

### 3.6. Whole powder pattern modelling: microstructure determination from powder diffraction data

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#### 3.6.1. Introduction

X-ray diffraction is a very simple technique, but is one of the most flexible and powerful tools for the analysis of materials. The diffraction pattern carries information about the atomic arrangement and motion at both the short and the long range; for nanostructured materials this means that a single technique can simultaneously provide structural and microstructural information.

Microstructure analysis *via* X-ray powder diffraction (XRD), often termed line-profile analysis (LPA), is mostly performed through the Scherrer (1918) formula. Just a few years after the discovery of X-ray diffraction, Scherrer derived a very simple relationship between the width of the diffraction peaks and the size of the so-called *Kristallchen* (translated as crystallites), the coherently scattering (nanocrystalline) domains composing the colloids that he was studying (the formula is rewritten here using an updated notation):

$$\langle D \rangle = \frac{K_w \lambda}{\text{FWHM}_{hkl} \cos \theta_{hkl}}. \quad (3.6.1)$$

The calculation of an ‘average size’  $\langle D \rangle$  is therefore immediate once the position and full-width at half-maximum of a peak ( $2\theta_{hkl}$  and  $\text{FWHM}_{hkl}$ , respectively), measured with X-rays of wavelength  $\lambda$ , are available. The constant  $K_w$  (the Scherrer constant) carries information on the shape of the domains and has an order of magnitude of 1. Values of the Scherrer constant can be found in the literature for both isotropic and anisotropic shapes (in the latter case leading to different sizes for different reflections  $hkl$ ): Table 3.6.1 contains the data of Langford & Wilson (1978) for common domain shapes. An elegant derivation of the Scherrer formula can be found in the work of Patterson (1939) and Warren (1990); a summary is also presented in Chapter 5.1.

Its simple mathematical nature is probably the main reason for the widespread (ab)use of equation (3.6.1). Simple, in fact, does not mean accurate.

The Scherrer formula and its variants are based on strong assumptions about the peak shape. In the original derivation [equation (3.6.1)] the peak was assumed to be Gaussian (see Appendix A3.6.1 for the definition of a unit-area Gaussian); in subsequent derivations, the peak-shape information is lost, as the peak is transformed into an equivalent rectangle *via* the use of the integral breadth (IB)  $\beta = A/I$ , where  $A$  and  $I$  are the area and the maximum intensity of the peak, respectively (see Table 3.6.1 for the corresponding Scherrer constant values). Together with this, we should consider that the size of the domains in a real

specimen is always disperse; it can be easily proven that the quantity  $\langle D \rangle$ , which is called the ‘average size’ or ‘mean size’, is actually not the mean (first moment) of the size distribution, but is related to its third moment (*i.e.* it is volume-weighted). If we add that the finite size of the domains is not the only source of peak broadening, we immediately see where the abuse of the Scherrer formula can lie.

To try to sort some of those issues out, Williamson & Hall (1953) proposed plotting the FWHM (or the IB) *versus* the reciprocal of the lattice spacing ( $d_{hkl}^* = 1/d_{hkl} = 2 \sin \theta_{hkl}/\lambda$ ). For spherical domains (*i.e.* size independent of the direction), a horizontal line is expected. An anisotropic shape would cause a scattering of the points, whereas other sources of broadening might also change the slope. Following the findings of Stokes & Wilson (1944), Williamson and Hall proposed writing the integral breadth in reciprocal space (reciprocal-space variable  $d^*$ ) as a combination of the Scherrer formula with the differential of Bragg’s law:

$$\beta(d^*) = \frac{K_\beta}{\langle D \rangle} + 2ed^*. \quad (3.6.2)$$

Equation (3.6.2) describes a line for which the intercept (extrapolation of the integral breadth to the origin of the reciprocal space, *i.e.* to  $d \rightarrow \infty$ ) is related to the reciprocal of the Scherrer size, and the slope parameter  $e$  accounts for the distribution of local strain inside the domains. For a Gaussian distribution of this local strain, the root-mean strain (also known as microstrain)  $\langle \varepsilon^2 \rangle^{1/2} = e\sqrt{2/\pi}$  can be obtained. The microstrain, which is mostly caused by the presence of imperfections, is often quoted together with the average size.

