Micro Reverse Monte Carlo Approach to EXAFS Analysis

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We have developed a new Reverse Monte Carlo code, called the micro Reverse Monte Carlo (m-RMC), which is applicable to structure analysis of nanomaterials and surface species. In the m-RMC, Reverse Monte Carlo is applied to an ensemble of replica files, each of which contains one molecule or one small cluster, because the Extended X-ray Absorption Fine Structure (EXAFS) is sensitive to short-range structures and has negligible interaction between molecules or clusters. We apply the m-RMC to face-centered cubic metals (Cu, Pd, and Pt) and discuss the advantages, validation, and problems of the m-RMC. The bond distance and some cumulant coefficients can be determined from the EXAFS using m-RMC. Some 50-100 replica files are sufficient to reproduce the EXAFS oscillations and radial distributions. The bond distance can be determined, including the asymmetric distributions, by m-RMC. We also apply m-RMC to α -MoO₃ and Au clusters. The m-RMC analysis of MoO₃ shows that three radial distribution peaks appear corresponding to three types of Mo–O bonds. The m-RMC analysis of Au cluster indicates the presence of Au₅₅ cuboctahedral structure with Au–Au distance at 0.288 nm. We obtain a 3 D image of Au₅₅ nanocluster from the unified file. The m-RMC method can be applied to the analysis of the EXAFS for chemical systems with appropriate care. [DOI: 10.1380/ejssnt.2014.322]

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I. INTRODUCTION

The Extended X-ray Absorption Fine Structure (EXAFS) is one of the most important tools for local structure analysis of nanomaterials and surface species [1]. Polarization dependent EXAFS is applied to metal species dispersed on the surface of oxide single crystal as a model supported catalyst and has provided three dimensional structures of surface metal species and the interaction between metal and surface [2].

However, the EXAFS method has several limitations. One weakness lies in the analysis of a system with an asymmetric radial distribution, which is often found in an amorphous structure [3, 4], where the coordination numbers and bond lengths are less reliable when the data are analyzed with a conventional EXAFS equation, because this assumes Gaussian or symmetric radial distribution curves.

Several methods have been proposed to treat the asymmetric atomic distribution such as cumulant expansion, regularization method and genetic algorithm [5–8]. In the cumulant expansion method [5], the EXAFS oscillation from one coordination shell is expressed as:

$$\chi(k) = S_0 \frac{N F_{\text{eff}}(k, r)}{k r^2} e^{(-2k^2 C_2 + \frac{2}{3} C_4 k^4 - \dots)} \times \sin(2kr + \phi_{\text{eff}}(k, r) - \frac{4}{3} C_3 k^3 + \dots), \quad (1)$$

where S_0 , N , r , and k are the inelastic reduction factor, coordination number, bond distance, and wave number of the photoelectron, respectively; F_{eff} and ϕ_{eff} are the effective backscattering amplitude and phase shift functions derived from theoretical calculations such as the FEFF code [9]; and C_2 , C_3 , and C_4 are the 2nd, 3rd, and 4th cumulant coefficients [5]. Here, C_2 is equal to the square of the Debye-Waller factor or the relative mean-square displacement and C_3 reflects the asymmetric distribution and is related to the thermal expansion [10]. C_4

describes the symmetric deviation from the Gaussian distribution [11]. They are directly related to anharmonic potential through path integral method [12–14]. If the EXAFS of one coordination shell with one type of coordinating element can be extracted from the total EXAFS oscillation by Fourier filtering, then the ratio method can be applied, which provides us with reliable cumulant coefficient [5, 15, 16]. However, the cumulant expansion analysis has two limitations. One is that it requires more fitting parameters than the conventional EXAFS analysis and the other is that there is no guarantee for the convergence of the cumulant expansion in a largely disordered system [4].

