Anomalous Small-Angle X-Ray Scattering of Core-shell Nanoparticles

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1 Introduction

The great potential of core-shell nanoparticles stems from the capacity to obtain combined structures with properties that neither individual material possesses [1]. Nanoparticles constitute a bridge between bulk materials and atomic structure, possessing exceptional electronic, magnetic and mechanical properties [3]. The aim of this project was the study of Co-Ag core-shell nanoparticles by anomalous small-angle x-ray scattering (ASAXS) method. Because of contrast variation provided by this method, it is powerful tool by which one can probe the nanoscale structure.

In this project computacional analysis was made which allowed the complete characterization of the core-shell nanoparticles. The determination of the partial structure factors (PSFs) of the core-shell and 'onion' sphere near and below the absorption edges of cobalt and silver elements was also possible. ASAXS simulations were also applied to polydisperse systems.

2 Theory

2.1 ASAXS Theory

The contrast variation in the ASAXS method arises from the variation of atomic scattering factor of elements near the absorption edges. By measuring small-angle x-ray scattering (SAXS) of systems consisting of two or more elements, for example, silver (Ag) and cobalt (Co), the scattering coming from these two elements cannot be distinguished easily. On the other hand, by adjusting the x-ray energies near and below the absorption edges of one of these elements (which is called "anomalous element") the determination of the partial structure factors (PSFs) for this system and the distinction of the scattering coming from different elements is in principle possible.

In the SAXS theory we can approximate the scattering factor as the atomic number of the element. However, we cannot do this approximation when the x-ray energies are adjusted near the absorption edge of the element; in this case, a complex anomalous dispersion correction is needed and the scattering factor is expressed by [5]:

$$f(q,E) = f_0(q) + f'(q,E) + if''(q,E), \tag{1}$$

where f_0 is the Fourier transform of the electron density of the atom, f' and f'' are, respectively, the real and imaginary part of the dispersion correction and q is the scattering vector, which is given by:

$$q = \frac{4\pi \sin\theta}{\lambda}, \tag{2}$$

where θ is half of the scattering angle and λ is the wavelength of the x-rays. At small angle and consequently at small q value this expression may be approximated by:

$$f(E) = Z + f'(E) + if''(E), \tag{3}$$

where Z is the atomic number of the element. The imaginary part of the dispersion correction in the equation (3) is related to the absorption of the x-rays. From this equation it can be seen that the dispersion correction factors are energy dependent and in the vicinity of the absorption edge these factors show strong variations [4]. In this present project, ASAXS intensities were analyzed at three energies below and near the cobalt and silver K absorption edges.

2.2 Partial Structure Factors (PSFs)

The scattering intensity is, by definition, the absolute square of the scattering amplitude:

$$I(q) = |A(q)|^2 = A(q)A^*(q) \tag{4}$$

In general we can calculate the scattering intensity through the Debye formula [2]:

$$I(q) = \sum_{n=1}^{N}\sum_{m=1}^{N} f_n f_m \frac{\sin(qx_{nm})}{qx_{nm}}, \tag{5}$$

where f_n and f_m are the scattering factors of point-like scattering of units n and m, located at a distance x_{nm} from each other. When the system is composed of two different types of elements, e.g. type 1 for cobalt and type 2 for silver, it can be separated in three parts, the so called partial structure factors (PSFs). Here this factors will be called $P_{11}(q)$, $P_{22}(q)$ and $P_{12}(q)$ and they will describe, respectively, the partial structure of element 1, element 2 and partial structure factor of the mixed elements 1 and 2. Then the x-ray scattering intensity for this system can be written by:

$$I(q) = P_{11}(q) + P_{12}(q) + P_{22}(q) \tag{6}$$

The calculation and determination of the PSFs were done using computational analysis and the methods used are described in the next section.

3 Method

3.1 Determination of core-shell nanoparticles coordinates

The construction and determination of the coordinates of the core-shell nanoparticles was the first step carried out in this project. Choosing the desired radius of the core and shell and the atomic scattering factors of the elements, several core-shell nanoparticles were constructed by mathematical calculations. The points of the coordinates were separated from each other by a distance of 2 Å and the radius of the core-shell varied from 0.6 to 5 nm.

