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The Influence of the Available Scattering-Vector Range on the Retrieval of Particle-Size Distributions from Small-Angle Scattering Intensity Data

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Abstract

The determination of the particle-size distribution [$D(r)$] from small-angle scattering intensity data is discussed. The influence of the maximum available scattering vector h_{max} on $D(r)$ retrieval is investigated with the help of numerical experiments with previously known solutions. The numerical corrector method provides a good answer even in cases where h_{max} is much smaller than those values necessary with other retrieval methods.

1. Introduction

The use of small-angle scattering (SAS) techniques (Guinier & Fournet, 1955; Glatter & Kratky, 1982) has steadily increased during recent years, partly due to the availability of powerful X-ray and neutron radiation sources. Analytical solutions and various numerical methods have been proposed (Glatter, 1977; Fedorova & Schmidt, 1978; Glatter, 1980; Mulato & Chambouleyron, 1996) to retrieve the size distribution [$D(r)$] of the particles producing the scattering from SAS intensity data [$I(h)$], where r is the particle characteristic size and h is modulus of the scattering vector defined by $4\pi \sin\theta/\lambda$, where θ is half the scattering angle and λ is the wavelength of the radiation used. The analysis of systems having scattering particles with varied size (polydisperse systems) is extremely involved because it is always an ill-posed problem, in which the inverse relationship between scattering intensity $I(h)$ and particle size $D(r)$ has to be worked out from a limited range of experimental information.

In the present paper, $D(r)$ will be considered to be a distribution of particles of varying size but identical shape (solid spheres) embedded in a matrix, thus forming a two-phase system. With the use of *gedanken* experiments, we analyse the influence of the available scattering-vector range on the retrieval process of $D(r)$ using the new recurrence numerical corrector method of Mulato & Chambouleyron (1996). Theoretical experiments will be performed to study the detrimental effects of truncated SAS intensity data, *i.e.* the maximum available scattering vector h_{max}, on the retrieved $D(r)$.

2. Numerical method for computing $D(r)$

The anti-transform integral equation relating $I(h)$ and $D(r)$ is (Fedorova *et al.*, 1978)

$$D(r) = (1/r^2) \int_0^\infty [I(h)h^4 - C_4]\{[1 - 2/(hr)^2] \cos 2hr - [1 - 1/2(hr)^2](2/hr) \sin 2hr\}\, dh, \quad (1)$$

where C_4 is the limit of $I(h) \times h^4$ for $h \to \infty$.

In a previous study, Mulato & Chambouleyron (1996) reported a numerical corrector method to compute $D(r)$ from truncated experimental $I(h)$ curves. The proposed fixed-point iteration may be written as

$$D_{k+1} = D_k + P_2\{T_3[I - T_1(D_k)]\}, \quad (2)$$

where P_2 represents the projector operator on the physical subspace where each $D(r)$ should belong, T_1 is the integral transformation that relates the SAS data to the original $D(r)$ and T_3 is the transformation described by (1) using the integration limits h_{min} and h_{max} in place of 0 and ∞. In (2), I is the original SAS intensity data. At each step, a new $D(r)$ curve is obtained based on a previous one.

3. Considerations on a safe h interval for the finding of a good C_4

The different Gaussian-like $D(r)$ used in the present work are given by

$$D(r) = (1/\text{Norm}) \exp\{-[(r - r_c)/w]^2\}, \quad (3)$$

where r_c is the center of the distribution, w its width and Norm a normalization constant. Fig. 1 shows (solid lines) two $D(r)$'s with $r_c = 5$ Å, $w = 2$ Å, Norm = 3.54 (Fig. 1*a*) and $r_c = 50$ Å, $w = 5$ Å, and Norm = 8.86 (Fig. 1*b*).

The theoretical scattering intensity function $I(h)$ of these particle-size distributions were obtained following the procedure described by Mulato & Chambouleyron (1996). Figs. 2(*a*) and (*b*) show $I(h) \times h^4$ as a function of h for the two $D(r)$ distributions of Figs. 1(*a*) and (*b*), respectively. This kind of plot is illustrative of the

most important aspects of the numerical calculation of the anti-transform integral equation: the determination of C_4 [Fedorova & Schmidt, 1978, see equation (3)]. It can be seen in Figs. 2(*a*) and (*b*) that: (i) the amplitude of the oscillations decreases with increasing h; (ii) the number of oscillations increases with increasing particle size (r_c); and (iii) the scattering-vector value for which $I(h) \times h^4$ becomes constant is smaller for $D(r)$'s having a larger r_c. Although not seen at the scale of the drawing of Fig. 2(*b*), the $I(h) \times h^4$ curve reaches a constant value only for $h > 0.6\,\text{Å}^{-1}$ (the oscillations in the [0.4–0.6 Å^{-1}] h interval can be easily seen on a different scale).

