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To cite this version:

Dragomir Tatchev. Structure Analysis of Multiphase Systems by Anomalous Small-Angle X-ray Scattering. Philosophical Magazine, 2008, 88 (12), pp.1751-1772. 10.1080/14786430802279760 . hal-00513925

HAL Id: hal-00513925

https://hal.science/hal-00513925v1

Submitted on 1 Sep 2010

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Structure Analysis of Multiphase Systems by Anomalous Small-Angle X-ray Scattering

Journal:	*Philosophical Magazine & Philosophical Magazine Letters*
Manuscript ID:	TPHM-08-Mar-0068.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	05-Jun-2008
Complete List of Authors:	Tatchev, Dragomir; Hahn-Meitner-Institut Berlin, SF3; Institute of Physical Chemistry - BAS
Keywords:	materials characterisation, SAS
Keywords (user supplied):	multiphase systems, partial structure factors

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Structure Analysis of Multiphase Systems by ASAXS *Philosophical Magazine*

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(recto) *Philosophical Magazine*

REVIEW ARTICLE

Structure Analysis of Multiphase Systems by Anomalous Small-Angle X-ray Scattering

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Abstract

The theory of the small-angle scattering is reviewed with special attention paid to the anomalous scattering and multiphase systems. A general equation describing the scattering of a multiphase system as a sum of scattering functions of each of the phases, as if it scattered alone in a two phase system, and interphase interference scattering functions is derived. These scattering functions depend only on the spatial distribution of the phase boundaries, but not on the scattering density. Contrast variation techniques are most rewarding when the scattering density of only one phase can be varied. For ASAXS, this means the most favorable is the case in which resonant atoms are contained in one phase only. The general equation involves $n(p\text{-}1)$ unknown partial atomic number density differences, where p is the number of phases and n - the number of the different atom types in the sample. These partial atomic number density differences can be found if a suitable structure model is applied to calculate the phase scattering functions. Then, the phase compositions and densities can be calculated by solving a system of linear equations incorporating the atom number conservation law. The partial structure factors formalism is also reviewed. Corresponding equations for a system of n types of atoms and p phases are derived. The number of independent partial structure factors is $p(p\text{-}1)/2$ and depends on the number of phases, but not on the number of the types of the atoms in the sample, as in the case of wide angle scattering.

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Keywords*:* anomalous small-angle scattering; multiphase systems; partial structure factors

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The theory of the small-angle scattering is reviewed with special attention paid to the anomalous scattering and multiphase systems. A general equation describing the scattering of a multiphase system as a sum of scattering functions of each of the phases, as if it scattered alone in a two phase system, and interphase interference scattering functions is derived. These scattering functions depend only on the spatial distribution of the phase boundaries, but not on the scattering density. Contrast variation techniques are most rewarding when the scattering density of only one phase can be varied. For ASAXS, this means the most favorable is the case in which resonant atoms are contained in one phase only. The general equation involves $n(p\text{-}1)$ unknown partial atomic number density differences, where p is the number of phases and n - the number of the different atom types in the sample. These partial atomic number density differences can be found if a suitable structure model is applied to calculate the phase scattering functions. Then, the phase compositions and densities can be calculated by solving a system of linear equations incorporating the atom number conservation law. The partial structure factors formalism is also reviewed. Corresponding equations for a system of n types of atoms and p phases are derived. The number of independent partial structure factors is $p(p\text{-}1)/2$ and depends on the number of phases, but not on the number of the types of the atoms in the sample, as in the case of wide angle scattering.

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1. Introduction

Small-angle scattering (SAS) of x-rays (SAXS) or neutrons (SANS) is a versatile tool for studying the structure of condensed mater on nanoscale dimensions. It is a technique sensitive to variation of the electron density or neutron scattering length density at distances of 1-1000 nm, and has applications in soft condensed mater, materials science and nanotechnology. The emergence of the synchrotron radiation enables the investigation of matter with anomalous small angle scattering (ASAXS). ASAXS uses tuneable x-ray energy near an absorption edge of a chemical element contained in the sample. This leads to reduction of the intensity scattered by the atoms of this element rendering the technique sensitive to chemical composition. ASAXS requires the investigated object to contain at least one element with a X-ray absorption edge in the instrumentally available energy range. Thus, it is used mainly to study solid matter; alloys [1-9], glasses [10, 11], metal catalysts [12-14] and polymer composites [15, 16]. ASAXS investigations of charged colloids [17-19] and soft mater objects [20] were also published. ASAXS has been done even at the S, P and Si absorption edges [21-23].

Since the 80-s, when the ASAXS appeared, three main approaches to the data interpretation were developed. Two of them borrow the partial structure factors (PSFs) formalism that is used in wide angle x-ray scattering (WAXS) [24]. De Fontaine, Lyon, and Simon and Regan and Bienenstock applied the partial structure factors, that are Fourier transforms of the atomic pair correlation functions, to the ASAXS data analysis [25-33]. The second method was proposed by Haubold [34, 35], and is often referred as the "Bhatia-Thornton" method. The method also determines partial structure factors. For a binary alloy, these three partial structure factors describe pure density (or topological) fluctuations, pure chemical fluctuations and a correlation factor.

An alternative method was devised by Stuhrmann [36]. Three scattering functions, resonant, non-resonant (or off-resonant) and a cross-term, are determined from at least three scattering curves at each available absorption edge. The resonant function originates from the spatial arrangement of the resonant atoms only, while the non-resonant is thought to be the scattering one could obtain by scattering of X-rays with energy far from any absorption edge [10, 18]. Similar equations were reported also by Epperson and Thiyagarajan [37].

All three methods treat scattering curves obtained near one and the same absorption edge. An attempt to generalize for two absorption edges was done only by Simon and Lyon [29]. Normally, one assumes the absorption edges are remote enough from each other, and the scattering curves measured at one edge are considered independent of the presence of the atoms that have remote absorption edges. Thus the mentioned

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data analysis methods are applied separately for each absorption edge. Simon and Lyon investigated ternary alloys, so they developed their method for binary and ternary alloys, though their equations also apply to multicomponent alloys. The use of Stuhrmann's method always supposes some pseudo binary representation of the studied object. The possible relations between the scattering functions obtained at different edges were never revealed. Haubold derived his equations for binary systems. He also mentioned the possibility to extend his method to ternary systems. Equations for close absorption edges were never derived.

All these methods form a system of linear equations for three unknown variables. The coefficients of the equations are being calculated from the atomic scattering factors of the resonant atoms. However, the system is often ill-conditioned [26,28], and a number of methods were proposed to solve it, including overdetermination by measuring at more then three energies, or omitting the smallest term in the system.

The two-phase approximation is dominating the small-angle scattering data analysis. Small-angle scattering of three phase systems were treated first by Peterlin [38]. Multiphase systems were considered in terms of "stick probability functions" [39-41]. The main concern was the evaluation of the correlation function for three phase system. This theory of three phase systems was applied mainly to catalysts supported by porous media [13,42], but coal [43] or zeolite studies are also available. Experimental data fitting with multiphase structures like core-shell particles is widespread. Turning to ASAXS, one seeks to fit the scattering contrasts at all x-ray energies, but they are not independent. General treatment of the anomalous scattering from multiphase systems is not available.

Many of the industrially important materials are multicomponent and often multiphase systems and ASAXS, as well as other types of contrast variation, is capable of revealing systems that do not comply with the two phase approximation. Anyway, the ASAXS theory and the theory of small-angle scattering from multiphase systems were never reviewed. These two topics are also only briefly mentioned or completely missing in the most popular monographs on small angle scattering [44-47]. This paper briefly revises the anomalous small angle scattering theory, with special accent to the multiphase systems.

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2. Theory

2.1. Small-angle scattering intensity

The elastic scattering of X-rays proceeds through interaction with the electrons of the atoms. The small-angle X-ray scattering is sensitive to the electron density fluctuations in the sample. The scattering contrast is calculated by products of the atom number density, n_i, and the number of electrons Z_i of each type, i, of

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atoms. This stems from the assumption that the atomic scattering factor far from absorption edge equals the number of electrons of the atom. However, this treatment prohibits the energy dependence of the scattering contrast. Near an absorption edge the atomic scattering factors, f_i, take complex values and deviate significantly from the number of electrons

$$f_i(\varepsilon) = f_{0i} + f_i'(\varepsilon) + if_i''(\varepsilon) \tag{1}$$

where $f_{0i} = Z_i$ and ε denotes the X-ray energy. The angular dependence of f_i is insignificant at small scattering angles. The energy variation of the atomic scattering factors at zero scattering angle are tabulated in the literature [48]. The tables of $f_i'(\varepsilon)$ show that it is different from zero for many elements even far from their absorption edges. Thus, it is more suitable to use the partial atomic number density

$$n_i(\vec{r}) = x_i(\vec{r})\eta(\vec{r}) \tag{2}$$

rather than electron density. Here, x_i denotes the atomic part of the atoms of type i and η - the number density of all types of atoms,

$$\eta(\vec{r}) = d(\vec{r})N_a / \sum M_i x_i(\vec{r}) \tag{3}$$

where $d(\vec{r})$ is the mass density, M_i - the corresponding atomic weights, and N_a is the Avogadro's number. The scattering amplitude from irradiated sample volume, V, reads [45]

$$F(\vec{q},\varepsilon) = \int_V \sum_i f_i(\varepsilon) n_i(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \tag{4}$$

with $\vec{q}$ being the scattering vector with magnitude

$$q = |\vec{q}| = \frac{4\pi}{\lambda}\sin(\theta)$$

where 2θ is the scattering angle and λ is the X-ray wavelength. The scattered intensity is then

$$I(\vec{q},\varepsilon) = F(\vec{q},\varepsilon)F(\vec{q},\varepsilon)^* = \left|\int_V \sum_i f_i(\varepsilon) n_i(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3}\right|^2. \tag{5}$$

