

ANALYSIS OF SMALL ANGLE SCATTERING DATA BY MODEL FITTING

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Abstract

Small angle scattering is a common technique for investigating fluctuations in materials, for sizes ranging from about ten to a few hundred Angstroms. The technique could be more widely used if data analysis were more convenient; however, expressions relating the small angle scattered intensity to materials parameters of interest tend to be complicated. Non-linear regression fitting of experimental small angle scattering data from metallurgical systems is discussed, and the analysis procedure is demonstrated for two models on data from a Ni-Si alloy undergoing phase separation. It is concluded that if sufficient information is available to permit the proper model to be identified, quantitative values for the relevant materials parameters can be extracted in a rather routine manner, provided the parameters are not too closely coupled.

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Introduction

To a first approximation, the small angle scattering (SAS) of neutrons or x-rays is not sensitive to the exact positions of atoms within the sample. Rather, the SAS is related to the size, shape and contrast of inhomogeneities contained in the sample. In this sense, SAS is a low resolution technique. The technique is concerned with investigating the scattering from structures with sizes ranging from about ten to a few hundred Angstroms, depending on the characteristics of the instrument being used. Roughly speaking, this covers the range of sizes from just above atomic dimensions to approaching what can be viewed with optical microscopy, a range of particle sizes that can be investigated with transmission electron microscopy (TEM). Also, the SAS range is partially overlapped by field-ion microscopy (small sizes) and scanning transmission electron microscopy (large sizes). The microscopy techniques are capable of resolving details of the object far better than can a small angle scattering experiment, but such data are tedious to reduce for large numbers of particles. The major advantage of SAS lies in the fact that a large volume is sampled (typically, on the order of 10^{16} - 10^{18} particles are sampled in a SAS experiment), and in a carefully done experiment the scattering pattern inherently contains statistically reliable information. As was pointed out so elegantly by Guinier (1969), scattering and microscopy techniques are complementary and, it will be argued presently, the SAS community could benefit by making more use of this fact. In particular, it will be concluded that additional information may be necessary to select the model which best represents the system being investigated with SAS. Then, techniques such as non-linear regression can be utilized to extract materials parameters of interest from the scattering data. Such information about inhomogeneities in this size range is useful to metallurgists because of the direct relationship between the physical and/or mechanical properties of a material and the size, composition and dispersion of particles contained in it.

In this paper, a brief discussion is given of the classical Guinier approximation for small angle scattering. It is then argued that for most real systems the assumptions inherent in the Guinier approximation are rarely satisfied. The consequence is that a specific model must be invoked for the microstructure of a given system, and one attempts to extract the relevant model parameters from analysis of the scattering data. Inasmuch as the mathematical expressions for the scattered intensity often become non-linear, data analysis has become onerous, or one has been forced to make undesirable approximations. The principal goal of this paper is to demonstrate that present-day computer techniques centered on general purpose, non-linear regression codes allow one to fit a specific model to an entire SAS profile in a routine manner. Of course, different models may be required for different systems of interest. This can be accommodated by provision to add models to the software menu and by allowing one to select a specific model at the time of execution.

Relevant Theoretical Background

Small angle scattering investigations have their origin in the work by Guinier (1939); excellent overviews of the subject have been given by Guinier (1963), Kratky (1982) and Porod (1982). Guinier considered a material which was homogeneous on a scale somewhat above atomic dimensions. He imagined a small grain of another homogeneous material embedded in the otherwise homogeneous matrix and asked what would be the scattering from the resulting system. Let the scattering length density (for neutrons, or electron density for x-rays)⁺ have the

⁺ We shall henceforth consider only the case for small angle neutron scattering.

