Folding a two-dimensional powder diffraction image into a one-dimensional scan: a new procedure

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A new procedure aimed at folding a two-dimensional powder diffraction pattern into a one-dimensional scan is presented. The sample-to-detector distance is the only parameter that, in this approach, needs to be adjusted in a separate step by using the 'standard' sample. The technique consists of three steps: tracking the beam centre by means of simulated annealing of the diffraction rings along the same axis, detector tilt and rotation determination by a Hankel Lanczos singular value decomposition and intensity integration by an adaptive binning algorithm. The X-ray powder diffraction (XRPD) intensity profile of the standard NIST Si 640c sample is used to test the performance. Results show the robustness of the method and its capability of efficiently tagging the pixels in a two-dimensional readout system by matching the ideal geometry of the detector to the real beam-sample-detector frame. The technique is a versatile and user-friendly tool for the one-dimensional folding of two-dimensional XRPD images.

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1. Introduction

X-ray powder diffraction (XRPD) is nowadays a well known tool to study crystalline properties, which provide important information for applications in many fields such as crystal structure solution, microstructure characterization, phase quantification and, more recently, in nanotechnology. In the future, high-brilliance X-ray facilities, like synchrotron radiation beamlines and X-ray free electron lasers, will open new frontiers in science with respect to discovering and probing new states of matter, understanding and following chemical reactions and biological processes in real time, imaging chemical and structural properties of materials on the nanoscale, and imaging noncrystalline biological materials at atomic resolution (see for instance the linac coherent light source report at <http://www-ssrl.slac.stanford.edu/lcls>). In these fields, digital integration area detector [imaging plate (IP) and charge-coupled device (CCD)] technology is advancing quickly (for instance the microstrip gas chamber at SPring-8 for time-resolved X-ray crystallography experiments) and data collection time is accordingly reducing (Takeda *et al.*, 2005). This kind of experiment produces large data sets, but for pixel detectors (like CCD detectors) this is not a problem; thus area detectors are preferred to other kinds of detectors (Hanley & Bonner Denton, 2005; Hammersley *et al.*, 1997; Muchmore, 1999; Phillips *et al.*, 2002; Suzuki *et al.*, 1999). When working with two-dimensional detectors, a crucial step is the folding of the two-dimensional powder diffraction image into a one-dimensional scan, especially if a subsequent Rietveld analysis has to be performed. In most widespread procedures (see for instance Hammersley *et al.*, 1997), folding requires a detector calibration step,

performed by means of a standard sample. This calibration allows one to find all the geometrical parameters necessary to extract a one-dimensional profile from a two-dimensional image. In addition, processing a large number of data sets can lead to some features being overlooked or misinterpreted if an automatic procedure is not implemented. In the present paper, a new automatic procedure aimed at folding a two-dimensional powder diffraction image into a one-dimensional scan is presented. This procedure allows all geometrical parameters used in folding to be set, except for the detector-to-sample distance, without any standard sample. The procedure works with a nominal value of the sample-to-detector distance; the precise determination of it (necessary to derive the 2θ angular coordinates correctly) is considered as a separate step, which can eventually be performed according to the traditional approach.

2. The method

The ideal X-ray powder diffraction geometry is cylindrical along the beam-sample axis. The diffraction cone with an opening angle 2θ and the apex on the sample reaches the imaging plate (a CCD detector for instance). Ideally, the imaging plate would be orthogonal to the beam-sample axis and it would collect a series of circles with radii corresponding to different momentum transfers: the larger the radius, the higher the momentum transfer (*i.e.* the resolution). Unfortunately, the imaging-plate axis rarely fits the ideal geometry and the circles become ellipses with an eccentricity ε and a rotation ϕ_0 parameterizing tilt and rotation of the detector frame. Furthermore, the beam rarely reaches the geometrical centre of the plate and a

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Table 1

Parameter estimation by HLSVD ($K = 3$) for a few ellipses.

	$a_0 (\times 10^4)$	$a_1 (\times 10^8)$	$\varphi_1 (^\circ)$	$\varepsilon (\times 10^2)$	$\phi_0 (^\circ)$	a
Ellipse 1	0.117	0.268	319	0.091	69.6	293
Ellipse 2	0.119	0.247	342	0.083	80.1	290
Ellipse 3	0.120	0.291	346	0.097	82.8	289
Ellipse 4	0.146	0.395	357	0.108	88.6	262
Ellipse 5	0.145	0.325	346	0.089	82.9	263

global shift of the rings is needed to perform a correct two-dimensional folding.