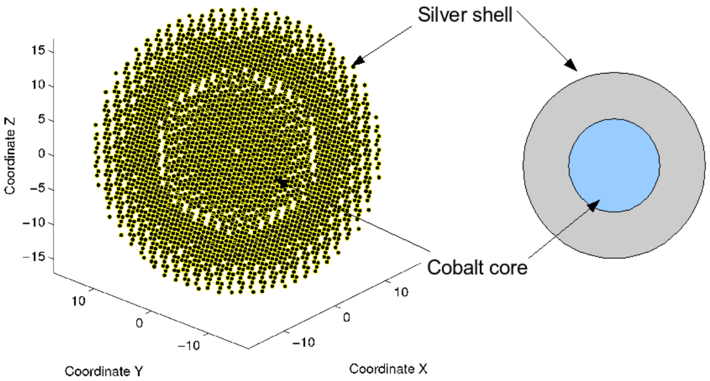

Figure 1: Schematic and 3-D versions of the core-shell nanoparticle.

Besides the core-shell coordinates, the coordinates of 'onion' sphere were also obtained. The atomic scattering number of the elements were present in the coordinate datas.

3.2 Determination of the partial structure factors (PSFs)

The datas obtained through the construction of the core-shell nanoparticles and other spheres were used to calculate the partial structure factors by Debye formula. For three different energies near the absorption edges and, consequently, three different values of anomalous scattering factors of Co and Ag elements, the computational analysis used determined the partial structure factors in the following way: for each q-value, if two atoms (or points) from the core-shell system coming from the same type of atoms (with the same atomic number Z) the scattering intensity calculated was separated into P_{11} term for Co elements and P_{22} term for Ag elements; on the other hand, if two points are of different type, then the intensity was separated into P_{12} term. The Figure 3 and Table 1 show the anomalous scattering factors and energies used to calculate the PSFs of the Co-Ag core-shell nanoparticles.

Element	Z	Energy (eV)	f'	f''
Cobalt (Co)	27	7300	-2.603	0.524
		7616	-4.061	0.485
		7700	-6.564	0.475
Silver (Ag)	47	25404	-4.652	0.571
		25475	-5.655	0.613
		25500	-6.662	0.746

Table 1: Anomalous scattering factors of Co and Ag elements at different energies near from their K absorption edge

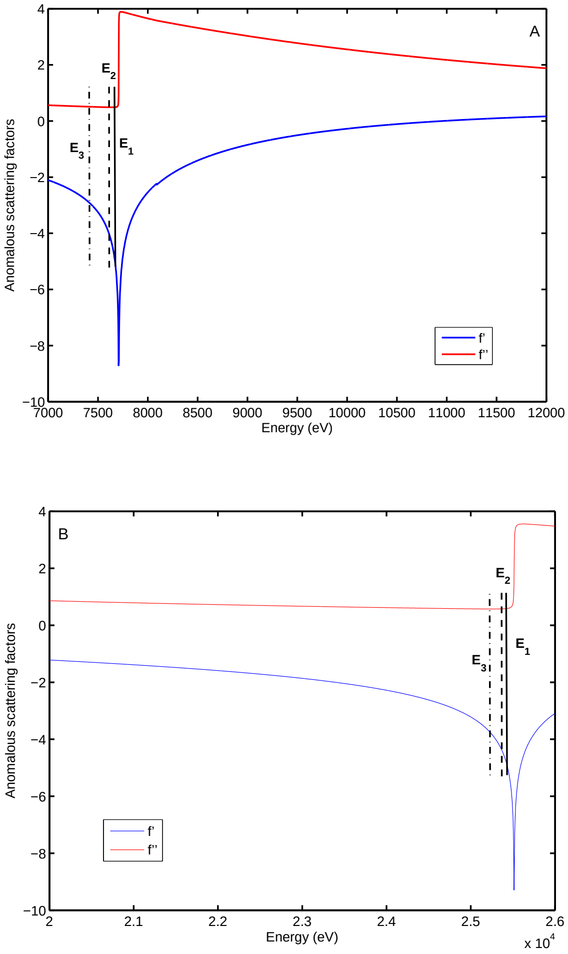

Figure 2: Anomalous scattering factor for (A) Co and (B) Ag absorption edge.

