

# A Brief Review of Two Theoretical Models Used to Interpret the SAXS Intensities Measurements in Heterogeneous Thin Films.

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## Abstract.

We present a brief review of two theoretical models adopted to interpret the experimental scattering intensity results  $I(q)$  obtained with the SAXS (small angle X-ray scattering) technique. They will be used to determine the fundamental structure of our nanoheterogeneous thin films fabricated by implanting gold ions into PMMA (polymethylmethacrylate) polymer and into DLC (diamond-like carbon).

*Keywords:* nanostructured materials, SAXS theories, metal-polymer conducting thin films.

## I. Introduction

In this paper we present a brief review of two different models, within the framework of the SAXS theory, that will be used to determine the structural properties of our heterogeneous PMMA-Au and DLC-Au thin films. The PMMA-Au and DLC-Au composite thin films have been fabricated by implanting Au ions into polymer and DLC. It will be assumed that the films are isotropic and formed by clusters of gold nanometric spherical particles named *monomers*. Usually, monomers are defined as the smallest gold nanoparticles found in the film. They have radius  $R$  and electronic density  $\rho(\mathbf{r})$ . The films are composed by an ensemble of clusters of monomers. All clusters form an *aggregate* or *sample*.

Detailed information about the structural properties of the films can be obtained, for instance, using the small angle X-ray scattering (SAXS)<sup>1,2</sup> technique. The X-ray scattering intensity  $I(q)$  is experimentally determined as a function of the scattering vector  $\mathbf{q}$  whose modulus is given by  $q = (4\pi/\lambda)\sin(\theta/2)$ , where  $\lambda$  is the X-ray wavelength and  $\theta$  is the scattering angle. Since our composite films are macroscopically isotropic the intensities will depend only on the modulus of  $q$  that for SAXS is given by  $q \approx (2\pi/\lambda) \theta$ . The SAXS technique is useful if relevant structural features are at a superatomic level, from a few tenths up to 100 nm. As well known, the SAXS measurements analyzed with suitable theoretical models

that accounts for disordered systems peculiarities are of fundamental importance in the characterization of nanostructured materials.<sup>3</sup>

In Section 1 is shown how to calculate the scattered intensity  $I_s(q)$  due to a single spherical monomer. In Section 2 we see how to obtain the scattered intensity  $I_s(q)$  due to a dilute cluster formed by  $N$  monomers. In Section 3 we present two different approaches to determine  $I(q)$  due to dense clusters of monomers: in Section (3.1) we show the Fractal Model and in Section (3.2) the Debye, Anderson and Brumberger Model or DAB Model.

### (1) Intensity $I_s(q)$ due to a single spherical monomer.

According, for instance, to Debye and Bueche<sup>4</sup> (see also references 1 and 2) the intensity  $I_s(q)$  of the scattered X-rays due to a *single monomer* is given by

$$I_s(q) = I_e(q) \int_{v_1} dv_1 \int_{v_2} dv_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \exp[i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] \quad (1.1),$$

where  $I_e(q)$  is the intensity scattered by one electron,  $v$  and  $\rho(\mathbf{r})$  are, respectively, the volume and the electronic density (or scattering power) of the monomer.

Assuming that z-axis is along the incident momentum  $\mathbf{q} = qz$ , where  $z$  is unit vector along the z-axis (1 and 2), putting  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ,  $\rho(\mathbf{r}) = \rho(r, \theta, \varphi)$  and  $dv = r^2 dr d\Omega = r^2 dr \sin\theta d\theta d\varphi$ , (1.1) is written as

$$I_s(q) = I_e(q) F^2 = I_e(q) \int_{v_1} \int_{v_2} \rho(r_1, \theta_1, \varphi_1) \rho(r_2, \theta_2, \varphi_2) \exp[iq(\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{z}] dv_1 dv_2 \quad (1.2),$$

where  $q = (4\pi/\lambda)\sin(\theta/2)$ .

