Scaling Functions for the Finite-Size Effect in Fractal Aggregates

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Abstract
An exact scaling function for the finite-sized fractal aggregates sharply bounded by a sphere of radius \( R \) has been established by using the convolution square of the shape function of aggregates and the inhomogeneity function, which is introduced to take into account the presence of inhomogeneity in fractal aggregates. The scaling function for an inhomogeneous aggregate is mainly determined by the geometric shape of the aggregate but is also dependent upon the degree of inhomogeneity present in the aggregate. The differences between the scaling function reported in this paper and the commonly used ones, \( \exp(-r/\xi) \) and \( \exp[-(r/\xi)^2] \), are discussed. The simulating calculations have shown that the use of different scaling functions will not only influence the cross-over behavior between the Guinier regime and the fractal regime, but also make the low-\( q \) scattering intensity converge to different values.

I. Introduction
Small-angle scattering (SAS) techniques (with neutrons, X-rays or light) have been widely applied to explore the structures of inhomogeneous fractal aggregates (Schaefer, Martin, Wiltzius & Cannel, 1984; Weitz, Huang, Lin & Sung, 1985; Aubert & Cannel, 1986; Honjo, Ohta & Matsushita, 1987; Hurd, Schaefer & Martin, 1987; Vacher, Woigner, Pelou & Courtens, 1988; Schmidt, 1991), which are often encountered in various fields related to the manipulation of ultrafine particles. Normally, a quantitative SAS investigation of aggregate structures involves a numerical fitting of the experimentally collected scattering profile to a specific physical model so as to characterize the microstructure by evaluating the structural parameters such as fractal dimension \( D_f \), the size of elementary blocks \( r_0 \) and fractal correlation length \( \xi \). Nevertheless, it has been proved that the satisfactory interpretation of scattering data by fractal aggregates is not always easy. To a large extent, whether or not the structure of aggregates is correctly characterized depends on the soundness and completeness of the model used. One of the major difficulties involved in building a good theoretical model may be a reasonable description of the scattering profile within the cross-over range (in the neighborhood of \( q = 1/\xi \), where the important boundary structural information of aggregates is contained. There have been several pioneering articles (Sinha, Freitoft & Kjems, 1984; Freitoft, Kjems & Sinha, 1986; Teixeira, 1988) in which a scaling function like \( \exp(-r/\xi) \) was phenomenologically introduced to take account of the finite-size effect of aggregates. The formula based on the scaling function \( \exp(-r/\xi) \) and the generally accepted power-law pair-correlation function \( g(r) \propto (r/r_0)^{d-D_f} \) has been effectively used to describe the experimentally measured scattering data by protein solutions (Chen & Teixeira, 1986), fumed silica aggregates (Freitoft, Kjems & Sinha, 1986) and gold colloids (Dimon, Sinha & Weitz, 1986). Quite often, it seems that the function \( \exp(-r/\xi) \) is taken as a scaling function whenever it is needed. To our knowledge, however, there seems to be no unambiguous and strict arguments in the literature as to the physical reason for using \( \exp(-r/\xi) \) as a scaling function. In the Lead Article by Martin & Hurd (1987), it was said that the scaling function was used to account for the fact that if \( r \) is much larger than the radius of the fractal \( R \), the correlation function must vanish. So the scaling function \( h(r/R) \) should be equal to 1 for \( r/R \ll 1 \) and vanish rapidly (faster than a power law) for \( r/R \gg 1 \). This argument is quite ambiguous and indefinite. Many choices can be made to satisfy these requirements. A recent study by Jullien (1992) declared that some choices were forbidden for scaling functions such as, for example, the simple Yeaviside function because it results in negative intensities. So Jullien wrote 'even for an object with a sharp boundary, scaling function must exhibit some
It is clear that the word ‘width’ is also too vague to give an unambiguous definition of a scaling function. Moreover, from the statements of Jullien, one might perceive some implication (not explicitly mentioned) that a Yeaviside function cannot be used as a scaling function since it leads to negative intensities. Consequently, it seems as if some functions similar to Yeaviside functions but with a particular ‘width’ to avoid the negative intensity could be used as scaling functions. This implication is entirely unfounded.

