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The determination of the single-scattering line profile from the observed spectrum

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Abstract. An analysis is given for the calculation of the single-scattering profile $S_1(x, y, z, \dots)$ from the observed spectrum $I(x, y, z, \dots)$, when $I(x, y, z, \dots)$ contains contributions from plural-scattering events. No assumptions are made concerning the line shape for $S_1(x, y, z, \dots)$, but a value for the unscattered intensity is required. Further, the analysis given requires that all the scattered intensity is collected, so that Poisson statistics are applicable to the scattering processes occurring in the specimen. The solution for $S_1(x, y, z, \dots)$ is then given as a series in $I(x, y, z, \dots)$, with appropriate weighting coefficients. The spectrum $I(x, y, z, \dots)$ must be corrected for the finite resolution of the spectrometer, before a solution can be obtained for $S_1(x, y, z, \dots)$. Computational tests and the limitations of the present analysis are given.

1. Introduction

Frequently the observed spectrum $I(x, y, z, \dots)$ obtained in an experiment is not suited to a direct comparison with a theoretical model. The ideal spectrum for comparison with theory is the distribution $S_1(x, y, z, \dots)$ that results after a single-scattering event, but in practice this is modified by subsequent scattering events within the specimen and one obtains instead the compound spectrum $S(x, y, z, \dots)$, which is the sum of 1, 2, 3, ..., m scattering events, i.e.

$$S(x, y, z, \dots) = \sum_{n=1}^{n=m} a_n S_n(x, y, z, \dots) \quad (1)$$

where

$$S_n(x, y, z, \dots) = \int_{-\infty}^{+\infty} S_1(x', y', z', \dots) S_{n-1}(x-x', y-y', z-z', \dots) dx' dy' dz' \dots$$

and a_n are normalizing constants which depend on the statistics of the scattering processes occurring within the specimen.

Equation (1) has been written in terms of a general multi-dimensional coordinate system (x, y, z, \dots) , for mathematical reasons only. In practice, the one-dimensional form of equation (1) is most frequently encountered in spectroscopy, but occasionally the two-dimensional form of equation (1) is appropriate in describing the scattering processes within the specimen, for example the measurement of the angular and energy coordinates of electrons which have been inelastically scattered in thin films.

Further, $S(x, y, z, \dots)$ may be modified by the finite resolution $M(x, y, z, \dots)$ of the spectrometer according to the convolution integral, to give the measured curve $I(x, y, z, \dots)$, i.e.

$$I(x, y, z, \dots) = \int_{-\infty}^{+\infty} S(x', y', z', \dots) M(x-x', y-y', z-z', \dots) dx' dy' dz' \dots \quad (2)$$

where $M(x, y, z, \dots)$ is normalized such that

$$\int_{-\infty}^{+\infty} M(x, y, z, \dots) dx dy dz \dots = 1.$$

Solutions of equation (2) for $S(x, y, z, \dots)$ in one dimension are well known (e.g. Jones and Misell 1967, Moore 1968, Ergun 1968, Hossfeld 1968), and in two dimensions the solution for $S(x, y, z, \dots)$, although a more difficult problem than the one-dimensional case may be solved by an iteration procedure (e.g. Burr 1966, Ergun 1968). The effect of not correcting $I(x, y, z, \dots)$ for resolution effects is that, in the present analysis, we would calculate a single-scattering curve which bears no simple relation to the required curve $S_1(x, y, z, \dots)$.

For simplicity in the present paper we shall consider only the one-dimensional solution of equation (1), but the method of calculation of $S_1(x, y, z, \dots)$ for the general multi-dimensional problem is similar and will be limited only by the computing facilities available. In particular, we shall consider the problem of the energy losses of fast electrons in thin films, where we have

$$S(E) = \sum_{n=1}^{n=m} a_n S_n(E) \quad (3)$$

with

$$S_n(E) = \int_{-\infty}^{+\infty} S_1(E-E') S_{n-1}(E') dE'$$

provided that we define $S_1(E) = 0$ for $E \leq 0$, i.e. the incident electron may only lose energy on being scattered in the specimen film.

