SMALL ANGLE NEUTRON SCATTERING OF AEROGELS: SIMULATIONS AND EXPERIMENTS

Anwar Hasmy, Marie Foret, Eric Anglaret, Jacques Pelous, René Vacher and Rémi Jullien
Laboratoire de Science des Matériaux Vitreux, UA 1119 CNRS, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France
(August 8, 1995)

A numerical simulation of silica aerogels is performed using diffusion-limited cluster-cluster aggregation of spheres inside a cubic box (with periodic boundary conditions). The volume fraction c is taken to be sufficiently large to get a gel structure at the end of the process. In the case of monodisperse spheres, the wavevector dependent scattered intensity I(q) is calculated from the product of the form factor P(q) of a sphere by the structure factor S(q), which is related to the Fourier transform of g(r) - 1, where g(r) is the pair correlation function between sphere centers. The structure factor S(q) exhibits large-q damped oscillations characteristics of the short range (intra-aggregate) correlations between spheres. These oscillations influence the I(q) curve in the q-region between the fractal regime and the Porod regime and quantitative comparisons are made with experiments on colloidal aerogels. Moreover, at small-q values, S(q) goes through a maximum characteristic of large range (inter-aggregate) correlations. Quantitative fits of the maximum in the experimental I(q) curves of base-catalyzed aerogels are presented. In the case of polydisperse spheres, I(q) is calculated directly from a single aggregate simulation. It is shown that increasing polydispersity shifts the location of the cross-over between the fractal and Porod regimes towards low q-value.

1. Introduction

As revealed by Small Angle X-rays Scattering (SAXS) or Small Angle Neutron (SANS) experiments, Silica Aerogels (13) are made of a disordered, but homogeneous, array of connected fractal clusters which result from the aggregation of primary particles (3). In the case of colloidal aerogel the form factor of the individual particles is well defined and one can extract the precise form of the structure factor S(q) from the scattered intensity I(q). The analysis of the wave vector dependence of S(q), and I(q), has permitted the determination of two characteristic length scales which are the average size, a, of the particles and the average size, ξ, of the clusters. Three distinct domains of wavevectors can be identified in both functions. At large q (q > a−1) S(q), and I(q), exhibits large-q damped oscillations, and the Porod law (I(q) ~ q−4), respectively. At intermediate values of q, for ξ−1 < q < a−1, the fractal nature of intra-cluster particle correlations is revealed by a power law behavior q−D, where D is the fractal dimension of the clusters. At last, at small q values, for q << ξ−1, the scattering function saturate and eventually decreases as q tends to zero.

Earlier studies (13) of the damped oscillations in the S(q) curve of colloidal aerogels have not been analyzed in terms of their all short range (intra-aggregate) features. On the other hand, the presence of a maximum in some S(q) and I(q) curves was puzzling for some authors (13) who tried to fit the experimental data by considering single aggregate theories like the formula due to Fisher and Burford (13) in which ξ plays the role of a radius of gyration. Others (2,3,6,14) have used a semi-empirical formula obtained by introducing a cut-off function to limit the fractal scaling, in which ξ enters as a correlation length. In all cases, these approaches do not take into account the inter-cluster interactions which give rise to a maximum in the scattering function. As far as long range properties are concerned, the single-aggregate approach is only valid for extremely diluted solutions of aggregated particles where the mean inter-aggregate distance ℓ is much larger than the mean radius of gyration R of the aggregates. Otherwise, the theoretical scattering function curve of a single aggregate, which saturates for q values smaller than R−1, in the so-called Guinier regime (3), is not valid down to q values of order ℓ−1, where inter-aggregate correlations start to have some influence. Recently, a hard sphere model have been introduced by Posselt et al. (16) to describe the packing of the connected clusters. However, their model does not take account of the fact that neglecting other scattering contributions such as scattering by thermally activated fluctuations, should cause S(q) and I(q) to vanish for q < ℓ−1, since, for distances larger than ℓ, the system becomes homogeneous and should no longer scatter the incident beam. Such behavior cannot be avoided in the case of aerogels where ℓ and R are of the same order of magnitude and should be replaced by ξ. If the experiments can be performed down to sufficiently small q-values, if no other artifactual inhomogeneities are present and if scattering by thermal fluctuations is small enough, all the experimental I(q) curves for gels or aerogels should exhibit a maximum. In practice, a maximum is observed, or not, depending on the range of q-values available. When it exists, this maximum is more or less pronounced, depending on preparation, i.e. catalysis conditions.

This paper is a review of a series of recent numerical studies which has been, in part, published elsewhere (11–19). We first study the large-q regime which is re-
lated to short interparticle distances within the aggregate. Then, we present quantitative results for the location and shape of the maximum of the \( I(q) \) curve at small- \( q \) values. Finally, the effect of particle size polydispersity in the cross-over between the fractal and Porod regime is discussed. The scattering functions \( S(q) \) and \( I(q) \) were obtained from numerical simulations of the full aerogel structure which is modeled by diffusion-limited cluster-cluster aggregation model (DLCA) in a box \([4,20,21]\) with a sufficiently large initial concentration, rather than the hierarchical model \([22]\) which is only able to build a single aggregate.

