A Cell Model for X-ray Scattering from Random Systems*

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Abstract

A model, belonging to the class of cell models previously introduced, is developed to calculate the small-angle X-ray scattering of random multiphase systems. This model, which is applied to supported metal catalysts, involves two cell sizes, one for the support and one for the metal. Interphase surface areas and the correlation function, related to the X-ray scattering intensity by a Fourier transform, are given in terms of these two parameters. By fitting the measured intensity $I(h)$ to that predicted by the model, values for the metal and support surface areas are obtained.

I. Introduction

With respect to their small-angle X-ray scattering, systems such as the supported metal catalysts used in the petroleum industry (Germain, 1969), may be described as random and multiphase. A phase is defined as the region of space occupied by matter of a particular homogeneous electron density, so that the electron density changes only at a phase boundary. For a γ-alumina–platinum catalyst, there are three phases: the alumina (support), the platinum (metal catalyst) and the interstitial void. Each phase occurs as inclusions of different sizes and shapes, with no regularity in their arrangement; hence the term ‘random’. If a model for the system can be parametrized to yield the experimental small-angle X-ray scattering, one can use it to obtain the interphase surface areas. A new class of models for this kind of system has been proposed (Goodisman & Coppa, 1981) and the simplest example of this class explored.

The present paper describes a model of this kind which is more realistic for many random multiphase systems and indicates how one uses the model to obtain interphase surface areas. A new class of models for this kind of system has been proposed (Goodisman & Coppa, 1981) and the simplest example of this class explored.

For an isotropic system, the theoretical small-angle X-ray scattering intensity $I(h)$ is related to the Fourier transform of the correlation function according to (Guinier, Fournet, Walker & Yudowitch, 1955; Porod, 1951):

$$I(h) = I_e(h) 4\pi V \int_0^{\pi} \frac{r^2 \gamma(r) \sin hr}{hr} dr,$$

where $h = 4\pi \lambda^{-1} \sin \theta$, $\lambda$ = wavelength of X-ray, $\theta$ = 1/2 scattering angle, $I_e(h)$ = scattering by a single electron, $V$ = illuminated volume, and $\gamma^2$ = mean-square electron density fluctuation. The correlation function $\gamma(r)$ for multiphase systems can be written (Goodisman & Brumberger, 1971):

$$\gamma(r) = 1 - \frac{\sum_{ij} P_{ij}(r)(n_i - n_j)^2}{\sum_i q_i(n_i - \bar{n})^2},$$

where $q_i$ is the volume fraction of phase $i$ with electron density $n_i$ and $P_{ij}(r)$ is the probability of finding two phases $i$ and $j$ separated by a distance $r$. The interphase surface areas $S_{ij}$ are related to the $P_{ij}$ by (Goodisman & Coppa, 1981; Goodisman & Brumberger, 1971; Coppa, 1980):

$$\left(\frac{dP_{ij}}{dr}\right)_{r=0} = S_{ij} 4V.$$

The single cell size (SCS) models proposed by Goodisman & Coppa (1981) are built by dividing space into identical space-filling polyhedra, or cells, and filling each with one of the several phases. In the simplest model each cell is independently assigned a phase according to some predetermined ratio. With this assumption, the correlation function $\gamma(r)$ and the interphase surface areas, which are the quantities of experimental interest, are calculated in terms of the properties of the polyhedra. The $P_{ij}$ depend on the volume fractions of the various phases and the ‘non-crossing probability’ (see equation 7 and preceding discussion) for the particular polyhedron (cell type) used in building the model (Coppa, 1980).

In the cubic SCS model the cells were cubes of length $l$; the surfaces can be obtained by finding the probability that any cube face belongs to the surface $S_{ij}$ and multiplying it by the total number of cube faces in the entire model, and by the area of one face. This

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probability is equal to \(2\varphi_i\varphi_j\) where the fraction of phase \(i\) is of course equal to the probability that any single cell is filled with phase \(i\). The factor of 2 is the number of ways two facing cells can be filled with phases \(i\) and \(j\). The total number of cells is \(3N\) for the cubic SCS model (where \(N\) is the number of cubes) so the surface areas are

\[
S_{ij} = 6N\varphi_i\varphi_j l^2 \quad (i \neq j) \tag{4}
\]

and the surface-to-volume ratios \((V = Nl^3)\) are

\[
\frac{S_{ij}(i \neq j)}{V} = \frac{6\varphi_i\varphi_j}{l}. \tag{5}
\]

Equation (5) can also be obtained with the appropriate probability function \(P_{ij}\) in (3).