value ρ_0 in the matrix and ρ in the particle, and let $s(r)$ be a form factor which is unity in the particle and zero outside. The amplitude of the scattered wave is given by a Fourier transform which involves a convolution of the Fourier transforms of the form factor and of the scattering length density. The observable small angle scattered intensity[†] is given by

$$S(\vec{q}) = (\rho - \rho_0)^2 \left| \sum(\vec{q}) \right|^2, \quad (1)$$

where $\sum(\vec{q})$ is the Fourier transform of the form factor, $(\rho - \rho_0)$ is the difference in scattering length density between the particle and matrix and q is the magnitude of the scattering vector, \vec{q} ,

$$q = \frac{4\pi}{\lambda} \sin \theta, \quad (2)$$

where θ is half the scattering angle and λ the wavelength of the radiation used in the scattering experiment. The important thing to note from eq. 1 is that it does not depend on the structure of the sample on an atomic scale; it depends only on the size, shape and contrast of the grain. The intensity decreases from a maximum at $q=0$ and becomes practically zero at a scattering angle on the order of magnitude of λ/d , where d is an average dimension of the grain. This consideration determines what size particles can be investigated with a given instrument.

The well know Guinier approximation is based on the assumption of a monodispersion of N non-interacting, well defined particles in an otherwise homogeneous matrix. The SAS is then just N times the intensity scattered by a single particle. Guinier showed that the central region of the scattering profile resulting from this original model could be represented adequately by a Gaussian function

$$S(q) = S(0) e^{-\frac{R_g^2 q^2}{3}}, \quad (3)$$

where R_g is a size parameter commonly called the Guinier radius (or radius of gyration). The Guinier radius equals the root-mean square of the distance of every atom from the center of mass of the particle

$$R_g^2 = \frac{\int_v r^2 \rho(r) dv}{\int_v \rho(r) dv}, \quad (4)$$

where r is a position variable, and the integration is over the volume of the particle. Provided the above stated assumptions are valid, a Guinier plot, i.e., $\ln S(q)$ vs q^2 , should be linear in the low- q region, and one can determine R_g from the slope in the linear region from the expression

$$R_g = \sqrt{-3 \frac{d(\ln S(q))}{d(q^2)}}. \quad (5)$$

[†] The full expression contains an additional term which represents the ordinary high angle diffraction pattern, but this is not of interest in the present context.

Unfortunately, not all metallurgical systems of interest satisfy the assumptions inherent in Guinier's original model, and we shall return to this problem presently.

The tail portion of the SAS pattern also contains useful information. Porod (1951) showed that for a system of particles with finite dimensions in all directions and with well defined interfaces the total interfacial area, in units of cm^2 per cm^3 of sample, can be determined from the asymptotic behavior of the tail portion (or Porod region) of the scattering curve

$$A = \frac{P_c}{2\pi(\Delta\rho)^2}, \quad (6)$$

where the Porod constant, P_c , is given by

$$P_c = \lim_{q \rightarrow \infty} q^4 S(q). \quad (7)$$

Here, and in the following discussion, it is assumed that the scattering data have been converted to absolute cross sections, cm^{-1} per steradian per cm^3 of sample, as has been reviewed by Wignall and Bates (1987) and by Russell, Lin, Spooner and Wignall (1988). It is worth noting that these Porod relationships are valid even if the particles have various shapes and sizes or are densely packed, provided the stated assumptions are fulfilled.

On the other hand, a range of particle sizes is reflected in the Guinier region, and this affects one's ability to extract a characteristic size. For a distribution of particles, $N(r)$, the SAS can be expressed as

$$S(q) = \int_0^{\infty} [V_p(r) \Delta\rho \Phi(qr)]^2 N(r) dr, \quad (8)$$

where $V_p(r)$ is the volume of a particle with radius r and $\Phi(qr)$ is the single particle structure factor which for a spherical particle with constant scattering length density is

$$\Phi(qr) = \frac{3}{(qr)^3} [\sin(qr) - (qr)\cos(qr)]. \quad (9)$$

The presence of a distribution of particle sizes in the sample causes the Guinier plot to be non-linear. In particular, the r^6 factor appearing in the integral in eq. 8 (i.e., V_p^2) causes the larger particles to be overemphasized. This has long been recognized as a problem in extracting particle size information from SAS data as discussed recently by Chen and Epperson (1991). A number of procedures have been developed to allow one to extract the particle size distribution from SAS data of the type just indicated; for example, by Brill and Schmidt (1968), by Vonk (1976), by Glatter (1980) and more recently the maximum entropy method (Potton, et. al. (1984, 1988)).