If the monomers are spheres with radius  $R$  and homogeneous, that is, with electronic density  $\rho(\mathbf{r}) = \text{constant} = \rho$  from (1.2) we get

$$\begin{aligned} I_s(q) &= I_e(q) \rho^2 (4\pi)^2 \int_0^R r_1^2 dr_1 [\sin(qr_1)/qr_1] \int_0^R r_2^2 dr_2 [\sin(qr_2)/qr_2] = \\ &= I_e(q) F(q)^2 = I_e(q) \{3\rho R [\sin(qR) - qR \cos(qR)]/(qR)^3\}^2 \quad (1.3), \end{aligned}$$

where  $v = (4\pi/3)R^3$  is the monomer volume and the function  $F_s(q)$ , named *single-particle form factor*, is given by

$$F_s(q) = 3\rho v [\sin(qR) - qR \cos(qR)]/(qR)^3 \quad (1.4).$$

A different approach to obtain (1.4) is shown in the Appendix 1. This approach, that is more suited to the treatment of heterogeneities of the electronic

density of the monomers, that was developed originally by Lord Rayleigh,<sup>5</sup> is shown in details in the paper of Stein, Wilson and Stidham.<sup>6</sup>

The calculation of the scattering function  $F(q)$  for inhomogeneous monomers are shown in the paper of Stein, Wilson and Stidham<sup>6</sup> and also in our Appendix 2.

## (2) Intensity $I_s(q)$ due to a Dilute Cluster with N Monomers.

If the scattering system is a cluster composed by N monomers that are separated from each other widely enough it is plausible that they will make independent contributions to the scattered intensity. In these conditions the total scattered intensity  $I_s(q)$  due to the (*dilute*) cluster is given by,<sup>1,2,7</sup>

$$I_s(q) = NI_s(q) = N \Delta\rho^2 \{3v [\sin(qR) - qR \cos(qR)]/(qR)^3\}^2 \quad (2.1),$$

omitting for simplicity,  $I_e(q)$  and where  $\Delta\rho = \rho - \rho'$  assuming that the monomers are embedded in a homogeneous medium with constant electric density  $\rho'$ .<sup>1,2</sup>

## (3) Intensity $I(q)$ due to a Dense Cluster with N Monomers.

Equation (2.1) gives the scattering intensity produced by a cluster composed by N monomers widely separated. However,<sup>1,2</sup> when these monomers form a dense cluster (as occurs, for instance, in liquids) (2.1) does not give satisfactory descriptions of scattering intensity. This is due to the entanglement of the scattering amplitudes generated by the different parts of the monomers that now are closer. Many theoretical models have been developed to explain this entanglement effects<sup>3,7</sup> in heterogeneous materials. However, in this work we will take into account only two scattering models: *Fractal Model* and *Debye-Anderson-Brumberger Model*.

### (3.1) Fractal Model.

As well known, it is widely recognized<sup>3,8,9</sup> that the complex microstructure and behavior of a large variety of materials and systems can be quantitatively characterized by using the ideas of fractal distributions. Fractal concepts give us an important tool for characterizing the geometry and surface structure of heterogeneous materials and long-range correlations that often exist in their morphology. Even if the material does not possess fractal properties at significant length scales the concepts of fractal geometry often provide useful means of obtaining deeper insights into the structure of the material.<sup>3</sup>

It is well known<sup>7</sup> the scattering amplitude  $I(q)$  for a dense fractal aggregate composed by N spherical *homogeneous monomers* with radius R is given by

$$I(q) = I_s(q) S^V(q) \quad (3.1.1),$$

where, according to (2.1),  $I_s(q)$  is given by

$$I_s(q) = N(\Delta\rho)^2 v^2 \{3[\sin(qR) - qR\cos(qR)]/(qR)^3\}^2 \quad (3.1.2)$$

and  $S^v(q)$  is the *structure factor of the particles centers* defined by

$$S^v(q) = \{1 + 4\pi\Phi \int_0^\infty [g(r) - 1] r^2 (\sin(qr)/qr) dr\} \quad (3.1.3)$$

and  $g(r)$  is the *pair correlation function* defined by

$$g(\mathbf{r}) = \int_V \rho(\mathbf{r}) \rho(\mathbf{r} + \mathbf{r}') d\mathbf{r}'$$

