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# Reverse Monte Carlo refinement of molecular and condensed systems by x-ray absorption spectroscopy

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Received 16 December 2004

Published 21 January 2005

Online at [stacks.iop.org/JPhysCM/17/S135](http://stacks.iop.org/JPhysCM/17/S135)

## Abstract

We have developed a successful method for structural refinement, based on the reverse Monte Carlo (RMC) algorithm, that can be applied simultaneously to diffraction and x-ray absorption (XAS) data. The method is designed to study molecular and condensed systems incorporating all of the advances related to the application of modern multiple-scattering (MS) codes and the  $n$ -body expansion for XAS data-analysis (GNXAS). Convergence properties and the dependence of the structural model upon specific features of the XAS spectra and calculation parameters are discussed. Limitations and advances of the method are elucidated in the light of the structural sensitivity of the XAS technique.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

X-ray absorption spectroscopy (XAS) is a powerful technique for investigating the very short-range structural properties of ordered and disordered substances. Its unique sensitivity to short-range atom–atom correlations can be successfully exploited in conjunction with other more standard structural techniques like x-ray and neutron diffraction. However, the underlying XAS physical mechanism is the photoexcitation of an electron from a deep core level which strongly interacts with surrounding matter and proper theoretical treatments and data-analysis methods have been developed only in recent times.

Current XAS data-analysis provides a structural refinement of the raw XAS data through multiple-scattering (MS) calculations of the x-ray absorption cross-section. In particular, the GNXAS *ab initio* data-analysis method for XAS data-analysis is designed to produce fast and accurate simulations of the  $\gamma^{(n)}$  MS XAS  $n$ -body signals, associated with the  $n$ -body distribution functions  $g_n$  describing the local structure around selected photoabsorbing

atoms [1, 2]. The standard XAS structural refinement is based on modelling the short-range distribution functions as a sum of distinct peaks associated with well-defined bonding distances and angles corresponding to first and further neighbours for the pair ( $g_2$ ) and higher-order ( $g_n, n > 2$ ) distribution functions [2, 3]. This approach is justified for molecules and in ordered condensed matter, where the assumption about the existence of distinct  $g_2$  and  $g_3$  peaks at short distances is fulfilled. In these systems, the ‘peak-fitting’ scheme represents a fast and efficient tool, usually able to guarantee a reliable reconstruction of the shape of the short-range distributions through a limited number of structural parameters. However, even in these cases, the problem of defining suitable model functions is particularly severe. Gaussian shapes work fine whenever the harmonic approximation for vibrations holds, but deviations have been observed and studied even at moderate temperatures. Non-Gaussian model functions have been devised and have been successfully used in a variety of cases [1–6], but their extensive application to pair and higher-order distribution functions is particularly difficult.

The ‘peak-fitting’ scheme has also been used in highly disordered substances, such as amorphous or liquid matter. In these systems, short-range peaks of the  $n$ -body distribution functions are usually merged into a long-range tail, and a meaningful XAS data-analysis can only be carried out using suitable physical constraints [4]. The application of this methodology has been shown to be successful in describing the short-range pair distribution function of ‘simple’ elemental melts, ionic binary liquids and aqueous solutions (see [4–9] and the review paper [10]). However, the extension of the ‘peak-fitting approach’ to disordered multi-component systems [11] and a reliable reconstruction of the shape of the higher-order distribution functions in liquids is a formidable task within the current strategies for XAS data-analysis.

Of course, advances in XAS data interpretation overcoming present limitations are particularly important, in view of the high potential of the XAS technique in measuring the local structure in highly disordered systems through pair and higher-order correlations. The additional information provided by XAS data is able to improve our ability in reconstructing the local geometry in disordered substances. Here we present a novel application of the reverse Monte Carlo (RMC) method [12–14] which fully incorporates all of the advances related to the application of multiple-scattering (MS) codes and the  $n$ -body expansion for XAS data-analysis (GNXAS). The new suite of programs is designed to apply the RMC algorithm simultaneously to diffraction and XAS data, allowing the construction of a tridimensional model for the disordered system compatible with the observables under consideration. In particular, XAS data probe the local structure around photoabsorbing centres, while diffraction data provide the necessary medium and long-range constraints.