In the last two equations $\vec{r}$ represents the radius vector of a point of the sample with atomic density of the i-th atom type equal to $n_i(\vec{r})$. With $f_i = Z_i$, the sum $\sum_i f_i(\varepsilon) n_i(\vec{r})$ obviously equals the electron density and represents the SAXS case. The energy dependence can be taken out of the integral sign

$$I(\vec{q},\varepsilon) = \left|\sum_i f_i(\varepsilon) A_i(\vec{q})\right|^2 \tag{6}$$

where

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$$A_i(\vec{q}) = \int_V n_i(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3}. \tag{7}$$

Expression (6) shows that the energy and the, q, dependence can be decoupled. There are several ways to do it. They all lead to a system of linear equations with coefficients that are functions of the parameters f_{0i}, $f_i'(\varepsilon)$ and $f_i''(\varepsilon)$ of the atomic scattering factors. The solution of the systems are partial structure factors. They all have the form $const.A_i(\vec{q})A_j(\vec{q})^*$ and can be an object of the usual SAXS formalism.

2.2 ASAXS partial structure factors (ASAXS-PSF) formalism

The most straightforward approach to equation (6) is the direct calculation. Thus one obtains the expression

$$I(\vec{q},\varepsilon) = \sum_{i,j} f_i(\varepsilon) f_j(\varepsilon)^* S_{ij}(\vec{q}) \tag{8}$$

with partial structure factors defined as

$$S_{ij}(\vec{q}) = A_i(\vec{q})A_j(\vec{q})^* = \int_V n_i(\vec{r}_a) n_j(\vec{r}_b) e^{-i(\vec{r}_a - r_b)\vec{q}} d\vec{r}_a^{\,3} d\vec{r}_b^{\,3}. \tag{9}$$

Though the PSF formalism is the same in SAXS and WAXS this definition of the partial structure factors, (8), does not coincide with any of the WAXS formalisms. The closest match is the Ashcrofth-Langreth (AL) PSF formalism [24, 49] $S_{ij} = \sqrt{\bar{x}_i \bar{x}_j} S_{ij}^{AL}$ where $\bar{x}_i$ denotes the mean sample composition. Obviously, $S_{ij}(\vec{q}) = S_{ji}(\vec{q})^*$ and $S_{ii}(\vec{q})$ is real, $S_{ij}(\vec{q})$ form an $n \times n$ Hermitian matrix. Therefore we could also write

$$I(\vec{q},\varepsilon) = \sum_{i=1}^{n} |f_i|^2 S_{ii} + 2\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \mathrm{Re}(f_i f_j^* S_{ij}). \tag{10}$$

Keeping in mind (2), we see that $S_{ii}(\vec{q})$ results from the spatial arrangement of the atoms of type i only. Equation (9) can be written in terms of cross- and selfconvolution, $\tilde{n}_{ij}(\vec{r})$, of the atomic densities

$$S_{ij}(\vec{q}) = \int_V \tilde{n}_{ij}(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \tag{11}$$

where

$$\tilde{n}_{ij}(\vec{r}) = \int_V n_i(\vec{r} + \vec{r}_b) n_j(\vec{r}_b) d\vec{r}_b^{\,3}. \tag{12}$$

The convolution functions can be safely replaced by a convolution of the atomic density differences. Within a quite good approximation the average atom density of species i can be defined as

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$$\overline{n}_i = \overline{x}_i \overline{\eta} \tag{13}$$

and

$$n_i(\vec{r}) = \Delta n_i(\vec{r}) + \overline{n}_i \ , \tag{14}$$

one obtains

$$\tilde{n}_{ij}(\vec{r}) = \int_V \Delta n_i(\vec{r} + \vec{r}_b) \Delta n_j(\vec{r}_b) d\vec{r}_b^{\,3} + const. \tag{15}$$

The Fourier transform of a constant is a delta function, so the contribution of the constant to the scattering curve is only at $\vec{q} = 0$. It is not measurable so the constant in (15) can be safely omitted. Thus, we can write also

$$I(\vec{q}, \varepsilon) = \left| \int_V \sum_i f_i(\varepsilon) \Delta n_i(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \right|^2 . \tag{16}$$

As the partial structure factors are Fourier transforms of the atom density convolutions $\tilde{n}_{ij}$, which are real, the former will be real when the later are even functions. This is the case of centrosymmetric objects. Another case with real PSFs are the statistically isotropic media. Then the scattering is an average over all spatial directions and the cosine part of the Fourier transform gives a $\sin(qr)/(qr)$ term, but the sine part (i.e the imaginary part) equals zero. Therefore, partial correlation functions and invariants can be introduced. Obviously, the SAXS invariant depends on the energy and is expressed by the partial invariants

$$Q(\varepsilon) = \int_0^\infty I(q, \varepsilon) q^2 dq = \sum_{i,j} f_i(\varepsilon) f_j(\varepsilon)^* Q_{ij} \ , \tag{17}$$

where the partial invariants, Q_{ij}, are

$$Q_{ij} = 2\pi^2 \int_V \Delta n_i(\vec{r}) \Delta n_j(\vec{r}) d\vec{r}^{\,3} \ , \tag{18}$$

As an example for the use of equation (8) we could consider a system of two types of atoms. Equation (8) then reads

$$I(\vec{q}, \varepsilon) = |f_1(\varepsilon)|^2 S_{11}(\vec{q}) + 2\,\mathrm{Re}\left[f_1(\varepsilon) f_2(\varepsilon)^* S_{12}(\vec{q})\right] + |f_2(\varepsilon)|^2 S_{22}(\vec{q}) \tag{19}$$

or

$$I(\vec{q}, \varepsilon) = |f_1(\varepsilon)|^2 S_{11}(\vec{q}) + o_{12}(\varepsilon)\,\mathrm{Re}\left[S_{12}(\vec{q})\right] + h_{12}(\varepsilon)\,\mathrm{Im}\left[S_{12}(\vec{q})\right] + |f_2(\varepsilon)|^2 S_{22}(\vec{q}) \tag{20}$$

$$o_{12}(\varepsilon) = 2\,\mathrm{Re}\left[f_1(\varepsilon) f_2(\varepsilon)^*\right] \ h_{12}(\varepsilon) = -2\,\mathrm{Im}\left[f_1(\varepsilon) f_2(\varepsilon)^*\right].$$

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A system of linear equations for the partial structure factors is formed by scattering curves measured at at least four energies near one or both edges. Thus, it seems possible to determine even the imaginary part $\mathrm{Im}[S_{12}(\vec{q})]$. The majority of the studied systems are either isotropic or contain centrosymetric particles. Then the PSFs are real, and three scattering curves measured at three different energies are enough to determine the system (20).

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For an n-component system we obtain from (10)

$$I(\vec{q},\varepsilon)=\sum_{i=1}^{n}\left|f_i(\varepsilon)\right|^2 S_{ii}(\vec{q})+\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}o_{ij}(\varepsilon)\,\mathrm{Re}\left[S_{ij}(\vec{q})\right]+\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}h_{ij}(\varepsilon)\,\mathrm{Im}\left[S_{ij}(\vec{q})\right]. \tag{21}$$

Measuring at several X-ray energies, also at different absorption edges, one obtains a system of linear equations (21) from which at least in principle the partial structure factors can be determined. The atomic scattering factors, however, are dominated mainly by f_{0i} even in the vicinity of the absorption edges.