If we consider an $S_1(E)$ which is composed of only a single loss distribution, then, provided that all scattered electrons are collected, it may be shown that (Burge and Misell 1968)

$$S(E) = \sum_{n=1}^{n=m} \left(\frac{t}{\lambda I_s} \right)^{n-1} \frac{S_n(E)}{n!} \quad (4)$$

where t is the specimen thickness, λ the mean free path for the scattering process and

$$I_s = \int_{-\infty}^{+\infty} S_1(E) dE.$$

The procedure of Burge and Misell (1968) was then to assume some profile for $S_1(E)$ defined by a set of unknown parameters and to curve-fit, by a least-squares method, the equation (4) to the experimental curve, when it was then possible to determine the parameters defining $S_1(E)$ and t/λ . However, there are a number of objections to this type of procedure, which, in particular, prevent the application of equation (4) to determine an $S_1(E)$ composed of several types of scattering processes:

(i) The assumption of a model for $S_1(E)$. Each scattering process in $S_1(E)$ is represented by an analytic curve, the form of which is governed by a reasonable theoretical model. As such, $S_1(E)$ is pre-determined to some extent, even though the parameters of the component curves are arbitrary.

(ii) Before the application of equation (4) to the observed spectrum, we must be certain of the exact number of processes which make up the single-scattering curve. This quantity we can never be certain about, owing to the possible overlap of the component curves of $S_1(E)$.

(iii) Owing to the non-physical nature of curve-fitting procedures, it is possible to fit almost any analytic function to the experimental curve provided that the number of variables is sufficiently large. Thus the $S_1(E)$ determined from curve-fitting must be subject to close scrutiny.

(iv) Some difficulty will arise from assigning certain peaks in the spectrum to single- or plural-scattering events, and this again leads to arbitrary solutions for $S_1(E)$.

In summary, the curve-fitting procedure predetermines $S_1(E)$ by the initial assumptions.

In this paper we shall give an analysis for the determination of $S_1(E)$, without any initial assumptions on its shape, in terms of the experimental curve $S(E)$, corrected for instrumental effects (equation (2)), and the unscattered (elastically scattered) electron intensity I_0 . This $S_1(E)$ may then be compared either directly with a theoretical curve or

fitted by a sum of curves, which represent the individual components of $S_1(E)$, but in this case the theory is introduced at a late stage and does not pre-determine the single-scattering curve.

2. Formulation of the plural-scattering problem

If the single-scattering curve is given as $S_1(E) = f_1(E) + g_1(E) + h_1(E) + \dots$, where $f_1(E)$, $g_1(E)$, $h_1(E)$, etc., are the component distributions of $S_1(E)$, then the resultant spectrum may be written as

$$S(E) = \sum_{n=1}^{\infty} \left(\frac{t}{\lambda_{av} I_s} \right)^{n-1} \frac{S_n(E)}{n!} \quad (5)$$

where, for the convenience of the subsequent analysis, the upper limit m of the summation has been replaced by infinity. This modification makes no difference to the physical significance of equation (5), since for $n > m$ it has been implicitly assumed that further terms in the summation make no significant contribution to $S(E)$.

$$I_s = I_f + I_g + I_h + \dots \quad (6)$$

and λ_{av} is the average mean free path for all single-scattering processes f, g, h, \dots

Further, we have that

$$\frac{1}{\lambda_{av}} = \frac{1}{\lambda_f} + \frac{1}{\lambda_g} + \frac{1}{\lambda_h} \quad (7)$$

and

$$I_f : I_g : I_h : \dots = \frac{1}{\lambda_f} : \frac{1}{\lambda_g} : \frac{1}{\lambda_h} : \dots \quad (8)$$

It must, however, be shown that equation (5) is the same equation as that which would be derived if we considered f, g, h, \dots as separate processes, each characterized by its own mean free path, i.e. it is necessary to determine the function $S(E)$ by the consideration of all combinations of the loss processes f, g, h, \dots with appropriate statistical weighting factors. Applying Poisson statistics to an $S_1(E)$ composed of just two types of losses f and g , we find for $S(E)$ the following expression:

$$\begin{aligned} S(E) = & \sum_{n=1}^{\infty} \left(\frac{t}{\lambda_f I_f} \right)^{n-1} \frac{f_n(E)}{n!} + \sum_{n=1}^{\infty} \left(\frac{t}{\lambda_g I_g} \right)^{n-1} \frac{g_n(E)}{n!} \\ & + \sum_{n=1}^{\infty} \sum_{p=1}^{\infty} \left(\frac{t}{\lambda_f I_f} \right)^{n-1} \left(\frac{t}{\lambda_g I_g} \right)^p \frac{f_n(E) * g_p(E)}{n! p!} \end{aligned} \quad (9)$$

where the $*$ indicates the convolution of $f_n(E)$ with $g_p(E)$. Applying equations (6), (7) and (8) to equation (5), we can readily show that equations (5) and (9) are identical term by term for a given number of plural-scattering events. Similarly, it may be shown that equation (5) is equivalent to an equation of a similar form as (9) for an $S_1(E)$ comprising three types of loss processes f, g, h . A detailed analysis showing the equivalence of equations (5) and (9) is given in the appendix. The analysis is of general validity for an $S_1(E)$ comprising an arbitrary number of component distributions.

