MICROSTRUCTURAL CHARACTERIZATION OF SURFACE FRACTALS USING SMALL-ANGLE SCATTERING

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Received August 28, 2017

Abstract. The microstructural properties of deterministic surface fractals with a directional growth pattern are determined from the small-angle scattering (SAS) intensity of neutrons, X-ray or light, as a function of the momentum transfer. The monodisperse intensities are calculated for a system consisting of a macroscopic number of randomly oriented surface fractals with uncorrelated positions. We show that, within the model, the scattering data can be used to determine surface thickness, the size of smallest building unit, the fractal dimension or the iteration number. The obtained microstructural quantities are related to the scaling factor of the fractal. We explain these correlations and illustrate the above findings on a model of hydrant deterministic fractal.

Key words: small-angle scattering, 3D hydrant deterministic fractal surfaces, structural properties, scaling factor, fractal form factor.

PACS: 05.45.-a, 61.43.Hv, 61.05.fg, 61.05.cf, 61.43.-j.

1. INTRODUCTION

The production of fractal surfaces is often intended [1, 2] in the synthesis of nano/micro patterned surfaces with predefined functional properties [3–7], and is usually achieved by electron beam or optical lithography. New materials, organized as deterministic fractal surfaces, with exact self-similarity, have improved, or at least similar, properties compared to their random, only statistically self-similar counterparts. This is also reflected by the scattering transfer image obtained from the random fractal structure, whose response can be close to that of a certain deterministic model geometry [8]. For example, a better agreement with the 3D Koch snowflake model was obtained in the interpretation of experimental small-angle neutron scattering (SANS) data from fractal supernucleosomal chromatin structures [9] when randomness was also taken in account, and introduced into the construction algorithm of the theoretical model.

Numerical computations applied to a more general class of deterministic mass fractals [10] recently extended the potential of the theory aided SAS data interpretation technique to describe experimental results obtained from formations with a vast structural diversity. In this sense, theoretical numerical computations performed using deterministic fractals, modeling existing natural or artificial formations, bear a major advantage, beside the lower computational time and resource requirements. Following this path, one can deduce analytic behavior of the variation of the aimed properties and geometric parameters, such as the SAS intensity spectrum or radius of gyration, as a function of the parameters considered during the modeling phase [11–15]. Then, using a sufficiently fine discretization of the model’s parameters in their applicability domains, a matrix with the indexed results can be constructed. This form is the optimal one, and is further used in fitting experimental measurements to obtain the physical quantities describing the experimental sample. That is why the framework of deterministic fractals provides “exactly solvable models”, crucial in the elucidation and description of the structural properties of the new generations of nano/micro-structured surfaces, studied using experimental SAS techniques.

It was recently proven that any surface fractal is composed of mass fractals of the same fractal dimension, so that the scattering amplitude of the surface fractal is the sum of the amplitudes of the composing mass fractals [16, 17]. One can apply this observation to a 3D surface Cantor-like fractal with a center of symmetry built from Cantor dust at various iterations. This is why, the structural information that can be extracted from experimental SAS data is the same as that for mass fractals [16]. However, although for surface fractals the maxima and minima have an approximate log-periodicity with the factor $1/\beta_s$, their nature is different as compared to periodicity in the case of mass fractals. In the latter case, the log-periodicity arises from the self-similarity of distances between scattering centers, while in the former case, it arises from the self-similarity in sizes of the scattering centers [17].

