

Linear Relations Among Small-Angle Scattering Intensities

Abstract

We give the general conditions to be fulfilled for the small-angle scattering intensities of samples, differing in their scattering densities and volume fractions, to be linearly related as well as the analytical expressions of the coefficients of the linear relations in terms of the above parameters. An application to a natural coal undergoing fluid extraction processes is also discussed.

Key words: multiphase systems, linearly related intensities, scattering density changes, slight geometrical changes.

Introduction

In this paper, we aim to draw people's attention to the existence of linear relations among the scattering intensities of samples of which the constituting phases have a fixed geometrical configuration while their scattering densities can be varied. More precisely, if the samples are made of N different homogeneous phases with a fixed geometry, once one has collected the scattering densities relevant to $N(N-1)/2$ different sets of scattering density values, the intensities collected for other sets of scattering density values are linear combinations of the first ones. The coefficients of the linear relations are known functions of the scattering density and volume fraction values and can be used to determine the latter quantities. These results can also be generalized to the case where the volume fractions are slightly varied. By definition, a variation is slight if the associated change in the internal geometry of the sample's phases is

such that the linearly independent auto-correlation functions, defined later, are left approximately unchanged. In fact, under this assumption, one finds that the scattering intensities are linearly related and the involved coefficients are again known functions of the scattering densities and volume fractions. It is stressed that the condition of slight variation can be checked experimentally by numerically verifying whether the linear relation among the collected intensities is obeyed throughout the explored scattering vector range or not and, in the positive case, the knowledge of the resulting numerical coefficient values can be used to determine the volume fractions and the scattering density values. The plan of the paper is as follows. In part entitled 'Basic relations', we report the basic equations of the small-angle scattering theory and we show that only $N(N-1)/2$ auto-correlation functions are linearly independent. In part entitled 'Three - phase samples', we specialize the previous results to the case of three-phase samples and we report the mathematical expressions of the coefficients involved in the linear relations, in terms of the volume fractions and scattering densities. We also mention briefly some interesting limiting cases corresponding to the cases where one of the constituting phases can be considered a collection of particles made up of simple films or threads. In part entitled 'Slight variation in the internal geometry', we

consider the case of slight variations in the internal geometry and a practical application. In part entitled 'Conclusions', we report our concluding remarks.

Basic relations

The fact that the spatial resolution achievable in small-angle scattering experiments does not exceed 1 nm led Debye et al. [1] to assume that the sample under analysis can be idealized as consisting of $N(=2)$ homogeneous phases with scattering densities (i.e. the electron or the scattering-length density for X-ray or neutron beams, respectively) n_i and volume fractions φ_i (with $i = 1, \dots, N$). Then, the scattering density function of the sample reads $n(\vec{r}) = \sum_{i=1}^N n_i \rho_i(\mathbf{r})$ where $\rho_i(\vec{r})$ is the function that defines the full geometry, i.e. the shape, the size and the location in space) of the i th phase since $\rho_i(\mathbf{r})$ is equal to one or zero depending on whether the tip of \mathbf{r} falls inside or outside phase i . The scattering density fluctuation function $\eta(\mathbf{r})$ is defined as

$$\eta(\vec{r}) \equiv n(\vec{r}) - \bar{n} = \sum_{i=1}^N (n_i - \bar{n}) \rho_i(\vec{r}) \quad (1)$$

where $\bar{n} = \sum_{i=1}^N n_i \varphi_i$ is the mean scattering density of the sample. The observed scattered intensity $I(\mathbf{q})$ is the square modulus of the Fourier transform of $\eta(\vec{r})$ and, for statistically isotropic samples, it only depends on q , the modulus of the scatter-

$$\gamma(r) \equiv \left(\frac{1}{4\pi V \eta^2} \right) \int d\vec{\omega} \int \eta(r\vec{\omega} + \vec{r}_1) \eta(\vec{r}_1) dv_1. \quad (3)$$

$$\begin{aligned} P_{i,j}(r) &\equiv \frac{1}{4\pi V} \int d\vec{\omega} \int \rho_i(r\vec{\omega} + \vec{r}_1) \rho_j(\vec{r}_1) dv_1 \\ &= \frac{1}{4\pi V} \int d\vec{\omega} \int_{V_i} dv_1 \int_{V_j} dv_2 \delta(r\vec{\omega} + \vec{r}_1 - \vec{r}_2) \end{aligned} \quad (4)$$

Equations 3 and 4.

