

W. Gille

Department of Physics,
Martin-Luther-Universität Halle-Wittenberg,
SAS-Laboratory, Hoher Weg 8,
D-06120 Halle, Germany
gille@physik.uni-halle.de

Models of small-angle scattering for the analysis of porous materials

1. Introduction

Controlled pore glasses (CPGs) with pore sizes of 0.3-1000 nm have applications in practice as carriers for catalysts or for functional materials, such as adsorbents, macromolecular sieves or host material in non-linear optic devices.

Porous glasses are ideal two-phase systems. The preparation of CPGs involves thermal treatment of sodium borosilicate glasses, followed by several leaching procedures [1,2,3].

Isotropic random particle systems can be studied by SAS [4,5]. Here, simple geometric models allow an interpretation of the scattering curves $I(h)$. Besides the SAS correlation function (c.f.), this includes the interpretation of the so-called transformed correlation function (t.c.f.) [6]. A selection of different order ranges L_i is possible. Other types of models concentrate more in detail on the shape of the pores. A transformation method was developed for establishing chord length distributions for infinitely long 'rods' of various cross-sections [7-10].

2. The order range L

A basic concept in the field of SAS is the description of the material by the use of such model particles for which so-called structure functions are available. Then, $I(h)$ can lead back to the structure functions by integral transformation. Here, the length parameter L influences all specific steps of data evaluation. One typical curve $I(h)$ selects one order range L . If exclusively small particles (pores) are analysed, then L must be fixed to those small values. Such a 'fixing procedure' consists in the application of well-defined experimental conditions, say $L=1.5$ nm, $h_{\max}=2/\text{nm}$ or $L=150$ nm, $h_{\max}=0.02/\text{nm}$ for studying larger particles. Different order ranges L_i have to be considered separately (in different experimental conditions), followed by specific procedures of data evaluation for the L_i considered. The order range L of a single particle is its largest particle di-

Abstract

Small-angle scattering (SAS) is used effectively to describe the morphology of isotropic porous materials. Beside other methods such as scanning electron microscopy (SEM), nitrogen adsorption (NA) and mercury intrusion (MI), scattering experiments allow a determination of random geometric length parameters in different order ranges. Examples for models and structure functions are discussed. Chord length distributions of infinitely long figures are useful for the interpretation of experimental results. In all cases investigated, the geometric arrangement of the macropores involves a high symmetry. A relatively restricted placing of the pore axis and the pore positions in space is found. Operating with the SAS correlation function, it is even possible to detect so-called filled macropores in the material.

Key words: macroporous/mesoporous glass, colloidal silica, stereology, specific surface area, order range L

ameter. Consequently, the c.f. of SAS must be studied for relatively large r -values (see Figure 1) in the cube and the ellipsoid cases.

A fixed position $r=L$ at the r -axis, where the c.f. 'disappears', does not exist, see Figure 1. In many cases L cannot be detected from the c.f. Then, the transformed correlation function (t.c.f.), [6,7,11] can be considered. This step is performed in Figure 2 using the data from Figure 1.

The order range L is the upper integration limit of the integrals of SAS for the integration procedure in real space, for example for the step from the c.f. to $I(h)$. In the following L is estimated from the t.c.f. of a tightly packed particle (mesopore/macropore) arrangement. The case of a mesoporous glass, see [6], is considered in Figure 3. The slope of the c.f. near the origin $r=0$ describes relatively small mesopores, $L_1=11$ nm. Otherwise, macropores exist which possess a long order range $L_2 \approx 120$ nm, which follows from an extrapolation procedure of the t.c.f. [6,16].

3. Geometric models for particular L

Assuming a so-called quasi-diluted particle system [7], based on the Babinet theorem, a porous system can be approximated (up to a certain maximum length) by the geometric shape of a typical single pore. If the largest particle dimension is smaller than the smallest distance between two particles, this approximation is correct.