In this paper we extend the applicability of the above results to the class of hydrant deterministic fractal surfaces [18], which exhibit a directional growth pattern. We show that for this class of surfaces, considered for the first time in this kind of studies, its thickness can be also obtained, from the interpretation of SAS data. This is in addition to the other structural information specific to surface fractals with a center of symmetry. As we shall see, the main prerequisite needed to explain these structural properties is the existence of a power-law distribution of sizes of units that build up the surface fractal.
2. MODEL AND FORMULATION

2.1. GENERAL CONSIDERATIONS

There are various methods to gather experimental data that can be used to determine the fractal parameters of different natural or artificial fractal-structured samples, such as scattering, imaging, adsorption or electron energy transfer experiments. A technique proven to be especially useful in the nano-/micro-metric range of dimensions is Small-angle scattering of waves such as light, X-rays or neutrons (SAS). It does not require any special sample preparation with the possibility to alter the fractal’s structure. The obtained quantities are averaged over a macroscopic volume. It can also differentiate between surface [19] and mass [20] fractals. These features of SAS allow investigation of a large class of surfaces and thin films [21–23].

Using the standard interpretation of experimental SAS data, the most frequently determined fractal parameter is the fractal dimension $D_s$, where $d - 1 < D_s < d$, and $d$ is the Euclidean dimension in which it is embedded. For a fractal surface in the 3D space, the envelope surface of all balls of radii $r$ centered on the phase boundary obeys $S(r) \propto r^{2-D_s}$. This leads to the well-known behavior of scattering intensity, which scales as $I(q) \propto q^{-(6-D_s)}$ with the scattering wave vector $q = (4\pi/\lambda)\sin\theta$, where $\lambda$ is the wavelength of the incident radiation and $\theta$ is the half of the scattering angle. When $D_s \to 3$ the surface is so heavily folded that it nearly fills the entire space. On the other hand, an almost perfectly smooth surface is obtained in the limit $D_s \to 2$.

When it comes to the interpretation of experimental SAS data, one can choose to study the variation of $I(q)$ vs. $q$ on a double logarithmic scale. This characteristic can exhibit a linear shape on a double logarithmic scale. Determining the slope of the best fitted line $\alpha = 2d - D_s$ leads to the value of $D_s$. The standard Beaucage model can be used [24] when the intensity graph also displays the Guinier and Porod regions, or possibly a succession of simple power-law decays with different slopes [14, 25], characteristic to fractal structure forming another fractal. The overall size of the fractal, and the size of each individual fractal structure can be thereby obtained. It is known that additional information about the structural properties of deterministic mass fractals with a single scale can be extracted from SAS data exhibiting generalized power-law decays of consecutive maxima and minima superimposed on simple power-law decays [13]. This includes the determination of the scaling factor, iteration number, or the number of units composing the fractal. Using the model derived for densely packed surface fractal aggregates [26], one obtains both the specific surface area of the aggregates, and the fraction of particle interfacial sub-surfaces at the aggregate perimeter.

In the formulation of the elastic single scattering of waves from a macroscopic sample, let us consider a large number of objects with uncorrelated positions and
scattering lengths of $b_j$, and denote the object positions with $r_j$. The scattering length density (SLD) is $\rho_s(r) = \sum_j b_j \delta(r - r_j)$, where $\delta$ is Dirac’s delta distribution. One can apply this definition to a two-phase system where the scattering units with a SLD of $\rho_f$ are dispersed in a solid matrix with a SLD of $\rho_{mat}$. Taking 3D fractals as constituent objects of the macroscopic sample, considering that $n$ is their concentration inside the sample, $V$ is the volume of each fractal, and $F(q) \equiv (1/V) \int_V e^{-iq \cdot r} dr$ is the normalized form factor (with $F(0) = 1$), the scattering intensity becomes [27, 28]:

$$I(q) = n |\Delta \rho|^2 V^2 \langle |F(q)|^2 \rangle.$$  (1)

The scattering contrast is given by $\Delta \rho = \rho_f - \rho_{mat}$. The symbol $\langle \cdots \rangle$ denotes an ensemble average over all orientation, so that for an arbitrarily function $f$, in spherical coordinates, one has:

$$\langle f(q_x, q_y, q_z) \rangle = \frac{1}{4\pi} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi f(q, \theta, \phi),$$  (2)

with $q_x = q \cos \phi \sin \theta$, $q_y = q \sin \phi \sin \theta$, $q_z = q \cos \theta$.