The method for deriving the surface area from the small-angle X-ray scattering curve is simple, since the SCS model involves only one parameter, \(l\), which is varied to fit the correlation function or the scattering intensity to that experimentally determined. Then, if the quality of the fit is good enough to justify use of the model, the surfaces are given by (4) and (5).

In the cases we have examined (supported metal catalysts) the SCS model does not work well. In fact, it is easily seen in electron micrograph studies (Prestridge, Via & Sinfelt, 1977; Sinfelt, 1979) on systems of this type that the particle size distribution for the support is not the same as for the metal catalyst. For certain silica-supported osmium catalysts, the average osmium particle size is an order of magnitude smaller than the average silica particle. The SCS model makes the particle size for all phases the same, which is unrealistic. We now propose a model that involves two (or more) cell sizes.

II. The MCS model

The procedure for building the multi cell size (MCS) model mimics somewhat the way in which supported metal catalysts are actually prepared: that is, first the support is constructed and then the metal is dispersed throughout the pore system of the support, for example, via precipitation from an infiltrating metal solution (Linsen, 1970). For the cubic MCS model the structure of the support is built by dividing space into cubes of side length \(l_s\), and independently filling each cube with support, with probability \(\varphi_s\), or leaving it empty, with probability \(\Phi_s = 1 - \varphi_s\). The eventual volume fractions of metal and void will add to \(\Phi_s\). At this stage, the result is like that of a two-phase SCS model. Next, the cubes not containing support are divided into smaller cubes of edge length \(l_c\) such that

\[
l_c = ml_s, \tag{6}
\]

where \(m\) is an integer. The cubes are sometimes referred to as large divided cubes. The small cubes (side length \(l_c\)) are then filled with either metal catalyst or void according to the probability \(\varphi_c/\Phi_c\) for metal catalyst, and \(\varphi_v/\Phi_v\) for void. The sum \(\varphi_c + \varphi_v + \varphi_s\) is unity, whereas \(\Phi_c = \varphi_c + \varphi_v\).

The final result is a random dispersion of metal-catalyst particles throughout a void system that itself is randomly dispersed throughout the support. Fig. 1 shows a two-dimensional analogy to such a model.

The correlation function for the MCS model can be derived according to (2). The \(P_{ij}\) will be given in terms of the volume fractions for the various phases and the 'non-crossing probabilities' for the two cell sizes. The 'non-crossing probability' \(P_0(r)\) for a lattice of cells is the probability that two points separated by a distance \(r\) will both be inside the boundaries of the same cell. \(P_0(r)\) for the cube as reported by Goodisman (1980) is:

\[
P_0(r) = 1 - 2r + \frac{2}{r^2} - \frac{1}{r} + \frac{3}{r^3}, \quad 0 \leq r < l
\]

\[
P_0(r) = -2 + \left(\frac{3}{4} - \frac{1}{4\pi}\right)\frac{l}{r} + \frac{3r}{2\pi l} + \frac{6r}{\pi l} \cos^{-1} \frac{l}{r} - \frac{r^3}{2\pi l}\pi, \quad l \leq r < l/\sqrt{2}
\]

\[
P_0(r) = \frac{3l}{2r} + \left(\frac{2l}{\pi r} - \frac{6r}{\pi l}\right) \cos^{-1} \left(\frac{r^2}{l^2} - 1\right)^{1/2} - \frac{5l}{4\pi r} + \frac{3r}{2l} (1 - \pi^{-1}) - \frac{4}{3}
\]

Fig. 1. Part of a two-dimensional analogy to a cell model involving three phases and two cell sizes; letters a-l correspond to probabilities of equations (8)-(13).
Here, \( a = \frac{4l^4(r^2 - 2l^2)}{\pi^2} \) and \( b = \frac{2l^2}{\pi^2} \). The function \( P_0 \) is everywhere continuous and with continuous slope. The non-crossing probabilities for cubes of side length \( l_c \) and \( l_s \) are denoted by \( P_{0c}(r) \) and \( P_{0o}(r) \), and obtained by substituting \( l_c \) and \( l_s \) respectively for \( l \) in (7).

