
\]  

(7)

where \( Q_\infty(x) \) is the autocorrelation function for the infinite lattice. Using the expression for \( P(x) \) and identifying the integration over \( x_1 \) as the autocorrelation function of the shape amplitude, we have

\[
Q_{\text{finite}}(x) = Q_\infty(x)Q_{\text{shape}}(x),
\]  

(8)

where

\[
Q_{\text{shape}}(x) = 1 - |x|/D.
\]  

(9)

We have derived this result in the same way as Hosemann (1963), while Vainshtein (1966) uses the fact that autocorrelation and intensity are a Fourier pair to arrive at the same expression.

The Fourier transform of \( N \) probability peaks \( F[Q_N(x)] \), excluding the shape function, using the convolution theorem, can be shown to be (Mark, 1988)

\[
F[Q_N(x)] = 1 + 2 \sum_{n=1}^{N} [I_1(s)]^n.
\]  

(10)

where \( I_1(s) \) is the Fourier transform of \( P_1(x) \), which gives

\[
I_1(s) = \exp(-a^2s^2 + ids),
\]  

(11)

where \( a^2 = \omega^2/2 \) for the Gaussian approximation [2].

The contribution from the shape amplitude can be determined from the following Fourier theorem (Sneddon, 1951):

\[
F[xQ_N(x)] = -id[\{F[Q_N(x)]\}] /ds
\]

so that

\[
F[(1 - |x|/D)Q_N(x)] = [1+(i/D)d/ds]\{F[Q_N(x)]\}. \]  

(12)

Summing the series in (9) and substituting into (12), we get an expression for the intensity from a finite paracrystal as

\[
I(s) = I_{N-1}(s) + I'_N(s),
\]  

(13)

where \( I'_N(s) \) is the modified intensity for the probability peak centred at \( D \). It has been shown that (Mark, 1988)

\[
I'_N(s) = (2a_N/D\pi^{1/2}) \exp(i\pi Ns) \times \{1 - a_N[2D(a_Ns) + i\pi^{1/2} \exp(-a_N^2s^2)]\},
\]  

(14)

where \( a_N^2 = N\omega^2/2 \) and \( D(a_Ns) \) is Dawson's integral or the error function with purely complex argument and can be easily computed. Simulated intensity profiles for various values of \( g \) and \( N \) are given in Fig. 2. Here, \( D \) is given by \( N\delta_{\text{hi}} \) or \( Nd \).

3. Results and discussion: statistical procedure for line simulation and matching

Using (13) and (14), one can generate intensity profiles consisting of 3-4 orders of reflections using the one-dimensional paracrystalline model outlined in the previous section. If the experimental profile is a first-order reflection, then a first-order reflection of the simulated profile is used for matching. Normally, the number of experimental points of an X-ray profile between \( s_0 \) (peak position) and \( s_0 + s_0 \) should be above the condition imposed by the sampling theorem of Young, Gerdes & Wilson (1967), wherein they consider the effect of the

![Fig. 1. Electron density of a finite paracrystal. All delta functions outside the dotted shape amplitude are neglected. The quantity \( x_2 \) allows different portions of the infinite lattice to fall within the shape amplitude.](image)
Table 1. Microcrystalline parameters obtained by matching of simulated and experimental profiles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present method</th>
<th>Multiple order method&lt;sup&gt;[a]&lt;/sup&gt;</th>
<th>Single-order method&lt;sup&gt;[b]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g (%)</td>
<td>⟨N⟩ (°)</td>
<td>⟨D⟩ (Å)</td>
</tr>
<tr>
<td>LDPE 110</td>
<td>0.01 (1)</td>
<td>7.5 (2)</td>
<td>30.7</td>
</tr>
<tr>
<td>LDPE 220</td>
<td>1.20 (1)</td>
<td>7.5 (2)</td>
<td>30.9</td>
</tr>
<tr>
<td>LDPE 200</td>
<td>2.00 (4)</td>
<td>11.1 (2)</td>
<td>43.3</td>
</tr>
<tr>
<td>LDPE 400</td>
<td>1.51 (2)</td>
<td>12.4 (2)</td>
<td>49.6</td>
</tr>
<tr>
<td>Kevlar 200</td>
<td>0.01 (1)</td>
<td>12.2 (4)</td>
<td>23.3</td>
</tr>
<tr>
<td>Kevlar 400</td>
<td>2.53 (3)</td>
<td>14.4 (2)</td>
<td>28.2</td>
</tr>
<tr>
<td>MgO 422</td>
<td>0.57 (1)</td>
<td>66.1 (5)</td>
<td>113.6</td>
</tr>
<tr>
<td>W 110</td>
<td>1.29 (2)</td>
<td>104.7 (9)</td>
<td>233.7</td>
</tr>
</tbody>
</table>