The PSFs can be seen on the Figure 3 (A). In this same figure (B, C and D) can be observed how the partial structure factors separately vary as function of energy. Note that each partial structure factors gives the scattering intensity pattern of the object studied. When the energy is adjusted near and below the absorption edge of the cobalt, for example, the P_{11} term shows the scattering pattern of the core, which is constituted by cobalt element, the P_{12} term shows the pattern of the mixed elements and the last term, P_{22}, shows the scattering pattern of the shell, constituted by silver elements. Note also that this last term does not vary as function of the energy since the energies were adjusted near and below the Co absorption edge. We can see also in this figure that the scattering intensity increases when the energy decreases. However, I have to point that in real experiment we never get the PSFs separetely, they always are summed in the scattering intensity form $I(q)$.

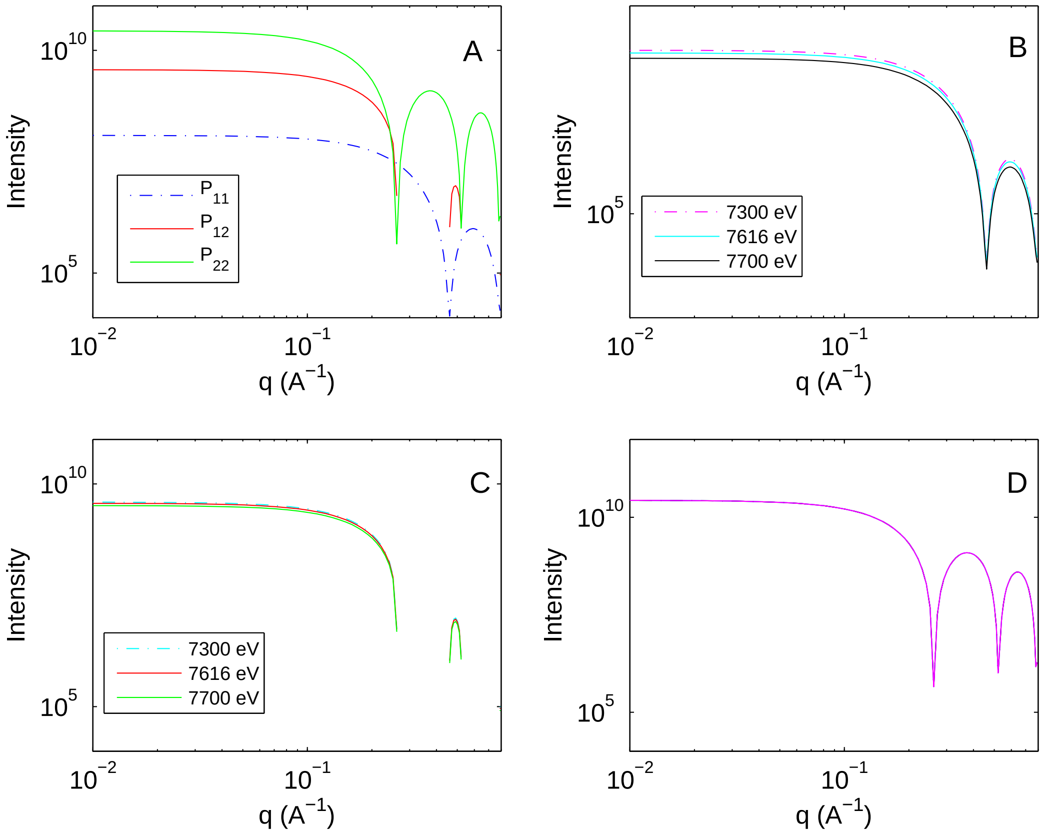

Figure 3: (A) Partial structute factors of Co-Ag core-shell at 7616 eV for Co energy; (B), (C) and (D) shows, respectively, the P_{11}, P_{12} and P_{22} term for three energies below and near the cobalt absorption edge. Note that in the last graphic there was a superposition of the curves at different energies.

3.2.1 Construction of scattering intensity patterns

The scattering intensity pattern of the core-shell nanoparticles was obtained through the sum of the partial structure factors. Figure 4 shows the scattering intensity pattern of the core-shell at three energies below and near the absorption edge of Co and Ag elements. There is also in both graphics the subtraction curve of two of these energies; note that some regions of the subtraction curve do not appear in the doublelogarithmic scale, because some values are negative. When two scattering intensity patterns are subtracted from each other, it is foreseen that the resulting scattering pattern shows the scattering of the core, if the cross term P_{12} can be assumed to be small. This is because, as seen in the Section 3.2, the P_{22} term is the same for all the energies. But according to these simulations, in case of core-shell nanoparticles, the P_{12} term cannot be neglected as small. On the other hand, if we adjusted the energies near and below the absorption edge of Ag, the subtraction scattering pattern is supposed to be only from shell (since this part is constituted by silver element).

