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**Radial Distribution Functions and
Structure Factors for
Dense Aggregates: Non−Fractal and
Fractal Approaches**

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Radial Distribution Functions and Structure Factors for Dense Aggregates: Non−Fractal and Fractal Approaches

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Abstract

In many books and papers are found the definitions and applications of Radial Distribution Function (RDF) and Structure Factor (SF) to study aggregate properties. The RDF and SF functions defined to determine the interaction potential between the particles of an aggregate are completely different from the respective ones defined to obtain the fractal properties of the aggregate. Since these differences are not found clearly displayed in the literature they will be pointed out and analyzed in details here. This article was written to graduate and postgraduate students of Physics.
Key words: pair correlation functions; structure factors; fractals.

Resumo

Em muitos livros e artigos encontramos as definições e aplicações da Função de Distribuição Radial (FDR) e do Fator de Estrutura (FE) para estudar as propriedades de agregados. As FDR e FE definidas para determinar o potencial de interação entre as partículas de um agregado são completamente diferentes das respectivas funções definidas para obter as propriedades fractais do agregado. Como essas diferenças não são encontradas claramente expostas na literatura elas são mostradas e analisadas em detalhes aqui. Esse artigo foi escrito para alunos de graduação e pós−graduação de Física.

(1) Pair Correlation Function.

To simplify our analysis we will assume that the material is composed by N identical nanometric spherical "particles" with radius r_o that occupy a volume V. These "particles" ("monomers") can be atoms, molecules or also nanometric agglomerates of atoms and molecules. In addition, it will be assumed that the particles distribution in the agglomerates have a spherical symmetry. In Statistical Mechanics[1,2,3] using the "two particles correlation function" or simply "pair correlation

function" $n^{(2)}(r)$ the "Radial Distribution Function" (RDF) $g(r)$ of the aggregate is defined by :

$$g(r) = (V/N)^2 \, n^{(2)}(r) \qquad (1.1)$$

The function $g(r)$, which is normalized to 1 for $r \rightarrow \infty$, gives the effective distribution of the particles localized at a distance r around a given particle placed at the origin. The number of particles $dN(r)$ between r and $r+dr$ is given by $dN(r) = 4\pi \, (N/V)g(r) \, r^2 dr$.

(2) Determination of the Interaction Potential between Particles.

With the intention to determine the interaction potential between the particles in a material the function $g(r)$ is sometimes written as[1,2]

$$g(r) = \exp\{- \varphi(r)/kT \} \qquad (2.1),$$

where k is the Boltzmann constant, T is the absolute temperature of the system and $\varphi(r)$ is the effective energy interaction potential between two particles. In Figure 1 is seen a typical $g(r)$ function for a liquid assuming that $\varphi(r)$ is a Lennard−Jones potential.[1,2] The shape of $g(r)$ that describes[2] how the particles are concentrated as a function of r can be easily understood taking into account that for $r \rightarrow 0$ the potential $\varphi(r) \rightarrow \infty$ due to a repulsive force ("hard core"), at $r = \sigma \sim 2r_0$ it passes by a negative minimum, due to an attractive force between the particles and for $r \rightarrow \infty$
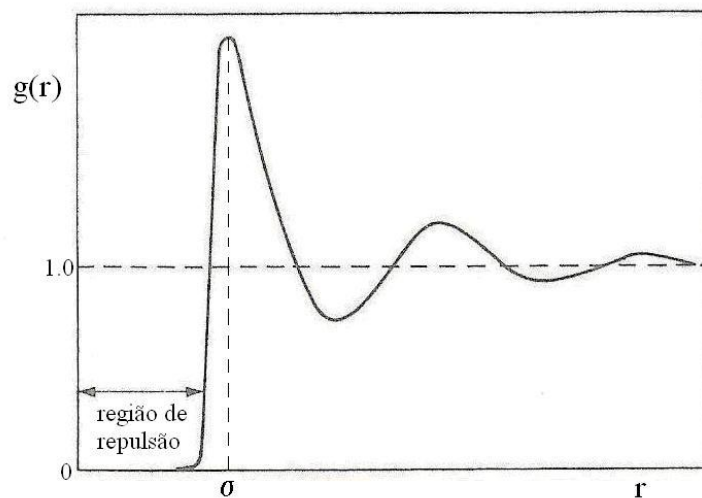

