A model of small-angle scattering from three-phase fractal systems

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Abstract. In small-angle scattering (SAS) intensities on a double logarithmic scale, one generically observes “knees” arising from changes of the power-law exponents. While the appearance of power-law behavior is associated usually with a fractal structure, the explanation of the knees is a more intricate problem in general. It is shown that the crossover between the exponents can be accounted for by various levels of the structures with different scattering length densities (SLD). Thus, the whole system is a multiphase system, composed of the homogeneous structures embedded into each other. In this way, one can explain the crossover between arbitrary exponents whose values vary from -4 to 0. In order to confirm this conclusion, we calculate the SAS intensity from a set of non-interacting, randomly oriented and uniformly distributed three-phase fractals with controllable Hausdorff dimension. We observe the appearance of crossover (knee), which depends on the values of the SLD of each phase and estimate its position. Random fractals are described as well within the developed model by taking the fractal sizes at random, which leads to polydispersity and, as a consequence, to smearing of the SAS intensity curves.

1. Introduction
Small-angle scattering (SAS) [1] has been proved to be a very useful technique to study structural properties of fractals [2]. In general, the SAS technique enables us to obtain the fractal dimension and the edges of the fractal region [3,4]. As was shown recently, the SAS intensity from deterministic fractal systems (DFS) can be used to extract the additional fractal parameters: the fractal iteration number, the scaling factor and the number of structural units of which the fractal is composed [5].

For a two-phase system, fractals are composed of homogeneous units, which are embedded into a homogeneous solid matrix. Then the SAS intensity from the system clearly shows a separate contribution of the two structural levels: the fractal itself and its building units [4–7]. Therefore, at low q the intensity is characterized by the Guinier region of the fractal (a plateau on a double logarithmic scale) and the fractal region \( I(q) \propto q^{-D} \), where \( D \) is the fractal dimension, while at high q the intensity is characterized by the second Guinier and Porod \( I(q) \propto q^{-4} \) regions of the building units. When the Guinier region of the building units is small enough, the intensity shows a crossover point (knee) at some value of the wave vector \( q_c \), where the scattering exponent changes from \(-D\) to \(-4\).

However, at the knee position, SAS experimental data often exhibit a transition between arbitrary values of the scattering exponents, whose values vary from \(-4\) to \(0\) [8–11]. In general, the values of the exponent lie within \(-3 < D_m < 0\) for a mass fractal, and within \(-4 < D_s < -3\) for a surface fractal, where \( D_m \) and \( D_s \) are mass and, respectively, surface fractal dimension [3, 4]. We argue that the crossover between the exponents can be accounted for by various levels of structures with different
scattering length densities (SLD). Thus, this kind of SAS intensity is typical for a multiphase system, composed of the homogeneous structures embedded into each other.

In order to check this statement, we suggest a model of three-phase system, where one of the phase is a DFS. In this model, a uniform matrix with scattering length density (SLD) $\rho_0$ (phase 1) contains balls with SLD $\rho_1$ (phase 2), in which a DFS with SLD $\rho_2$ (phase 3) are embedded, see Fig. 1. We model the DSF phase by means of the generalized Cantor fractals (GCF) [7], which is a mass fractal with controllable fractal dimension (Fig. 2). A random fractal can be modeled by this system as well if we consider an ensemble of DSFs, whose sizes are taken at random (polydisperse DFS system) [4–7].

This paper examines both monodisperse and polydisperse SAS intensities from a set of randomly oriented and uniformly distributed three-phase fractals and focuses on studying of the knee on the scattering intensity. We investigate the effects of variation of the SLD values on the contribution of the individual structural levels to the total scattering intensity.

2. The model

The three-phase model is a solid matrix with uniform SLD $\rho_0$ that includes a macroscopic number of spherical regions with SLD $\rho_1$, and each of them contains the 3D generalized Cantor fractals (GCF) with SLD $\rho_2$ (see the left diagram in Fig. 1). The fractal dimension can be controlled by varying its scaling factor $\beta$. The GCF is constructed [7] with the help of a cube by iterations called approximants (Fig. 2). The zero-order iteration (initiator) is a ball of radius $r_0 = l_0/2$, where $l_0$ is the length of the cube edge. The radius of the ball surrounding the fractal is $R = kl_0$, where $k \geq \sqrt{3}/2$ (Fig. 1). It is assumed that the spatial positions and orientations of these constructions in the solid matrix are uncorrelated.