Recently, it has been proven that surface fractals can be constructed as sums of mass fractals [16, 17], and therefore the normalized scattering amplitude of the surface fractal can be calculated as a sum of that of the composing mass fractals. Thus, for the $m$th iteration of a surface fractal, with a total volume $V_{tot}$, scaling factor $\beta_s$, and initial size $l_0$, one can write [16, 17]:

$$F_{SF}^m(q) = \frac{1}{V_{tot}} \left( V_0 F_0(l_0 q) + \sum_{i=1}^m V_i^{MF} F_i^{MF}(q) \right).$$  (3)

Here $V_i^{MF}$ is the volume of the constituent mass fractal at $i$th iteration, $F_0(q)$ is the form factor of its basic unit and:

$$F_{MF}^m(q) \equiv F_0(\beta_s^m l_0 q) \prod_{i=0}^{m} G_i(q).$$  (4)

The generative function $G_i(q)$ gives the positions of the units inside the fractal, at each iteration. Using Eq. (3), the SAS intensity, given by Eq. (1), averaged over the solid angle, becomes:

$$I_m(q)/I_m(0) = \langle |F_{SF}^m(q)|^2 \rangle,$$  (5)

where $I_m(0) \equiv n |\Delta \rho|^2 V^2$.

2.2. THE HYDRANT DETERMINISTIC FRACTAL MODEL

For the construction of the hydrant deterministic surface (Fig. 1) embedded in the 3D Euclidean space, a top-down approach can be used, repeatedly adding smaller
structures to a fixed size initial one, according to a specified rule.

The hydrant fractal surface model, used as a working example in this study, is obtained applying this iterative method. We start with a square planar surface of size \( l_0 \) \((m = 0)\), as shown in Fig. 1 for scaling factors \( \beta_s = 0.28 \) (upper part) and respectively \( \beta_s = 0.33 \) (lower part). This square is divided in 9 squares of size \( l_1 = \beta_s l_0 \), where \( \beta_s = 1/3 \) is the scaling factor. At the first iteration \( m = 1 \), a cube is added above the central square. At the step with \( m = 2 \) the same procedure is repeated for each previously obtained square, so that 13 cubes of edge size \( l_2 = \beta_s^2 l_0 \) result. In the limit of high iteration numbers the algorithm leads to a hydrant fractal surface [18]. The total number of cubes at the \( m \)th iteration \((m = 1, 2, \cdots)\) is:

\[
N_m = 13^{m-1}, \tag{6}
\]

and the edge size is:

\[
l_m = \beta_s^m l_0. \tag{7}
\]

For a big iteration number, the fractal dimension of the total volume of the cubes, coincides with that of the total surface, so that the fractal dimension of the total surface can be written as:

\[
D_s \equiv \lim_{m \to \infty} \frac{\log N_m}{\log (1/\beta_s^m)}. \tag{8}
\]

In order to avoid overlapping of the scattering centers, we have to consider \( \beta_s < 1/3 \) and since \( N_m \) is constant, we obtain \( D_s < 2.31 \). But, for a surface fractal embedded in 3D Euclidean space we have \( D_s > 2 \), and thus \( \beta_s \gtrsim 0.28 \).

One can note from Eq. (7) that the cube sizes from each iteration follow a discrete power-law distribution. The quantity responsible for the behavior of the scattering intensity in the fractal region is the exponent of the power-law distribution [16].

