Multiple Small-Angle Scattering: an Experimental Investigation

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Abstract

The results of multiple small-angle neutron scattering (SANS) experiments carried out using a low-resolution instrument on two bidisperse \( \text{Al}_2\text{O}_3 \) samples, with particle sizes much larger than the limit accessible under the single-scattering approximation, have been analyzed in the light of a recently developed formalism for multiple small-angle scattering. It is shown that the extraction of realistic structural parameters that are in good agreement with those calculated from prior knowledge of the samples is only possible when both multiple scattering and bidispersity of the samples have been accounted for.

I. Introduction

In traditional small-angle scattering (SAS) experiments, one can study the structural features of inhomogeneities with sizes ranging from 1 nm to 1 \( \mu \text{m} \), depending upon the resolution of the instrument. The upper limit of the extractable size range bears a reciprocal relation to the minimum value of the accessible wave-vector transfer \( q \), which is generally limited by the finite width of the direct beam.

A primary feature of multiple scattering is the broadening of the scattering profile. It should therefore be possible to exploit this beam-broadening feature of multiple scattering, using suitably thick samples, to probe very large inhomogeneities that are otherwise not measurable because their single-scattering profiles are too sharp to yield significant signals in the region well outside the incident-beam profile. Furthermore, as a result of the large thickness of the sample in a multiple scattering experiment, the incident beam can be scattered almost completely, yielding much improved signal-to-background ratios up to very high wave-vector transfers.

Recently, we have developed a formalism for multiple small-angle scattering, described in detail in Mazumder & Sequeira (1992), which indicates the nature of the structural information extractable from different limiting regimes of the multiple-scattering profile, for different types of scattering media. It was shown (Mazumder & Sequeira, 1992) that, when the scattering mean free path of the radiation is very large compared with the linear dimensions of the inhomogeneities, the polydisperse scattering medium can be treated as a statistically average medium; such a medium has been termed an effective medium. For an effective medium, the nature of the information extractable from the Guinier regime of the profile is given by

\[
\left( \sum_{i=1}^{N_i} N_i R_i^2 \right)^{-1/2},
\]

where \( N_i \) stands for the number of scattering interactions the radiation has undergone with the \( i \)th type of inhomogeneity with linear dimension \( R_i \), while passing through the sample. It should be recalled (Mazumder & Sequeira, 1992) that the corresponding information in the case of single scattering from a monodisperse medium is given by \( R \).

The present experiment is intended to verify this aspect of the theory, by studying multiple small-angle scattering from two bidisperse \( \text{Al}_2\text{O}_3 \) samples of known composition. It also shows the extent of the errors incurred when the scattering data from thick samples are analyzed without accounting for multiple scattering.

II. Experimental

A. Raw materials

For the preparation of SAS samples, two different grades of \( \text{Al}_2\text{O}_3 \) powder (used for the polishing of specimens for the microstructural investigation of bulk materials) were chosen. The nominal particle sizes for these powders, as indicated by the suppliers, were 600 and 2500 \( \AA \), respectively. Here, 'size' refers to the diameter of a sphere of equal volume.

B. Powder characterization

Phase analysis of the starting powders by X-ray diffraction revealed that specimen (I), with particle size 600 \( \AA \), was amorphous in nature, while specimen (II), with particle size 2500 \( \AA \), was found to be in the \( \alpha \) phase. Helium-gas pycnometry indicated a theoretical
Table 1. Dimensional and compositional characteristics of SANS samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>600 Å powder content (g)</th>
<th>2500 Å powder content (g)</th>
<th>Diameter (cm)</th>
<th>Thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (I)</td>
<td>12.1040</td>
<td>9.0847</td>
<td>3.0193</td>
<td>2.622</td>
<td>1.864</td>
</tr>
<tr>
<td>Sample (II)</td>
<td>12.9862</td>
<td>3.3817</td>
<td>9.6045</td>
<td>2.622</td>
<td>1.530</td>
</tr>
</tbody>
</table>

density of 3.756 g cm\(^{-3}\) for particles of specimen (I). The theoretical density \(\rho_T\) of \(\alpha\)-phase particles is known to be 3.986 g cm\(^{-3}\). To determine the shape characteristics, both the specimens were examined using scanning electron microscopy (SEM). Samples of \(\text{Al}_2\text{O}_3\) from both batches were dispersed in ethanol and ultrasonicated. One drop of alcohol suspension was taken on the stub and a thin copper coating was given to the dried surface to make it conducting, for SEM examination. Figs. 1 and 2 show the SEM photographs of the \(\text{Al}_2\text{O}_3\) particles from specimens (I) and (II), respectively. As expected, greater agglomeration is clearly evident in the fine particles [specimen (I)]. Fig. 1 also shows the spherical shape of the particles in specimen (I). The particle shape in specimen (II), however, is found to vary slightly. The particle size as measured by SEM agrees fairly well with that reported by the supplier.

