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Characterization of Static Disorder by Cumulant Analysis of EXAFS: an Investigation on a Two-Gaussian Distribution

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The EXAFS of a two-Gaussian distribution is simulated. It is shown that the cumulant analysis of an EXAFS signal in the case of static disorder allows the reconstruction of the corresponding asymmetric interatomic distance distribution by the splice method. In addition, the relationships between the parameters of two Gaussians and the leading cumulants of their superposition are derived. The possibility of determining the parameters of the two Gaussians by analytical means is investigated.

Keywords: EXAFS; static disorder; Gaussian analysis.

1. Introduction

In the single-scattering approximation the EXAFS $\chi(k)$ of a given coordination shell is related to the distribution $\rho(r)$ of the absorber–backscatterer interatomic distances through the Fourier transform (characteristic function) of the effective distribution $P(r,\lambda) = \rho(r)\exp(-2r/\lambda)/r^2$:

$$k\chi(k) = S_0^2\, N\, |f(k,\pi)|\, \mathrm{Im}\left[\exp(2i\varphi) \times \int_0^\infty P(r,\lambda)\exp(2ikr)\,\mathrm{d}r\right] \quad (1)$$

where k is the photoelectron wavevector, N the coordination number, $f(k,\pi)$ the backscattering amplitude, φ the total phase shift experienced by the photoelectron, and λ the photoelectron mean free path. S_0^2 is an amplitude reduction due to the relaxation of the wavefunctions of the 'passive' electrons in the excited atom (Crozier, Rehr & Ingalls, 1988).

The shape of $\rho(r)$ and $P(r,\lambda)$ depends on the degree of thermal and static disorder. For systems with a low degree of disorder, $\rho(r)$ is a narrow Gaussian, $P(r,\lambda)$ can also be assumed to be Gaussian and the standard analysis of EXAFS (Lee, Citrin, Eisenberger & Kincaid, 1981) can be applied. However, it has long been recognized that non-Gaussian asymmetric distributions must be taken into account for a correct determination of bond lengths and coordination numbers in systems with moderate to large disorder (Eisenberger & Brown, 1979). In fact, EXAFS is naturally very sensitive to the details of the distribution due to the high values of momentum transfer, $q = 2k$, twice that of a conventional diffraction experiment.

In principle, an accurate reconstruction of $P(r,\lambda)$ [hence $\rho(r)$] should be obtained from (1) by taking the inverse Fourier transform of $k\chi(k)$. However, this is not straightforward in the analysis of an experimental EXAFS, since the single-scattering approximation limits the application of (1) to values of $k \geq 2$–3 Å^{-1} ($q \geq 4$–6 Å^{-1}). Contrary to the low q values achievable in a diffraction experiment, this means loss of information on the broad features of the distribution and on the intermediate range correlations. Typically, as in powder diffraction experiments on disordered systems or in structural characterization of metal-binding sites in protein crystallography, diffraction experiments give a description of the global structure whereas X-ray absorption spectroscopy is used to probe the details of the radial distribution function around the selected atomic species.

The limited k range, especially in the low-k region, has led to model-dependent analyses of EXAFS when the effects of disorder must be taken into account in the asymmetry of $P(r,\lambda)$: either monotonic exponentially decaying distributions (De Crescenzi *et al.*, 1981) or two-Gaussian subshell models (Sadoc, Raoux, Lagarde & Fontaine, 1982) have been utilized.

When only one atomic species is present in the coordination shell, the cumulant analysis of EXAFS allows a model-independent reconstruction of $P(r,\lambda)$ and $\rho(r)$ by recovering the low-k missing part of the EXAFS signal. The method relates to the expansion in a series of cumulants C_n around $k = 0$ of the *effective* distribution (Bunker, 1983; Dalba, Fornasini & Rocca, 1993):

$$\ln\int_0^\infty P(r,\lambda)\exp(2ikr)\mathrm{d}r = C_0 + \sum_{n=1}^{\infty}\frac{(2ik)^n}{n!}C_n. \quad (2)$$

The zero-order cumulant, C_0, depends on the normalization of $P(r,\lambda)$. The first cumulant, C_1, is the mean value and the second cumulant, C_2, is the variance (mean-square relative displacement, MSRD) of $P(r,\lambda)$. The cumulants of order higher than two measure the deviation from a Gaussian shape: they are zero for Gaussian distributions

of $P(r,\lambda)$.