ing vector \vec{q} , related to the scattering angle θ and the ingoing beam wave-length λ as

$$q = \left(\frac{4\pi}{\lambda}\right) \sin\left(\frac{\theta}{2}\right).$$

Hence, one generally has

$$I(q) = \left(\frac{1}{4\pi}\right) \int d\vec{\omega} \left| \int dv \eta(\vec{r}) e^{iq\vec{\omega} \cdot \vec{r}} \right|^2 \quad (2)$$

which, in principle, applies to both isotropic and anisotropic samples since the first integral amounts to angularly averaging over all the possible directions ($\vec{\omega}$) of \vec{q} . Equation (2) can also be written as

$$I(q) = \frac{4\pi V \bar{\eta}^2}{q} \int_0^\infty r \sin(qr) \gamma(r) dr, \quad (2a)$$

where $\gamma(r)$, the correlation function of the sample, is defined as Equation (3).

Here, V and $\bar{\eta}^2 \equiv \sum_{1 \leq i < j \leq N} (n_i - n_j)^2 \varphi_i \varphi_j$ (this equality is proved in Ref. [2]) denote the sample's volume and mean square density fluctuation, respectively. After substituting Equations (1) in (3) and putting Equation (4) [where $\delta(\cdot)$ is the three-dimensional Dirac function and V_i (V_j) the region occupied by phase i (j)], the correlation function (CF) takes the form.

$$\gamma(r) = \sum_{1 \leq i < j \leq N} \frac{(n_i - \bar{n})(n_j - \bar{n})}{\bar{\eta}^2} P_{i,j}(r). \quad (5)$$

Even though Equations (5) and (6) were first derived in Ref. [1] in the case of two-phase samples, they apply whatever the value of N , as it was first noticed in Refs. [3-5]. According to Debye [1], function $P_{i,j}(r)$ is the stick probability function (SPF) of phases i and j . In fact, it represents the probability density that, after having randomly tossed a very large number of times a stick of length r (where *randomly* means that the angular distribution of the tossed sticks as well as the spatial distribution of one of the stick's ends are uniform), one end of the stick falls within phase i and the other within j . Definition (4) makes it clear that each $P_{i,j}(r)$ only depends on the spatial configurations of phases i and j and that the following properties hold true [2-5]:

$$P_{i,j}(r) = P_{j,i}(r), \quad i, j = 1, \dots, N, \quad (6a)$$

$$\sum_{j=1}^N P_{i,j}(r) = \varphi_i, \quad i = 1, \dots, N, \quad (6b)$$

$$P_{i,j}(0) = \varphi_i \delta_{i,j}, \quad i, j = 1, \dots, N, \quad (6c)$$

$$P_{i,j}(\infty) = \varphi_i \varphi_j, \quad i, j = 1, \dots, N. \quad (6d)$$

From Equation (6b) it follows that each $P_{i,j}(r)$ can be written in terms of φ_i and the SPFs with $i \neq j$ and from (6a) that each SPF with $i > j$ is simply equal to that with $i < j$. Hence, one can choose as linearly independent only those SPFs with indices such that $i < j$. Using these observations, Equation (5) converts into

$$\gamma(r) = \sum_{1 \leq i < j \leq N} \frac{(n_i - n_j)^2 \varphi_i \varphi_j}{\bar{\eta}^2} \Gamma_{i,j}(r) \quad (7a)$$

with

$$\Gamma_{i,j}(r) \equiv 1 - \frac{P_{i,j}(r)}{\varphi_i \varphi_j}, \quad 1 \leq i < j \leq N, \quad (7b)$$

as it was shown in Ref. [2]. Function $\Gamma_{i,j}(r)$ only depends on the spatial configuration of phases i and j . Besides, due to conditions (6c) and (6d), it obeys the following boundary conditions

$$\Gamma_{i,j}(0) = 1 \quad \text{and} \quad \Gamma_{i,j}(\infty) = 0, \quad (8)$$

and for this reason it can be named the correlation function of phases i and j . Taking the Fourier transform (FT) of Equation (7a) and putting

$$\widetilde{\Gamma}_{i,j}(q) = \frac{4\pi}{q} \int_0^\infty r \sin(qr) \Gamma_{i,j}(r) dr, \quad (9)$$

from Eq.~(2a), it follows that

$$I(q) = V \sum_{1 \leq i < j \leq N} \kappa_{i,j} \varphi_i \varphi_j \widetilde{\Gamma}_{i,j}(q) \quad (10)$$