In the present paper, we present a discussion on the scaling function for finite-sized fractal aggregates. A detailed theoretical derivation of the small-angle scattering by fractal aggregates is also presented. The main advantages of our treatment of scattering behavior by aggregates are that the fundamental principles of diffraction are closely followed so as to find a method of taking into account the aggregate size effect and that the scaling function is set up in a natural and strict manner. We introduce an inhomogeneity function $K(r)$ and use the convolution of an aggregate shape function to describe the inhomogeneity and the size effect of fractal aggregates.

With the present treatment, we clarify the physical implication of the scaling function involved in the SAS intensity formula and discuss the differences between the scaling function derived in the present paper and that used usually, $\exp(-r/\xi)$, and also $\exp[-(r/\xi)^2]$, which was introduced by Jullien (1992). We believe that obtaining a thorough understanding of scaling functions by starting from an ideal fractal aggregate will greatly help to reach realistic and more complicated modifications of scaling functions.

II. Fundamental scattering formulae

It is well known that, in the framework of scattering theory for point-like scatterers, the scattering intensity $I_{sc}(q)$ from a single aggregate composed of identical particles can be generally written as (in electronic units)

$$I_{sc}(q) = f(q)^2 \int_{-\infty}^{+\infty} \rho(u)\rho(u')\sigma(u)\sigma(u') du' \cdot$$

$$\times \exp(-iuq) \exp(iu'q) \, du \, du', \quad (1)$$

where $q$ is the scattering vector with $q = 4\pi(\sin \theta)/\lambda$, $f(q)$ and $\rho(u)$ are, respectively, the particle scattering ability and the number density distribution function that is defined in the whole space; the function $\sigma(u)$ is introduced to describe the aggregate shape and size. For a real finite-sized aggregate, the particle number density must vanish to zero everywhere beyond the aggregate. So $\sigma(u)$ is assumed to have the following definition:

$$\sigma(u) = \begin{cases} 1 & \text{inside aggregate} \\ 0 & \text{outside aggregate}. \end{cases} \quad (2)$$

With $u' = u - r$ and a structure-related Patterson function defined as

$$P(r) = \int_{-\infty}^{+\infty} \rho(u)\rho(u + r)\sigma(u)\sigma(u + r) \, du,$$  

(1) can be simply rewritten as

$$I_{sc}(q) = f(q)^2 \int_{-\infty}^{+\infty} P(r) \exp(-iqr) \, dr. \quad (4)$$

It is easy to note that the definition of the aggregate shape function, (2), actually circumscribes an effective integration domain for (3), which varies with the translation vector $r$. Only the overlapping part of $\sigma(u + r)$ and $\sigma(u)$, i.e. the shaded area shown in Fig. 1, contributes to the integral. Therefore, one has

$$P(r) = \int_{V(r)} \rho(u)\rho(u + r) \, du$$

$$= V(r)V(p(u))g(r)K(r), \quad (7)$$

where $V(r) = V'(r)/V$, with $V'(r)$ the volume of the overlapped parts of $\sigma(u)$ and $\sigma(u + r)$ and $V$ is the total volume of the aggregate; $\langle \rho(u)\rho(u + r)\rangle_{V(r)}$ is the average value of the function $\rho(u)\rho(u + r)$ over the overlapping domain $V(r)$.

If into (5) is put an ensemble average correlation function $g(r)$, which is generally defined as

$$g(r) = \langle \rho(u)\rho(u + r)\rangle_{V}/\langle \rho(u)\rangle_{V}, \quad (6)$$

the Patterson function becomes

$$P(r) = V(r)V(p(u))g(r)K(r)$$

$$= N_p V(r)K(r)g(r), \quad (7)$$

where $N_p$ is the total number of particles within the aggregate; the newly introduced function $K(r)$, which we call the inhomogeneity function is defined as

$$K(r) = \langle \rho(u)\rho(u + r)\rangle_{V}/\langle \rho(u)\rangle_{V} \quad (8)$$

It is a function that takes into account the contributions of density inhomogeneity present in aggregates.
SCALING FUNCTIONS

to the Patterson function. Certainly, as indicated in (8), for a homogeneous object, the function \( K(r) \) behaves as a constant of unity with no effect on the Patterson function.