Even and odd cumulants contribute separately to the amplitude and phase of the EXAFS signal, respectively. In fact, the EXAFS function of one coordination shell [equation (1)] can be written as

$$k\chi(k) = A(k)\sin\Phi(k) \tag{3}$$

where, from (2), the phase $\Phi(k)$ and the amplitude $A(k)$ are given by:

$$\Phi(k) = 2kC_1 - \frac{4}{3}C_3k^3 + \frac{8}{15}C_5k^5 + \ldots + \varphi(k) \tag{4a}$$

$$A(k) = S_0^2\, N\, |f(k,\pi)|\exp(C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 + \ldots). \tag{4b}$$

In principle, the cumulants C_n of the effective distribution of an unknown sample can be estimated by comparison with a reference compound from a best fit to the phase difference and the logarithm of amplitude ratio (the so-called 'ratio method') through the following expressions (Bunker, 1983; Crozier, Rehr & Ingalls, 1988; Dalba, Fornasini & Rocca 1993):

$$\Phi_s(k) - \Phi_r(k) = 2k\Delta C_1 - \frac{4}{3}k^3\Delta C_3 + \frac{8}{15}k^5\Delta C_5 + \ldots \tag{5a}$$

$$\ln\frac{A_s(k)}{A_r(k)} = \ln\frac{N_s}{N_r} + \Delta C_0 - 2k^2\Delta C_2 + \frac{2}{3}k^4\Delta C_4 + \ldots \tag{5b}$$

where $\Delta C_n = C_n^s - C_n^r$ and s and r label the sample and the reference compound, respectively. In (5*b*), ΔC_0 is often negligible.

Since the cumulant expansion (2) is a series expansion around $k = 0$, it will diverge at high k depending on the degree of disorder, *i.e.* on the shape of $\rho(r)$ and $P(r,\lambda)$. Actually, the phase and amplitude analysis of an experimental EXAFS signal yields a limited number of polynomial coefficients (typically two from the phases and two from the amplitudes), which will correspond to the cumulants C_n only if the cumulant series is rapidly convergent. In the case of thermal disorder, the convergence of the cumulant series can be evaluated from the temperature dependence of the cumulants (Dalba, Fornasini & Rocca, 1993; Dalba, Fornasini, Gotter & Rocca, 1995).

For systems with low to moderate disorder, the fitted C_n can be directly used to reconstruct $P(r,\lambda)$ by inverting (1). The real distribution, $\rho(r)$, can then be recovered if the photoelectron mean free path, λ, is given (Dalba, Fornasini & Rocca, 1993; Stern, Ma, Hanske-Petitpierre & Bouldin, 1992).

In systems with large disorder, the cumulant series converges only at low k values and cannot be simply inverted to give $P(r,\lambda)$. For such cases the 'splice' method has been proposed (Crozier, Rehr & Ingalls, 1988; Dalba, Fornasini, Grazioli, Gotter & Rocca, 1995; Stern, Ma, Hanske-Petitpierre & Bouldin, 1992): the cumulant expansion is used to extrapolate $k\chi(k)$ to $k = 0$ while the actual filtered experimental EXAFS is used in the high-k region.

The aim of this work is to give an insight into the potentialities of the cumulant analysis of EXAFS in the presence of static disorder. The simplest and physically interesting cases are two close-lying shells that cannot be resolved by Fourier transform techniques. In fact, two Gaussian subshells are often utilized to model asymmetric distributions of absorber–backscatterer distances as in distorted octahedral sites [*e.g.* NiO_6 octahedra in $LiNiO_2$ (Rougier, Chadwick & Delmas, 1994)] and metal–metal or metal–metalloid distances in metallic glasses [*e.g.* Cu_xZr_{1-x} (Sadoc & Lasjaunias, 1985); Fe_xZr_{1-x} (Sadoc & Chouteau, 1988); CoP (Lagarde, Rivory & Vlaic, 1983)]. In this respect, it has also been pointed out (Lagarde, Rivory & Vlaic, 1983) that although the overall distribution is the really important factor to be determined, whenever the existence of two different bonds around the absorbing species can be reasonably assumed, a detailed characterization of the two underlying subshells seems more appealing from the point of view of the structural interpretation.

Therefore, we will simulate the EXAFS signal of a reasonable two-Gaussian distribution and verify whether the cumulant analysis and the splice method can yield an adequate model-independent reconstruction. Moreover, we will derive the relationships between the parameters of two Gaussians and the leading cumulants of their superposition and investigate the possibility of developing reliable models of static disorder by analytical means.