2. Constraints on Theory

2.1. The Model

We have considered a three dimensional off-lattice extension of the original cluster-cluster aggregation model \([20,21]\) in the case of a sufficiently large particle concentration to get a gelling network at the end of the process. Such a model was previously proposed by Kolb and Herrmann \([23]\) to describe the formation of gels, but, at this time, they considered a two-dimensional model on a lattice. Initially, identical spherical particles of unit diameter are randomly disposed in a cubic box of edge length \( L \) (here \( L \) is not necessary an integer) using a standard sequential addition procedure: attempts are made to center particles, one after another, at points whose coordinates are random numbers uniformly distributed between 0 and \( L \). If a particle overlaps a previous one, it is discarded and a new trial is made. If the process generates \( N \) particles, the dimension-less concentration, or volume fraction, \( c \) is given by:

\[
c = \frac{\pi N}{6 L^3}
\]  

(1)

From previous studies \([24]\), it is known that, with this procedure, \( c \) cannot exceed an upper limit which is called the “jamming concentration”, \( c_j \approx 0.385 \). Let us consider the starting configuration as a collection of aggregates containing one particle each. At a later time, one obtains a collection of \( N_a \) aggregates, the \( i \)-th aggregate containing \( n_i \) particles, so that:

\[
\sum_{i=1}^{N_a} n_i = N
\]  

(2)

The algorithm proceeds as follows. An aggregate \( i \) is chosen at random according to a probability, \( p_{n_i} \) which depends on the number of particles \( n_i \) that it contains given by:

\[
p_{n_i} = \frac{n_i^\alpha}{\sum n_i^\alpha}
\]  

(3)

In most of our simulations, we have taken \( \alpha \approx -0.55 \), a value close to \(-\frac{1}{3}\), where \( D \approx 1.78 \) is the fractal dimension of the resulting aggregates built in 3d \([25]\), in order to insure that the diffusion coefficient of the aggregates varies with the inverse of their radius. Then a space direction is chosen at random among the six directions \( \pm 1, \pm 1, \pm 1 \) and an attempt is made to move the cluster by a step of one unit length in that direction (note that this choice corresponds to perform a random translational brownian motion on a lattice but, since the original coordinates of the particles are not integers, the aggregates themselves are built off lattice). If the cluster does not collide any other cluster during this motion, the displacement is performed and the algorithm goes on by choosing again a cluster at random, etc... If instead a collision occurs, the cluster is translated in the chosen direction by the shortest distance insuring that one of its particles becomes tangent to one particle of the collided cluster. Then the collection of clusters is updated: the two colliding clusters are discarded and a new cluster, formed by sticking together the colliding clusters, is added to the collection. After that, one cluster is chosen at random, etc... Periodic boundary conditions are used at the edges of the box. The process is stopped when a single aggregate is reached. If the concentration is larger than a characteristic gel concentration \( c_g \), the final aggregate spans the box from edge to edge in the three space directions. This is the usual convention to define a gel network.

A series of calculations has been done to determine the gel concentration \( c_g \) as a function of the box size \( L \). In practice we have varied the concentration and we have performed twenty independent runs for each concentration. The gel concentration has been defined as being the concentration at which ten runs end up with a gel. The results are given in figure 1 as a log-log plot of \( c_g \) versus \( L \). As already found by Kolb and Herrmann \([23]\), the gel concentration tends to zero in the infinite \( L \) asymptotic limit. Since, at the gelling threshold, an aggregate of fractal dimension \( D \) reaches the size \( L \) of the box, one should have:

\[
c_g \sim \frac{L^D}{L^3} \sim L^{-(3-D)}
\]  

(4)

Our data are well fitted with the slope \(-1.28 \pm 0.05 \), giving \( D \approx 1.72 \pm 0.05 \), a value slightly smaller but quite close to the fractal dimension \( D \approx 1.78 \) of DLCA at the gel point in three dimensions \([26]\).

In all the calculations reported below, we have considered \( c \) values much larger than \( c_g \), in order to get a gel far above the gelling threshold and to be sure that the correlation length \( \xi \) is smaller than the box size \( L \). Typical examples of gel networks for two different concentrations are depicted in figure 2a and 2b where we have visualized a two-dimensional projection of a slice of the box. The slice thickness has been chosen to be proportional to \( \frac{1}{L} \) in order to get the same mean coverage in projection. Thus the only difference between the two pictures is in the way the apparent local densities deviate from the mean. As one sees larger holes in case (a), it is apparent that the mean cluster size is larger in that case where the concentration is smaller than in case (b). For comparison,
we show in figure 2c a micrograph of a colloidal aerogel sample.

2.2. The correlation function \( g(r) \)

As usual the two points correlation function \( g(\mathcal{P}) \) is defined such as \( g(\mathcal{P})d^3r \) is proportional to the probability of finding a particle center in a volume \( d^3r \) at a distance \( \mathcal{P} \) from a given particle center. Consequently, for an isotropic material, the number of particle centers \( dn \) located between \( r \) and \( r + dr \) from a given particle center is proportional to \( g(r)4\pi r^2dr \). Knowing from eq. 1 that, in average, the number of particle centers per unit volume is \( \frac{6c}{\pi} \), one can normalize \( g(r) \) to unity when \( r \) tends to infinity, by writing:

\[
dn = \frac{6c}{\pi} g(r)4\pi r^2dr = 24cg(r)r^2dr
\]  

(5)

We have used this formula to compute \( g(r) \) in the gels resulting from our simulations. For each particle in the box, we have counted the number of particle centers located between spheres of radius \( r \) and \( r + \Delta r \) taking care of the periodic boundary conditions when investigating regions outside of the box. Then we have averaged the result over all the \( N \) particles in the box and divided it by \( 24\pi r^2 \Delta r \). Moreover, \( g(r) \), obtained that way, has been averaged over a large number of independent simulations.