The other method is the reverse Monte Carlo (RMC) method [17–19]. The RMC method is used to solve an inverse problem in neutron and X-ray diffraction [17]. The EXAFS is reproduced by a large number of atoms, N , ($N = 10^2$ – 10^3) confined in a large cell with periodic boundary conditions. The N atoms are allowed to walk randomly to reduce the residual (R -factor) between the calculated and experimental EXAFS spectra in a Metropolis algorithm. After many cycles of random walks, the R -factor has negligible changes, which is identified as equilibrium in this paper. When equilibrium has been reached, we can derive the radial distribution function (RDF) and several structure parameters (r , C_2 , and C_3) from the statistical analysis of the RDF [18]. The RMC uses a three-dimensional real-space structure and, thus, the multiple scattering paths are automatically included with the assistance of an EXAFS calculation program such as FEFF [9]. The RMC is mainly applied to the EXAFS analysis of condensed matters, e.g., amorphous Si [18], liquid KPb [20], undercooled Cu [21], water [22], Li₂Fe₂O₃ [23], and Ca(Zr,Ti)O₃ solid solutions [24].

In contrast, RMC is rarely applied to discrete systems composed of molecules and small clusters, in which chemists and nanoscientists are interested. Although some examples were found in the application of the conventional RMC analysis to liquid molecular systems such as water [22, 25], a large number of independent molecules or clusters are present in a large cell, though EXAFS is mostly determined by the structure inside the components

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(molecules or clusters) and the contribution to EXAFS from the interaction between the components (molecules and clusters) is negligible. In this sense, the conventional RMC is inefficient. In this paper, we propose another RMC, called a micro reverse Monte Carlo (m-RMC), which is designed for the discrete system. The m-RMC utilizes a small file without periodic boundaries, in which only one molecule or one cluster is present, so that we completely neglect the interaction between molecules or clusters. However, one file is insufficient to represent the entire system, so many replica files are prepared. The RMC procedure is applied to each replica file while the EXAFS oscillation is calculated for each file and averaged in order to compare the calculated EXAFS oscillation with the experimental data. After the residual between the calculated and experimental values achieves equilibrium, we derive the RDF from the ensemble of replica files. Each file is expected to be a virtual model of the real molecule or cluster, which may provide us with a three-dimensional structure. The merit of m-RMC method is as follows.

- (1) The neglect of the intermolecular interaction increases the calculation speed.
- (2) We can recognize a molecule or a small cluster directly from each file.
- (3) It is easy to combine m-RMC with the local force field calculation.

The concept of m-RMC was already published by Di Cicco *et al.* [26], who applied it to molecular Br₂. However, there has been no systematic study of the m-RMC method. In this research, we apply the m-RMC method to face-centered cubic (fcc) metal foils, particularly Pd, in order to validate the method. Cu, Pd and Pt foils have advantages that we can measure good EXAFS data and can compare the results with the literature. Many physical properties of fcc metals are available in the literature, enabling us to measure the EXAFS more precisely. We would like to answer the following questions:

1. Is the m-RMC applicable to EXAFS analysis?
2. How many files are necessary to determine the structure?
3. What kind of information do we derive from the m-RMC?
4. Can each file be a virtual model structure of the real system?

In the final part, we briefly report the results on m-RMC applied to MoO₃, a highly distorted oxide and Au nanocluster.

II. 2. CALCULATION AND EXPERIMENT

A. m-RMC method and algorithm

In principle m-RMC method follows the conventional RMC procedure. In m-RMC each molecule or cluster was

divided into independent file. The initial model structure was assumed, and then the initial configurations were copied to replica files. The necessary number of replica files was discussed below. Each $\chi_{\text{cal}}^i(k)$ was calculated using an FEFF8.4 code [9] based on the atomic configuration in each replica file. Consequently multiple scattering effects are included. In the analysis of fcc metals and MoO₃ only the central atoms were regarded as X-ray absorbing atoms and the other atoms were treated as electron-scattering atoms for simplicity. In the analysis of Au₅₅ cluster, we treated all Au as absorbing atoms.