2.3 The dispersion analysis or curve separation technique (Stuhrmann's method) [36]

It is possible to distinguish f_{0i} from $f_i'(\varepsilon)$ and $f_i''(\varepsilon)$. By substituting (1) in (21) and collecting the energy dependent terms, one obtains

$$\begin{aligned} I(\vec{q},\varepsilon)=&\sum_{i=1}^{n}(f_i'^2+f_i''^2)S_{ii}+2\sum_{i=1}^{n}f_{0i}f_i'S_{ii}+2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left[\left(f_i'f_j'+f_i''f_j''\right)+\left(f_{0i}f_j'+f_i'f_{0j}\right)\right]\mathrm{Re}(S_{ij})+\\ &-2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\left[\left(f_i''f_j'-f_i'f_j''\right)+\left(f_i''f_{0j}-f_{0i}f_j''\right)\right]\mathrm{Im}(S_{ij})+\sum_{i=1}^{n}f_{0i}^2S_{ii}+2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}f_{0i}f_{0j}\,\mathrm{Re}(S_{ij}) \end{aligned}. \tag{22}$$

This is a generalized multiatom equation for the dispersion analysis method. Here we recognize resonant terms and a pure non-resonant energy independent term

$$\begin{aligned} I_{Ri}&=S_{ii}\\ I_0&=\sum_{n=1}^{n}f_{0i}^2S_{ii}+2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}f_{0i}f_{0j}\,\mathrm{Re}(S_{ij}) \end{aligned}. \tag{23}$$

It is easy to be seen from (10) and (19) that the non-resonant term is the SAXS scattering far from all edges and within the approximation $f_i'=f_i''=0$. The other terms of (22) may form their own contribution or add to the non-resonant term, depending on the change of the corresponding f' and f'' near the selected absorption edge(s). To illustrate this, we will consider the case of curves obtained only near one edge, say of atom type 1. Then (22) takes the form

$$I(\vec{q},\varepsilon)=(f_1'^2+f_1''^2)I_{R1}(\vec{q})+f_1'I_{0R1}'(\vec{q})+f_1''I_{0R1}''(\vec{q})+I_{01}(\vec{q}) \tag{24}$$

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where

$$\begin{aligned} I_{R1} &= S_{11} \\ I'_{0R1} &= 2\left\{ f_{01}S_{11} + \sum_{j=2}^{n}\left[\left(f_{0j}+f'_j\right)\mathrm{Re}(S_{1j}) + f''_j\mathrm{Im}(S_{1j})\right]\right\} \\ I''_{0R1} &= 2\sum_{j=2}^{n}\left[f''_j\mathrm{Re}(S_{1j}) - \left(f_{0j}+f'_j\right)\mathrm{Im}(S_{1j})\right] \\ I_{01} &= I_0 + \textit{all remaining terms from } (22) \end{aligned} \quad . \tag{25}$$

The last equation shows that the non-resonant scattering curves determined at different edges should in principle not be equal. A term proportional to f''_1 will be present even for real S_{ij} If one uses x-ray energies only at one side of the absorption edge then f''_1 may be considered as a constant and its contribution adds to I_{01}. A simplification can be obtained if we consider the SAXS approximation $f'_i = f''_i = 0$ for all atoms except the resonant ones. Then

$$\begin{aligned} I_{R1} &= S_{11} \\ I'_{0R1} &= 2\left\{ f_{01}S_{11} + \sum_{j=2}^{n} f_{0j}\,\mathrm{Re}(S_{1j})\right\} \\ I''_{0R1} &= -2\sum_{j=2}^{n} f_{0j}\,\mathrm{Im}(S_{1j}) \\ I_{01} &= I_0 \end{aligned} \tag{26}$$

and $I''_{0R1} = 0$ for centrosymetric objects and statistically isotropic media so that (24) reduces to its usual form [10, 36]. Anyway, for multiatom systems containing elements with closely situated edges (25) or (22) should be used.

2.4 The Bhatia-Thornton partial structure factors (BT-PSF) formalism

Equations (2) and (8)-(16) show that all scattering functions depend on the product of the variations of the atomic fractions $\Delta x_i(\vec{r})$ and atomic number density $\Delta\eta(\vec{r})$ of all types of atoms. A partial scattering factor depending only on $\Delta\eta(\vec{r})$ can be constructed by the following way. The atomic density difference is

$$\Delta n_i(\vec{r}) = \bar{x}_i\Delta\eta(\vec{r}) + \Delta x_i(\vec{r})\eta(\vec{r}) . \tag{27}$$

Defining a composition average of the atomic scattering factor as

$$\bar{f}(\varepsilon) = \sum_i f_i(\varepsilon)\bar{x}_i . \tag{28}$$

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and accounting also that $\sum_{i=1}^{n}\Delta x_i = 0$ we can replace Δx_n with $-\sum_{i=1}^{n-1}\Delta x_i$,

so that the scattering amplitude is

$$F(\vec{q},\varepsilon) = \int_V \left[\bar{f}(\varepsilon)\Delta\eta(\vec{r}) + \sum_{i=1}^{n-1}\Delta f_i(\varepsilon)\Delta x_i(\vec{r})\eta(\vec{r}) \right] e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \tag{29}$$

with $\Delta f_i = f_i - f_n$.

The following numbering convention can be applied

$$A'_n(\vec{q}) = \int_V \Delta\eta(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \text{ and } A'_i(\vec{q}) = \int_V \Delta x_i(\vec{r})\eta(\vec{r}) e^{-i\vec{r}\vec{q}} d\vec{r}^{\,3} \quad 1 \le i \le n-1 \tag{30}$$

and equations equivalent to (8) and (9) can be written

$$I(\vec{q},\varepsilon) = \sum_{i,j} g_i(\varepsilon) g_j(\varepsilon)^* S'_{ij}(\vec{q}) \tag{31}$$

with

$$g_i(\varepsilon) = \Delta f_i(\varepsilon)\,,\ 1 \le i \le n-1,\ g_n(\varepsilon) = \bar{f}(\varepsilon) \text{ and } S'_{ij}(\vec{q}) = A'_i(\vec{q}) A'_j(\vec{q})^* \tag{32}$$

keeping the indexes *i* and *j* running from 1 to *n*. This means that all equations derived for S_{ij} in the previous sections hold also for S'_{ij}. Namely, a system of equations can be formed and S'_{ij} can be found. Moreover, since $g_i(\varepsilon)$ can also be written as

$$g_i(\varepsilon) = g_0 + g'_i(\varepsilon) + i g''_i(\varepsilon)\ , \tag{33}$$

a new decomposition follows from (22) with the corresponding *f*-s replaced by *g*-s

Equation (31) could be easily recognized as the Bhatia-Thornton decomposition if rewritten in the form

$$I(\vec{q},\varepsilon) = \left|\bar{f}\right|^2 S'_{nn} + \sum_{i=1}^{n-1}\left|\Delta f_i\right|^2 S'_{ii} + 2\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\mathrm{Re}(g_i g_j^* S'_{ij}) \tag{34}$$

In ASAXS, this decomposition scheme was firstly proposed by Haubold [34] for binary systems *n*=2

$$I(\vec{q},\varepsilon) = \left|\bar{f}\right|^2 S'_{22} + \left|\Delta f_i\right|^2 S'_{11} + 2\,\mathrm{Re}(\Delta f_1 \bar{f}^* S'_{12}) \tag{35}$$

or for centrosymetric particles or statistically isotropic media $\mathrm{Re}(S'_{ij}) = S'_{ij}$ so that

$$I(q,\varepsilon) = \left|\bar{f}\right|^2 S'_{22} + \left|\Delta f_1\right|^2 S'_{11} + 2\,\mathrm{Re}(\Delta f_1 \bar{f}^*) S'_{12} \tag{36}$$

[35].

Using (15) and (27), a connections between S_{ij} and S'_{ij} can be found similarly to the WAXS case. They are

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$$
\begin{aligned}
S_{ij} &= \bar{x}_i \bar{x}_j S'_{nn} + \bar{x}_j S'_{jn} + \bar{x}_i S'_{ni} + S'_{ij} \quad 1 \le i, j \le n-1 \\
S_{in} &= \left(1 - \sum_{k=1}^{n-1} \bar{x}_k\right)\left(\bar{x}_i S'_{nn} + S'_{in}\right) - \sum_{k=1}^{n-1}\left(\bar{x}_i S'_{nk} + S'_{ik}\right) \quad 1 \le i \le n-1 \\
S_{ni} &= S^*_{in} \qquad\qquad 1 \le i \le n-1 \\
S_{nn} &= \left(1 - \sum_{k=1}^{n-1} \bar{x}_k\right)^2 S'_{nn} - \left(1 - \sum_{k=1}^{n-1} \bar{x}_k\right)\sum_{k=1}^{n-1} \mathrm{Im}(S'_{nk}) + \sum_{k=1}^{n-1}\sum_{j=1}^{n-1} S'_{kj}
\end{aligned}
\quad . \tag{37}
$$

The relations for binary system given by Haubold [34] are obtainable directly from (37).