where  $V$  is cluster volume and  $\Phi = (N/V)$ . As well known,  $\Phi g(r)$  represents the probability per unit of volume to find a particle at a distance  $r$  from a particle situated at the origin that for a fractal aggregate is given by

$$\Phi g(r) = (D/4\pi r_0^D) r^{D-3} \exp(-r/\xi) \quad (3.1.4),$$

where  $D$  is the volume (or mass) *fractal dimension* of the aggregate and  $\xi$  is a *correlation distance*. Putting (3.1.4) into (3.1.3) we get

$$\begin{aligned} S^v(q) &= 1 + (D/R^D) \int_0^\infty r^{D-1} \exp(-r/\xi) [\sin(qr)/qr] dr \\ &= 1 + (1/qR)^D \{D \Gamma(D-1) / [1 + 1/(q\xi)^2]^{(D-1)/2}\} \sin[(D-1) \tan^{-1}(q\xi)] \quad (3.1.5). \end{aligned}$$

According to the momentum uncertainty relation (MUR)  $\Delta p \Delta r \geq \hbar$  where  $\Delta p = \hbar q$  we see that the radius  $R^* \sim \Delta r$  of the region inside which the x-ray scattering is produced can be estimated by  $R^* \sim 1/q$ . In this context, let us obtain the function  $I(q)$  given by (3.1.1)–(3.1.3) for some special limits of  $q$  for three  $q$  different regions.

(I)  $q\xi \ll 1$  and, consequently,  $qR \ll 1$

In this case  $I(q) \rightarrow N(\Delta\rho)^2 v^2$  and  $S^v(q) \rightarrow \Gamma(D+1)(\xi/R)^D \{1 - [D(D+1)/6]q^2\xi^2\}$  resulting a  $I(q)$  function which has a Guinier-type behavior

$$\begin{aligned} I(q) &= N (\Delta\rho)^2 v^2 \Gamma(D+1)(\xi/R)^D \{1 - [D(D+1)/6]q^2\xi^2\} \\ &\approx N (\Delta\rho)^2 v^2 \Gamma(D+1)(\xi/R)^D \exp[-D(D+1)\xi^2 q^2/6] \quad (3.1.4). \end{aligned}$$

According to (3.1.4) the *generalized gyration radius*  $R_g(D, \xi)$  for spherical particles is given by

$$R_g(D, \xi) = [D(D+1)/2]^{1/2} \xi \quad (3.1.5)$$

instead of  $R_g = (3/5)^{1/2}R$  predicted by Guinier<sup>1</sup> that is valid when the fractality is negligible. The cluster radius is defined by (3.1.5). Inside the sphere with radius  $R_g \sim \xi$ , where the monomers are assembled, there is a correlation effect between them. The correlation length  $\zeta$  represents the characteristic distance above which the mass distribution is no longer described by a fractal law.

According to the MUR, the momentum transfer  $q$  in the cluster region is given approximately by  $q \sim 1/R_g \sim 1/\xi$ .

(II)  $1/\xi \ll q \ll 1/R$

In this  $q$  range  $I(q) \rightarrow N(\Delta\rho)^2 v^2$ ,  $S^v(q) \sim q^{-D}$  and, consequently,  $I(q) \sim q^{-D}$ . In this region the  $\log I(q) \times q$  plot is generally used to estimate the fractal dimension<sup>7</sup> measuring the slope of the curve. For Euclidean (homogeneous) materials,  $D = 3$ , we obtain  $I(q) \sim q^{-3}$ . Since  $D \leq 3$  we verify that as  $q$  increases,  $I(q)$  becomes larger for mass fractal than for homogeneous aggregates.

In this fractal range, that is, when  $1/\xi \ll q \ll 1/R^*$ , the radius  $R^*$  of the scattering regions are in the interval  $\xi > R^* > R$ .

(III)  $qR \gg 1$

In this case  $S^v(q) \rightarrow 1$  and there are two possibilities for  $I_o(q)$ : when the surfaces of the monomers are fractal, with fractality dimension  $D_s$ .