The $\chi_{\text{cal}}^i(k)$ was obtained from the initial configuration using the following equation:

$$\chi_{\text{cal}}^i(k) = S_0 \sum_j^N \frac{F_{\text{eff}}(k, r_{ij})}{kr_{ij}^2} \sin(2kr_{ij} + \phi_{\text{eff}}(k, r_{ij})),$$

$$k = \sqrt{\frac{2m}{\hbar^2}}(h\nu - E_0) \quad (2)$$

where r_{ij} is the bond distance between the j -th atoms in the i -th file. E_0 and m were the origin of photoelectron kinetic energy and mass of electron, respectively. S_0 and E_0 were obtained from the EXAFS data of the corresponding reference compounds.

The $\chi_{\text{cal}}^i(k)$ values were then averaged over all replica files to give the total $\chi_{\text{cal}}(k)$, which was then compared with $\chi_{\text{exp}}(k)$ (from experimental data). The degree of fitting was estimated by an R factor, $R^2 = (\sum[k^3\chi_{\text{exp}}(k) - k^3\chi_{\text{cal}}(k)]^2) / \sum(k^3\chi_{\text{exp}}(k))^2$, which was minimized by the m-RMC method. One atom in each replica file was chosen and then randomly walked to produce a new configuration. In order to avoid the unphysical overlap of surrounding atoms, we used a hard sphere model for each atom with radius of 0.24 nm. If the random walk caused the distance between the two atoms less than this value, the movement was automatically rejected. Otherwise a new $\chi_{\text{cal}}(k)$ was calculated using the new atomic configuration to obtain a new R factor (R_{new}). When R_{new} was smaller than the R factor before the random walk, R_{old} , the new configuration was accepted. When R_{new} was larger than R_{old} , the Metropolis algorithm was applied, i.e., the new configuration was accepted with a probability of $\exp(-(R_{\text{new}}^2 - R_{\text{old}}^2)/\tau)$, where τ is a controlling parameter to determine the accept/reject ratio.

R was normally varied by approximately 1×10^{-4} in the final optimization process, the τ factor was set at 10^{-6} because the number of replica files was typically 100. In order to avoid being trapped at the local minimum and to decrease the calculation time, τ was first set at a large value of approximately 0.01 and was then gradually decreased to obtain an accept/reject ratio nearly unity. We repeat the random walk procedure on the next atom. After 10^4 - 10^5 steps in the walk, the R factor reached equilibrium. The RDFs and cumulant coefficients from the final configurations are given by the following equations:

$$r = \langle C_1 \rangle = \langle r \rangle, \quad (3)$$

$$C_2 = \langle (r - \langle r \rangle)^2 \rangle, \quad (4)$$

$$C_3 = \langle (r - \langle r \rangle)^3 \rangle. \quad (5)$$

FIG. 1: Experimental data for $k^3\chi(k)$ (a-c) and their Fourier transforms (A-C) for Cu (a, A), Pd (b, B), and Pt (c, C).

B. EXAFS measurements

The EXAFS spectra were measured in a transmission mode at the Photon Factory (PF) of the Institute of Materials Structure Science, of the High Energy Accelerator Research Organization (KEK-IMSS-PF). The Cu K- α , Au L $_3$ - and Pt L $_3$ -edges were measured at room temperature at the beam line BL12C of the PF storage ring (2.5 GeV, 500 mA) using a Si(111) double crystal monochromator. The Mo K- and Pd K-edges were measured at beam line NW10A in the PF-AR (Photon Factory Advanced Ring) operated at 6.5 GeV, 50 mA using a Si(311) double crystal monochromator. The data were processed using REX 2000 [27–29]. Figure 1 shows the experimental data for $k^3\chi(k)$ and their Fourier transforms for Cu, Pt, and Pd. The Fourier transformation range was $30\text{--}160 \text{ nm}^{-1}$. @ MoO $_3$ was purchased from Wako Chemicals. @ Au nanoclusters were prepared according to the previously reported way to deposit Au(PPh $_3$)NO $_3$ on Fe(OH) $_3$ followed by 673 K calcination [30, 31].