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2.5 Multiphase systems

No any assumption about the nature of the scattering object was made so far. The derived equations are valid for any multiatom system suitable for ASAXS. We will consider now a system consisting of p homogeneous phases divided by sharp interfaces. This means that the differences of the atomic number densities can be described as [40]

$$
\begin{aligned}
&\Delta n_{i\alpha}(\vec{r}) = \Delta n_{i\alpha} \Pi_\alpha(\vec{r}) \\
&\Pi_\alpha(\vec{r}) = \begin{cases} 1 & \textit{if the end of } \vec{r} \in V_\alpha \\ 0 & \textit{otherwise} \end{cases}.
\end{aligned}
\tag{38}
$$

Here, α is an index designating the phase and V_α is the volume of this phase. The function $\Pi_\alpha(\vec{r})$ differs from zero only if the end of $\vec{r}$ is within the volume of the phase α. $\Delta n_{i\alpha}(\vec{r})$ represent correspondingly the difference of the atomic density of the component i in the phase α from the average $\bar{n}_i = \bar{x}_i \bar{\eta}$. Obviously, $\Pi_\alpha(\vec{r})$ describes the geometry (or topology) of the phase α. Then from equations (15) and (16) we obtain

$$
S_{ij}(\vec{q}) = \sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} \Delta n_{i\alpha} \Delta n_{j\beta} \hat{S}_{\alpha\beta}(\vec{q}) \tag{39}
$$

where

$$
\hat{S}_{\alpha\beta}(\vec{q}) = \int_V \tilde{\Pi}_{\alpha\beta}(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r}^{\,3}, \quad \hat{S}_{\beta\alpha}(\vec{q}) = \hat{S}_{\alpha\beta}(-\vec{q}) = \hat{S}_{\alpha\beta}(\vec{q})^* \tag{40}
$$

and

$$
\tilde{\Pi}_{\alpha\beta}(\vec{r}) = \int_V \Pi_\alpha(\vec{r} + \vec{r}_b) \Pi_\beta(\vec{r}_b) d\vec{r}_b^{\,3} = \Pi_\alpha \bullet \Pi_\beta \tag{41}
$$

is the convolution of the geometry functions of the phases α and β that we will denote with $\bullet$ for convenience. The functions $\hat{S}_{\alpha\beta}(\vec{q})$ can be named phase scattering functions ($\alpha = \beta$), or cross-phase

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scattering functions ($\alpha \neq \beta$). The functions $\tilde{\Pi}_{\alpha\beta}(\vec{r})$ differ from the "stick probability functions" as defined by [40, 43] only by multiplier and directional averaging. Within a normalization factor, $\tilde{\Pi}_{\alpha\beta}(\vec{r})$ represent correlation functions that can be named phase correlation functions ($\alpha = \beta$) or cross-phase correlation functions ($\alpha \neq \beta$). Equation similar to (39) is given by Simon and Lyon [26], but with $\Delta x_{i\alpha}\Delta x_{j\beta}$ instead of $\Delta n_{i\alpha}\Delta n_{j\beta}$. This is justified as long as the density difference between the phases is zero, as in the cases they studied.

The simplest case is $\alpha, \beta = [1, 2]$

$$\begin{aligned}
\hat{S}_{11} &= \int_V \Pi_1 \bullet \Pi_1 e^{-i\vec{q}\vec{r}} d\vec{r}^3 \\
\hat{S}_{12} = \hat{S}_{21}^* &= \int_V \Pi_1 \bullet (1-\Pi_1) e^{-i\vec{q}\vec{r}} d\vec{r}^3 = V_1\delta(q) - \hat{S}_{11} = -\hat{S}_{11} \\
\hat{S}_{22} &= \int_V (1-\Pi_1) \bullet (1-\Pi_1) e^{-i\vec{q}\vec{r}} d\vec{r}^3 = \hat{S}_{11}
\end{aligned} \quad . \tag{42}$$

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$\hat{S}_{12} = \hat{S}_{21}^* = \int_V \Pi_\alpha \bullet (1-$
$\hat{S}_{22} = \int_V (1-\Pi_\alpha) \bullet (1-$

which means that for two phase systems all three partial structure factors will be real and proportional to each other. This result was also obtained earlier [26]. Indeed from (39)

$$\begin{aligned}
S_{ii} &= (\Delta n_{i1} - \Delta n_{i2})^2 \hat{S}_{11} = (n_{i1} - n_{i2})^2 \hat{S}_{11} = (x_{i1}\eta_1 - x_{i2}\eta_2)^2 \hat{S}_{11} \\
S_{ij} &= S_{ji} = (\Delta n_{i1} - \Delta n_{i2})(\Delta n_{j1} - \Delta n_{j2})\hat{S}_{11} = (x_{i1}\eta_1 - x_{i2}\eta_2)(x_{j1}\eta_1 - x_{j2}\eta_2)\hat{S}_{11}
\end{aligned} \tag{43}$$

Deleted: $S_{ii} = (\Delta n_i^\alpha - \Delta n_i^\beta)^2 \hat{S}_{11}$
$S_{ij} = S_{ji} = (\Delta n_i^\alpha - \Delta n_i^\beta$

As expected, only differences of the atomic number density between the two phases take part in the last equations.

The same approach can be applied to the Bhatia-Thornton PSFs. From (27) and (44)

$$\begin{aligned}
\Delta\eta_\alpha(\vec{r}) &= \Delta\eta_\alpha \Pi_\alpha(\vec{r}) \\
\Delta x_{i\alpha}(\vec{r})\eta_\alpha(\vec{r}) &= \Delta x_{i\alpha}\eta_\alpha \Pi_\alpha(\vec{r})
\end{aligned} \tag{44}$$

and substitution in (30) and (32) results in

$$\begin{aligned}
S'_{ij} &= \sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} \Delta x_{i\alpha}\eta_\alpha \Delta x_{j\beta}\eta_\beta \hat{S}_{\alpha\beta} \quad 1 \le i, j \le n-1 \\
S'_{in} = S'^*_{ni} &= \sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} \Delta x_{i\alpha}\eta_\alpha \Delta\eta_\beta \hat{S}_{\alpha\beta} \quad 1 \le i \le n-1 \\
S'_{nn} &= \sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} \Delta\eta_\alpha \Delta\eta_\beta \hat{S}_{\alpha\beta}
\end{aligned} \quad . \tag{45}$$

Again, for two phase systems, we have $\hat{S}_{12} = \hat{S}_{21} = -\hat{S}_{11}$ and $\hat{S}_{22} = \hat{S}_{11}$ so that

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$$
\begin{aligned}
S'_{ii} &= \left(\Delta x_{i1}\eta_1 - \Delta x_{i2}\eta_2\right)^2 \hat{S}_{11} \quad 1 \le i \le n-1 \\
S'_{ij} &= S_{ji} = \left(\Delta x_{i1}\eta_1 - \Delta x_{i2}\eta_2\right)\left(\Delta x_{j1}\eta_1 - \Delta x_{j2}\eta_2\right)\hat{S}_{11} \quad 1 \le i, j \le n-1 \\
S'_{in} &= S_{ni} = \left(\Delta x_{i1}\eta_1 - \Delta x_{i2}\eta_2\right)\left(\Delta\eta_1 - \Delta\eta_2\right)\hat{S}_{11} \quad 1 \le i \le n-1 \\
S'_{nn} &= \left(\Delta\eta_1 - \Delta\eta_2\right)^2 \hat{S}_{11}
\end{aligned}
\tag{46}
$$

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$$
\begin{aligned}
S'_{ii} &= \left(\Delta x_i^{\alpha}\eta^{\alpha} - \Delta x_i^{\beta}\eta^{\beta}\right. \\
S'_{ij} &= S_{ji} = \left(\Delta x_i^{\alpha}\eta^{\alpha} - \right. \\
S'_{in} &= S_{ni} = \left(\Delta x_i^{\alpha}\eta^{\alpha} - \right. \\
S'_{nn} &= \left(\Delta\eta^{\alpha} - \Delta\eta^{\beta}\right)^2 \hat{S}
\end{aligned}
$$

which means that the BT-PSFs will also be proportional to each other. The quantity η_α in these equations is also defined by equation (3) applied to the phase α.

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Since each point of the sample belongs to only one phase

$$\sum_{\alpha=1}^{p} \Pi_\alpha(\vec{r}) = 1 \quad \forall \vec{r} \tag{47}$$

the $\hat{S}_{\alpha\beta}(\vec{q})$ functions are not independent

$$\sum_{\alpha}^{p} \hat{S}_{\alpha\beta} = \sum_{\beta}^{p} \hat{S}_{\alpha\beta} = 0\,. \tag{48}$$

Solving equation (47) against Π_p and substituting in (39) - (41) one obtains a general expression

$$S_{ij}(\vec{q}) = \sum_{\alpha=1}^{p-1}\sum_{\beta=1}^{p-1} \Delta\xi_{i\alpha}\Delta\xi_{j\beta}\hat{S}_{\alpha\beta}(\vec{q}) \tag{49}$$

for the ASAXS-PSFs and

$$S'_{ij}(\vec{q}) = \sum_{\alpha=1}^{p-1}\sum_{\beta=1}^{p-1} \Delta\zeta_{i\alpha}\Delta\zeta_{j\beta}\hat{S}_{\alpha\beta}(\vec{q}) \tag{50}$$

for BT-PSFs, where

$$\Delta\xi_{i\alpha} = x_{i\alpha}\eta_\alpha - x_{ip}\eta_p \quad 1 \le i \le n; \quad 1 \le \alpha \le p-1 \tag{51}$$

and

$$
\begin{aligned}
\Delta\zeta_{i\alpha} &= \Delta x_{i\alpha}\eta_\alpha - \Delta x_{ip}\eta_p \quad 1 \le i \le n-1 \quad 1 \le \alpha \le p-1 \\
\Delta\zeta_{n\alpha} &= \eta_\alpha - \eta_p \qquad\qquad i = n; \quad 1 \le \alpha \le p-1
\end{aligned}
\tag{52}
$$

The relation

$$\Delta\zeta_{i\alpha} = \Delta\xi_{i\alpha} - \bar{x}_i\Delta\zeta_{n\alpha} \quad 1 \le i \le n; \quad 1 \le \alpha \le p-1 \tag{53}$$

holds. Equations (49) and (50) are mathematically equivalent to (8) and can be also presented in the form of (10). Since $\hat{S}_{\beta\alpha}(\vec{q}) = \hat{S}_{\alpha\beta}(-\vec{q}) = \hat{S}_{\alpha\beta}(\vec{q})^*$ (49) and (50) show that there are $p(p-1)/2$ independent $\hat{S}_{\alpha\beta}$ functions which is exactly the number of the linearly independent "stick probability functions" [39, 41]. We should also

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note that equation (39) is symmetric regarding the phases in the sample, but $\hat{S}_{\alpha\beta}$ are not independent. Equations (49) and (50) are not symmetric regarding the phases, since one phase, p, is selected and all atom number density differences are calculated against this phase, but $\hat{S}_{\alpha\beta}$ are independent.