2.3. The scattering functions \( S(q) \) and \( I(q) \)

From the single scattering theory, the structure factor \( S(q) \) of a macroscopic system containing identical particles with mean volume fraction \( c \) is given by 26:

\[
S(q) = 1 + \frac{6c}{\pi} \int_0^{\infty} (g(r) - 1) \frac{\sin qr}{qr} 4\pi r^2 dr
\]  

(6)

The infinite boundary of the integral means that the incident beam is scattered by the particles located within the whole macroscopic volume. The presence of \( g(r) - 1 \) means that one has subtracted the intensity scattered by a quasi-infinite homogeneous object having the same boundaries as the considered macroscopic system. As a consequence, with formula (6), \( S(q) \rightarrow 0 \) when \( q \rightarrow 0 \) (because the \( q \approx 0 \) contribution of the boundaries has been suppressed). Quantitatively, this \( q = 0 \) limit results from the following sum rules:

\[
\frac{6c}{\pi} \int_0^{\infty} g(r)4\pi r^2 dr = M - 1 \tag{7a}
\]

\[
\frac{6c}{\pi} \int_0^{\infty} 4\pi r^2 dr = M \tag{7b}
\]

where \( M \) is the total number of particles contained in the macroscopic volume.

When applying formula (6) to real systems, it should be remembered that the underlying theory considers only the single scattering by static (quenched) particles. Therefore the scattering by thermally activated (and correlated) motions of these particles is not considered. It is known that in the case of liquids, the latter contribution (which corresponds to scattering by thermally activated density fluctuations) gives a non-zero contribution at \( q = 0 \) proportional to the product of temperature, bulk density and isothermal compressibility 23. Since in the following, the formula will be applied to solid aerogels, of quite low compressibility, we will assume that such contribution is negligible.

In practice, we have numerically calculated \( S(q) \) from the preceding \( g(r) \) results, by replacing formula (6) by:

\[
S(q) = 1 + \frac{6c}{\pi} \int_0^{\infty} (g(r) - g_0) \frac{\sin qr}{qr} 4\pi r^2 dr
\]  

(8)

Here, \( g_0 \) is a parameter which is very close, but not strictly equal, to one, \( r_m \) is an upper cut-off and the integral is numerically computed as a discrete sum. We have chosen \( r_m = \frac{4}{3} \), to avoid the boundary artifact mentioned above but also we have averaged \( g(r) \) over many simulations and we have limited ourselves to concentrations sufficiently greater than the gel concentration to obtain a significant range of \( r \) values below \( r_m \) where \( g(r) \approx 1 \). Nevertheless, the truncation of the integral implies that the numerical results for \( S(q) \) become meaningless for \( q \) values smaller than:

\[
q_{\min} = \frac{\pi}{r_m}
\]  

(9)

and, indeed, we have observed that for \( q < q_{\min} \) the precise shape of the computed \( S(q) \) curve depends on both \( r_m \) and \( g_0 \). To avoid this problem, we have forced the sum rules (7a) and (7b) to be verified, and, instead of using \( g_0 = 1 \), we have computed this parameter from:

\[
g_0 = \frac{\int_0^{r_m} g(r)4\pi r^2 dr + \frac{\pi}{r_m} \int_0^{\infty} 4\pi r^2 dr}{\int_0^{\infty} 4\pi r^2 dr}
\]  

(10)

where, to compute the integrals, we have used the same discretisation as in formula (8). We have checked that \( g_0 \) is always equal to 1 within less that 0.001, however using (10) instead of \( g_0 = 1 \), insures that \( S(q) \rightarrow 0 \), exactly, when \( q \rightarrow 0 \). This trick, which allows to obtain a continuation of \( S(q) \) below \( q_{\min} \), is expected to give a reasonably correct result if, in the corresponding infinite system, \( g(r) \) is supposed to stay constant for \( r > r_m \). This has been checked a posteriori by verifying that the numerical results are the same (within the numerical uncertainties) for different \( L \)-values.

For systems formed by monodisperse particles, the scattered intensity \( I(q) \) can be obtained by using:

\[
I(q) = S(q)P(q)
\]  

(11)

where \( P(q) \) is the normalized form factor for spherical particles of unit diameter:

\[
P(q) = \left(24 \frac{\sin \frac{q}{2} - \frac{q}{2} \cos \frac{q}{2}}{q^3} \right)^2
\]  

(12)
If the system contains polydisperse particles one can no longer calculate the scattered intensity \( I(q) \) as a product of \( P(q) \) and \( S(q) \). One should go back to the calculation of the scattered amplitude \( \tilde{A} \), which is proportional to:

\[
\tilde{A} = \sum_i \int e^{i\vec{q} \cdot (\vec{r}_i + \vec{x})} d^3x
\]

(13)

where \( \vec{r}_i \) refers to the center of the \( i \)-th particle and \( \vec{x} \) refers to a running point inside the volume of the \( i \)-th particle with respect to its center. The integral inside the sum, which should be performed over the volume of the \( i \)-th particle, can be calculated as a function of \( a_i \), assuming isotropy and homogeneity inside the sphere, leading to:

\[
\tilde{A} = \sum_i e^{i\vec{q} \cdot \vec{r}_i} A_i(q)
\]

(14a)

with:

\[
A_i(q) = 4\pi \frac{\sin(qa_i)}{qa_i} - \frac{\sin(qa_i - qa_i)}{qa_i}
\]

(14b)

Then, assuming a random orientation of the aggregate over the direction of \( \vec{q} \), the scattered intensity \( I(q) = |\tilde{A}|^2 \) can be written as:

\[
I(q) = \sum_{i,j} A_i A_j \frac{\sin(qr_{ij})}{qr_{ij}}
\]

(15)

where \( r_{ij} = |\vec{r}_i - \vec{r}_j| \).