A constant shift of the SLD in the overall sample is important only for small values of wave vector, unattainable with the SAS technique. Therefore, by subtracting the solid matrix density $\rho_0$, the model can be reduced to the fractals with SLD $\rho_2 - \rho_0$ and the volume $V_2 = 8^m \beta^m_2 4\pi r_0^3/3$, embedded into the surrounding balls with SLD $\rho_1 - \rho_0$ and the volume $V_b = 4\pi R^3/3$ (Fig. 1). Thus, the model can be considered as if the balls were “frozen” in a vacuum and had the density

$$\rho(r) = \begin{cases} 
\rho_2 - \rho_0 & \text{in } V_2, \\
\rho_1 - \rho_0 & \text{in } V_b \setminus V_2.
\end{cases}$$

Effectively, this procedure allows us to reduce the three-phase system to the two-phase system. We will call this construction, shown in Fig. 1, the three-phase fractal.

Figure 1. A three-phase fractal system is equivalent to a two-phase one in a vacuum, where the building units of the fractal have SLD $\rho_2 - \rho_0$ and the surrounding ball of radius $R$ has SLD $\rho_1 - \rho_0$. 
Figure 2. The 2D projection of the 3D generalized Cantor fractal (GCF): initiator \((m = 0)\) and first two iterations \((m = 1\) and \(m = 2)\). Vectors \(a_j\) connect the center of the ball of radius \(r_0\) with the centers of balls of radii \(r_1\) (see Ref. [7] for details).

3. Calculation of the scattering intensity

The scattering intensity (the differential cross section per unit volume of the sample) can be calculated if we take into account the randomness of orientations and spatial positions of the three-phase fractals. Then they scatter the incident beam independently, which leads to [1]

\[
I(q) = n \langle |A(q)|^2 \rangle, \quad (2)
\]

\[
A(q) \equiv \int_{V_b} \rho(r) e^{-iqr} dr, \quad (3)
\]

where the quantity \(A(q)\) is the scattering amplitude of the three-phase fractal. Its effective SLD is given by Eq. (1). Here \(n\) is the number of fractals per unit volume, the brackets \(\langle \cdots \rangle\) stand for the ensemble averaging over all orientations of \(q\).

It is convenient to write down the intensity in terms of the normalized scattering amplitudes. The normalized amplitude is defined in general as

\[
F(q) \equiv \int_{V_b} \rho(r) e^{-iqr} d^3r / \int_{V_b} \rho(r) d^3r. \quad (4)
\]

It follows from the definition that \(F(0) = 1\), and for a homogeneous system \(A(q) = \rho V F(q)\). A straightforward substitution of Eq. (1) into Eq. (3) yields after a little algebra

\[
A(q) = V_b (\rho_1 - \rho_0) \alpha^{-1} \left[ \alpha F_b(qR) + (1 - \alpha) F_2^{(m)}(q l_0) \right], \quad (5)
\]

where we introduce by definition the “contrast parameter”

\[
\alpha \equiv \left( 1 + \frac{\rho_2 - \rho_1 V_2}{\rho_1 - \rho_0 V_b} \right)^{-1}, \quad (6)
\]

and \(F_b(qR)\) and \(F_2^{(m)}(q l_0)\) are the normalized form factors of a homogeneous ball of radius \(R\) [1] and of the fractal at the \(m\)th iteration [7], respectively. They are calculated analytically in terms of elementary functions. Thus, the final expression for the scattering amplitude takes the form

\[
I_m(q) = n V_b^2 (\rho_1 - \rho_0)^2 \alpha^{-2} \left\langle \left| \alpha F_b(qR) + (1 - \alpha) F_2^{(m)}(q l_0) \right|^2 \right\rangle. \quad (7)
\]
In a real physical system, scatterers almost always have different sizes. Therefore, a more realistic description should involve size polydispersity. Here we consider an ensemble of the three-phase fractals with different sizes. Specifically, we choose the log-normal distribution of the sizes with the average fractal size $l_0$ and its relative dispersion $\sigma_r$ (see Refs. [5, 7] for details). Thus, the average in Eq. (7) is taken over the both angles and sizes. Polydispersity obviously smears the intensity curves, and the oscillations disappear at strongly developed polydispersity [5, 7].
4. Results and Discussions