When the surface is rough, taking into account the monomer fractal boundary surface  $D_s > 2$  the scattered intensity, instead of (3.1.6), is given by<sup>7</sup>

$$I_s(q) \approx \pi N_o(\Delta\rho)^2 \Gamma(5 - d) \sin[\pi(D_s - 1)/2]/q^{(6 - D_s)} \quad (3.1.6),$$

where  $\Gamma(x)$  is the gamma function of argument  $x$ ,  $d$  is the Euclidian dimension of sample and  $D_s$  is the fractal dimension of the monomer surface.

When the surface is smooth, that is, when  $D_s = 2$  we get, from (3.1.6):

$$I(q) = 2\pi(\Delta\rho)^2 A_m/q^4 \quad (3.1.7),$$

where  $A_m = N_o\pi R^2$  is the total area of the monomers. Equation (3.1.7) which predicts an intensity  $I(q) \sim 1/q^4$  is known as *Porod law*.<sup>1,2</sup>

*Polydispersive Fractal Aggregates of Homogeneous Monomers.*

As shown above, the scattered intensity  $I(q)$  due to a dense cluster formed by  $N$  homogeneous spherical monomers is given by (3.1.1)–(3.1.5). The cluster radius is defined the *radius of gyration*  $R_g = [D(D+1)/2]^{1/2} \xi$ . If the aggregate is composed by an *ensemble* of dense clusters all them with the same  $R_g$  we say that the aggregate is *monodisperse*. When it is composed by many clusters with different  $R_g$  we say that an aggregate is *polydisperse*. All clusters are assumed to have the same mass fractal dimension  $D$ .

Thus, let us assume that our aggregate is polydisperse formed by a collection  $i = 1, 2, \dots, n$  of fractal clusters which have radius  $\{R_{ci}\}_{i=1, \dots, n}$ , each one with  $N_i$  monomers. Indicating by  $N(i)_{i=1, \dots, n}$  the number of clusters with radius  $R_{ci}=R_{gi}$  we see, following the formalism presented in Section (3.1), that the SAXS intensity generated by this polydisperse aggregate is proportional to  $I_{pol}(q)$  that is given by:

$$I_{pol}(q) = \sum_{i=1..n} N(i) I_i(q) \quad (3.1.7),$$

where, according to (2.1) and (3.1.5),  $I_i(q) = I_{si}(q) S_i^v(q)$ ,

$$I_{si}(q) = N_i (\Delta\rho)^2 v^2 P(q) = N_i (\Delta\rho)^2 v^2 \{3[\sin(qR) - qR \cos(qR)]/(qR)^3\}^2 \quad \text{and}$$

$$S_i^v(q) = 1 + (1/qR)^D \{D \Gamma(D-1)/[1 + 1/(q\xi_i)^2]^{(D-1)/2}\} \sin[(D-1) \tan^{-1}(q \xi)] \quad (3.1.8).$$

Note that all clusters have the same fractal dimension  $D$  but different clusters have a different correlation length  $\xi_i$  since  $R_{ci} = [D(D+1)/2]^{1/2} \xi_i$ .

Taking into account that the factor  $(\Delta\rho)^2 v^2 P(q)$  is the same for all clusters  $I_{pol}(q)$ , given by (3.1.7), can be put in a more compact form:

$$I_{pol}(q) = (\Delta\rho)^2 v^2 P(q) \sum_{i=1..n} N(i) N_i S_i^v(q) \quad (3.1.9).$$