Note that, since the \( i \) and \( j \) dependent product \( A_i A_j \) appears inside the sum, the result cannot be split in two parts. In particular one cannot use the correlation function \( g(r) \) to calculate an intermediate structure factor \( S(q) \). Here the double sum should be calculated directly. We have used such formula to calculate \( I(q) \) for single aggregates built using a hierarchical model.

3. Results

In figure 3 we show typical \( g(r) \) curve that result from an average over 20 simulations with \( L = 57.7 \) and \( c = 0.05 \). In this figure one observes a strong peak at \( r = 1 \), a discontinuity at \( r = 2 \), and a weaker singularity at \( r = 3 \) (discontinuity of the derivative). At large \( r \), \( g(r) \) goes through a minimum and becomes very close to one (in order to avoid artifactual correlations due to the periodic boundary conditions, we have used \( c \) values bigger than \( c_q \) to insure that the the homogeneous regime (when \( g(r)=1 \) can be reached for \( r < \frac{L}{2} \)). For small \( c \) values, one can observe the fractal regime, at intermediate \( r \) values, where \( g(r) \) follows the power law:

\[
g(r) \propto r^{-(3-D)}
\]

(16)

The range of this fractal regime decreases as \( c \) increases. Note that in the inset in figure 3, where \( c = 0.1 \), it is almost inexistant.

The strong peak at \( r = 1 \) is due to the non-zero proportion of distances \( r = 1 \) corresponding to bonds between contacting particles. The non-zero value of \( g(r) \) for \( r = 1 \) and the discontinuity at \( r = 2 \) can be understood if one considers that \( g(r) \) can be written as:

\[
g(r) = g_1(r) + g_2(r)
\]

(17)

where \( g_1(r) \) is the contribution of couples of particles that are tangent to the same third one and where \( g_2(r) \) contains all the other contributions. We have observed that, while \( g_2(r) \) is continuously varying from \( r = 1 \), where \( g_2(1) = 0 \), up to the largest distance, going through a maximum around \( r = 2 \), \( g_1(r) \) exists only between \( r = 1 \) and \( r = 2 \) and reaches non-zero values at both limits. The weaker singularity at \( r = 3 \) can be explained by analyzing distances between spheres tangent to each sphere of a dimer in a manner very similar to the discontinuity at \( r = 2 \).

In the inset in figure 3 we show the \( g(r) \) curves obtained for \( L = 57.7 \) and different \( c \) values by emphasizing the region near the minimum. One can see that the location of the minimum strongly depends on \( c \). The minimum corresponds to distances between particles located at the periphery of the clusters where the local density is smaller. Therefore the value of \( r \) at the minimum gives a good estimate of the mean cluster size, let us call it \( \xi \).

The dependence of \( \xi \) with \( c \) is reported in the log-log plot of figure 4. Assuming that the clusters are fractal with fractal dimension \( D \), one should get:

\[
\xi \sim c^{-\frac{1}{3-D}}
\]

(18)

The value \( \xi = 3 \) reported for the largest concentration \( c = 0.1 \) should be considered as artifactual since for such concentration the minimum of \( g(r) \) sticks on the singularity at \( r = 3 \), as seen in the inset of figure 3. A straight line fit of the remaining points for the largest box size gives a slope of \(-0.77 \pm 0.03 \), leading to \( D = 1.70 \pm 0.06 \), again slightly smaller but quite close to the fractal dimension \( D = 1.78 \) of 3d DLCA aggregates. We point out that in this model \( D \) increases when \( c \) increases as showed elsewhere [28,29]. However, the above value \( D \) can be understood by analyzing the time evolution during the aggregation process at the instant where the system can be considered as a gelling network the fractal dimension of the clusters is \( D \approx 1.78 \) and the characteristic length \( \xi \) value does not change compared with to measured \( \xi \) value at the end of the aggregation process [29].

Typical \( S(q) \) curves are reported in figure 5 for different concentrations and for \( L = 57.7 \). The location of \( q_{\text{min}} \) is indicated by the arrow. All the curves exhibit the same damped oscillations at large \( q \). In this figure, one observes a large minimum at about \( q \approx 4 \) followed by damped oscillations. The oscillations can be attributed to the \( \delta \)-peak of \( g(r) \). If one considers only the distance contributions of the delta peak the correlation function \( g(r) \) writes:

\[
g_1(r) = \frac{z}{24c} \delta(r - 1)
\]

(19a)
reported the numerical estimates of $\zeta$ which can be usefully compared to $\xi$. However the large minimum at $q \approx 4$ is not accounted for by this contribution only. Not only the delta-peak at $r = 1$ influences the shape of the first minimum of $S(q)$, but also the others short range features of the system, as the discontinuity at $r = 2$ and the singularity at $r = 3$, play some role.