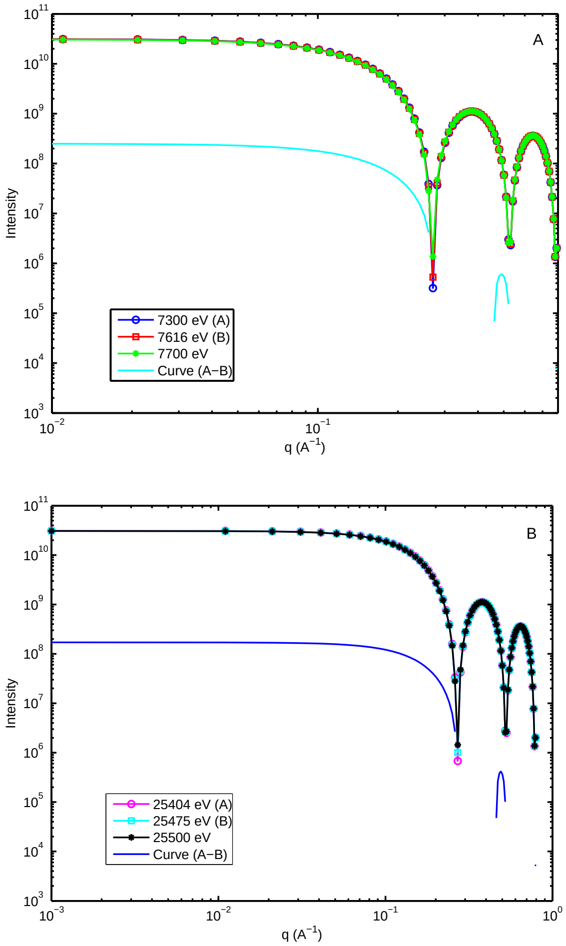

Figure 4: Scattering intensity patterns for core-shell nanoparticle at energies below and near the K absorption edge of Co (A) and Ag (B) elements and subtraction curve of two scattering intensity patterns in loglog scale.

Figure 5 shows the cobalt subtraction curve in linear scale, where the negative regions of the subtraction curve, which do not appear in the Figure 4, can be seen. From comparison of the subtraction curve in Figure 4 and the PSFs in Figure 3 (B) and 3 (C) it can be concluded that the subtraction curve is very similar to the cross term P_{12} and not to the PSF from core. This means that the P_{12} term have a strong contribution in the data analysis.

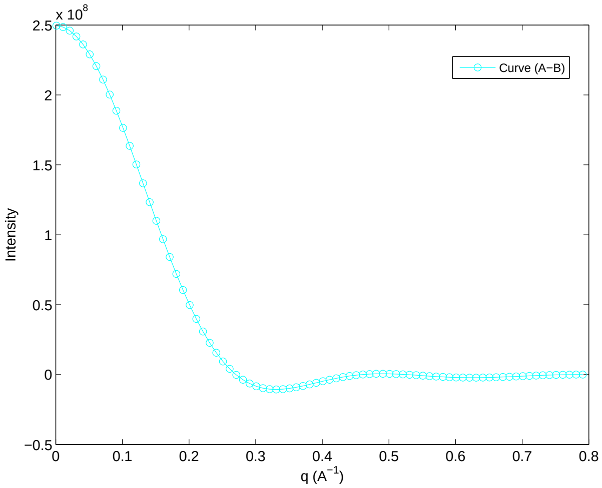

Figure 5: Subtraction curve in linear scale of two scattering intensity patterns at two energies at cobalt edge.

The subtraction curve for the case of core-shell nanoparticles with core constituted by silver and shell by cobalt element was also obtained in order to compare with the subtraction curves obtained in the Figure 4. The Figure 6 shows that the subtraction curve does not look like the shell unit (since the energies were adjusted at cobalt absorption edge). This fact confirms again that the P_{12} term dominates in the case of core-shell nanoparticles.

