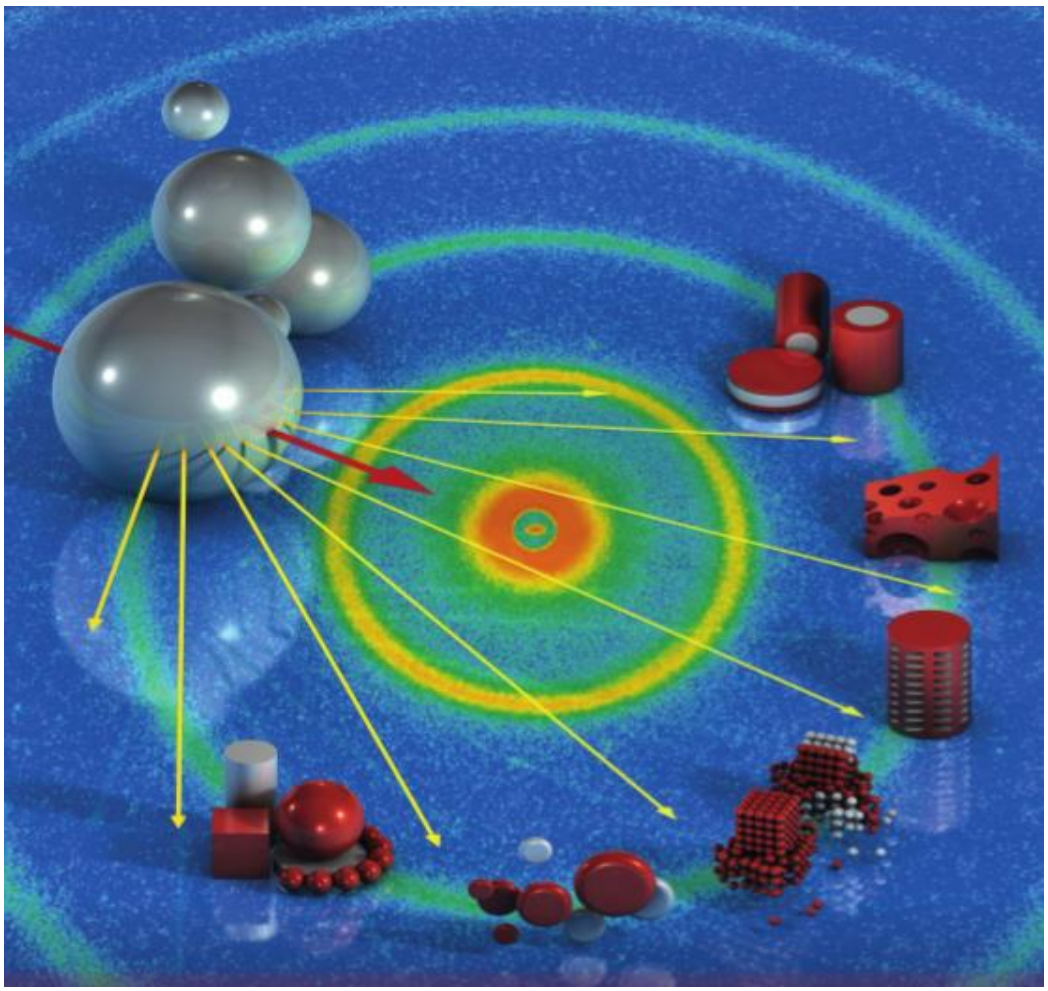
SAXS IN A GLIMPSE



This document is not dedicated to one specific scattering instrument or one particular application area, but aims to give a global overview of the main instrumentation and applications.

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Contents

1. Preface

Small-angle X-ray scattering is an increasingly important tool in studying the diverse fields of material science. This process is performed with the availability of latest high-performance laboratory instruments along with the availability of powerful data-analysis programs.

To achieve this, it's important to know how a SAXS instrument works and how SAXS analysis is done. What is collected in this document is related to the introduction, basics, instrument, analysis, scientific and Industrial application of SAXS device. It will give you a broad perspective because you should select SAXS and how to fulfill your aim.