2. Study of a two-Gaussian distribution

2.1. *EXAFS analysis and reconstruction of the interatomic distance distribution*

To work on a realistic two-Gaussian sample distribution, we chose the model Ni pair distribution function around Ni atoms (two Ni atoms at 2.40 Å with $\sigma = 0.08$ Å, and four Ni atoms at 2.55 Å, with $\sigma = 0.12$ Å), reported by Sadoc, Raoux, Lagarde & Fontaine (1982) as the best fit to the EXAFS of the Ni_2Y glassy alloy at the Ni K edge (Fig. 1*a*). The first five cumulants of both the real and the effective distribution, with $\lambda = 7$ Å, have been calculated (Table 1). The EXAFS has been simulated in the range k = 2–15 Å^{-1}. The application of the ratio method requires that the EXAFS of a harmonic reference compound which satisfies phase and amplitude transferability is also measured. Therefore, in order to simulate the analysis of an experimental EXAFS, a reference $\chi(k)$ has been created from a physically reasonable narrow Gaussian centred at $R = 2.5$ Å with $\sigma = 0.05$ Å and normalized to $N = 6$. Both the sample and the reference $k\chi(k)$ were Fourier-transformed using a Gaussian window. The respective main peaks in the r space were isolated and backtransformed in the momentum space. The phase difference and the logarithm of amplitude ratio are plotted in Fig. 2 *versus* k and k^2, respectively (full

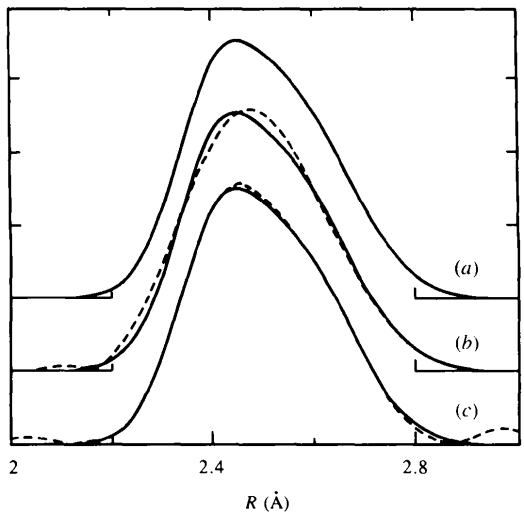

Figure 1
(*a*) The two-Gaussian distribution reported by Sadoc, Raoux, Lagarde & Fontaine (1982): two atoms at 2.40 Å with σ = 0.08 Å and four atoms at 2.55 Å with σ = 0.12 Å. (*b*) The distribution as reconstructed from the first five 'experimental' cumulants without splicing to the filtered simulated $k\chi(k)$ (dashed line). The original two-Gaussian distribution is also reported for comparison (full line). (*c*) The distribution as reconstructed from the first four 'experimental' cumulants by splicing to the filtered simulated $k\chi(k)$ (dashed line). The original two-Gaussian distribution is also reported for comparison (full line).

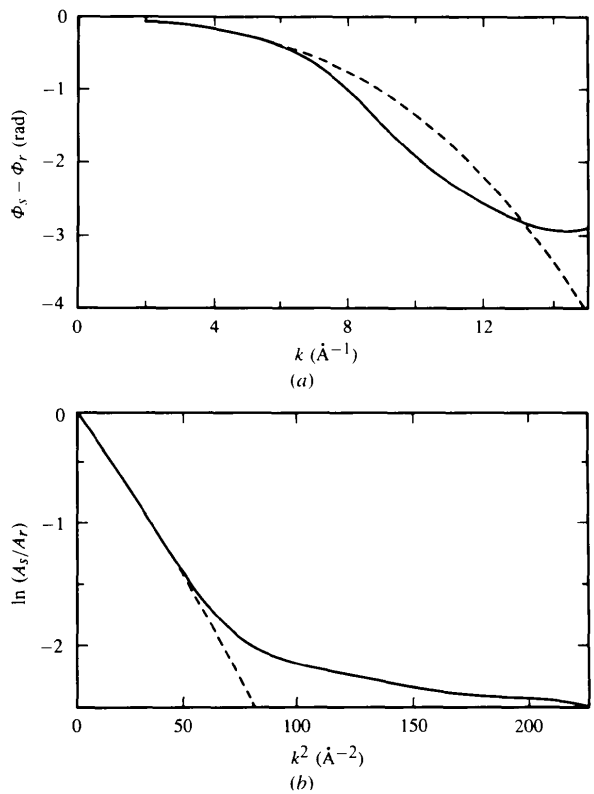

Figure 2
(*a*) Sample (Φ_s) and reference (Φ_r) phase difference as a function of k (full line). The dashed line is the fitting curve in the range k = 2–6 Å^{-1}. (*b*) Logarithm of the sample (A_s) and reference (A_r) amplitude ratio as a function of k^2 (full line). The dashed line is the fitting curve in the range k = 2–7 Å^{-1}.

