Small-Angle X-Ray Scattering from Spherical Particles of Non-Uniform Electron Density

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The scattering functions for spherical particles with the Gaussian distribution of electron density and for particles with the cosine distribution of electron density are calculated and compared with scattering from the sphere of uniform electron density. The scattering curves of dilute systems of various degrees of polydispersity are also calculated for all three models considering the statistics both of mass and of the number of particles.

Introduction

This paper deals with the scattering of spherical particles in which the electron density is not uniformly distributed but falls off gradually from the centre outwards. Such a distribution of electron density may occur when clusters of atoms of one of the components develop in binary solid solutions, e.g. in spherical silver-rich G.P. zones in aluminum-silver solid solutions.

Two models of particles of non-uniform electron density have been studied. The scattering of dilute polydisperse systems of particles has been calculated on the basis of a suitable particle-size distribution law. All the scattering curves obtained have been compared with the well-known scattering curves of dilute monodisperse and polydisperse systems of spheres of uniform electron density.

The scattering and other curves were calculated on a Univac 1106 computer.

Three models of electron-density distribution inside a spherical particle

Three models of particles, all having spherical symmetry but differing in electron-density distribution, were studied. If \( r \) is the distance from the centre, and \( \varrho_e (r) \) is the difference between electron density at a point inside a particle and the constant electron density outside the particle, these models are:

(a) A sphere of radius \( R \) of constant electron density \( \varrho_e \) (in the following abbreviated as H-EDD for homogeneous electron-density distribution)

\[
\varrho_e = \begin{cases} 
\varrho_0 & \text{for } 0 \leq r \leq R \\
0 & \text{otherwise}
\end{cases}
\]

(b) The electron-density distribution has the form of a cosine function:

\[
\varrho_e = \frac{\varrho_0}{2} \left( 1 + \cos \pi \frac{r}{R} \right) \text{ for } 0 \leq r \leq R
\]

\[
= 0 \quad \text{otherwise}
\]

(abbreviated as Cos-EDD).

(c) Electron density diminishes from the centre according to a Gaussian curve (abbreviated as Gauss-EDD)

\[
\varrho_e = \varrho_0 \exp \left( -\frac{r^2}{2\sigma^2} \right) \text{ for } 0 \leq r \leq \infty.
\]

\( \varrho_0 \) is the difference between the electron density at the centre of the particle and in the matrix.

The radius of gyration is a convenient size parameter by means of which the sizes of particles of different types can be compared. The radii of gyration of the three types of particles are for H-EDD

\[
R_g = \sqrt{\frac{2}{3}} R,
\]

for Cos-EDD

\[
R_g = \sqrt{\frac{3}{2}} \left( \frac{\pi^4}{\pi^2 - 6} - 20 \right)^{1/2} R,
\]

and for Gauss-EDD

\[
R_g = \sqrt{3} d.
\]

Formulae (4), (5) and (6) make it possible to express the electron density \( \varrho_e \) in terms of \( r/R_g \).

Thus for H-EDD we have

\[
\varrho_e = \varrho_0 \text{ for } 0 \leq \frac{r}{R_g} \leq \sqrt{\frac{2}{3}} ;
\]

for Cos-EDD

\[
\varrho_e = \frac{\varrho_0}{2} \left( 1 + \cos \frac{r}{C R_g} \right) \text{ for } 0 \leq \frac{r}{R_g} \leq \frac{\pi C}{2}.
\]

where

\[
C = \left[ \frac{\pi^4}{\pi^2 - 6} - 20 \right]^{-1/2} = 0.56762,
\]

and for Gauss-EDD

\[
\varrho_e = \varrho_0 \exp \left( -\frac{3}{2} \left( \frac{r}{R_g} \right)^2 \right) \text{ for } 0 \leq \frac{r}{R_g} \leq \infty.
\]

In Fig. 1 the distributions of electron density along the diameters of the three types of particles of the same \( R_g \) and of the same number of excess or deficit electrons with respect to the matrix are compared.
Scattering functions for the three types of particles

The scattering amplitude of a spherically symmetric particle is given by

\[ \Phi(k) = \frac{4\pi r^2 \rho_e(r)}{4\pi r^2 \rho_e(r)} \int_0^R \sin(kr) \, dr \]  

(11)

(Guinier & Fournet, 1955), where \( R \) is the radius of the particle and \( k = \frac{2\pi n}{\lambda} \), \( n \) being the scattering angle. The denominator represents the excess or deficit of electrons within the particle with respect to the matrix and it normalizes the amplitude \( \Phi(k) \) to unity at zero scattering angle.