Substituting the Patterson function (7) into (4), one arrives at the scattering intensity formula for a single aggregate:

\[
I_{\text{eu}}(q) = N_p I_f(q) I^2 \left[ 1 + \int V(r)K(r)g'(r) \exp(-iqr) \, dr \right]
\]

or

\[
I_{\text{eu}}(q) = N_p I_f(q) I^2 \left[ 1 + \int V(r)K(r)g'(r) \exp(-iqr) \, dr \right] + \int V(r)K(r)g'(r) \exp(iqr) \, dr
\]

(9)

if the correlation function is written as \( g'(r) = \delta(0) + g'(r) \), with \( \delta(0) \) referring to the case where the interparticle distance or the correlation length \( r = 0 \). It should be pointed out that this treatment requires the function \( g'(r) \) to be always equal to zero at \( r = 0 \).

It is not difficult to understand that the same procedure as above can be followed to work out the general scattering-intensity formula for an aggregate system composed of a large number of identical aggregates:

\[
I_{\text{eu,di}}(q) = N_q I_f(q) I^2 \left[ 1 + \int V(r)K_d(r)g'_d(r) \exp(-iqr) \, dr \right]
\]

(10)

where \( F(q) \) designates the scattering ability of each aggregate, \( N_q \) is the number of aggregates concerned in the aggregate assembly, \( V_d(r) \) and \( K_d(r) \) stand for the volume function and inhomogeneity function, respectively, for the aggregate system and \( g'_d(r) \) corresponds to the aggregate pair-correlation function determined by an imagined point array with all the points occupied by the aggregate centroids.

Generally, it is very difficult to write down all the functions involved in (10) for a particular system. But the common aggregate systems that develop under a single growth mechanism may possibly be regarded as homogeneous on a scale larger than the dimension of individual aggregates. In this case, the inhomogeneity function \( K_d(r) \) can be statistically approximated to unity. Moreover, when the amount of sample illuminated by a radiation beam is much larger than the individual aggregates, the interference effect among aggregates will be concentrated in such a narrow range centered at the origin of reciprocal space that it is beyond the range over which the interparticle interference effect can be experimentally observed. This fact can be easily seen from the following relation:

\[
\int V_d(r)K_d(r)g'_d(r) \exp(-iqr) \, dr = V_d(q) \ast G'_d(q),
\]

(11)

where \( V_d(q) \) and \( G'_d(q) \) are the Fourier transforms of the aggregate pair-correlation function and the volume function of the irradiated sample, respectively. When the sample size is relatively large, \( V_d(q) \) will differ from zero only in the vicinity of \( q = 0 \). As a result, the interference between aggregates will be merged into the primary beam and thus be difficult to observe. To make this matter clearer, a simple quantitative estimate can be performed. Suppose the irradiated portion of the sample is like a sphere of radius \( R' = 1 \) mm, then \( V_d(q) = V_0 \left[ 3(\sin R'q - R'q \cos R'q)/(R'q)^3 \right]^2 \). When \( R'q \) increases to about 4.5, the corresponding \( V_d(q) \) decays to zero. After this point, there occur several submaxima but their peak values are too small to be observed (about \( V_0/1000 \)). One may therefore take this point as a limit for the observable \( V_d(q) \); the range of \( q' \) over which the interaggregate interferences are evident enough to be observed is about \( 1/R' \approx 4 \times 10^{-7} \) Å\(^{-1}\). Obviously, this range is too small to be reached by the usual small-angle scattering techniques. Finally, (10) can be reduced to a very simple form:

\[
I_{\text{eu,di}}(q) = N_q I_f(q) I^2.
\]

(12)

This approximation indicates that, in the usual cases, the total scattering intensity by an aggregate assembly may be equal to an averaged sum of the scattering intensities by all the individual aggregates. So, if all the aggregates concerned are identical, the total scattering intensity formula will be

\[
I_{\text{eu,di}}(q) = NI_f(q) I^2 \left[ 1 + \int V(r)K(r)g'(r) \exp(-iqr) \, dr \right]
\]

(13)

where \( N = N_p N_q \), the total number of particles constituting the aggregate assembly. It should be pointed out that, in the above derivation of the scattering-intensity formula, the polydispersity in the sizes of particles and aggregates was not considered for the sake of simplicity. But, since our interests in the present paper are confined to the clarification of the scaling function, the formula derived without considering polydispersity will offer the same generality in the results. The sophisticated formula including various polydispersities and the relevant discussion will be published elsewhere.

