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):

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

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 FWHM_{hkl}, respectively), measured with X-rays of wavelength λ, 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.

Table 3.6.1
Scherrer constants (K_w and K_β) for various domain shapes (Langford & Wilson, 1978)

Shape	K_w (FWHM)	K_β (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

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:

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

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 $d\to\infty$) 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

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