2. SAXS introduction

SAXS is an analytical method to determine the structure of particle systems in terms of averaged particle sizes or shapes. The materials can be solid or liquid and they can contain solid, liquid or gaseous domains of the same or another material in any combination. Generally speaking, Transmission mode is state when X-rays are sent through the sample and every particle that happens to be inside the

beam will send out its signal. Thus, the average structure of all illuminated particles in the bulk material is measured. It is very important to know what are the similarities and differences between scattering and microscopy and when to use them.

Scattering and absorption are the first processes in any technique that uses radiation, such as an optical microscope. Although the operation of a scattering instrument is identical to the first process that takes place in a microscope, its result is complementary to that of a microscope. The second process in an optical microscope is the reconstruction of the object (particle) from the scattering pattern that is done with the help of a lens system. Instead, the scattering pattern must be recorded and the reconstruction must be attempted in a mathematical way rather than in an optical way. The constitutes the main difference between microscopy and X-ray scattering is that in the recording process the phases of the detected waves the scattering pattern due to the lost phases, it is not possible to achieve a holographic representation of the object in a direct way, as it would be possible with a lens system.

In brief:

Microscopy: The scattered waves are processed into a picture (reconstructed) by a lens. SAXS: The scattered intensity is recorded by a detector and is processed mathematically, as a replacement for the actions of a lens.

In addition, in microscopy one object or a small part of a sample is magnified and investigated but with scattering techniques the whole illuminated sample volume is investigated. As a consequence, average values of the structure parameters are obtained by SAXS.

It is worth mentioning that the resolution criteria in SAXS are the same as those in microscopy.

Eventually, in order to get the complete picture of an unknown sample one needs to make use of both methods, because their results are complementary.

3. SAXS basics

There are two main interactions of X-rays with matter: absorption and scattering. In order to obtain high-quality SAXS data the absorption must be kept small. Scattering can occur with (different wavelength[A]) or without (same wavelength[B]) loss of energy.

A: Compton scattering [1] (inelastic scattering)

B: Rayleigh[1] or Thomson scattering[2] [2, 3] (elastic scattering)

Whatever the type of detector, only the intensity is accessible. Thus, the result of a structure analysis by scattering will always be ambiguous and the data must be interpreted with some knowledge about the sample (e.g., from microscopy or from an understanding of the sample's chemistry).

Scattering pattern is usually called "the structure in reciprocal space" and scattering patterns are presented as functions of q. The lower limit q_{min} is due to the presence of the primary beam and is governed by the quality of the collimation system. The upper limit q_{max} is due

1. *The incident radiation is visible light.*
2. *The case of X-rays and neutrons.*

to the fading of the signal into the noise level (see „collimation system “on page 8).

When X-rays interacted with matter atoms they are scattered by electrons and only the interfering photons carry information on the structure. The scattering of the matrix material also carries information (on atomic distances). In practice, one subtracts the blank scattering (of sample holder and matrix) from the sample scattering. The visibility increases with the difference in electron density between the two materials. This is called contrast.

4. SAXS instrument

The basic components of all SAXS instruments are a source, a collimation system, a sample holder, a beam stop and a detection system.

- **Source:** The source(X-rays) irradiate the sample and they are sent through the sample and every particle that happens to be inside the beam will send out its signal. Thus, the average structure of all illuminated particles in the bulk material is measured. In most cases the source is a sealed X-ray tube, a microfocus X-ray tube or a rotating anode.

- **Collimation system**: In SAXS a collimation is required, as divergence of the incoming beam must be kept small. The collimation system makes the beam narrow and defines the zero-angle position. The two collimation systems used in SAXS instruments (point and line collimation). It is also very difficult to obtain a narrow and clean beam with a point-collimation set-up, which generally results in poor resolution. Mostly the resolution can be improved a bit by increasing the sample-to-detector distance.
- **Sample holder**: One of the most complicated parts of a SAXS system is the sample holder. Everything that is put inside an X-ray beam, even air, produces scattering. It is therefore good idea to keep the sample-to detector distance in vacuum. Unfortunately, most samples cannot stand the vacuum, which is required to keep background scattering low. Therefore, special sample holders are necessary to keep the samples fit for the scattering experiments. The samples are in liquids, pastes, solids and powders forms.