C. Sample fabrication

Two samples for the multiple small-angle scattering experiment were prepared, by mixing the two powder specimens in different proportions. The mixed powders were then pelletized by applying a load of 2268 kg, in order to obtain pellets with the requisite strength for further handling. The dimensional and compositional characteristics of the pellets are given in Table 1. Henceforth, we will refer to the two mixtures as sample (I) and sample (II).

D. SANS experiment

Small-angle neutron scattering (SANS) profiles with the above mentioned two pellets were recorded using the SANS facility (Desa, Mazumder, Sequeira & Dasannacharya, 1985) at the CIRUS reactor at Trombay. The wavelength distribution, \(f(\lambda)\), of the incident beam is depicted in Fig. 3 by open circles. The solid line represents the continuous distribution obtained from an eighth-order polynomial fitted to the data points. From the fitted continuous distribution, we have several moments of \(f(\lambda)\), such as \(\langle \lambda \rangle\) (5.266 Å), \(\langle \lambda^2 \rangle\) (27.844 Å\(^2\)), \(\langle \lambda^{-2} \rangle\) (0.0365 Å\(^{-2}\)) and \(\langle \lambda^{-4} \rangle\) (0.00135 Å\(^{-4}\)) etc., which we will make use of in the analysis of the scattering data. It should be noted that \(\langle \lambda^n \rangle = \int [f(\lambda)\lambda^n] d\lambda[/f(\lambda) d\lambda].\)
Table 2. Volume fractions, number densities and packing fractions of samples (I) and (II)

<table>
<thead>
<tr>
<th>Sample (I)</th>
<th>$p_1$</th>
<th>$p_2$</th>
<th>$\rho_1$ (cm$^{-3}$)</th>
<th>$\rho_2$ (cm$^{-3}$)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample (I)</td>
<td>0.2404</td>
<td>0.0753</td>
<td>21.27 $\times$ 10$^{14}$</td>
<td>0.0921 $\times$ 10$^{14}$</td>
<td>0.3157</td>
</tr>
<tr>
<td>Sample (II)</td>
<td>0.109</td>
<td>0.2918</td>
<td>9.6441 $\times$ 10$^{14}$</td>
<td>0.3569 $\times$ 10$^{14}$</td>
<td>0.4008</td>
</tr>
</tbody>
</table>

The scattering profiles of the two samples and of the blank run are depicted in Fig. 4 as plots of $\ln$ (intensity) versus scattering angle $\theta$. The minimum $q$ obtainable with the instrument is 0.017 Å$^{-1}$, which corresponds to a maximum accessible size of 369.45 Å for the inhomogeneity.

III. Data analysis

In this section, we discuss the result of an analysis of the SANS data, depicted in Fig. 4 as plots of scattering intensity versus scattering angle $\theta$. It should be noted that the multiple-scattering profile does not bear the signature of interparticle interference to any significant level. This is expected, since it is the second moment of the single-scattering cross section which predominates (Mazumder & Sequeira, 1992) in the Guinier regime of the multiple-scattering profile. Since the interparticle interference function changes sign with wave-vector transfer, it is the contribution of the second moment of the particle form factor towards the second moment of the single-scattering cross section that is significant. That is how, unlike the single-scattering profile, the multiple-scattering profile remains practically unaffected by interparticle interference.

Let us now introduce some notation and sample parameters for the convenience of further discussion.

A. Notations and some sample parameters

$Z$ denotes the thickness of the sample, which contains two ($i = 1, 2$) types of inhomogeneities, i.e. Al$_2$O$_3$ particles of specimens (I) and (II). We assume that the particles are spherical in shape with radius $R_i$ and volume $V_i$. $p_i$, $\rho_i = p_i/V_i$ and $D_i$ denote, respectively, the volume fraction, number density and neutron-scattering-length density of the $i$th type of inhomogeneity in the matrix. $\phi$ denotes the packing fraction of the sample. Table 2 lists the values of $p_i$, $\rho_i$ and $\phi$ for the two samples.