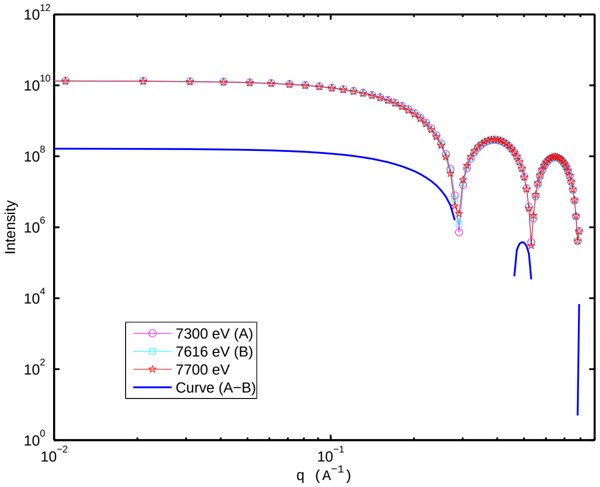

Figure 6: Scattering intensity patterns for core-sehll nanoparticle with core and shell constituted by cobalt and silver, respectively at Co absorption edge.

3.2.2 Scattering intensity pattern of the 'onion' sphere

To simulate a sphere constituted by mixed elements, a sphere constituted by different slices of cobalt and silver elements was made. From the 'onion' coordinates, the scattering intensity pattern was calculated at three energies near and below the Co absorption edge. The subtraction curve of two different energies was also obtained.

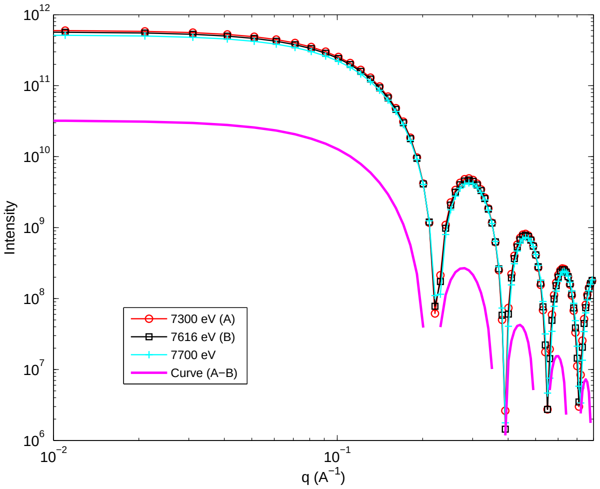

Figure 7: Scattering intensity patterns for 'onion' nanoparticle at energies below and near the K absorption edge of Co and subtraction curve of two scattering patterns at two energies in loglog scale.

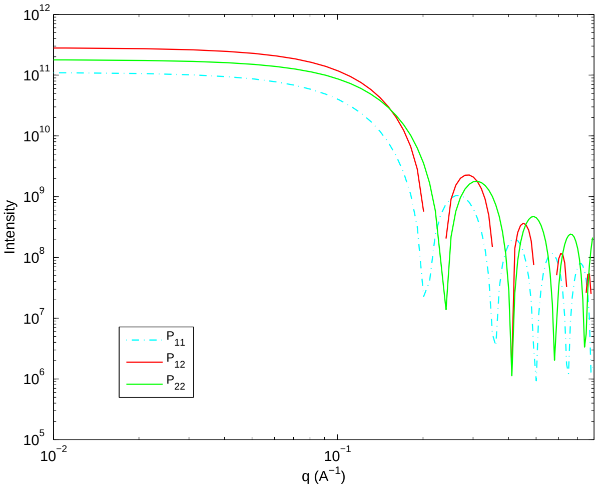

Figure 8: Partial structure factors of 'onion' sphere at 7616 eV (Co edge), in loglog scale.

The partial structure factors of 'onion'sphere can be seen on the Figure 8. The graphic above shows that all the PSFs have the same behaviour, there are only some differences in the intensities between the curves. This means that the 'onion' sphere simulates a sphere constituted by mixed elements since we cannot distinguish the scattering pattern coming from the Co and Ag elements.

3.2.3 Scattering intensity patterns of core-shell nanoparticles with several sizes

In order to compare the core-shell nanoparticles with different sizes, several core-shell were built keeping the core and shell volumes equal. The scattering intensity patterns from these core-shells can be seen in Figure 9, where there is also a schematic figure with the sizes of the core-shells. We can see on this graphic that the scattering intensity increases when the size of the particle increase.