Liquid samples: in transmission mode are measured inside a thin-walled capillary the thickness of which should be around 1mm when the liquid contains mainly water or hydrocarbons. Solvents that contain heavy atoms, e.g., chlorine must be measured in thinner capillaries. Liquids that are so viscous are better measured in a paste cell.

Pastes rubbers, and vacuum sensitive materials in general have to be squeezed into a sample holder that has removable windows. The most widely used window material certainly is a foil made of Kapton®.

Solids: can be clamped onto frames with or without additional window foils for protection against the vacuum. In case of special atmospheric requirements, such as a specified relative humidity or a gas reaction, the sample must be put into a small compartment which is then inserted into the vacuum.

Powders: can be measured between two layers of sticky tape or in (disposable) capillaries. The crystallinity on the atomic scale (in WAXS) or on the nanoscopic scale (in SAXS) are the only reasons why one would make scattering experiments (finding internal structure elements) on powders.

Sometimes materials must be prepared on a substrate in order to investigate thin-film properties. Normally one would choose to measure these samples in reflection mode (GISAXS).

- **Beam stop:** The function of the beam stop is to prevent that the intensive direct beam hitting the detector which would overshadow the relatively weak scattering of the sample and would even destroy some of the detectors. Two different types of beam stops are in use. One type consists of dense materials, such as lead or tungsten. The other type is made of transparent materials.
- **The detector:** The detector measures the radiation coming from the sample in a certain range of angles. Four different types of detectors are in use with SAXS. Wire detectors, CCD detectors, imaging plates and solid-state (or CMOS) detectors.

5. SAXS analysis

When the sample is in (or on) the holder the actual measurement can begin. This is done by exposing the sample to the beam. It is important to note that one measurement always consists of two experiments. The scattering of the matrix material (e.g., the solvent)

and of the particle system must be measured in two separate experiments.

After the sample is measured, the data are analyzed. This is done in various ways and in various extents, depending on the type of sample and on the intent of the investigation. The SAXS signal can be optimized by employing a large illuminated sample volume (scattering volume). In transmission mode (SAXS) a thick sample is not desirable due to the increased sample absorption. So, the only way to maintain a large scattering volume is to widen up the beam dimensions and to keep the optimum sample thickness, which (for water-based samples and copper radiation) is about 1 mm. Typical sample sizes are 50 μL for liquids and 1×1mm^2 (point collimation) to 1×20 mm^2(line collimation) for solid samples or pastes. In reflection mode (GISAXS) the sample thickness is of no concern, because only the topmost surface layers are probed. The only way to maintain a large scattering volume is to increase the sample length. In SAXS experiments, i.e., for ($2\theta < 10°$), the polarization is usually ignored, but not in XRD experiments.

5.1. Data interpretation

Once the intensity of a sample is recorded and background corrected, the question arises as to which information can be obtained from it. The most of factors are: The resolution, Radius of gyration, Surface per volume, Molecular weight, Particle structure, Polydispersity analysis, Particle interaction, Degree of orientation and Degree of crystallinity. In the part of particle interaction: every particle produces a form factor that is characteristic to its structure. The slope of the form factor at small angles is primarily determined by the overall size and the final slope at large angles bears the information of the surface. The information about the shape and the internal density distribution lies in the oscillating part in the middle section of the form factor ("Central part ", according to Porod[4]).

A rough classification into globular, cylindrical and lamellar shape (with axial ratios bigger than 5) can be quickly done by investigating the power law of the form factor at small angles (see Fig. 5.-1). In a double logarithmic plot an initial slope of 0, -1 or -2 indicates globular, cylindrical or lamellar shape, respectively. If the slope is steeper than that (e.g., -3 or -4) then the particles are larger than the

resolution limit and the Porod region is the only part of the form factor that can be observed.