References: (a) Warren & Averbach (1950, 1952); (b) Hall & Somashekar (1991); (c) D. Balzar, private communication; (d) McKeehan & Warren (1953); (e) Aqua & Wagner (1964); (f) Van Berkum (1994); (g) Van Berkum, private communication.

* Using all the available reflections.

finite number of sampling points and conclude that a minimum of about 3–4 must fall within the intensity profile at half height.

The experimental profile between \( s_0 \) and \( s_0 + s_0/2 \) (or \( s_0 \) and \( s_0 + B/2d \) if there is truncation of the profile \( B < 1 \)) is matched with the corresponding simulated order of reflection between \( s_0 \) and \( s_0 + s_0/2 \) (or \( s_0 \) and \( s_0 + B/2d \)) using the one-dimensional paracrystalline model for various values of \( N \) and \( g \) to minimize the difference between the calculated and experimental normalized intensity values. For minimization, we have used a *SIMPLEX* multidimensional algorithm (Press, Flannery, Teukolsky & Vetterling, 1987). The simplex is a geometrical figure that, in \( N \)-dimensional space, has \( N + 1 \) vertices, with interconnecting edges and faces (in three dimensions it is a tetrahedron), and the minimization algorithm makes use of this concept. If there are \( n \) variables to be adjusted, the procedure starts with \( n + 1 \) estimates forming a simplex. The vertex leading to the highest \( \Delta^2 \) is found and this is reflected in the opposite face, the new point normally having a lower \( \Delta^2 \), and the simplex is either expanded or contracted along this line seeking a still lower value. The high point is then rejected and the procedure is repeated. The results obtained do not depend on the initial estimates of the parameters. The minimum value of the standard deviation indicates a good fit, since this is comparable with experimental uncertainty.

Using this procedure, the values of \( N \) and \( g \) obtained for the X-ray reflections of low-density polyethylene (LDPE) (110, 220, 200 and 400) and of Kevlar49 (200 and 400) are given in Table 1 along with standard deviations. The experimental procedure and various corrections are given in an earlier paper (Somashekar, Hall & Carr, 1989). Also, in Table 1, we have included the results obtained by the Warren–Averbach multiple-order method (Warren & Averbach, 1950, 1952) and the single-order method (Hall & Somashekar, 1991). We find that there is good agreement with the results obtained using different orders of reflection from the same set of planes and the Warren–Averbach multiple-order method. The inherent difficulties in the single-order method have been discussed in an earlier paper (Hall & Somashekar, 1991).