Even though the Williamson–Hall idea is straightforward, there is no physical reason why the two terms in equation (3.6.2) should be added: the only case where breadths are additive is when the peaks are Lorentzian (see Appendix A3.6.1 for the definition of a unit-area Lorentzian). The Williamson–Hall equation is therefore valid for Lorentzian peaks and under the condition that both the size and strain contributions are Lorentzian as well. We therefore immediately envisage a problem here, as the size contribution, described by the Scherrer equation, was derived in the Gaussian limit. This inconsistency is seldom reported or considered in the literature. The fact that, in the end, the profiles are often highly Lorentzian in character mathematically justifies the separation of a size and a strain term, but dilutes the quantitative meaning of the result.

Modification of the Williamson–Hall approach to remove the inconsistency of the size- and strain-broadening terms has been extensively discussed by Balzar & Popović (1996). Using Voigtians (*i.e.* the convolution of a Gaussian  $G$  and a Lorentzian  $L$ ; see Appendix A3.6.1) to describe a profile, four combinations are possible for the size and strain terms:  $L-L$ ,  $L-G$ ,  $G-L$  and  $G-G$ . The Williamson–Hall method corresponds to the  $L-L$  case, whereas the combinations involving a Gaussian size term are more compatible with the Scherrer formula. Even in those cases, though, ‘The pure-Gauss size-broadened profile is incompatible

**Table 3.6.1**

Scherrer constants ( $K_w$  and  $K_\beta$ ) for various domain shapes (Langford & Wilson, 1978)

Shape	$K_w$ (FWHM)	$K_\beta$ (integral breadth)
Sphere	0.89	1.07
Cube	0.83–0.91	1.00–1.16
Tetrahedron	0.73–1.03	0.94–1.39
Octahedron	0.82–0.94	1.04–1.14

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with the definitions of surface-weighted domain size and column-length distribution function' (Balzar & Popović, 1996): integral breadth methods are therefore intrinsically limited for the microstructure analysis of real materials. This is in stark contrast to the fact that equation (3.6.2) is used, for example, by a large number of Rietveld refinement codes to describe the observed trend in line-profile broadening (and to perform a rough microstructure analysis). This situation can be improved a little by properly considering at least the anisotropic broadening component, as performed, for example, in the modified Williamson–Hall method (MWH; Ungár & Borbély, 1996; Ungár, 2001; Scardi *et al.*, 2004). The results are more accurate and related to some physical quantities (a dislocation density and a stacking fault probability), but they are still tightly bound to a Voigtian profile approximation.

An alternative to the integral breadth methods was developed by Warren & Averbach (1950, 1952) almost simultaneously with the idea of Williamson and Hall, but took longer to be fully employed owing to the lack of fast computing tools. It is based on the extensive use of Fourier transforms and represents the starting point of modern line-profile analysis techniques. The whole profile carries information on the microstructure, as each point in reciprocal space is related to the Fourier transform of real space (and thus to the size and shape of the domains and also the deviation from perfect three-dimensional periodicity). Each profile also contributes to a better picture of the microstructure, as it samples along a different direction in space.

For decades, these Fourier methods were only used in a very small number of scientific areas; the availability of fast computers and the fast Fourier transform has contributed greatly to their further diffusion. It is, however, only in recent years that the full power of the Fourier approach has been unveiled, with the development of whole-pattern methods and the extension of most models to a wider range of materials.

#### 3.6.2. Fourier methods

##### 3.6.2.1. Definitions

In the following, the diffraction peaks for a powder will be described in reciprocal space with reference to the Bragg position  $d_{\{hkl\}}^*$  expected for the  $\{hkl\}$  reflection family in the absence of any type of defect. The coordinate  $s$ , where

$$s = d^* - d_{\{hkl\}}^* = \frac{2}{\lambda} (\sin \theta - \sin \theta_{\{hkl\}}), \quad (3.6.3)$$

will be employed. Moving from reciprocal to diffraction space (' $2\theta$  space') involves a trivial but nonlinear change of variables: peaks that are symmetrical in reciprocal space will become asymmetrical in  $2\theta$  space and *vice versa*.

