Disentangling instrumental broadening

Antonio Cervellino$^{a,b}$, Cinzia Giannini$^b$, Antonietta Guagliardi$^b$ and Massimo Ladisa$^{b,\star}$

$^a$ Paul Scherrer Institute CH-5232, Villigen PSI, Switzerland

$^b$ Istituto di Cristallografia (IC-CNR), Via G. Amendola 122/O, I-70126, Bari, Italy

(November 13, 2018)

Abstract

A new procedure aiming at disentangling the instrumental profile broadening and the relevant X-ray powder diffraction (XRPD) profile shape is presented. The technique consists of three steps: denoising by means of wavelet transforms, background suppression by morphological functions and deblurring by a Lucy–Richardson damped deconvolution algorithm. Real XRPD intensity profiles of ceria samples are used to test the performances. Results show the robustness of the method and its capability of efficiently disentangling the instrumental broadening affecting the measurement of the intrinsic physical line profile. These features make the whole procedure an interesting and user-friendly tool for the pre-processing of XRPD data.

$^\star$ Corresponding author, E-mail: massimo.ladisa@ic.cnr.it, Phone: +39 0805929166, Fax: +39 0805929170
I. INTRODUCTION

Precise knowledge of X-ray diffraction profile shape is crucial in the investigation of the microstructural properties of polycrystalline materials (Snyder et al., 1999). A reliable instrumental line-broadening analysis is thus a pre-processing step in most of the whole powder pattern fitting softwares. A new procedure aiming at disentangling the instrumental profile broadening and the intrinsic physical diffraction profile is presented and applied for the first time to XRPD data. The technique consists of three steps: denoising by means of wavelet transforms, background suppression by morphological functions and deblurring by a Lucy–Richardson damped deconvolution algorithm. Real XRPD intensity profiles of ceria samples (Balzar et al., 2004) are used to test the performances. Results show the robustness of the method and its capability of efficiently disentangling the instrumental broadening affecting the microstructural information. These features make the whole procedure an interesting and user-friendly tool for the pre-processing of XRPD data.

II. THE METHOD

Four different raw datasets were downloaded \(^1\) in pairs. For each pair, one dataset was collected on the annealed ceria specimen - representing the instrumental broadening - and the other was collected on the broadened sample. The selected pairs are those measured at the University of Birmingham (a high resolution x-ray laboratory) and at the National Synchrotron Light Source (NSLS X3B1).

In order to extract the intrinsic physical profile, each broadened pattern has to be first corrected for the instrumental contribution. Several methods have been devised so far to deal with this problem. Among the others we quote the Stokes method (Stokes, 1948), a Bayesian approach (Richardson, 1972) and the fundamental parameter approach (Cheary,

\(^1\)www.du.edu/~bbalzar/ssrr.htm, www.boulder.nist.gov/div853/balzar, www.ccp14.ac.uk
1992). The main drawbacks of these methods can be attributed to the difficulty in evaluating the background level, mainly due to peak overlapping.

The technique proposed in this paper is a modified version of the one presented by Balzar et al, 2004. A blurred or degraded XRPD pattern can be approximately described by a Volterra equation $g = \mathcal{H} \otimes f + n$, where $g$ is the blurred XRD pattern and $\mathcal{H}$ is the distortion operator due to several causes, also called point spread function (PSF) in an optics/signal processing terminology; $f$ is the original XRPD pattern and $n$ is an additive noise, introduced during data acquisition, that corrupts the signal. Strictly speaking in a typical diffraction experiment we deal with a poissonian noise, that is a multiplicative noise. Moreover the Poisson distribution function resembles the Gaussian one provided a sufficiently large statistics in photons counting.

Our strategy in disentangling the profile broadening out of the experimental sample relies on a three steps procedure which we sketch in the sequel.

A. Denoising

The noise was determined by means of wavelet transforms for the whole XRPD spectrum and subtracted prior to the background suppression. Wavelets is a well established method to perform several kinds of analyses on signals (see for instance Daubechies, 1992). The attention on this scale-based analysis from a frequency-based one (i.e. a pure Fourier approach) started when it became clear that an approach measuring average fluctuations at different scales might prove less sensitive to noise. Since then the wavelet domain has been growing very quickly in several fields. Among them signal denoising has been deeply investigated and wavelets filter can be considered as the state of art on this subject.