The problem reduces to the nonlinear fit of the parameters appearing in the Cartesian equation of an ellipse: $x^2/a^2 + y^2/b^2 = 1$, where a/b is the major/minor semi-axis. For a generic beam-sample-plate geometry, the following equations hold:

$$\begin{aligned} x &= x_c + \Delta x_c + a \cos(\phi - \phi_0) / [1 + \varepsilon \sin^2(\phi - \phi_0)]^{1/2}, \\ y &= y_c + \Delta y_c + a \sin(\phi - \phi_0) / [1 + \varepsilon \sin^2(\phi - \phi_0)]^{1/2}, \end{aligned} \quad (1)$$

where Δx_c and Δy_c the discrepancies along the x and y axes between the beam centre and the imaging-plate centre (x_c, y_c). ε is the ellipse eccentricity $a^2/b^2 - 1$ and $\phi = \phi_0 + \arctan[(y - y_c)/(x - x_c)]$. The Cartesian equation for the ellipse finally reads:

$$\frac{\rho^2}{a^2} [1 + \varepsilon S^2] - 1 = 2\rho \left(\frac{\Delta x_c C}{a^2} + \frac{\Delta y_c S}{b^2} \right) - \left(\frac{\Delta x_c^2}{a^2} + \frac{\Delta y_c^2}{b^2} \right), \quad (2)$$

where $\rho = [(x - x_c)^2 + (y - y_c)^2]^{1/2}$, $S = \sin(\phi - \phi_0)$ and $C = \cos(\phi - \phi_0)$.

In equation (2), the left-hand side is $\mathcal{O}(\varepsilon)$, while the right-hand side is $\mathcal{O}[(\Delta x_c \Delta y_c / ab)^{1/2}]$ and, since usually $\varepsilon \ll (\Delta x_c \Delta y_c / ab)^{1/2}$, equation (2) finally decouples. The rationale of equation (2) decoupling can be understood by performing an angular integration over the ϕ variable to single out the order of magnitude of both the left-hand side and the right-hand side. By using the values listed in Table 1, for instance, we obtain an order 10^{-3} for the left-hand side and a few percent for the left-hand side. Such a conclusion is independent of the ellipse we choose in Table 1 and, therefore, the problem of finding the ring's centroid can be solved independently of the ε/ϕ_0 determination, which is indeed a 'fine tuning' with respect to the former task. Needless to say that the attempt to find the ring's centroid cannot be accomplished by using the equation (2) itself, where both ε and ϕ_0 are unknown at this stage.

We claim that almost all the parameters necessary to the folding procedure can be obtained independently of the detector-to-sample distance calibration. Let us suppose that we know the detector-to-sample distance exactly. The two-dimensional folding procedure presented here will allow us to determine the geometrical parameters, namely eccentricity, rotation and centre coordinates, without any need for a standard sample. The procedure is accomplished by three steps: beam centroid determination, tilt/rotation angle fitting and radial intensity integration.

2.1. Beam centroid hunting

This task is carried out by using a simulated annealing (SA) algorithm (see Metropolis *et al.*, 1958; Pincus, 1970; Kirkpatrick *et al.*, 1982, 1983; Kirkpatrick, 1984) to search for a minimum of the XRPD ring's centroid position on the imaging plate. As known, the algorithm employs a random search which not only accepts changes that decrease objective function f , but also some changes that increase it. Changes decreasing f are accepted with a probability $p = \exp(-\delta f/T)$, where δf is the decrease in f and T is a control parameter, which by analogy with the original application is known as the system

temperature irrespective of the objective function involved. Here the objective function f is the sharpness (defined *e.g.* as the inverse normalized variance) of the radial distribution function of the highest intensity rings recorded on the imaging plate, and the system 'temperature' is the domain size around the trial beam centre during the random search. f is computed with respect to the trial ring centre. In Fig. 1, the sharpness of the radial distribution function is shown before (*a*) and after (*c*) the SA. The increase of f sharpness is dramatic and it follows the correct positioning of the beam centre onto the imaging plate (see the two spots in Fig. 1*a*).

2.2. Detector tilt and rotation determination

Once the beam centre has been positioned, *i.e.* $\Delta x_c = \Delta y_c = 0$, the eccentricity ε and rotation ϕ_0 computation is straightforward; in fact, equation (2) reads

$$1/\rho^2 \simeq 1/a^2 [1 + \varepsilon \sin^2(\phi - \phi_0)].$$

The detector tilt and rotation are determined by using a subspace-based parameter estimation method called Hankel Lanczos singular value decomposition (HLSVD) technique (Laudadio *et al.*, 2002). The HLSVD method works as follows. Let us model the $1/\rho^2$ by samples $1/\rho_n^2$ collected at angles $\phi_n, n = 0, \dots, N - 1$, as the sum of K exponentially damped complex sinusoids,

$$1/\rho_n^2 \simeq \sum_{k=1}^K a_k \exp(-d_k \phi_n) \cos(2\pi f_k \phi_n + \varphi_k), \quad (3)$$