III. Scaling functions and discussions

For an aggregate assembly composed of aggregates with a spherical symmetry, (13) can be further simplified. In this case, one may obtain a familiar scattering intensity formula

\[
I_{\text{eu}}(q) = NI_f(q) I^2 \left[ 1 + 4\pi \int V(r)K(r)g'(r) \sin(qr)r \, dr \right]
\]

(14)
where \( f(\mathbf{q}) \) is usually called the form factor and denoted as \( P(\mathbf{q}) \) and the subsequent term is the structure factor \( S(\mathbf{q}) \), which is completely determined by the nature of the aggregate structure. Comparing (14) with the formulae used in the literature (Sinha et al., 1984; Teixeira, 1988; Jullien & Botet, 1987), one can immediately see that the product of the convolution square of the particle shape factor \( \sigma(u) \) and the inhomogeneity function \( K(r) \) exactly takes the place of the scaling function \( \exp \left(-r/\xi \right) \), with \( \xi \) interpreted as the correlation length or the size of the aggregates. As mentioned before, the function \( \exp \left(-r/\xi \right) \) was first phenomenologically introduced by comparison with percolation phenomena. It has a rather simple form but its validity is still an open question. In contrast, by looking at the derivation of (14), one can easily see that the function \( V(r)K(r) \) actually arises as a natural outcome from the mathematical treatment when the aggregates have finite sizes. Physically, this means that an ideal finite aggregate, like a spherical portion isolated from an infinite aggregate characterized by a correlation function \( g'(r) \), has its own correlation function:

\[
\Phi(r) = V(r)K(r)g'(r).
\]

(15)

It is in this sense that the function \( V(r)K(r) \) can be thought of as a scaling function, which serves to reduce the correlation function \( g'(r) \) with increasing \( r \) to give a new correlation function \( \Phi(r) \) for the finite aggregate. Here it is worth remembering that the function \( g'(r) \) is often used in the case of finite aggregates with no justification simply because any finite aggregate isolated from an infinite fractal aggregate of correlation function \( g'(r) \) has the same fractal structure pattern as the infinite one. However, this does not necessarily imply that they have the same correlation function. The correlation function for a finite-sized aggregate should be \( \Phi(r) \). It gives the averaged probability, over all centroids of the particles and all aggregate orientations, of finding the particle pairs with separation \( r \) inside the aggregate. Therefore, for any given aggregate containing \( N_p \) particles, the function is supposed to be normalizable into \( N_p - 1 \), namely

\[
N_p = 4\pi \int_0^\infty \Phi(r) r^2 dr + 1.
\]

Obviously, this property restricts the arbitrary choice of scaling functions.

As seen from (15), the scaling function \( V(r)K(r) \) is determined both by the geometry of the aggregates and the inhomogeneity present in the aggregates. This fact shows, on the one hand, that the scaling function is not only a function of aggregate size as implied by \( \exp \left(-r/\xi \right) \) but also depends on the fractal structure that is characterized by the fractal dimension \( D_f \). On the other hand, the scaling function is different from the shape function, which is used for describing the cut-off behavior of the density function \( \rho(r) \) at the edge of finite-sized aggregates. Generally, any finite aggregate with a largest dimension \( \zeta \) in some direction will be allowed to have a non-zero probability of finding two particles separated by a distance \( r < \zeta \) but to have a zero probability for \( r > \zeta \). Undoubtedly, this requires the scaling function to have zero values at \( r > \zeta \). With a spherical fractal aggregate of radius \( R \) as an example, it is easy to find that this kind of aggregate will have largest correlation length \( 2R \). So the corresponding scaling function is supposed to vanish to zero for \( r > 2R \) rather than \( r > R \) as in the case of the shape function. In addition, the shape function may be a Yeaviside-like function with a constant 1 for \( r < R \) and 0 for \( r > R \) whereas a scaling function for a finite object will be expected to show a continuously decaying behavior with a maximum of 1 at \( r = 0 \). Accordingly, it is clear that any function like a shape function previously used or a Yeaviside function even with some ‘width’, as mentioned by Jullien (1992), may not be used as a correct scaling function.