Thus, it can be useful to consider the scattering behaviour of single infinitely long geometric bodies, such as cylinders, elliptic cylinders, rectangular rods or triangular rods, in order to approximate the scattering behaviour of pores possessing a constant cross-section. The chord length distributions (c.l.d.'s) of several infinitely long geometric figures were analysed, [4]. Procedures exist which allow the calculation of the c.l.d. $A(l)$ of three-dimen-

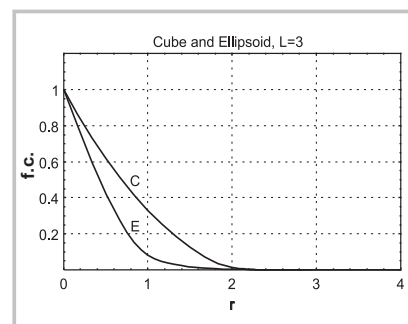


Figure 1. The c.f. of a cube and an ellipsoid with $L=3$ in both cases. L cannot be detected directly from the c.f.

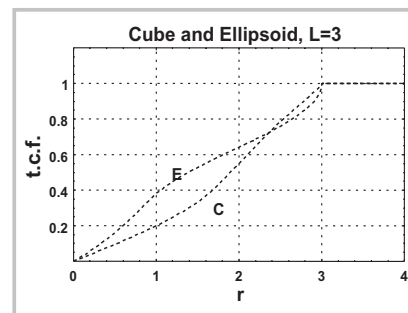


Figure 2. The exact value $L=3$ follows from the t.c.f. The method is limited to positive values of c.f.s. Extrapolation procedures are useful in order to estimate fL 's upper limit.

sional figures based on the c.l.d. $P(x)$ of the one-dimensional cross-section (see Figure 4). Here, an interesting result lies in the fact that the position of the pole of the c.l.d. of an infinitely long circular cylinder as well as the first moment of $A(l)$ agree with the diameter d of the cylinder. Consequently, peaks in $A(l)$ functions nearly agree with the diameters of the corresponding infinitely long figures.

A new transformation allows the evaluation of the chord length distribution $A(r,a,b)$ of an infinitely long elliptical cylinder based on the chord length distribution of the ellipse $P(x,a,b)$, see [9,10].

Certainly, such considerations are always limited to relatively small r -values, because of inter-particle interference. More general considerations of stochastic geometry for tightly packed particle systems are necessary, for example, Boolean models could be studied [11]. Such models have been used for the macroscopic description of bakery products.

In order to study inter-particle interference, the case of two parallel infinitely long cylinders of diameter d , the centres of which are separated by a distance s , was considered in [12]. Fig. 5 shows the example of touching cylinders A and B. The calculation really includes all random distances between A and B.

There is a general theory of c.l.d.s which includes the case considered in Fig. 5 as a special case, [13-16]. It also holds in the case of non-convex particles (like hollow spheres or hollow cylinders), including so-called one-chord distributions (OCD) and multi-chord distributions (MCD).

Here, the interpretation of the second derivative of the c.f. (Figure 5) is the following, see [12]: Two types of chord lengths exist: m_i outside the cylinders (the first peak, near the origin) and l_i inside the cylinders (the second peak, main peak). Additionally sums of chord lengths must be considered. The third peak reflects OCD lengths.

The singularity at $r=d$ also exists for a single cylinder A. The mean chord length of each cylinder is $4 \cdot V/S \rightarrow d$. The Cauchy principle holds. Because of the infinite volume of the pair AB, the fourth moment of the c.l.d. does not exist, $12 \cdot V^2/(\pi \cdot S) \rightarrow \infty$. As a consequence of the existing vicinity of the straight line of contact between A and B, a very high number of very small chord lengths between the cylinders results. Otherwise, the number of extremely large chords outside AB is small. The local maximum at $r=2d$ reflects the distribution law, OCD, of unpaired sums of chord lengths $l_i+m_i+l_i$. A local minimum, reflecting l_i+m_i , lies between the second and the third peaks.

4. Analysis of filled and empty pores

Controlled Pore Glasses (CPGs) can be prepared from alkali borosilicate glasses by phase separation and combined acid and alkaline extraction. After a temperature-dependent phase separation, two different phases can be obtained.

