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Reverse Monte Carlo modelling of crystalline disorder

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Abstract

The reverse Monte Carlo (RMC) modelling method, although initially developed for interpreting structural data from liquids and amorphous materials, has been extensively applied to similar data from crystalline systems. This has been especially beneficial for materials which display a large amount of disorder. The work in this area will be briefly reviewed here, including a summary of the range of crystalline materials which have been studied using RMC modelling. Recent developments made specifically to improve the RMC modelling method for crystalline systems will also be described.

1. Introduction

The reverse Monte Carlo (RMC) computer modelling method is an inherently straightforward procedure. Atoms within a three-dimensional configuration are chosen randomly and moved randomly one at a time; after each move, calculated structural functions are compared with equivalent experimentally determined functions. If the move improves the agreement, then the move is accepted; if it worsens, then the move is accepted with a reduced probability. Atoms continue to be moved in this manner until the agreement with the data is minimized and subsequent moves only cause the agreement factor to deviate by small amounts around the minimum. The resulting configuration of atoms may then be considered as a representative three-dimensional structure consistent with the experimental structural data. Further information relating to the general RMC method may be found in other articles in this issue, or recent reviews on the subject (for example [1, 2]).

It is easy to see why such a modelling scheme is attractive to those researchers investigating liquid and amorphous structures. Total scattering structure factors and radial distribution functions from neutron or x-ray scattering experiments may be used as the experimental data and the method provides a mechanism for 'fitting' a structural model to these data in a way which is loosely similar to the familiar Rietveld refinement method for powder diffraction data.

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It is also one of the very few practical methods for producing three-dimensional models of liquid and amorphous structures without recourse to simulations using interatomic potentials. It is therefore natural that the RMC method was developed with these systems in mind; forerunners of the method were developed for selenium-based glasses [3, 4] and early RMC papers considered liquid argon [5] and silica glass [6] amongst other systems.

In contrast, it is less obvious why the RMC method might be able to make a significant contribution to the understanding of the structures of crystalline materials. On the one hand, extremely effective methods already exist for determining crystal structures from diffraction data (including the Rietveld method mentioned above) and, on the other hand, the feature of the RMC method of emphasizing disorder in a structure is likely to be inappropriate for ordered crystalline materials. However, and perhaps surprisingly, some of the earliest RMC publications concerned the behaviour of crystalline AgBr [7–9]. These papers described total scattering studies of powdered samples of AgBr as a function of temperature very close to the melting temperature. The aim was to determine whether it was possible to use these data to identify structural characteristics which may be associated with either the onset of superionic behaviour or with the proposed pre-melting disorder. The data were analysed using RMC modelling and it was found that a small, but increasing proportion of silver ions began to occupy the interstitial tetrahedral sites in the rock salt structure as the temperature was raised. In addition, the models could be used to identify the mechanism for cation mobility and to determine the anisotropic shape of the cation distributions. It was surmised that the disorder would lead to a ‘true’ superionic state in AgBr, although this is interrupted by the melting transition. This conclusion was subsequently supported by later structural work on the high-pressure rock salt phase of AgI which does undergo a gradual transition to a superionic phase with the same mechanism as AgBr [10].

2. Disorder in crystals

In the context of this paper, the significance of the work on AgBr (described above) was that the authors identified a circumstance where the RMC method provided additional information which could not be obtained unambiguously from ‘traditional’ crystallographic structure determination. In this case, characterizing the structural disorder associated with ionic conduction was essential in order to understand the physical processes in AgBr close to melting. In more general terms, it was the local instantaneous deviations from the time-average long-range structure which were important.

Rietveld refinement, and other structure refinement methods which rely solely on the Bragg peak positions and intensities, produce an average structural model. This gives information about space group symmetry, unit cell metrics and average atom positions within the unit cell. These are of fundamental importance for all structural investigations. However, when a material displays deviations from this average structure, whether as a result of thermal vibrations, substitutional disorder, short-range distortions or something else, an average structural model has limited flexibility to accommodate these local effects. This is because each local region within the structure no longer accurately mimics the average: the deviations are now significant. The average structure is able to invoke large anisotropic atomic displacement parameters and an increased number of partially occupied sites to reflect these increased local deviations, but the average structural model is, by definition, unable to characterize correlated structural deviations.