with

$$\kappa_{i,j} \equiv (n_i - n_j)^2. \quad (11)$$

Equation (10) is particularly interesting. It shows that the scattering intensities of samples that have a fixed internal geometry and differ only in the scattering densities are always linear combinations of the $N(N-1)/2$ quantities $\widetilde{\Gamma}_{i,j}(q)$ that depend on the only geometry of the homogeneous phases that make up the samples. The coefficients of the linear combinations are $V\varphi_i\varphi_j$ times $\kappa_{i,j}$. The last quantity according to Equation (11) defines the contrast between phases i and j . The only $\kappa_{i,j}$ s can be varied by isotopic substitution in the case of neutron scattering [6, 7]. In the case of X-ray scattering, the variation can be made by anomalous scattering [8, 9] or, when the sample has a porous structure, by filling the pores with different fluids or gases at different pressures, assuming that the pores are rather large and fully accessible [10]. These remarks imply that, given an N -phase sample with a particular internal geometry, if one performs M (greater than $N(N-1)/2$) different scattering density variations and collects

the corresponding M scattering intensities, denoted by $I_a(q)$ with $a=1, \dots, M$, these according to Equation (10) obey

$$I_a(q) = \sum_{1 \leq i < j \leq N} \kappa_{a,i,j} \varphi_i \varphi_j \widetilde{\Gamma}_{i,j}(q), \quad a = 1, \dots, M, \quad (10a)$$

with $\kappa_{a,i,j} = (n_{i,a} - n_{j,a})^2$. The first $N(N-1)/2$ of these equations can be used to determine the $\widetilde{\Gamma}_{i,j}(q)$ s in terms of $I_1(q), \dots, I_{N(N-1)/2}(q)$. Then, substituting the resulting expressions into the remaining $(M - N(N-1)/2)$ Equation (10a), the $I_a(q)$ s with $a = N(N-1)/2 + 1, \dots, M$ are expressed as linear combinations of the $I_a(q)$ s with $a = 1, \dots, N(N-1)/2$. These conditions can easily be verified by fitting each intensity of the previous set to those of the second set and checking whether the agreement is satisfactory or not. In the affirmative case, one is sure that the internal geometry has not been modified by the manipulations required to vary the scattering densities (or that all the pores are accessible, if one is sure that the internal geometry cannot change). Besides, in such a case, the coefficients appearing in the linear combinations can be used to determine some of the scattering densities and, what is more important, from the measured intensities one can determine all the $\widetilde{\Gamma}_{i,j}(q)$ s.

Recalling that the values of the three first derivatives of $P_{i,j}(r)$ s at $r=0$ have known integral expressions in terms of the (i,j) interfaces [1, 11-15], one can use these relations to extract from the $\widetilde{\Gamma}_{i,j}(q)$ s further structural information on the internal geometry of the sample. For simplicity, we only report here the relation relevant to the first derivative. In this case, one knows [12] that

$$P'_{i,j}(0) = (-1)^{\delta_{i,j}} \frac{S_{i,j}}{4V}, \quad (12)$$

where $\delta_{i,j}$ is the Kronecker symbol and $S_{i,j}$ denotes the area of the (i,j) interface while $S_{i,i} = \sum_{1 \leq j \leq N} S_{i,j}$ (the prime denotes that j cannot be equal to i) is the total area of the surface bounding phase i . Combining Equations (9), (7b) and (12), one finds at a large q that

$$\widetilde{\Gamma}_{i,j}(q) \approx \frac{2\pi S_{i,j}}{\varphi_i \varphi_j q^4}. \quad (13)$$

Finally, the well-known Porod law [11] is recovered by substituting Equation (13) into Equation (10).

■ Three-phase samples

The previous results will now be specialized to the case of three-phase samples

where only three SPFs are linearly independent. Different choices of the linearly independent SPFs are possible. For instance, for some polymeric three-phase samples, Miyazaki *et al.* [16] found it convenient to choose $P_{1,1}(r)$, $P_{2,2}(r)$ and $P_{1,2}(r)$, while Wu [17] and Ciccariello and Riello [18] considered the choice: $P_{1,1}(r)$, $P_{2,2}(r)$ and $P_{3,3}(r)$. In the following, we shall confine ourselves to this choice, which is the most symmetric one, but it should be clear that most of the results reported later can be extended, *mutatis mutandis*, to other choices of the linearly independent SPFs. In order to deal with the linearly independent $P_{1,1}(r)$, $P_{2,2}(r)$ and $P_{3,3}(r)$, we need to define the auto-CF of phase i as