3. Derivation of an equation for $S_1(E)$

From equation (5) it is possible to derive an expression for $S_1(E)$ in terms of a series in $(t/\lambda_{av} I_s)$ and $S(E)$, but an equation of the form (9) would not be so amenable to the present analysis. The first step in the solution of equation (5) for $S_1(E)$ involves taking the Fourier transforms of both sides of (5), where we define the Fourier transform of the function $S(E)$ by

$$\bar{S}(w) = \int_{-\infty}^{+\infty} S(E) \exp(-iwE) dE. \quad (10)$$

Hence equation (5) becomes

$$\bar{S}(w) = \sum_{n=1}^{\infty} \frac{C^{n-1} \bar{S}_n(w)}{n!} \quad (11)$$

where we have written C for the quantity $(t/\lambda_{av} I_s)$ ($=1/I_0$, I_0 is the unscattered intensity).

From the properties of the Fourier integral it is known that (e.g. Titchmarsh 1948, Sneddon 1951)

$$\bar{S}_n(w) = \int_{-\infty}^{+\infty} dE \int_{-\infty}^{+\infty} S_{n-1}(E') S_1(E-E') \exp(-i\omega E) dE' = \bar{S}_1(w) \bar{S}_{n-1}(w).$$

Hence equation (11) becomes

$$\bar{S}(w) = \frac{1}{C} \sum_{n=1}^{\infty} \frac{C^n \bar{S}_1(w)^n}{n!}. \quad (12)$$

We then obtain from equation (12) the following expression for $\bar{S}_1(w)$:

$$C \bar{S}_1(w) = \ln\{C \bar{S}(w) + 1\} \quad (13)$$

and, for $|C \bar{S}(w)| < 1$, the logarithmic term may be expanded in a power series, i.e.

$$\bar{S}_1(w) = \bar{S}(w) - \frac{1}{2} C \{\bar{S}(w)\}^2 + \frac{1}{3} C^2 \{\bar{S}(w)\}^3 - \frac{1}{4} C^3 \{\bar{S}(w)\}^4 \dots \quad (14)$$

Taking inverse Fourier transforms of equation (14) gives for $S_1(E)$

$$S_1(E) = S(E) - \frac{1}{2} C \{S(E) * S(E)\} + \frac{1}{3} C^2 \{S(E) * S(E) * S(E)\} - \dots \quad (15)$$

where

$$S(E) * S(E) = \int_{-\infty}^{+\infty} S(E') S(E-E') dE' \quad \text{and} \quad C = \frac{1}{I_0}.$$

Thus $S_1(E)$ is determined by $S(E)$, the experimental curve corrected for resolution effects, and the parameter C , which is the inverse of I_0 . The major consideration is the validity of the expansion in equation (13), on which the correctness of equation (15) depends. It may be shown that for a Gaussian $S_1(E)$ the expansion (13) is valid, provided that the average number of scattering events occurring in the specimen (t/λ_{av}) is less than 0.69; this upper limit for (t/λ_{av}) is dependent on the nature of the $S_1(E)$ profile (which determines $S(E)$ by equation (5)), but we can expect (15) to be valid for at least $(t/\lambda_{av}) = 0.5$ (see § 4 for a detailed consideration of this question). In electron energy-loss work we should expect λ_{av} values of approximately 500–1000 Å, and this indicates that the film thickness t must be in the range 250–500 Å for (15) to be applicable to the electron energy-loss spectrum, and t values of this order are not impractical. In any case, the determination of the single-scattering curve by a fitting procedure based on equations of the form (9) and its more complicated extensions would seem to be a formidable computing problem.

The $S_1(E)$ computed from an experimental curve by the use of equation (15) is not necessarily the unique solution of (5), but a repetition of the computations for several film thicknesses (within the range for which equation (15) is valid) should give a consistent set of $S_1(E)$ curves, within the experimental error. The solution for $S_1(E)$ is unique only in the case of error-free data (see § 4).