Unlike conventional techniques, wavelet decomposition produces a family of hierarchically organized decompositions. The selection of a suitable level for the hierarchy will depend on the signal and experience. Often the level is chosen based on a desired low-pass cutoff.
frequency. At each level j, we build the j-level approximation $A_j$, or approximation at level j, and a deviation signal called the j-level detail $D_j$, or detail at level j. We can consider the original signal as the approximation at level 0, denoted by $A_0$. The words approximation and detail are justified by the fact that $A_1$ is an approximation of $A_0$ taking into account the low frequencies of $A_0$, whereas the detail $D_1$ corresponds to the high frequency correction. One way of understanding this decomposition consists of using an optical comparison. Successive images $A_1, A_2, A_3$ of a given object are built. We use the same type of photographic devices, but with increasingly poor resolution. The images are successive approximations; one detail is the discrepancy between two successive images. Image $A_2$ is, therefore, the sum of image $A_4$ and intermediate details $D_3, D_4$, i.e.: $A_2 = A_3 + D_3 = A_4 + D_4 + D_3$. The organizing parameter, the scale $a$, is related to the level j by $a = 2^j$. Since the resolution is $1/a$ then the greater the resolution, the smaller and finer are the details that can be reproduced. Thus the size of the details, at jth level, is proportional to the size of the region where the analysing function (wavelet) of the rescaled variable $x/a$ differs from zero.

Generally speaking, the denoising procedure involves three steps. The basic version of the procedure follows the steps described below.

- **Decompose.** Choose a wavelet, choose a level N. Compute the wavelet decomposition of the signal s at level N.

- **Threshold detail coefficients.** For each level from 1 to N, select a threshold and apply soft thresholding to the detail coefficients. As to the thresholding, let $t$ denote the threshold. The hard threshold signal is $x$ if $|x| > t$, and is 0 if $|x| \leq t$. The soft threshold signal is $\text{sign}(x)(|x| - t)$ if $|x| > t$ and is 0 if $|x| \leq t$. As can be seen the hard procedure creates discontinuities at $x = \pm t$, while the soft procedure does not (see Birgé, L. & Massart, P., 1997). Thus once we take a reference level called $J$, there are two sorts of details, those associated with indices $j \leq J$ correspond to the scales $a = 2^j \leq 2^J$ (the fine details) and the others, corresponding to $j > J$ (the coarser details). Choosing $j$ is crucial to define $A$‘s and $D$‘s: most of wavelet algorithms use
an entropy-based criterion to select the most suitable decomposition of a given signal by quantifying the information to be gained by performing each split.

- Reconstruct Compute wavelet reconstruction using the original approximation coefficients of level N and the modified detail coefficients of levels from 1 to N.

There are different types of wavelet families whose qualities vary according to several criteria. Among them we quote their support: the wavelets having a compact support are used in local analysis. Therefore in our denoising approach we used the Daubechies wavelets family: they are compactly supported wavelets with highest number of vanishing moments for a given support width. We address the reader to Daubechies (1992) for further details.

**B. Background suppression**

The background was determined by means of morphological transforms for the whole XRPD spectrum and subtracted prior to the deconvolution. Morphology is a technique of image processing based on shapes. The value of each pixel in the output image is based on a comparison of the corresponding pixel in the input image with its neighbours. By choosing the size and shape of the neighbourhood, you can construct a morphological operation that is sensitive to specific shapes in the input image. Thus morphological functions are used to perform common image processing tasks, such as contrast enhancement, noise removal, thinning, skeletonization, filling, and segmentation (see Serra, 1994).

In our background suppression procedure the XRPD pattern is reshaped and padded into a two-dimensional image by building the $m \times n$ matrix whose elements are taken columnwise from the one-dimensional XRPD data (with $m \times n \simeq N$, being $N$ the length of the XRPD data). Then morphological functions play their role on it; in particular dilation and erosion are used in combination to implement image processing operations. A disk with a radius of three pixels is used as structuring element both for erosion and for dilation. As to the
erosion (dilation), pixels beyond the image border are assigned the maximum (minimum) value afforded by the data type. The morphological opening removes small objects from the image while preserving the shape and size of larger objects in the image. The overall result is a peak smearing effect while the background intensity remains unaltered.

Restoring the original one-dimensional pattern provides the XRPD spectrum background. We compared our findings to the traditional interpolation method and we found a satisfactory agreement. Up to our knowledge, this technique has never been applied to XRPD spectrum background suppression and it provides a reliable and user independent estimate of it.

C. Deblurring

The XRPD pattern plugged in the deblurring algorithm is noise-background free since it has been already pre-processed by the wavelets filter + morphological background suppressor.