$$\Gamma_{i,i}(r) \equiv \frac{P_{i,i}(r) - \varphi_i^2}{\varphi_i(1 - \varphi_i)}, \quad 1 \leq i \leq 3, \quad (14)$$

which will more simply written as $\Gamma_i(r)$. Due to Eqs. (6c) and (6d), one has

$$\Gamma_i(0) = 1, \quad \text{and} \quad \Gamma_i(\infty) = 0 \quad (15a)$$

and, as consequence of the first relation,

$$\int_0^\infty q^2 \tilde{\Gamma}_i(q) dq = 2\pi^2, \quad (15b)$$

which, combined with Eq. (10), yields the Porod invariant expression. The total contrast of phase i with the remaining two is defined as

$$\kappa_i \equiv (n_i - n_j)^2 + (n_i - n_k)^2 - (n_j - n_k)^2 \quad (16)$$

i, j, k being a circular permutation of 1, 2, 3. By simple algebra, one easily converts Equations (7a) and (2a) into

$$\gamma(r) = \sum_{i=1}^3 \frac{\kappa_i \varphi_i (1 - \varphi_i)}{2\eta^2} \Gamma_i(r) \quad (17)$$

$$\text{and} \quad I(q) = V \sum_{i=1}^3 \frac{\kappa_i \varphi_i (1 - \varphi_i)}{2} \tilde{\Gamma}_i(q) \quad (18)$$

where $\tilde{\Gamma}_i(q)$ is the three-dimensional FT of $\Gamma_i(r)$. It is noted that $\tilde{\Gamma}_i(q)$, multiplied by V , is the scattering intensity of a sample (of volume V) formed by phase i , with unit scattering density and a void phase filling the remaining region of the sample. At a large qs , $\tilde{\Gamma}_i(q)$ has the following leading asymptotic behaviour:

$$\tilde{\Gamma}_i(q) \approx \frac{2\pi S_i}{\varphi_i(1 - \varphi_i)q^4},$$

which substituted into Equation (18) allows us to recover Porod's law. At this point, we make a short diversion by adding two remarks. First, we observe that the previous equations reduce to those of two-phase samples, letting the scattering densities of two phases become equal or the volume fraction of one phase go to zero. Second, it is possible that one phase, say phase 3, has a constant thickness δ_3 as it happens for the surfactant in a water-oil-surfactant mixture (see, *e.g.*, [19]). Assuming that δ_3 is very small, as it was first discussed by Teubner [20], the contribution to the scattering intensity from the surfactant phase can be considered as being due to a film. This contribution is easily worked out from the last expression in Equation (4). In fact, dv_1 and dv_2 can fairly be written as $\delta_3 dS_1$ and $\delta_3 dS_2$ so that $P_{3,3}(r)$, the SPF of the surfactant, becomes

$$\frac{\delta_3^2}{4\pi V} \int d\vec{\omega} \int_{S_3} dS_1 \int_{S_3} dS_2 \delta(\vec{r}_1 + r\vec{\omega} - \vec{r}_2)$$

and, by Eq. (14), $\Gamma_3(r)$ becomes Equation (19).

If one compares the above integral expression with that of the second-order derivative of an SPF, worked out by Ciccariello *et al.* (*i.e.* Eq. (3.1) of Ref. [12]), one sees that the latter's integrand contains the expression $(\vec{\omega} \cdot \vec{v}_1)(\vec{\omega} \cdot \vec{v}_2)$, which is not present in Equation (19). Recalling that \vec{v}_1 and \vec{v}_2 respectively denote the unit vectors orthogonal to dS_1 and and that the second derivative of any SPF tends to zero as $r \rightarrow 0$ if the interface is smooth [12], it is now clear that the limit of (19) must be singular as $r \rightarrow 0$ because the vanishing factor $(\vec{\omega} \cdot \vec{v}_1)$ is not present in (19). In fact, a more careful analysis [20, 21] shows that

$$\Gamma_3(r) \approx \frac{S_3 \delta_3^2}{2\varphi_3(1 - \varphi_3)V r} \quad (20a)$$

as $r \rightarrow 0$ and, consequently,

$$\tilde{\Gamma}_3(q) \approx \frac{2\pi S_3 \delta_3^2}{\varphi_3(1 - \varphi_3)V q^2} \quad (20b)$$

as q becomes large. From Equation (18), one would obtain, in the q range where $q\delta_3 \ll 1$ and $qL_3 \gg 1$ with L_3 denoting the mean distance among the points of the surfactant phase, that

$$I(q) \approx \frac{\pi \delta_3^2 \kappa_3 S_3}{q^2} + \frac{V}{2} \sum_{i=1}^2 \kappa_i \varphi_i (1 - \varphi_i) \tilde{\Gamma}_i(q). \quad (21)$$