2.6 Conservation of the number of atoms

In an *ex situ* small-angle scattering experiment, the sample does not usually change. The number of atoms of each type per unit volume is preserved which invokes the atom number conservation law. The average system composition $\bar{x}_i$ and the average atom density $\bar{\eta}$ are usually known or can be easily determined. These values refer to the sample as if it was homogeneous. Whatever the distribution of the atoms among the phases is, these average values should remain constant. Therefore some new relations should be introduced. For the case of homogeneous phases, these are

$$\bar{x}_i\bar{\eta} = \sum_{\alpha=1}^{p} \varphi_\alpha \eta_\alpha x_{i\alpha} \quad or \quad \bar{x}_i\bar{\eta} - x_{ip}\eta_p = \sum_{\alpha=1}^{p-1} \varphi_\alpha \Delta\xi_{i\alpha} \quad 1 \le i \le n \tag{54}$$

$$\bar{\eta} = \sum_{\alpha=1}^{p} \varphi_\alpha \eta_\alpha \quad or \quad \bar{\eta} - \eta_p = \sum_{\alpha=1}^{p-1} \varphi_\alpha \Delta\zeta_{n\alpha} \tag{55}$$

where φ_α represents the volume fractions of the phases. Additional relations must be included in case the components of the system are molecules in order to account for the molecule stoichiometry. Alternatively, one can calculate average molecular scattering factor, molecular fractions and number densities and use them instead of atomic ones. This applies for small molecules which structure does not contribute to the SAXS pattern. Macromolecules should be treated differently. According (38) ,

$$\varphi_\alpha = V_\alpha / V = \frac{1}{V}\int_V \Pi_\alpha(\vec{r})d\vec{r}^{\,3} \tag{56}$$

with V denoting the irradiated sample volume. Equations connecting the volume fractions can be obtained by using the partial invariants, Q_{ij}. Using (18) and (38), we obtain relations similar to (39)

$$Q_{ij} = 2\pi^2 \sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} \Delta n_{i\alpha}\Delta n_{j\beta} \int_V \Pi_\alpha(\vec{r})\Pi_\beta(\vec{r})d\vec{r}^{\,3}. \tag{57}$$

However, all integrals with $\alpha \ne \beta$ will give zero since the different phases have no common points. The integrals with $\alpha = \beta$ will give the volume, V_α, of the corresponding phase. Thus, per unit sample volume one obtains

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$$Q_{ij} = 2\pi^2 \sum_{\alpha=1}^{p} \Delta n_{i\alpha} \Delta n_{j\alpha} \varphi_\alpha \tag{58}$$

Using (54) the last equation can be rewritten in variables $\Delta\xi_{i\alpha}$

$$Q_{ij} = 2\pi^2 \left[\begin{array}{l} \sum_{\alpha=1}^{p-1} \left(\Delta\xi_{i\alpha} - \sum_{\beta=1}^{p-1} \varphi_\beta \Delta\xi_{i\beta} \right) \left(\Delta\xi_{j\alpha} - \sum_{\gamma=1}^{p-1} \varphi_\gamma \Delta\xi_{j\gamma} \right) \varphi_\alpha + \\ + \left(\sum_{\beta=1}^{p-1} \varphi_\beta \Delta\xi_{i\beta} \sum_{\gamma=1}^{p-1} \varphi_\gamma \Delta\xi_{j\gamma} \right) \left(1 - \sum_{\alpha=1}^{p-1} \varphi_\alpha \right) \end{array} \right]. \tag{59}$$

For 2-component two phase systems (n=2, p=2) one obtains

$$Q_{ij} = 2\pi^2 \Delta\xi_{i1} \Delta\xi_{j1} \varphi_1 (1 - \varphi_1) \tag{60}$$

from (59) and

$$Q(\varepsilon) = 2\pi^2 \left[\sum_{i,j} f_i(\varepsilon) f_j(\varepsilon)^* \Delta\xi_{i1} \Delta\xi_{j1} \right] \varphi_1 (1 - \varphi_1) \tag{61}$$

which is the well known relation [45]. Similar decomposition is available for the BT formalism and can be obtained from (59) using (53).

2.7 Models

For a completely unknown system under study, both the scattering functions $\hat{S}_{\alpha\beta}$ and the atomic number density differences $\Delta\xi_{i\alpha}$ and $\Delta\zeta_{i\alpha}$ in equations (49)-(53) are unknown. One needs other methods to determine the phase compositions and densities and therefore $\Delta\xi_{i\alpha}$ and $\Delta\zeta_{i\alpha}$. Then, $\hat{S}_{\alpha\beta}$ can be determined by solving the system of linear equations (49) or (50). Alternatively, one may use electron microscopy to determine the geometrical structure and to try to calculate the phase scattering functions $\hat{S}_{\alpha\beta}$. The later approach is often followed since the compositions of the phases can also be an aim of the ASAXS experiment. The calculation of $\hat{S}_{\alpha\beta}$ for different geometries is beyond the scope of this paper. We will limit ourselves to two simple examples of dilute systems of randomly distributed particles from which, however, more general conclusions can be derived.

2.7.1 Homogeneous spherical particles in a homogeneous matrix

The scattering from a system of homogeneous particles in a homogeneous matrix is described by [46]

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Deleted: The equations (49)-(53) of the previous section show that even for two phase system both the scattering functions $\hat{S}_{\alpha\beta}$ and the atomic number density differences $\Delta\xi_{i\alpha}$ and $\Delta\zeta_{i\alpha}$ are unknown.

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$$I(q,\varepsilon)=\int_0^\infty \Delta\rho^2(\varepsilon)N(R)V^2(R)\Psi^2(q,R)dR \tag{62}$$

where $\Psi(q,R)$ is the normalized scattering amplitude of a sphere with radius R, $N(R)$ is the size distribution and $V(R)$ is the particle volume. As far as the squared contrast, $\Delta\rho^2(\varepsilon)$, does not depend on the particle radius, it can be taken out of the integral sign. The system has obviously only two phases. By definition

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$$\Delta\rho^2(\varepsilon)=\left[\sum_{i=1}^{n} f_i\left(x_{i\alpha}\eta_\alpha - x_{i\beta}\eta_\beta\right)\right]\left[\sum_{i=1}^{n} f_i\left(x_{i\alpha}\eta_\alpha - x_{i\beta}\eta_\beta\right)\right]^* . \tag{63}$$

Performing the multiplication and rearranging the terms, we obtain

$$\Delta\rho^2(\varepsilon)=\sum_{i=1}^{n}\sum_{j=1}^{n} f_i f_j^*\left(x_{i\alpha}\eta_\alpha - x_{i\beta}\eta_\beta\right)\left(x_{i\alpha}\eta_\alpha - x_{i\beta}\eta_\beta\right) \tag{64}$$

Therefore,

$$I(q,\varepsilon)=\sum_{i=1}^{n}\sum_{j=1}^{n} f_i f_j^*\left(x_{i\alpha}\eta_\alpha - x_{i\beta}\eta_\beta\right)\left(x_{j\alpha}\eta_\alpha - x_{j\beta}\eta_\beta\right)\int_0^\infty N(R)V^2(R)\Psi^2(q,R)dR \tag{65}$$

and comparing with (8) and (40), we find

$$\hat{S}_{11}(q)=\int_0^\infty N(R)V^2(R)\Psi^2(q,R)dR \tag{66}$$

and of course all PSF are given by (43). The same derivation can be done for the BT-PSFs and the corresponding result is obtained; $\hat{S}_{11}$ is given by (66), S'_{ij} by (46) and the scattering curve by (36). Thus, the relationship between the model-free PSF (curve separation) techniques and model fit parameters, the scattering contrast in this case, are established.