Up to now, C_4 was calculated in the region of the $I(h) \times h^4$ curve tail where no oscillations exist. This tail would represent the interval between $h_{C4} = 0.6$ and $h_{max} = 0.8\,\text{Å}^{-1}$ in Fig. 2(*b*). In fact, this h range can be imagined as an h safety interval needed to obtain a good C_4. If the available h_{max} is smaller than this h_{C4} value, increasing problems can be expected. The obtained C_4 value will not be representative of the $\lim_{h\to\infty} [I(h) \times h^4]$. As a consequence, the retrieved $D(r)$ might not be the correct one and the method fails.

It is clear that the safety h interval and the relative values of h_{max} and h_{C4} necessary to obtain a reliable C_4 will depend on the specific particle-size distribution under analysis. The dependence is shown in Fig. 3, where minimum h_{C4} values have been represented as a function of r_c for different Gaussian-like distributions of spherical scatterers. The parallel dotted lines represent different w values; from bottom to top, w = 25, 15, 10 and 5 Å, respectively. The dashed horizontal line at $h_{C4} = 0.8\,\text{Å}^{-1}$ is a limit; for $w \leq 2$ Å, a safe h_{C4} does not exist for $h < 0.8\,\text{Å}^{-1}$, which is our maximum theoretical scattering-vector value. It should be noted that the spacing between dotted lines does not scale linearly with variations of w. The figure also indicates that some safe h_{C4} values are larger than the h_{max} values achievable in conventional small-angle scattering experiments (for example, h_{max} of the order of $0.3\,\text{Å}^{-1}$). This means that a particle-size distribution having $r_c < 80$ Å and $w < 25$ Å would not be correctly retrieved. According to Fig. 3, the retrieval of particle-size distributions as the ones given in Figs. 1(*a*) and (*b*) would require h_{max} values much larger than 0.8 and $0.6\,\text{Å}^{-1}$, respectively.

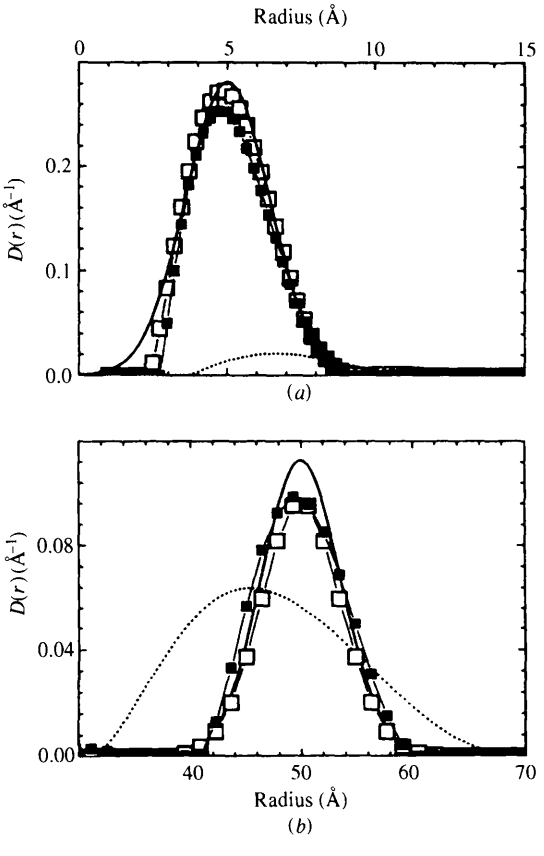

Fig. 1. Gaussian-like particle-size distributions (see text). (*a*) Original: solid line (r_c = 5 Å, w = 2 Å, Norm = 3.34). Retrieved: open squares ($h_{max} = 0.8\,\text{Å}^{-1}$), solid squares ($h_{max} = 0.63\,\text{Å}^{-1}$ and $h_{C4} = 10^{-3}\,\text{Å}^{-1}$), and dotted line ($h_{max} = 0.4\,\text{Å}^{-1}$ and $h_{C4} = 10^{-3}\,\text{Å}^{-1}$). (*b*) Original: solid line (r_c = 50 Å, w = 5 Å, Norm = 8.86). Retrieved: open squares ($h_{max} = 0.8\,\text{Å}^{-1}$), solid squares ($h_{max} = 0.2\,\text{Å}^{-1}$), and dotted line ($h_{max} = 0.1\,\text{Å}^{-1}$).

