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Determination of partial structure factors by reverse Monte Carlo modelling—a test of the method

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Abstract

The reverse Monte Carlo modelling technique is commonly applied for the analysis of the atomic structure of liquid and amorphous substances. In particular, partial structure factors of multi-component alloys can be determined using this method. In the present study we use the example of the liquid Ni₃₃Ge₆₇ alloy to investigate the impact of different input data on the result of RMC modelling. It was found that even two experimental structure factors might be sufficient to obtain reliable partial structure factors if the contrast between them is high enough.

1. Introduction

Detailed description of a multi-component liquid or amorphous alloy requires the knowledge of the partial structure factors and partial pair distribution functions. However, a conventional diffraction experiment allows obtaining only the total structure factor. Applying the Faber–Ziman formalism [1], the total structure factor in an alloy with K constituents can be expressed as a weighted sum of the partial ones:

$$S(Q) = \sum_{i,j}^K w_{ij}^n(Q) S_{ij}(Q). \quad (1)$$

The coefficients w_{ij} depend on the composition of the sample and the scattering behaviour of the components, which differs with the type n of diffraction experiment carried out. These factors read

$$w_{ij}^X(Q) = \frac{c_i c_j f_i(Q) f_j(Q)}{\langle f(Q) \rangle^2}, \quad w_{ij}^N = \frac{c_i c_j b_i^{\text{coh}} b_j^{\text{coh}}}{\langle b^{\text{coh}} \rangle^2} \quad (2)$$

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Table 1. Coefficients relating the partial structure factors to the total ones as given by (2).

	$^{58}\text{Ni}_{33}\text{Ge}_{67}$	$^{60}\text{Ni}_{33}\text{Ge}_{67}$	$^*\text{Ni}_{33}\text{Ge}_{67}$
w_{NiNi}^n	0.216	0.056	0.146
$2w_{\text{NiGe}}^n$	0.497	0.327	0.473
w_{GeGe}^n	0.287	0.617	0.381

for x-ray (superscript X) and neutron (N) diffraction experiments, respectively. Herein c_i denotes the molar fraction of component i , $f(Q)$ the Q -dependent atomic form factor in case of x-ray scattering, b_i^{coh} the coherent scattering length for neutron diffraction and

$$\langle f(Q) \rangle = \sum_i^K c_i f_i(Q), \quad \langle b^{\text{coh}} \rangle = \sum_i^K c_i b_i^{\text{coh}}. \quad (3)$$

Generally speaking, (1) can be solved with respect to the $S_{ij}(Q)$ if $K(K+1)/2$ experimental diffraction curves are at hand. There exist a number of experimental techniques to determine the partial structure factors of binary alloys, e.g. diffraction experiments using different radiations [2], neutron scattering with isotopic substitution (NDIS) [3, 4] or the anomalous x-ray scattering method (AXS) [5]. All these methods have proved to be powerful techniques. Nevertheless, their application is often limited by low availability, high costs or insufficient accuracy.

Approximative approaches have been developed, such as assuming partial structure factors which are independent of the concentration (e.g. [6]). By means of computer modelling techniques, especially the reverse Monte Carlo method [7], partial distribution functions can be derived from less than $K(K+1)/2$ diffraction experiments. This technique is frequently applied for modelling a large variety of materials. In particular, diffraction data for amorphous and liquid alloys have been evaluated by RMC calculations. Recently, data from EXAFS-experiments have been included successfully [8]. However, the question arises whether this approach leads to accurate results.

In this work we aim to demonstrate that the reverse Monte Carlo modelling technique (RMC) in certain cases allows the determination of reliable partial structure factors for a binary alloy from only two independent measurements. For this purpose we chose the example of the liquid $\text{Ni}_{33}\text{Ge}_{67}$ alloy. For this particular alloy, NDIS data are available [4]. This provides an unique possibility to elucidate how different input data affects the result of the RMC modelling.