Table 1
The first five cumulants of both the real and the effective distribution and the 'experimental' cumulants.

A: Cumulants of the real two-Gaussian model distribution; *B*: cumulants of the effective two-Gaussian model distribution; *C*: 'experimental' cumulants as determined from the polynomial fit to the phase difference (without C_5) and the logarithm of amplitude ratio; *D*: odd 'experimental' cumulants as determined from the polynomial fit to the phase difference with C_5.

Cumulant	*A*	*B*	*C*	*D*
C_1 (Å)	2.50	2.48	2.48	2.48
C_2 (Å^2)	1.67×10^{-2}	1.62×10^{-2}	1.6×10^{-2}	
C_3 (Å^3)	5.5×10^{-4}	6.2×10^{-4}	8×10^{-4}	5×10^{-4}
C_4 (Å^4)	-7.5×10^{-5}	-5.1×10^{-5}	-8×10^{-5}	
C_5 (Å^5)	-2.13×10^{-5}	-2.34×10^{-5}		-2×10^{-5}

lines). The beating expected at $(\pi/2)(\Delta R)^{-1}$ = 10.5 Å^{-1}, where ΔR is the difference between the mean values of the two Gaussians underlying the sample model distribution, is clearly visible. Conversely, a rough estimate of the inter-shell separation, ΔR, can be obtained from the position of the minimum in the amplitude ratio and that of the inflection point in the phase difference (Bunker, 1983), but this is not so relevant as soon as we are interested in a detailed reconstruction of the overall radial distribution $\rho(r)$.

The phase and amplitude analysis was made through equations (5*a*) and (5*b*) truncated at the third-order and fourth-order term, respectively. A reasonable fit to the phase difference and logarithm of amplitude ratio curves can be made in a range $k_{min} - k_{max}$, with k_{min} = 2 Å^{-1} and k_{max} well below the beating (Fig. 2, dashed lines), and allows ΔC_1, ΔC_2, ΔC_3 and ΔC_4 of the two-Gaussian effective distribution to be estimated relative to the narrow-Gaussian effective distribution. In particular, good fits were obtained by keeping $k_{max} \leq 7$ Å^{-1} in the amplitude fitting and $k_{max} \leq 6$ Å^{-1} in the phase fitting. Actually, in this simulation, a reasonable phase fit could also be obtained by extending the range to k_{max} = 9 Å^{-1} and increasing the number of the fitting parameters up to the fifth cumulant. In this way, the two-Gaussian distribution C_5 could also be estimated and a lower value of C_3 was obtained (Table 1).

The absolute values of the cumulants C_n of the sample effective distribution were determined by following, for the reference distribution, the common assumption that the differences between the cumulants of order higher than one of the real and of the effective distribution are negligible. Hence, C_1 has been evaluated by adding ΔC_1 to the mean value of the *effective* reference distribution, while C_2 has been evaluated by adding ΔC_2 to the variance of the *real* reference distribution. As regards C_3 and C_4, since the cumulants of order higher than two of the reference Gaussian distribution are zero, $C_3 = \Delta C_3$ and $C_4 = \Delta C_4$. It must be noted that in this simulation the variance of the reference distribution is known, while in the experimental cases it has to be evaluated from temperature-dependent measurements and fit to vibrational dynamics models (Dalba, Fornasini & Rocca, 1993). The absolute val-

ues of the cumulants obtained from the simulated analysis ('experimental' cumulants) are reported in Table 1 together with those calculated from the original distribution: they are a good estimate of the order of magnitude of the correct cumulants.

Nonetheless, a bad reconstruction of $\rho(r)$ (Fig. 1*b*) is obtained from the Fourier transform of the characteristic function of $P(r,\lambda)$ as determined directly from the cumulant expansion (2), using either the 'experimental' cumulants (Fig. 3, full line) or the original ones, with or without C_5. This means that the cumulant expansion is correct only for k values well below the beating and cannot interpret the high-k part of the EXAFS signal, as expected.