Application of the RMC method for XAS data-analysis was already suggested by Gurman and McGreevy [13], and preliminary applications to silver bromide and crystalline and amorphous silicon were presented. The method was also applied for data-analysis of liquid GaSb and InSb [15]. A successful application of the RMC algorithm to XAS data has been carried out more recently by Winterer [16]. We have now developed an RMC program using state-of-the-art simulation techniques for calculating the XAS signal starting from ensembles of either molecular replicas or a box with cyclic boundary conditions. In the latter case, the RMC refinement is applied both to XAS experimental data and the  $g(r)$  curve obtained by diffraction techniques.

## 2. Method

X-ray absorption spectroscopy is known to be a suitable technique for studying the short-range structure, especially in disordered and ill-ordered systems.

The structural XAS signal is the modulation of the x-ray absorption coefficient above a deep core electron excitation edge. The XAS oscillations are usually referred to as x-ray absorption fine structure (XAFS). More precisely, XAFS is defined as the relative oscillation with respect to a smooth total atomic absorption cross-section  $\sigma_0^l$  normalized to the atomic cross-section of the edge under consideration  $\sigma_0$ , i.e.  $\chi(k) = [\sigma(E) - \sigma_0^l(E)]/\sigma_0(E)$ , where  $k = \sqrt{2m(E - E_c)}/\hbar$  is the modulus of the photoelectron wavevector ( $E_c$  being the threshold energy).

For a single-component system the structural XAS signal is related to the  $n$ -body distribution functions by

$$\begin{aligned} \langle \chi(k) \rangle = & \int_0^\infty dr 4\pi r^2 \rho g_2(r) \gamma^{(2)}(r, k) \\ & + \int dr_1 dr_2 d\theta 8\pi^2 r_1^2 r_2^2 \sin(\theta) \rho^2 g_3(r_1, r_2, \theta) \gamma^{(3)}(r_1, r_2, \theta, k) \\ & + \dots \quad \dots \end{aligned} \quad (1)$$

where the short-range nature of the  $n$ -body XAS  $\gamma^{(n)}$  signals limits the integral in a region of linear dimensions of the order of few ångströms.

The implementation of the RMC method [12, 14] for XAS data-analysis has been done by developing a new package of programs (RMC-GNXAS, based on the GNXAS suite of programs) designed to work for structural refinement of both molecular and condensed systems. For molecular systems the programs produce an ensemble of replicas of the given molecule, while for condensed ordered or disordered systems the atom positions are defined in a cubic box of selected size where cyclic boundary conditions are applied.

The initial atomic configuration is provided by a program (`crymolrmc`) specifying either the number of molecular replicas or the size of the cubic box and the number, type and initial positions of atoms involved in the calculation. The initial model generally includes Gaussian disorder around selected average (equilibrium) atomic positions. In this way the starting configuration is a disordered crystalline or molecular model with well-defined average distances, number and type of atoms, and density (or number of molecules).

For the purpose of XAS refinement of liquids or amorphous systems, this initial configuration can be successively refined to reproduce the shape of the pair distribution function  $g(r)$  obtained by diffraction experiments or by computer simulations. This is done, for example, by using directly the `rmcxas` program and executing an RMC procedure limited to the known  $g(r)$ . Therefore, the starting configuration for XAS refinement of liquid or amorphous systems can be a truly disordered structure already compatible with previous experiments or calculations. This is an important aspect of the successive RMC refinement, because the XAS sensitivity is limited to a few ångströms, and medium-range and long-range order has to be constrained using complementary information from different techniques.

The practical implementation of the RMC method is done simply by calculating the XAS signal defined by equation (1) for any given set of atomic coordinates of the ensemble. To this purpose, the relevant  $\gamma$  signals are calculated for a selected range of distances and atom types and interpolated for all of the actual distances of the model structure. The programs `phagen` and `gnxas` (included in the GNXAS package) are used for calculating the table of XAS  $\gamma$  signals. Appropriate standard calculation strategies have been implemented for optimizing the calculation of the variation of the XAS signal associated with the modification of the atomic positions during the RMC loops. The main difference with the application described in [13] is the use of sophisticated MS calculations within the  $n$ -body expansion and of the relationship given by equation (1). Note also that a term ( $g_2-1$ ) instead of  $g_2$  appears in the integral in [13].