$L_i$ denotes the scattering mean free path of the radiation in the matrix with respect to the $i$th type of inhomogeneity, whereas $L = (L_1L_2/(L_1 + L_2))$ denotes the total scattering mean free path in the matrix. $N_i = Z/L_i$ denotes the number of scattering interactions the radiation undergoes with the $i$th type of inhomogeneity while traversing the sample thickness $Z$; $N(\sum_{i=1}^{2} N_i)$ denotes the total number of scattering interactions. The subscript $i (i = 1, 2)$ is used for particles of specimens (I) and (II), respectively.

The neutron scattering-length density $D$ is calculated from the relation

$$D = \sum_{i=1}^{2} b_i/V_i,$$

where $b_i$ is the coherent neutron scattering length of the $i$th nucleus in the unit cell of volume $V_i$ and the sum is defined over the unit cell. The above expression simplifies to

$$D = N_A \langle b \rangle \rho_T \text{/molecular weight},$$

where $N_A$ is Avagadro’s number, $\langle b \rangle$ is the arithmetical average of the scattering lengths over the chemical-formula unit and $\rho_T$ is the theoretical density of the specimen. From (2), it is found that $D_1$ and $D_2$ take the following values: $D_1 = 5.396 \times 10^{-6}$ and $D_2 = 5.726 \times 10^{-6}$ Å$^{-2}$.

To estimate the severity of the multiple scattering, we have calculated $N_i$, the average number of scattering interactions the radiation undergoes with the $i$th type of inhomogeneity. $N_i$ is given by

$$N_i = 2\pi \rho_i Z \lambda^2 D_i^2 R_i^4,$$
where the subscripted quantities represent the quantities corresponding to the $i$th type of inhomogeneity. With account being taken of the wavelength distribution of the incident beam, the above expression for $N_i$ is modified to

$$N_i = 2\pi \rho_i Z \langle \lambda^2 \rangle D_i^2 R_i^*.$$  \hfill (4)

From (4), we obtain $N_1 = 16.36$, $N_2 = 24.04$ and $N = 40.40$ for sample (I) and $N_1 = 6.09$, $N_2 = 76.47$ and $N = 82.56$ for sample (II).

B. Extraction of the measure of the radius of curvature of a scattering profile

In the following, we confine our discussion to the normalized scattering profile $I(\theta)$, for which $I(\theta = 0) = 1$. The scattering profile is characterized by the value of $M$, which is a measure of the radius of curvature of the scattering profile at $\theta = 0$. It should be recalled that, for a curve $Y = f(x)$, the radius of curvature at $x$ is given by

$$1/(2M) = \left[1 + (dY/dx)^2\right]^{3/2}/(d^2Y/dx^2).$$  \hfill (5)

$M$ is a measure of the negative gradient of the Guinier plot. It should be noted that for single scattering from a monodisperse population of spheres of radius $R$, the value of $M$ is given by $(2\pi R/\lambda)^2/5$, while, for multiple scattering from a monodisperse population of spheres, the $M$ value is given by $(2\pi R/\lambda)^2/5N$.

Since the incident-beam profile has a finite width, the scattering profiles of the samples must be corrected for the angular spread of the incident beam, to obtain the radius of curvature of the scattering profiles corresponding to a zero-divergence incident beam.

For the deconvolution of the scattering profiles of the samples from the incident-beam profile, we have carried out a least-squares analysis to justify the choice of the functional forms of the scattering profile and the blank run. In the procedure adopted here, the functional forms of the incident- and the scattered-beam profiles are determined by least-squares analysis employing the Pearson function,

$$I_0(\theta) = \left[1 + (M/n)\theta^2\right]^{-n},$$  \hfill (6)

which is known to reduce to a functional form such as a parabola ($n = -1.0$), semicircle ($n = -0.5$), Lorentzian ($n = 1.0$) or Gaussian ($n \rightarrow \infty$) for different values of $n$. Furthermore, irrespective of the value of $n$, $I_0(0) = 1$ and has the common radius of curvature $1/(2M)$ at the origin, $\theta = 0$.

We have determined the value of $n$ for each data set by least-squares analysis. The value of $n$ turns out to be very large ($> 10^{14}$) for the scattering profiles of the two samples, as well as for the blank run. The very large value of $n$ indicates that the three profiles, as shown in Fig. 4, can be assumed for all practical purposes to be Gaussian.

The function $I(\theta) = \exp\left(-m\theta^2\right)$ has been used to fit the scattering profiles of the two samples as well as of the blank run. The $m$ values obtained are $m_1 = 1490.59$ (41.78) for sample (I), $m_2 = 2409.07$ (66.61) for sample (II) and $m = 25896.29$ (2160.42) for the blank run. The numbers in parentheses are the standard deviations of the estimated quantities. The estimated standard deviations include contributions from the angular resolutions of the measurements and the estimated standard deviations calculated purely on the basis of the fitting of the data set to a Gaussian curve. While fitting the data set to a Gaussian, the data points have been taken up to $\theta_{\text{max}}$ such that $m^{1/2}\theta_{\text{max}} \leq 1$. $\theta_{\text{max}}$ gives an estimate of the maximum value of $\theta$ for which the Gaussian approximation for the scattering profile is valid.