We calculated the scattering amplitude for Cos-EDD and Gauss-EDD particles using relations (8) and (10) which define \( R \) and the functions \( \rho_e(r) \). The scattering function \( \Phi^2(k) \) which is proportional to the scattered intensity but normalized to unity at zero scattering angle, can be expressed in terms of \( kR_g \). The scattering function of a homogeneous sphere is well known (Guinier, 1939; Guinier & Fournet, 1955):

\[ \Phi^2(kR_g) = \Phi^2(u) = \left[ \frac{3}{u^3} \sin u - u \cos u \right]^2 \]  

(12)

where

\[ u = \sqrt{\frac{3}{\pi}} \cdot kR_g = kR. \]  

(13)

The scattering function for Cos-EDD was found to be

\[ \Phi^2(kR_g) = \Phi^2(z) \]  

\[ = \left[ \frac{D}{z^2(1-z^2)} \left( \frac{1-3z^2}{1-z^2} \sin \pi z - \pi z \cos \pi z \right) \right]^2 \]  

(14)

where

\[ \pi z = kR, \]  

\[ z = CkR_g, \]  

\[ D = \frac{3}{\pi(\pi^2 - 6)} = 0.24678, \]  

(15)

(16)

and the value of \( C \) is given in (9).

The scattering function of Gauss-EDD:

\[ \Phi^2(kR_g) = \exp \left[ -\frac{(kR_g)^2}{3} \right] \]  

(17)

is a function of Gaussian type because the amplitude \( \Phi(kR_g) \), being the Fourier transform of the electron density, is also a function of the Gaussian type.

When developed as power series, all three scattering curves have the first two terms equal:

\[ \Phi^2(kR_g) = 1 - \frac{(kR_g)^3}{3} \pm \ldots, \]  

(18)

which has been proved to be a general feature of all scattering curves of particles (Guinier, 1956) and is widely used under the name of the Guinier approximation.

In order to show the trend of the three scattering functions given in formulae (12), (14) and (17) over a large range of scattering angles they had to be presented in a \([\log \Phi^2(kR_g) \text{ vs. } (kR_g)]\) plot (Fig. 2). Both the H-EDD and the Cos-EDD scattering curves oscillate. The oscillations are damped, approaching a curve which can be derived from the scattering function by omitting the oscillating terms. These curves, showing the average asymptotic behaviour of scattering curves, are indicated in Fig. 2 by dot-dashed lines, and their equations are

![Fig. 1. Distribution of electron density along the diameter of three types of particle containing the same number of electrons. Full line: homogeneous sphere. Dotted line: cosine distribution. Dashed line: Gaussian distribution.](image)

![Fig. 2. Scattering functions of a homogeneous sphere (full line), a particle with the cosine distribution of electron density (dotted line) and a particle with the Gaussian distribution of electron density (dashed line). The dot-dashed lines indicate the curves to which the first two scattering curves approach asymptotically at large \( kR_g \).](image)
for H-EDD particles (Guinier, 1956) and

\[ A_c(kR_g) = A_c(z) = \frac{D^2}{2(1-z^2)^2} \left( \frac{1}{z^6} + \frac{\pi^2 - 6}{z^4} \right. \]

\[ + \left. \frac{9 - 2\pi^2}{z^2} + \pi^2 \right) \]

(20)
or, in the form of a power series

\[ A_c(z) = \frac{D^2}{2} \left( \frac{\pi^2}{z^6} + \frac{9 + 2\pi^2}{z^4} + \frac{3(\pi^2 + 10)}{z^2} \right. \]

\[ + \frac{4\pi^2 + 67}{z^2} \right) \]

(20a)

for Cos-EDD particles.