Another effect of structural disorder in crystalline materials is the observation of an increase in diffuse scattering intensity in diffraction experiments. Diffuse scattering can be analysed in many ways, depending on the type of disorder responsible for the scattering and which approximations can be justified [11]. For situations where the disorder is substantial and complex, and where the scattering data are limited (many analyses rely on single-crystal diffuse scattering data), molecular dynamics computer simulation has had a major impact, particularly for materials where the disorder is dynamic in nature. The RMC modelling method also has a role to play in this area, insofar as it can access structural detail that is not straightforward to extract using other methods. This is because it typically relies on total scattering from powdered samples, it is completely general and it is not dependent on potential functions. Total scattering (i.e. the Bragg and diffuse scattering contributions in a diffraction experiment) is the routine measurement for liquid and amorphous samples. Once the data have been rigorously corrected, they may be Fourier transformed to produce real space pair correlation functions [12]. These functions correspond to a 'snapshot' of the structure and as such provide complementary information to the time-average structure obtained from Bragg scattering alone. The implications of this for interpreting crystalline disorder will be developed further in the following sections.

It should also be pointed out that there is a growing interest in the effect of structural disorder on the physical properties of crystalline materials and in developing tools for understanding and characterizing this disorder. Examples of this might be high-temperature superconductors (oxygen disorder), CMR materials (local dynamic distortions), zeolites (host–guest systems), NTE materials (anomalous thermal vibrations) and C_{60} and related compounds (molecular disorder). It is therefore a highly topical area of scientific study.

3. RMC method developments for crystalline systems

There have been two major developments of the RMC method to improve its effectiveness for crystalline systems. The first, resulting in the program RMCPow [13], calculates the scattering functions in three dimensions and then performs a powder average to compare with total scattering data. The second, producing the program RMCProfile [14], calculates the total scattering via real space radial distribution functions but with the addition of a calculation of the Bragg peak profile function. The latter RMCProfile approach will be considered first, since it retains elements of the 'standard' RMC methodology, and the development in RMCPow will lead naturally from the discussion of RMCProfile. However, before discussing either approach, it is important to consider the total scattering data themselves.

3.1. Total scattering data from powders

The long-range ordered nature of crystals means that it is even more important to measure total scattering data to high Q with good instrumental resolution. Unlike total scattering from many liquids, the scattering often does not become flat and featureless until very high values of momentum transfer, Q, are reached, because the local structure may be extremely well defined. Also, at low temperatures, the Bragg peak intensities may not be suppressed until very high Q is reached by the Debye–Waller factors. Equally, the experimental resolution is important because Bragg peak widths are often resolution limited and a good separation of peaks improves the structural models.

The GEM powder neutron diffractometer at ISIS [15] balances effective, rapid powder diffraction measurements with accurate total scattering data obtained from liquids and amorphous materials. It therefore has all the attributes required for making total scattering measurements of crystalline materials. The instrument receives pulses of neutrons from the cold methane moderator at ISIS that scatter from the sample into a wide solid angle of detectors, arrayed in seven detector banks between $2\theta \simeq 2°$ and 159°. Careful beam collimation and an oscillating radial collimator between the sample and detectors keep backgrounds to a minimum.

Rigorous data correction is possible using the GUDRUN program (based on the ATLAS suite of programs [16]), to produce quantitative total scattering structure factors, $S(Q)$, from each bank of detectors.

