Model for neutron total cross-section at low energies for nuclear grade graphite

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Abstract

At subthermal neutron energies, polycrystalline graphite shows a large total cross-section due to small angle scattering processes. In this work, a new methodology to determine pore size distributions through the neutron transmission technique at subthermal energies is proposed and its sensitivity is compared with standard techniques. A simple model based on the form factor for spherical particles, normally used in the Small Angle Neutron Scattering technique, is employed to calculate the contribution of small angle effect to the total scattering cross-section, with the width and center of the radii distributions as free parameters in the model. Small Angle X-ray Scattering experiments were performed to compare results as a means to validate the method. The good agreement reached reveals that the neutron transmission technique is a useful tool to explore small angle scattering effects. This fact can be exploited in situations where large samples must be scanned and it is difficult to investigate them with conventional methods. It also opens the possibility to apply this method in energy-resolved neutron imaging. Also, since subthermal neutron transmission experiments are perfectly feasible in small neutron sources, the present findings open new possibilities to the work done in such kind of facilities.

1. Introduction

Advanced materials have nowadays a wide variety of applications in rapid development, like in the storage of information in magnetic disks, or in improvements in the mechanical properties of steel, high-impact plastics and super alloys and the current carrying in superconductors. The properties of these materials are critically determined by their structure at nanometric scale. Supported by this technological interest, a method to explore the bulk structure in a fast way which gained relevance in recent times is the thermal neutron transmission technique [1]. With the same rationale, the subthermal neutron transmission has been employed to study nanometric structures, as recently tested for the first time in graphite [2] (a material of great interest in nuclear industry), as an alternative to the well-known Small Angle Neutron Scattering technique. The total cross-section of subthermal neutrons in graphite had been repeatedly measured by different research teams in the last few decades, revealing that for neutrons of energies below 0.0018 eV (i.e. slightly less than that of the first Bragg edge) the experimental value varies from 4 to 8 barns, depending on the porosity level. In contrast, calculations using standard theoretical models that compute the crystal structure, but not the structure at nanometric scale (as employed in the nuclear data processing code NJOY [3]), produce a value of 0.2 barns. Recent experimental studies [2] have shown that this difference in the total cross-section is due to neutrons scattered at small angles, i.e. refractions and reflections in the great number of existent solid/air interfaces due to the graphite porosity, not taken into account by NJOY.

Graphite is widely used in nuclear installations, due to its ability to moderate fast neutrons and reflect slow neutrons. Examples are the proposed nuclear fuel made of graphite balls containing uranium oxycarbide or uranium dioxide employed in Very High-Temperature Gas reactors (one of the reactor concepts for the next generation of nuclear power plants), or the cylindrical graphite bricks that form the core of the Advanced Gas Reactors (widely employed in the United Kingdom), serving both as neutron moderator and structural components. In the latter case, years of neutron irradiation caused profound microscopic changes in the material that resulted in shrinking of the graphite bricks. But because the neutron bombardment does not spread evenly through the brick material, the rates of recession are also irregular. This causes tension and eventually cracking, affecting the safe operation of the power plants. Thus, a good characterization of the
porosity of materials is particularly significant in graphites employed in the nuclear industry. Nuclear grade graphites are those with a density greater than 1.7 g/cm³ (the theoretical value being 2.2 g/cm³), which defines an upper bound on its porosity, that is an important parameter in reactor calculations.

Most of the methods to characterize the porosity of materials are based on adsorption properties [4]. Widely employed techniques are the mercury porosimetry, vapor–liquid equilibrium method [5], and liquid–solid thermoporometry [6]. The most popular method, known as the Brunauer–Emmett–Teller (BET) method [7], is based on gas adsorption. As this method is based on the area that is occupied by gas molecules, it is inaccurate either when the surface is too rough, or when the pores are too small or completely closed. Avnir et al. [8,9] found that the surfaces of most materials are fractals at the molecular size range. As a consequence of this is that the routine analyses that employ the BET technique overestimate the effective area, since they consider an extra adsorption caused by the surface roughness. As an example, in the study of Kaneko et al. [10] BET measurements of the specific area in microporous carbons showed an overestimation of 40% due to capillary condensation. Besides the mentioned problem, the extra pressure applied to the gas can lead to pore deformation. On the other hand, microscopy techniques, besides not being representative of the whole volume, cannot be applied to microporous materials (pore sizes less than 2 nm).

