Small-Angle X-ray Scattering and Nanostructured Materials

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Abstract. Basic theoretical and experimental aspects of the small-angle X-ray scattering (SAXS) method and some of its applications to studies of nanostructured materials are described. Particular attention is given to experimental studies of processes of formation of nanomaterials and mechanisms associated with structural and phase transformations. Comparisons of experimental SAXS results and theoretical predictions associated with these phenomena are also outlined. Furthermore, basic theories of related techniques such as anomalous SAXS, grazing incidence SAXS and X-ray reflectometry, as well as some of their applications, are described. Novel applications will soon be possible by using newly designed SAXS beam lines connected to extremely bright fourth-generation synchrotron sources, such as that to be in operation from 2019 at LNLS, Brasil.

Key words: SAXS, nanostructured materials, ASAXS, GISAXS.

The first step of the classical single-crystal X-ray diffraction procedure is determining a set of complex structure factors, \( F_{\text{hkl}} \), corresponding to hkl points of the reciprocal lattice. This is followed by a Fourier synthesis that yields the average atomic structure within the unit cells. As is well known, the resolution of the structure derived in this way can be increased by increasing the limit in reciprocal space up to which the intensities of Bragg diffraction peaks are experimentally determined. On the other hand, X-ray scattering patterns produced by imperfect crystals contain, in addition to Bragg diffraction peaks, a diffuse background related to the existence of crystalline defects. The small-angle X-ray scattering (SAXS) intensity produced by imperfect crystals refers only to the part of diffuse scattering corresponding to a small volume of reciprocal space near its origin or, in other words, within the small scattering angle range. The first application of SAXS method to materials science was the detection and further characterization of Cu-rich nanoplates (GP zones) coherently embedded in a single-crystalline Al alloy [1].

Taking into consideration that in SAXS experiments there is a practical limit for the lowest angle to be reached and because of the low maximum scattering angle up to which intensity is recorded, the information derived from experimental patterns is exclusively associated with low-resolution structural features of nanometric particles or zones. In all cases, the shape of the SAXS curve is independent of the atomic nanoparticle structure.

The main aspects of the SAXS theory applied to nanostructured materials are presented [2,3]. Particularly, this experimental method allows for studying materials whose low-resolution structure can be well described by a simple two-electron-density model consisting of homogeneous nanoparticles embedded in an also homogeneous medium or, alternatively, two-phase bicontinuous nanostructures. Examples of these materials are solutions of inorganic colloidal particles, nanoporous materials, nanocomposites consisting of metallic nanoparticles embedded in glass, nanoparticles of oxides dispersed in polymeric matrices and proteins in liquid solution. SAXS measurements can provide useful structural information such as shape, average size, size distribution, average electron densities, number density and spatial correlation of isolated nanoparticles embedded in homogeneous media.

The basic characteristics of classical laboratory SAXS setups and those of beam lines associated with synchrotron radiation sources are described. Notice that SAXS measurements are performed in transmission mode. In practice, the optimum sample thickness for achieving maximum SAXS intensity depends on material composition and X-ray wavelength. For CuK\( \alpha \) radiation, typical optimum sample thicknesses are a few microns for metals such as Cr, Fe and Co and approximately 1 mm for materials containing light elements such as water and simple polymers. Before further analysis, the parasitic contribution to the total SAXS intensity - coming from the X-rays scattered by collimation slits, air volume and thin windows – is subtracted. If necessary, experimental data are corrected for smearing effects associated with the sizes of the incoming beam cross-section and X-ray detector pixels. Methods for determining SAXS intensity in absolute scale are also described.
A few examples of applications of basic concepts of the SAXS theory to two-phase systems are presented, starting from those consisting of dilute or dense sets of size-monodisperse or size-polydisperse spherical nanoparticles [3]. The expected features of SAXS intensity curves corresponding to fractal nano-objects and bicontinuous systems are also described. Some SAXS studies conducted by the author and collaborators dealt with in situ investigations of mechanisms of formation and isothermal growth of Bi nanoparticles [4]. In most cases, the time-dependent structural parameters determined from SAXS results were compared with those derived from previous theoretical predictions. Other investigations were performed by combining SAXS and WAXS (wide angle X-ray scattering) results, which allowed for determining the crystal-to-liquid (melting) and liquid-to-solid (freezing) transition temperatures of spherical Bi nanoparticles and their dependences on nanoparticle radius [5]. The experimental results derived from these works are in good agreement with predictions of classical theories. It was also recently demonstrated that the melting and freezing temperatures of very dilute and nearly size-monodisperse sets of Pb nanoparticles can be precisely determined by using only SAXS data recorded at varying temperatures [6].

A particular method that requires several SAXS measurements using different X-ray wavelengths is named anomalous or resonant SAXS (ASAXS). This method is applied for studying more complex materials such as those that can be described by three electronic density models. Another widely used technique is grazing incidence SAXS (GISAXS), which is applied to structural studies of thin nanostructured films deposited on flat substrates and nanostructures close to the surface of different materials. The basic theory of GISAXS is presented [7] and in situ studies of the formation and coherent growth of CoSi$_2$ thin nanoplates buried into flat Si single-crystal substrates are described [8]. Finally, the basic theory of X-ray reflectometry (XR) is outlined. This experimental procedure is widely applied for characterizing thin films deposited on flat substrates or modified layers near external surfaces of bulk materials. The quantitative parameters derived from experimental XR studies of thin films are their thickness, average mass density and roughness. In order to also characterize the internal nanostructure of thin films, the XR method is usually applied together with the GISAXS technique.

A fourth generation synchrotron source (Sirius) - under construction at the National Synchrotron Light Laboratory (LNLS) in Campinas, Brasil - will be open to users in 2019. Relevant features of the new SAXS beam line to be connected to Sirius and some of its novel applications are described. Since Sirius will have a very low emittance and, consequently, an extremely high brightness, the new beam line will allow for in situ studies of fast structural transformations and high-resolution SAXS mapping. The large volume of coherence of the X-ray beam delivered by Sirius will also allow for performing statistical speckle studies, which can be applied to characterizations of dynamic properties of soft materials. Theories for analysing SAXS data derived from experiments using coherent X-ray beams have been recently developed but they are outside the scope of the here referenced books [2,3,7].

References