Typically, for liquid and amorphous samples, the structure factors from the different detector banks are merged to form one $S(Q)$ encompassing the entire measured range of Q. The merged $S(Q)$ may then be Fourier transformed to produce a total radial distribution function, $G(r)$. This procedure causes problems for total scattering from crystalline materials because each detector bank has a different resolution and the merged $S(Q)$ therefore contains data with a complex combined resolution function varying with Q. Resolution broadening also reduces the intensities of the high-r features in $G(r)$. To counter both of these resolution effects, inverse methods of obtaining $G(r)$ from $S(Q)$, such as MCGR [17], have been modified to incorporate the resolution functions for the different detector banks. The program MCGRtof [18] takes a representative $G(r)$ and fits its Fourier transform, convoluted with the appropriate resolution functions, to the $S(Q)$ from the different detector banks. The representative $G(r)$ is then varied until good agreement is achieved. This accounts for effects of instrumental resolution and, provided that a suitably large r-range is used, bypasses high-Q truncation.

In parallel with the above data treatment and manipulation, models of the average structure are refined using the Rietveld method, fitting the diffraction data from the different detector banks separately. This not only serves as a starting model for further refinement using RMCProfile or RMCPow, but also provides the parameters for the resolution functions needed for MCGRtof and RMCProfile (see below).

3.2. RMCProfile

RMCProfile extends the basic RMC method in two ways. First, it accounts for the instrumental resolution by convoluting the calculated $S(Q)$ with the appropriate resolution functions prior to comparison with the data and, secondly, it introduces an additional term to the χ^2 comparison function comparing the Bragg profiles in the powder pattern. The χ^2 comparison function for RMCProfile typically looks like this:

$$\chi^2_{\mathrm{RMC}} = \chi^2_{\mathrm{Data}} + \chi^2_{\mathrm{Constraints}} \tag{1}$$

where

$$\chi^2_{\mathrm{Data}} = \sum_k \sum_n \left[S_{\mathrm{calc}}(Q_i) - S_{\mathrm{exp}}(Q_i)\right]^2/\sigma(Q_i) + \sum_m \left[T_{\mathrm{calc}}(r_i) - T_{\mathrm{exp}}(r_i)\right]^2/\sigma(r_i) + \sum_j \left[I_{\mathrm{calc}}(t_j) - s' I_{\mathrm{exp}}(t_j)\right]^2/\sigma_{I(i)}(t_j) \tag{2}$$

summing over the n points in each of the k structure factors, $S(Q)$, the m points in the radial distribution function, $T(r)$, and the j points of the powder profile, $I(t)$. The σ parameters determine the relative weighting of the different functions in the comparison. ($T(r)$ and $S(Q)$ are representative real and reciprocal space correlation functions, respectively; other functions with different normalizations may equally be used. See [12] for details.) $I_{\mathrm{calc}}(t_j)$ is given by

$$I_{\mathrm{calc}}(t_j) = \sum_{hkl} L_{hkl} |F(hkl)|^2 R_{hkl}(t_j - t_{hkl}) + B(t_j) \tag{3}$$

where $R_{hkl}(t_j - t_{hkl})$ is the peak shape of the hkl reflection arising from the instrumental resolution. s' is a scale factor and $B(t)$ is the background in the diffraction pattern arising from the diffuse scattering component of the total scattering. These parameters are determined from a Rietveld refinement of the same diffraction pattern, and for GEM data are a function of the neutron time of flight, t_j. L_{hkl} is the Lorentz factor of the hkl reflection and $F(hkl)$ is the structure factor given by

$$F(hkl) = \frac{1}{N_c} \sum_j \bar{b}_j \exp(\mathrm{i}\mathbf{Q}_{hkl} \cdot \mathbf{r}_j) \tag{4}$$

where N_c is the number of unit cells in the configuration and $\mathbf{Q}_{hkl}$ is the scattering vector of the hkl reflection. The summation in equation (3) is over all hkl, including symmetry related sets and those expected to be absent due to translational symmetry (screw axes and glide planes). The second term in equation (1) refers to additional terms in the χ^2 comparison which may be used to constrain the model to follow known local chemical arrangements (bond lengths, angles, average coordinations etc) and topologies. An example of how these constraints work in practice can be found in a paper on amorphous silica in this issue [19].