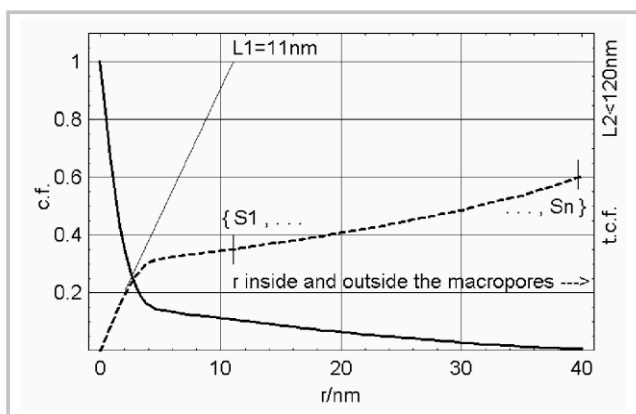


Figure 3. c.f. and t.c.f. of a macroporous glass describe two different order ranges L_1 and L_2 . There is a superposition of $L_{1,2}$ distances, $3nm < r < 6nm$. The region $10nm < r$ is exclusively influenced by the scattering behaviour of the macropores [5].

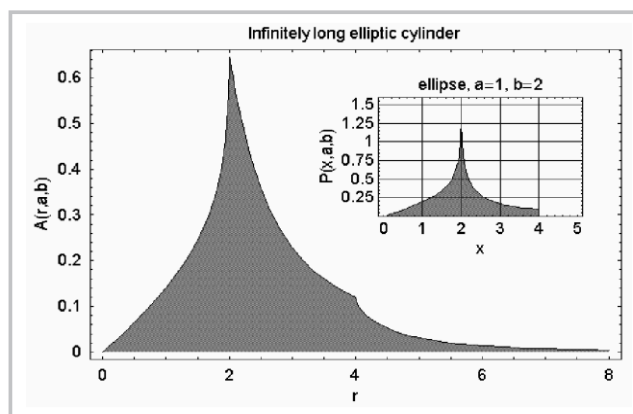


Figure 4. CLD of ellipse $P(x,a,b)$ and infinitely long elliptical cylinder $A(r,a,b)$. Here, the two-dimensional cross section of the geometric figure is analysed to determine the chord length distribution of the three-dimensional infinitely long figure (ellipse with semi-axes $a < b$).

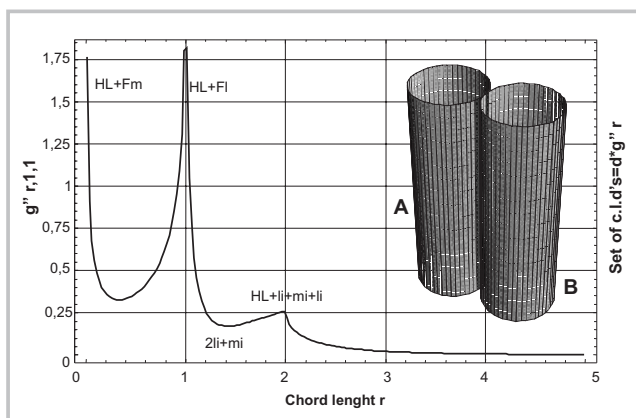


Figure 5. The c.l.d. of an arrangement of two infinitely long parallel circular cylinders AB in the case $s=d$. MCDs and OCDs exist. The spike significantly marks the diameter d .

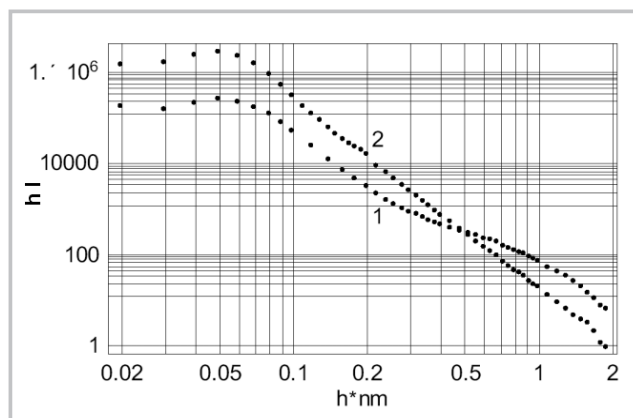


Figure 6. SAXS intensities of MePG(1) and MaPG(2). Here, $h_{min} = 0.02/nm$ was used. The upper resolution limit is 150nm. There is a very similar scattering behaviour for small h -values. Here, the curves differ by a constant factor.