The 'splice' method overcomes this problem by using the cumulant expansion in the low-k missing part of the experimental signal while the actual filtered experimental EXAFS is retained in the high-k part. To this aim, a suitable $k\chi(k)$ (for $2 < k < 15\,\text{Å}^{-1}$ in the present simulation) has to be recovered (Fig. 3, dashed line) from the Fourier filtered signal and after extraction of the reference EXAFS phase shift $[\varphi(k)]$ and amplitude $[S_0^2\,|f(k,\pi)|]$: this also ensures that windowing effects are compensated for, provided that the sample and the reference are analyzed in the same way. Then, an adequate splice interval $k_{\min} - k_{\max}$ has to be chosen within the experimental k range. The final $k\chi(k)$ is obtained by taking the cumulant expansion for $0 < k < k_{\min}$ and the filtered experimental $k\chi(k)$ for $k > k_{\max}$, while a weighted linear combination of them is used in the intermediate range $k_{\min} < k < k_{\max}$ to join the low-k and the high-k part.

In our case, as a first step, only the first four cumulants have been considered. As regards the optimization of the splice range $k_{\min} - k_{\max}$, an accurate reconstruction of $\rho(r)$, with a small residual difference with respect to the original distribution, has been obtained by taking $k_{\min} = 2.5\,\text{Å}^{-1}$ and $k_{\max} = 6.5\,\text{Å}^{-1}$, that is near the corresponding lower and upper limits of the phase and amplitude fitting intervals (Fig. 1*c*). The same $\rho(r)$ is obtained if the cumulants of the effective original sample distribution are used instead of the 'experimental' ones. This means that the small residual difference between the reconstructed $\rho(r)$ and the original is not due so much to a poor determination of the cumulants C_3 and C_4 as to an unavoidable inaccuracy in the recovered $k\chi(k)$. Moreover, the same $\rho(r)$ is also found if the fifth cumulant C_5 is added in the low-k cumulant expansion.

The above discussion shows that in the case of static disorder the cumulant analysis can yield an adequate model-independent determination of the interatomic distance distribution, provided that the low-k cumulant expansion is 'spliced' to the high-k part of the experimental EXAFS.

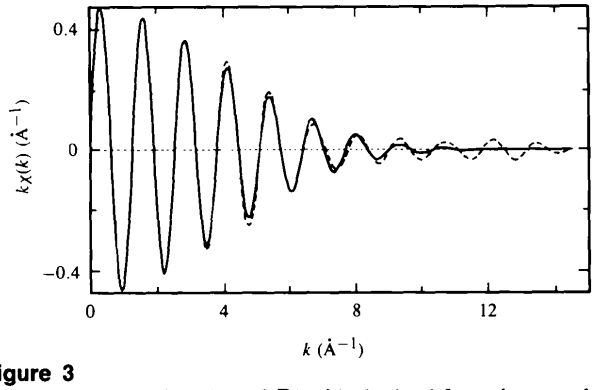

Figure 3
The characteristic function of $P(r,\lambda)$ obtained from the cumulant expansion using the first four 'experimental' cumulants as determined from the phase and amplitude analysis (full line) and $k\chi(k)$, simulated from the two-Gaussian model distribution after the Fourier filtering procedure and the phase and amplitude extraction (dashed line).

2.2. *Analytical determination of the parameters of two Gaussians from the leading cumulants of their superposition*

The next step is to investigate whether the parameters of the two underlying Gaussians may be analytically determined from the knowledge of the leading cumulants of the distribution.

First of all, the relations between mean values (R_1 and R_2), variances ($v_1 = \sigma_1^2$ and $v_2 = \sigma_2^2$) and normalization constants (N_1 and N_2) of two Gaussians and the first five cumulants C_1, C_2, C_3, C_4 and C_5 of their superposition will be derived. In fact, since the total coordination number ($N = N_1 + N_2$) is known from the amplitude analysis, five equations are needed for five unknowns (*e.g.* N_1, R_1, R_2, v_1 and v_2).

If $\rho(r)$, $\rho_1(r)$ and $\rho_2(r)$ are three distributions normalized to unity, such that $\rho(r)$ is a linear combination of $\rho_1(r)$ and $\rho_2(r)$,

$$\rho(r) = (N_1/N)\rho_1(r) + (N_2/N)\rho_2(r), \tag{6}$$

from the series expansion of their characteristic functions, it follows that the same relation as (6) holds for the corresponding ith-order moments, m_i, $m_i^{(1)}$ and $m_i^{(2)}$:

$$m_i = (N_1/N)m_i^{(1)} + (N_2/N)m_i^{(2)} \tag{7}$$

where $m_i = \langle r^i \rangle$.