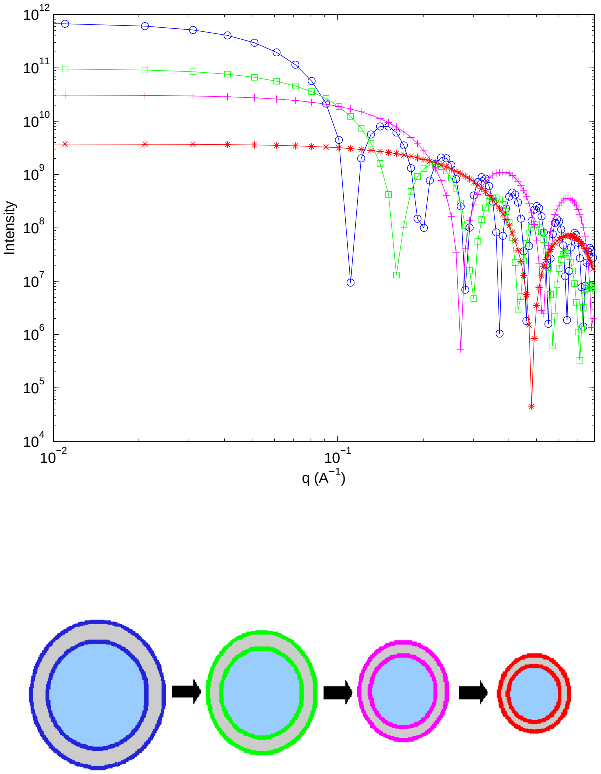

Figure 9: Scattering intensity patterns for core-shell nanoparticles with several sizes. The colorful rims depict each scattering intensity pattern with the same color.

In real experiments, however, the samples often are systems consisting more than one kind of sizes. Such systems are called polydisperse. Figure 10 shows the 'more realistic' scattering patterns coming from this system.

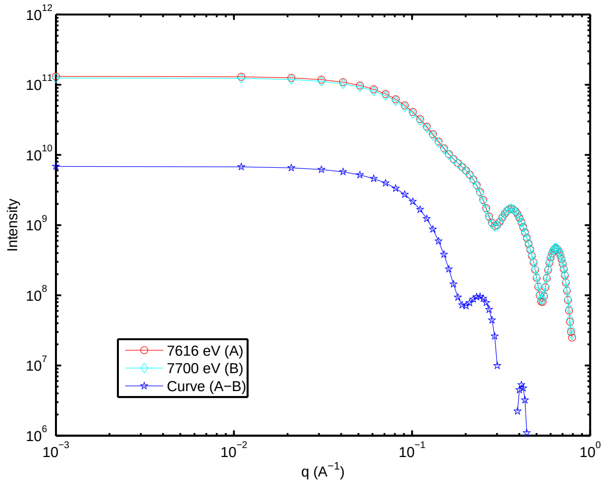

Figure 10: Scattering patterns and subtraction curve coming from polydisperse system at cobalt absorption edge.

We can note also that the subtraction curve has some negative regions and this is a confirmation that the system under study is constituted by core-shell nanoparticles.

4 Conclusion

Several computational calculations were done to describe the ASAXS intensities of core-shell nanoparticles. Although SAXS is the mostly used and known method, it cannot distinguish easily the scattering intensity coming from systems constituted of two or more elements. By adjusting the energies below and near the absorption edge of the elements under study it is possible to separate the sacttering pattern coming from different elements through the determination of the partial structure factors (PSFs). In this project were showed that each PSFs represents the scattering pattern coming from core and shell unit and their form depending of the energy chosen (near and below the cobalt or silver K absorption edge). The scattering intensity patterns of core-shell nanoparticles were also built for three energies below and near the Co and Ag absorption edges and the subtraction curves were obtained for two closest energies. The analysis of the subtraction curve revealed that this pattern does not look like the scattering pattern coming from only the core (in case of Co edge) and shell (in case of Ag edge) unit and it can be concluded that the cross term P_{12} cannot be neglected when the datas are analyzed. When the samples studied are polydisperse systems ASAXS method can be used to identify if the particles which constitutes the sample are core-shell or not.

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