The `rmcxas` program of the RMC-GNXAS package is fully interfaced with GNXAS [2, 3] and performs standard RMC structural refinements of both molecular and condensed structures. The  $\chi^2$  function at each RMC step is simply given by

$$\chi^2 = \sum_{i=1}^{N_{\text{XAS}}} [\chi^{\text{E}}(k_i) - \chi^{\text{C}}(k_i)]^2 / \sigma_i^2 + \sum_{j=1}^{N_g} [g_2^{\text{E}}(r_j) - g_2^{\text{C}}(r_j)]^2 / \sigma_j^2 \quad (2)$$

where in the first term of the rhs  $\chi^{\text{C}}$  is calculated by the program starting from the actual atomic coordinates using equation (1) and the  $\gamma^{(2)}$  signals given by GNXAS,  $\chi^{\text{E}}$  is the raw XAS signal determined by a preliminary data-analysis (performed using the `fittheo` program, GNXAS suite) and  $\sigma_i^2$  the noise function obtained from the experiment (evaluated by application of `fittheo`). In the second term, omitted in molecular cases,  $g_2^{\text{C}}$  is the pair distribution associated with the atomic coordinates of the RMC box,  $g_2^{\text{E}}$  is a model pair distribution obtained by neutron/x-ray diffraction or computer simulations, and  $\sigma_j^2$  is the variance associated with the pair distribution.

### 3. Test application to Br<sub>2</sub>

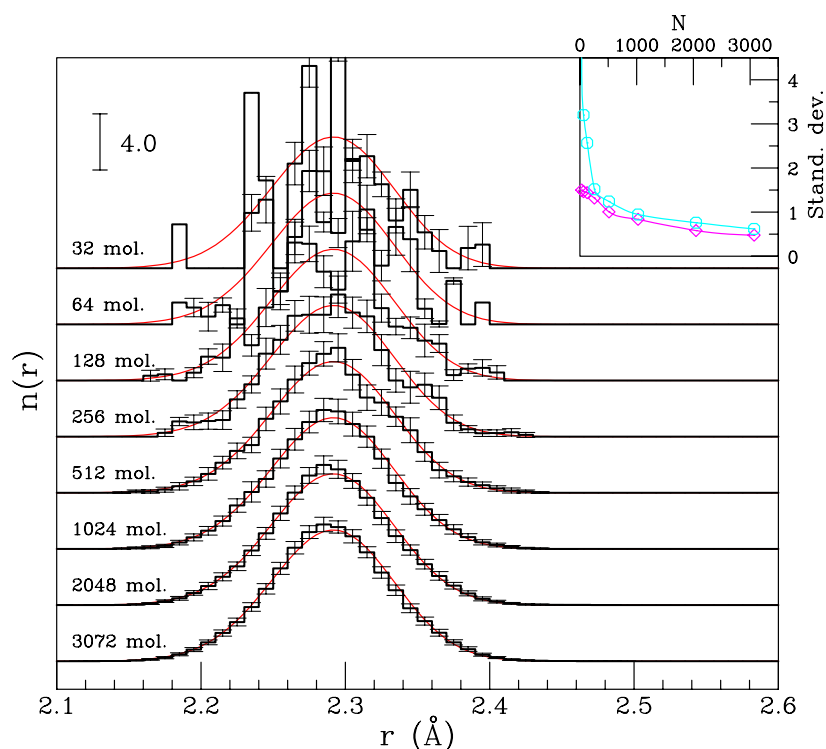
A suitable test of the structural refinement capabilities of the RMC method as applied to XAS data, using the present `rmcxas` program, is the application to a simple diatomic molecule. In such a case, the existence of reliable experimental and theoretical models for the structure and the pure two-body nature of the structural problem are essential features to understand the advantages and limitations of the present approach. In particular, we shall present test RMC applications to Br K-edge experimental data of gaseous bromine (Br<sub>2</sub>). The bond distribution of the Br<sub>2</sub> molecule has been investigated by XAS by several authors (see for example [17, 18] and references therein), in agreement with previous electron diffraction and spectroscopic studies. Data-analysis was originally performed using a standard Gaussian ‘peak-fitting’ approach (average distance  $R = 2.288 \text{ \AA}$  and bond variance  $\sigma^2 = 0.0019 \text{ \AA}^2$  for the XAS data under consideration; see [18] and references therein).