III. RESULTS AND DISCUSSION

A. m-RMC results for the first shell of the Pd foil

Since EXAFS oscillation is mainly determined by the first nearest neighbor (FNN), the EXAFS oscillation of the FNN was extracted from the data via inverse Fourier transformation of the first peak in Fig. 1(B), filtered in the range of $0.16\text{--}0.31 \text{ nm}$. Since only the FNN was considered, the replica file contains thirteen atoms with one X-ray absorbing atom and 12 FNNs. The calculated

FIG. 2: (a) Comparison of $k^3\chi(k)$ calculated using m-RMC (black solid curve) and Fourier filtered data of Pd foil (red broken curve) and (b) the radial distribution curve at the equilibrium after the m-RMC steps.

FIG. 3: Conventional curve fitting results of the Pd K-edge EXAFS data. The black solid curve shows the fitted data and the red broken line shows the experimental data. (a) $C_3 = 0.0 \text{ nm}^3$, (b) $C_3 = 2.0 \times 10^{-7} \text{ nm}^3$.

$k^3\chi_{\text{cal}}(k)$ was obtained by averaging a hundred $k^3\chi_{\text{cal}}^i(k)$ values of each file. Figure 2(a) presents a comparison of the Fourier-filtered data of the experimental $k^3\chi(k)$ for Pd foil and the calculated values for $k^3\chi(k)$ (denoted as $k^3\chi_{\text{exp}}(k)$ and $k^3\chi_{\text{cal}}(k)$). The R factor at equilibrium was 0.096. Figure 2(b) shows the RDF (histogram) derived from the m-RMC results. The RDF was normalized by the number of files so that its integration was equal to the coordination number of FNNs (12). The r , C_2 , and C_3 values were $0.276 \pm 0.001 \text{ nm}$, $(6.5 \pm 1.0) \times 10^{-5} \text{ nm}^2$, and $(2 \pm 1) \times 10^{-7} \text{ nm}^3$, respectively (Table I). Figure 3a shows the conventional curve fitting analysis using Eq. (2). The R factor was 0.12. Figure 3b also shows the curve fitting result with optimized $C_3 = 2.0 \times 10^{-7} \text{ nm}^3$. The fitting was improved and the results were summarized in Table I.

The measured bond distance was 0.274 nm , a little shorter than the value obtained from the m-RMC. The contraction of the bond distance was due to the asymmetric distribution effect. The asymmetric distribution effect can be corrected by using the cumulant expansion analysis expressed in Eq. (1). In fact, we carried out curve fitting analysis including C_3 and found that $r = 0.275 \pm 0.002 \text{ nm}$, with $C_2 = (6.5 \pm 1.0) \times 10^{-5} \text{ nm}^2$ and $C_3 = (2 \pm 1) \times 10^{-7} \text{ nm}^3$. The m-RMC automatically includes the asymmetry effects.

The C_2 value of Pd could be calculated from the Debye

TABLE I: Comparison of m-RMC and curve fitting results.

Method	r (nm)	$C_2/10^{-5}$ (nm ^{2})	$C_3/10^{-7}$ (nm ^{3})	R
m-RMC 100 files	0.276 ± 0.001	6.5 ± 1.0	2 ± 1	0.096
Curve fitting w/o C_3	0.274 ± 0.002	6.9 ± 1.0	—	0.12
Curve fitting w/ C_3	0.276 ± 0.002	6.5 ± 1.0	2 ± 1	0.11

FIG. 4: The normalized radial distribution curves determined by m-RMC for Pd foil: (a) 1 file, (b) 2 files, (c) 10 files, and (d) 50 files, and (e) the corresponding R factors.

model using the Debye temperature (275 K) [32]. The value of C_2 is $6.7 \times 10^{-5} \text{ nm}^2$, which is in good agreement with the values of C_2 obtained from EXAFS.

B. Dependence on the number of files

One of the most important parameters of the m-RMC method is the number of replica files. Too small a number cannot reproduce the real distribution of atom positions. The more files that are used for the simulation, the more accurate the result will be. However, too large a number of files will increase the computing time. Therefore, an appropriate number of files must be chosen. Here, we discuss how many files are necessary and sufficient to reproduce the oscillation.

