Small-angle scattering from generalized self-similar Vicsek fractals

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Abstract.
An analytical approach for calculating the small-angle X-ray or neutron scattering (SAXS/SANS) from generalized self-similar Vicsek fractals (GSSVF) is presented; each fractal consists of spherical subunits. The system considered is a mass-fractal, generated iteratively from a regular 3D Vicsek fractal structure. Its fractal dimension is controllable and increases with increasing the value of the scaling factor. Small-angle scattering (SAS) intensity is determined from a set of non-interacting, randomly oriented and uniformly distributed GSSVF fractals. It is shown that in the fractal region, the curve \( I(q) \propto q^{-D} \) is approximately log-periodic with the period equal to the scaling factor of fractal; here \( D \) and \( I(q) \) are the fractal dimension and the SAS intensity, respectively. In particular, the positions of deepest minima and highest maxima are log-periodic, and their number coincides with the number of fractal iterations. The log-periodicity of the scattering curves is a consequence of the self-similarity of GSSVF.

1. Introduction
Small-angle scattering (SAS) [1, 2] from fractal systems [3] provides valuable information about the structure at nano-micro scales [4, 5, 6]. The SAS intensity decays in the momentum space according to the power law [7]:

\[ I(q) \propto q^{-D}. \] (1)

Here \( q \) and \( D \) are the absolute value of the scattering vector and the fractal dimension of the fractal, respectively. This type of scattering is often referred to as the power-law decay. Equation (1) is valid within the reciprocal fractal region, given by

\[ 1/l \lesssim q \lesssim 1/l_{\text{min}}. \] (2)

Here \( l \) is the size of the fractal and \( l_{\text{min}} \) is the minimal distance between the scattering centers.

In the fractal region, the scattering intensity is proportional to the Fourier transform of the pair distribution function \( g(r) \), describing the spatial correlations between particles inside a fractal. Equation (1) leads to

\[ g(r) \propto r^{-D-3}, \] (3)

by Erdélyi’s theorem for asymptotic expansion of Fourier integrals [3]. This equation is satisfied within the fractal region in real space

\[ l_{\text{min}} \lesssim r \lesssim l. \] (4)
Therefore, three parameters can be extracted from experimental fractal scattering intensities: the exponent and the edges of the fractal region in the $q$-space, which appear as “knees” in the scattering line on a logarithmic scale. For random fractals, it is rather difficult to extract more information from the scattering, because a fine structure of particle correlations is usually smeared due to the randomness. One can expect that deterministic fractals, being more ordered, allow us to obtain additional information from the scattering data.

Analytical calculations of SAS intensity from the 3D triadic Cantor and Vicsek sets were reported in Ref. [10]. In the previous paper [12], the generalized 3D Cantor set was suggested, whose dimension can vary from zero to three by means of varying the scaling factor. If the SAS is considered from monodispersive sets, which are randomly oriented and placed, then the scattering intensities represent minima and maxima superimposed on a power-law decay, with the exponent equal to the fractal dimension of mass fractal. This dependence of the intensity on momentum is called the generalized power-law decay.

Recently, it was shown [13] that in the reciprocal fractal region, the curve $I(q)q^D$ is approximately log-periodic with the period equal to the scaling factor of the fractal. In this paper we relate this log-periodicity with the self-similarity of generalized self-similar Vicsek fractals (GSSVF) and explicitly show that the pair distribution function $g(r)$, describing spatial correlations between positions of the fractal subunits, also obeys the generalized power law only on the average, and polydispersity smears the spatial correlations between the units composing the fractal.

We present a scheme, first introduced in Ref. [13], for estimating the iteration number, the scaling factor and the total number of structural units in GSSVF from the scattering curves. The present analysis of GSSVF is based on the method of calculating the scattering amplitude, developed in Refs. [14, 15, 16, 17].