2. Experimental details

Total structure factors of the eutectic $\text{Ni}_{33}\text{Ge}_{67}$ alloy at a temperature of 780 °C have been measured by neutron diffraction with isotopic substitution by Halm and co-workers [4]. Alloys with ^{58}Ni ($b_{\text{Ni}}^{\text{coh}} = 14.4$ fm), the natural isotopic mixture (in the following denoted as $^*\text{Ni}$, $b_{\text{Ni}}^{\text{coh}} = 10.3$ fm) as well as a mixture of $^*\text{Ni}$ and ^{60}Ni (for simplicity denoted as ^{60}Ni , $b_{\text{Ni}}^{\text{coh}} = 5$ fm) have been measured at diffractometer 7C2 of the Léon Brillouin laboratory (LLB), Saclay. The experimental details as well as the data treatment are described in [4] and the total structure factors are shown in figure 1.

For each of the three experimental total structure factors the coefficients defined by (2) are listed in table 1. By applying (1) the partial structure factors shown in figure 2 have been calculated. Please note that no smoothing has been applied. In the following discussion, we will assume that these partial structure factors are the correct ones and thus use them to examine the results of the RMC modelling.

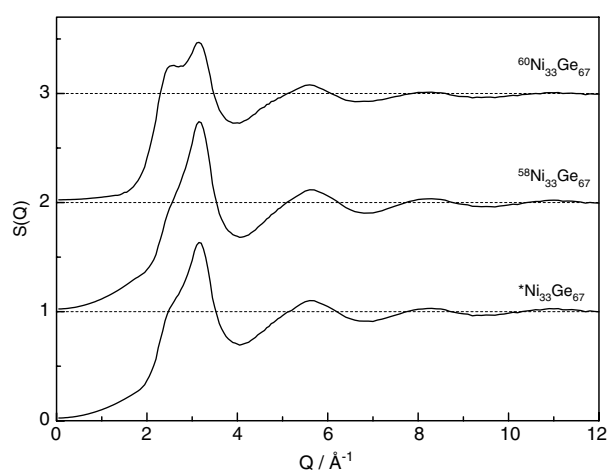


Figure 1. Experimental total structure factors of the $\text{Ni}_{33}\text{Ge}_{67}$ alloy obtained by neutron diffraction with isotopic substitution [4].

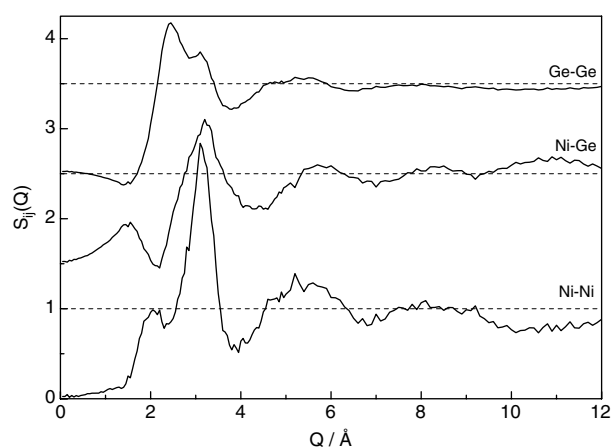


Figure 2. Partial structure factors $S_{ij}(Q)$ obtained from the experimental structure factors by solving (1).

3. Reverse Monte Carlo modelling

The reverse Monte Carlo modelling technique, which was described first by McGreevy and Pusztai in 1988 [7], is a modification of the conventional Metropolis Monte Carlo algorithm. An actual survey and discussion with a broad variety of examples is to be found in [9].

Instead of pair potential total structure factors, total pair correlation functions or EXAFS experimental data are used to obtain a three-dimensional atomic configuration describing the system under investigation. Furthermore, constraints can be imposed on the atomic configuration. In general, the average number density ρ_0 (which determines the configuration size for a given number of particles) and distances of closest approach of atoms are fixed. In addition a certain coordination behaviour of the constituents can be assumed.

To start with, an initial atomic configuration can be created either from random positioning of the atoms, from a known crystalline structure or from a hard-core model. The partial

pair correlation functions in this configuration are determined from the averaged number of neighbouring atoms $n_{ij}(r)$ in a certain interval Δr of the radial distance r from the centre atom:

$$g_{ij,\text{RMC}}(r) = \frac{\langle n_{ij}(r) \rangle}{4\pi\rho_0 r^2 \cdot \Delta r}. \quad (4)$$

The $g_{ij}(r)$ are then Fourier transformed to Q -space to obtain partial structure factors. By applying (1) and (2) the total structure factors corresponding to the given experimental ones are calculated. The deviation between each set of the model total structure factor $S_{\text{RMC}}(Q)$ and the experimental total structure factor $S(Q)$ is given by

$$\chi^2 = \frac{1}{\sigma^2} \sum_i [S_{\text{RMC}}(Q_i) - S(Q_i)]^2. \quad (5)$$

For a number of data-sets the individual values of χ^2 have to be added to obtain a measure for the overall deviation.