The experimental $k^3\chi_{\text{exp}}(k)$ values are obtained by inverse Fourier transformation. The Fourier transform range (Δk) and the inverse Fourier transform range (Δr) were $130 (= 160 - 30) \text{ nm}^{-1}$ and 0.15 nm , respectively so that the number of degrees of freedom [33] was $N_{\text{free}} = 2\Delta k\Delta r/\pi + 2 = 14.4$. In Eq. (2), the only adjustable parameters were r_{ij} and one file only had twelve adjustable parameters. This is less than N_{free} and not large enough to accurately reproduce the experimental data with only one file.

Figures 4(a)-(d) show the radial distribution curves derived from different numbers of replica files. Figure 4(e) shows the R factors for each number of files. As ex-

FIG. 5: EXAFS oscillations (left) and their Fourier transforms (right) of (a) Cu, (b) Pd, and (c) Pt foils. The black solid curves and the red broken curves correspond to the m-RMC data and observed data, respectively.

pected, one file was insufficient to accurately reproduce $\chi(k)$ ($R = 0.18$). In the analysis with two files, the R factor was much better ($R = 0.13$). However, looking at the RDF of the two files case shown in Fig. 4(b), the peak is rather rough and split into two, even though the average bond distance and C_2 were 0.276 nm and $6.0 \times 10^{-5} \text{ nm}^2$, respectively, corresponding well to those obtained with 100 files. Five files improved the R factor to 0.11. Ten files accurately reproduced the $\chi(k)$ and we acquire a Gaussian-like distribution curve with an R factor of 0.106. The r , C_2 , and C_3 are $0.276 \pm 0.001 \text{ nm}$, $(6 \pm 2) \times 10^{-5} \text{ nm}^2$, and $(4 \pm 3) \times 10^{-7} \text{ nm}^3$, respectively.

When we calculated $\chi(k)$ with more than ten files, we did not greatly improve the R factor (by around 0.10 or a little less). We concluded that at least ten files are necessary and 50-100 files were sufficient for the calculation of the distribution and other structure parameters in the analysis of Pd foil. The number of adjustable bond lengths was 12 times the number of files, which was between 600 (for 50 files) and 1200 (for 100 files). This number corresponds well to the number of bond lengths necessary for the reproduction of EXAFS oscillation suggested by Di Cicco *et al.* in their model mimicking the Br_2 molecule [21].

C. Cu, Pt, and Pd fcc foils

Figure 5 shows the EXAFS data of Cu, Pt, and Pd foils measured at room temperature and calculated by m-

FIG. 6: RDFs of (a) Cu, (b) Pd, and (c) Pt derived from m-RMC analyses of EXAFS measured at room temperature. The red dotted vertical lines indicate the distances given in the crystallography.

TABLE II: Cumulant parameters derived from m-RMC.

Sample	r (nm)	$C_2/10^{-5}$ (nm ²)	$C_3/10^{-7}$ (nm ³)	R
Cu	0.255 ± 0.001	9.0 ± 1.0	5 ± 3	0.18
Pd	0.276 ± 0.001	6.5 ± 1.0	2 ± 1	0.19
Pt	0.277 ± 0.001	4.8 ± 1.0	1 ± 1	0.18

RMC. The m-RMC calculations were produced based on 100 replica files with larger clusters composed of 55 atoms. The only absorbing atom was the central atom and the other 54 atoms were scatterers in this calculation. After a large number of random walks of all atoms in 100 files, the R factors were reduced to 0.18, 0.19, and 0.18, for Cu, Pd, and Pt foils, respectively, and reached equilibrium. The R factors were a little worse than the results shown above because we included four shells for the calculations in Fig. 5, while the previous calculation was conducted only on the first shell. Fitting was actually a little worse in the higher coordination shells as shown in the Fourier transformation (Fig. 5(A)-(C)).