The starting configuration typically consists of a supercell of the crystal unit cell with the atoms in their ideal average positions as determined by Rietveld refinement. Various forms of substitutional disorder may also be introduced into the starting model, as appropriate. The minimization then follows standard RMC procedures, effectively refining the starting model, since the final model should also replicate the Rietveld refined average structure. To this end, the weighting on the Bragg profile term in equation (2) is usually set at a level such that it dominates the fitting. The final configuration consists of a three-dimensional supercell of the crystal structure, which has a reliable average structure (it produces good agreement with the powder diffraction profile) whilst simultaneously reproducing the local instantaneous deviations from the average (it also replicates the experimental $S(Q)$ and $T(r)$). This model may then be interrogated to identify structural features that are important for understanding the system under study (see examples below).

3.3. RMCPow

The program RMCPow [13] is a development of the RMC method intended specifically for total scattering from powdered crystalline materials. $S(Q)$ is calculated using the following equation [20] and assuming that the configuration is a supercell (sc) of the crystal unit cell:

$$S(Q) = 2\pi^2 \frac{N}{V} \sum_{hkl_{\mathrm{sc}}} |F(hkl_{\mathrm{sc}})|^2 \frac{R(Q - Q_{hkl_{\mathrm{sc}}})}{Q^2_{hkl_{\mathrm{sc}}}} \tag{5}$$

where N is the number of atoms within the configuration of volume V and R is the experimental resolution function. hkl_{sc} are the allowed 'Bragg' positions of the supercell and

$$F(hkl_{\mathrm{sc}}) = \frac{1}{N} \sum_j \bar{b}_j \exp(\mathrm{i}\mathbf{Q}_{hkl_{\mathrm{sc}}} \cdot \mathbf{r}_j) \tag{6}$$

(analogous to equation (4)). The calculation is carried out for all $\mathbf{Q}_{hkl_{\mathrm{sc}}}$ where $|\mathbf{Q}|$ is within the range of Q of the measured $S(Q)$. Equation (6) is therefore calculated at Bragg positions for the crystal (when $hkl_{\mathrm{sc}} = hkl$) and at diffuse scattering positions (when $hkl_{\mathrm{sc}} \neq hkl$).

There are several benefits of the RMCPow method. First, as with RMCProfile, the experimental resolution function may be readily incorporated in the comparison with the data. Secondly, because of the form of the scattering function, magnetic neutron scattering may be readily included in the RMCPow refinement [20]. This aspect may be used to find solutions to average magnetic structures. The program has also been developed to include moves which can be used to mimic substitutional disorder, by randomly swapping atoms. Both these latter two enhancements are only being developed within RMCProfile at present. There are however, two drawbacks of the method, both a consequence of forming a continuous one-dimensional scattering function from a summation of a three-dimensional function calculated on a discrete lattice. At low Q, few $\mathbf{Q}_{hkl_{\mathrm{sc}}}$ are available unless a very large configuration is used and hence the diffuse scattering data must be smoothed. At high Q, the number of $\mathbf{Q}_{hkl_{\mathrm{sc}}}$ within a given ΔQ range becomes very large and the calculation becomes very time-consuming. This is because the number of $\mathbf{Q}_{hkl_{\mathrm{sc}}}$ scales linearly with V, the volume of the supercell configuration and, more importantly, as Q_{max}^3. This has meant that most studies using this method have tended to use data with a limited range of Q (e.g. $Q_{\mathrm{max}} \leqslant 10$ Å^{-1}).

4. Analysing the RMC models

There is considerable scope for detailed analysis of the RMC refined models. Since the model is a supercell of the crystal unit cell, it is possible to average the model onto a single unit cell. This can be used to generate atom density maps or isosurfaces and also to calculate average atom positions within the unit cell for comparison with those determined by Rietveld refinement of the Bragg profile. Given that these density maps mimic the distributions of the disordered atoms, they can be compared with the average anisotropic atomic displacement parameters (adps). Any differences can then be ascribed to ‘unusual’ disordering behaviour, which cannot be readily described with adps. Programs such as atomeye [21] are extremely useful for viewing both the full configuration and the averaged unit cell distributions.