More insidious is the fact that in many metallurgical systems of interest, the particles are distributed non-randomly or are present in high concentration, the result being that the various particles do not scatter independently. Rather, interference among the scattered waves occurs, and a broad peak is observed in the resulting SAS profile. Although this form of the scattering

function was in violent contradiction to the concept of a linear, low- q region of a Guinier plot, before the advent of digital computers, it was necessary to attempt to extract particle size information from the Guinier plot. While extracting a Guinier radius from the high angle side of the diffuse maximum sufficed to allow one to monitor relative changes in the system, it was nonetheless disconcerting to ignore the most prominent feature in the small angle scattering pattern. A comprehensive discussion of small angle scattering theory and of earlier methods of analyzing SAS data was given by Gerold (1957), and a more recent review was given by Weertman (1981).

A useful discussion of interparticle interference has been given by Porod (1982). While a general, but operational, theory for interparticle interference is lacking, Yarusso and Cooper (1983) have considered the case for liquid-like order among the positions of the scattering particles. They also reviewed several explicit models that have been put forth. Yarusso and Cooper proposed a variation of the hard-sphere, liquid-like interference model

$$S(q) = N \left[V_p(r) \Delta\rho \Phi(qr) \right]^2 \frac{1}{1 + 8 \left(\frac{V_{R_{CA}}}{v_p} \right) \varepsilon \Phi(2qR_{CA})} \quad (10)$$

where ε is a constant close to unity, v_p is the mean system volume per particle, $V_{R_{CA}}$ is the excluded volume and R_{CA} is the radius of closest approach. They were successful in quantitatively modelling small angle x-ray scattering data from sulfonated polystyrene ionomers. Note that a single particle size is assumed in eq. 10.

As has been indicated previously, metallurgical systems almost always contain a range of particle sizes, and one would like to include such a possibility in the scattering function, along with interparticle interference. There is evidence from the literature (de Hoff (1965) and Harkness, Gould and Hren (1969)) that a log-normal distribution may be useful for this purpose. Furthermore, the log-normal distribution has the advantage of tractability in that two geometric parameters define the frequency function. Incorporating this log-normal distribution, along with a modification of the Yarusso-Cooper expression for the interparticle interference function, the scattering function becomes

$$S(q) = \int_0^{\infty} D(r) \left[V_p(r) \Delta\rho \Phi(qr) \right]^2 \frac{1}{1 + 8 \left(\frac{V_{R_{CA}}^*(r)}{v_p} \right) \Phi(2qR_{CA}^*(r))} dr. \quad (11)$$

Here the log-normal frequency distribution is

$$D(r) = \frac{1}{r\sqrt{2\pi \ln \sigma}} \exp \left\{ -1/2 \left[\frac{\ln \bar{r} - \ln r}{\ln \sigma} \right]^2 \right\}, \quad (12)$$

where \bar{r} is a mean particle size which will be discussed more fully in a later section and σ is the standard deviation which defines the width of the frequency distribution function. For reasons

of tractability, we take the radius of closest approach to be a constant times the particle radius, r ($R_{CA} = kr$). Regression techniques are clearly needed if one wishes to extract the relevant materials parameters from eq. 11, and some results are discussed in the following section.

Results and Discussion

To demonstrate the kinds of model fits that can be achieved on real data, some small angle neutron scattering data from a Ni-12.5 at.% Si alloy undergoing phase separation (Polat, Chen and Epperson (1988)) were selected. Transmission electron microscopy reported by Polat, Chen and Epperson (1989) and by Chen and Epperson (1991) demonstrated the γ precipitates (Ni_3Si) to be nearly spherical, hence eq. 9 is a valid representation of the structure factor for this alloy system. If one further assumes that the log-normal particle size distribution is a reasonable representation and that the interparticle interference is of the liquid-like type as discussed in the previous section, eq. 11 can be utilized. A general, non-linear regression code written by Gibson (1985) and obtained from Miller (1985) was modified and extended for the present work.