Figure 1. Typical plot of $g(r)$ x r for a liquid.[2] The maximum of $g(r)$ is found at $r \sim \sigma \sim 2r_0$.

it tends to 1 since $\varphi(r) \rightarrow 0$. In this way, $g(r) = 0$ for $r \leq 2r_o$, it passes by a maximum value at $r \sim \sigma$, in the region of the first neighbors, and for $r > \sigma$ it oscillates representing the effects of the more distant neighbors. The amplitudes of the oscillations decrease as r increases and for $r \rightarrow \infty$, where the particles density (distribution) becomes uniform, $g(r) \rightarrow 1$.

Putting $\Phi = (N/V)$, where V is the system volume, the total number of particles $N(r)$ which is inside a sphere with radius r, taking a particle at the origin $r = 0$, is given by

$$N(r) = \Phi \int_0^r g(r) \, 4\pi \, r^2 \, dr \qquad (2.2).$$

To determine microscopic properties of a material we can measure, for instance, the scattering intensity $I(q)$[3–5] of neutrons, electrons, or photons (X−rays). It is given by $I(q) = I_o(q) S(q)$ where $I_o(q)$ is the scattering generated individually by the N mononers and $S(q)$ is the "structure factor" (SF) defined[1,2,3–5]

$$S(q) = 1 + 4\pi\Phi \int_0^\infty [g(r) - 1] \, r^2 \, (\sin(qr)/qr) \, dr \, \} \qquad (2.3),$$

and q is the momentum change of the scattered photon, neutron or electron. The SF takes into account the correlated scattering between the monomers. In the case of elastic collision $q = 2k \sin(\theta/2)$ where $k = 2\pi/\lambda$ is the wave vector of the incident particle and θ is the scattering angle. According to the quantum position−momentum uncertainty relation $\Delta p \Delta r \geq \hbar$ if in the collision there is a momentum change $\Delta p = \hbar q$ the region where this effect is produced must have a dimension R given by a $R \sim 1/q$. As, in general, $\varphi(r)$ is different zero[2] in the interval $0 < r \leq 10 \, \text{Å} = 1$ nm the details of the function $\varphi(r)$ can be obtained only if the scattering are observed when $1/q < 10 \, \text{Å} = 1$ nm, that is, only when the momentum change q are given by $q > 1 \, \text{nm}^{-1}$. If the particle wavelength $\lambda \sim 1$ Å we verify that $q = (4\pi/\lambda) \sin(\theta/2) \sim 4\pi \sin(\theta/2)$. This implies that to have $q > 1 \, \text{nm}^{-1}$ the scattering angle θ must be $\theta > 10°$, that is, the effective scattering must occur at "large angles".

In Figure 2 is seen a typical function $S(q)$ as a function of q for a liquid in the case of a "large scattering angle". The value of $S(q)$ at $q = 0$ is given, as is shown in the Appendix, by $S(0) = \Phi\chi_T kT$, where $\chi_T = (\partial\Phi/\partial P)_{V,T}/\Phi$ is the isotermic compressibility of the material.[2]
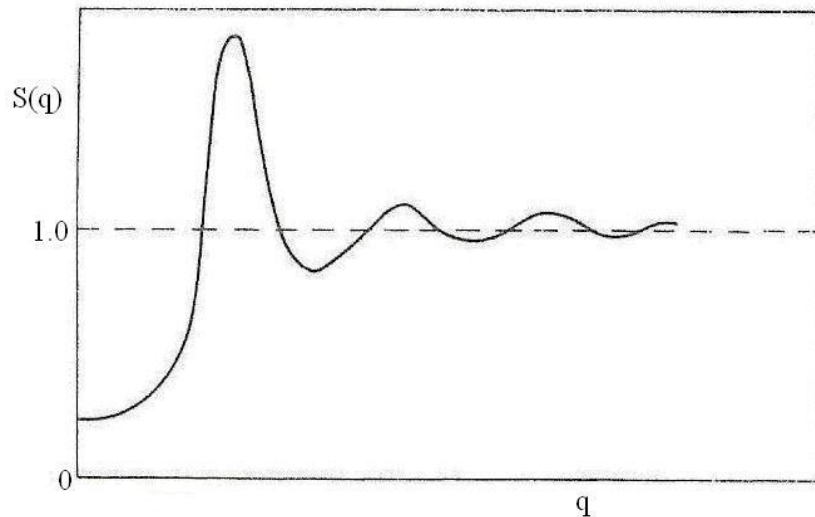
Figure 2. Typical plot[2] of S(q) x q for a liquid for "large scattering angles". q is usually measured in nm^{-1} or Å^{-1}.