2.7.2 Core-shell spherical particles in a homogeneous matrix

Core-shell particles in a matrix are an example of a three phase system. The scattered intensity is

$$I(q,\varepsilon)=\int_0^\infty N(R)V_C^2(R)\left|\Delta\rho_{cs}\Psi(q,R)+\Delta\rho_{ms}\gamma^3\Psi(q,\gamma R)\right|^2 dR \tag{67}$$

where $\Delta\rho_{\alpha\beta}$ $\alpha=c,s,m$ is the (complex) contrast between the core, c, the shell, s, and the matrix, m, $\gamma>1$ is the ratio between the shell and the core radii, R is the core radius, $V_C(R)$ is the core volume and $N(R)$ is the size distribution of the cores. After derivation similar to the homogeneous spheres, we obtain

$$S_{ij}=(x_{ic}\eta_c - x_{is}\eta_s)(x_{jc}\eta_c - x_{js}\eta_s)\hat{S}_{cc}+(x_{ic}\eta_c - x_{is}\eta_s)(x_{jm}\eta_m - x_{js}\eta_s)\hat{S}_{cm}+(x_{im}\eta_m - x_{is}\eta_s)(x_{jm}\eta_m - x_{js}\eta_s)\hat{S}_{mm} \tag{68}$$

where

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$$\hat{S}_{cc} = \int_0^\infty N(R)V_C^2(R)\Psi^2(q,R)dR$$
$$\hat{S}_{cm} = \hat{S}_{mc} = \int_0^\infty N(R)V_C^2(R)\gamma^3\Psi(q,R)\Psi(q,\gamma R)dR \ . \qquad (69)$$
$$\hat{S}_{mm} = \int_0^\infty N(R)V_C^2(R)\gamma^6\Psi^2(q,\gamma R)dR$$

2.8 General presentation of the scattered intensity

A general expression for the small angle scattering intensity is obtained by combining (8) and (49) or (50)

$$I(\vec{q},\varepsilon) = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{\alpha=1}^{p-1}\sum_{\beta=1}^{p-1} f_i(\varepsilon)\Delta\xi_{i\alpha}\hat{S}_{\alpha\beta}(\vec{q})\Delta\xi_{j\beta}f_j^*(\varepsilon)\,. \qquad (70)$$

According to the definition of the $\hat{S}_{\alpha\beta}$ functions as Fourier transforms (40) of the convolutions (41) of the functions describing the phase geometry, the $\hat{S}_{\alpha\alpha}$ represent the scattering of the phase α only, as if it was the only phase in the sample and had unit electron density difference with its ambiance. This equation reduces the scattering of multiphase system to a sum of scattering of two phase systems and interphase interference scattering terms. The SAXS correlation function is inverse Fourier transform of the scattered intensity. Thus corresponding to (70) and due to linearity of the Fourier transform, one can write

$$\gamma(\vec{r},\varepsilon) = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{\alpha=1}^{p-1}\sum_{\beta=1}^{p-1} f_i(\varepsilon)\Delta\xi_{i\alpha}\hat{\gamma}_{\alpha\beta}(\vec{r})\Delta\xi_{j\beta}f_j^*(\varepsilon) \qquad (71)$$

where $\gamma(\vec{q},\varepsilon)$ is the global correlation function and $\hat{\gamma}_{\alpha\beta}$ are the already mentioned phase and cross-phase correlation functions. The value of the first derivative of $\hat{\gamma}_{\alpha\beta}$ at the origin will give the specific area of the surface of the corresponding phase when $\alpha = \beta$, or the interface area between the phases α and β when $\alpha \neq \beta$.

The meaning of the phase scattering functions can be clarified by the example of the core-shell particle in Section 2.7.2. The phase scattering functions and correlation functions are shown in Figure 1. The first integral of (69), $\hat{S}_{cc}$, describes the scattering of a two phase system of spheres (the cores only) in a matrix. The third integral, $\hat{S}_{mm}$, also describes a scattering of a two phase system of spheres, but with γ times larger radius than $\hat{S}_{cc}$, i.e. the matrix with the shells (including cores) as holes in it. Thus equation (70) describes

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also the possibility to extract two-phase scattering patterns from the scattering of a multiphase system, which is the aim of the contrast variation studies.

Guinier and Porod approximations can apply to the $\hat{S}_{\alpha\beta}$ functions, and give unique topological parameters (energy and composition independent) in the case $\alpha = \beta$. Functions with $\alpha \neq \beta$ describe interference between the phases, so they would not in general obey the Guinier approximation with the Guinier radius treated as a characteristic of size. In the case of $\alpha = \beta$ the Porod constant is proportional to the specific surface area of the phase α. To find the specific surface area between different phases, the first derivative at $\vec{r} \to 0$ of the inverse Fourier transform of $\hat{S}_{\alpha\beta}$ (i.e. of the first derivative of the corresponding cross-phase correlation function) must be calculated despite that $\hat{S}_{\alpha\beta}$ may apparently follow the Porod law. The case of the core shell particle presented in Figure 1 is a good example. Though $\hat{S}_{cm}$ obeys the Porod law, Figure 1b, with a Porod constant comparable to $\hat{S}_{cc}$ the first derivative of the inverse Fourier transform of $\hat{S}_{cm}$ at $\vec{r} \to 0$ is zero, Figure 1d, which corresponds to the fact that the core and the matrix have no common surface. The actually measured Guinier radius and Porod slope follow from the linear combination (70). They obviously depend on the X-ray energy and their interpretation is not straightforward. An exception is the system of two homogeneous phases, since all partial scattering factors are proportional to $\hat{S}_{11}$.

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Equation (70) suggests also a simplified data fitting procedure when $\hat{S}_{\alpha\beta}$ are known, or assumed by a model, and the phase compositions are sought. Several scattering curves obtained by ASAXS measurement at x-ray energies near one or more absorption edges or by other type of contrast variation technique can be fitted simultaneously by (70). The number of fit variables is then equal to the number of $\Delta\xi_{i\alpha}$ (or $\Delta\zeta_{i\alpha}$), namely $n(p\text{-}1)$, plus the number of possible parameters determining the $\hat{S}_{\alpha\beta}$ functions. To find the compositions of the phases, one has to solve a linear system of equations. In case of no stoichimetric relations are involved, the system is $AX = B$ where

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$$X_{i\alpha} = x_{i\alpha}\eta_\alpha \text{ no summation over } \alpha,\ 1 \le \alpha \le p$$

$$B_{i\alpha} = \Delta\xi_{i\alpha}\ ,\ 1 \le \alpha \le p-1;\quad B_{ip} = \bar{x}_i\bar{\eta} - \sum_{\alpha=1}^{p-1}\varphi_\alpha \Delta\xi_i^\alpha \tag{72}$$

and the compositions are found from

$$\sum_i X_{i\alpha} = \eta_\alpha\ ;\ x_{i\alpha} = X_{i\alpha}/\eta_\alpha \tag{73}$$

For the BT formalism, we have correspondingly

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$$X_{i\alpha} = \Delta x_{i\alpha}\eta_\alpha \text{ no summation over } \alpha,\ 1 \le i \le n-1,\ \ X_{n\alpha} = \eta_\alpha$$

$$B_{i\alpha} = \Delta\zeta_{i\alpha},\ \ 1 \le \alpha \le p-1,\ B_{ip} = \bar{\eta} - \sum_{\alpha=1}^{p-1}\varphi_\alpha \Delta\zeta_{i\alpha} \tag{74}$$

and

$$\sum_i X_{i\alpha} = \eta_\alpha\ ;\ x_{i\alpha} = \bar{x}_i + X_{i\alpha}/\eta_\alpha \tag{75}$$

For both cases, the matrix A is

$$A = \begin{pmatrix} E_{(p-1)\times(p-1)} & -1 \\ 0 & -1 \end{pmatrix}_{p\times p},\ \text{where } E_{(p-1)\times(p-1)} = \delta_{ij}\ , \tag{76}$$

the solution complies the relation $\sum_i x_{i\alpha} = 1$, and the atom number conservation law is fulfilled.

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The quantities of the average composition, $\bar{x}_i$ and atomic density $\bar{\eta}$, involved in (72), (74) and (75), can be measured. However, the p-1 phase volume fractions also appear as unknown variables in these equations. As far as the model is determined the volumes V_α in (38) are known and therefore the volume fractions can be calculated from (56). In most cases the structure model will depend on some parameter set, $P = P(P_1 \ldots P_k)$, $\hat{S}_{\alpha\beta} = \hat{S}_{\alpha\beta}(q,P)$ therefore the volume fractions will also depend on these parameters, $\varphi_\alpha = \varphi_\alpha(P)$. Unfortunately, if the $\hat{S}_{\alpha\beta}$ are parameterized in such a way that the volume fractions of the phases (except phase p) are determined with accuracy of a multiplier the variables $\Delta\xi_{i\alpha}$ (or $\Delta\zeta_{i\alpha}$) can also be determined only with an accuracy of a multiplier. Then at least one composition or density value should be known in advance. This is general behaviour following from (70), but not a drawback of the proposed analysis scheme.

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As an alternative one may use the partial structure invariants Q_{ij} (59) to introduce other $n(p-1)$ equations without involving new unknown variables. This will determine the volume fractions, so the dependence $\varphi_\alpha = \varphi_\alpha(P)$ will decrease the number of parameters by one. Anyway, care should be taken during the invariants calculation since it requires extrapolations of the scattering curves to $q = 0$ and $q = \infty$. Another option could be to use the sample x-ray transmission.