As seen in Fig. 2, at small angles the Cos-EDD curve lies between the curves of H-EDD and Gauss-EDD and can be approximated by a Gaussian up to greater angles than can the scattering curve of a homogeneous sphere. The relative percentage deviation of both the H-EDD and Cos-EDD curves from the Gaussian curve is presented in Fig. 3. It will be seen that a deviation of about 2.5% is reached for the H-EDD curve at \( kR_g = 1.3 \) and for the Cos-EDD curve at \( kR_g = 1.5 \).

The zero points of the Cos-EDD curve lie closer together than those of the H-EDD curve, i.e. at \( kR_g = 4.164; 6.008; 7.810; 9.597; 11.376; 13.150; \) \ldots \ The maxima of the Cos-EDD curve lie at \( kR_g = 0; 4.797; 6.708; 8.546; 10.355; 12.149; 13.935; \) \ldots \ The values of the Cos-EDD function at maxima are several orders of magnitude lower and fall off more rapidly than in the case of the H-EDD curve; their values are: \( 1; 2.351 \cdot 10^{-4}; 1.484 \cdot 10^{-5}; 2.069 \cdot 10^{-6}; 4.379 \cdot 10^{-7}; 1.207 \cdot 10^{-7}; 4.005 \cdot 10^{-8}; \) \ldots \n
Scattering by polydisperse dilute systems of particles

Since the scattered intensity \( I \) of a dilute system of \( N \) identical particles is

\[ I(kR_g) \propto N n_e^2 \Phi^2(kR_g), \]

(21)
where \( n_e \) is the number of excess or deficit electrons in the total volume of the particle in relation to the number of electrons in an equal volume of the surrounding substance, and since

\[ n_e \propto R_g^2, \]

the scattering of a polydisperse system of particles of the same shape but of different sizes will be

\[ I(kR_g) \propto \int_0^\infty N(R_g) R_g^2 \Phi^2(kR_g) dR_g \]

(22)

where \( N(R_g) dR_g \) is the number of particles with gyration radii between \( R_g \) and \( R_g + dR_g \).

If \( M(R_g) dR_g \) is the mass of particles with gyration radii between \( R_g \) and \( R_g + dR_g \), the intensity will be

\[ I(kR_g) \propto \int_0^\infty M(R_g) R_g^2 \Phi^2(kR_g) dR_g. \]

(23)

Various size-distribution functions \( M(R_g) \) (Maxwellian, Gaussian and rectangular) have been applied to calculate the scattering curves of particles of various shapes but of uniform electron density (Shull & Roess, 1947; Roess & Shull, 1947). More recently Mittelbach & Porod have applied the following size-distribution function:
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\[ g(R_g) = \frac{a^{n+1}}{n!} R_g^n \exp\left(-a R_g\right) \]  

(24)

for which the relation between the statistical parameters describing the system and the parameters \( a \) and \( n \) is very simple (Mittelbach & Porod, 1964; Mittelbach, 1965). The average particle size (the arithmetic mean) is

\[ \langle R_g \rangle = \frac{n+1}{a} . \]  

(24a)

The degree of polydispersity is usually described by the statistical parameter \( \sigma \), the square of which \( (\sigma^2) \) is defined as the ratio of the mean square of fluctuations of \( R_g \) to the square of the mean value of \( R_g \). \( \sigma \) depends only on parameter \( n \):

\[ \sigma^2 = \frac{\langle R_g^2 \rangle}{\langle R_g \rangle^2} - 1 = \frac{1}{n+1} . \]  

(24b)

Thus the smaller \( n \) is, the greater is the polydispersity. For a monodisperse system \( n = \infty \). The first factor in equation (24) normalizes the function \( g(R_g) \) in the sense that

\[ \int_0^\infty g(R_g) dR_g = 1 . \]

We shall refer to the function (24) as the M–P particle-size distribution (after Mittelbach & Porod). Introducing the variable

\[ x = \frac{R_g}{\langle R_g \rangle} \]  

(25)

and eliminating \( a \) by means of (24a), the function (24) becomes

\[ g(x) = \frac{(n+1)^{n+1}}{n!} x^n \exp\left[-(n+1)x\right] . \]  

(26)