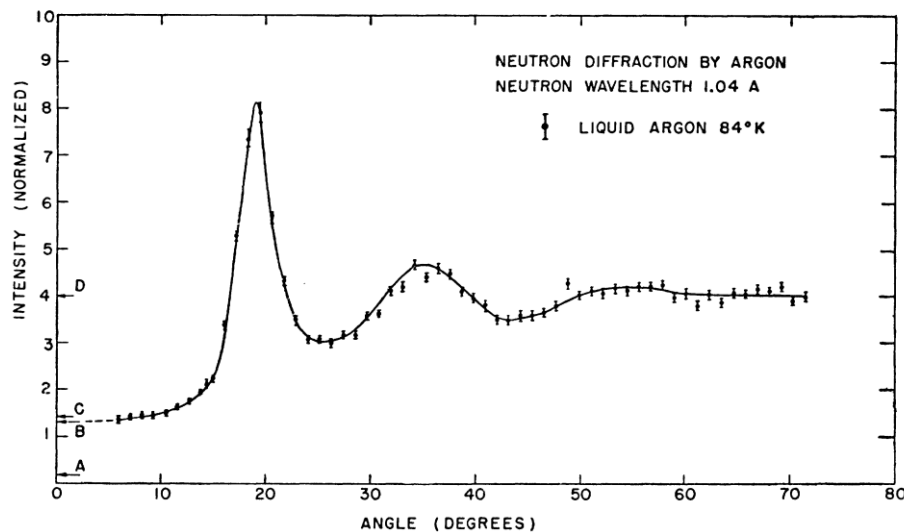In Fig.3 we see S(q) as a function of "large scattering angles" θ of neutrons[2,6] by liquid Ar at 84 K.

Figure 3. S(q) x θ measured in degrees, obtained for "large scattering angles" θ of neutrons by liquid Ar at 84 K.[6]

From S(q) we determine g(r) using (2.3). In Figure 4 are shown the experimental results[2,7] of S(q) as a function of q to liquid Rb at 40°C, obtained by scattering of neutrons at "large angles" compared with the values of S(q) calculated using (2.3) and (2.1) assuming a hard−sphere potential φ(r).[1,2,7]
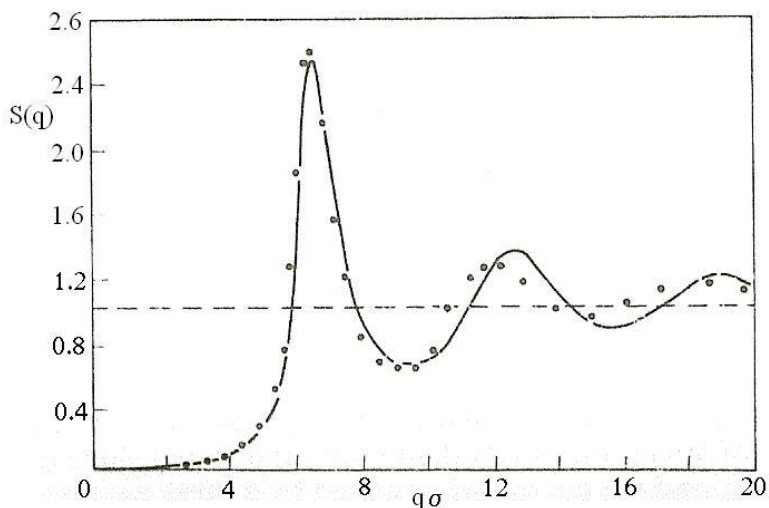
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Figura 4. Function S(q) x qσ obtained measuring "large angle" neutron scattering[2] (represented by black dots) to the Rb at 40° C compared with calculations (continuous line) performed assuming a hard−sphere interaction between the atoms.[1,2.7]