For a *monodisperse* sample formed by  $J$  identical clusters the intensity  $I_{mon}(q)$ , using(4.3) is simply given by

$$I_{mon}(q) = J I_s(q) P(q) S^v(q) \quad (3.1.10).$$

Now, let us apply (3.1.9) to study the simplest polydisperse aggregate formed only by two clusters with radius  $R_{c1}$  and  $R_{c2}$ . Supposing  $R_{c1} > R_{c2}$  we have  $\xi_1 > \xi_2$ . In the  $q$  region where  $q\xi_1 \ll 1$  and  $qR \ll 1$  we have

$$I_1(q) \sim \Gamma(D+1)(\xi_1/R)^D \exp[-R_{c1}^2 q^2/3], \quad (3.1.11)$$

where  $R_{c1}=[D(D+1)/2]^{1/2}\xi_1$ , according to (2.1.4) and (2.1.5), respectively. Similarly, in the region where  $q\xi_2 < 1$  and  $qr_0 \ll 1$  we have

$$I_2(q) \sim \Gamma(D+1)(\xi_2/R)^D \exp[-R_{c2}^2 q^2/3], \quad (3.1.12)$$

with  $R_{c2}=[D(D+1)/2]^{1/2}\xi_2$ . Consequently,

$$I_{\text{pol}}(q) \sim f_1 I_1(q) + f_2 I_2(q), \quad (3.1.13)$$

where  $f_1$  and  $f_2$ , with  $f_1 + f_2 = 1$ , are the percentages of clusters 1 and 2, respectively.

With a  $\log I_{\text{pol}}(q) \times q^2$  plot<sup>7,10,11</sup> we can estimate the clusters radius  $R_{c1}$  and  $R_{c2}$  measuring the slopes of the curves  $I_1(q)$  and  $I_2(q)$ .

If  $f_1$  and  $f_2$  are known the equation  $I_{\text{pol}}(q) \sim P(q) [f_1 S_1(q) + f_2 S_2(q)]$  can be used to fit the experimental data  $I(q)$  in terms of the adjustable parameters  $D$ ,  $\xi_1$ ,  $\xi_2$  and  $R$  that, in this way, can be determined.

### (3.2) Debye–Anderson–Brumberger Model.

Let us suppose that the monomers which are implanted at random in the film are, in average, almost equally distant one from another forming an aggregate that can be taken approximately as a periodic lattice with period  $d$ . In these conditions, we will assume that the scattered intensity  $I(q)$  due to this kind of aggregate could be explained by the Debye, Anderson and Brumberger model<sup>12-14</sup>:

$$I(q) = 4\pi V \langle \eta^2 \rangle \int_0^\infty \gamma(r) [\sin(qr)/(qr)] r^2 dr \quad (3.2.1),$$

where  $V$  is the volume of the sample “illuminated” by the X-rays,  $\langle \eta^2 \rangle = \langle (\rho - \rho_{\text{av}})^2 \rangle$  is the mean square fluctuation of the scattering density  $\rho$ ,  $\rho_{\text{av}}$  is the average value of  $\rho - \rho'$ ,  $r$  is the distance between inhomogeneous regions of the sample and  $\gamma(r)$  is a the *correlation function* defined by

$$\gamma(r) = [\sin(2\pi/d)/(d/2\pi r)] \exp(-r/\delta),$$

$\delta$  being a *correlation length*. It is clear that there are two length scales involved in  $\gamma(r)$ :  $d$ , which is characteristic of the domain size or periodicity of the inhomogeneous regions of the film (due to monomers) and  $\delta$  is the *correlation length* which is responsible for the decay of the correlations between these regions as  $r$  increases. Integrating (3.2.1) one can verify that<sup>13,14</sup>  $I(q)$  is given by a function

$$I(q) \sim 1/(a_2 + c_1 q^2 + c_2 q^4) \quad (3.2.2),$$

where  $a$  and  $c_i$  ( $i=1,2$ ) are coefficients that can be obtained from the expansion of the phenomenological Landau<sup>13-15</sup> free energy  $F$  for an heterogeneous medium in terms of the order parameter  $\psi$ :

$$F = \int f(\psi, \nabla\psi, \nabla^2\psi) d^3r,$$

where  $f = a_0 + a_1\psi + a_2\psi^2 + \dots + c_1(\nabla\psi) + c_2(\nabla^2\psi)^2 + \dots$