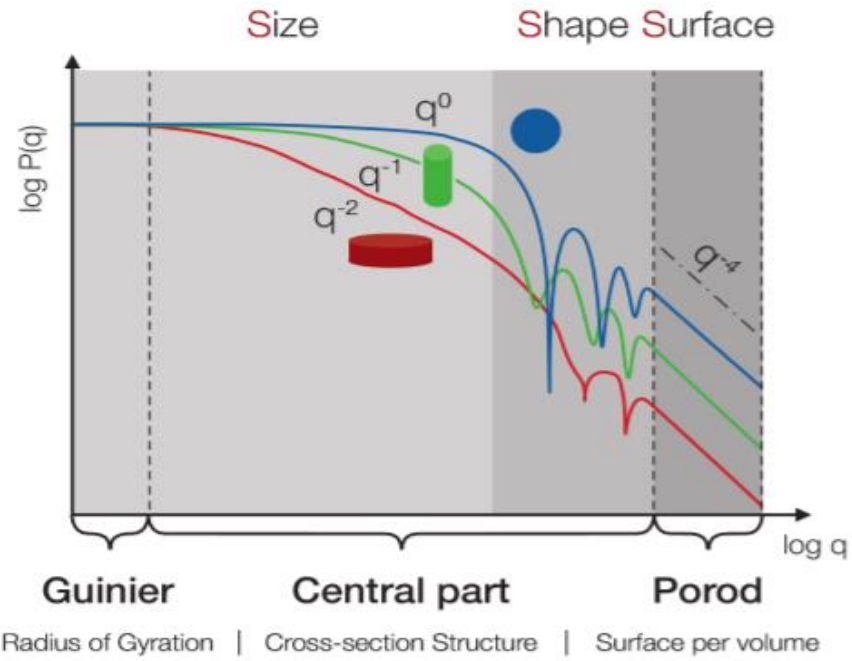

Fig. 5.-1. The information domains of a particle form factor

Finally, as a conclusion of this part we should summarize the parameters that affect the scattered intensity and, thus, have an influence on the SAXS-signal quality are: Size (the intensity of the scattering signal goes with the sixth power of the particle size. The larger the particles are, the more intensity will be detected from them), Volume (the sample volume increases the intensity linearly. Twice the illuminated sample volume will give twice the intensity and √2-times the signal quality), Contrast (the electron-density difference

between particles and matrix material (e.g., the solvent) increases the intensity quadratically), Sample-to-detector distance, Resolution and Collimation (every collimation has its function. The function of point collimation is to resolve orientation effects, not to improve the signal quality or resolution. Similarly, the function of line collimation is to improve signal quality and resolution, not to investigate orientation effects).

6. Scientific application

Now a days GISAXS has developed into an important tool to study nanostructured surfaces and thin films. Also, it is important to know SAXS is a powerful tool for studying the structure and dynamics of biomolecules and biomolecular complexes in solution [5]. The SAXS studies of structural biology contain some basics about biomolecular and biological, the polynucleotides: DNA and RNA, the polypeptides: Proteins and Complex biomolecular assemblies and integrative methods. In addition to structural information, SAXS can provide information regarding the stoichiometry of subunits [6], and binding affinities [7, 8]. Particularly powerful for studying complexes is a combination of SAXS and SANS (small-angle neutron scattering) and contrast variation [9, 10]. Well-known examples are conjugated

polymers and molecules for organic electronics (typical d-spacings from 1 nm to 10 nm), lipids (3 nm to 30 nm), nanoparticles (3 nm to 30 nm), as well as block copolymers (10 nm to 100 nm). Such systems are of interest to use with industrial coating and printing techniques for flexible consumer electronics, medical sensors, and many other applications.

SAXS provides detailed insights into the structures and conformations of material molecules and can probe a wide range of dimensions, as well as nano-material dynamics. At the same time, there have been significant developments in determinations constituent phases, microstructures, data interpretation, detailed modeling and structural modeling tools [11, 12, 13].

7. Industrial application

The SAXS method is accurate, non-destructive and usually requires only a minimum of sample preparation. Application areas are very broad and include biological materials, polymers, colloids, chemicals, nanocomposites, metals, minerals, food and pharmaceuticals and can be found in research as well as in quality control.

A key driver in the development of modern materials of today has been the ability to control their structure and functional properties and its relationship to the potential applications in the emerging fields of nano-materials. The self-assembled and hierarchical structures and the functions offered by these self-assemblies, such as micelles, liquid crystals, emulsions, liposomes, and solid-gels, consisting of amphiphilic organic polymers, are utilized in a wide variety of industrial fields. In addition, not only self-assemblies of organic amphiphiles, but also nano-structured inorganic materials, such as composite TiO2 particles and mesoporous silicas and modified biological substances (e.g., recombinant and purified proteins) are in great demands.