In Figure 5 is shown g(r) calculated taking into account the experimental S(q) values[2,6] obtained with "large angle" neutron scattering for liquid Ar at 84 K assuming φ(r) as a Lennard−Jones potencial.[1,2,6]
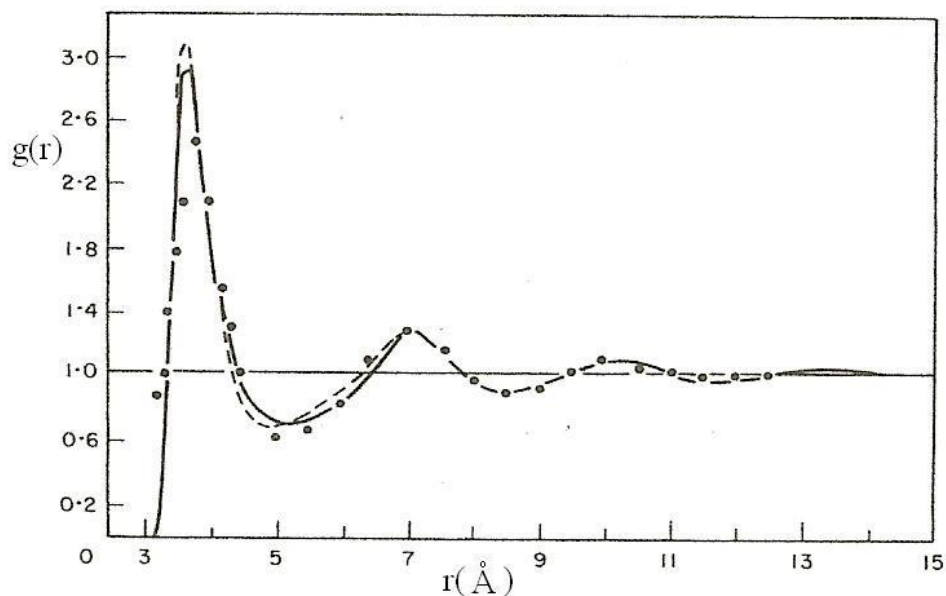

Figure 5. Function g(r) x r obtained from the experimental S(q) values of Ar at 84 K measured[6] with "large angle" neutron diffraction (black dots). The function g(r) was calculated (continuous and dashed lines) assuming φ(r) as a Lennard−Jones potential.[1,2,6,8]

(3) Determination of Fractal Properties of Aggregates.

Let us see how to determine the fractal properties of aggregates analyzing the scattering of neutrons, electrons or fotons (X−Ray). To do this we first show how to calculate the volume and mass fractality of systems composed by identical spherical monomers with radius r_o. To do a more complete and general study about fractality we suggest the lecture, for instance, of the books de Mandelbrot [9] and Feder. [10]

Let us consider a sphere (or circle) filled with identical monomers ("small balls") each one with radius r_o. Let us assume that the radius of the sphere R_n and the number of monomers N_n contained in the sphere are written as

$$R_n = a^n r_o \qquad e \qquad N_n = b^n \qquad (n = 1,2,3,..) \qquad (3.1).$$

Note that in our approach it will be assumed that $R_n \gg r_o$, that is, we have a very large number N_n of balls inside the sphere with radius R_n.