Then, if $\tilde{\Gamma}_1(q)$ and $\tilde{\Gamma}_2(q)$ do not appreciably change in the above-defined q range, the observed scattered intensity decreases as q^{-2} , as it happens in the case of plane lamellae, because the scattering behaviour is dominated by the film phase. For completeness, it is also mentioned that the scattering intensity can show a q^{-1} behaviour [21] if one phase has a thread-like structure.

We go back now to discuss the implications of Equation (18). Assume we have M samples made up of three homogeneous phases with a fixed internal geometry and different scattering densities that assume the values $n_{i,a}$ with $i=1,2,3$ and $a=1,\dots,M$ with $M \geq 3$. The corresponding scattering intensities will be $I_a(q)$, $a=1,2,\dots,M$. According to Equation (18), they only depend on the three $\tilde{\Gamma}_i(q)$ s. Therefore, the $\tilde{\Gamma}_i(q)$ s can be obtained from three $I_a(q)$ s, *e.g.* from $I_1(q)$, $I_2(q)$ and $I_3(q)$. In fact, solving the resulting system of linear equations, one finds

$$\tilde{\Gamma}_i(q) = \sum_{a=1}^3 \frac{A_{i,a}}{2V\varphi_i(1 - \varphi_i)} I_a(q) \quad (22)$$

with Equation (23), where (i, j, k) , (a, b, c) and (a', b', c') are circular permutations of (1, 2, 3), respectively determined by

$$\Gamma_3(r) \approx \frac{\delta_3^2}{\varphi_3(1 - \varphi_3)} \left[-\frac{S_3^2}{V^2} + \int d\vec{\omega} \int_{S_3} dS_1 \int_{S_3} dS_2 \frac{\delta(\vec{r}_1 + r\vec{\omega} - \vec{r}_2)}{4\pi V} \right]. \quad (19)$$

$$A_{i,a} \equiv \frac{(n_{j,b} - n_{k,b})(n_{j,c} - n_{k,c})}{[\sum_{1 \leq a' \leq 3} n_{a',a}(n_{b',b} - n_{c',b})][\sum_{1 \leq a' \leq 3} n_{a',a}(n_{b',c} - n_{c',c})]}, \quad (23)$$

$$C_{m,i} \equiv \frac{[\sum_{a=1}^3 n_{a,m}(n_{b,j} - n_{c,j})][\sum_{a=1}^3 n_{a,m}(n_{b,k} - n_{c,k})]}{[\sum_{a=1}^3 n_{a,i}(n_{b,j} - n_{c,j})][\sum_{a=1}^3 n_{a,i}(n_{b,k} - n_{c,k})]}. \quad (25)$$

$$\sum_{a=1}^3 n_{a,2}(n_{b,3} - n_{c,3}) = n_{1,2}(n_{2,3} - n_{3,3}) + n_{2,2}(n_{3,3} - n_{1,3}) + n_{3,2}(n_{1,3} - n_{2,3}) \\ = (n_{1,2} - n_{2,2})(n_{2,3} - n_{3,3}) + (n_{2,2} - n_{3,2})(n_{2,3} - n_{1,3}), \quad (26)$$

$$D_{m,i'} \equiv \sum_{a'=1}^3 \left(\frac{\varphi_{a'}(1 - \varphi_{a'})}{\varphi_{a'}(1 - \varphi_{a'})} \right) \cdot \frac{(n_{a',m'} - n_{b',m'})(n_{a',m'} - n_{c',m'})(n_{b',j} - n_{c',j})(n_{b',k} - n_{c',k})}{[\sum_{a'=1}^3 n_{a',i}(n_{b',j} - n_{c',j})][\sum_{a'=1}^3 n_{a',i}(n_{b',k} - n_{c',k})]}, \quad (30)$$

Equations 19, 23, 25, 26 and 30.

the first value of i , a and a' . The remaining intensities $I_a(q)$, with $a = 4, \dots, M$, can be expressed as linear combinations of the first three intensities by Equations (22) and (23) and the explicit relation is

$$I_m(q) = \sum_{i=1}^3 c_{m,i} I_i(q), \quad m = 4, \dots, M, \quad (24)$$

with Equation (25).