### 1.1. Background on small-angle scattering

Here we restrict ourselves to two-phase systems, which are composed from homogeneous units of “mass” density $\rho_m$. The units are immersed into a solid matrix of “pore” density $\rho_p$. Then [1, 2] we can consider the system as if the units were “frozen” in a vacuum and had the density $\Delta \rho = \rho_m - \rho_p$. The density $\Delta \rho$ is called scattering contrast. The scattering intensity (that is, the cross section per unit volume of the sample) is given by

$$I(q) = n|\Delta \rho|^2V^2 \langle |F(q)|^2 \rangle,$$

where $n$ is the fractal concentration, $V$ the “mass” volume of each fractal, and $F(q)$ the normalized form factor

$$F(q) = \frac{1}{V} \int_V e^{-iq \cdot r} \, dr,$$

obeying the condition $F(0) = 1$. The brackets $\langle \cdots \rangle$ stand for the ensemble averaging over all orientations of $q$. Therefore, the SAS intensity at zero angle will be $I(0) = n|\Delta \rho|^2V^2$. Once a deterministic fractal is composed of the same objects, say, $N$ balls of radii $R$, then (see, e.g., Ref. [13])

$$F(q) = \rho_q F_0(qR)/N,$$

with $\rho_q = \sum_j e^{-iq \cdot r_j}$ the Fourier component of the density of the balls, and $r_j$ are the center-of-mass positions of balls. Here the ball form factor of unit radius is given by [2]

$$F_0(z) = 3(\sin z - z \cos z)/z^3.$$

By substituting Eq. (7) into Eq. (5), we obtain for the scattering intensity

$$I(q) = I(0)S(q)|F_0(qR)|^2/N,$$

where $S(q)$ is the structure factor.
The quantity $S(q)$ is called structure factor, and it is intimately connected to the pair distribution function, see Eq. (21) below. In the fractal region $q \lesssim 1/R$ because of $R \leq l_{\text{min}}$, and hence $F_0(qR) \simeq 1$. This implies that the scattering intensity is proportional to the structure factor in the fractal region.

### 1.2. Construction of 3D generalized self-similar Vicsek fractals

We follow the procedure described in Ref. [13] by starting with a cube with edge $l_0$ and placing in its center a ball of radius $l_0/2$. This is zero fractal iteration, called the initiator. The iteration rule (generator) is to replace the initial ball by nine smaller balls of radius $\beta_s l_0/2$ (Fig. 1). We choose the Cartesian coordinates such that the origin lies in the cube center, and the axes are parallel to the cube edges. The position of one ball is at the origin, while the centers of the eight other balls are shifted from the origin by the vectors

$$a_j = \{\pm \beta_t l_0, \pm \beta_t l_0, \pm \beta_t l_0\},$$

with all the combinations of the signs, where

$$\beta_t \equiv (1 - \beta_s)/2.$$  

Repeating the same operation to each ball $m$ times, we arrive at the $m$th approximant, which is composed of the $N_m = 9^m$ balls of radius $r_m = \beta_s^m l_0/2$.

The ideal GSSVF is obtained in the limit $m \to \infty$. Its Hausdorff (fractal) dimension can be derived from the condition $[3] N_1 \beta_s^{D} = 1$. For GSSVF it takes the explicit form

$$D = \frac{2 \log 3}{\log \beta_s},$$

where the restriction $\beta_s < \sqrt{3}/(\sqrt{3} + 2)$ is imposed on the scaling factor in order to avoid overlapping of the balls.
Figure 2. (Color online) Scattering intensities \((16)\) for the first four iterations of monodisperse GSSVF. The scattering curve for the \(m\)th iteration is scaled up, by the factor \(10^\beta (m-1)\). Black at low \(q\) shows the Guinier regions \((q \lesssim 1/l)\); light gray (orange) represents fractal regions, given by Eq. \((2)\); dark gray (blue) at high \(q\), Porod regions \((q \gtrsim 1/r_m)\).

2. Form factor

One can obtain \([11, 12, 13]\) an analytical formula for the monodisperse form factor

\[
F_m(q) = F_0(r_m q) \prod_{i=1}^{m} G_i(q),
\]

for \(m = 1, 2, \cdots\). Here the generative function reads

\[
G_m(q) = \frac{[1 + 8 \cos(u_m q_x) \cos(u_m q_y) \cos(u_m q_z)]}{9},
\]

with \(u_m \equiv l_0 \beta_s l_0^{m-1}, m = 1, 2, \cdots\). Then SAS intensity is obtained with the help of Eq. \((5)\)

\[
I_m(q)/I_m(0) = \langle [F_m(q)]^2 \rangle,
\]

see Fig. [2].