Mittelbach (1965) applied the distribution (26) as a mass distribution \( M(R) \) and calculated the scattering curves for systems of homogeneous spheres of various degrees of polydispersity, using a modified equation (23):

\[ I(k\langle R_g \rangle_m) = \sum_{x=0}^{\infty} \frac{(n+1)^{n+4}}{(n+3)!} x^{n+3} \times \exp\left[-(n+1)x\right] \Phi^2(k\langle R_g \rangle_m) dx . \]  

(27)

We applied the same M–P distribution law to the number of particles \( N(R_g) \) and calculated the scattering curves of polydisperse systems for all three models of particles, using a modified relation (22):

\[ I(k\langle R_g \rangle_n) = \sum_{x=0}^{\infty} \frac{(n+1)^{n+7}}{(n+6)!} x^{n+6} \times \exp\left[-(n+1)x\right] \Phi^2(k\langle R_g \rangle_n) dx . \]  

(28)

The scattering functions (27) and (28) are normalized so that \( I = 1 \) at \( k = 0 \). The size distribution functions (26) for various \( n \) are presented in Fig. 4, and the cor-

Fig. 5. Scattering curves for dilute systems of homogeneous spheres of various degrees of polydispersity. The size distributions shown in Fig. 4 represent the number statistics of particle sizes. The dotted line shows the scattering from a monodisperse system.

Fig. 6. The same as in Fig. 5 but for Cos–EDD particles.
responding scattering curves for the systems of H–EDD, Cos–EDD and Gauss–EDD particles are shown in Figs. 5, 6 and 7 respectively. \( \langle R_g \rangle \) in these cases means the number average size of particles.

The scattering curves are presented in log–log plot to show the characteristic behaviour of polydisperse systems at large angles. The larger the degree of polydispersity, the more damped are the oscillations of H–EDD and Cos–EDD curves. Lower polydispersity is needed to smooth oscillations completely in the case of Cos–EDD curves. Porod's law \( I \propto k^{-4} \) is fulfilled only for homogeneous spheres because for such systems alone there exists a well-defined interface between the regions of two different electron densities. It is seen in Fig. 6 that the Cos–EDD curves also show a simple asymptotic behaviour which can be represented by

\[
I \propto k^{-8}
\]  

when the \( k \langle R_g \rangle \) values are so large that the value of the function \( A_c \) in equation (20a) does not differ much from its first term. The departure of the slope of the \((\log I \text{ vs. } \log (k \langle R_g \rangle))\) curves from \(-8\) amounts to 3% at \( k \langle R_g \rangle = 17.3 \).

**Comparison of scattering curves when the same particle-size distribution function is applied to both the mass and the number of particle**

If we compare the scattering curves of the mixtures of homogeneous spheres presented in Fig. 5, where the particle-size distribution given by equation (24) was applied as the distribution of the number of particles \( N(R_o) \), with the curves presented in Fig. 2 in Mittelbach’s paper (1965), where the same distribution law was applied to the mass of particles \( M(R_o) \), we notice a striking difference. In both cases the further the curves are removed from the curve of a monodisperse system the higher is the degree of polydispersity, but they appear to lie on the opposite side of that curve. However, this difference may only be apparent because the curves in Mittelbach’s plot are not well resolved in the small-angle region. In order to study the disposition of curves in greater detail we recalculated Mittelbach’s curves for H–EDD and calculated also the analogous curves for the Cos–EDD and Gauss–EDD types of particles.

Let us see in an example, firstly what influence the use of the same distribution function in the number and the mass statistics will have on the scattering curves, and secondly, what the relation is between the number- and mass-statistical parameters describing the same system. If curve \( A \) in Fig. 8 shows the distribution given by equation (26) for \( n = 30 \), the scattering curves in Fig. 9 denoted by \( n = 30 \) and \( m = 30 \) correspond to the same distribution law but applied to the number and to the mass of particles respectively. The \( \langle R_g \rangle \) value appearing in the variable on the abscissa should be the number average \( \langle R_g \rangle_n \) in the first case and the mass average \( \langle R_g \rangle_m \) in the second case. The system for
which curve $A$ in Fig. 8 represents the number statistics has the mass distribution represented by curve $B$ which has the form

$$M(x) = \frac{(n+1)^{n+4}}{(n+3)!} x^{n+3} \exp \left[-(n+1)x \right].$$

(30)