For an example of how a probability function is derived \( P_{uv}(r) \) is considered. \( P_{uv}(r) \), the probability that there will be void at both ends of a line segment of length \( r \), is composed of three terms. The first is the probability that both points are within the same small cube. That probability is equal to the volume fraction of small void cubes, \( \sigma_v \), multiplied by the probability that the line connecting the points is contained within a single small cube, \( P_{0o}(r) \). The second term is the probability that the points are in different small void cubes, both of which are contained in a single large divided cube. To calculate this, we note first that the probability that end \( A \) of a line segment lies in void is \( \sigma_v \), and the probability that the other end, \( B \), lies in the same large cube is \( \sigma_v P_{0o}(r) \). The probability that end \( B \) lies in the same small void cube being \( \sigma_v \), the probability that end \( A \) is in void and end \( B \) is in the same large cube as \( A \), but not the same small cube, is \( \sigma_v [P_{0o}(r) - P_{0o}(r)] \). Since we require that end \( B \) be in fact in void, we must multiply this by the volume fraction of void cubes in the divided cube, \( \sigma_v(\sigma_v + \sigma_c) \). The third term is the probability that the points are in void cubes situated in different large divided cubes. It is the product of the volume fractions of void cubes, \( \sigma_c^2 \), multiplied by the probability that the distance \( r \) spans more than one large divided cube \([1 - P_{0o}(r)]\). Thus,

\[
P_{uv}(r) = \sigma_v P_{0o}(r) + \sigma_v [\sigma_v(\sigma_v + \sigma_c)] [P_{0o}(r) - P_{0o}(r)] \\
+ \sigma_c^2 [1 - P_{0o}(r)].
\]

With these functions in (2) the correlation function reduces to

\[
\gamma(r) = P_{0o}(r) - \frac{P_{0o}(r) - P_{0o}(r)(n_e - n_o)^2}{n^2 - \bar{n}^2} \frac{\sigma_v \sigma_c}{\sigma_v + \sigma_c},
\]

where

\[
\bar{n} = \sum_i n_i \phi_i \\
\bar{n}^2 = \sum_i n_i^2 \phi_i.
\]

If \( P_{0o}(r) = P_{0o}(r) \) (i.e. \( l_c = l_s \), \( m = 1 \)), equation (14) is exactly the correlation function for the cubic SCS model (Goodisman & Coppa, 1981), since there is then only one cube size. Fig. 2 shows the effect on the correlation function of changing \( l_c \) for fixed \( l_s \). The increase at larger values of \( r \) reflects the presence of the large cubes (edge length \( l_c \)). The values of \( \gamma(r) \) at small \( r \) are dominated by the small cubes (edge length \( l_s \)). The correlation function is smoothly decaying and becomes zero for \( r > l_s/\sqrt{3} \). Fig. 3 shows the corresponding scattering intensity weighted by \( h^2 \).
For the case of three phases there are three different surface areas. To use equations (3) for the surfaces we need \(\frac{dP_0}{dr}\) at \(r = 0\), which is \(-\frac{1}{2}\) according to (7). Then

\[
S_{xc} = 6V\varphi_c\varphi_c/l_s
\]

(15)

\[
S_{xt} = 6V\varphi_t\varphi_t/l_s
\]

(16)

\[
S_{tx} = 6V\varphi_t\varphi_c/l_s + 6V[\varphi_c\varphi_c/(\varphi_c + \varphi_t)](l_c^{-1} - l_t^{-1})
\]

(17)

By a method similar to that used for the SCS model, the MCS model also yields the surfaces by direct counting of faces, giving results in exact agreement with equations (15) through (17).

III. Application

The Fourier transform of \(\gamma(r)\), required for the calculation of \(I(h)\) according to (1), requires the Fourier transform of the non-crossing functions, which has already been discussed for cubes (Goodisman, 1980; Goodisman & Coppa, 1981). We may write the intensity as

\[
I(h) = C \int_0^\infty h^{-1}r \sin hr \left(P_0(r)(n_c - n_t)^2\varphi_c\varphi_c(\varphi_c + \varphi_t)^{-1}
\right.

\[
+ P_0(r)[(n_c^2 - \bar{n}^2)
\right.

\[
- (n_c - n_t)^2\varphi_c\varphi_c(\varphi_c + \varphi_t)^{-1}] dr,
\]

(18)

where the constant \(C\) is \(I_c(h)4\pi V\). Given the volume fractions and electron densities of the phases, only two parameters remain, \(l_c\) and \(l_t\). In principle one could choose their values to make (18) fit the measured intensity as well as possible.