Fourier transform (3.2.1) fixes the proportionality constant  $C$  of (3.2.2),<sup>13</sup>

$$I(q) = C/(a_2 + c_1 q^2 + c_2 q^4),$$

where  $C = 8\pi V \langle \eta^2 \rangle c_2 / \xi$ . In this general case the parameters  $\xi$  and  $d$  are given by

$$\xi = [(a_2/c_2)^{1/2}/2 + (c_1/c_2)/4]^{-1/2} \quad \text{and} \quad d = [(a_2/c_2)^{1/2}/2 - (c_1/c_2)/4]^{-1/2}.$$

It can be shown<sup>13,14</sup> that when  $c_1 < 0$  the intensity function  $I(q)$  given by (3.2.2) yields a single broad maximum  $I_{\max}$  at  $q = q_{\max}$ . In the neighborhood of  $q_{\max}$  the function  $I(q)$  would be represented by

$$I(q) = I_o / \{ (1 - I_o/I_{\max})(q^2/q_{\max}^2 - 1)^2 + I_o/I_{\max} \} \quad (3.2.3),$$

decaying proportional to  $q^4$ , according to Porod law for  $q > q_{\max}$ .  $I_{\max}$  and  $q_{\max}$  can easily be obtained from the experimental data and  $I_o$  is an adjustable parameter which can be used to narrow or broaden the peak. The two characteristic lengths,  $d$  and  $\delta$ , within the material that can be obtained by fitting (3.2.3) are given by<sup>13,14</sup>

$$d = 2\pi \{ (1/2)q_{\max}^2 [ 1/(1 - I_o/I_{\max})^{1/2} + 1 ] \}^{-1/2}$$

and

$$(3.2.4).$$

$$\delta = \{ (1/2)q_{\max}^2 [ 1/(1 - I_o/I_{\max})^{1/2} - 1 ] \}^{-1/2}$$

The relations between the parameters  $d$  and  $\delta$  with the coefficients  $a_i$  and  $c_i$  ( $i = 1,2,\dots$ ) that appear in the expansion of  $F$  in term of  $\psi$  are shown explicitly in papers mentioned above.<sup>13,14</sup>

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**APPENDIX 1. Calculation of  $F_s(q)$  following Lord Rayleigh.**

In this approach is taken into account a correlation function for the internal structure of the monomers. If the product of the  $\rho$ 's depends only upon the separation of the scattering elements, one may integrate over angle and the coordinates of one of the scattering elements, keeping the separation between them constant. In these conditions from (2.1.2) we obtain,<sup>4,6,12</sup>

$$F_s(q)^2 = 4\pi v \int_0^{\infty} \langle \rho_1 \rho_2 \rangle_{12} [\sin(qr_{12})/qr_{12}] r_{12}^2 dr_{12} \quad (2.1.5),$$

where  $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$ ,  $\rho_n=\rho(r_n,\theta_n,\varphi_n)$ , and  $\rho_1\rho_2$  stands for the product at a fixed value of  $r_{12}$  averaged over all positions of one of the scattering elements.

Now, for a homogeneous sphere,  $\rho_1 = \rho_2 = \text{constant} = \rho$ , since both scattering elements of volume lie within the sphere, one can show that<sup>4,6,12</sup>

$$\langle \rho_1 \rho_2 \rangle_{12} = \rho^2 \gamma_o(r) \quad (2.1.6),$$

where  $\gamma_o(r)$  is a *correlation function* given by

$$\gamma_o(r) = 1 - (3/4)[r_{12}/R] + (1/16)[r_{12}/R]^3, \quad \text{for } r_{12} < 2R$$

and (2.1.7).

$$\gamma_o(r) = 0, \quad \text{for } r_{12} \geq 2R$$

If a scattering element of volume is taken at the point 1, (2.7) expresses the probability to find an element 2 at a distance  $r_{12}$  from 1.

Thus, (2.1.5) is written as

$$\begin{aligned} F_s(q)^2 &= 4\pi v \rho^2 \int_0^{2R} \gamma_o(r_{12}) [\sin(qr_{12})/qr_{12}] r_{12}^2 dr_{12} \\ &= 4\pi v \rho^2 \int_0^{2R} \{1 - (3/4)[r_{12}/R] + (1/16)[r_{12}/R]^3\} [\sin(qr_{12})/qr_{12}] r_{12}^2 dr_{12} \\ &= \{3\rho v [\sin(qR) - qR \cos(qR)]/(qR)^3\}^2 \end{aligned} \quad (2.1.8),$$

which is identical to (2.1.3).