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3. Discussion

Before discussing the main result of this paper, namely equation (70), we should mention some considerations concerning the partial structure factors. Despite the partial structure factors formalism being

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the same in WAXS and SAXS, there are two major differences that follow from the fact that WAXS aims single phase materials while SAXS is applied mainly to materials containing at least two phases. Thus, the density difference between the phases is not accounted for in the WAXS PSF equations. For example, the equation used by Simon and Lyon is obtained by setting $\Delta\eta(\vec{r})=0$ in (27) and replacing $\Delta x_n = -\sum_{i=1}^{n-1}\Delta x_i$ in (15). Therefore $S_{ij}=S'_{ij}$ for $1\le i,j\le n-1$ and $S'_{ij}=0$ for either $i=n$ or $j=n$. Only in this case (8) reduces to

$$I(q,\varepsilon)=\sum_{i,j}\left(f_i(\varepsilon)-f_0\right)\left(f_j(\varepsilon)-f_0\right)^{*}S_{ij}(q) \tag{77}$$

where f_0 is the atomic form factor of the majority (or matrix) element. The application of this expression is, however, limited to systems containing phases with different compositions, but same density, like the phase separation on an undistorted lattice studied by the mentioned authors.

The second difference is seen already from equation (49) and (50). The number of the independent $\hat{S}_{\alpha\beta}$ functions is $p(p-1)/2$. Therefore, S_{ij} will not be linearly independent when $n>p-1$. The maximum number of the independent S_{ij} is the smaller of $n(n+1)/2$ and $p(p-1)/2$. Since the condition $n\ge p-1$ is satisfied in most cases, $p(p-1)/2$ will determine the number of independent partial structure factors. This number in small-angle scattering is determined by the number of phases, but not by the number of atom types of the sample, as in the wide angle scattering [24]. Variations of the electron density at space length of the order of the interatomic distances are responsible for the wide angle scattering. In the case of SAXS, the atoms are "invisible", and the electron density behaves as a continuum. Only the difference of the electron density between the (homogeneous) phases causes the scattering, and therefore the number of these phases should determine the number of the independent structure factors.

Since the SAXS formalism for two phase systems is well developed and understood the reduction (70) of the scattering of multiphase systems to a sum of scattering from two-phase systems and additional terms is essential. As shown by the examples that will follow, this was the aim of many contrast variation studies. In fact, equation like (71) for three phase system was derived by Peterlin [38], and was used by most authors that addressed systems with more than two phases. Anyway, the phase correlation functions were not decoupled from the atomic number densities, equation (70) was not derived and the possible opportunities for interpretation of the contrast variation experiments were not elucidated.

Performing the summations over *i* and *j* in (70) one obtains

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Deleted: The determination of the partial structure factors remains, however, non-trivial. For example, the full solution of the system (22) for two edges with mutual influence will contain nine unknown variables. This means first, that measurements at only three energies at each edge are not enough. The minimum is totally nine energies at both edges. Anyway, some of the terms in (22) may not vary so strongly, and one may decide to fix them, thus reducing the number of the unknown variables. Moreover, the full system could be expected to be ill-conditioned. Important is the simple relation $I_{Ri}=S_{ii}$. Under certain conditions, it allows to extract two phase scattering curves from ASAXS data of multiphase system. Also at least in principle, it allows to determine S_{ii} by Stuhrmann's method and after that to attempt finding S_{ij} from (8). The same applies for the decomposition scheme (31), (33) and (22) with *f*-s replaced by *g*-s from (33). ¶

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$$I(\vec{q}) = \sum_{\alpha=1}^{p-1}\sum_{\beta=1}^{p-1} \Delta\rho_\alpha \Delta\rho_\beta^* \hat{S}_{\alpha\beta}(\vec{q}) . \tag{78}$$

where $\Delta\rho_\alpha$ represent the (complex) scattering contrast of phase α against phase p. The last equation has exactly the mathematical form of equation (8) but phase scattering functions take the place of the partial structure factors, and the scattering contrast replace the atomic scattering factors. The validity of (78) for any kind of contrast variation is not its only advantage to (8). The PSFs usually contain information for all phases in the sample (eq. (49) and (50)) which renders their interpretation as difficult as the original scattering curves, while the $\hat{S}_{\alpha\beta}$ functions have clear physical meaning and for $\alpha = \beta$ one could unleash the entire SAS formalism developed for two phase systems. It is to be noted that in all derivations no any assumption about phase p was made, so p could be any phase, not necessarily the phase with highest volume fraction (matrix or solvent). Obviously, varying the x-ray energy, the composition, x, and/or density, d, of one of the phases (excluding p in this form of equation (74)) an equation of the form (considering only real atomic scattering factors and $\hat{S}_{\alpha\beta}$ functions)

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$$I(q,x,d) = \Delta\rho(x,d)^2 I_c(q) + \Delta\rho(x,d) I_{cs}(q) + I_s(q) \tag{79}$$

is obtained for $p \geq 3$. Such an equation is widely used in the study of macromolecules. The large molecules are considered as a phase, and $\Delta\rho(x,d)$ is the average scattering contrast of the molecule with respect to the solvent. The contrast variation is achieved by varying the composition and/or density of the solvent, assuming the molecules are impenetrable for the solvent. The ratio D_2O/H_2O is used in case of neutron scattering. The functions $I_i(q)$ $i = c, cs, s$ are called basic functions [45]. Actually, for p=3, $\Delta\rho = \Delta\rho_1$, $I_c = \hat{S}_{11}$, $I_{cs} = 2\Delta\rho_2 \hat{S}_{12}$ and $I_s = (\Delta\rho_2)^2 \hat{S}_{12}$. The use of equation (79) with the average molecule scattering contrast against the solvent defines also the contrast $\Delta\rho_2$ as the contrast of the "internal" part of the molecule against the average molecule contrast. According to our derivation $I_c = \hat{S}_{11}$ is the scattering function of the solvent. Keeping in mind that the molecules are treated as particles with same shape, the later statement matches exactly the meaning of I_c as "shape scattering function". The basic function I_s is treated as the scattering function of the internal part of the molecule. Actually, to be really internal part the first derivative of the inverse Fourier transform of $\hat{S}_{12}$ (i.e. of I_{cs}) at $r \to 0$ must be zero, which will mean that the solute and the molecule internal part have no common surface. Equation (79) is a three phase approximation of a macromolecule solution in this case.

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Equation (79) holds for any number of phases, as far as only the contrast of one phase varies and the scattering function of this phase is always $\hat{S}_{11} = I_c$. The same relations apply also for ASAXS, so that we can draw the conclusion that ASAXS is most fruitful if the resonant element, at whose absorption edge the measurement is performed, is contained in only one phase. Then, using (49) and (51), one obtains that the corresponding partial structure factor is proportional to the scattering function of the phase containing the resonant atoms

$$S_{ii} = x_{ik}\eta_k \hat{S}_{kk} \tag{80}$$

where i denotes the resonant element and k - the only phase that contains it. S_{ii} can be found by the Stuhrman's method since, as already shown, S_{ii} equals the resonant curve I_R. Therefore the Stuhrman's method could be quite useful for systems like supported metallic catalysts or colloids containing metallic ions. We should also note that the application of (79) requires the compositions of the phases to be known in order to form a system of equations. ASAXS is a favourable exception, in this case since the atomic scattering factors have to be known, but not necessarily the phase compositions.

The majority of the studies of systems with three or more phases try to use models of the phase structure, so that either the scattering curves are directly fitted or the correlation function is parameterized by certain small number of parameters and the scattering curves are fitted again. In the later case [38, 41, 50], the most frequently used model involves exponential correlation function, but Gaussian and other functions were also used. The studies went in this direction, since it is not possible to determine by SAXS the phase surface areas in system with more than two phases without assuming a structure model. However, this is possible according to equation (70) or (78), provided suitable contrast variation technique is available. In practice, the success of this procedure will depend also on the magnitude of the contrasts in (78), and the limits of the possibility of their variation.