For the experimental data available to us, the nature of the samples (powder) did not permit determination of \(V\) (Brumberger, 1980) so absolute intensities were not available. Therefore, we work with the three quantities

\[
L = \lim_{h \to \infty} h^2 I(h)
\]

\[
M_2 = \int_0^\infty h^2 I(h) dh
\]

\[
M_1 = \int_0^\infty h I(h) dh
\]

The value of \(M_2\), aside from the value of \(C\), is independent of the form of \(\gamma\), so it may be used to determine \(C\):

\[
M_2 = C\eta^2 \int_0^\infty h^2 dh \int_0^\infty r^2 dr (\sin hr)(hr)^{-1} \gamma(r)
\]

\[
= C\eta^2 \pi/2
\]

It may also be shown (Goodisman & Coppa, 1981; Guiner et al., 1955, p. 18) that

\[
M_1 = C\eta^2 \int_0^\infty \gamma(r) dr
\]

Experimental measurement of \(M_1\) and \(M_2\) requires intensities out to large \(h\); in the example presented below, intensities were extrapolated using the fact that \(I\) must decrease as \(h^{-4}\) for large \(h\). For \(L\) we integrate by parts to find

\[
L = C\eta^2 \lim_{h \to \infty} \{h^3 \int_0^\infty (\sin hr)(r\gamma) dr\}
\]

\[
= C\eta^2 \lim_{h \to \infty} \{[(\cos hr)(2r\gamma' + r\gamma'')]_0^\infty\}
\]

where primes mean differentiation with respect to \(r\) and we have used the continuity of \(\gamma\) and \(\gamma'\). Since \(\gamma''\) is not continuous at \(l_c, l_c\sqrt{2}, l_c\sqrt{3}, l_t, l_t\sqrt{2},\) and \(l_t\sqrt{3}\), one also should evaluate \(r\gamma''\cos hr\) at these points, but these contributions give oscillating functions of \(h\), averaging to zero. Therefore we have for \(L\) only \(-2C\eta^2\gamma'(0)\).

The experimental quantities of interest are thus

\[
M_1/M_2 = (2/\pi) \int_0^\infty \gamma(r) dr
\]

(19)

\[
L/M_2 = (-4/\pi)\gamma'(0)
\]

(20)

The intensities measured were slit-smeared, i.e. one obtained

\[
\bar{I}(h) = \int_{-\infty}^\infty I(u) du
\]

where \(u^2 = h^2 + x^2\), and converted properties of \(\bar{I}(h)\) to properties of \(I(h)\). For instance,

\[
\bar{I}(0) = 2 \int_0^\infty I(h) dh
\]

so that the slit-smeared intensity for zero angle yields the first moment of \(I\) needed for \(M_1\). Reliable experimental intensities \(\bar{I}(h)\) could not be obtained for \(h\) below 0.008 Å\(^{-1}\) and a linear extrapolation of \(\ln \bar{I}\) vs \(h^2\).
was used. The uncertainties for small $h$ affect $M_1$ most, $M_2$ less, and $L$ not at all. For the platinized alumina catalyst, the measured slit-desmeared parameters are given in Table 1.

To calculate (19) we need the integrals of $P_6$ and $P_7$ from $r=0$ to $r=\infty$, which, according to a previous evaluation (Goodisman & Coppa, 1981), are $0.4483 l_5$ and $0.4483 l_6$, respectively. Thus,

$$\frac{M_1}{M_2} = 0.2854 \left[ \frac{l_5 - l_6}{(n_5 - n_6)^2 \varphi_c \varphi_e} \right]$$

and

$$\frac{L}{M_2} = 1.9099 \left[ \frac{1}{l_6} - \frac{(l_5^{-1} - l_6^{-1})(n_c - n_e)^2 \varphi_c \varphi_e}{(n_5^2 - n_6^2)(\varphi_c + \varphi_e)} \right]$$

where we have used $P_6(r) = -3/2 l_5$. By using only the ratios $M_1/M_2$ and $L/M_2$, we avoid the necessity for obtaining absolute values of intensities and for evaluating sample thickness or sample volume. We may solve (21) and (22) for $l_5$ and $l_6$. The substitution of $l_5$ from (21) into (22) gives a quadratic equation for $l_6$. Having determined $l_6$ and $l_5$ (two solutions), we compute surface areas. One solution yields a negative surface area; rejecting this choice, we are left with $l_6 = 119$, $l_5 = 10.8 \AA$.