As to the deblurring procedure we implement the damped Lucy–Richardson algorithm. This function performs multiple iterations, using optimization techniques and Poisson statistics. In our approach the PSF is the raw dataset downloaded for the ceria sample - the instrumental standard - resembling the instrument profile (Balzar et al., 2004). The algorithm maximizes the likelihood that the resulting image, when convolved with the PSF, is an instance of the blurred image, assuming Poisson noise statistics. This function can be effective when you know the PSF but know little about the additive noise in the image. The Lucy–Richardson algorithm implements several adaptations to the original maximum likelihood algorithm that address complex image restoration tasks. Using these adaptations, you can reduce the effect of noise amplification on image restoration, account for nonuniform image quality (e.g., bad pixels, flat-field variation) and improve the restored image resolution by subsampling. As already stressed by Balzar et al, 2004, the main drawbacks in applying such algorithm to the single peak deconvolution are the noise amplification and the peak fitting
bias. Noise amplification is dramatically reduced by both the denoising procedure and the small (some five) number of iterations used in the algorithm. Moreover the damp in the algorithm specifies the threshold level for the deviation of the resulting image from the original image, below which damping occurs. For pixels that deviate in the vicinity of their original values, iterations are suppressed. As to the peak fitting bias, unlike the Balzar approach, our procedure uses the instrumental standard pattern (with no overlapping) as the PSF to deconvolve the whole XRPD pattern and then we extract the deconvoluted/deblurred XRPD pattern in the same range of the PSF used for the deconvolution itself. The rationale of this choice relies on the fact that while the PSF peaks have no overlap, this is not the case for the broadened sample peaks and, thus, the peak ranges can be defined starting on the annealed sample rather than the broadened one. Moreover the discrete Fourier transform (DFT), used by the deblurring functions, assumes that the frequency pattern of an image is periodic. This assumption creates a high-frequency drop-off at the edges of an overlapping peaks cluster. This high-frequency drop-off can create an effect called boundary related ringing in deblurred images, that is a systematic error affecting any further investigation on the physical meaning of the deconvolved spectrum. To reduce ringing our whole pattern deconvolution, as described above, resembles an edgetaper function removing the high-frequency drop-off at the edge of an image by blurring the entire image and then replacing the center pixels of the blurred image with the original image. In this way, the edges of the image taper off to a lower frequency.

III. RESULTS AND CONCLUSIONS

The whole procedure described above has been carried out by using few routines of Matlab and toolboxes implemented therein. In Figure 1 the results of the denoising/background suppression procedure described above are shown for the ceria XRPD pattern collected at Birmingham. Since the two different raw datasets for the ceria sample overlap on a reduced support, we focused our analysis on the first five peaks: extending the whole procedure
described above to a more realistic XRPD pattern is straightforward. The dataset pair collected at NSLS X3B1, treated with the present procedure, is analyzed within the paper submitted to Phys. Rev. B (2005). The final result is an XRPD pattern with narrower peaks in the same positions of the original ones. The integrated intensity remains constant during the whole procedure while the FWHM (full width at half maximum) for each peak is significantly reduced, as clearly reported in Table 1.

It is worth noting that once the deblurred, noise-background free XRPD spectrum is convoluted back to the PSF and added to the noise+background signal singled out at the beginning of the procedure, the XRPD pattern resembles the original one with satisfactory agreement, as clearly reported on the bottom in Figure 1 ($R_w = 0.03$).
REFERENCES

[1] Balzar, D., Audebrand, N., Daymond, M.R., Fitch, A., Hewat, A., Langford, J. I., Le Bail, A., Louer, D., Masson, O., McCowan, C.N., Popa, N.C., Stephens, P.W. & Toby, B.H. (2004), Journal of Applied Crystallography, 37, 911-924.

[2] Biemond, J., Lagendijk, R.L., Mersereau, R.M. (1990), Iterative methods for image deblurring, Proceedings of the IEEE, 78, 5, 856-883.

[3] Birgé, L. & Massart, P. (1997), From model selection to adaptive estimation, D. Pollard (ed), Festchrift for L. Le Cam, Springer, 55-88.

[4] Cervellino, A., Giannini, C., Guagliardi, A. & Ladisa, M. (2005), Nanoparticle size distribution estimation by full-pattern powder diffraction analysis, submitted to Physical Review B.

[5] Cheary, R.W. & Coelho, A.J. (1992), Journal of Applied Crystallography, 25, 109-121.

[6] Daubechies, I. (1992), Ten lectures on wavelets, SIAM.

[7] Lucy, L.B. (1972) An iterative technique for the rectification of observed distributions, The Astronomical Journal, 8, 243-246.

[8] Richardson, W.H. (1972), Journal of Optical Society of America A, 62, 55-59.

[9] Serra, J. (1994) Morphological filtering: an overview, Signal Processing, 38, 3-11.

[10] Snyder, R.L., Fiala, F. & Bunge, H.J. (1999), Defect and Microstructural Analysis by Diffraction, International Union of Crystallography, Oxford University Press, New York.

[11] Stokes, A.R. (1948), Proc. Phys. Soc. (London), 61, 382-391.
TABLE I. Performance of the deblurring. Units are degrees.

| peak number | 1   | 2   | 3   | 4   | 5   |
|-------------|-----|-----|-----|-----|-----|
| FWHM (before) | 0.3281 | 0.3428 | 0.3436 | 0.3673 | 0.4056 |
| FWHM (after)  | 0.3062 | 0.3200 | 0.3148 | 0.3433 | 0.3872 |
FIGURES

FIG. 1. Top: original XRPD pattern. Middle: XRPD pattern after denoising and background suppression. Bottom: residue between final XRPD pattern re-convoluted to the PSF together with noise and background and the original XRPD pattern. On y-axes XRPD intensities are reported on an arbitrary units scale.