The linear fractal regime is quite narrow and is more extended for low concentrations. It corresponds to a fractal dimension $D \approx 1.7$. We point out that in a system of homogeneous connected fractal clusters of finite size, the fractal dimension is only an “apparent fractal dimension” as showed elsewhere [29,30]. At lower $q$ values, all the curves exhibit a maximum. The location of the maximum, $q_m$, as well as the intensity of the maximum, $S(q_m)$, have been reported as a function of $c$ in table I together with the corresponding values of $\xi$. If one forget the artificial situation $c = 0.1$, the product $q_m\xi$ is almost constant, so that one has approximately:

$$q_m \approx \frac{2.75}{\xi} \quad (20)$$

On the other hand one observes that the intensity of the maximum $S(q_m)$ is roughly proportional to $c\xi^3$, which is the number of particles contained in a sphere of diameter $\xi$:

$$S(q_m) \approx 0.75c\xi^3 \quad (21)$$

For very low $q$-values (smaller than $q_m$) we get a linear behavior with slope $+2$. This is consistent with the low-$q$ expansion of formula (7), which predicts:

$$S(q) \approx \zeta^2 q^2 \quad (22a)$$

with:

$$\zeta^2 = \frac{6c}{\pi} \int_0^{r_m} (g_0 - g(r))4\pi r^4 dr \quad (22b)$$

This result is derived from a Taylor expansion of $\sin qr/qr$ inside the integral of (8). Note that, for an infinite system (where $r_m = \infty$ and $g_0 = 1$), such procedure is mathematically justified if $g(r) - 1$ tends to zero more quickly than any power law when $r$ tends to infinity. Our numerical results, which leads to a quite size-independent result for $\zeta$, strongly support a large-$r$ exponential decay for $g(r) - 1$. This defines another characteristic length $\zeta$ which can be usefully compared to $\xi$. In table I, we have reported the numerical estimates of $\zeta$ from our computed $S(q)$ curves for the different $c$ values considered. We find that $\zeta$ is roughly proportional to $\xi$, and therefore $\zeta$ does not bring any new information on the structure.

As it should be expected, the characteristics of the maximum of $S(q)$ do not depend only on the mean cluster size $\xi$, but also on the extension of the cluster size distribution. The cluster size distribution is reminiscent of the size distribution of the aggregates observed during the aggregation process and therefore it strongly depends on the nature of the aggregation mechanism. As a consequence, all the quantitative analysis done above, as well as the values of the constants appearing in formulae (20) and (21), are only valid for DLCA where it is known that the aggregate size distribution presents a well defined maximum.

When the cluster perform a ballistic random motion instead of diffusion brownian during the aggregation process described in section 2.1., one obtains the ballistically-limited cluster-cluster aggregation (BLCA) model which is able to describe the aerosols in the Knudsen regime. In BLCA the polydispersity of cluster sizes is larger than in the DLCA model. On the other hand, when a very small sticking probability is introduced in the DLCA model one obtains the chemically-limited cluster-cluster-aggregation (CLCA) model where it is known that the aggregate size distribution is broader than the DLCA and BLCA models. In figure 6 we show that this polydispersity features are observed in the $S(q)$ curves, where the broadest peak at $q_m$ corresponds to the CLCA model.

The log-log plots of $I(q)$ versus $q$ for different concentrations are reported in figure 7. As a result of the multiplication by $P(q)$ and the use of the logarithmic scale, the maximum appears to be relatively less pronounced than in the $S(q)$ curves. The large-$q$ oscillations in the Porod region are due to the monodisperse particles forming the system. These oscillations become more and more damped when one increases the particles polydispersity [19] as it will be showed in figures 10.

4. Discussion

In this section we would like to discuss the theoretical results in the light of experimental data.

4.1. Short-range correlations (large $q$-values)

Colloidal silica aerogels have been prepared using the process described in ref. [10]. They have densities ranging from 0.070 to 0.380 $g/cm^3$. They are made of small colloidal spherical particles with a quite low diameter polydispersity as it has been checked on electron micrographs such as figure 2c. We have checked that the intensity scattered by the correspondingly diluted sol can be fitted by an averaged form factor $\overline{P}(Q)$ given by:

$$\overline{P}(Q) = \int_0^\infty P(Q,a)g(a)da \quad (23a)$$

where $P(Q,a)$ is the form factor of a spherical particle of diameter $a$ and $g(a)$ a truncated gaussian distribution given by:

$$g(a) \sim e^{-\frac{a^2}{2\sigma^2}} \quad (23b)$$
The same analysis has been done for all our experimental data and in the following we give the results for the structure factor as being the ratio of $I(Q)$ by $P(Q)$ as a function of the reduced wavevector $q = Q\alpha_0$. All the experimental $S(q)$ curves, determined this way, have been normalized such that $S(q) \to 1$ for $q \to \infty$. It has been shown \cite{17} that using formula (11) in presence of small polydispersity, in spite of this approach, the $S(q)$ curves present the same broad minimum.