The numerical results for the scattering intensity (7) are represented in Fig. 3 for different values of the contrast parameter $\alpha$. One can clearly see the appearance of the crossover points (knees on a double logarithmic scale). In order to estimate their positions, let us make simple approximations in the limit of strongly developed polydispersity (see Fig. 3b)

$$\langle |F_b(qR)|^2 \rangle \propto \begin{cases} 1, & q \lesssim 1/R, \\ (qR)^{-4}, & q \gtrsim 1/R, \end{cases}$$

and

$$\langle |F_2^{(m)}(ql_0)|^2 \rangle \propto \begin{cases} 1, & q \lesssim 1/l_0, \\ (ql_0)^{-D}, & 1/l_0 \lesssim q \lesssim 1/l_m, \\ (qr_m)^{-4}, & q \gtrsim 1/r_m, \end{cases}$$

where $l_m = \beta_m l_0$ and $r_m = \beta_m r_0$ are the mean length of cube’s edge and the mean radius of the composing balls at the $m$th iteration. Note that the radius of surrounding sphere $R$ is always bigger than the fractal size $l_0$.

For a given $q$, the ball amplitude $F_b(qR)$ and the fractal amplitude $F_2^{(m)}(ql_0)$ in the r.h.s. of Eq. (7) can be of different orders of magnitude, provided the corresponding exponents are not equal. Then one of the amplitudes dominates. The knee position can be found by equating the corresponding intensities $\alpha^2 \langle |F_b(qcR)|^2 \rangle \simeq (1-\alpha)^2 \langle |F_2^{(m)}(ql_0)|^2 \rangle$ and using the estimations (8). This gives us

$$qc \simeq \begin{cases} 1/R \sqrt{|\alpha| / (1-\alpha)}, & 1/R \lesssim qc \lesssim 1/l_0, \\ 1/l_0 \left( |\alpha| l_0^2 / (1-\alpha) R^2 \right)^{1/2}, & 1/l_0 \lesssim qc \lesssim 1/l_m. \end{cases}$$

If $1/R \lesssim qc \lesssim 1/l_0$ (say, for $\alpha = 0.999$ in Fig. 3b), one can see all the regions in the intensity curve: the Guinier and Porod regions of the surrounding ball, and the Guinier, fractal, and Porod regions of the fractal. When the contrast $\rho_2 - \rho_1$ between the ball and fractal is suppressed or the fractal volume is small enough, the contrast parameter $\alpha$ gets closer to one. As a consequence, a part of the fractal curve is “absorbed” by the ball curve. For instance, at $\alpha = 0.9999$ one can see the direct transition between the Porod and fractal regions. At sufficiently small values of $|1-\alpha|$, the fractal region can not be observed by the SAS technique at all.

5. Conclusions

We develop a model that describes multi-phase fractal systems, where one phase (GCF) is embedded into another phase (ball) and altogether the combined system is further put into a third phase (matrix). We derive an analytical expression for the SAS intensity from such a system and observe the appearance of various knees between the power-law regimes. The knee positions and the contributions of the different structural levels to the total scattering intensity are controlled by the effective contrast parameter $\alpha$ (6), depending on the relative values of the SLD of each phase and their volumes. The found estimations (9) for the knee positions can be used to answer the question of principle: whether the fractal region is observable at a given contrast by the SAS method or not.

In order to explain the transition between arbitrary scattering exponents, the developed model can be generalized to complex multilevel structures embedded into each other.

References

[1] Feigin L A and Svergun D I, *Structure Analysis by Small-Angle X-Ray and Neutron Scattering* (Plenum Press, 1987, NY).
[2] Mandelbrot B B, *The Fractal Geometry of Nature*, (Freeman, 1982, San Francisco).
[3] Martin J E and Hurd A J, *J. Appl. Cryst.*, 20, 61 (1987).
[4] Schmidt P W, *J. Appl. Cryst.*, 24, 414 (1991).
[5] Cherny A Yu, Anitas E M, Osipov V A and Kuikin A I, *Phys. Rev. E*, 84, 036203 (2011).
[6] Cherny A Yu, Anitas E M, Kuklin A I, Balasoiu M and Osipov V A, J. Surf. Invest., 4, 903 (2010).
[7] Cherny A Yu, Anitas E M, Kuklin A I, Balasoiu M and Osipov V A, J. Appl. Cryst., 43, 790 (2010).
[8] Schaefer D W and Justice R S, Macromolecules, 40, 8501 (2007).
[9] Kravchuk K V, Gomza Yu P, Pashkova O V, Vyunov O I, Nesin S D and Belous A G, J. Non. Crys. Sol., 355, 2557 (2009).
[10] Schneider G J and Goritz D, J. Chem. Phys., 132, 154903 (2010).
[11] Singh M, Sinha I, Singh A K and Mandal R K, J. Nanopart. Res., 13, 69 (2011).