We should also note that the definition of phase is given here by (38) and does not necessarily connect to thermodynamic phases. One example is the already discussed scattering from solutions of macromolecules where the macromolecules are considered actually to be presented by two phases. Another good example is the ASAXS study of the primary crystallization of Ni(P) particles in an amorphous NiP alloy [5]. A composition size dependence was found for these particles, which means that the $\Delta\xi_i^\alpha$ variables depend on the particle size. The particles of different size and composition are treated as different phase, and due to the low volume fraction the interparticle interference can be neglected, which eliminates also the cross-phase scattering functions. The total scattered intensity can be presented as

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Deleted: The three phases of a metallic catalyst on a porous support are the support, the catalyst and the voids. It is often treated by subtracting scattering curves measured at two X-ray energies. This is strictly justified when no mutual interference occurs between the catalyst and the pores or the support [50]. Then, $\hat{S}_{\alpha\beta} = 0$ for $\alpha \neq \beta$ and $I_{cs}(q) = 0$ and the difference of two ASAXS curves is proportional to the scattering of a two phase system (i.e. proportional to $I_c = \hat{S}_{11}$). The later relations were proven to hold for three-phase Debye-random system [13]. ¶ Another approach is to measure the scattering of the support alone and subtract it from the scattering of the support plus catalyst under the assumption, that the support is not altered by the introduction of the metal. This procedure obviously subtracts the phase scattering function of the voids (or the support, which is the same), but does not subtract the corresponding cross-phase scattering functions between the catalyst, the voids and the support. ¶

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Deleted: The "pore masquant technique" is another example where (79) could apply. The scattering power of only one phase (pores in a porous media) is changed by filling the pores with gas or liquid. The conclusion that the scattered intensities obtained by varying the gas pressure are linearly related [43] follows from (79) also. ¶

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$$I(q) = \sum_{\alpha=1}^{m} \left[\Delta\rho_\alpha(\varepsilon, R_\alpha)\right]^2 \hat{S}_{\alpha\alpha} \tag{81}$$

where m equals the number of points (bins) in the particle size distribution, and R_α is the radius of the particles of the phase α. $\hat{S}_{\alpha\alpha}$ has the form of (66), but the integration is done in a short interval around R_α.

The multiphase approximation (38) obviously concerns systems with phases separated by sharp surfaces. Interesting is also the case of slowly varying scattering density without well formed phase boundaries. The conditions for best two-phase approximation of such system were studied by Ciccariello [51] and it was proven that the position of the surface dividing the two phases depends on the actual scattering density profile. Thus, if contrast variation is applied then the scattering density profile will change and therefore the dividing surface between the two phases will also change resulting in variable size of the features of the sample structure. If the multiphase approximation is applied, then the number of "phases" used to approximate the variable scattering density can be increased until the scattering data can be fit with phases with constant phase boundaries. The resulting scattering density profile can be regarded as several steps approximation of the variable scattering density. An analogy with the black and white images (two phase approximation) and greyscale images (multiphase approximation) can be proposed.

The possibility to find the scattering function of a single phase trough (78) and (79) was discussed until now. Another task of the ASAXS experiment is to find the phase compositions. Such a procedure is outlined in section 2.8. It requires the phase scattering functions to be known. The usual approach is to introduce a kind of idealized model like homogeneous spheres or spherical core-shell structure. The key point for determining the number of composition and density values from ASAXS experiment remains the solution of the system of equations formed by (70). The solution of similar systems of bilinear equations is done by least squares method (i.e. curve fitting), but it seems that there is still no systematic study of the conditions for existing and uniqueness of the solution [52]. The introduction of the structure model parameters, P, can also lead to dependences that will decrease the number of atomic number differences and correspondingly the number of compositions and densities that can be determined, in the worst case with k. Therefore, multiple solutions could still be possible. They will define the composition and density ranges of the phases in the sample. Some of the values of the composition or density variables are often known. This would allow the determination of the unknown compositions even with reduced number of $\Delta\xi_{i\alpha}$ (or $\Delta\zeta_{i\alpha}$) variables determined by ASAXS. It is also tempting to try using numerical Fourier transform [53] to calculate $\hat{S}_{\alpha\beta}$ from

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binary maps obtained from electron microscopy or 3D atom probe. Such an approach would eliminate the need to stick to regular particle shapes.

4. Conclusions

In a very general terms, the small angle scattering curve of a system of n types of atoms (components) and p homogeneous phases can be presented as a linear combination of phase scattering functions, $\hat{S}_{\alpha\beta}(\vec{q})$ $(\alpha = \beta)$, representing the scattering of each phase as if it scattered alone in a two phase system, and cross-phase scattering functions, $\hat{S}_{\alpha\beta}(\vec{q})$ $(\alpha \neq \beta)$, that represent the interference scattering between each pair of phases – equation (70). The coefficients of this linear combination consist of the partial atomic density differences, $\Delta\xi_{i\alpha}$, that depend only on the phase compositions and densities, and the atomic scattering factors, f_i, that depend on the X-ray energy only. The functions $\hat{S}_{\alpha\beta}(\vec{q})$, do not depend on either the X-ray energy or the phase compositions or densities, but only on the spatial distribution of the phases in the sample.

This representation of the scattering of the multiphase system combined with contrast variation techniques allows extraction of structural information about one or two phases, which are of interest in a multiphase sample. The contrast variation techniques, including ASAXS, are most useful if the scattering density of only one phase can be varied independently from the scattering densities of the other phases. Thus, if the resonant element is present in only one phase the Stuhrmann's resonant curve is proportional to the corresponding phase scattering function and can be treated as if it scattered in a two phase system. If suitable contrast variation is possible, the area of the surfaces of all phases and the interfaces between the phases can be found without introducing any model for the structure of the phases.

For a system of n types of atoms and p homogeneous phases the number of independent partial structure functions is $p(p-1)/2$ and is determined by the number of phases, rather then by the number of the atom types in the sample. Anyway, $n(p-1)$ partial structure factors could be sufficient to determine the atom number density differences between the phases, provided the phase scattering functions are known. The phase compositions and densities of homogeneous phases can be found by solving simple $p \times p$ system of linear equations that incorporates also the atom number conservation law.

Acknowledgments

The author expresses his thanks to Prof. R. Kranold, Dr. A. Hoell and Dr. A. Heinemann for their comments on the manuscript.

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Deleted: Thus the basic functions approach (equation (79)), used in the study of macromolecular solutions, is a three phase approximation of potentially multiphase system. It is applicable to other systems in which the scattering density of only one phase can be varied independently from the scattering density of the other phases.

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Deleted: the measurement can be done near the x-ray absorption edge of an element contained in only one phase. The scattering function of this phase is proportional to the corresponding partial structure factor (80) which is equal to the resonant scattering curve in the Stuhrmann's method. Equation (70) shows also that, at least theoretically, i

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Figure Caption.

Figure 1. Monodisperse system of core-shell particles with core radius 4 nm and shell radius 6 nm: phase scattering functions, core-core - $\hat{S}_{cc}$, matrix-matrix - $\hat{S}_{mm}$ and cross-phase scattering function core-matrix $\hat{S}_{cm}$, a); the cross-phase scattering function core-matrix in linear and logarithmic vertical axis, b); the corresponding correlation functions, c); and their derivatives, d), $\hat{\gamma}'_{cm}(0) = 0$, $\hat{\gamma}'_{mm}(0) = \gamma^2 \hat{\gamma}'_{cc}(0)$.

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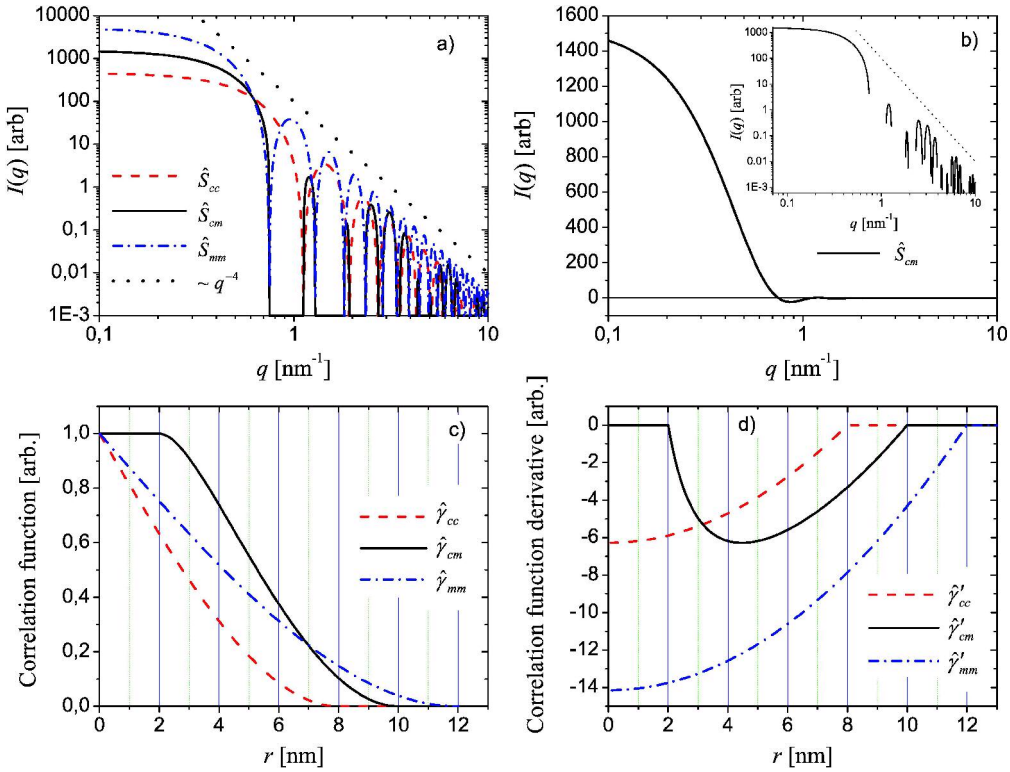

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