

## 1. INTRODUCTION

However, it was not long before the method was extended to X-ray powder diffraction. The quality of the data and the computation power available these days have allowed the technique to develop enormously, to the point that even the (successful) Rietveld refinement of small protein structures from synchrotron powder diffraction data is now possible (see Chapter 7.1). Another development is the extension of the Rietveld method towards parametric refinement on large numbers of complimentary data sets with various as-yet unexplored new applications. Rietveld refinement is so important it is described in detail in Chapter 4.7, but we describe a number of important fundamentals of the method here by way of introduction.

The basic idea behind the Rietveld method is simple: Instead of extracting the integrated intensities of Bragg peaks and fitting models to these, as would be done in single-crystal and early powder diffraction studies, the full powder pattern, for example available as step-scanned intensity data, is fitted using a model whose parameters are refined using a least-squares procedure. The model parameters are varied in such a way as to minimize the sum of the squares of the difference between the  $n$  observed  $Y_{\text{obs}_i}$  and  $n$  calculated  $Y_{\text{calc}_i}(\{p\})$  step-scan intensities in the powder pattern, where the latter are calculated from a model containing a set of parameters  $\{p\}$ . The function that is minimized is usually the profile-weighted residual function, or  $R$  factor, given by

$$R_w = \sum_{i=1}^n w_i (Y_{\text{obs}_i}(2\theta) - Y_{\text{calc}_i}(2\theta; \{p\}))^2. \quad (1.1.91)$$

The weight  $w_i$  is derived from the variance of the values of  $Y_{\text{obs}_i}$ , while all covariances between different  $Y_{\text{obs}_i}$  values are assumed to be zero.

The calculated intensity  $Y_{\text{calc}_i}$  is expressed by combinations of mostly nonlinear and analytic or non-analytic functions as

$$Y_{\text{calc}_i} = \sum_{ph=1}^{\text{phases}} \left( S_{ph} \sum_{hkl(ph)} \left( K_{hkl(ph)} |F_{hkl(ph)}|^2 \Phi_{hkl(ph)}(2\theta_i - 2\theta_{hkl(ph)}) \right) \right) + b_i(\text{obs}). \quad (1.1.92)$$

The outer sum runs over all phases  $ph$  present in the powder pattern, while the inner sum runs over all reflections  $hkl$  of a phase  $ph$  that contribute to the intensity at the position  $i$  in the powder pattern. A scaling factor  $S_{ph}$  is assigned to the reflection intensities for each phase; the scaling factor is proportional to the weight fraction of the phase.  $K_{hkl(ph)}$  represents the product of various correction factors to the square of the structure-factor amplitudes,  $|F_{hkl(ph)}|^2$ , which may depend on the diffraction geometry and/or individual reflections. The value of the profile function  $\Phi_{hkl}(2\theta_i - 2\theta_{hkl})$  is given for the profile point  $(2\theta_i - 2\theta_{hkl})$  relative to the position of the Bragg reflection  $hkl$ . The observed background at position  $i$  in the powder pattern is denoted as  $b_i(\text{obs})$ . Parameters in the model such as atomic positions, lattice parameters and experimental factors that affect peak shape and background are varied, using a least-squares approach, until the agreement between the calculated and measured diffraction profiles is optimized. In a least-squares approach, optimization consists of minimizing a cost function that is the weighted sum of the squared differences. This is a refinement method: a good initial guess at, or knowledge of, the structure is required and this model is refined by small adjustments.

This approach requires the modelling of the *entire* powder pattern. To simplify this complex task, the information content of

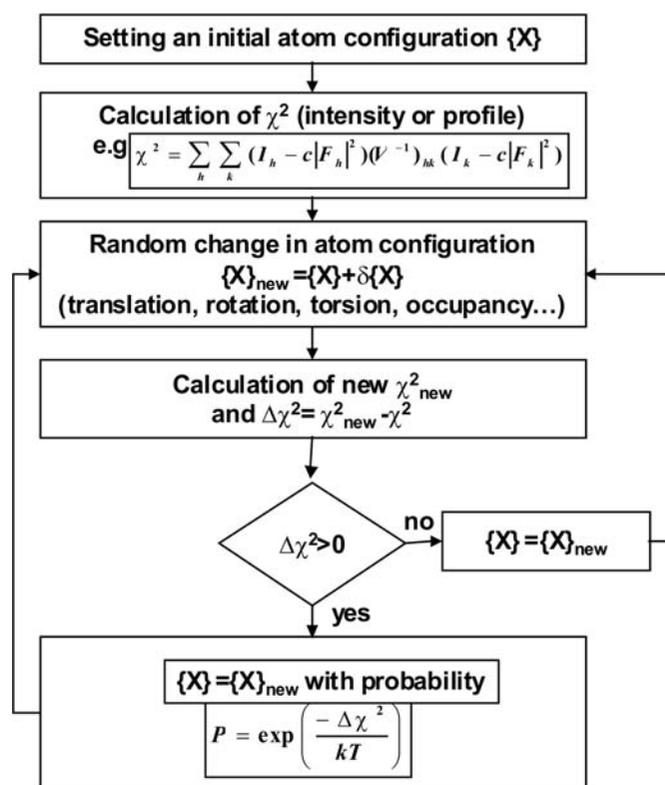


Figure 1.1.25

Flow diagram of a simulated-annealing procedure used for structure determination from powder diffraction data (from Mittemeijer & Welzel, 2012).  $F$  in the double sum is the structure factor from the structural model at each step of the optimization. Each sum runs over all reflections.  $h$  and  $k$  are summation indices representing  $hkl$  and  $h'k'l'$ , respectively.

the powder pattern can be divided into several parts (Fig. 1.1.1), allowing the separation of groups of parameters with respect to their origin:

- the peak intensity  $|F_{hkl(ph)}|^2$  – the time- and space-averaged crystal structure and geometrical contributions;
- the peak position – crystallographic lattice and symmetry, and instrumental contributions;
- the peak shape  $\Phi_{hkl}(2\theta_i - 2\theta_{hkl})$  – microstructural parameters and instrument profile;
- the background  $b_i(\text{obs})$  – local structure and instrumental conditions.

Each part contains contributions from the sample and the instrument.

Rietveld refinement is a nonlinear least-squares process and requires starting values for all parameters. It is generally implemented with a local, rather than a global, optimizer and it is important for the starting parameters to be close to those of the actual solution to ensure that it is in the valley in parameter space that contains the global minimum. It is usual to guide the refinement into the (relatively narrow) range of convergence by hand by adding the parameters to the refinement sequentially. In this sense, Rietveld refinement takes some time to learn, but with care it can provide robust quantitative structures and a wealth of information can be extracted from the data.

Of course, there is no reason (other than computational efficiency) why the minimization algorithm could not be a more robust global optimizer, and this is now starting to be implemented in modern Rietveld codes. The most common and most easily implemented global optimizer, though one of the least efficient, is the Metropolis or simulated-annealing (SA) algo-