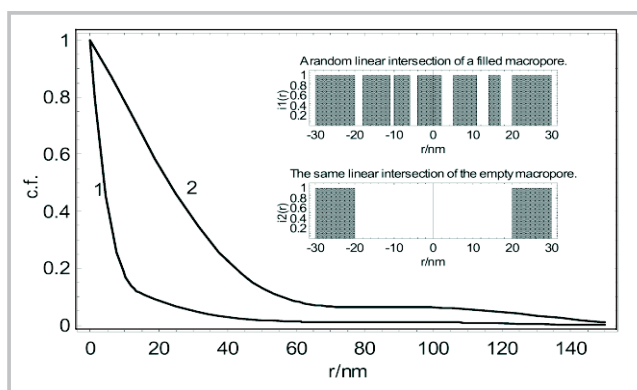


Figure 7. The c.f.s of MePG(1) and MaPG(2), $2\text{nm} < r < 150\text{nm}$, were calculated, based on $I(h)$, see Fig. 6. Both c.f.s possess a different initial slope. This is a consequence of the different inner surface areas of both states. The insert exemplifies this. The indicator functions $i_1(r)$ and $i_2(r)$ describe a filled macropore and an empty one. The results obtained by means of other methods such as SEM, NA and MI [3] with these results. However, there are systematic deviations concerning absolute values of the specific surface area S_v . This will be discussed in the following chapter.

The first one is pure silica, which is assumed to stay unchanged in the following (the solubility of silica in acidic media is low). The other one is an alkali-rich borate phase with different amounts of silica.

After the extraction, finely dispersed silica remains in the cavities of the main silica framework and affects the pore structure of a mesoporous glass of state 1, MePG. By leaching with a basic solution this mesoporous secondary structure, which completely fills each macropore, can be properly removed. Thus, results in obtaining macroporous glass in the state 2 (with the denotation (MaPG) [17].

By use of chemical measurements, it seems impossible to compare the geometric arrangement of state 1 and state 2 directly, but it seems to be a logical fact that no decisive difference between the inherent property for the macropores in the glass (state) and their real existence (state 2) can exist. The system of so-called filled (1) and empty (2) macropores of diameter 52nm has been investigated by use of SAS [6,16,17].

The shape of the macropores is nearly fixed, independent of their degree of filling. The shape and size of the macropores coincide with the shape and size of the borders of the finely dispersed silica-gel.

5. The specific area surface S_v

In the case of isotropic two-phase systems, the porosity c can be obtained from Rosiwal's linear integration principle from the mean chord lengths. Otherwise, a mean average chord length $d_m = 2/s_v = (\langle l \rangle + \langle m \rangle) / 2$ can be obtained. Here, the symbols $\langle l \rangle$ and $\langle m \rangle$ denote the mean chord lengths of the pores and of the walls. □

However, differences exist in the specific area surfaces S_v as determined by

SAS, MI, NA. These differences can be completely explained by the specificities of the individual technique [18,19]. It is known that s_v , determined by SAS mostly reflects reality. Here, based on stereological principles, a mean volume over a very large sample volume is obtained, without any destructuring of the materials at all. On the other hand, the structure parameters obtained by a special method reflect the specificities of the method itself. In order to describe these deviations qualitatively, the parameter $q = S_v / s_v$ describes the exactness of the arrangement of the pores of the equilibrium state of the glass. In the idealised case, $q = 1$.

6. Summary

The analysis of the scattering intensity yields information about the microstructure for a certain L . The geometric differences between a filled macropore and an empty one can be investigated based on $I(h)$.

Operating with the circular cylinder model (one single cylinder or two adjacent cylinders), the mean pore diameter, the mean distance between adjacent pores, porosity (application of the linear integration principle of Rosiwal, 1898) and the specific surface area can be obtained from first geometric principles. The approximation of pores by cylinders can be applied. But, a macropore possesses a certain curvature in its length direction. Models containing curvature parameters are being worked on. The estimation of pore-curvature parameters and of a typical (mean) length of a pore from a scattering experiment is a complex procedure. □

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