Small-angle scattering from Apollonian packings using Monte Carlo simulations

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Abstract. Analytic expressions for form factors of several simple deterministic fractals have been derived in the last years, including mass-, surface-, fat and multi-fractals. Such expressions are very useful for extracting various structural parameters such as the fractal dimensions, lower and upper limits of the fractal, iteration number or the scaling factor. However, for more complex structures such as Apollonian packings (AP), where the fractal symmetry can not be easily exploited, analytic expressions are not available and we have to resort to other methods. Here, we calculate the pair-distance distribution function and small-angle scattering intensity of 3D AP using Monte Carlo simulations, and show that the corresponding fractal dimension is $D \approx 2.46$, which is very good agreement with theoretical predictions. Thus, Monte Carlo simulations can be used successfully to characterize complex deterministic systems at nano- and micro-scales.

1. Introduction

In recent years analytic expressions for calculating the small-angle scattering (SAS) intensities from various types of deterministic fractals have been derived [1]. This includes, single scale mass [2–4] and surface [4–9] fractals, as well as heterogeneous fractals such as fat [10–12] and multifractals [1]. This theoretical development is mainly based on the advances in materials science and nanotechnology, and which bring innovative ways in preparation of complex fractal nanomaterials with predefined functions and properties [13–22].

However, a fundamental challenge in improving their physical properties relies on a detailed knowledge of their nano- and micro-structure. To this aim the structural properties provided by the existing theoretical models are very useful but they are intended to model specific structures such as Menger sponge [23] and Vicsek [2] mass fractals, Cantor-like [5] and Koch snowflake [6] surface fractals. While in the case of symmetric mass fractals, derivation of an analytic expressions for SAS intensity is a relatively simple procedure [2, 10], in the case of SAS from surface fractals this can be a tedious task, since any surface fractal can be decomposed into a sum of mass fractals of the same fractal dimension, and thus the scattering amplitude of a surface fractal can be written as a sum of amplitudes of the composing mass fractals [5, 6, 8, 9]. Such a decomposition is not always obvious, and in some cases it requires some ingenuity in revealing a useful recurrence relationship between the various mass fractal iterations, as well as which exactly are the components of a given mass fractal iteration [6].

It is known that Monte Carlo simulations can be successfully used to calculate the SAS intensity for virtually any type of shapes, from basic Euclidean shapes such as cylinders, to complex structure such as truncated models of the human hepatitis B viral capsid structure [24]. Comparison with theoretical...
results show very good agreement also for multi phase systems [25], such as those consisting of Janus particles [26]. Here, we extend the range of applicability of Monte Carlo methods to deterministic surface fractals as well. We show that although this method can reveal, in a relatively simple manner, important information about the fractals, such as the fractal dimension or the edges of the fractal region, some other properties like the scaling factor or the fractal iteration number can hardly be obtained. This is due to the intrinsic property of Monte Carlo methods, which involve a random distribution of points within the volume of the fractals, and which leads to a partial smearing of the pair-distance distribution function (pddf) \( p(r) \).

### 2. Theoretical background on small-angle scattering

Physically, SAS involves interaction of an incident beam with the electrons in the sample (in the case of SAXS) or with the atomic nuclei or magnetic moments (in the case of SANS). Thus, the Fourier transforms of spatial density-density correlations in the sample can be obtained as the differential elastic cross section of SAXS) or with the atomic nuclei or magnetic moments (in the case of SANS). Thus, the Fourier transforms of spatial density-density correlations in the sample can be obtained as the differential elastic cross section 

\[ \frac{\partial \sigma}{\partial \Omega}(q) = q^2 V^2 \langle |F(q)|^2 \rangle, \]

where where \( n \) is the fractal concentration, \( V \) is each fractal’s volume, and \( F(q) \) is the form factor given by:

\[ F(q) = \frac{1}{V} \int_V e^{-iqr} \, dr, \]

obeying the boundary condition \( F(0) = 1 \). Here, the notation \( \langle \cdots \rangle \) stands for ensemble averaging over all orientations of the fractal.

Recall that SAS has the ability to distinguish, between mass [28] and surface [29] fractals through the value of the scattering exponent \( \tau \) of the SAS curve in the fractal region, and thus Eq. (1) can be rewritten as [29][30]:

\[ I(q) \sim q^{-\tau}, \]

with

\[ \tau = \begin{cases} D_m, & \text{for mass fractals,} \\ 2d - D_s, & \text{for surface fractals,} \end{cases} \]

where \( d \) is the Euclidean dimension of the embedding space in which the fractal is embedded, and \( D_m \) and \( D_s \) are the mass and surface fractal dimensions. Note that in a two-phase configuration in a \( d \)-dimensional space, one usually considers that one phase (i.e. mass) with dimension \( D_m \) has a complement phase (i.e. pores), with dimension \( D_p \). [31]. The boundary between the two phases form also a set with surface fractal dimension \( D_s \). In the case of mass fractals \( D_s = D_m < d \) and \( D_p = d \), while for a surface fractal we have \( D_m = D_p = d \) and \( d - 1 < D_s < d \). Experimentally, having determined the slope \( \tau \) of the scattering curve then if the measured value is smaller that \( d \) then the object is classified as a mass fractal with dimension \( D_m = \tau \), while if \( d < \tau < d + 1 \) the object is a surface fractal with surface fractal dimension \( D_s = 2d - \tau \). Since here we are dealing only with surface fractals, we denote in the following \( D = D_s \). Also, we will make use of the fact that the scattering intensity can be written in terms of pddf, which gives the probability distribution for the distance between two arbitrary points within the scattering volume. Thus one can write [32]:

\[ I(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} \, dr. \]
3. Results and discussions

3.1. Model and method

Apollonian packing (AP) is a space filling process which involves a set of disks/balls whose radii follow a power-law distribution of sizes, and thus it generates a surface fractal whose initiator \((m = 0)\) is a set of mutual tangent disks (in 2D) or balls (in 3D). The first iteration \(m = 1\) of AP is obtained by inscribing additional disks/balls of smaller radii between the mutually tangential disks/balls at \(m = 0\) and tangent to them \([33]\). In 2D the classical AP is obtained in the limit \(m \rightarrow \infty\) and is constructed starting from an initial configuration consisting from three mutually tangent disks and by recursively filling the space with the osculatory packing down to arbitrarily small diameters. Fig. 1 (left side) shows a 3D AP of balls at \(m = 3\), where the initiator consists from 5 balls. The fractal dimension of such this packing is known to be \(D \simeq 2.46\) \([34]\).