where a_k is the amplitude, φ_k the phase, d_k the damping factor and f_k the frequency of the k th sinusoid, $k = 0, \dots, K$, with K the number of damped sinusoids. This multiparametric functions family has been successfully used (Laudadio *et al.*, 2002) for modelling NMR signals, because these functions are intrinsically related to the physical description of an NMR signal. It has been shown, however, that this family has a great approximating power for many kinds of signals, including some of the natural functions used to describe crystal diffraction patterns, namely the Dirichlet kernel, related to the Laue interference function (see Beylkin & Monzón, 2005, §5.1 therein). Practical tests (Ladisa *et al.*, 2005*a,b*; Cervellino *et al.*, 2005*a,b*) have also confirmed their effectiveness. SVD gives this method its main advantage, that is flexibility, since the number of parameters is not fixed and it is determined only by the desired agreement level between the model and the real peak profile shape. A 'fast' SVD decomposition is achieved by the Lanczos bidiagonalization algorithm with partial reorthogonalization. This algorithm is based on FFT, but a discussion of details is beyond the scope of this paper (see Laudadio *et al.*, 2002, and references therein). Values for the parameters $\hat{a}_k$ and $\hat{f}_k$ so obtained are inserted into the model equation (3), which yields the set of equations

$$1/\rho_n^2 \simeq \sum_{k=1}^K a_k \exp(-\hat{d}_k \phi_n) \cos(2\pi \hat{f}_k \phi_n + \varphi_k), \quad (4)$$

with $n = 0, \dots, N - 1$. The least-squares solution of equation (4) provides the amplitude $\hat{a}_k$ and phase $\hat{\varphi}_k$ estimates of the model sinusoids which are used in the next step.

Equation (4) and the left-hand side of equation (2) formally match for $K = 3$ and the parameters ε and ϕ_0 finally read $\varepsilon = 2a_1/(a_0 - a_1)$ and $\phi_0 = (\varphi_1 - \pi)/2$. In passing, we also quote the major semi-axis of the ellipse, $a = 1/(a_0 - a_1)^{1/2}$.

2.3. Tagging pixels and radial integration

We shall focus on the pixel tagging problem. We do not apply data reduction procedures (detector response, diffraction corrections,

Figure 1
 (a) Original XRPD pattern: the beam centres before and after SA are indicated on the image. (b) Radial distribution function before SA. (c) Radial distribution function after SA. (d) Original XRPD pattern: the beam centre after SA together with a few ellipses tagged by the HLSVD procedure are indicated.

Bragg peaks removal, etc.) at this stage, since we are not interested in them; their inclusion will not affect our conclusions (see Hammersley *et al.*, 1996, for instance).

Tagging pixels onto the two-dimensional detector is a crucial step in the XRPD intensity profiling problem. In fact, the final XRPD intensity profile follows the radial integration over the ellipses domains. Pixels are actually labelled by an adaptive binning algorithm. Adaptive binning is an analysis technique that involves subdividing a signal into samples that are more homogeneous than the whole signal (see Sanders & Fabian, 2001, and references therein for instance). This technique reveals information about the structure of the signal. Here we have adopted the following scheme. The two-dimensional XRPD image is divided into a set of annuli with common centre and eccentricity/phase computed in the previous steps. Then each annulus is tested to see whether it meets some criterion of homogeneity (e.g. whether all the pixels in the annulus are within a specific dynamic range); here we have chosen a conservative criterion: the same statistical representation within each annulus, *i.e.*

the same number of pixels per annulus. More complicated criteria can be devised to account for other features (detector response and diffraction correction for instance). If an annulus meets the criterion, it is not divided any further. If it does not meet the criterion, it is subdivided again and the test criterion is applied to the new annuli. This process is repeated iteratively until each annulus meets the criterion. The result might have annuli of several different sizes. Finally the two-dimensional scanning is achieved by integrating the two-dimensional XRPD intensity profile over the annular domains tagged in the previous step. In order to position the radial integrated intensity profile on the resolution axis, either expressed in angles or in vectors, it is necessary to refine the detector-to-sample distance, fixed at the beginning. The latter step requires a standard sample as done in other approaches. The resulting intensity profile corresponding to Fig. 1(d) is shown in Fig. 2, together with the corresponding one-dimensional pattern extracted by the program *Fit2D* (Hammersley *et al.*, 1997). The difference profile is also plotted, showing the good agreement between the patterns.

Figure 2
Comparison of XRPD intensity profiles corresponding to image (d) of Fig. 1 obtained by our procedure and by *Fit2D* software. The difference profile is plotted at the bottom. For clarity, both intensity profiles have been lowered by 25 000 counts.

3. Results and conclusions

We have considered a new approach to the two-dimensional folding used for powder diffraction experiments using two-dimensional detectors. The sample-to-detector distance is the only parameter that needs to be determined by using the standard sample. Our method relies on the decoupling of two main problems: the beam centre positioning and the calculation of eccentricity and rotation of the set of ellipses recorded. The two tasks are respectively accomplished with by a simulated annealing and a Hankel Lanczos singular value decomposition, two well known and feasible techniques widely applied in several optimization problems. Results of the HLSVD are summarized in Table 1; for the sample test, the average estimated values for the eccentricity ε and the rotation ϕ_0 are respectively $0.93 (1) \times 10^{-3}$ and $82 (5)^\circ$. The task of tagging pixels is achieved by an adaptive binning algorithm by which the whole image is partitioned in a set of annuli with the same statistics. Integration over the

annular domains finally provides the 2θ intensity profile. This approach has been successfully applied to a set of XRPD CCD images of samples of the NIST standard Si 640c collected with a KappaCCD Nonius diffractometer.

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