In order to clarify further the properties of scaling function \( V(r)K(r) \), some analytical and numerical comparisons with the function \( \exp \left(-r/\xi \right) \) have been made. First, a non-fractal homogeneous aggregate is examined. This can also be taken as an approximation of the weak fractal aggregates. In such cases, the inhomogeneity function \( K(r) = 1 \) and the scaling function is exactly \( V(r) \). For spherical aggregates of radius \( R \), \( V(r) \) has a very simple analytical expression (Hosemann & Bagchi, 1962):

\[
V(r) = \begin{cases} 
1 - 3/4(r/R) + 1/16(r/R)^3 & r < 2R \\
0 & r > 2R.
\end{cases}
\]

(16)

This function has a maximum of 1 at \( r = 0 \) and shows a monotonous decrease down to zero with \( r \) increasing up to \( 2R \). A schematic comparison between \( V(r) \), \( \exp \left(-r/\xi \right) \) and \( \exp \left[-(r/\xi)^2 \right] \) is given in Fig. 2, where \( \xi \) is assumed to be the radius \( R \). It can be seen that, on the whole, the functions \( \exp \left(-r/\xi \right) \) and \( \exp \left[-(r/\xi)^2 \right] \) both show decaying trends similar to \( V(r) \). In fact, their similar properties enable us to understand why the function \( \exp \left(-r/\xi \right) \) can be used to describe the experimental data in some cases. But the differences between them are quite evident. The scaling function \( V(r) \) is reasonably equal to zero for \( r > 2R \), whereas the functions \( \exp \left(-r/\xi \right) = 0.1353 \) and \( \exp \left[-(r/\xi)^2 \right] = 0.0183 \) at \( r = 2R \) and approach zero only when \( r \to \infty \). Undoubtedly, the tailing effect in the latter case will inevitably cause errors in the scattering-data analysis. An example is given below using different scaling functions to perform a normalization treatment.

From (14), the following relation will hold when \( q = 0 \):

\[
S(0) = 1 + 4\pi \int_0^\infty h(r)g'(r)r^2 dr = N_p.
\]

(17)
where $h(r)$ represents the scaling function and $N_p$ the total number of particles involved in the aggregate. Supposing that an aggregate has a fractal structure characterized by a pair-correlation function

$$g'(r) = AD_f r^{D_f-4}/4\pi r_0^{D_f}$$

and then substituting (16) and (18) into (17), one obtains

$$N_p(r_0/R)^{D_f} = 2^{D_f} A \left[ 1 - \frac{3}{2} \left[ \frac{D_f}{(D_f + 1)} \right] \right]$$

$$+ \frac{D_f}{2(D_f + 3)}$$,

where $A$ is a proportionality constant and $r_0$ is the radius of the particles. When $D_f = 3$, the left side of the above equation exactly equals the proportionality constant $A$, i.e. $N_p(r_0/R)^3 = A$. This result indicates that the constant $A$, in fact, can be regarded as the packing density $N_p(r_0/R)^3$ of the aggregate when its fractal structure is extrapolated to the state $D_f = 3$. So when $A$ is supposed to be 0.637, the extrapolated aggregate is a hard-sphere densely packed system bounded by a sphere of radius $R$; when $A$ is supposed to be unity as in the treatment of Teixeira (1988), the aggregate may be interpreted as a compact spherical object. Clearly, these results are both practically plausible.

Substituting $h(r)$ in (17) by $\exp(-r/\xi)$ and $\exp[-(r/\xi)^2]$ for the same aggregate, however, one may reach the following quite different outcomes for $D_f = 3$, respectively:

$$N_p(r_0/R)^3 = 6A$$ and $$N_p(r_0/R)^3 = 3/2 \Gamma(3/2) A = 1.33A.$$ Evidently, in these two cases, at least one of the two parameters $\xi$ and $A$ will have unreasonable values in the numerical analysis if the scaling functions $\exp(-r/\xi)$ or $\exp[-(r/\xi)^2]$ are used. If one wants to keep $\xi$ equal to the real value of the aggregate $R$, the parameter $A$ will be only $1/6$ or $1/1.33$ that of the real value. Otherwise, one has the same $A$ as in the case where $V(r)$ is used as a scaling function but $\xi$ will be smaller than $R$ by a factor $1/1.82$ or $1/1.10$. Certainly, some more complicated intermediate cases are also likely to occur in a particular data-fitting process, in which a compromise must be made between $A$ and $\xi$.