IV. Discussion

The corresponding surface areas, (15)-(17), are $S_{cv}/V = 0.00832 \text{ Å}^{-1}$, $S_{ce}/V = 0.000174 \text{ Å}^{-1}$, and $S_{cv}/V = 0.000813 \text{ Å}^{-1}$. The last figure corresponds to $253 \text{ m}^2 \text{ g}^{-1}$ of platinum (density of Pt assumed to be 21.4 Mg m$^{-3}$), a reasonable figure for catalysts of this kind with no heat treatment (Mout & Moscou, 1965), but rather high for the present sample. If the platinum particles were spheres of equal size, their radius would be 5.56 Å.

The ratio $m = l_5/l_6$ is about 11. The small size of the catalyst-support surface is due to the model; at the small Pt volume fraction, statistical considerations show the Pt is overwhelmingly in isolated small cubes and half of these are found, unphysically, surrounded by void. It would be possible to modify our model to allow Pt only in small cubes connected to metal or to support. However, one should not take the model as a literal description of the shape of these phase volumes. Interestingly enough, Renouprez, Hoang-Van & Compagnon (1974) used the assumption $S_{cv} = 0$ as the basis of their method for interpreting X-ray scattering from these systems.

The fact that reasonable surface areas result from application of the model does not, of course, prove that the system is well described by it. This would require further comparison of the intensity with predictions of the model. For instance, the zeroth moment is predicted to be

$$M_0 = \int_0^{\infty} I(h)dh = I_0(h)\eta^2 2\pi V_0 \int_0^{\infty} \gamma rdr$$

$$= C\eta^2 \left[ \frac{0.2353(l_5^2 - l_6^2)(n_c - n_e)^2 \varphi_c \varphi_e}{(n_5^2 - n_6^2)(1 - \varphi_s)} \right]$$

$$= 1673.4M_2.$$  

Although we have no reliable experimental value for $M_0$, our extrapolation of $\bar{I}$ to $h=0$, which was used in obtaining $M_1$ and $M_2$, corresponds to $M_0 = 17740$. It is possible that $I(h)$ passes through a maximum for some $h$ below 0.008 Å$^{-1}$, making our extrapolation poor, but the discrepancy is disturbing. Together with the large value of $S_{cv}/V$, it suggests the present model does not describe this sample well. Supporting this view is the fact that $L/M_2$ seems to be approximately the same for the support without platinum as for the catalyst: if the metal had a characteristic length much smaller than that of the support, the introduction of metal would markedly change the intensity at large $h$.

The lack of a reliable value for $M_0$ also prevents application of a previous theory (Goodisman & Brumberger, 1971) for random multiphase systems, since that theory requires four parameters. It may be noted, however, that the formulas of that theory simplify considerably for the present case, where one volume fraction (say $\varphi_3$) is very small. If one can neglect $S_{31}$ or $S_{32}$ compared to $S_{21}$, and put $\varphi_1 + \varphi_2$ equal to unity, the correlation function becomes

$$\gamma(r) = f \exp(2\lambda_2 r/8V) + (1 - f) \exp(2\lambda_3 r/8V),$$

with $\lambda_2 = -2S_{21}/\varphi_1 \varphi_2$ and $\lambda_3 = -2(S_{31} + S_{32})/\varphi_3$. Here, $f$ is a function of surfaces and volume functions. Depending on whether $\lambda_2$ or $\lambda_3$ is larger in size, the large-$r$ behavior of $\gamma$ may be dominated by either surface. In deriving this model, all the phases are treated equivalently, and the numbering of $\lambda_1, \lambda_2, \lambda_3$ is not related to the numbering of phases.

The two theories seem to start from quite different assumptions and introduce the random character of the system differently. They make different predictions about the scattering intensity and, from a limited portion of the $I(h)$ curve, would derive different surface areas. It is important to get accurate scattering data for this type of system so that it may be ascertained which, if either, of the theories fits and can be used to measure surface areas. This we presently hope to do.

<table>
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<th>Volume fractions</th>
<th>Electron densities</th>
<th>Moments of intensity</th>
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<tr>
<td>$\varphi_e$</td>
<td>$\varphi_c$</td>
<td>$\varphi_v$</td>
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References