Figure 1 illustrates the log-normal with interference model fits to two representative sets of Ni-12.5 at.% Si data; Fig. 1a, 29 hrs. at 505°C and Fig. 1b, 22 hrs. at 550°C.

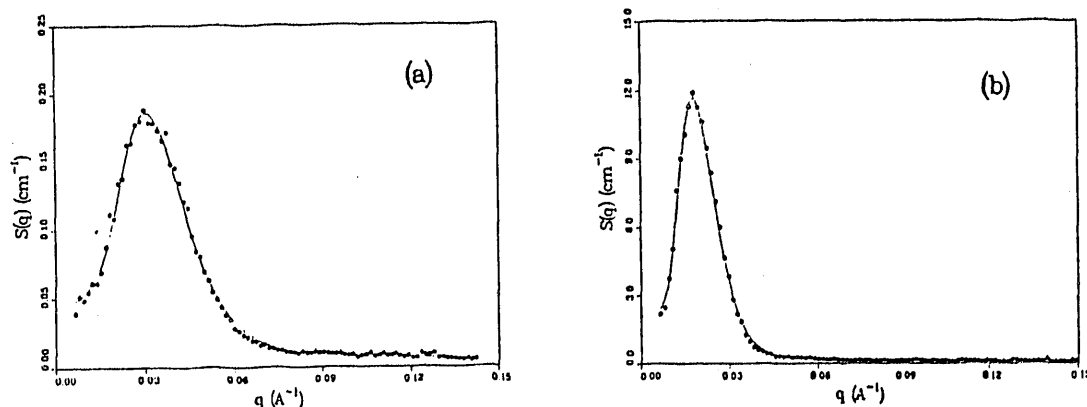


Fig. 1. Log-normal size distribution with interparticle interference model fits to the small angle neutron scattering from Ni-12.5 at.%Si: a) 29 hrs. at 505°C and b) 22 hrs. at 550°C.

The filled circles are the experimental data and the solid lines are the model fits. The values of the fitted parameters are given on the left side of Tables I and II, respectively. The fits are quite satisfactory, except at the base on either side of the interference maxima. Other models can, of course, be fitted to these data. As a means of illustrating this point, the sphere with interference model (eq. 10) was fitted to the same two data sets. The fits are shown graphically in Fig. 2, and the fitted parameters are given in the middle of Tables I and II. Clearly, attempting to model these data with a single particle size results in a qualitatively less satisfactory fit, as one would intuitively expect. The right sides of Tables I and II give the spherical radii estimated from Guinier fits to the data on the high angle side of the interference maxima. Attempting a Guinier fit to such SAS data characterized by an interference maximum is, however, not recommended.

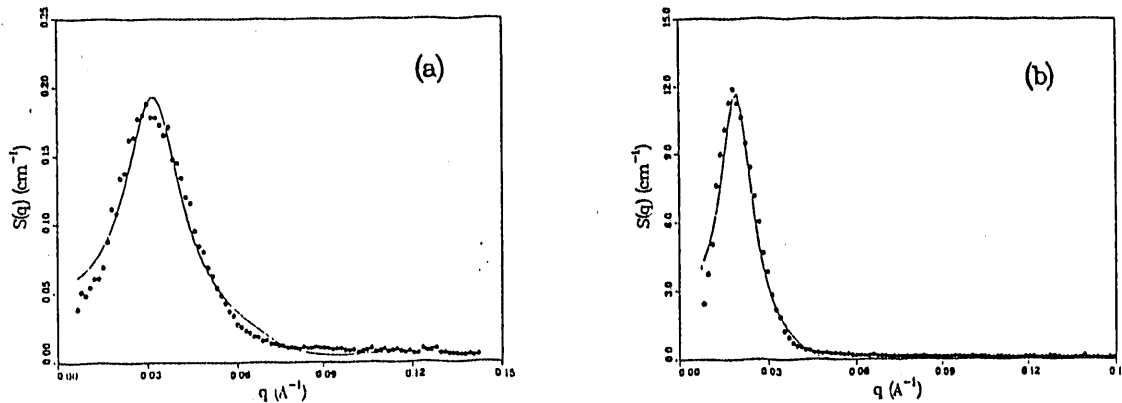


Fig. 2. Sphere of uniform size with interparticle interference model fits to the small angle neutron scattering from Ni-12.5 at.%Si: a) 29 hrs. at 505°C and b) 22 hrs at 550°C.