In order to get the results derived using the scaling functions $\exp(-r/\xi)$ or $\exp[-(r/\xi)^2]$ closer to the real case, one possibility is to regard $\xi$ as a radius of gyration of the aggregate. For a spherically symmetrical aggregate, the radius of gyration $R_g$ is given by

$$R_g^2 = \int_0^\infty \rho(r)\sigma(r)r^4 dr \int_0^\infty \rho(r)\sigma(r)r^2 dr.$$ (20)

By using the power-law density distribution function $\rho(r) \propto r^{D_f-3}$ for fractal aggregates, it follows that $R_g = R[D_f/(D_f + 2)]^{1/2}$. Therefore, one has $R_g = (3/5)^{1/2} R$ when $D_f = 3$. Comparison of $R_g$ with the above results shows that such a reduction is still not enough for the scaling function $\exp(-r/\xi)$ but a little too much for the function $\exp[-(r/\xi)^2]$.

Not only does the use of the scaling functions $\exp(-r/\xi)$ and $\exp[-(r/\xi)^2]$ cause problems in the normalization treatment but it also results in large differences in the description of the scattering behavior compared with the case using $V(r)$. We still examine a homogeneous (or quasihomogeneous) aggregate. So the function $K(r) = 1$ and the fractal dimension is taken as 3. Consequently, the corresponding pair-correlation function $g'(r)$ in (18) will be reduced to a constant $AD_f/4\pi r_0^4$ over the whole $r$ range if the local fluctuation of $g'(r)$ in the short range can be neglected. Taking into account these properties of the aggregate and using (16), we derive the structure factor:

$$S(q) \sim 1 = A(R/r_0)^3[3(\sin Rq - Rq \cos Rq)/(Rq)^3]$$

(21)

Obviously, this result has the same form as the well known form factor of particles when the particles are assumed to be homogeneous spheres of radius $R$. Certainly, (21) has an approximation of Guinier form, $A(R/r_0)^3 \exp[-q^2 R^2/5]$ when $Rq$ is quite small, and its envelope demonstrates a Porod's law when $Rq$ is quite large.

In contrast, a different situation will occur if the scaling functions $\exp(-r/\xi)$ and $\exp[-(r/\xi)^2]$ are substituted into the above procedure. For these two
scaling functions, the following structure factors are obtained, respectively:

\[ S(q) - 1 = \left(3A/qro\right)(\xi/r_0)^2 \times \sin \left[2 \arctan \left(\xi/q\right)\right]/\left[1 + (\xi/q)^2\right] \]  
\[ S(q) - 1 = 1.334A(\xi/r_0)^3 \exp \left[-(\xi/q)^2/4\right]. \]

(22)

(23)

The differences between these three structure factors can be seen in Fig. 3, where the curves are calculated by setting \( A = 1, \xi = R \) and \( R/r_0 = 10 \). Compared with the structure factor given by \( V(r) \), the structure factors given by (22) and (23) do not show any oscillations over the whole \( q \) range. The lack of these oscillations is obviously due to the superfluous contribution from the tails in \( \exp(-r/\xi) \) and \( \exp[-(r/\xi)^2] \). In addition, in the low-q range, the structure factor calculated with \( \exp(-r/\xi) \) is much larger than the normal structure factor; the one calculated with \( \exp[-(r/\xi)^2] \) has values close to normal. It is easy to understand that the different results of normalization using different scaling functions should be responsible for the above differences.

Now let us turn our discussions to an inhomogeneous fractal aggregate system, where the fractal dimension \( D_f < 3 \), and thus the presence of inhomogeneity must be taken into account. In other words, the function \( V(r) \) will be multiplied by a factor, the inhomogeneity function \( K(r) \), to form the scaling function in comparison with the homogeneous cases.