In order to examine the convergence properties and dependence of the resulting structural model from specific characteristics of the input XAS signal we have performed a series of refinements where  $\chi^{\text{E}}$  is a theoretically calculated XAS signal in the range  $4\text{--}15 \text{ \AA}^{-1}$ , used in place of the actually measured data. This allowed us to exclude the possible effects of systematic errors affecting real experimental spectra. This fictitious signal has been calculated from a given Gaussian  $n(r)$  distribution with average distance ( $R = 2.2897 \text{ \AA}$ ) and variance ( $\sigma^2 = 0.0018 \text{ \AA}^2$ ), close to that measured in previous works. A Gaussian noise of amplitude of  $10^{-4}$  has been added to the calculated  $\chi(k)$  in order to mimic a real XAS measurement.

Several RMC models, using different numbers  $N$  of Br<sub>2</sub> molecular replicas, have been tested. The starting configuration was chosen to reproduce a Gaussian distribution with displaced values with respect to those chosen for the model  $n(r)$ .

Complete simulations lasted for 200 RMC steps, each RMC move corresponding to  $N$  molecular distance moves (the current speed is about 2 ms for each molecular distance move on a 3 GHz Intel<sup>®</sup> Pentium<sup>®</sup> IV CPU). Convergence of  $\chi^2$  near to the expected value,  $E[\chi^2] = N_p$ , where  $N_p$  is the number of data points (450 in the present case) is reached very rapidly, after 10–20 RMC moves.

In figure 1, we show the average  $n(r)$  calculated over the last 150 RMC moves (thick histograms) for increasing number of molecules  $N$  in the RMC model. The thin (red) curve, reported for comparison, is the model  $n(r)$  corresponding to the theoretical signal used in place of  $\chi^{\text{E}}$  in this refinement. Maximal deviations of the resulting  $n(r)$  distributions from the model

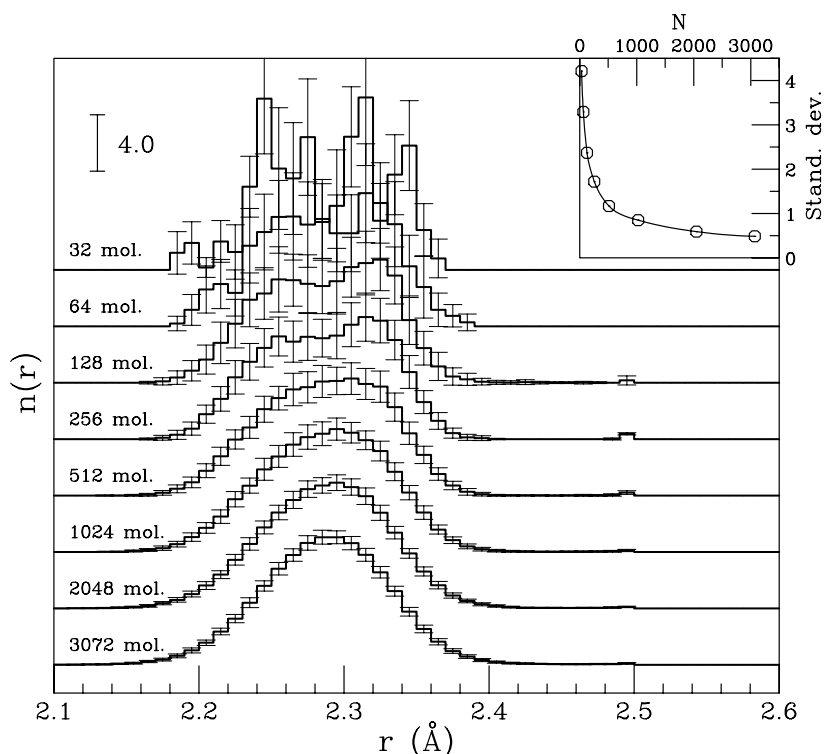


**Figure 1.** Pair distribution functions  $n(r)$  (thick histograms) resulting from the RMC refinement of an XAS signal corresponding to a Gaussian distribution (thin curve). The  $n(r)$  resulting from different RMC models containing an increasing number of molecules are shown (shifted by 4). Error bars correspond to fluctuations of the  $n(r)$  associated with equilibrium configurations. Maximal deviations of the  $n(r)$  from the model are also shown in the inset (circles), in comparison with maximal statistical fluctuations (diamonds).

one are shown in the inset (circles) as a function of  $N$ . The statistical fluctuations (standard deviation) of the  $n(r)$  associated with the RMC sampling of the equilibrium configurations are reported as error bars in figure 1. The maximal fluctuations, observed usually near the  $n(r)$  maxima, are reported also in the inset (diamonds).