A real physical system is almost always composed of scatterers of different sizes, and, therefore, a more realistic description should include polydispersity. The distribution function \(D_N(l)\) of the scatterer sizes is defined in such a way that \(D_N(l) dl\) gives the probability of finding a fractal whose size falls within the interval \((l, l + dl)\). We consider a log-normal distribution function of the fractal size

\[
D_N(l) = \frac{1}{\sigma l (2\pi)^{1/2}} \exp \left( - \frac{[\ln(l/l_0) + \sigma^2/2]_2}{2\sigma^2} \right),
\]

where \(\sigma = [\ln(1 + \sigma^2)]^{1/2}\). The mean length and its relative variance are

\[
l_0 \equiv \langle l \rangle_D, \quad \sigma_r \equiv \langle (l^2)_D - l_0^2 \rangle^{1/2}/l_0,
\]

with \(\langle \cdots \rangle_D = \int_0^{\infty} \cdots D_N(l) dl\).

The resulted intensity is the average of \((16)\) over \((17)\) [see Figs. 3(a) and 3(b)]

\[
I_m(q) = n |\Delta \rho|^2 \int_0^{\infty} \langle [F_m(q)]^2 \rangle V_m^2(l) D_N(l) dl,
\]

where \(V_m = N_m \beta_s^3 m V_0\) is the total volume of “mass” in the \(m\)th iteration.
3. Pair distribution function
The pair distribution function gives information about the spatial correlations inside the fractal [2]. It can be written as

\[
g(r) = \frac{r^3}{4\pi r^2} \frac{2}{N(N-1)} \sum_{k<j} \langle \delta(r - r_{jk}) \rangle_D,
\]

where \(r_{jk} = |r_j - r_k|\) are the relative distances between the ball centers. It gives the probability density to find a particle at the distance \(r\) from another particle, provided a position of the latter particle is given. Then, the structure factor \(S(q)\) of the fractal system can be related to \(g(r)\) through

\[
S(q) = 1 + (N-1) \int_0^{+\infty} dr \frac{4\pi r^2}{l_0^3} g(r) \frac{\sin qr}{qr}.
\]

The polydispersity effect in Eq. (20) can be taken into account by averaging over [17] [Fig. 4(a) and 4(b)].

4. Discussions of the Results
The properties in real-space of \(g(r)\) are shown in Fig. 4(a) and 4(b). The self-similarity of GSSVF manifests itself in the periodicity, on the double logarithmic scale, of the minima and highest maxima. Explicitly, in the fractal region of real space, \(g(r)\) has the property (Fig. 4(b)):

\[
g(\beta_s r) \left(\frac{\beta_s^D}{r_s^D} \right)^{D-3} = g(r) \frac{r^D}{r_s^D}.
\]

This is a consequence of the log-periodicity of \(S(q)q^D\) in the fractal region in reciprocal space, which follows from Eq. (21). Conversely, the log-periodicity of \(S(q)q^D\) results from the log-periodicity of \(g(r)r^{3-D}\).

5. Conclusions
- We develop a model of deterministic fractal, which allows explicit analytic solutions for the scattering amplitude.
Figure 4. The influence of polydispersity on $g(r)$. Scattering curves for the distribution width $\sigma_r = 0.2, 0.4$ are scaled-up for clarity by $10$ and $10^2$ respectively. (a) expression (20) for various values of the relative variance $\bar{\chi}$ and (b) the quantity $g(r)r^3 - D$ clearly shows the log-periodicity. The period in the log scale is equal to $\log_{10}(1/\beta_s)$, where $\beta_s$ is the scaling factor of the fractal.

- We derived analytical expressions for the form factor and the pair distribution function.
- We suggest a scheme for interpreting the experimental data in the framework of deterministic mass fractals with a single scale. Once we a priori know that the fractal is of that kind then we can extract a number of parameters from the scattering intensity (Fig. 3):
  (i) The fractal dimension from the generalized power law.
  (ii) The fractal scaling parameter from the period on the logarithmic scale.
  (iii) The number of fractal iteration, which is equal to the number of periods of function $I(q)q^D$.
  (iv) The lower and upper fractal edges from the diagram $I(q)q^D$ as the beginning and end of “periodicity region”.
  (v) The total number of structural units, from which the fractal is composed, by the relation $N_m = (1/\beta_s)^mD$.

- The results can be applied for a various number of structures, whose geometries are based on an iteration of a fractal system.

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