The usual tools to explore the structure of solids and liquids in the nanometric scale are small angle X-ray and neutron scattering techniques (SAXS and SANS, respectively). While SAXS requires high-flux radiation facilities and good properties of longitudinal coherence (as provided by synchrotron radiation sources) and is sensitive to inhomogeneities in the electronic density of the sample, the SANS technique explores inhomogeneities in scattering length density and requires neutron facilities (e.g. reactors) to produce a monochromatic beam of cold neutrons. Both techniques explore the scale range from 1 to 100 nm and are applicable to both amorphous and crystalline materials. Some typical applications of SANS and SANS include the determination of the pore size distribution and the estimation of the specific area in nanocellular systems.

As commented above, subthermal neutron transmission proved recently to be a tool to explore SANS effects. The interest in developing techniques based on neutron transmission is twofold. On the one hand it reinforces the role of small neutron facilities (e.g. reactors) to be used, leading to more isometric particles than needle-coke graphite. The resulting material is more dense than the needle coke graphite. Although the sample has a smoother surface than pitch coke graphite, pores are still visible to the naked eye. Spherical samples were machined out from a rod.

• Needle coke graphite is the most porous species [32]. Samples were cut from a 24 cm cube provided by the RA-6 Nuclear Reactor, of the Centro Atómico Bariloche, Argentina. The density of the material is 1.681 ± 0.008 g/cm³. Elemental composition determined by EXAFS is C 99.815%, S 0.102%, Ca 0.047%, Si 0.026%, Al 0.009%, and K 0.001%. Pores of around 1 mm are visible to the naked eye.

• Pitch-coke graphite is a byproduct of pitch produced by heat treatment, leading to more isometric particles than needle-coke graphite. The resulting material is more dense 1.725 ± 0.004 g/cm³ than the needle coke graphite. Although the sample has a smoother surface than pitch coke graphite, pores are still visible to the naked eye. Spherical samples were machined out from a rod.

• Isostatic-pressed graphite is manufactured from finer coke particles, and has very uniform and isotropic properties, that makes it suitable to be used as neutron moderator. Spherical samples were molded by isostatic pressing. These samples presented the largest density (1.740 ± 0.004 g/cm³).

2. Experimental

2.1. Samples

Three different types of graphite were examined in this work, needle-coke, pitch coke and isostatic-pressed graphite, which differ in the way they were manufactured:

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2.2. Experimental techniques

SAXS experiments, performed in transmission mode, were done in the SAXS1 beamline at the Laboratorio Nacional de Luz Sincrotron (LNLS) in Campinas, Brazil. The beamline works with a fixed energy of 8 keV and a beam size of 1.5 mm (horizontal) × 0.5 mm (vertical). The X-ray detection was performed with a solid state detector PILATUS 300 K with a resolution of 0.1(ΔE/E). To increase the statistics, the detection threshold was set at 7 keV. Two ranges of q were measured, 0.11 nm⁻¹ < q < 4 nm⁻¹ and 0.03 nm⁻¹ < q < 1.5 nm⁻¹, to cover the highest possible range of momentum transferred. Seven graphite samples were employed, four corresponding to needle-coke and three to pitch-coke.
The samples were sectioned to 0.7 mm width, with a PetroThin® sectioning system. These thickness was chosen so an attenuation factor of 1/e for X-rays of 8 keV was obtained. The samples produced by this method had a rectangular shape of approximately 2 cm × 3 cm. In order to explore possible inhomogeneities of the porosity, squares of 3 mm × 3 mm were cut from the center and the edge of the samples.