If the scattering profiles, corresponding to $\delta(\theta)$ incident beam, of samples (I) and (II) are expressed as $\exp\left(-M_1\theta^2\right)$ and $\exp\left(-M_2\theta^2\right)$, respectively, then $M_1$ and $M_2$ are obtained from $m$, $m_1$ and $m_2$ using the relation

$$M_i = m m_i/(m - m_i); \quad i = 1, 2.$$  \hfill (7)

From the values of $m$, $m_1$ and $m_2$, we obtain $M_1 = 1581.6286$ (195.517) and $M_2 = 2656.162$ (332.514).

C. Classification of the scattering medium

Multiple small-angle scattering theory and the expression of the scattering profile become drastically simplified when the mean free path of the radiation is very large compared to the linear dimensions of the inhomogeneities. Such a medium has been termed an effective medium, whereas the usual one is termed a statistical medium. Since the constitution of the medium is known, we can estimate the scattering mean free path $L$, the expression for which is

$$L = 1 \left\{\frac{2\pi \lambda^2}{\sum_{i=1}^{2} \rho_i D_i^2 R_i^*}\right\}.\hfill (8)$$

The above expression is based on the assumption that the particles are spherical in shape. Since the incident radiation is not monochromatic in the present experiment, the expression for $L$ is altered to

$$L = \langle \lambda^{-2}\rangle \left\{\frac{2\pi}{\sum_{i=1}^{2} \rho_i D_i^2 R_i^*}\right\}.\hfill (9)$$

Using the above expression for $L$, we obtain $L = 0.0461$ cm for sample (I) and $L = 0.0188$ cm for sample (II). The $L$ values in both the samples are very much greater than the linear dimensions of the particles, which suggests that the samples qualify to be treated as effective media as far as the multiple small-angle scattering is concerned.
D. Curvatures of Guinier regions as expected from the theory

Here we estimate the $M$ values, which give a measure of the curvature of the scattering profile in the Guinier regime, for the two samples, as expected from the theory. From the theory of multiple small-angle scattering from an effective bidisperse medium, the scattering profile $I(\theta)$ in the vicinity of $\theta \to 0$ can be written as

$$I(\theta) = \exp \left[ -(2\pi/\lambda)^2 \sum_{i=1}^{2} N_i / R_i^2 \right].$$ \(10\)

The above expression is normalized at $\theta = 0$, that is $I(0) = 1$. From (3), (10) can be rewritten as

$$I(\theta) = \exp (-A\theta^2),$$

where

$$A = (2\pi/5Z)\left[ \lambda^4(\rho_1 D_1^2 R_1^2 + \rho_2 D_2^2 R_2^2) \right].$$

When the incident beam has a wavelength distribution $f(\lambda)$, as it has in our experiment, the expression for $I(\theta)$ becomes

$$I(\theta) = \left[ \int f(\lambda) \exp (-A\theta^2) \, d\lambda \right] \left[ \int f(\lambda) \, d\lambda \right].$$ \(11\)

For the scattering profile, as expressed by (11), the expression for $M$ is

$$M = (2\pi/5Z) \langle \lambda^{-4} \rangle / \left( \rho_1 D_1^2 R_1^2 + \rho_2 D_2^2 R_2^2 \right).$$

From knowledge of the sample, as well as of the wavelength distribution of the incident beam, we have evaluated the value of $M$ for both the samples. We found that $M = 1505.41$ (0.55) for sample (I) and $M = 2545.66$ (0.93) for sample (II). The estimated standard deviations of $M$, given in parentheses, are obtained by taking into account only the error involved in fitting the wavelength distribution of the incident beam to an eighth-order polynomial.