The system of Cartesian coordinates that can be used for the hydrant deterministic fractal surface shown in Fig. 1 has its origin coinciding with the center of the cube from first iteration \( m = 1 \) with edge size \( l_1 \). The axes are parallel with this cube’s edges. Choosing the \( z \)-axis perpendicular to the plane surface considered at iteration \( m = 0 \), the thickness of the surface at the \( m \)-th iteration is:

\[
t_m = \frac{1}{2} (1 - \beta_s^m), \tag{9}
\]

and the size of the surface along either the \( x \)- or \( y \)-direction is:

\[
a_m = 1 - 2\beta_s^m. \tag{10}
\]
Fig. 1 – (Color online) First three iterations of the deterministic hydrant fractal surface model embedded in the 3D Euclidean space. Upper part: $\beta_s = 0.28$. Lower part: $\beta_s = 0.33$. 
3. RESULTS AND DISCUSSION

3.1. SCATTERING FORM FACTOR

For an arbitrary iteration $m > 1$, the positions of the cubes forming the surface fractal, are given by the recurrence relation:

$$G_{m}^{oz}(q) = h^{oz}(q)G_{m-1}^{oz}(\beta_{s}q) + l^{oz}(q)G_{m-1}^{ox}(\beta_{s}q) + l^{oy}(q)G_{m-1}^{oy}(\beta_{s}q),$$  

with $G_{0}^{oz}(q) = G_{0}^{oy}(q) = G_{0}^{ox}(q) = 0$, and $G_{1}^{oz}(q) = G_{1}^{oy}(q) = G_{1}^{ox}(q) = 1$, while for the $x$- and $y$-directions, the generative functions are:

$$G_{m}^{ox}(q) = h^{ox}(q)G_{m-1}^{ox}(\beta_{t}q) + l^{ox}(q)G_{m-1}^{oz}(\beta_{t}q) + l^{oy}(q)G_{m-1}^{oy}(\beta_{t}q),$$  

$$G_{m}^{oy}(q) = h^{oy}(q)G_{m-1}^{oy}(\beta_{t}q) + l^{oz}(q)G_{m-1}^{oz}(\beta_{t}q) + l^{ox}(q)G_{m-1}^{ox}(\beta_{t}q).$$  

Here, we defined:

$$l^{oz}(q) \equiv 2\cos(u_{z}/2),$$  

$$l^{ox}(q) \equiv 2\cos(u_{x}/2),$$  

$$l^{oy}(q) \equiv 2\cos(u_{y}/2),$$  

$$h^{oz}(q) \equiv 4C(q) + (l^{oz}(q)/2)(2\cos(u_{x}) + 2\cos(u_{y}) + 1),$$  

$$h^{ox}(q) \equiv 4C(q) + (l^{ox}(q)/2)(2\cos(u_{y}) + 2\cos(u_{z}) + 1),$$  

$$h^{oy}(q) \equiv 4C(q) + (l^{oy}(q)/2)(2\cos(u_{z}) + 2\cos(u_{x}) + 1),$$

and denoted $u_{i} = q_{i}l_{0}\beta_{t}$, $i = x, y, z$; $C(q) \equiv \cos(u_{x})\cos(u_{y})\cos(u_{z})$, $\beta_{t} \equiv (1 - \beta_{s})/2$.

Now we take into account that the surface fractal consists of cubes with a power-law distribution of sizes, which can be decomposed into a sum of mass fractals for an arbitrary iteration of the fractal [17]. Using Eq. (3), the form factor of the surface fractal for any $m$ can be written as:

$$F_{m}^{SF}(q) = \frac{1}{V_{tot}^{m}} \left( V_{1}F_{1}(q) + \sum_{i=2}^{m} \frac{1}{13^{i-1}}V_{i}F_{i}(\beta_{t}^{-1}q)G_{i}^{oz}(q) \right).$$
Here $V_{m}^{\text{tot}}$ is the total volume of the cubes considered at all iterations $i = 1, \cdots, m$, and $V_i$ is the volume of the cubes at $i$th iteration. The form factor of a cube of edge length $l_1$ is given by:

$$F_1(q) = \frac{\sin(q_x l_1/2) \sin(q_y l_1/2) \sin(q_z l_1/2)}{q_x l_1/2 \cdot q_y l_1/2 \cdot q_z l_1/2}.$$ \hfill (21)

### 3.2. MONODISPERSE SCATTERING INTENSITY

The normalized monodisperse SAS intensities, computed using Eqs. (21), (20) and (5), are shown in Fig. 2. In these representations the iterations are considered up to $m = 5$ and for three values of the scaling factor $\beta_s$. For each case, the intensity curves are characterized by the presence of four main regions. From each region one can extract structural properties of the surface.