One notes from Tables I and II that there are large differences for the volume fractions of second phase (f_v) and for the contrast ($\Delta\rho$) from the two models. Although the log-normal with interference model is more plausible for this alloy system and the fits to the experimental data are consistently better, this point needs further critical investigation.

Table I. Model Fitting of SANS Data for Ni-12.5 at.%Si Annealed 29 Hours at 505°C

<u>Log-normal with interference</u>	<u>Sphere with interference</u>	<u>Guinier approximation</u>
\bar{r} 40.6Å	\bar{r} 47.6Å	R_{sph} 59.3Å
f_v 0.254	f_v 0.076	
$\Delta\rho$ $1.31 \times 10^9 \text{ cm/cm}^3$	$\Delta\rho$ $2.56 \times 10^9 \text{ cm/cm}^3$	
σ 1.285	R_{CA} 83.97Å	
k_{RCA} 1.464	B_{kg} 0.0053 cm^{-1}	
B_{kg} 0.0059 cm^{-1}		

Table II. Model Fitting of SANS Data for Ni-12.5 at.%Si Annealed 22 Hours at 550°C

<u>Log-normal with Interference</u>	<u>Sphere with interference</u>	<u>Guinier approximation</u>
\bar{r} 74.2Å	\bar{r} 85.5Å	R_{sph} 118.6Å
f_v 0.540	f_v 0.110	
$\Delta\rho$ $2.63 \times 10^9 \text{ cm/cm}^3$	$\Delta\rho$ $7.14 \times 10^9 \text{ cm/cm}^3$	
σ 1.313	R_{CA} 137.8Å	
k_{RCA} 1.278	B_{kg} 0.0374	
B_{kg} 0.1069		

It is worthwhile noting that the surface represented by the intensity expression can be relatively complicated. In particular, one should be aware that it may contain local minima. In such instances, the "solution" obtained from non-linear regression fitting will be sensitive to the direction of approach. Some probing, using various initial estimates for the parameters, may be necessary to be sure that the proper solution has been found. Also, if the value of any parameter is known independently, it can be held constant while the remaining parameters are fitted.

Because there will be a need to compare results from non-linear regression fitting of SAS data with results obtained from other means, it is worthwhile considering some of the properties of the log-normal distribution, eq. 12. Figure 3 shows log-normal particle size distributions calculated for $\bar{r} = 25\text{\AA}$ and $f_v = 0.10$, for selected values of σ . These frequency functions are normally distributed about $\ln \bar{r}$. By differentiation of eq. 12 and setting the result equal to zero, one finds the most probable radius to be

$$r^* = \exp(\ln \bar{r} - \ln^2 \sigma). \quad (13)$$

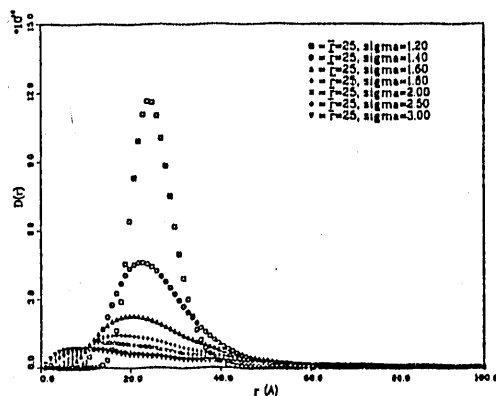


Fig. 3. Log-normal particle size distributions calculated for $\bar{r} = 25\text{\AA}$ and $f_v = 0.10$ for selected values of σ , as given in the figure.

The width of the log-normal distribution as characterized by σ can have a dramatic effect on the most probable radius of the distribution as illustrated by Fig. 4a.