Looking at figure 1, it is evident that the reliability of the reconstruction of the  $n(r)$  distribution gradually increases with the number of molecules  $N$ . In particular, the shape of the  $n(r)$  is satisfactorily reproduced starting from 256 molecules. This can be appreciated by looking at the inset of figure 1, where we can see that the noise of the simulations approaches asymptotic values for increasing  $N$ . In particular, it appears that a reasonable choice for this example could be  $N \geq 512$  molecular replicas. It is interesting to note also that the intrinsic fluctuation (diamonds) of the reconstructed  $n(r)$  is much smaller than the observed deviation (circles) from the original model for smaller  $N$ . This can be a consequence of the possibility of reproducing the XAS signal with a reduced set of parameters.

Therefore, this systematic series of tests performed using a calculated signal for  $\chi^E$  has shown that RMC refinement of XAS data is able to reproduce the model  $n(r)$  when using a sufficiently large ensemble of molecular replicas (e.g. at least 256 molecules). It is thus interesting to apply a similar study of convergence properties and fluctuations to real experimental XAS data.

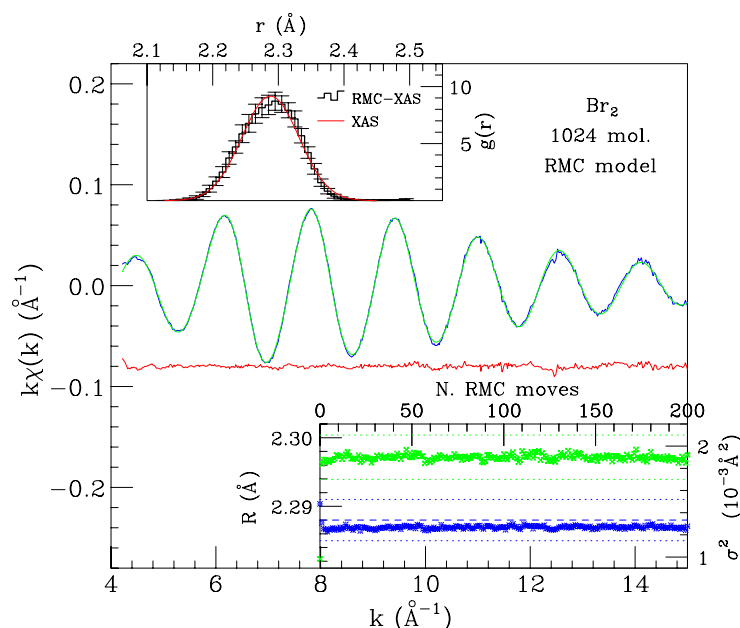


**Figure 2.** Histograms of the  $n(r)$  distributions for the RMC refinement of an XAS signal measured for gaseous bromine.  $n(r)$  distributions are associated with different RMC models obtained by increasing the number of molecules  $N$  (from top to bottom). Error bars correspond to fluctuations of the  $n(r)$  associated with equilibrium configurations. The dependence of maximal fluctuations on the number of molecules is reported in the inset.

The experimental data considered in this work are those measured at LURE, beamline D42, and published in [17]. The XAS signal has been extracted in a preliminary analysis using the `fittheo` program (GNXAS suite).

In figure 2, we show the calculated  $n(r)$  (thick histograms) for increasing number of molecules  $N$  in the RMC model. As previously discussed in reference to figure 1, the statistical fluctuations of the  $n(r)$  provide us with a measure of the accuracy in the determination of the  $n(r)$  distribution from experimental data. Maximal standard deviations (reported in the inset as a function of  $N$ ) are found to decrease for increasing  $N$  towards a limiting value. In particular, it appears from figure 2 that a nearly Gaussian shape of the  $n(r)$  distribution, compatible with previous measurements, can be obtained with a number of molecules  $N$  greater than 512.