Figure 6 shows the RDFs determined by m-RMC up to the fourth shell. The parameters in the first shell are given in Table II. The peaks derived from m-RMC agreed well with the positions calculated from the lattice constant. The Debye model provided the C_2 values as 7.8×10^{-5} , 6.7×10^{-5} , and 4.8×10^{-5} nm² for Cu, Pd, and Pt, respectively, which agreed well with the C_2 values obtained from m-RMC analysis. The C_3 values of Cu, Pd, and Pt

FIG. 7: (a) Comparison of $k^3\chi(k)$ calculated using m-RMC (black solid curve) and from experimental data (red broken curve) of MoO₃ and (b) the radial distribution curve at the equilibrium after the m-RMC steps. Black vertical bars indicated the distances in the crystallographic data. Purple RDF in the range of 0.1-0.3 nm indicated Mo-O while red RDF in the range of 0.3-0.45 nm indicated the Mo-Mo. The Mo-O interaction in this 0.3-0.45 nm was not shown here in order to simplify the figure.

could be obtained from the thermal expansion (α) using the equation [10]:

$$C_3 = 2\alpha r T C_2, \quad (6)$$

yielding 2.3×10^{-7} , 1.3×10^{-7} , and 0.7×10^{-7} nm³ for Cu, Pd, and Pt, respectively. These were found in the literature as 1.3×10^{-7} , 0.90×10^{-7} , and 1.1×10^{-7} nm³ for Cu [34], Pd [16, 35], and Pt [36], respectively, which correspond well to the values given in Table II. Consequently, the m-RMC method can reproduce the structure parameters, such as the bond distance and the C_2 and C_3 cumulants.

D. Preliminary applications to MoO₃ and Au nanoparticles

The m-RMC method was applied to the MoO₃ and Au nanoparticle. Preliminary results are presented here to discuss the future directions. First example is MoO₃. Mo oxide nanocluster and surface thin layer are catalytically important oxides for the selective oxidation reactions [37–40]. Since MoO₃ has an anisotropic structure with 5 different bond lengths at 0.167, 0.176 0.195 $\times$ 2, 0.225 and 0.233 nm [41, 42], it is difficult to determine the bond distances correctly by conventional EXAFS analysis [43], though such anisotropic structure has an important role in the selective oxidation reaction [44–46]. We carried out the m-RMC analysis on MoO₃. Figure 7(a) shows the comparison between the $k^3\chi(k)$ calculated by the m-RMC method and the observed one. The frequency of

FIG. 8: (a) Comparison of $k^3\chi(k)$ calculated using m-RMC (black solid curve) and from experimental data (red broken curve) of Au nanoparticles and (b) the radial distribution curve at the equilibrium after the m-RMC steps.

FIG. 9: The cluster image obtained from m-RMC for Au nanocluster. The all m-RMC replica files were unified to one file and all atoms were plotted. Each overlapping small balls indicated the presence of Au atoms in different replica files.

the oscillation was well reproduced. Figure 7(b) shows the radial distribution functions. The vertical bars in the figure indicated the Mo–O positions determined by the crystallography. There were three peaks appearing at the corresponding Mo–O positions to those of the crystal data in the range of 0.15–0.3 nm. The first peak was composed of two Mo–O bondings at 0.167 and 0.173 nm. It was difficult to distinguish the two Mo–O bonds owing to the finite k range ($30\text{--}140\text{ nm}^{-1}$) which gave the bond distance resolution as $0.014\text{ nm} = \pi/2\Delta k$. Thus a peak in m-RMC simulation appeared at 0.170 nm just at the average position of the two Mo–O bonds. In the present m-RMC simulation the second peak appeared at 0.197 nm shifted

from the MoO_3 crystal data by 0.002 nm. A broad peak was observed around 0.237 nm which corresponded to the long Mo–O bonds at 0.225 and 0.235 nm. The deviation in the position and broadening were due to the smaller contribution of the Mo–O bond to XAFS oscillation. Actually in the polarization dependent XAFS measurement of MoO_3 , the peak of Mo–O at 0.225 nm was less than a half of 0.173 nm peak [42, 43]. Figure 7(b) also shows the Mo–Mo radial distribution function. Three peaks appeared at 0.343 nm, 0.370 nm and 0.396 nm corresponding to the three Mo–Mo distances in MoO_3 crystal as shown in Fig. 7(b). Note that there was a broader peak at 0.370 nm than the other two Mo–Mo peaks. The direction of 0.370 nm peak corresponded to [001] in Pbnm space group which showed smallest thermal expansion and compression [47]. Further studies using polarization and temperature dependence measurement are interesting to reveal the anisotropic behavior of Mo–Mo lattice interaction.