It is noted that coefficients $A_{i,a}$ and $c_{m,i}$ depend on the differences of the scattering densities because each sum present in Equations (23) and (25) is a sum of the terms that involve the product of two scattering density differences. To make this point clear, consider for instance $\sum_{a=1}^3 n_{a,m}(n_{b,j} - n_{c,j})$ and take $m = 2$ and $j = 3$. One finds Equation (26) and the property appears evident. We briefly discuss the structural information that can be obtained by the previous equations. First, to determine fully the $\tilde{r}_i(q)$ s by Equation (22), we only need to know the scattering densities of the phases of the three samples because the knowledge of

the φ_i s follows the requirement that sum-rules (15b) are obeyed. The measurement of further scattering intensities, relevant to samples with the same internal geometry, allows us to check whether the resulting intensities are linearly related to the outset three intensities throughout the explored q range, and to determine the numerical values of coefficients $c_{m,i}$. If the linearity is obeyed, one is sure that the contrast variation technique, or any other technique used to vary the scattering densities, has not modified the internal geometry of the samples. Moreover, from the knowledge of the numerical values of the $c_{m,i}$ s, one can determine the scattering densities of the m th sample if the scattering densities of the outset three samples are known, otherwise one can only determine the scattering density differences of the m th sample with those of the first three. The knowledge of the $\tilde{r}_i(q)$ s allows us to determine the areas of the S_i s and to extract further information on the structure of these surfaces such as, for instance, the presence of edges [12] and their average curvatures [13]. If

phase i has a monodispersed particulate structure, one can use the well-known relation [22]

$$\tilde{r}_i(q) = N_i F_i(q) S_i(q) \quad (27)$$

(with N_i , $F_i(q)$ and $S_i(q)$ equal to the particle number, the particle angularly averaged form-factor and the structure function, respectively) to obtain further geometrical and statistical-mechanical information on the structure of phase i .

Finally, we mention that the above results can usefully be applied to metallic catalysts. Whenever the pores are rather large and fully accessible to a fluid, by letting the pressure of the latter vary so as to approach the critical point, the scattering density of the filled pores should vary enough for the collected scattering intensities to differ enough to make the application of the above results useful. In this case, the above formulae simplify since one varies the scattering density of a single phase. The corresponding equations can be found in [18], where most of the above ideas were already discussed.

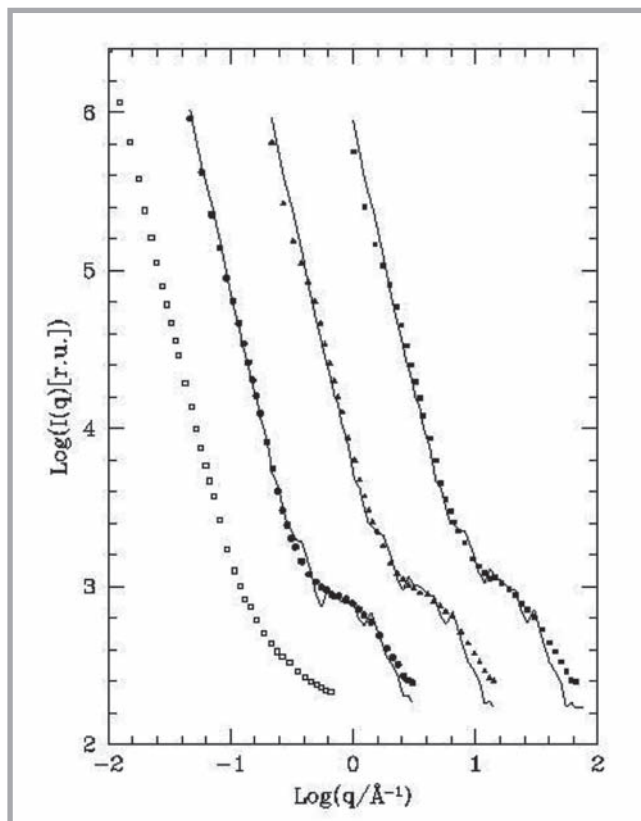


Figure 1. SAXS intensities of the Wyodak coal at $T=120^\circ\text{C}$ in an Argon atmosphere at 0.1 MPa (void square) and, after the first extraction process described in part entitled 'Slight variation in the internal geometry' at 120°C in a THF atmosphere at 0.1 MPa (full circles), 4.5 MPa (full triangles) and 15.2 MPa (full squares). [For greater clarity, each intensity has been shifted from the nearest left one by $2/3$.] The continuous lines are the results of best fitting a linear combination of the three intensities shown in Figure 2 to each intensity collected after the first extraction process.