This is no longer the M–P distribution law and therefore the mass-average size is given by a different expression:

$$\langle R_\theta \rangle_m = \frac{n+4}{a} = \langle R_\theta \rangle_n \cdot \frac{n+4}{n+1}. \quad (30a)$$

The degree of polydispersity is given by

$$\sigma^2_m = \frac{1}{n+4} = \sigma^2_n \cdot \frac{n+1}{n+4}. \quad (30b)$$

When the M–P distribution (26) (curve $A$ in Fig. 8) is applied as a mass distribution, curve $C$ in Fig. 8 will show the distribution of the number of particles in the same polydisperse system, which is given by

$$N(x) = \frac{(n+1)^{n-2}}{(n-3)!} x^{n-3} \exp \left[-(n+1)x \right]$$

(31)

and for which

$$\langle R_\theta \rangle_n = \frac{n-2}{a} = \langle R_\theta \rangle_m \frac{n-2}{n+1}. \quad (31a)$$

and

$$\sigma^2_n = \frac{1}{n-2} = \sigma^2_m \frac{n+1}{n+2}. \quad (31b)$$

Curve $D$ in Fig. 8 shows a symmetric distribution of particle sizes given by the relation

$$N(x) = (1 + \cos 2\pi x) \quad \text{for} \quad 0.5 \leq x \leq 1.5$$

for which $\sigma$ is the same as for the M–P distribution with $n=30$ (18%). This distribution has been proposed (Baur & Gerold, 1964) on the basis of actual measurements of the sizes of G.P. zones in aluminum–silver alloys by means of transmission electron microscopy. The scattering curves for this distribution differ only slightly from curves with $n=30$.

We see in Fig. 9 that the (log $I$) curves for polydisperse H–EDD (full lines) and Cos–EDD (dot-dashed lines) systems are parallel at large scattering angles. This is the consequence of their asymptotic behaviour which does not depend on the particle-size distribution. At small angles, however, the dependence on particle-size statistics is rather pronounced as seen in Figs. 10 and 11 where the Guinier plots of the scattering curves for H–EDD and Cos–EDD systems for various degrees of polydispersity are presented. Parameters $n$ and $m$ refer to $N(R_\theta)$ and $M(R_\theta)$ distributions. In this region the scattering curves of low-polydispersity systems are bent downwards but may also appear as straight lines, while the scattering curves of Gauss–EDD would invariably be bent upwards throughout the entire angular range. We see now that the slope of all scattering curves of polydisperse systems, presented as Guinier plots, at very small scattering angles is greater than the slope of the scattering curve of a single spherical particles of non-uniform electron density.
Discussion

Although the particle with the Gaussian electron density distribution is not a particle in the true sense because it has no definite boundaries, it may still be considered as a particle owing to the rapidly diminishing electron density (see the dashed curve in Fig. 1). The scattering curves of such particles have the Gaussian form throughout the entire angular range and not at small angles only. In the case of the hypothetical polydisperse systems of such particles, therefore, the often-used procedure of decomposing scattering curves into a few Gaussian curves (Jellinek, Solomon & Fan-kuchen, 1947) to find the size and fractional number or mass of particles of the same size would seem justified.

Such a procedure, however, if applied to real systems, may lead to wrong conclusions. Let us mention an example which we actually met while studying the scattering of G.P. zones in aluminum–silver alloys quenched both from the melt and from the solid state (Kranjc & Stubičar, 1973). Suppose that we have two polydisperse systems differing only in the mean size of the particles which in the first system is much smaller than in the second. Although theoretically the scattering curves of both systems are represented by the same function of \( k(R_o) \), the experimental scattering curves may differ greatly because, for the same angular range \( k \), the scattering curve of the first system will be known up to much smaller values of \( k(R_o) \). For example, if the scattering curves are determined up to \( k=0.6 \), the Guinier plot of the scattering from the system of smaller particles \( (R_o)_1 \leq 5 \text{ Å} \) may appear as a nearly straight line [the curve \( n=30 \) up to \( (k(R_o))^2 = 9 \) in Fig. 11] which – if interpreted by decomposition into Gaussian curves – would suggest a rather monodisperse system. The scattering curves of the system of larger particles \( (R_o)_2 \leq 10 \text{ Å} \) would show the upward curvature indicating polydispersity [the dot-dashed curve \( n=30 \) up to \( (k(R_o))^2 = 36 \) in Fig. 9].