In figure 8a one gives log $S(q)$ versus log $q$ for different aerogels made of particles of the same size ($\alpha_0 = 96\,\text{Å}$) but with densities ranging from 0.070 to 0.250 $\text{g/cm}^3$. On this figure, one observes the same characteristic broad minimum followed by damped oscillations that we have observed in the simulated curves, and the density fixes the size $\xi$ of the clusters. In figure 8b we compare two experimental $S(q)$ curves for the same aerogel density ($\rho = 0.10\,\text{g/cm}^3$) with the simulated curve in the diffusion limited case. It is clear in this figure that the agreement between theory and experiments is only qualitative. Even if the data are very noisy for large $q$ values it seems that the large $q$ oscillations of the experimental curves are more damped. But we would like to focus on the larger discrepancy which is that the minimum is wider and deeper in the experimental curves. This discrepancy is systematically more important for bigger particles, and its cannot be attributed to the kind of restructuring as showed in ref. \cite{17} because a restructuring mechanism in DLCA aggregates increases its coordinations number resulting in the $S(q)$ curves a deeper minimum but not wider. Since it is difficult to imagine some other realistic restructuring mechanisms able to fully account for the observed discrepancies, we do not trust the earlier interpretations which were considering quite large coordination numbers \cite{4,8,14}. One might invoke other possible explanations for the discrepancies such as small-$q$ modifications of the form factor or corrections to the scattered intensity due to some shape deformation of the particles near their contact zone. This last effect might be approximately taken into account by considering a different length for the particle-diameter and for the center-to-center distance between contacting particles. However all these considerations, if they might sometimes give a better fit, appear to be too “ad hoc” to really improve the comprehension of the problem.

Here we would like to propose another tentative interpretation. In general a complete theory of scattering (including multiple scattering, shadowing, refraction etc...) should consider two dimensionless parameters, $Qa$ and $ka = 2\pi\frac{\lambda}{\lambda_0}$. The fact that the theoretical $S(q)$ curve considered above does not depend on the extra parameter $ka$ comes from all the considered approximations. However the simple scattering theory should be recovered in the limit $ka \to 0$. Some corrections might appear for large $ka$ values. The fact that in figure 8b the theoretical curve can be considered as the limit of the experimental ones when $a \to 0$ support this analysis. Moreover the parameter $ka$ is quite large in our case. We used a combination of two incident neutron wavelengths of $6\,\text{Å}$ and $18\,\text{Å}$ in the experimental set-up. Thus our $ka$ values are in the range 30 to 300, close to the values involved in the geometrical optics approximation. It is reasonable to admit that corrections to the simple scattering theory, such as shadowing, refraction, multiple scattering effects, cannot be neglected for such large values.

4.2. Long-range correlations (small $q$-values)

As is known, colloidal aerogels are formed by particles bigger than standard aerogels. This fact impedes to obtain information about its long-range correlations (small $q$-values). For study the long range correlations we have considered SANS experiments on standard silica aerogels \cite{3,4}. They are prepared by chemical reactions (hydrolysis and condensation) of organosilicates. According to the $p_H$ value of the hydrolysis aqueous solution, we can distinguish “basic” and “neutral” aerogels. The basic aerogels \cite{44} are made of larger sized, but strongly polydisperse, primary particles while, for the neutral aerogels \cite{9}, particle sizes are smaller and extend down to the atomic scale. According to previous studies \cite{3,4,43,34}, only colloidal and basic aerogels can be considered as grown according to DLCA while the neutral aerogels are more likely grown according to the chemically-limited cluster-cluster aggregation process \cite{12,13,14}. Three experimental $I(q)$ curves for basic aerogels with different densities are compared with simulations in figure 9. The concentrations that we have used for the fit are those corresponding to the aerogel density $\rho$, according to the formula:

$$c = \frac{\rho}{\rho_0}$$

(24)

where $\rho_0 = 2.2\,\text{g/cm}^3$ is the density of silica. The only two adjustable parameters are the mean particle diameter value and a multiplicative constant for the intensity. Note that varying these parameters in a log-log plot does not change the shape of the curve but only leads to translations along the $x$ and $y$ directions. The three fits have been performed together using the same values for these parameters. A discrepancy occurs in the Porod region where the experimental curves stay slightly below the maxima of the large-$q$ oscillations of the theoretical curves. Such discrepancy can be attributed to the strong polydispersity of the primary particles \cite{4} and will be discussed in section 4.3.

We point out that, our DLCA model neglects rotational diffusion, aggregates deformations as well as all kinds of restructuring effects. However, as mentioned above, large restructuring is certainly not present, at least in the early stages of the aggregation process. But, in the last stages, when the gel structure is under formation, the diffusion process looses its leading character and it might be that restructuring and rotational motions have some influence on the gel structure and the inter-clusters correlations.

4.3. Effect of the particle size polydispersity
To study the influence of the particle size polydispersity we have calculated $I(q)$, using formula (15), for hierarchical aggregates made of spheres whose diameter are distributed according to a truncated gaussian distribution characterized by $\sigma_{eff} = \frac{a_0}{a_0}$, where $a_0$ and $\sigma$ are the mean value and the standard deviation of their diameters [18].

It has been shown [18] that the crossover wave-vector $q_c$ between the fractal and Porod regime, for $\sigma_{eff} > 0.1$, varies as:

$$q_c = \frac{2\pi}{a_0} (1 - 1.6\sigma_{eff})$$

(25)