The Guinier region (I) is determined by the overall size of the fractal. It extends up to $q \lesssim 2\pi/a_m$, where $a_m$ is given by Eq. (10). Furthermore, expanding Eq. (20) in power series of $ql_1$, and using Eq. (5), the radius of gyration for arbitrary iteration $m$ can be obtained [13, 14]. According to Eq. (10), the lateral dimension of the surface increases with increasing iteration number $m$, thus the end of the Guinier region is shifted left. It is marked by a vertical dotted line in Fig. 2 for $m = 5$ (magenta curve).

The intermediate region (II) is given by the size of the lateral dimensions, which are all equal in our case, and the height of the surface. These dimensions are found to obey the inequality $2\pi/a_m \lesssim q \lesssim 2\pi/t_m$, where the thickness $t_m$ is given by Eq. (9). The exponent of the power-law decay is -2, and the surface appears like a 2D object. Because, as in the case of lateral dimensions, the thickness increases with increasing iteration number $m$, the end of region II is also shifted left with increasing $m$. However, since the rate of thickness increase with iteration number $m$ is slower than that of the lateral dimension, the overall length of region II will increase with $m$. This effect is also illustrated in Fig. 2, where the longest region II is obtained for $m = 5$, and its end is marked by an other vertical dotted line. Please note that for the considered model, according to Eqs. (9) and (10), the thickness of the surface and its size along either the $x$ or $y$ directions, differ only by a factor of 2 in the limit of high number of iterations. Imposing additional restrictions on the construction of the surface, such as allowing only the thickness to increase, while the lateral size is kept constant, can largely increase the length of the intermediate region (II). In this case an even more accurate thickness determination can be performed when interpreting experimental data.

The fractal region (III) is determined by the overall thickness of the surface and the size $l_m$ of the smallest cube that enters in its composition at a certain iteration, as formulated in Eq. (7).
Fig. 2 – (Color online) Monodisperse SAS intensity for the first five iterations of the hydrant fractal surface. Scattering intensities are shifted up vertically by a factor of $20^{m-1}$ for clarity.
This is why a generalized power-law decay (superposition of maxima and minima on a simple power-law decay) is observed in the range $2\pi/t_m \lesssim q \lesssim 2\pi/l_m$. The numerical results from Fig. 2 confirm this behavior for all iterations. Here, the size $l_m$ decreases much faster with $m$ than the increase of thickness $t_m$. This means that, on a double logarithmic scale, the end of the fractal region will be shifted to the right, in discrete steps, with increasing iteration $m$. Thus, the log-periodicity of minima in Fig. 3 arises from the self-similarity of the sizes of the basic structural units. This is in contrast with the periodicity of the minima for mass fractals, which arise from the self-similarity of the distances between the structural units. These properties have been discussed in details in Refs. [13, 16]. In Fig. 2 the end of the fractal region for $m = 5$ is marked by the third vertical dotted line.

The Porod region (IV) occurs for $q \gtrsim \pi/l_m$. The Euclidean dimension of the space in which the fractal is embedded can be calculated from the exponent of the power-law decay. The value -4 for the exponent indicates that the fractal, that was used in our example, is embedded in the 3D space, as expected. From this region, one can obtain additional information about the specific surface of the fractal [27, 28], when the scattering experiments are performed on an absolute scale.