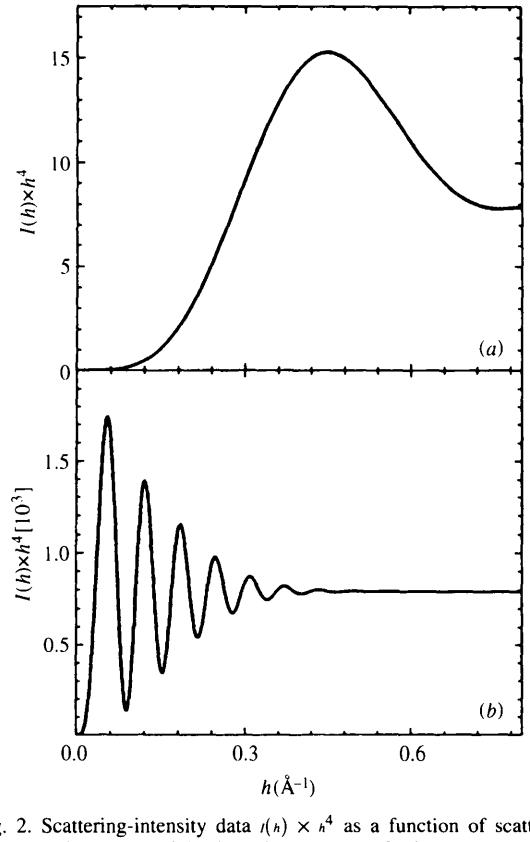

Fig. 2. Scattering-intensity data $I(h) \times h^4$ as a function of scattering vector for the particle-size distributions of Figs. 1(*a*) and (*b*), respectively.

4. Improved results with smaller h_{max} values

Advantage can be taken from the fact that the numerical corrector method is based on a fixed-point iteration process. As a different procedure, C_4 will now be determined as the mean value of $I(h) \times h^4$ in a selected tail interval.

Consider the original $D(r)$ (solid line) of Fig. 1(*a*) and its corresponding $I(h)$ (Fig. 2*a*). Using $h_{max} = 0.8$ and $h_{C4} = 0.6\,\text{Å}^{-1}$, the present numerical corrector method retrieved the particle-size distribution shown as open squares in Fig. 1(*a*). If h_{max} is chosen equal to or smaller than $0.6\,\text{Å}^{-1}$ and h_{C4} is chosen as 75% of h_{max}, the corrector method does not work correctly. It is interesting to note that when h_{max} is chosen as $0.63\,\text{Å}^{-1}$ and h_{C4} as $10^{-3}\,\text{Å}^{-1}$, the retrieved $D(r)$ is the one shown as solid squares in Fig. 1(*a*). In fact, a substantive portion of the original particle-size distribution was retrieved. Pinning h_{C4} at $10^{-3}\,\text{Å}^{-1}$ and decreasing the h_{max} value even more leads to a poor result in the retrieved $D(r)$. The dotted line in Fig. 1(*a*) corresponds to $h_{max} = 0.4\,\text{Å}^{-1}$. In summary, decreasing h_{max} leads to a retrieved particle-size distribution having a smaller area and also to a shifted $D(r)$ peak.

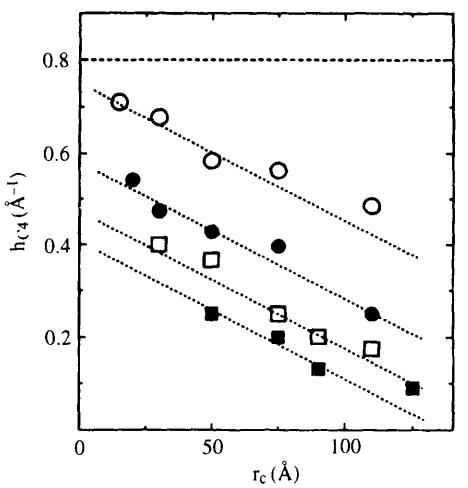

Fig. 3. Theoretical h_{C4} limit as a function of r_c (see text). h_{C4} are safe h values, above which the $I(h) \times h^4$ function reaches its constant value (C_4). The parallel dotted lines from bottom to top represent different $D(r)$'s where w = 25, 15, 10 and 5 Å, respectively. For w equal to or less than 2 Å, h_{C4} stays above the horizontal dashed line at $0.8\,\text{Å}^{-1}$.

Consider now the example shown in Fig. 1(*b*). As previously stated, h_{C4} was chosen as 75% of h_{max} in all cases. The results given by the numerical corrector method are shown in Fig. 1(*b*) as open squares (for $h_{max} = 0.8\,\text{Å}^{-1}$), solid squares (for $h_{max} = 0.2\,\text{Å}^{-1}$) and dotted line (for $h_{max} = 0.1\,\text{Å}^{-1}$). For $h_{max} < 0.1\,\text{Å}^{-1}$, increasing failures in the retrieval process were observed. Under such extreme conditions, the method does not work any longer.

5. Conclusions

In summary, the numerical corrector method works reasonably well even for h_{max} and h_{C4} values much smaller than those predicted by a safe h_{max} value, which determines the interval where no oscillations exist in the $I(h) \times h^4$ curve. This is a clear advantage of the fixed-point iteration process, which improves the retrieval at each new step. The weak dependence of the method on h_{max} makes the numerical generation of tails of the scattering intensity data unnecessary. The retrieval of narrow particle-size distributions centered at small r_c values requires a high h_{max}. Broad and intense r_c-centered $D(r)$'s, on the other hand, can be retrieved from $I(h)$ scattering data with relatively small h_{max} values.

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