where $\sigma_{eff}$ is the dimensionless standard deviation, or polydispersity. Note that, when $\sigma_{eff} = 0$ the crossover wave-vector $q_c$ is equal to $\frac{2\pi}{a_0}$ as can be verified in figure 7. In figure 9 the experimental curves exhibits the crossover take place at $q_c$ approximately equal to $\frac{2\pi}{a_0}$ and according the above equation $\sigma_{eff}$ should be equal to 0.25. We have computed, for simplicity, a single aggregate with a particle number $N$ equal to 32 using the hierarchical procedure [22] with a particle polydispersity $\sigma_{eff} = 0.25$, the theoretical $I(q)$ curve has been calculated using equation (15) and has been averaged over 32 simulations. The resulting curve is shown in figure 10a (solid line) in a log-log plot of $I(q)$, emphasizing the large-$q$ region, and for comparison we have depicted the case when $\sigma_{eff} = 0$(dashed line) and the experimental curve for $c = 0.043$(open circles). We can note in this figure that introducing a polydispersity not only the large-$q$ damped oscillations disappear, but also $q_c$ shifts towards low-$q$ values. This result can be attributed to the fact that larger particles dominate the scattering. Even if a single aggregate does not account for the realistic long-range correlations, figure 10a shows the good agreement at large $q$-values between the theoretical $I(q)$ curve for $\sigma_{eff} = 0.25$ and the experimental ones. Figure 10b shows a log-log plot of $I(q)$ versus $q$. Here the dashed line represents the numerical $I(q)$ results at the low-$q$ values in a system of connected fractal clusters for $c = 0.043$, and solid line represents results obtained at large-$q$ values of a single aggregate made of polydisperse particles. In this figure the agreement between the simulation and the entire experimental results (open circles) is remarkable.

**Conclusion**

In this paper we have shown that the diffusion-limited cluster-cluster aggregation model (DLCA) can explain the structure of “colloidal” as well as “basic” aerogels, as revealed by small-angle neutron scattering experiments since in most cases the full $I(q)$ curve can be quantitatively accounted for. This is a real progress compared to previous approaches which were focusing on the intermediate-$q$ fractal regime only. Such modelization is now used to study some other physical properties of aerogels. In the present issue we give two examples of application which are numerical calculations of aerogel sintering [33] and simulations of phase transitions in the pores of aerogels [34]. We also present a numerical study of the evolution of the $I(q)$ curve during the aggregation process [24]. Other applications are under progress. Further investigations are needed to account for the experiments on “neutral” aerogels which exhibit a larger fractal dimension than DLCA aggregates. Neutral aerogels are made of very small and strongly polydisperse particles whose sizes extend down to the atomic scale. It might be that their growing mechanism is closer to chemically-limited aggregation (CLCA) than DLCA but also there might exist some complex restructuring mechanisms due to their flexibility.

One of us (A. H.) would like to acknowledge support from CONICIT (Venezuela).

[1] D. W. Schaefer, J. E. Martin and K. D. Keefer, Phys. Rev. Letters, 56, 2199 (1986)
[2] T. Frelink, J. K. Kjems, and S. K. Sinha, Phys Rev. B, 33, 269 (1986)
[3] R. Vacher, T. Woigner, J. Pelous, and E. Courtens, Phys. Rev. B, 37, 6500 (1988)
[4] R. Jullien and R. Botet, Aggregation and Fractal Aggregates, (World Scientific, Singapore, 1987)
[5] B. M. Mandelbrot, Fractals: Form Chance, and Dimension (Freeman, San Francisco, 1977)
[6] P. Dimon, S. K. Sinha, D. A. Weitz, C. R. Safinya, G. Smith, W. A. Varady and H. M. Lindsay, Phys. Rev. Letters, 57, 595 (1986)
[7] T. Frelink, Thesis, Riso-M-report 2570 (Riso, Roskilde, 1986).
[8] F. Grey and J. K. Kjems, Physica D, 38, 154 (1990)
[9] S. K. Sinha, Physica D, 38, 310 (1990)
[10] M. Foret, J. Pelous and R. Vacher, J. Physique I (France), 2, 791 (1992)
[11] G. Dietler, C. Aubert, D. S. Cannell and P. Wiltzius, Phys. Rev. Letters, 57, 3117 (1986)
[12] B. Cabane, M. Dubois, F. Lefaucheux and M. C. Robert, J. of Non-Cryst. Sol., 119, 121 (1990)
[13] M. E. Fisher and R. J. Burford, Phys. Rev., 156, 583 (1967)
[14] F. Ferri, B. J. Frisk blinking D. S. Cannell, Phys. Rev. Letters, 67, 3026 (1991)
[15] A. Guinier and J. Fournet, Small Angle Scattering of X-rays, (Wiley Interscience, New York, 1955)
[16] D. Posselt, J. S. Pedersen, and K. Mortensen, J. of Non-Cryst. Solids, 145, 128 (1992)
[17] A. Hasmy, M. Foret, J. Pelous and R. Jullien, Phys. Rev. B, 48, 9345 (1993).
[18] A. Hasmy, R. Vacher and R. Jullien, Phys. Rev. B: Rap. Comm., 53, 1305 (1994)
[19] A. Hasmy, E. Anglaret, M. Foret, J. Pelous and R. Jullien, Phys. Rev. B, 50, 6006 (1994).
[20] P. Meakin, Phys. Rev. Letters, 51, 1119 (1983)
[21] M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Letters, 51, 1123 (1983)
R. Botet, R. Jullien, and M. Kolb, J. Phys. A, 17, L75 (1983)
M. Kolb and H. Herrmann, J. Phys. A, 18, L435 (1985)
D. W. Cooper, Phys. Rev. A, 38, 522 (1988)
P. Meakin, J. Coll. and Int. Sci., 102, 491 (1984)
L. A. Feigin and P. I. Svergun, Structure Analysis by Small Angle X-rays and Neutron Scattering, (Plenum, New York and London, 1987)
P. A. Egelstaff, “An Introduction to the Liquid State”, Academic Press (London and New York, 1967)
H. F. van Garderen, E. Pantos, W. H. Dokter, T. P. M. Beelen and R. A. van Santen, Mod. Sim. Mater Sci. Eng., 2, 295 (1994).