In the next step an atom to be moved is chosen randomly. This atom is shifted by a random vector applying periodic boundary conditions. The total structure factors of the changed configuration are then obtained as described above and another figure of merit $\hat{\chi}^2$ is calculated. If $\chi^2 > \hat{\chi}^2$ the changed configuration substitutes the old one. In the opposite case, the new configuration is used for further modelling only with a probability

$$P \sim \exp\left[-\frac{\hat{\chi}^2 - \chi^2}{\sigma^2}\right]. \quad (6)$$

Continuous application of this algorithm yields a good agreement between the experimental and the model structure factors and χ^2 will start to oscillate around a certain value. However, by accepting a number of moves which do increase the value of χ^2 the algorithm reduces the probability that the algorithm will be caught in local minima.

The parameter σ can be regarded as a measure of the experimental error inherent in the given total structure factors. By comparing (6) to the case of conventional Metropolis Monte Carlo simulations it becomes obvious that σ plays the role of a numerical temperature. It can thus be used to improve the agreement between experiment and model by annealing the atomic configuration (this procedure is often referred to as ‘simulated annealing’).

In our study, reverse Monte Carlo modelling has been performed with (a) all three experimental structure factors given in section 2, only either (b) the $^{60}\text{Ni}_{33}\text{Ge}_{67}$ or (c) the $^{58}\text{Ni}_{33}\text{Ge}_{67}$ structure factor combined with the $^*\text{Ni}_{33}\text{Ge}_{67}$ total experimental structure factor and (d) the $^*\text{Ni}_{33}\text{Ge}_{67}$ neutron scattering structure factor only. For all RMC runs $\rho_0 = 0.049 \text{ \AA}^{-3}$ and $r_{\text{min,Ni-Ni}} = r_{\text{min,Ni-Ge}} = r_{\text{min,Ge-Ge}} = 1.8 \text{ \AA}$ but no coordination constraints have been applied.

All RMC runs have been performed in three steps. First, a random configuration of 500 atoms has been prepared. The modelling process has been started with $\sigma = 0.025$, which has been decreased stepwise to $\sigma = 0.010$ whenever χ^2 was oscillating around a certain value, which is a sign of an equilibrium state. Then the size of the simulation box has been doubled in each direction, thus a configuration of 4000 atoms was at hand. With this arrangement of atoms σ has been further decreased to a value of $\sigma = 0.003$. Finally, the simulation box has again been doubled in each direction and contained 32 000 atoms. The modelling process has been continued to reach $\sigma = 0.001$.

For all RMC simulations a very good agreement between model structure factor and experimental structure factor has been achieved. As an example, this is illustrated for the case of the RMC run with three experimental structure factors (case (a)) in figure 3. The computed partial structure factors are shown in figure 4 in comparison with the ones determined

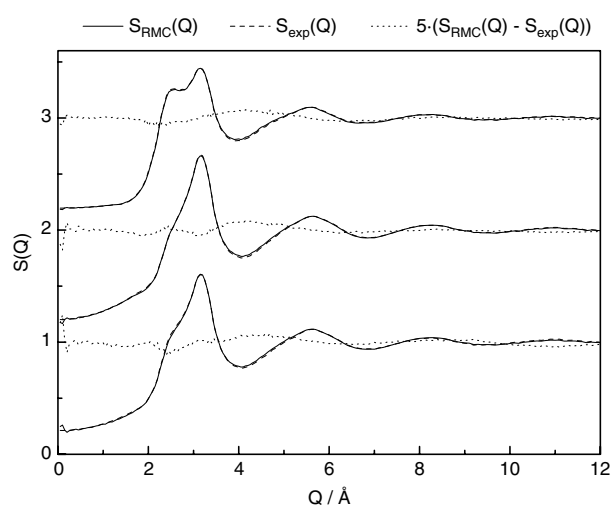


Figure 3. Comparison between model for case (a) (solid lines) and experimental (dashed lines) total structure factors. Note the good agreement between the experiment and RMC result (the difference has been scaled up by a factor of five).