Porod’s law, which holds for systems of homogeneous spheres, allows the specific surface to be determined from the measured constant value of the product \( I_{abs} \cdot k^4 \) at large angles. According to (29), in the case of Cos–EDD systems the product \( I_{abs} \cdot k^8 \) will be constant at large angles. Although the measurement of this value cannot supply information on the specific surface of the system, some information can still be obtained. If we express the number of excess or deficit electrons in the particle in terms of \( R_o \):

\[
n_e = \int_0^{nC R_o} 4r^2 \pi r_0 \left( 1 + \cos \frac{r}{C R_o} \right) dr = 2\pi r_0 \frac{C^3}{D} R_o^3
\]

and modify relation (21) to describe a polydisperse system of constant \( g_0 \), for which the scattering function \( \Phi^2(kR_o) \) can be substituted by the first term in equation (20a), we obtain:
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\[ I_{ab} k^8 = \frac{2 \varrho_0 \pi^4}{C^2} \int_0^\infty \frac{N(R_0)}{R_0^2} \, dR_0. \]

Taking for \( N(R_0) \) the function (24), we obtain the relation between the constant value \( I_{ab} k^8 \) and the parameters describing the system:

\[ I_{ab} k^8 = \frac{2 \varrho_0 \pi^4 (n + 1)^2}{C^2 n(n - 1) \langle R_0 \rangle^2} \text{ for } n > 1. \]  

(32)

If the assumed distribution law were correct and if the experimental scattering curve could be fitted to one of the calculated scattering curves, it would be possible to determine the values of \( \langle R_0 \rangle \) and \( n \). In this case \( \varrho_0 \) could be determined from equation (32) and the relative density of the whole particle with respect to the matrix would be known.

As the \( k^{-8} \) dependence of intensity at high angles is characteristic for Cos-EDD particles independently of the statistical features of the system, it may be used as a criterion for whether such particles are present. However, with the common small-angle cameras we can measure the scattering up to about \( k = 0.6 \) (or \( \varepsilon \approx 8^\circ \) for Cu K\( \alpha \) radiation). In order to verify the \( k^{-8} \) law we must reach experimentally \( k \langle R_0 \rangle \) greater than about 18 and therefore the mean \( \langle R_0 \rangle \) of the system should exceed 30 \( \AA \). At high angles the scattered intensity would be a few orders of magnitude weaker than the scattering of the statistically analogous system of homogeneous spheres.

For systems of smaller particles the scattering curve in the \( k^{-8} \) region cannot be measured, and only a comparison with the calculated scattering curves will make it possible to determine whether the particles correspond to the Cos-EDD model. And this, as often emphasized, is a procedure which does not lead to conclusive answers, because completely different systems can give nearly identical scattering curves. Even if we knew that all the particles were spherical and had the same electron density distribution, it would be difficult – purely on the basis of scattering curves – to determine unambiguously the model for the particles and the statistical parameters.

The shapes of many actual distributions of particle sizes of various substances measured by means of electron microscopy are symmetric or fall more steeply on the side of the larger particles. In such cases the application of not only the M-P distribution but also the Maxwellian and Gaussian distributions to describe the number and not the mass statistics of the system appears more justified.

References


Spinodal Decomposition in Al-Base Alloys Quenched from the Liquid State – A Small-Angle X-ray Scattering Study

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Small-angle X-ray scattering has been used to study early-stage spinodal decomposition in Al-base Zn and Al-base Ag alloys which were liquid-quenched at rates of the order of \( 10^6 \)°C/sec. Such ultra-rapid cooling yields a well-quenched specimen having a narrow solute cluster-size distribution, which persists at ambient temperature. Al–Zn alloys, up to 22 at. % Zn, have been studied and show clear linear spinodal behaviour for aging at temperatures below 100°C. The situation is less certain for Al–Ag, but liquid quenching does clarify the early-stage phase decomposition behaviour. In alloys in the range of 15 at. % Ag, spinodal decomposition is observed to be the initial mode of phase decomposition.