



Volume 55 (2022)

Supporting information for article:

Determination of the specific surface of a granular porous material by the USAXS-SAXS intensity of a loosely packed powder sample

Salvino Ciccariello

The two aforesaid Debye-idealizations of the given powder sample essentially imply that we are geometrically considering the sample as a three phase one in so far the set \underline{V} , occupied by the full sample, is divided into three sets \underline{V}_1 , \underline{V}_{2M} and \underline{V}_{2m} that are respectively occupied by the bulk matter, the macropores and the micropores. Assume now that these three sets are filled by matter of density respectively equal to n_1 , n_2 and n_3 . The first idealization, *i.e.* the one yielding $\overline{I_D(q)}$, corresponds to the choice: $n_1 = n$, $n_2 = n_3 = 0$, while that relevant to $\underline{I_D(q)}$ to the choice: $n_1 = n_3 = \bar{n}$, $n_2 = 0$. The SAXS theory of three phase samples has been thoroughly investigated. We refer to Ciccariello & Riello (2007) for its greater completeness and for a full list of references. This paper assumes that the molar scattering densities are given in units Λ and shows that the scattering intensity is given by

$$I_D(q) = \frac{4\pi}{q} \int_0^\infty r \gamma_D(r) \sin(qr) dr, \quad (1)$$

where $\gamma_D(r)$, the correlation function of the three homogeneous phase sample, reads

$$\gamma_D(r) = \sum_{1 \leq i < j \leq 3} (n_i - n_j)^2 \phi_i \phi_j \gamma_{D,i,j}(r), \quad (2)$$

with

$$\gamma_{D,i,j}(r) \equiv 1 - \frac{P_{i,j}(r)}{\phi_i \phi_j}, \quad (3)$$

and

$$P_{i,j}(r) \equiv \frac{1}{4\pi V} \int d\hat{\omega} \int \rho_i(\mathbf{r}_1) \rho_j(\mathbf{r}_1 + r\hat{\omega}) d\mathbf{v}_1 = \mathbf{P}_{j,i}(\mathbf{r}). \quad (4)$$

$P_{i,j}(r)$ is the so-called stick probability function (SPF) relevant to the i th and j th phase. It was first introduced by Debye *et al.* (1957) and written in the above form, ensuring the function isotropy, by Ciccariello *et al.* (1981). In particular, the outer integral is performed over all the directions of the unit vector $\hat{\omega}$ and the inner integral over all the space owing to the definition of the $\rho_i(\mathbf{r}_1)$ s while dv_1 is the infinitesimal volume element set at point \mathbf{r}_1 . Besides, $\rho_i(\mathbf{r}_1)$ is the characteristic function of set \underline{V}_i and is defined as being equal to 1 if the tip of \mathbf{r}_1 falls inside \underline{V}_i and to 0 elsewhere. A remark worths to be made: if we change the scattering densities of the phases without changing the phases' geometry, from equations (4) and (3) it follows that the resulting $P_{i,j}(r)$ s and $\gamma_{D,i,j}(r)$ s do not change and, from equation (2), that we cannot have more than three linearly independent $\gamma_D(r)$ s. Now, since we have only measured $I_D(q)$ and $\overline{I_D(q)}$, the inverse FTs of these functions will respectively yield $\gamma_D(r)$ and $\overline{\gamma_D(r)}$. These, using the reported scattering

density values, take the form

$$\begin{aligned} \gamma_D(r) = n^2(\phi_1\phi_{2M} - P_{1,2M}(r)) + n^2(\phi_1\phi_{2m} - P_{1,2m}(r)) = \\ n^2\phi_1(\phi_{2m} + \phi_{2M}) - n^2(P_{1,2M}(r) + P_{1,2m}(r)) \end{aligned} \quad (5)$$

and

$$\overline{\gamma_D}(r) = \bar{n}^2(\phi_1 + \phi_{2m})\phi_{2M} - \bar{n}^2(P_{1,2M}(r) + P_{2m,2M}(r)). \quad (6)$$

Thus, of the three linearly independent SPFs (*i.e.* $P_{i,j}(r)$ with $i < j$), we only determine the combinations $[P_{1,2M}(r) + P_{1,2m}(r)]$ and $[P_{1,2M}(r) + P_{2m,2M}(r)]$. A further measurement is necessary to determine each of the three independent $P_{i,j}(r)$ s. This would be possible if we should succeed in filling the only macropores with a liquid of known scattering density without modifying the relative geometrical dispositions of the porous material grains. After measuring the scattering intensity, we could determine the three independent $P_{i,j}(r)$ s ($1 \leq i < j \leq 3$). At this point, the areas of the three interfaces would be determined by the relations $P'_{i,j}(0) = -S_{i,j}/4V$ (Ciccariello *et al.*, 1981). Consequently, we would know $S_{2,3} = S_{2m,2M}$, the interface between the macropores and the micropores, *i.e.* the area corresponding to the red segments of Fig. 1. [Note that the knowledge of $S_{2m,2M}$ is not surprising because this interface is now physically defined by the liquid filling the only macropores.] Finally, we would find that the previous S and \bar{S} obey to $S = S_{1,2m} + S_{1,2M}$ and $\bar{S} = S_{1,2M} + S_{2m,2M}$.

References

- Ciccariello, S. & Riello, P. (2007). *J. Appl. Cryst.* **40**, 282-289.
- Ciccariello, S., Cocco, G., Benedetti, A., & Enzo, S. (1981). *Phys. Rev. B* **23**, 6474-6485.
- Debye, P., Anderson, H.R. & Brumberger, H. (1957). *J. Appl. Phys.* **28**, 679-683.