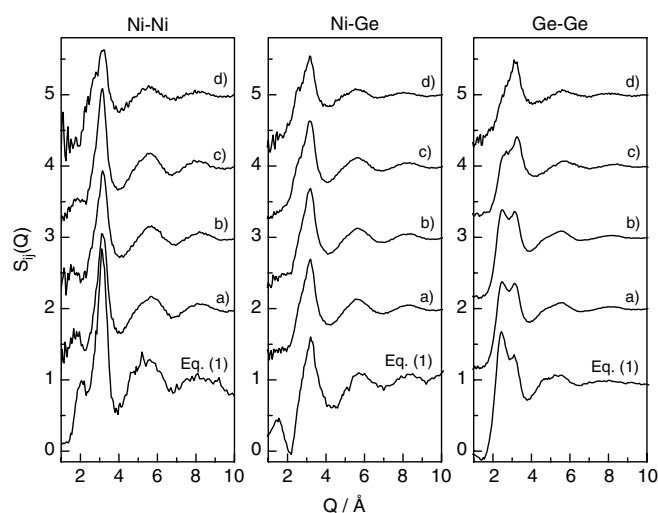


Figure 4. Partial structure factors obtained using different input data: application of (1) and RMC runs with (a) $^{58}\text{Ni}_{133}\text{Ge}_{67}$, $^{60}\text{Ni}_{133}\text{Ge}_{67}$, $^*\text{Ni}_{133}\text{Ge}_{67}$, (b) $^{60}\text{Ni}_{133}\text{Ge}_{67}$, $^*\text{Ni}_{133}\text{Ge}_{67}$, (c) $^{58}\text{Ni}_{133}\text{Ge}_{67}$, $^*\text{Ni}_{133}\text{Ge}_{67}$, and (d) only $^*\text{Ni}_{133}\text{Ge}_{67}$ total structure factor used.

by application of (1). No smoothing procedure has been applied to these partial structure factors. Instead, modelling of sufficiently large atomic configurations yields a good statistics in determining the partial pair correlation functions and thus smooth Fourier transformed functions. Furthermore, the cut-off value is then high enough to avoid truncation effects in the Fourier transformation.

Table 2. Figure of merit R judging the relative information content of the different sets of total structure factors used for the RMC modelling and deviation coefficient Γ describing the agreement between the RMC model and solving (1).

Used structure factors	R	Γ
(a) $^{58}\text{Ni}_{133}\text{Ge}_{67}$, $^{60}\text{Ni}_{133}\text{Ge}_{67}$ and $^{*}\text{Ni}_{133}\text{Ge}_{67}$	0.47	0.030
(b) $^{60}\text{Ni}_{133}\text{Ge}_{67}$ and $^{*}\text{Ni}_{133}\text{Ge}_{67}$	0.42	0.033
(c) $^{58}\text{Ni}_{133}\text{Ge}_{67}$ and $^{*}\text{Ni}_{133}\text{Ge}_{67}$	0.37	0.039
(d) $^{*}\text{Ni}_{133}\text{Ge}_{67}$	0.33	0.056
— $^{*}\text{Ni}_{133}\text{Ge}_{67}$, x-ray	0.38	—

4. Discussion

It is obvious that a different amount of information on the partial structure factors is inherent in each of the data-sets used. McGreevy and Pusztai proposed a figure of merit R for assessing the relative information content of different sets of total structure factors as follows [10]. For a particular total structure factor the coefficients w_{ij}^n given by (2) form a $K(K+1)/2$ component vector \mathbf{C}^n , the unit vector being $\hat{\mathbf{C}}^n$. The difference in information between the total structure factors from two experiments α and β is then represented by the angle

$$\phi_{\alpha\beta} = \arccos(\hat{\mathbf{C}}^\alpha \cdot \hat{\mathbf{C}}^\beta) \quad (7)$$

between the unit vectors corresponding to the experiments. A third total structure factor is taken into account by calculating the angle $\phi_{(\alpha\beta)\gamma}$ between the plane given by $\hat{\mathbf{C}}^\alpha$ and $\hat{\mathbf{C}}^\beta$ and the remaining vector $\hat{\mathbf{C}}^\gamma$. With the arbitrary choice $\phi_\alpha = \pi/2$ for the first measurement, the relative information content is the maximum value of