It should be observed that these calculated values of the parameter $M$, for both samples, are systematically lower than those obtained from the experimental scattering profiles. This observation can be explained by the fact that there must be a size distribution, however narrow it may be, of particles in the two specimens of Al$_2$O$_3$ used for making the SANS samples. The quoted sizes of 600 and 2500 Å are only indicative of the average particle sizes. It is important to note that the asymmetry of the particle shape can only have the opposite effect (Mazumder & Sequeira, 1992) that the $M$ value from the Guinier regime of a scattering profile from a polydisperse population of spheres, having the same scattering-length density, is given by $(2\pi/\lambda)^2 \langle R^6 \rangle / 5 \langle R^6 \rangle$. But when the polydispersity of the sample is ignored and the sample is assumed to be a monodisperse population of spheres of radius $\langle R \rangle$, the structural information from the Guinier plot of the profile is interpreted as $(2\pi/\lambda)^2 \langle R^6 \rangle / 5$. It can be shown that $\langle R^6 \rangle / \langle R^6 \rangle \geq \langle R \rangle^2$. For proof, let us consider a bidisperse population of spheres with the same scattering-length density. For a bidisperse medium, the following relation holds good, irrespective of the values of $R_1$, $R_2$, $\rho_1$ and $\rho_2$.

$$(R_2 - R_1)(R_2^2 - R_1^2)(\rho_1 + \rho_2) + (R_2^6 - R_1^6)(\rho_1 R_1 + \rho_2 R_2) \geq 0.$$ \(12\)

From the above relation, after some algebraic manipulation, we arrive at

$$(\rho_1 + \rho_2)^2(\rho_1 R_1^6 + \rho_2 R_2^6) \geq (\rho_1 R_1^6 + \rho_2 R_2^6)(\rho_1 R_1 + \rho_2 R_2)^2$$

or

$$(\rho_1 R_1^8 + \rho_2 R_2^8)((\rho_1 R_1^6 + \rho_2 R_2^6)) \geq [(\rho_1 R_1 + \rho_2 R_2)]^2$$

or

$$\langle R^6 \rangle / \langle R^6 \rangle \geq \langle R \rangle^2.$$ \(13\)

We have proved the above relation by taking the example of a bidisperse medium, but in general it is also valid for a polydisperse medium. The above analysis indicates that the parameter $M$ extracted from the Guinier plot of the scattering profile of a polydisperse medium can only be higher than the value expected on the basis of average particle size.

E. Interpretation of scattering data, ignoring the multiple-scattering effect

When multiple scattering is not accounted for and the sample is assumed to be a monodisperse population of spherical particles of radius $R$, the $M$ value extracted from the scattering data is given by

$$M = 4\pi^2 R^2 \langle \lambda^{-2} \rangle / 5.$$ \(14\)

From the above relation, we obtain $R = 74.1$ Å for sample (I) and $R = 96.03$ Å for sample (II). Both values are much too small in comparison with the actual values: 300 and 1250 Å. The above analysis shows the importance of accounting for multiple scattering in analyzing the data from thick samples. The higher value of $R$ obtained for sample (II) (relative to that for sample I) is because sample (II) has a higher proportion of 2500 Å particles.
F. Interpretation of multiple-scattering data, assuming the sample to be monodisperse

Now let us estimate the particle size, assuming that multiple-scattering data has been obtained from a monodisperse population of spheres. For monochromatic radiation of wavelength $\lambda$, the Guinier regime of the multiple-scattering profile from a monodisperse population of spheres of radius $R$ is given by (Mazumder & Sequeira, 1992)

$$I(\theta) = \exp \left[-\frac{(2\pi R/\lambda)^2 \theta^2}{5N}\right]. \quad (13)$$

To account for the wavelength distribution of the incident beam, the above expression is modified to

$$I(\theta) = \frac{\int f(\lambda) \exp \left[-\frac{(2\pi R/\lambda)^2 \theta^2}{5N}\right] \, d\lambda}{\int f(\lambda) \, d\lambda}. \quad (14)$$

Replacing $N$ with $3Z\varphi \lambda^2 D^2 R/2$ in the above expression, we obtain

$$M = \frac{8\pi^3 R \langle \lambda^{-4} \rangle}{(15Z\varphi D^2)}. \quad (15)$$

Now, equating the above expression for $M$ with the value extracted from the scattering profiles from samples (I) and (II), we obtain $R = 429.86$ Å for sample (I) and $R = 750.77$ Å for sample (II). The above values are very much larger than the corresponding number-density-weighted particle sizes [310.12 Å for sample (I) and 333.93 Å for sample (II)].

IV. Concluding remarks

We have discussed the method of analysis of multiple small-angle scattering data from an effective medium and experimentally investigated an element of a recently proposed formalism. It has been shown that the values of the parameters extracted from the multiple-scattering profile are in excellent agreement with the values expected from the formalism. It has also been shown that, when multiple scattering is not accounted for, the values of the parameters extracted from the scattering profile can be quite far from the actual values of the parameters. It has also been demonstrated that multiple scattering can be exploited to study very large inhomogeneities, which are otherwise not measurable.

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References