In figure 3 we compare the raw  $k\chi^E(k)$  XAS signal with the signal  $k\chi^C(k)$  calculated in the RMC simulation for a model of 1024 molecular replicas. The experimental signal is almost perfectly reproduced, as shown by the residual curve. In the lower panel, we have reported average distance (lower curve) and variance (upper curve) for successive RMC moves of the 1024 molecular replicas. Both parameters are found to converge rapidly towards equilibrium values which are in excellent agreement with those evaluated by using the GNXAS peak-fitting procedure in the Gaussian approximation on the same data set (dashed lines) [17]. In the upper panel of figure 3 we have reported the average  $n(r)$  with the error bars (estimated from fluctuations of the equilibrium configurations) in comparison with the Gaussian distribution



**Figure 3.** Experimental XAS data ( $k\chi^E(k)$ ) compared with the RMC calculation ( $k\chi^C(k)$ ) for a model containing 1024 molecular replicas. The experimental signal is perfectly reproduced, as shown by the residual (lower curve). The RMC  $n(r)$  is shown in comparison with the Gaussian distribution measured in a previous work [17] (upper inset). Lower inset: average molecular distance  $R$  (lower curve) and distance variance  $\sigma^2$  (upper curve) calculated for the set of RMC coordinates at each simulation step. The average distance and variance evaluated using the GNXAS peak fitting procedure [17] are shown as dashed lines (error bars indicated as dotted lines).

measured in a previous work [17]. The results of the peak-fitting procedure and of the RMC refinement are clearly compatible, confirming the reliability of the approach.

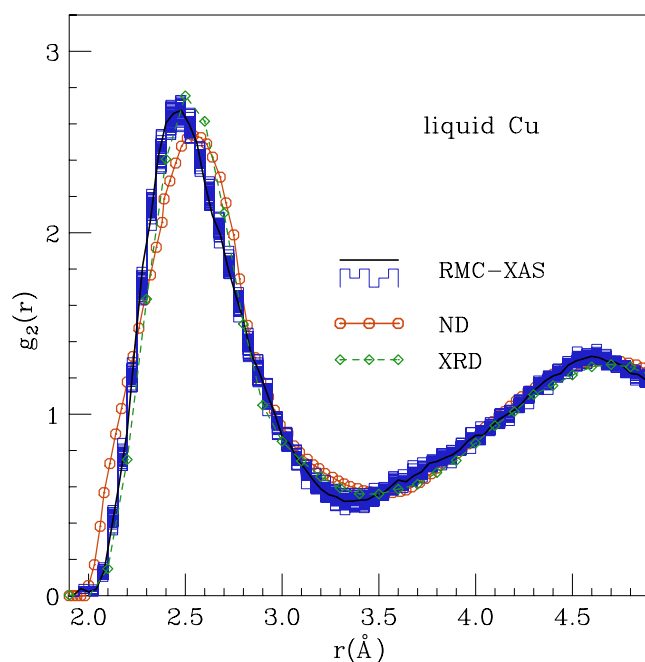
#### 4. Liquid copper

A first application of the new RMC-XAS package to condensed matter is the study of the short-range structure of liquid copper, for which full details have been reported elsewhere [19].

XAS spectra at the Cu K-edge of liquid and undercooled liquid copper were measured at the ESRF (BM29). Here we report on the results of an RMC data-analysis of XAS data of liquid copper (l-Cu) at 1398 K. The RMC simulation was performed using an 864-atom cubic box of fixed density and considering both the XAS experimental data and the published  $g_2(r)$  curve obtained by neutron diffraction (ND) [20], constraining for the long-range behaviour (see equation 2). The initial atomic configuration for the combined XAS and ND refinement was chosen to be compatible with the ND  $g_2$ .