$$R = \frac{\phi_\alpha + \phi_{\alpha\beta} + \phi_{(\alpha\beta)\gamma}}{3\pi/2} \quad (8)$$

for all possible permutations of the experimental structure factors. If x-ray structure factors are taken into account this orthogonality parameter is Q dependent. However, the changes in R over the whole Q -range are small compared to the differences between several sets of experimental data. The values of R for the cases under discussion as well as a combination of x-ray structure factor and neutron structure factor obtained from the natural isotopic composition (calculated for $Q = 0 \text{ \AA}^{-1}$) are given in table 2.

The shape as well as peak-heights of the partial structure factors depend strongly on the information provided for the modelling process. In particular, in the case of $S_{\text{GeGe}}(Q)$ the differences become prominent. Solving (1) gives the main peak position at $Q_1 = 2.45 \text{ \AA}^{-1}$ and there is a shoulder on the right-hand side. The result of the RMC run with the same input data is a split peak but at the right position. Less information results in completely different peak shapes and positions. However, the peak positions of the other partial structure factors remain practically unchanged when changing the information provided for the modelling process.

In order to quantify the deviations between the ‘correct’ and the modelled partial structure factors the value

$$\Gamma := \frac{1}{3Z} \sum_{i,j \geq i} \sum_k^Z [S_{ij,\text{RMC}}(Q_k) - S_{ij,\text{Eq.(1)}}(Q_k)]^2, \quad (9)$$

with the number Z of data points available, has been calculated for the results of all RMC runs (see table 2). The dependence $\Gamma(R)$ can be described approximately as an exponential law. This emphasizes that data-sets with high R -values indeed allow the determination of reliable partial structure factors even if fewer than $K(K+1)/2$ experimental $S(Q)$ are provided (compare

data-sets (a) and (b)). On the other hand, the same number of total structure factors with less relative information provided to the modelling process yields huge uncertainties in the obtained partial structure factors.

In this study we compare the results of RMC modelling to partial structure factors obtained by a direct inversion of (1). However, in an early work Edwards *et al* [11] showed that within this procedure small experimental errors in the total structure factors might be scaled up to huge errors in the partial structure factors and proposed an iterative procedure for the treatment of NDIS data. Throughout the present discussion we should therefore keep in mind that even the partial structure factors which we assumed to be the correct ones are affected by experimental errors.

As Soper pointed out recently [12], any computer modelling approach implicitly imposes constraints on the partial pair correlation function and thus also on the partial structure factors: the $g_{ij}(r)$ are obtained from a three-dimensional arrangement of atoms at the given density. In contrast to the direct inversion approach, this makes sure that the site–site pair distribution functions are non-negative over the whole r -range and atomic overlap does not occur.

5. Conclusions

In the present study we used the example of the liquid Ni₃₃Ge₆₇ alloy to perform reverse Monte Carlo calculations providing different input data with different relative information inherent in them. It can be stated that reliable partial structure factors can be determined even from two diffraction experiments if the contrast between these two experimental structure factors is high enough (see data-set (b)). The figure of merit R as proposed by McGreevy and Pusztai proved to be a useful measure for the relative information content of the sets of experimental structure factors at hand. For the practical application this means that partial structure factors can be obtained by combining one experimental structure factor obtained by x-ray diffraction and one experimental structure factor obtained with neutron diffraction with natural isotopic mixtures of the elements by means of the RMC technique if only the value of R is sufficiently high.

Application of constraints, e.g. the known coordination behaviour of certain components in the material under investigation, may have a strong impact on the result of RMC simulations. However, it has to be stressed that reliable information of this kind is scarce in most cases and thus constraints have to be used with great care in order to obtain unbiased results.

The above discussion restricts the determination of partial structure factors as the comparison between modelled structure and experimental data is done in terms of structure factors. However, the initial result of the RMC modelling is a three-dimensional atomic model of the material under investigation which reproduces the given experimental total structure factors. This model can be further analysed, e.g. in terms of pair correlation functions, coordination numbers, the distribution of atoms in the coordination shells, bond-angle distribution and other methods.

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