In terms of the definition of the inhomogeneity function in §II and in view of the fact that every point that belongs to the fractal object has the same type of environment, it can be verified that, for a finite-sized fractal aggregate, the function \( K(r) \) can be simply written as

\[ K(r) = \frac{\langle \rho(u) \rangle_{V(r)}}{\langle \rho(u) \rangle_V} = \frac{N'_p/N_p V(r)}{\int_{V(r)} \rho(r) \, dV/V} \]

(24)

where \( N'_p \) and \( N_p \) are the numbers of particles involved within the overlapping domain \( V'(r) \) and the whole aggregate \( V \), respectively. Adopting the power-law density function for fractal aggregates, \( p(r) \propto r^{-D_f-d} \) and, taking into account the spherical symmetry, we have

\[ K(r) = J/2 D_f R^D V(r), \]

(25)

where \( J = 1/2\pi \int_{V(r)} r^D p(r)^3 \, dV \). The relationships of \( K(r) \) with the correlation distance \( r \) and the fractal dimension \( D_f \) are given in plots in Fig. 4.

It is interesting to note that \( K(r) \) is not a monotonous function like \( V(r) \). With \( r \) increasing, it first increases and reaches its maximum above 1, then it decreases steadily to a particular value below 1 before an upward turn takes place as the overlapping volume approaches zero. Moreover, the lower the fractal dimension \( D_f \) is, the larger the deviations from

![Fig. 3. Structure factors (R/r_0 = 10, D_f = 3) for three different scaling functions: (1) exp(-r/R); (2) V(r); (3) exp[-(r/R)^2].](image)

![Fig. 4. Inhomogeneity functions K(r) for (1) D_f = 2.8, (2) 2.6, (3) 2.4, (4) 2.2, (5) 2.0, (6) 1.8 and (7) 1.6.](image)
1 the function $K(r)$ will have. It should be pointed out that the approximated inhomogeneity function $K(r)$ shows a divergence at the boundary $r = 2R$ since the function $V(r)$ converges to zero faster than the integral $J$ does with $r$ approaching $2R$. However, this property will not make the scaling function unreasonable. The scaling functions, as a product of $V(r)$ and $K(r)$, are also calculated for different fractal dimensions and plotted in Fig. 5, where the curves for $\exp\left(-\frac{r}{\xi}\right)$ and $\exp\left[-\left(\frac{r}{\xi}\right)^2\right]$ are given for comparison. It can be observed that the inhomogeneity present in fractal aggregates modifies the function $V(r)$ in such a way that the scaling function decreases more slowly in the first half of the range compared with the function $V(r)$, but faster in the second half of the range. In other words, with decreasing fractal dimension $D_f$, the scaling function shifts from close to $\exp\left(-\frac{r}{\xi}\right)$ towards $\exp\left[-\left(\frac{r}{\xi}\right)^2\right]$ in the first half of the range; while, in the second half of the range, it moves away from $\exp\left[-\left(\frac{r}{\xi}\right)^2\right]$ and much further from $\exp\left(-\frac{r}{\xi}\right)$.

Nevertheless, on the whole, it seems that the modifications by the inhomogeneity function $K(r)$ do not change the function $V(r)$ as much as the functions $\exp\left(-\frac{r}{\xi}\right)$ and $\exp\left[-\left(\frac{r}{\xi}\right)^2\right]$ deviate from $V(r)$ in the second and first half of the range, respectively.

Combining the scaling function with different fractal dimension $D_f$ as plotted in Fig. 5, we have calculated the structure factor $S(q)$ with the results presented in Fig. 6. It can be seen that weak fractal structure is characterized by strong oscillations in the structure-factor curves. So in these cases there seems no possibility to extract a correct fractal dimension from the slope of $S(q)$ in a log–log plot. But this kind of oscillation can be rapidly suppressed as the fractal dimension decreases and almost no oscillation can be observed above $D_f = 2.2$. Additionally, one finds that, accompanying the suppression of the oscillations, the structure-factor curves fall in the lower-$q$ range and stretch further to the right in the higher-$q$ range with the result that a wider linear regime is developed. These results are caused by the number $N_p$ of particles involved in the aggregates of the same dimension $R$ and the packing manner related to the constant $A$, which will become smaller as the fractal dimension $D_f$ decreases, and subsequently the interparticle interferences will be weakened.