The  $g_2(r)$  obtained by the last 400 RMC steps reproduces almost exactly those given by ND [20] and XRD [21] above about 4 Å, while the first-neighbour peak shape, measured with very high accuracy, is different. This is clearly shown in figure 4, where we report the pair distribution  $g_2(r)$  obtained during the last 200 steps (20 representative configurations) of the RMC-XAS refinement of liquid Cu. The first-neighbour peak is found to be narrower and the rise is steeper. The maximum of the first peak is shifted to shorter distances while the foot moves





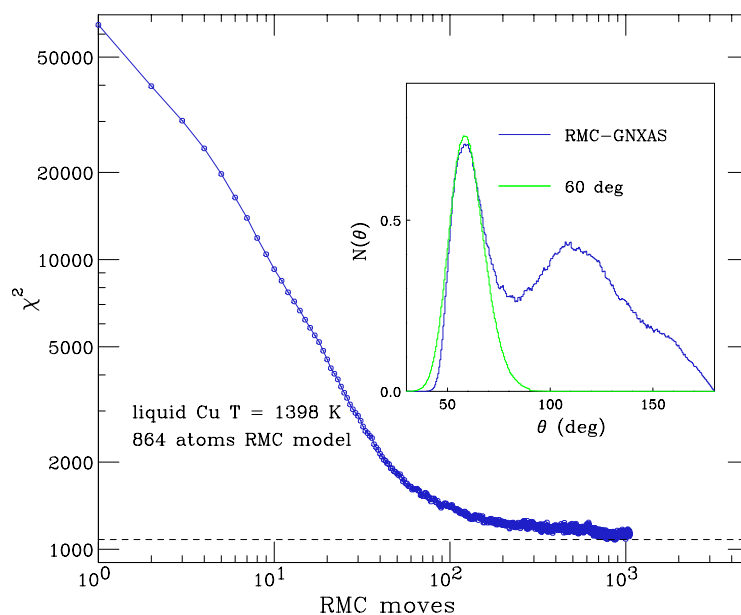
**Figure 4.** Histograms of the pair distribution  $g_2(r)$  obtained during the last 200 steps of the RMC-XAS refinement of liquid Cu. The oscillations in the  $g_2(r)$  shape for 20 representative equilibrium configurations are associated with the uncertainty of the present refinement for given experimental data and model parameters. The average  $g_2(r)$  is shown as a thick curve. The short-range shape of the  $g_2(r)$  is measured by XAS with very high accuracy.

to slightly longer distances with respect to the corresponding curve measured by ND [20]. The oscillations in the  $g_2(r)$  shape shown in figure 4 for different equilibrium configurations are associated with the uncertainty of the present refinement for given experimental data and model parameters.

The RMC refinement of liquid Cu obviously needs more steps and longer times for equilibration as compared with the  $\text{Br}_2$  molecule. Convergence of the RMC refinement to the expected  $\chi^2$  value for l-Cu is reported in figure 5. Equilibration to the expected minimum is reached after about 100–500 steps. As reported in detail in a previous publication [19], three-body effects are important in XAS spectra of liquid copper. Therefore, the local shape of the three-body distribution can be measured. The RMC bond-angle distribution shown in the inset of figure 5 is calculated by counting the number of triangular configurations per atom up to a selected limiting distance ( $R_{\text{cut}} = 2.98 \text{ \AA}$ ). The typical shape of the distribution for close-packed liquid metals contains a distinct peak around  $60^\circ$  associated with equilateral configurations and a second broad hump at about  $110^\circ$ . The three-body contribution of the equilateral configurations is found to be very important to reproduce the XAS signal. The detailed consequences of our understanding of the local structure of liquid Cu are discussed in detail elsewhere [19].

## 5. Conclusions

We have developed an XAS data-analysis program based on the RMC approach that incorporates the advanced features of the GNXAS method. In particular, simultaneous



**Figure 5.** Trend of the  $\chi^2$  residual function in liquid Cu at 1398 K. The full bond-angle  $N(\theta)$  distribution resulting from the RMC simulation is compared in the inset with that of equilateral triangles.

refinement of raw XAS and diffraction data is possible, giving realistic reconstructions of the local structure compatible with the results of both techniques. This is particularly important in disordered systems where the RMC model provides a tridimensional model compatible with the observables without the intrinsic limitations of the previous peak-fitting XAS data-analysis approach based on model functions.

The validity of the method has been put to a test on a simple molecular case ( $\text{Br}_2$ ) where the results of a standard data-analysis have been reproduced. For this simple diatomic molecule, several refinements have been performed in order to understand how the convergence properties, reliability of the calculated  $n(r)$  and statistical fluctuations depend on the number of molecular replicas used to model the system.

The application of this method to the study of the structure of liquid copper shows that realistic pair and triplet distribution functions can be measured and analysed by XAS.

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