##### 3.6.2.2. Peak profile and the convolution theorem

Each peak profile  $h(s)$  in a powder diffraction pattern can be described as the convolution of an instrumental profile  $g(s)$  with a function  $f(s)$  accounting for sample-related effects (microstructure; see, for example, Jones, 1938; Alexander, 1954; Klug & Alexander, 1974; and references therein):

$$h(s) = \int_{-\infty}^{\infty} f(y)g(s-y) dy = f \otimes g(s). \quad (3.6.4)$$

The calculation of the integral in equation (3.6.4) can be simplified through the use of a Fourier transform (FT). In fact,

the convolution theorem states that the FT of a convolution is the product of the Fourier transforms of the functions to be folded:

$$\mathcal{C}(L) = \text{FT}[h(s)] = \text{FT}[f(s)] \times \text{FT}[g(s)]. \quad (3.6.5)$$

In this equation,  $L$  is the (real) Fourier variable conjugate to  $s$ . The properties of the Fourier transform allow equation (3.6.4) to be rewritten as

$$h(s) = \text{FT}^{-1}[\mathcal{C}(L)] = \text{FT}^{-1}[\text{FT}[h(s)]] = \text{FT}^{-1}[\text{FT}[f(s)]\text{FT}[g(s)]]. \quad (3.6.6)$$

This equation is the basis of the Warren–Averbach approach and also of all modern LPA methods.

##### 3.6.2.3. The Warren–Averbach method and its variations

The convolution theorem can be employed to disentangle the specimen-related broadening contributions described by  $f(s)$ . In fact, let us suppose, as in the Williamson–Hall method, that size and microstrain are the only two sources of specimen-related broadening. We call the Fourier transform of the profiles broadened by size and distortion effects only  $A_{hkl}^S(L)$  and  $A_{hkl}^D(L)$ , respectively. As the size and distortion profiles are folded into  $f(s)$ , the following holds:

$$A(L) = \text{FT}[f(s)] = \text{FT}[h(s)]/\text{FT}[g(s)] = A_{hkl}^S(L)A_{hkl}^D(L). \quad (3.6.7)$$

The separation of the size and distortion terms is straightforward for spherical domains: the size effects for a sphere are independent of the reflection order, whereas those related to distortions (causing the change in the slope of the Williamson–Hall plot) are order-dependent. To describe the distortion term it is convenient to follow the idea of Bertaut (1949*a,b*, 1950), considering the specimen as made of columns of cells along the  $\mathbf{c}$  direction. The profile due to distortions is calculated by taking the average phase shift along the column due to the presence of defects. The analytical formula for the distortion term is thus of the type  $A_{hkl}^D(L) = \langle \exp(2\pi i L n \varepsilon_L) \rangle$ , where  $\varepsilon_L = \Delta L/L$  is the average strain along  $\mathbf{c}$  calculated for a correlation distance (*i.e.* Fourier length)  $L$ .

As a first-order approximation, the distortion terms give no profile asymmetry;  $A_{hkl}^D(L)$  is just a cosine Fourier transform. We can thus expand it as (Warren, 1990)

$$A_{hkl}^D(L) = \langle \cos(2\pi L n \varepsilon_L) \rangle = 1 - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle. \quad (3.6.8)$$

If we now rewrite equation (3.6.7) on a log scale, taking equation (3.6.8) into account, we obtain

$$\begin{aligned} \ln[A_{hkl}(L)] &= \ln[A_{hkl}^S(L)] + \ln[A_{hkl}^D(L)] \\ &= \ln[A_{hkl}^S(L)] + \ln[1 - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle] \\ &= \ln[A_{hkl}^S(L)] - 2\pi^2 L^2 n^2 \langle \varepsilon_L^2 \rangle. \end{aligned} \quad (3.6.9)$$

Equation (3.6.9) represents a line in the variable  $n^2$ : the intercepts at increasing  $L$  values provide the logarithm of the Fourier size term, whereas the slopes give the microstrain directly (Warren, 1990). From the size coefficients, we can obtain an average size, again following the idea of Bertaut (1949*a*, 1950), related to the properties of the Fourier transform:

$$\langle D \rangle = \left[ \left. \frac{\partial A_{hkl}^S(L)}{\partial L} \right|_{L=0} \right]^{-1}. \quad (3.6.10)$$

This average size is thus related to the initial slope of the Fourier coefficients [assuming that they are well behaved, *i.e.* that the tangent is always below the  $A_{hkl}^S(L)$  curve].