In the next example we tested Au nanoparticles deposited on $\text{Fe}(\text{OH})_3$. Au nanoparticle drew attentions because of its high low temperature CO oxidation activity [48, 49]. We constructed Au_{55} cuboctahedron cluster since the conventional EXAFS gave the 7.7 as coordination number. Then the replica files were optimized by the m-RMC method. In this case all Au atoms in the file were regarded as x-ray absorbing atoms and EXAFS oscillations were calculated for all of them. 5×10^4 cycles of FEFF calculations were applied and the simulated curve was obtained as shown in Fig. 8(a). The radial distribution was obtained as shown in Fig. 8(b). The bond distance, coordination number and C_2 for the first shell were 0.288 nm, 7.7 and $3.1 \times 10^{-5}\text{ nm}^2$, respectively. The bond distance was almost the same as the one in the crystal. We are now developing a program by changing the number of Au atoms in each cluster during the m-RMC process to obtain the size distribution.

E. The potential of m-RMC and conclusions

In this work, we have discussed the potential of the m-RMC method by comparing the experimental and calculated EXAFS oscillations of Cu, Pd, and Pt fcc metals. We raised four questions and tried to answer them:

1. Is the m-RMC method applicable to EXAFS analysis?
The m-RMC method can be applicable to the analysis of EXAFS and can determine the bond length exactly by including the correction of the asymmetric distribution.
2. How many files are necessary to determine the structure?
At least ten files are required to reproduce the data and 50–100 files are sufficient for the full calculation in the case of Pd foil.
3. What kind of information do we derive from the m-RMC?

We obtain the RDF and:

$$r = \langle C_1 \rangle = \langle r \rangle, \quad (7)$$

$$C_2 = \langle (r - \langle r \rangle)^2 \rangle, \quad (8)$$

$$C_3 = \langle (r - \langle r \rangle)^3 \rangle. \quad (9)$$

We can of course calculate C_4 but will still have a large error compared to the absolute value of C_4 , which is very small in the fcc metal. Therefore, we have not discussed it in the above work. This might play an important role in a more disordered system.

4. Can each file be a virtual model of the real system? We cannot currently confirm this because of the following reasons.

- (1) R_i (R -factor of i -th file) is larger than R (overall R -factor determined from the m-RMC method) because there is no necessity that each $\chi_{\text{cal}}^i(k)$ should converge to the $\chi_{\text{exp}}(k)$. Actually R_i values of some replica files were more than 1 even after the over-all R was nearly 0.1. We could apply some regulation on each R_i (For example, R_i should be less than the minimum value that one replica file could achieve, namely 0.18 as shown in Sec III.B) and we had the overall R -factor nearly 0.1. However each replica file does not completely reproduce the results because of small number of atomic pair available in each file. The unification of all files would give more reasonable 3 D image with distributions. Figure 9 shows Au₅₅ nanocluster image where every site contains Au atoms in all replica files. Since each replica file has an identical structure, it is easy to find the corresponding atomic coordinates from independent files.

- (2) In the m-RMC analysis of the fcc metal discussed above where only the EXAFS oscillation from the central atom was taken into account, we got little information about bond angles because the multiple scattering effect in the EXAFS region was usually smaller than the single scattering except collinear case. This point could be improved in the analysis of Au₅₅ nanocluster where correlations of all Au atoms were included. The force field constrain will be helpful [25, 50–52]. In this work we have included hard sphere interaction to avoid unphysical overlap of atoms. Another remedy is to combine the m-RMC with the polarization dependent XAFS analysis. As mentioned in introduction, polarization dependent XAFS can be obtained from metal species on the single crystal oxide surface which determined the bond angle and 3 D structure [53–57]. The m-RMC method will provide the distributions of the bond angle.

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