Now, under the hypothesis that $\rho_1(r)$ and $\rho_2(r)$ are Gaussians, by expressing the moments of the two Gaussians as functions of their mean values and variances and utilizing the relationships between the cumulants and the moments of a distribution (Guedenko, 1976; Cramer, 1966), the following equations can be derived:

$$C_1 = \frac{N_1}{N}R_1 + \frac{N_2}{N}R_2 \tag{8a}$$

$$C_2 = \frac{N_1}{N}v_1 + \frac{N_2}{N}v_2 + \frac{N_1N_2}{N^2}(R_1 - R_2)^2 \tag{8b}$$

$$C_3 = 3\frac{N_1N_2}{N^2}(R_1 - R_2)(v_1 - v_2) + \frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)(R_1 - R_2)^3 \tag{8c}$$

$$C_4 = 3\frac{N_1N_2}{N^2}(v_1 - v_2)^2 + 6\frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)(R_1 - R_2)^2(v_1 - v_2) + \frac{N_1N_2}{N^2}\left(1 - 6\frac{N_1}{N}\frac{N_2}{N}\right)(R_1 - R_2)^4 \qquad (8d)$$

$$C_5 = 15\frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)(v_1 - v_2)^2(R_1 - R_2) + 10\frac{N_1N_2}{N^2}\left(1 - 6\frac{N_1}{N}\frac{N_2}{N}\right)(v_1 - v_2)(R_1 - R_2)^3 + \frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)\left(1 - 12\frac{N_1}{N}\frac{N_2}{N}\right)(R_1 - R_2)^5 \qquad (8e)$$

As a matter of fact, the same expressions for C_2 and C_4 are obtained directly from a Taylor-series expansion around $k = 0$ of the natural logarithm of the amplitude modulus of the Fourier transform of the sum of two Gaussians in r space, as suggested by Crozier, Rehr & Ingalls (1988). It can be noted that C_3, C_4 and C_5 depend only on the differences $(R_1 - R_2)$ and $(v_1 - v_2)$, while the absolute mean values and variances enter the equations for C_1 and C_2, respectively.

From a mathematical point of view, if the first five cumulants C_n of a distribution $\rho(r)$ are known, (8) can be utilized to determine two Gaussians whose superposition has the same C_n as leading cumulants. By deriving $(v_1 - v_2)$ from (8*c*) and substituting it into (8*d*) and (8*e*), a system of two non-linear equations, depending only on C_3, C_4 and C_5 and not on C_1 and C_2, is found, with two unknowns, N_1/N and $(R_1 - R_2)$:

$$-2\left(\frac{N_1N_2}{N^2}\right)^2\left(1 - \frac{N_1N_2}{N^2}\right)(R_1 - R_2)^6 + 4\frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)C_3(R_1 - R_2)^3 - 3\frac{N_1N_2}{N^2}C_4(R_1 - R_2)^2 + (C_3)^2 = 0, \qquad (9a)$$

$$\frac{N_1N_2}{N^2}\left(\frac{N_2}{N} - \frac{N_1}{N}\right)\left(8 - 6\frac{N_1N_2}{N^2}\right)(R_1 - R_2)^5 - 20\left(1 - 3\frac{N_1N_2}{N^2}\right)C_3(R_1 - R_2)^2 + 15C_4\left(\frac{N_2}{N} - \frac{N_1}{N}\right)(R_1 - R_2) - 3C_5 = 0. \qquad (9b)$$

From symmetry considerations, the solutions of (9) that we are interested in are those with $0 < N_1/N \leq 0.5$. For each real solution of the system (9), *i.e.* for each pair of values of N_1/N and $(R_1 - R_2)$, the difference $(v_1 - v_2)$ can be determined from (8*c*). Then, v_1 and v_2 can be separately obtained from (8*b*). The obvious requirement that $v_1 > 0$ and $v_2 > 0$ in (8*b*) implies that only the solutions which satisfy the following relations can be retained:

$$\frac{N_1}{N}(v_1 - v_2) + \frac{N_1N_2}{N^2}(R_1 - R_2)^2 < C_2 \qquad (10a)$$

$$\frac{N_2}{N}(v_2 - v_1) + \frac{N_1N_2}{N^2}(R_1 - R_2)^2 < C_2. \qquad (10b)$$

Finally, R_1 and R_2 can be determined from (8*a*).