## APPENDIX 2. *Inhomogeneous Monomers.*

Let us assume now that the scattering power  $\rho$  of the monomers are inhomogeneous but with a radial symmetry, that is,  $\rho = \rho(r)$ . In this case, integrating (2.1.2) over angles we obtain, instead of (2.1.5)

$$F_{si}(q)^2 = 4\pi v \int_0^R \langle \rho(r_1) \rho(r_2) \rangle_{12} [\sin(qr_{12})/qr_{12}] r_{12}^2 dr_{12} \quad (2.1.9),$$

where  $\langle \rho(r_1) \rho(r_2) \rangle_{12}$  is the average over all positions 1 and 2 of the scattering elements separated by the distance  $r_{12}$ . If the sphere has internal structure, one may write<sup>6</sup>

$$\rho(r_1) = \rho_1 (1 + \mu_1) \quad \text{and} \quad \rho(r_2) = \rho_2 (1 + \mu_2) \quad (2.1.10),$$

where  $\rho_i$  is the scattering power of the homogeneous sphere at the position  $r_i$  and  $\mu_i$  are the fluctuations from this due to non homogeneous structure of the sphere. Then,

$$\langle \rho(r_1) \rho(r_2) \rangle_{12} = \langle \rho_1 \rho_2 \rangle_{12} + \langle \rho_1 \rho_2 \mu_1 \rangle_{12} + \langle \rho_1 \rho_2 \mu_2 \rangle_{12} + \langle \rho_1 \rho_2 \mu_1 \mu_2 \rangle_{12} \quad (2.1.11).$$

If the internal fluctuations  $\mu_n$  are random, positive and negative with equal probabilities, independent of the positions  $r_n$  we have

$$\langle \rho_1 \rho_2 \mu_1 \rangle_{12} = \langle \rho_1 \rho_2 \mu_2 \rangle_{12} = 0 \quad (2.1.12).$$

If the internal correlations  $\mu_1 \mu_2$  are independent of the correlations  $\rho_1 \rho_2$ , then

$$\langle \rho_1 \rho_2 \mu_1 \mu_2 \rangle_{12} = \langle \rho_1 \rho_2 \rangle_{12} \langle \mu_1 \mu_2 \rangle_{12} \quad (2.1.13).$$

Writing the internal correlations as

$$\langle \mu_1 \mu_2 \rangle_{12} = \langle \mu^2 \rangle_{av} \gamma_i(r_{12}) \quad (2.1.14),$$

where  $\gamma_i(r_{12})$  is the correlation function for internal fluctuations and  $\langle \mu^2 \rangle_{av}$  is the mean square amplitude of fractional refractive index variation. Thus, taking into account (2.1.6), (2.1.11)–(2.1.14) one obtains

$$\langle \rho(r_1) \rho(r_2) \rangle_{12} = \rho^2 \gamma_o(r_{12}) + \rho^2 \gamma_o(r_{12}) \langle \mu^2 \rangle_{av} \gamma_i(r_{12}) \quad (2.1.15).$$

In this way, (2.1.9) is written as

$$F_{si}(q)^2 = 4\pi v \rho^2 \int_0^R \gamma_{eff}(r_{12}) [\sin(qr_{12})/qr_{12}] r_{12}^2 dr_{12} \quad (2.1.16),$$

where  $\gamma_{eff}(r_{12}) = \gamma_o(r_{12}) [1 + \langle \mu^2 \rangle_{av} \gamma_i(r_{12})]$ . According to studies performed on scattering at large angles,<sup>6</sup> Debye and Bueche<sup>4</sup> have shown that the function  $\gamma_i(r) = \exp(-r/\xi)$ , where  $\xi$  is correlation distance, fits very well the experimental results.

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