In the method used here, the volume occupied by the fractal is filled with a high number of \(N\) points whose coordinates are generated using Monte Carlo simulations, as shown in Fig. 1 (right side). Then, the distances between arbitrarily two points is calculated and their values are distributed in a histogram with \(M\) bins, in order to approximate the frequency function between pairs of these points \([25,26]\). This histogram provides the pddf directly. Finally, the scattering intensity is calculated by using Eq. (5). Note that since the investigated fractal, as well as any other physical structure, has a maximum dimension \(D_{\text{max}}\), and which is obtained when \(p(r) \rightarrow 0\) at high values of \(r\), the upper integration limit in Eq. (5) shall be replaced by \(D_{\text{max}}\) \([32]\).

3.2. Pddf and scattering intensity of Apollonian packings

The numerical results describing the pddf of AP at iteration number \(m = 4\) are shown in Fig. 2a (black circles). The simulations have been performed by generating a number of \(N = 8 \times 10^4\) points, and distributing the corresponding distances into a histogram with \(M = 200\) bins. For comparison, the pddf of a ball of the same maximum size is included (red - squares). The results show that the pddf of AP is characterized by a sharp decrease up to \(r/a \simeq 0.15\), which reveals a relatively high degree of asymmetry at small scales present in AP, as compared to the ball. For \(0.15 \lesssim r/a \lesssim 0.44\), the pddf of AP has a less pronounced increase with a succession of small maxima and minima. This superposition of maxima and minima is a reflection of the self-similarity property of AP. Note that if we would have considered the
Figure 2. (Color online) (a) Pair distance distribution function $p(r)$ of AP (black - circles) at iteration number $m = 4$ and of a ball of the same maximum size as AP (red - squares). (b) The corresponding scattering intensities $I(q)$ of AP (black - upper curve) and of a ball of the same maximum size (red - lower curve). The scattering exponent of the curve in the fractal region is $\tau \approx 3.54$ and thus, according to Eq. (4), $D \approx 2.46$.

Points found only at the centers of each particle in AP, instead of the whole volume, more pronounced maxima and minima are to be expected, as seen also in other self-similar systems such as in 3D Vicsek fractals. The highest maxima at $r/a \approx 0.44$ corresponds to the maximum number of distances in AP. Note that this number is smaller as compared to the maximum number of distances within a ball, due to the geometry of AP, which restricts some of the distances. The "oscillating" decrease of pddf at $r/a \gtrsim 0.44$ reflect also the assymetry of AP, this time at large scale. Pddf becomes effectively zero at $r/a \approx 0.80$, which corresponds to the maximum dimension $D_{\text{max}}$ inside AP.

The corresponding scattering intensity of AP is shown in Fig. 2b (black-curve). In the calculated $q$-range, one can observe the presence of two main regions. At $q \lesssim \pi/D_{\text{max}} \approx 3.93$ a Guinier region is present, whose length reveals also the radius of gyration of AP. At $q \gtrsim 3.93$ a fractal region is present, with the scattering exponent $\tau \approx 3.54$, and thus $D = 6 - \tau \approx 2.46$. This value is in very good agreement with theoretical values reported elsewhere (see Ref. [34]). The upper edge of the fractal region is given approximately by $q_{\text{max}} \approx \pi/\beta_s D_{\text{max}} \approx 319$ (see also Ref. [5,6]), where $\beta_s = 1/3$ is the scaling factor of AP, i.e. the ratio of radii at two consecutive iterations. At $q \gtrsim 319$ we expect a Porod region with scattering exponent $\tau = 4$. Thus, the values of $M$ and $N$ used here are enough to reveal the radius of gyration and the fractal dimension of AP. However, if we are interested in extracting additional structural information from SAS data such as the scaling factors or the iteration number, a more clearly defined succession of maxima and minima is needed. Although an increase of the number of bins $M$ and the number of points $N$ could partially solve this issue, in some cases, such as those for which maxima and minima are intrinsically not very well defined, the limitations of this approach can play an important role.

4. Conclusion

In this work, Monte Carlo simulations have been performed to calculate the SAS intensity from AP. The process consists in generating a large number of random points distributed within the volume of AP, calculating all the distances between them, then arranging their values into a histogram, and followed
by determination of the corresponding pddf. Finally, the scattering intensity is obtained as a Fourier transform of pddf.

The results show that, when the number of generated points is about $10^5$ and the number of histogram bins in the pddf is 200 the scattering intensity shows the presence of the Guinier region followed by a fractal one. From the end of the Guinier region, as well as from the property that pddf tends to zero at large values of ratio $r/a$, where $a$ is the overall size of AP, the maximum distance inside AP can be determined. It is also shown that the fractal region decays proportionally to $q^{-6+D}$, where $D = 2.46$ is the fractal dimension of AP. Since the length of the fractal region is at least one decade, the obtained value of $D$ can be reliably used to assert the surface fractal nature of AP.

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