In principle, we may find one or more sets of values (N_1, R_1, σ_1; N_2, R_2, σ_2), or none. No solution means that no pair of Gaussians exists whose superposition has the same first five cumulants as $\rho(r)$. It would then be concluded that $\rho(r)$ cannot be considered as the sum of two Gaussians.

On the other hand, finding one or more pairs of Gaussians that give the same five leading cumulants as $\rho(r)$ would not necessarily imply that it or each one really reproduces $\rho(r)$: this should be verified by comparing the distributions.

Let us apply the above discussion to the original cumulants of the sample model distribution. Finding out the parameters of the two exact original underlying Gaussians requires, first of all, an accurate determination of N_1/N and $(R_1 - R_2)$ from (9), and $(v_1 - v_2)$ from (8*c*), which, in turn, depends on the accuracy of C_3, C_4 and C_5. If only one significant figure is retained in C_3, C_4 and C_5, the corresponding pair of Gaussians ($N_1 = 2.6$, $R_1 = 2.41$ Å,

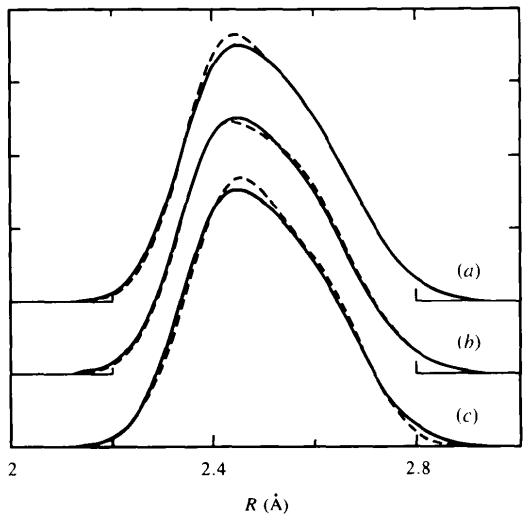

Figure 4
(*a*) Superposition of the two Gaussians as determined from the first five cumulants of the original distribution when only one significant figure is retained in C_3, C_4 and C_5 (dashed line). The original distribution is also shown for comparison. (*b*) The two different pairs of Gaussians as determined from the first five exact cumulants when two non-zero digits are retained in C_3 and C_4 and three in C_5: the fully reproduced original (full line) and the other (dashed line). (*c*) Superposition of the two Gaussians obtained from the first five cumulants directly calculated from the distribution as reconstructed by the splice method (dashed line). The original distribution is also shown for comparison (full line).

$\sigma_1 = 0.08$ Å, and $N_2 = 3.4$, $R_2 = 2.57$ Å, $\sigma_2 = 0.11$ Å) is not the original one, nor is the model distribution exactly reproduced (Fig. 4*a*). Indeed, the correct parameters are found if at least one more significant digit is retained in C_3 and C_4 and two more in C_5. Moreover, in this case, (8) and (9) also give another solution: a different pair of Gaussians ($N_1 = 1.5$, $R_1 = 2.39$ Å, $\sigma_1 = 0.071$ Å, and $N_2 = 4.5$, $R_2 = 2.536$ Å, $\sigma_2 = 0.124$ Å) whose superposition has the same first five cumulants but is slightly different from the original one (Fig. 4*b*).

3. Application to the cumulant analysis of experimental EXAFS

The aim of the analysis of an experimental EXAFS is to gain information about the local structure around the selected atomic species. In systems affected by static disorder, the shape of the absorber–backscatterer interatomic distance distribution, $\rho(r)$, cannot be *a priori* assumed to be Gaussian. In these cases, the cumulant analysis should allow, in principle, not only a reliable evaluation of the absorber–backscatterer interatomic mean distance and coordination number, but also a model-independent reconstruction of $\rho(r)$.

The present simulation has shown that, even in the case of static disorder, the phase difference and logarithm of amplitude ratio analysis can yield a good estimate of the first four, even five, cumulants of the original distribution, and that the original distribution itself can be adequately reconstructed. This is a non-trivial result: the radial distribution function obtained can be directly compared with theoretical models, such as molecular dynamics calculations, or inserted as input in reverse Monte Carlo calculations.

In some cases, when the existence of two different bonds around the absorbing species can be reasonably assumed, it would also be interesting to obtain an indication of their relative weights, bond lengths and MSRD. In this respect, the present simulation has shown that (8) and (9) allow the analytical determination of the exact two Gaussians underlying $\rho(r)$ provided that the first five cumulants of the *real* distribution are known with high accuracy. Otherwise stated, while the reconstructed $\rho(r)$ seems not to be very sensitive to the uncertainties in the cumulants from which the low-k missing part of the $k\chi(k)$ is recovered, the analytical determination of the parameters of the two Gaussians underlying $\rho(r)$ strongly depends on the accuracy in the values of the cumulants used to solve (8) and (9).