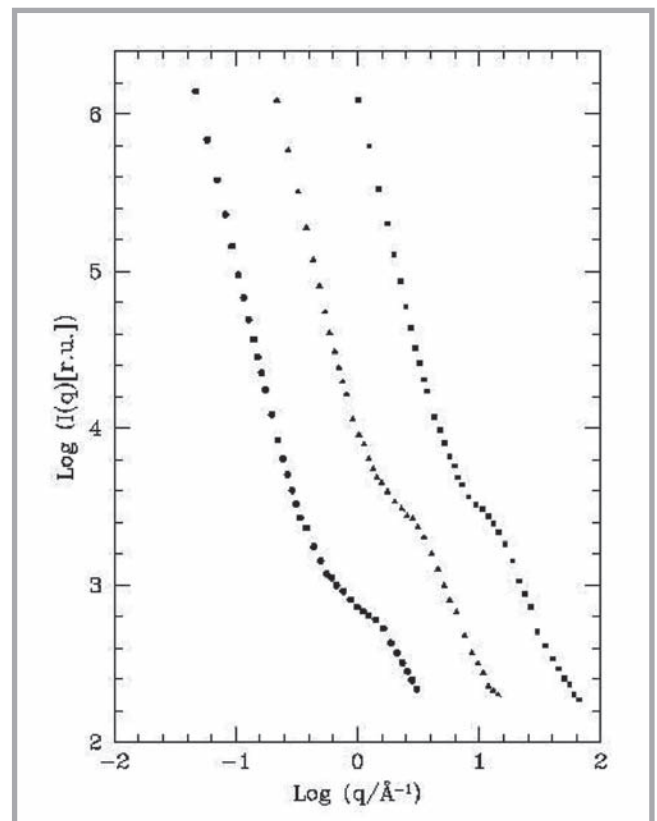


Figure 2. SAXS intensities of the Wyodak coal after the second extraction process at $T=120^\circ\text{C}$ and $P=0.1$ MPa (full circles), 4.5 MPa (full triangles) and 15.2 MPa (full squares). The q values are the same as in Figure 1. It is noticeable that, as the pressure decreases, the width of the shoulder increases while its intensity is at first nearly constant and then considerably decreases. These changes are accounted for by the numerical changes of the n_i and φ_i reported in the table of [18].

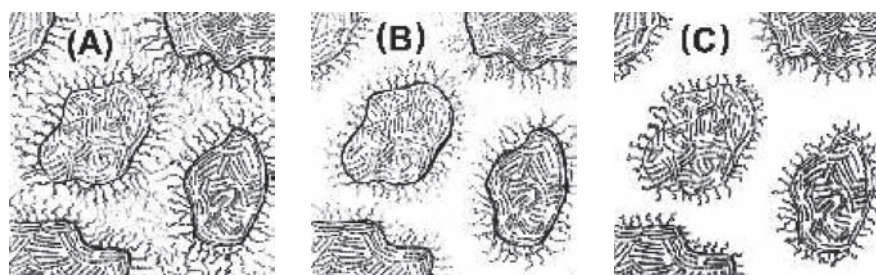


Figure 3. a) Schematic view of a natural coal section the islands are made up of small, distorted graphitic layers; the wavy lines depict aliphatic chains that, having a biological origin, contain amino acids and other atomic species and tend to be volatile, b) view of the coal after the first extraction process; the THF flow has reduced the filament region creating pores, c) the second extraction has further reduced the chain region and enlarged the pore one.

Slight variation in the internal geometry

So far, we have insisted on the condition that the internal geometry is fixed. It is, however, possible that small changes in the internal geometry leave the $\Gamma_i(r)$ s practically unmodified. On the basis of Equation (15a), the values of each $\Gamma_i(r)$ at the origin and at infinity do not change even if the interfaces are considerably modified. Hence, it appears sensible to assume that, if the interfaces are shifted by a small amount δ orthogonally to each point of the interfaces (so that the latter's shapes and topologies do not change), we can set

$$\Gamma_i(r)' = \Gamma_i(r), \quad i = 1, 2, 3, \quad (28)$$

where the outermost prime (which must not be confused with the derivative symbol) denotes that the quantities refer to the varied sample. When the conditions (28) are obeyed, we shall say the two samples are related by a *slight* variation. The main consequence of this assumption, already discussed in Ref. [18] in a more restricted case, is that the intensities $I_m(q)'$ of the slight modified samples (with different scattering densities and fixed internal geometry) are linearly related to the intensities $I_i(q)$ ($i = 1, 2, 3$) of the three initial samples (differing among themselves only in the scattering densities) as follows