Equation (3.1) can also be written as

$$R_n/r_o = a^n \qquad and \qquad N_n = b^n \qquad (3.2),$$

from which we get (omitting for simplicity the n index from R_n and N_n)

$$n = \ln(R/r_o)/ \ln(a) = \ln(N)/\ln(b) \qquad (3.3),$$

that is,

$$\ln(b)/\ln(a) = D = \ln(N)/\ln(R/r_o) \qquad (3.4).$$

Equation (3.4) shows that

$$N = (R/r_o)^D, \text{ onde } D = \ln(b)/\ln(a) \qquad (3.5).$$

The parameter D is defined as "fractal dimension" of the system. The system can be linear (1−dim), circular disk (2−dim), sphere (3−dim),…
A system embedded in an Euclidean space with dimension E is named "fractal" when $D < E$ and "Euclidean" when $E = 3$.

Comments.

(A) To deduce Eqs.(3.3)−(3.5) no hypothesis have been done about the structure of the material (it could be crystalline or amorphous) or that the volume is partially or "completely" filled with the small balls. To analyze this let us assume that the aggregate which has a volume V is formed by N identical particles with radius r_o. Putting $R = 10^X r_o$ and $N = 10^Y$ we verify, using (3.4), that $D = \ln(N)/\ln(R/r_o) = Y/X$. So, for instance, in a 3−dim space, depending on X and Y, the system is Euclidean or fractal system if

Y/X = 3 or Y/X < 3, respectively. The fractality will depend on the empty spaces among the monomers that occupy the volume V. Thus, if the volume occupied by the particles is $V_{ocup} = N (4/3)\pi r_o^3 = 10^Y (4/3)\pi r_o^3$ and putting the available volume $V_{avail} = (4/3)\pi R^3 = (4/3)\pi r_o^3 10^{3X}$ we see that the ratio $V_{ocup}/V_{disp} = 10^{Y-3X}$. In this way, we verify that $V_{ocup} < V_{avail}$ if Y < 3X which is the fractal condition, that is, non−Euclidean. We have an Euclidean case when $V_{ocup} = V_{disp}$, that is, when Y = 3X, or D = Y/X=3.

(B) Note that the volume V is never "completely" filled with the small spherical particles, that is, the condition $V_{ocup} = V_{disp}$ is only approximately valid; there are always voids among the particles. This kind of problem was analyzed mathematically, for instance, by Thomas Harriot[11] around 1587 after a question on the better way of piling canon balls on ships posed to him by Rayleigh. This problem is known as the "close−packing of spheres". How to dispose the spheres in space in order to achieve this highest density or how they can be disposed in order to occupy the minimum space. In geometry, "close−packing of spheres" is a dense arrangement of equal spheres in an infinite,regular arrangement (or lattice). If N is the number of spheres inside a sphere with radius R the density ρ of spheres is given by $N = \rho(R/r_o)^3$. Gauss[12] proved that the highest average density, that is, the greatest fraction of space occupied by spheres that can be achieved by a regular arrangement is given by (see also Feder[10])

$$\rho = \pi/3\sqrt{2} \approx 0.74048 \qquad (3.6).$$

According to Kepler (17th−century) this highest density can be achieved by any arrangement of spheres, either regular or irregular. This is known as "Kepler conjecture". Recently T.C. Hales[13] claimed to have proved[14] this conjecture that has evaded certain confirmation for 400 years using computational methods.

In the 2−dim case, for a close−packed collection of N disks with radius r_o inside a circle with radius R it can be shown that its highest density ρ which is defined by $N = \rho(R/r_o)^2$ is given[10]

$$\rho = \pi/2\sqrt{3} \approx 0.9069 \qquad (3.7).$$

For the 1−dim case (straight line) a close−packed collection of N disks that occupy a "volume" L = 2R has its highest density ρ defined by $N = \rho(R/r_o)^1$ given by

$$\rho = 1 \qquad (3.8).$$

In conclusion, for close−packed systems formed by N identical spheres (or disks) with radius r_o we have the following equations of N as functions of (R/ro), for 1−dim, 2−dim and 3−dim, respectively

$$N = (R/r_o)^1, \quad N = (\pi/2\sqrt{3})(R/r_o)^2 \quad \text{and} \quad N = (\pi/3\sqrt{2})(R/r_o)^3 ,$$

showing that close−packed systems are Euclidean, as occurs, for instance with many crystal structures. For non−Euclidean aggregates, that is, for fractal systems we have[9,10]

$$N = \rho(R/r_o)^D \tag{3.9},$$

where ρ is a constant and D is not integer.