The models are also able to provide instantaneous bond lengths, as distinct from the average bond lengths which are determined from analysis of Bragg scattering alone. The instantaneous value and average may be very different for a disordered material, since the former is formed from the average of all bonds in the model (i.e. ⟨A–B⟩) and the latter is the separation of two average positions (i.e. ⟨A⟩–⟨B⟩). To a degree, this information is available directly from the peak positions in total radial distribution functions. However, for crystalline materials, ⟨A–B⟩ can be calculated for subsets of atom types A and B, such as bonds that are symmetry related to each other. Similar selective bond angle distributions can be calculated from the models. In this way, it is possible to investigate small instantaneous distortions in bonded polyhedra.

A more formal parametrization of the above characterization of the local environment has been developed using a geometrical analysis of the difference between polyhedra within two independent configurations [22, 23]. Polyhedra from one configuration are optimally mapped onto equivalent polyhedra in another using translations and rotations. The amount of residual distortion (bond stretching, bending etc) is then calculated. The relative proportion of rotational and distortive disorder can then be used to assess the nature of the disorder across, for example, a disordering phase transition.

Very recently, the extent to which RMC models can be used to extract dynamical information has been assessed using a statistical analysis of a large number of configurations [24]. The phonon dispersion curves for MgO produced in this way reproduced the experimental results in both the low-energy regime and in the energy scale, but were unable to capture the detail of the high-energy features. However, this method shows promise for systems where low-energy features are important (for example rigid unit modes in linked polyhedra and soft mode induced phase transitions) and where the lack of large single crystals prevents inelastic scattering measurements.

5. A very brief summary of scientific applications

RMC modelling has made valuable contributions to the understanding of the structures of superionic materials (reviewed in [25]) such as those based on the silver and copper halides, where conduction pathways have been mapped out and disordering mechanisms identified. RMC modelling has been used to investigate the possible 'paddle-wheel' ion conduction mechanism in superionic Li_2SO_4: the models were used to assess the interplay between the Li ion diffusion and sulfate group rotation.

Network systems have also been extensively investigated. The structures of many polymorphs of silica have been analysed using RMC modelling (summarized in [26]). These studies have been used to investigate similarities and differences between the local structural environments of the tetrahedral crystalline phases of silica and silica glass: the high-temperature disordered cristobalite and tridymite phases are found to be locally similar to the glass. RMC analysis of total scattering data across the α–β phase transition in quartz provides a holistic interpretation of the phase transition. This showed that the symmetry change is evident on a short length scale and the phase transition is therefore inconsistent with microscopic domain models. The RMC models have also been used to interpret high-temperature piezoelectric behaviour in quartz [27].

A range of molecular materials have also been analysed, including the molecular crystal SF_6 [26] and the behaviour of the NO_3 groups through the phase transition in $NaNO_3$ [2]. The structural changes through a number of phase transitions have also been effectively analysed using RMC modelling. As well as those mentioned above, the distortions associated with the low-temperature phase transition in $SrTiO_3$ have been characterized using RMC modelling [28].

There has also been recent work on a range of magnetic systems including an RMC analysis of the dynamical correlations of the frustrated Kagomé magnet $SrCr_{9x}Ga_{12-9x}O_{19}$ [29] and a solution for the magnetic structure of Ba_2FeWO_6 [30].

It is not possible to include all crystalline applications of RMC modelling in this brief introductory review and indeed much of the work has already been summarized [1]. Recent work is also contained in this Special Issue and readers are referred to these articles for further details of current scientific applications of the RMC technique.

6. Conclusions and future prospects

As stated in section 2, understanding disorder in crystalline materials is becoming increasingly important. This is reflected in the increasing number of total scattering diffractometers available and being developed at spallation neutron sources and synchrotron x-ray facilities worldwide. A major component of their experimental programmes involves measurements of total scattering from powdered samples. RMC refinement (whether using RMCProfile or RMCPow) is ideally placed to exploit these high-quality measurements and is one of the few methods available for analysing these data effectively. Both RMC programs are still being improved to make them more generally applicable and there is no doubt that total scattering data, analysed with RMC methods, will continue to make major contributions to the understanding of structural disorder in crystalline materials for many years to come.

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