4. Computational tests

In order to ascertain the validity of equation (15) and also to determine an upper limit for t/λ_{av} , we have generated test $S(E)$ curves by using suitable line shapes for $S_1(E)$ in equation (5), for example a sum of Lorentzians or Maxwellians and for a range of t/λ_{av} values. This $S(E)$ and I_0 ($= I_s \lambda_{av}/t$) were then treated as experimental data subjected to combined errors in the range 0–20%. The experimental single-scattering curve $S_1'(E)$ was then calculated from equation (15) and the fit of this curve to the generating $S_1(E)$ was

assessed by the quantity $\sigma\%$, where

$$\sigma = \left[\frac{1}{r} \sum_{j=1}^{j=r} \left\{ \frac{S_1(E) - S_1'(E)}{S_1(E)} \right\}^2 \right]^{1/2} \times 100\%$$

for r points on the $S(E)$ curve.

The results of these computations for t/λ_{av} values in the range 0.25–1.00 are summarized in table 1. The σ values given represent average values calculated for varying types, number,

Table 1. The effect of error in the experimental data $S(E)$ on the computed single-scattering curve $S_1(E)$ (equation (15))

Experimental error (%)	σ (%)†			
	$t/\lambda_{av} = 0.25$	$t/\lambda_{av} = 0.50$	$t/\lambda_{av} = 0.75$	$t/\lambda_{av} = 1.00$
0.0	0.0	0.0	0.0	0.0
2.0	1.5	2.4	3.2	4.0
4.0	3.3	4.9	6.5	8.1
6.0	4.3	7.4	9.8	12.2
8.0	5.7	9.9	13.1	16.3
10.0	7.2	12.4	16.5	20.4
12.0	8.7	14.9	19.8	24.6
14.0	10.1	17.4	23.2	28.8
16.0	11.6	19.4	26.6	33.1
18.0	13.0	22.4	30.1	37.5
20.0	14.5	25.0	33.6	41.6

† Resultant error in $S_1(E)$.

half-widths and position of the maxima of distributions comprising $S_1(E)$. In the case of error-free data the maximum value of t/λ_{av} for which equation (15) is valid is unity. However, in the case of experimental data the maximum value of t/λ_{av} for which equation (15) is useful will be given by the criterion that σ should not be much larger than the experimental error. With the present test data this indicates a maximum value of t/λ_{av} of about 0.5. In practice, the error in $S_1(E)$ need not be as large as indicated in table 1, since we may analyse a number of experimental spectra for different t values or even different scans for the same specimen. An averaging procedure over all computed $S_1(E)$ curves should yield a satisfactory single-scattering curve.

5. Discussion of the analysis and its limitations

The present analysis gives a method, suitable for computer evaluation, for determining the single-scattering curve from an experimental profile, which is composed of a sum of repetitions of the primary scattering event. The advantages of the present analysis in relation to curve-fitting procedures for calculating $S_1(E)$ arise from the rigidity imposed on the solution for $S_1(E)$ by the use of the latter method and the initial information required concerning the number of processes which comprise $S_1(E)$. An $S_1(E)$ obtained by the above method may be then subjected to any model analysis required without the restrictions of a fitting procedure. Equation (15) may readily be rewritten for a two-dimensional experimental curve $S(x, y)$, but the increased computing time required to find a solution for $S_1(x, y)$ may prove a major difficulty. In this case curve-fitting procedures would also be difficult to apply. It is, however, necessary to point out the limitations of the present analysis:

(i) The series solution for $S_1(E)$ (equation (15)) is only slowly convergent, whereas equation (5) converges rapidly with increasing n .

(ii) The effect of experimental error in the solution of equation (15) becomes serious if the number of terms required becomes large, and could eventually lead to a divergence of the series for $S_1(E)$, when the value of C is near the upper limit allowed for the expansion in equation (13). Thus the analysis is only ideal for small C values, when the number of terms required to describe $S_1(E)$ in (15) is also small. Section 4 dealt with this problem in some detail.

(iii) There is the possibility that, when experimental errors are large, several solutions for $S_1(E)$ may be determined that fit the experimental curve equally well, and even a study of the variation of $S(E)$ with t may not be sufficient to determine a useful $S_1(E)$ curve.

(iv) The statistics of the scattering processes must be known for the analysis to be applicable. However, this limitation also can apply to curve-fitting procedures.