(C) For a 3−dim space the volume occupied $V_o(n)$ by n small identical balls with radius r_o, each one with $v_o = (4/3)\pi r_o^3$ and the available volume V(n) can be written, respectively, by

$$V_o(n) = N_n v_o = b^n v_o$$
and
$$V(n) = (4/3)\pi R_n^3 = (4/3)\pi (a^n r_o)^3 = a^{3n} v_o \tag{3.10}$$

Since, in the general case, $V(n) \geq V_o(n)$ from (3.10) we obtain $a^{3n} \geq b^n$, that is, $3n \ln(a) \geq n \ln(b)$, which implies, using (3.5) that

$$D \leq 3 \tag{3.11}$$

When the occupied volume $V_o(n)$ is equal to the available volume V(n), that is, when
$$V(n)/V_o(n) = 1 = (b/a^3)^n$$

we must have $b = a^3$ giving, using (3.5), $D = \ln(b)/\ln(a) = 3$ and, consequently, omitting for simplicity the index n, that $N = (R/r_o)^3$ which is the Euclidean case, D = 3.

(3.a) Mass Fractality and Density Fractality.
First let us consider the case of particles placed in a 3−dim space. If m_o is the mass of each monomer, using (3.5) the total mass M(R) of the system is given by

$$M(R) = N m_o = m_o(R/r_o)^D \tag{3.12}$$

and its density $\rho = M/[(4/3)\pi R^3]$ is written as

$$\rho(R) = (3m_o/4\pi r_o{}^D)(R/r_o)^{D-3} \sim (R/r_o)^{D-3} \qquad (3.13).$$

Let us consider a particle at $r = 0$. The number of particles $N(r)$, the mass $M(r)$ and the density $\rho(r)$ inside a sphere ("cluster") with radius r will be given by

$$N(r) = (r/r_o)^D, \quad M(r) = m_o(r/r_o)^D \quad e \quad \rho(r) = (3m_o/4\pi r_o{}^D)(r/r_o)^{D-3} \quad (3.14).$$

In this way the density $\rho(r)$ can be written as

$$\rho(r) = (3m_o/4\pi r_o{}^D)(r/r_o)^{D-3} = A\,(r/r_o)^{D-3} \qquad (3.15),$$

where the parameter $A = (3m_o/4\pi r_o{}^D)$ depends on the mass, the radius of particles and the fractality of aggregate where the particles are immersed. Since for a fractal material $D < 3$ Eq.(3.15) shows that the density of a fractal cluster decreases as its radius r increases. The cluster density is constant only when $D = 3$, that is, when D is equal to the Euclidean dimension E of the space where the cluster is placed.

In the general case of a cluster immersed in a Euclidean space with dimension E the density (3.15) is given by [9,10]

$$\rho(r) = C\,r^{D-E} \qquad (3.16),$$

where C is a constant showing that the density is constant when $D = E$ in agreement with Sections (3.b) and (3.c).

Note that $N(r)$, $M(r)$ e $\rho(r)$ displayed above are valid only for $r \gg r_o$ resulting, consequently, that available volume $V \gg v_o$.

(3.b) Correlation Function for a 3−dim Fractal Aggregate.