We have also extended our work to the case of tungsten and MgO specimens, since the cold deformation of tungsten shows dominant strain broadening caused by the introduction of numerous dislocations, whereas the thermal decomposition of MgCO₃ gives rise to size-
Fig. 3. Matching of simulated intensity profiles, employing different column-length distributions with sample profiles. (a) LDPE 110, (b) LDPE 220, (c) LDPE 200, (d) LDPE 400, (e) Kevlar 200, (f) Kevlar 400, (g) W 110 and (h) MgO 422.
only broadening. The physically broadened line profiles of W 110 and MgO 422 obtained by the Fourier–Stokes deconvolution method, collected and sent by Dr D. Balzar of NIST, Colarado, USA, were used to determine the size and strain by matching with the simulated line profile as discussed in this paper; the values are given in Table 1. Figs. 3(a) to (h) give the experimental and simulated profiles from the one-dimensional paracrystalline model for all the reflections. All the programs necessary for the calculations are written in Fortran77 and computations were carried out using an IBM AT/486; normally, two to three hours are required for the analysis of a profile. These results are based on Hosemann’s paracrystalline model, wherein the distribution of column lengths is a delta function. With the crystal size \((N)\) and lattice distortion \((\delta)\) obtained above as input parameters, we have also used two symmetric (Gaussian and top-hat) and two asymmetric (exponential and Reinhold) column-length distributions.

**Gaussian:**

\[ P(i) = \left(\frac{\sigma}{(2\pi)^{1/2}}\right)^{-1} \exp\left\{ -\frac{1}{2}(i-N)^2/\sigma^2 \right\}. \]

\(\sigma\) is the standard deviation and \(p = N - 2\sigma\).

**Top hat:**

\[ P(i) = \begin{cases} 
0 & \text{for } i < p \\
1/(2(i-p)) & \text{for } p < i < 2N - p \\
0 & \text{for } i > 2N - p 
\end{cases} \]

**Reinhold:**

\[ P(i) = \begin{cases} 
0 & \text{for } i < p \\
\beta^2(i-p) \exp\left[-(\beta(i-p))\right] & \text{for } i > p 
\end{cases} \]

where \(\beta = 2/(N-p)\).

**Exponential:**

\[ P(i) = \begin{cases} 
0 & \text{for } i < p \\
\alpha \exp\left[-\alpha(i-p)\right] & \text{for } i > p 
\end{cases} \]

where \(\alpha = 1/(N-p)\).

\(\alpha\) and \(\beta\) represent the width of the distribution, which has been varied to fit the experimental results. \(p\) is the smallest number of unit cells in a column (Hall & Somashekar, 1991). Figs. 3(a)–(h) give the experimental and simulated profiles from the one-dimensional paracrystalline model for all the reflections using these column-length distribution functions. From these figures, it is evident that the best fit is obtained for LDPE 110 (exponential, \(\alpha = 0.341, \delta = 3\%\)), LDPE 220 (Reinhold, \(\beta = 0.167, \delta = 9\%\)), LDPE 200 (exponential, \(\beta = 11.550, \delta = 3\%\)), LDPE 400 (Reinhold, \(\beta = 0.084, \delta = 7\%\)), Kevlar 200 (exponential, \(\beta = 0.274, \delta = 7\%\)), Kevlar 400 (Reinhold, \(\beta = 0.058, \delta = 9\%\)), MgO (Reinhold, \(\beta = 0.019, \delta = 3\%\)) and W 110 (Reinhold, \(\beta = 0.023, \delta = 3\%\)), where the corresponding column-length distributions, widths and mean-square deviations are given in parentheses. In some cases, different column-length distribution functions approach delta-type functions (e.g. LDPE 200) and, in certain other cases, symmetric functions do not give a minimum, which is highlighted in the MgO 422 and W 110 reflections. From these, it is evident that the method suggested here is far better than any earlier single-order method. The results in Table 1 justify this observation. In fact, the accuracy can be improved by increasing the number of steps between \(s_0\) and \(s_0 + s_0/2\) of the simulated profile, depending on the working memory capacity of the computer.

**4. Conclusions**

Nowadays, there is a popular trend towards the use of full-pattern-fitting software, such as some Rietveld-refinement programs, that already includes refinable parameters corresponding to the domain size and strain. Such automated line-broadening analysis is very often inaccurate because of the inadequate models used in these programs. The model suggested in this paper is based on Hosemann’s paracrystalline model, wherein the distribution of column lengths is a delta function or symmetric or asymmetric function and can be easily incorporated in any full-pattern-fitting procedures that give the size and strain in a straightforward manner without much complication, using one order of reflection.

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**References**