In conclusion, the present analysis, despite the above limitations, would seem to provide a flexible approach to the determination of the primary- (single-) scattering event, when the experimental curve is derived from a sum of terms, each term representing the scattering due to a given number of repetitions of the primary scattering.

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Appendix

Suppose $S_1(E)$ is made up of two distributions $f_1(E)$ and $g_1(E)$. Let us divide the film thickness t into n strips, each of elemental thickness Δt . Let the probability of collision f_1 in the thin strip be α , and of g_1 be β . After passing through the first strip, the electron probability (magnitude) is by definition (for an incident electron beam of unit intensity)

$$(1 - \alpha - \beta) + \alpha + \beta$$

where the terms represent those electrons which are unscattered and those electrons which undergo collisions f_1 and g_1 respectively.

After two thicknesses Δt , Δt the electron probability distribution is

$$(1 - \alpha - \beta)^2 + \alpha^2 + \beta^2 + 2(1 - \alpha - \beta)\alpha + 2(1 - \alpha - \beta)\beta + 2\alpha\beta.$$

After n collisions we obtain

$$\begin{aligned} \{(1 - \alpha - \beta) + \alpha + \beta\}^n &= (1 - \alpha - \beta)^n + \binom{n}{1}(1 - \alpha - \beta)^{n-1}(\alpha + \beta) \\ &\quad + \binom{n}{2}(1 - \alpha - \beta)^{n-2}(\alpha + \beta)^2 + \dots + (\alpha + \beta)^n. \end{aligned}$$

In the limit $n \rightarrow \infty$, $\Delta t \rightarrow 0$, such that the probability of scattering (totally, not in a 'thin' strip) is finite,

$$\left. \begin{aligned} n\alpha &\rightarrow \frac{t}{\lambda_f} \\ n\beta &\rightarrow \frac{t}{\lambda_g} \end{aligned} \right\} \text{from the definition of mean free path.}$$

Thus

$$\begin{aligned} \lim_{n \rightarrow \infty} &\left[\left\{ 1 - \frac{t}{n} \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right) \right\}^n + \binom{n}{1} \left\{ 1 - \frac{t}{n} \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right) \right\}^{n-1} \frac{t}{n} \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right) + \dots + \frac{t^n}{n^n} \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right)^n \right] \\ &= \exp \left\{ -t \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right) \right\} \left\{ 1 + t \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right) + \dots + \frac{t^n}{n!} \left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g} \right)^n \right\} \end{aligned}$$

where each power of $1/\lambda_f$ is associated with an f_1 collision, each $1/\lambda_g$ with a g_1 collision. The above equation represents the distribution of the magnitudes of scattering. Inserting the actual distributions, we obtain

$$\exp\left\{-t\left(\frac{1}{\lambda_f} + \frac{1}{\lambda_g}\right)\right\} \left[\delta(E) + t\left\{\frac{f_1(E)}{I_f\lambda_f} + \frac{g_1(E)}{I_g\lambda_g}\right\} + \left\{\frac{t^2}{2!} \frac{f_1(E)*f_1(E)}{I_f^2\lambda_f^2} + \frac{t^2}{2!} \frac{g_1(E)*g_1(E)}{I_g^2\lambda_g^2} + t^2 \frac{f_1(E)*g_1(E)}{I_f I_g \lambda_f \lambda_g} + \dots\right\} \right]$$

where the * indicates the convolution of two functions. It has been assumed that the incident electron beam may be represented as a delta function. Now, $S_1(E)$ is a sum of simple collisions, i.e.

$$S_1(E) = \text{constant} \times \left\{ \frac{f_1(E)}{I_f\lambda_f} + \frac{g_1(E)}{I_g\lambda_g} \right\}$$

but by definition

$$S_1(E) = f_1(E) + g_1(E).$$

Thus

$$I_f\lambda_f = I_g\lambda_g$$

and we obtain the following expression for $S(E)$ for an $S_1(E)$ comprising two distributions $f_1(E)$ and $g_1(E)$:

$$S(E) = \sum_{n=1}^{\infty} \left(\frac{t}{\lambda_{av} I_s} \right)^{n-1} \{f_1(E) + g_1(E)\} *^{(n \text{ convolutions})} \frac{1}{n!}$$

which is identical with equation (5).

The extension of the above analysis to an $S_1(E)$ composed of an arbitrary number of component distributions is quite straightforward.

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