From $N(r)$ given by (2.2) and (3.14) we get, respectively,

$$dN(r) = \Phi g(r)4\pi\,r^2\,dr \qquad \text{and} \qquad dN(r) = (D/r_o{}^D)\,r^{D-1}\,dr \qquad (3.17).$$

From (3.16) results

$$\Phi g(r) = (D/4\pi r_o{}^D)\,r^{D-3} \qquad (3.18).$$

Since for fractal systems [9,10] $D < 3$, $g(r)$, according to (3.18), would tend to zero when $r \to \infty$. This is a non physical result because for large r values the cluster shows an almost uniform density, with negligible fluctuations.[1,2] As is known from liquid theory,[1,2] $g(r) \to 1$ when $r \to \infty$. To correctly describe the behavior of a medium for large r it is introduced[15,16] a cutoff distance ξ, named "correlation distance" obtaining:

$$\Phi[g(r) - 1] = (D/4\pi r_o{}^D) \ r^{D-3} \ \exp(-r/\xi) \qquad (3.19).$$

ξ represents a characteristic distance larger than which the mass distribution in a cluster is no more described by a fractal law.[13]

(3.c) Structure Factor S(q) for a 3−dim Fractal Aggregate.

Note that the fractal relation (3.19) describes correlations between monomers only for $r \gg r_o$. On the other side, $g(r) = \exp\{-\varphi(r)/kT\}$ describes correlations between monomers for r values that are only a few times larger than the distances between the monomers.

In this way, (3.19) would be able to give precise information only for $r \gg r_o$. As analyzed in Section (2), according to the quantum position − momentum uncertainty relation $\Delta p \Delta r \geq \hbar$ if the momentum change of the scattered particle is a $\Delta p = \hbar q$ the dimension R of the region where this effect is produced would be given by a $R \sim 1/q$. Consequently, in order to investigate fractal properties the condition $R > r_o$, must be obeyed, that is, $1/q > r_o$. Taking into account that $q = (4\pi/\lambda) \sin(\theta/2)$ we verify that we must have $(4\pi r_o/\lambda) \sin(\theta/2) < \alpha$ where $\alpha \sim 1$. If the incident particle (photon, neutron or electron) has a wavelength $\lambda \sim 1.5$ Å = 0,1 nm and $r_o \sim 1.5$ nm the scattering angles obey the condition $40\pi \sin(\theta/2) < \alpha$ which implies that they must be very small at maximum equal to 3 ~ 4º. This means that the diffraction must be performed at "small angles" like in SANS ("Small Angle Neutron Scattering") ou SAXS ("Small Angle X−ray Scattering").[4,5]

Substituting (3.18) in (2.3) we can show that [17,18]

$$S(q) = 1 + (D/r_o{}^D) \int_0^\infty r^{D-1} \exp(-r/\xi) \ [\sin(qr)/qr] \ dr$$

$$= 1 + (1/qr_o)^D \{D \ \Gamma(D-1)/[1+1/(q\xi)^2]^{(D-1)/2}\} \ \sin[(D-1)\tan^{-1}(q\xi)] \quad (3.19)$$

The function S(q) is obtained integrating r from r = 0 because the radius and the volume of the monomer are taken as negligible compared with the dimensions of the aggregate. According to the SAXS theory[17−19] (or SANS) the fractal dimension D is determined analyzing S(q) in the interval $1/\xi \ll q \ll 1/r_o$ where $S(q) \sim q^{-D}$. For very small q values such as $q\xi \ll 1$ (consequently, $qr_o \ll 1$) we have $S(q) \approx \Gamma(D+1)(\xi/r_o)^D\{1 - [D(D+1)/6]q^2\xi^2\}$ with which is determined the "giration radius" $R_g(D,\xi) = [D(D+1)/2]^{1/2} \ \xi$. For large q values such as $qr_o \gg 1$ the function $S(q) \rightarrow 1$. In these conditions[18,19] the scattered intensity I(q) is described essentially by $I_o(q)$ due to the individual monomers, $I(q) \sim I_o(q) \sim q^{(Ds - 6)}$, where D_s is the fractal dimension of the monomers surfaces. For smooth particles $D_s = 2$ giving $I(q) \sim I_o(q) \sim q^{-4}$, which is the Porod law.