The information about inter-particle interactions in dense systems can be deduced by analyzing the structure factor with various potential models assuming repulsive or attractive interactions.

The most important topics in the industrial and health fields relevant to the mentioned discussion are:

1. self-assembled structures [14, 15, 16]

    1.1 Personal health care (cosmetics, toiletry and sanitary)

1.2 Pharmaceutical materials

1.3 Food and nutrients

1.4 Nano-structured inorganic materials

2. Nanocomposites
3. Biological nanocomposites
4. Liquid crystals [17]
5. Bio-compatible polymers

5.1 Polymers for gene therapy

5.2 Silicon-urethane copolymers

6. Mesoporous materials [18]
7. Membranes
8. Protein crystallization [19]
9. Lipoproteins [20, 21, 22]
10. Cancer cells [23, 24]
11. Carbohydrates [25, 26]
12. Building materials [27, 28]
13. Minerals

Finally, an important question may create:

SAXS? or DLS?

Size distribution is an important structural aspect in order to rationalize relationship between structure and property of materials utilizing polydispersity nanoparticles. One may come to mind the use

of dynamic light scattering (DLS) for the characterization of the size distribution of particles [29]. However, only solution samples can be analyzed and even for those, the solution should be transparent or translucent because of using visible light. It is needless to say that solid samples are out of range. Furthermore, the size distribution only in the range of several tens of nanometers can be characterized, so DLS is useless for particles in the range of several nanometers. Therefore, the small-angle X-ray scattering (SAXS) technique is much superior when considering the determination of the size distribution in several nanometers' length scale for opaque solutions and for solid specimens. Furthermore, the SAXS technique is applicable not only for the spherical particle but also for platelet (lamellar) and rod-like (cylindrical) particles. In particular, for systems forming complicated aggregations, this methodology is useful. Not only 'can the size distribution of a bunch of grapes' but also the size distribution of all grains of grapes in the bunch be evaluated according to this methodology. This is very much contrasted to the case of the DLS technique by which only 'a bunch of grapes' is analyzed but 'grains of grapes in the bunch' cannot be. It is because the DLS technique in principle evaluates diffusion constants of particles and all of the

grains in the same bunch of grapes diffuse as a whole. Thus, the methodology is important to highlight versatility and diversity in real materials, especially in soft matter, both in the liquid and in the solid states.

8. Conclusion

Now a days, small-angle X-ray scattering has become an increasingly important tool in studying the diverse fields of material science. This process has been accelerated by the accessibility of large-scales facilities and the availability of latest high-performance laboratory instruments along with the availability of novel and powerful data-analysis programs. Judging from the momentum that was gained in the last decade by using SAXS and the technique's inherent and unique capability in addressing the steadily up-coming developments in nanomaterials suggests that, in future, SAXS will further strengthen its position as a mainstream method for the analysis in a multiplicity of fields in material-science research.

9. Applied field SAXS instrument and sample conditions for SAXS test in Center for Nanoscience & Nanotechnology-Institute for Convergence Science & Technology (ICST) Sharif University of Technology

Typical values and conditions for SAXS experiment at commonly used states are summarized in Table 9.1.:

Table 9.1. The SAXS test values and conditions

Sample holder	sample type/application
Holder for solids	fibers, polymers, powders, For solid samples maximum 7mm × 21mm
µ-cell (Quartz)	volume liquids(100µL),
collimation instruments	Point-collimation instrument The beam dimensions at the sample position are typically 0.3 x 0.3 mm^2

In order to obtain high-quality SAXS data the absorption must be kept small and thus thickness must be appropriate. The optimum sample thickness d_{opt} depends on the linear absorption coefficient [30]. Typical values for d_{opt} at commonly used wavelengths for cu-k_α anode is summarized in Table 9.2.:

Table 9.2. The optimum sample thickness d_{opt} in [μm] of various matrix materials at commonly used X-ray wavelength

Radiation Wavelength	Cu-k_α 0.1542 nm	Density [g/mL]
Water, 4°C	980.8	1.00
Quartz glass	126.6	2.203
Chloroform, 15°C	70.5	1.498
Iron metal	4.22	7.86
Tungsten metal	3.08	19.3

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