$$I_m(q)' = \sum_{i=1}^3 \mathcal{D}_{m,i}' I_i(q) \quad (29)$$

with Equation (30) where the previous conventions on indices (i, j, k), (a', b', c') and (a, b'', c) have been used. The above $\mathcal{D}_{m,i}'$ s reduce to Equations (36)-(38) of Ref. [18] since there it was assumed that:

$$n'_{1,j} = n_{1,j} = n_1, \quad n_{2,j}' = n_{2,j}', \quad n_{2,j} = n_2$$

for $j = 1, 2, 3$ and $\varphi_1' = \varphi_1$.

As shown in [18], Equations (29) and (30) can usefully be applied to analyse the small-angle X-ray intensities of a natural coal that underwent fluid extraction processes. The experiments were performed by Nemmers, Horne and Bale [23] on a subbituminous coal (named *Wyodak*). The coal was first dried at 393 K and then put into a properly devised cell connected to an apparatus able to let tetrahydrofuran (THF) flow through the coal within the sealed cell at controlled temperatures and pressures. The intensity of the original coal, collected at 393 K before any extraction process, is shown in **Figure 1**. Then, the temperature was raised to 593 and the THF flowed through the cell at a pressure of 4.5 MPa. After stopping the flow, the temperature was lowered to 393 K and the SAXS intensities were collected at the THF pressures of 0.1, 4.5 and 15.2 MPa. **Figure 1** shows a substantial change in the intensity shapes. Comparing these with those reported in **Figure 1** of Ref. [24], it appears evident that the internal structure of the initial subbituminous coal is now similar to that of medium-volatile ones. The second fluid extraction consisted of raising the cell temperature to 553 K and again letting the THF flow through the cell at a pressure of 15.2 MPa. After stopping the flow, the cell was again brought to 393 K and the SAXS intensities were collected at pressures of 0.1, 4.5 and 15.2 MPa. These intensities are shown in **Figure 2**. **Figure 3** schematically shows the modifications that occurred in the internal structure of the coal by the fluid extraction processes. The initial configuration of the subbituminous coal is shown in **Figure 3a**. It consists of islands, made up of very disordered and distorted graphitic regions, and further aliphatic chains, also containing atomic species different from carbon as it usually happens in organic materials [25, 26]. The THF, flowing

through the coal, mainly takes this second component away. **Figures 3b** and **3c** schematically show the coal's internal configuration after the first and second treatments, respectively. The removal of part of the aliphatic chains leads to the formation of pores, which are filled by THF at different pressures during the SAXS measurements. Thus, the intensities of **Figure 1** (leaving aside that collected before fluid extraction) and those of **Figure 2** refer to three-phase samples where phase 1 (namely the one formed by the graphitic regions) has not been modified while phase 2 (that formed by the chains) was reduced in its volume fraction and to some extent varied in its scattering density and, finally, phase 3 is the resulting void region filled with THF at different pressures. If the variation of the coal structure from the first to the second extraction processes is slight, each of the scattering intensities collected after the first treatment ought to be a linear combination of those collected after the second extraction (or vice versa). The continuous lines of **Figure 1** are the fit results and show that the linearity condition is reasonably met. From the coefficients of the resulting linear combinations, it is possible to determine the volume fractions and the scattering density values as reported in **Table 1** of Ref. [18], to which one should refer for further details.

Conclusions

Starting from basic Equation (10), it has been shown that the scattering intensities of $M (> \frac{N(N-1)}{2})$ samples, made up of N homogeneous phases and different only in the scattering densities, are linearly related among themselves. In the case of three-phase samples ($N=3$), it is possible to determine the auto-CF of each single phase from three scattering intensities relevant to three different sets of scattering densities. This property can be used in the case of a porous sample by filling the pores with a fluid at different pressures (near the fluid critical point). For some samples that also differ in their internal geometry, it is possible to check whether the modification is slight or not by looking at the existence of linear relations among the scattering intensities. If this happens, the resulting coefficients of the linear combinations can be used to determine (some of) the n_s and φ_s using analytic expressions (30) of the coefficients that, in this paper, have been explicitly worked out for the most general case. This procedure has already

been usefully employed [18] to analyse the scattering intensities of a natural coal that had undergone fluid extraction processes.



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