As an example we calculate S(q) using (3.19) for a PMMA−Au analised[19] with SAXS where we have found D = 1.70, r_o = 1.64 nm e ξ

=13.08 nm. Considering these values and using (3.19) we have calculated S(q) as a function of $X = q r_o$, shown in Figure 6. As pointed out above, this function S(q) is completely different from the S(q) seen in Figures 2−4.

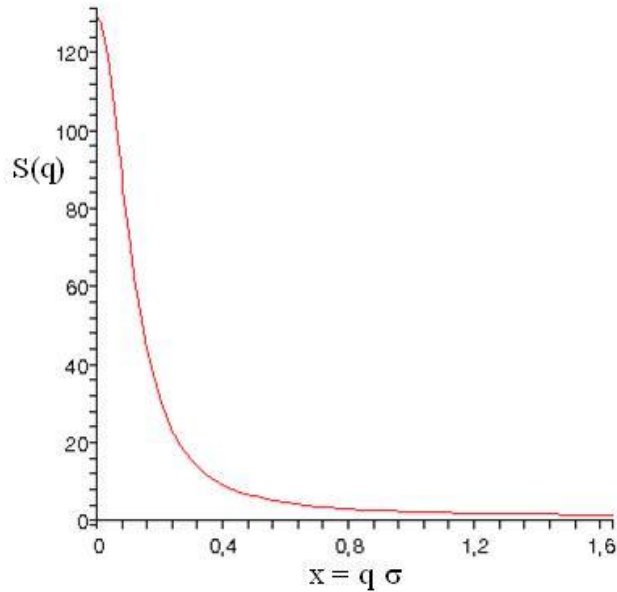**Figura 6.** S(q) defined by (3.19) as a function of $X = q r_o$ for a fractal a PMMA−Au film analyzed [19] with SAXS for which was obtained $D = 1.70$, $r_o = 1.64$ nm and $\xi = 13.08$ nm.

As a final remark, let us analyze S(q) given by (3.19) in the Euclidean case ($D = 3$) as occurs in a closed−packed system, like a perfect crystal. So, due to a long range order in the aggregate we have $\xi \rightarrow \infty$ and, consequently, $q\xi \rightarrow \infty$ resulting $\sin[2\tan^{-1}(q\xi)] = 0$. This implies that S(q) $\rightarrow$ 1, that is, the scattering intensity I(q) becomes $I(q) = I_o(q) S(q) \rightarrow I_o(q)$ where $I_o(q)$ is due only to the individual monomers.[4,5,17−19]

4) Conclusions.

According to Sections 1−3 if the intention is to determine the effective interaction potential between the particles of an aggregate using, for instance, neutron or X−ray difraction we must use *the large angle scattering*. If the intention is to determine fractal properties of the material we must use *small angle scattering* (SANS and SAXS). The structure functions S(q) for large and small angles scattering from which we obtain the necessary information, are completely different.

Appendix.

Putting $q = 0$ in (2.3) we get

$$S(0) = 1 + 4\pi\Phi \int_0^\infty [g(r) - 1]\, r^2\, dr = 1 + 4\pi\, (N/V) \int_0^\infty [g(r) - 1]\, r^2\, dr =$$

$$= 1 + (N/V)\{ -4\pi\, r_o^3/3 + \int_0^\infty [g(r) - 1]\, r^2\, dr \}$$

$$= 1 - V_o/V + v/V = (V - V_o)/V + v/V$$

where $v = N \int_{ro}^\infty [g(r) - 1]\, r^2\, dr$ and $V_o = 4\pi N r_o^3/3 =$ volume occupied by the small balls. The difference $V - V_o$ is effectively the empty volume that would exist in the aggregate if all balls were compacted. The volume v is the "probable" empty volume in the system created by the statistical fluctuations of the particles density Φ. It can be shown that[2] $S(0) = \Phi \chi_T kT$, where $\chi_T = (\partial\Phi/\partial P)_{V,T}/\Phi$ is the isothermal compressibility.

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