| $c$  | $\xi$ | $q_m$ | $q_m \xi$ | $S(q_m)$ | $\frac{S(q_m)}{c \xi^3}$ | $\zeta$ | $\frac{\xi}{\zeta}$ |
|-----|------|------|---------|----------|-----------------|-------|----------------|
| 0.025 | 10.7 | 0.26 | 2.78 | 24.7 | 0.81 | 38.5 | 3.6 |
| 0.033 | 8.4 | 0.31 | 2.60 | 16.0 | 0.82 | 28.1 | 3.3 |
| 0.038 | 7.8 | 0.37 | 2.88 | 12.8 | 0.71 | 25.9 | 3.3 |
| 0.043 | 6.7 | 0.40 | 2.68 | 10.5 | 0.81 | 21.0 | 3.1 |
| 0.050 | 6.3 | 0.43 | 2.71 | 8.3 | 0.66 | 18.4 | 2.9 |
| 0.061 | 5.3 | 0.52 | 2.76 | 6.2 | 0.68 | 15.5 | 2.9 |
| 0.100 | 3.0 | 0.80 | 2.40 | 3.3 | 1.22 | 10.0 | 3.3 |

TABLE I. For each concentration $c$ considered in the simulations, we have reported the location $\xi$ of the minimum of $g(r)$, the location $q_m$ of the maximum of $S(q)$, the product $q_m \xi$, the intensity of the maximum $S(q_m)$ and the ratio $\frac{S(q_m)}{c \xi^3}$, the characteristic length $\zeta$ entering the low-$q$ expansion of $S(q)$ and the ratio $\frac{\xi}{\zeta}$. We recall that $q$ is here a dimensionless quantity which is, in fact, equal to $2Qr_0$ where $Q$ is the dimensioned wavevector and $r_0$ is the radius of the primary particles and also that $S(q)$ has been normalized to unity for large $q$. 

2
FIG. 1. Log-log plot of the gel concentration $c_g$ as a function of the box size $L$. The fit by a straight line is shown which gives a slope of $-1.28 \pm 0.05$.

FIG. 2. Two dimensional projections of the particles contained in a slice of thickness $\ell$ after obtaining a gel in a box of size $L = 57.7$. Cases (a) and (b) corresponds to $c = 0.0095$, $\ell = 34.6$ and $c = 0.038$, $\ell = 8.65$, respectively. Cross sections of particles that are cut by the front slice edge are shown in black. (c) Micrograph of a 270 Å colloidal aerogel sample.

FIG. 3. Plot of $g(r)$ versus $r$ for $L = 57.7$ and $c = 0.05$. Inset: $g(r)$ curves for different $c$ values ($c = 0.025, 0.05, 0.1$). These curves result from averages over 20 simulations.

FIG. 4. Log-log plot of $\xi$, location of the minimum of $g(r)$, versus $c$, for $L = 28.8$ and $L = 57.7$. The fit by a straight line of the $L = 57.7$ data, excluding the $c = 0.1$ point, is shown giving a slope of $-0.77 \pm 0.03$.

FIG. 5. $S(q)$ versus $q$ for $L = 57.7$ and different $c$ values: $c = 0.025$, $c = 0.05$, $c = 0.1$. The dotted line correspond to $S_{\infty}(q)$. Here and in the following figures the location of $q_{\text{min}}$ is indicated by the arrow.

FIG. 6. Log-log plot of $S(q)$ versus $q$ for $L = 57.7$ and $c = 0.05$, the solid line, dashed line and dotted line, correspond to DLCA, BLCA and CLCA model, respectively. These curves result from average over 20 simulations.

FIG. 7. Log-log plot of the scattering intensity curve $I(q)$ versus $q$ for different $c$-values. The parameters are the same as in figure 5.

FIG. 8. (a) Experimental $S(q)$ curves (obtained as explained in text) for the 96Å -colloidal aerogel family. Samples are labeled by their densities. (b) Experimental $S(q)$ curves for samples of various particle diameters but with the same density, $\rho = 0.10g/cm^3$, and the simulated $S(q)$ curve in the diffusion-limited case.

FIG. 9. Comparison between simulations and experiments for three base catalyzed aerogels of the same family. The concentrations used in the simulations $c = 0.033, 0.043, 0.05$ are calculated from the aerogel densities ($\rho = 0.073, 0.095, 0.110g.cm^{-3}$) using formula (11). The two adjustable parameters, which are a multiplicative constant for the intensity and the particles diameter, taken to be 46Å, are the same for the three curves. The curves have been arbitrarily shifted vertically for clarity.

FIG. 10. (a)Log-log plot of $I(q)q^4$ vs. $q$ for $\sigma_{eff} = 0$ and $c = 0.043$ (dashed line), and for $\sigma_{eff} = 0.25$ with $N = 32$ (solid line). The open circles represent the experimental curve for $c = 0.043$. (b) Same data as in (a) but with a more extended $q$ interval and represented in a log-log plot of $I(q)$ vs. $q$. 

9
Fig 1
Fig 2a
Fig 4

![Graph showing data points for L=28.8 and L=57.7.](image-url)
Fig 5

![Graph of S(q) versus q with curves for different values of c: 0.1, 0.05, 0.025.](Image)
Fig 6
Fig 7

$I(q)$

c

- 0.025
- 0.05
- 0.1