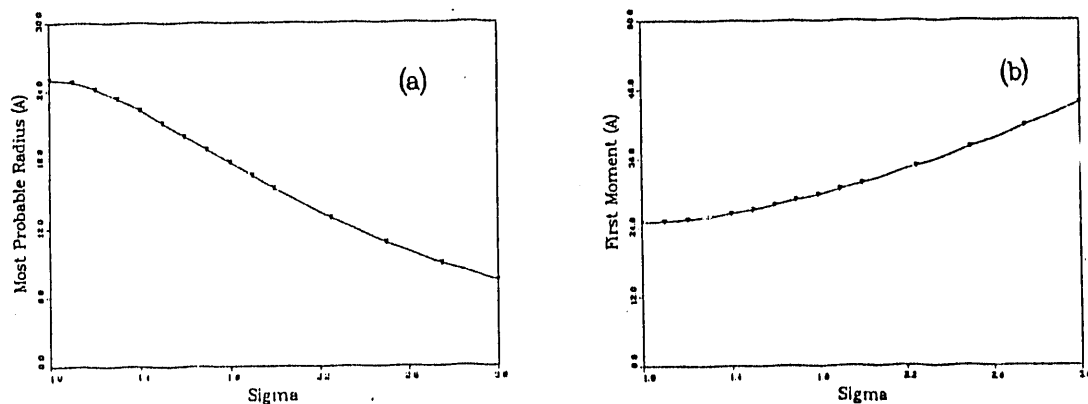


Fig. 4. Some characteristics of the log-normal distribution for the simulated data shown in Fig. 3: a) most probable radius vs. sigma and b) first moment vs. sigma.

The n'th moment, of the log-normal distribution is given by

$$M_n = \exp \left[n \ln \bar{r} + \frac{n^2}{2} \ln^2 \sigma \right]. \quad (14)$$

Note that the geometric mean of the distribution corresponds to \bar{r} only for the case when $\sigma=1.0$, i.e. for a delta function. The first moment as a function of σ is shown in Fig. 4b for the distributions shown in Fig. 3. Unless recognized, these properties could conceivably result in meaningless comparisons of SAS size information with that obtained by other methods.

Conclusions

It has been demonstrated that non-linear regression techniques can be used in a reasonably routine manner to fit a specific microstructural model to an entire small angle scattering profile from a metallurgical sample. This method is now practical, even if there is interparticle interference in the scattering pattern and if a distribution of particle sizes exists. It must be kept in mind, however, that no mathematically unique solution for the scattering function exists in terms of microstructural parameters. The computer codes can only obtain the best values for the model used. The task of the investigator is to find the proper model which yields a small angle scattering profile equivalent, within experimental error, to the observations. Selecting the model is not a trivial task; other models than the two discussed above can, for example, produce an interference peak. Two obvious examples are: 1). depletion zones about a system of randomly dispersed nuclei as proposed by Walker and Guinier (1953), or 2). spinodal decomposition as characterized by weak fluctuations of composition about the mean value, but correlated over relatively long distances, as described by Cahn (1961, 1962), Cahn and Hilliard (1958, 1959), and Cook (1970). While good agreement of the model fit to the experimental data is necessary, that alone is not sufficient to claim the best model has been chosen. Additional information is generally needed for model selection. It is recommended that higher resolution techniques such as transmission electron microscopy or atom-probe field-ion microscopy be used, when practical, to aid in this selection process.

Since the software package can be constructed to contain any number of models, with one being selected for use at the time of execution, the non-linear regression fitting as discussed here should evolve into a versatile data analysis tool.⁺ Only by utilizing such advanced tools can one hope to extract maximum information from the SAS data. Note, for example, that if one knows the particle size distribution, related information such as the total interfacial area and number density of particles is immediately accessible. The method cannot, however, resolve materials parameters if they are too closely coupled in the intensity expression.

A major deficiency exists with regards to our present understanding of interparticle interference. References have been cited in which general discussions of this topic have been given. Unfortunately, many of the expressions that have been put forth are not explicit, and hence are not usable. Additional theoretical guidance is needed.

⁺ Nothing inherent in the formalism restricts its usage to small angle scattering applications, or even to scattering data analysis.

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