The neutron transmission experiments were performed at the Bariloche electron linear accelerator (LINAC) facility (Argentina), and described in Refs. [2,33], so only a brief overview will be given here. A general scheme of the transmission experimental setup is shown in Fig. 1. The accelerator operated at a frequency of 50 Hz, and a 25-μA mean electron current. Neutrons were moderated in a 20 mm thick polyethylene slab. Measurements were carried out at room temperature, employing the “sample in-sample out” technique every 10 min. The detector bank consisted of seven $^3$He proportional counters (10 atm filling pressure, 6 in. active length, 1 in. diameter) placed on the incident beam path at 8.27 m from the sample. The number of pores divided by the total number of atoms can be written as

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where $\rho_{\text{por}}$ is the porosity defined as the ratio $V_p / V_T$. Furthermore, we can write

$$V_p / V_T = \frac{1}{N_C} \frac{\phi}{n_c (1-\phi)},$$

where $n_c$ is the number of carbon atoms per unit of volume in an ideal material without pores. The total volume of the pores can be

$$V_p = \int_0^\infty 4 \pi r^2 n(r) dr,$$

where $\phi$ is the porosity defined as the ratio $V_p / V_T$. Furthermore, we can write

$$V_p / V_T = \frac{1}{N_C} \frac{\phi}{n_c (1-\phi)}.$$
evaluated through the theoretical \( \rho_s \) and measured \( \rho_m \) densities as

\[
V_P = M \left( \frac{1}{\rho_m} - \frac{1}{\rho_s} \right) \tag{7}
\]

with \( M \) being the sample mass. Now, using Eqs. (2)–(7) in the total cross-section of SANS (1), the following expression can be written as

\[
\sigma_{\text{SANS}}(k_0) = \frac{1}{2k_0^2} \int_0^{2k_0} \int_0^{\infty} \left( \Delta \rho \right)^2 v(r)^2 \times \frac{9}{q^2} \cos(qr)^2 \eta(q) \, dq \, dr.
\tag{8}
\]

In this work a log-normal pore radius distribution \( n(r) \) was used:

\[
n(r) = \exp \left( -\frac{1}{2} \left( \frac{\ln r - \ln r_0}{\sigma} \right)^2 \right) \frac{1}{r \sigma \sqrt{2\pi}} \quad \tag{9}
\]

so the free parameters in Eq. (8) are the width of the pore size distribution \( \sigma \), and the maximum of the distribution \( r_0 \).

4. Results and discussion

4.1. SAXS results

In Fig. 2(a), the normalized X-ray scattered intensities \( l(q) \) for the different sections of pitch and needle coke samples in the measured range \( 0.03 \text{ nm}^{-1} < q < 0.1 \text{ nm}^{-1} \) are shown. A monotonous decrease of \( l(q) \) as a function of the transferred momentum \( q \) is observed in all the samples, which indicates that no signature of a preferential pore size is observed. The curves that belong to the edge and center of the pitch coke sample show no evident differences. This fact indicates that Guinier’s law is not followed. The steep increase of the scattered intensity at very low angles is caused by inhomogeneities in the material on a larger scale [34].

An interpretation of the integral intensities of the \( l(q) \) curves shown in Fig. 2 can be found in the theory of small angle scattering. We evaluated the integral value of \( l(q) \) weighted by \( q^2 \), known as the Porod invariant [34], which can be related to the volume fraction of the pores \( \phi \) as

\[
Q = \int_0^{\infty} q^2 l(q) \, dq = 2\pi^2 \rho_s^2 \phi (1 - \phi) \tag{10}
\]

where \( \rho_s \) is the carbon electron density. \( Q \)-values evaluated by integration between the experimentally accessible upper and lower limits of \( q \) show that the ratio of the pore volume to the total volume is around 20%, consistently with the value determined by Eq. (7).

A closer examination of the curves shows interesting features to analyze. The asymptotic behavior of \( l(q) \) for large \( q \) values can be represented as \( l(q) \propto q^{-\alpha} \), where \( \alpha \) is related to the roughness of the interface for a system composed of two electronic densities (for smooth surfaces a value of 4 is expected). The fitted \( \alpha \) values were 3.496 ± 0.003 for needle coke and 3.411 ± 0.002 for pitch coke (see Fig. 2(b)). The fact that the values obtained are not integers and lower than 4 indicates a fractal surface behavior. The fractal surface dimensions, defined as \( D_m = 6 - \alpha \) [37], are approximately equal to 2.5, which implies that the material has a rough pore–solid interface [38].