In Fig. 7, two sets of structure-factor curves are given, which are calculated using scaling functions $V(r)K(r)$ and $\exp\left(-\frac{r}{\xi}\right)$ with respect to different fractal dimensions. On the whole, the structure factors from different scaling functions with the same fractal dimensions $D_f$ show similar values in the higher-$q$ ranges, while in the intermediate- and lower-$q$ ranges they are quite different. In the intermediate-$q$ range, the structure factor calculated by $V(r)K(r)$ for each $D_f$ seems to be very close to the structure factor calculated by $\exp\left(-\frac{r}{\xi}\right)$ with a $D_f$ value about 0.2 larger. Obviously, such differences may result in a
positive variance in the fractal dimension if the scaling function \( \exp \left( -r/\xi \right) \) is used in a practical data-fitting process. In the lower-\( q \) range, the structure factor from \( V(r)K(r) \) always converges to a lower value than does the structure factor from \( \exp \left( -r/\xi \right) \) for the same fractal dimension \( D_f \), as is shown in Fig. 3. This kind of difference reflects the fact that the use of different scaling functions will lead not only to different cross-over behavior between the Guinier regime and the fractal regime, but also cause the structure factors to converge to different values after their cross overs if the microstructure parameters are evaluated with the same set of values in each case. In other words, for a given set of experimental SAS data, different values of the structural parameters may be obtained when the scaling functions adopted are different. Therefore, it is important to have a correct scaling function that really describes the fractal structure of the aggregates before a data-fitting process is started. Otherwise, the obtained structure information may not be true and reliable owing to the inappropriate use of a scaling function even though the fitting looks good from the mathematical point of view.

**IV. Concluding remarks**

In summary, in the present paper, we have shown that the scaling function for finite-sized fractal aggregates can be expressed by a product of the convolution square of the shape function and the inhomogeneity function. Through a strict derivation, it is believed that the correct scaling function for finite-sized aggregates of sharp boundaries is \( V(r)K(r) \), rather than \( \exp \left( -r/\xi \right) \) or \( \exp \left( -r/\xi^2 \right) \). This conclusion has obtained support from the above discussions on the problems caused by using \( \exp \left( -r/\xi \right) \) or \( \exp \left( -r/\xi^2 \right) \). The simulating calculations for structure factors has demonstrated that large differences in structure factors can occur in the intermediate- and lower-\( q \) ranges when the function \( V(r)K(r) \) is substituted by \( \exp \left( -r/\xi \right) \) with the same values for the structure parameters. This result indicates that the structural parameters may be evaluated with erroneous values if the scaling function \( \exp \left( -r/\xi \right) \) is used in a practical data-fitting treatment for a monodispersed and sharply bounded aggregate assembly. It should be pointed out that most real cases may be more or less complicated than the case described in the present paper but, starting from this point, one may find a way of solving the particular problems. The non-sharp boundaries of fractal aggregates can be described by a Yeaviside function with a certain ‘width’ given by the shape function \( \sigma(r) \). The polydispersity in the aggregate radius can also be taken into account on the basis given above. We would like to point out that a scaling function like \( \exp \left( -r/\xi \right) \) could be taken as an approximation to the averaged \( V(r)K(r) \) for a widely polydispersed aggregate system, where the radii of aggregates are distributed over a wide range and the parameter \( \xi \) is thus a distribution-related statistical quantity. In addition, taking into account the particle-size distribution and short-range non-fractal correlation between particles is another significant study, which is closely related to the correct description of a scattering profile in the upper cross over. We have combined Sinha’s model (Freitolf, Kjems & Sinha, 1986) with the particle-size distribution to construct a lower-end scaling function, with \( V(r)K(r) \) at the higher end, so as to describe the cross over from the fractal regime to Porod’s law. Detailed simulation work on these aspects is under progress. In this paper, we emphasize the establishment of a correct scaling function for finite-sized fractal aggregates through a strict derivation because such a process provides the possibility to describe scattering contributions from both fractal interparticle correlation and the geometrical details of the aggregates.

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