This result suggests that, when one is faced with the analysis of an experimental EXAFS, the best choice would be to solve (8) and (9) using the cumulants directly calculated from the reconstructed $\rho(r)$. In this case, problems may arise from the unavoidable side ripples which appear in the reconstruction and prevent an accurate determination of the cumulants. As an example, in the present simulation the cumulants of the reconstructed $\rho(r)$ were calculated by truncating $\rho(r)$ (Fig. 1*c*) at $R = 2.11$ and 2.87 Å. The pair of Gaussians found ($N_1 = 4$, $R_1 = 2.44$ Å, $\sigma_1 = 0.093$ Å, and $N_2 = 2$, $R_2 = 2.62$ Å, $\sigma_2 = 0.086$ Å), which is not the correct one, does not reproduce even the reconstructed $\rho(r)$ (Fig. 4*c*).

However, one could try to obtain some reliable indication about the characteristics of the two underlying bonds from the cumulants of the *effective* distribution directly obtained from the phase and amplitude analysis. Indeed, when the 'experimental' cumulants reported in Table 1 are utilized in equations (8) and (9), a pair of Gaussians is found whose superposition is very similar to the original, and whose parameters ($N_1 = 2.3$, $R_1 = 2.40$ Å, $\sigma_1 = 0.08$ Å, and $N_2 = 3.7$, $R_2 = 2.56$ Å, $\sigma_2 = 0.11$ Å) are well inside the error bars ($\Delta N = 0.5$, $\Delta R = 0.02$ Å) determined by Sadoc, Raoux, Lagarde & Fontaine (1982) from their best-fitting analysis on the Ni_2Y glassy alloy.

It must be noted, however, that in the present simulation the 'experimental' cumulants differ from the original cumulants of the model distribution at most only within ±10%, while in the analysis of an experimental EXAFS lower accuracies have to be expected. As an example, if we use a reasonably different value of C_3, $C_3 = 0.0004$ Å^3 instead of $C_3 = 0.0005$ Å^3, the corresponding pair of Gaussians ($N_1 = 3.6$, $R_1 = 2.43$ Å, $\sigma_1 = 0.092$ Å, and $N_2 = 2.4$, $R_2 = 2.6$ Å, $\sigma_2 = 0.099$ Å) is no more near to the correct one.

These results indicate that, as regards the analysis of an experimental EXAFS, when there are reasons for assuming the existence of two different bonds around the absorbing species, a reliable analytical determination of the parameters of the two corresponding Gaussians will not be possible, even though the cumulant analysis can yield a good reconstruction of the overall distribution.

4. Conclusions

The potentialities of the cumulant analysis of EXAFS in the case of static disorder have been investigated by simulating the EXAFS of a two-Gaussian distribution, $\rho(r)$.

It has been shown that the 'ratio method' allows the first four, even five, leading cumulants of the effective distribution, $P(r, \lambda)$, to be estimated by fitting the phase difference and the logarithm of amplitude ratio in the low-k region. Using these values, the low-k missing part of the experimental EXAFS signal can be recovered and by 'splicing' to the high-k part, a reliable model-independent reconstruction of $\rho(r)$ can be obtained once the mean free path, λ, of the photoelectron is given.

Moreover, the relationships between the parameters of two Gaussians and the first five cumulants of their superposition have been derived. In principle, the knowledge of the leading first five cumulants of the distribution would allow the two underlying Gaussians to be determined through (8) and (9). However, this analytical determination

strongly depends on the accuracy of the values of the cumulants used to solve (8) and (9). As regards the analysis of an experimental EXAFS, the present simulation has shown that an accurate determination of the leading first five cumulants of the reconstructed distribution is prevented due to unavoidable side lobes; on the other hand, the cumulants estimated from the phase and amplitude analysis cannot be confidently utilized due to uncertainties of the data-analysis procedure.

It can then be concluded that a careful analysis of an experimental EXAFS in case of static disorder can yield a reliable model-independent reconstruction of the absorber–backscatterer interatomic distance distribution, together with a good estimate of the leading cumulants of the distribution. However, when the existence of two different bonds around the absorbing species may be reasonably assumed, it does not seem possible to obtain a reliable indication about the parameters of the two corresponding underlying Gaussians by analytical means.

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