In order to determine a rough estimation of the pore size (which is useful as an initial parameter guess in subsequent refinements), the tangent method [36] was applied. This method consists in fitting a linear function in a suitable range where \( l(q) \) behaves linearly with \( q^2 \). The slope of this line allows us to have an estimation of the representative pore radius. This method gave a radius of gyration of about 10 nm for all samples.

SAXS data were fitted with the SAXSFit software [39]. A model of spherical pores with a log-normal pore radius distribution was used (Eq. (9)). The center and the width of the distributions resulted in \( 41 \pm 2 \text{ Å} \) and \( 0.12 \pm 0.05 \text{ Å} \), respectively, for pitch coke samples. For the needle coke samples the centers of the distributions were \( 27 \pm 2 \text{ Å} \) and \( 31 \pm 2 \text{ Å} \) at the center and the edge, respectively, whereas the widths were \( 0.11 \pm 0.05 \text{ Å} \) and \( 0.12 \pm 0.05 \text{ Å} \).

4.2. Neutron transmission results

The total cross-section was calculated considering the various contributions existent in the wavelength range from 7 to 9 Å. On the one hand, the contributions from the crystal structure (elastic
coherent and incoherent terms), and vibrations (inelastic incoherent component) were calculated employing the NJOY code [3], resulting in about 0.5 barns per atom throughout the range of interest. On the other hand, the one-phonon coherent scattering was assessed, based on the work of Al-Qasir et al. [31], resulting in a contribution of about 0.3 barns per atom in the range of interest. Finally, the small angle scattering contribution was calculated from Eq. (8) keeping $r_0$ and $\sigma$ as fitting parameters. The results of such fittings are shown in Fig. 3(a) and in Table 1. Due to the difficulty in the convergence process of $\sigma$, this value was kept fixed in a value where the parameter $r_0$ showed good convergence. The final values of $r_0$ were insensitive to changes in $\sigma$ of about 30%. For this reason we report a representative value of $\sigma$ without errors. In Fig. 3(b) we show the radial distributions (Eq. (9)), with the parameters fitted from neutron transmission data.

Comparative results between SAXS and Neutron Transmission are shown in Table 1. As can be seen, there is an agreement between the mean pore radii obtained with both techniques, and the pore distributions’ widths ($\sigma$) employed to analyze Neutron Transmission data are lower, although relatively insensitive, what sets a limit in the ability of the Neutron Transmission technique to determine $\sigma$. This is a result of the dependency of the total cross-section on $\sigma$ as evidenced by observing Eq. (8), where $\sigma$ affects only the function $n(r)$. The integral in (8) is not very sensitive to a variation of $\sigma$. Thus, the parameter $\sigma$ can be used only as a rough comparison of the polydispersion level between the samples studied.

5. Conclusions

In this paper we have shown that the subthermal neutron transmission technique has the capability to investigate small angle scattering effects. Its sensitivity to the pore size confers the Neutron Transmission the potential to be a useful tool for the study of materials at nanoscale. This is evidenced in the good compatibility of the values of the mean pore radii determined in this work with this technique and SAXS, which is established as a standard technique in the domain of nanoscales.

We must highlight that Eq. (8) formulated in this work constitutes a useful link between the intensity $I(q)$ observed in SANS experiments and the total cross-section (measured in barns), observed in neutron transmission experiments. In the analysis we showed that the form factors commonly used as trial functions in the SANS technique can also be adopted in neutron transmission data analysis. We envisage a wide field of applicability of this technique even in the case of the study of complex systems in which the density and the chemical composition are not clearly defined. In such case it is still possible to fit the form factor parameters and an overall scaling constant which is the factor in square brackets in Eq. (8).

The results shown in this work are in agreement with those reported in the literature for similar samples [36] employing SANS, which supports the soundness of the present results. Experiments of this kind can be performed quickly, permitting the scanning of large samples and allowing to perform experiments in small facilities. As a future prospect, we propose to employ the present data analysis procedure to determine the spatial variation of the porosity in large Graphite blocks using energy-resolved neutron imaging. This kind of studies could be performed with instruments like ENGIN-X (ISIS facility, United Kingdom) using an MCP detector [18], a field under promising development.

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