The above numerical results illustrate the applicability of SAS technique for the determination of the structural properties of surface fractals, which exhibit a directional growth pattern at all scales. Viewed from a distance larger than its lateral dimension $a_m$, or in a low $q$ region in the reciprocal space, the fractal will appear as a 0D object, resulting in a plateau on a double logarithmic scale as in Fig. 2, region I. When it is observed from a smaller distance that $a_m$, which is still larger than $t_m$, the surface fractal will look like a 2D object (Fig. 2, region II). For distances shorter than $t_m$, but bigger than $l_m$, the self-similarity is revealed, and the fractal dimension can be calculated (Fig. 2, region III). The fractal appears as a 3D object (Fig. 2, region IV), if it is viewed at distances closer than $l_m$. If we were to deal with a regular surface, the fractal region would be absent, and the analysis would be reduced to a scattering from regular 3D objects [29].

### 3.3. POLYDISPERSE SCATTERING INTENSITY

Most often, a real sample consists of fractals of different sizes. This can be taken into account introducing polydispersity in the scatterer’s initial size. The distribution function $D_N(l)$ is defined so that $D_N(l)dl$ gives the probability of finding a fractal whose size is in the range $(l, l + dl)$. By choosing a log-normal distribution, with the mean length $l_0$, and relative variance $\sigma_r$ given by:

$$l_0 \equiv \langle l \rangle_D, \quad \sigma_r = ((\langle l^2 \rangle_D - l_0^2)^{1/2}/l_0,$$  (22)
where $\langle \cdots \rangle_D = \int_0^\infty \cdots D_N(l)dl$, the polydisperse scattering intensity becomes (Fig. 3)

$$I_{m}^{\text{poly}}(q) = \frac{\int_0^\infty (F^S_{m}(q))^2 \left(V_{m}^{\text{tot}}(l)\right)^2 D_N(l)dl}{\int_0^\infty (V_{m}^{\text{tot}}(l))^2 D_N(l)dl}. \quad (23)$$

The polydisperse scattering intensities, obtained based on Eq. (23), are represented in Fig. 3. These are plotted for the first five iterations of the deterministic hydrant surface, when the relative variance is $\sigma_r = 0.4$. As expected, the scattering curves become smoother. In this case their shape is much closer to what is obtained experimentally. The scattering exponents are preserved as for the generalized power-law decays shown in Fig. 2. Thus, the simple power-law decay obtained in Fig. 3 can be used to determine very precisely the values for the fractal dimension of the surface.

4. CONCLUSIONS

In this article, we considered scattering from the class of deterministic fractal surfaces exhibiting directional growth pattern, representing deterministic hydrant surfaces [18]. The fractals are built from basic units, taken as cubes as a working example, with sizes that follow a power-law distribution. This property allows us to recover the value of the fractal dimension, by fitting a power-law dependence in the fractal region [17]. We obtained analytic expressions for the form factor of the mono- and polydisperse fractals embedded in the 3D Euclidean space at an arbitrary iteration number $m$. The suggested model represents a generalizations of surface fractal models with a center of symmetry, whose structural properties were recently reported in Refs. [16, 17].

We have shown that the scattering intensity describes both the geometrical and the main fractal characteristics of the surface, and that the parameter needed to obtain them is the fractal scaling factor $\beta_s$. The overall size of the fractal along the orthogonal directions can be determined from the ending point of the Guinier region. The intermediate region (denoted by II in Fig. 2) gives the surface thickness. From the fractal region (in Fig. 3) one can compute the fractal dimension related to the slope of the power-law decay, the number of iterations as the number of the most pronounced minima, and the scaling factor from the periodicity of the most pronounced minima. From the Porod region one can determine the specific surface of the fractal.

The suggested approach can be used to describe growth phenomena on various nano- and micro-structured surfaces such as of biological, organic or inorganic aggregates.
Fig. 3 – (Color online) Polydisperse SAS intensity for first five iterations of the hydrant fractal surface. Scattering intensities are shifted up vertically by a factor of $20^{m-1}$ for clarity. The slopes are preserved as in the monodisperse case.
Acknowledgements. This work was supported by the Joint Institute of Nuclear Research Dubna [project number 27/95]; Technical University of Cluj-Napoca [project number 27/96]; based on joint research protocol 4517-3-16/18.

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