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The cluster model: A hierarchically-ordered assemblage of random-packing spheres for modelling microstructure of porous materials

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Abstract

A new structural model based on the premises widely used for describing the structure of random materials, and especially aerogels, is introduced. Aerogels are described as an assemblage of randomly-packed spheres in several hierarchically-ordered levels. A new algorithm has been developed for constructing structural models from these premises using computer simulation. Subsequently, several techniques based both on the Monte Carlo technique and on geometrical considerations for characterizing real systems have been simulated, and textural parameters of the models have been obtained, including specific surface area, specific porous volume and the apparent density of the systems. This characterization process yields a set of parameters used for testing the capacity of the models to reproduce the structure of several real systems, like aerogels. Special attention has been paid to the pore size distribution calculations: the Monte Carlo integration and the triangulation algorithms have been compared.

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Keywords: Porosity; Monte Carlo simulations; Aerogels

1. Introduction

Silica aerogels are chemically inert, highly porous, nanostructured materials, synthesized by the well-known sol–gel method [1], and dried by the supercritical drying process conceived by Kistler [2] for preventing cracking. In this way we obtain the silica aerogels, more porous materials than the conventionally-dried gels, which are also known as xerogels. Their particular structure is responsible for the most interesting properties of the aerogels, such as low thermal conductivity and very high specific surface area, which can reach values of around 1000 m^2/g or more. Incidentally, an aerogel is currently the solid with the lowest density ever synthesized [3], with a value of 1.9 mg/cm^3.

The structure of aerogels has been described as an assembly of randomly-packed spherical particles in several hierarchically-ordered levels [4–7]. Knowledge of the aerogel structure has been acquired using computer simulation techniques taking inputs from several sources, such as the understanding of the sol–gel process, and the relationship

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between the structure and the mechanical properties. The structure formation process has been studied using the molecular dynamics technique [8]; this was first applied by Garofalini et al. to the sol–gel process in 1994 [9] using the Feuston–Garofalini potential [10], and they concluded that the structure formation starts with a slow growth process of the individual clusters, followed by the faster growth of the structure due to cluster–cluster aggregation.

It is generally admitted that the cluster–cluster aggregation regimes (DLCA – diffusion limited cluster aggregation, RLCA – reaction limited cluster aggregation) describe quite well the typical structures obtained via sol–gel. One of the goals pursued most by researchers is to reproduce the formation and growth processes of the aerogels, using the RLCA or DLCA algorithms or some modifications of these [11,12]. Scherer et al. [13] used structures generated with DLCA-modified algorithms, characterizing them by their fractal dimension, to achieve the power law exponent and they have presented some models to explain the relationship between structure and mechanical properties [14,15]. Then Woignier et al. introduced a new technique for characterizing these porous systems [16,17], and concluded that pore size distribution and hydroxyl content are relevant for understanding the mechanical properties of these materials [18]. In a previous study, Woignier and Phallipou proposed one approach starting from a cubic structural model [19] and for a rigid assembly of cohesive spheres [20]. Emmerlig and Fricke also studied this problem, for elasticity and conductivity, through the scaling properties obtained by their simulated aerogel structures [11]. The cluster model that is introduced here has also been applied as an initial approach to the study of mechanical properties [7].

Computer simulation techniques have been used to characterize models from several points of view. On the one hand, there are some simulation techniques for studying the texture (specific surface, apparent density, porous volume, porosity ...). Gelb and Gubbins have directed their work towards the development of characterization applications based on the Monte Carlo (MC) technique, for the porous structures generated by simulation [21] and also for testing the validity of the BET [22] or the BJH [21] methods for analysing the adsorption/desorption isotherms. Hasmy has also worked on characterization, studying the behavior of the characteristic cluster size and the influence of the simulation box size [23]. One of the most frequently studied features of porous materials is the pore size distribution (PSD), which is experimentally calculated by several techniques, such as N_2 adsorption or Hg porosimetry [24]. Similarly, the PSD of different porous structural models has been also pursued by several research groups, using different strategies or different concepts for describing a pore [16,25–27].

We have also applied our models to simulate titania (TiO_2) porous systems. These are widely used in the field of photocatalysis and new-generation photovoltaics [28]. The use of mesoporous morphology allows for a very high light-harvesting efficiency due to the large internal surface area of the material [29]. Furthermore it has been observed that transport and recombination in mesoporous solar cells is limited by point defects located on the surface of the titania nanoparticles [30]. For this reason it is of considerable practical interest to have a theoretical estimation of the surface area as a function of parameters like the particle size or the apparent density.

2. The cluster model: algorithm and characterization techniques

We are proposing a new algorithm based on the premise of randomly-packed spheres in several hierarchically-ordered levels for building the cluster models. The aim of this technique is to build structural models emulating the real systems. Its best quality is its versatility: by tuning the geometric parameters of the model we can obtain very different assemblies of randomly-packed spheres for representing very different porous systems. The main structural parameters in this model are the elementary particle radius, the contact distance, the number of shells of each level and the number of hierarchical levels. However, models constructed by this procedure are intended to describe not the growth process of real systems, but the final state of such systems. They are categorised as static models [31].

FORTRAN 90 programming language on a Pentium 4 (3.5 GHz) processor running under *Linux Ubuntu* OS was used; while only a few seconds was taken to construct these systems, several hours were spent in characterizing them. In the course of this article, reduced units (particle diameter) have been considered.

2.1. Algorithm

Fig. 1 displays a diagram explaining the building process. The algorithm works as follows: first we place one *elementary* sphere in the centre of our system. Then we randomly place as many other spheres as are needed to cover fully the surface of the first one; this produces the first random shell. Every sphere has to be *in contact* at least

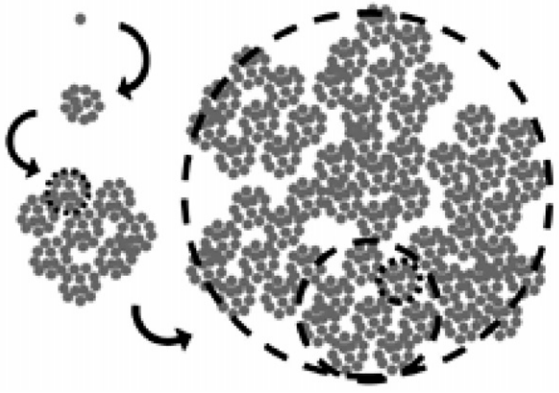

Fig. 1. Diagram of the cluster model algorithm.

with one other; that is, it must be at a previously defined distance. One can build as many shells of random spheres as are required. Then the *basic aggregate* of the first hierarchical level is built, and its diameter is measured. This diameter will be taken as the diameter of a *secondary sphere*.

The following hierarchical level is built in the same way, taking the basic aggregate as if it were an elementary sphere, that is, building the second level with *secondary spheres*. After building this new aggregate, each secondary sphere is replaced with one basic aggregate, to obtain a two-level hierarchically-ordered assembly of randomly-packed spheres. Then, the size of this system is measured again and is taken as the diameter of a *tertiary sphere*, if the intention is to build a third hierarchical level. In this case, an aggregate of *tertiary spheres* can then be built and, lastly, each *tertiary sphere* is replaced by the two-level system; in this way a three-level hierarchically-ordered system is obtained. This process can be repeated as many times as required. Typical values of our models are 1000–60 000 particles organised in 2–4 shells of random-packed spheres and 2 or 3 hierarchical levels; their contact distance d usually is found in the interval $0.85D < d < 1.0D$, D being the particle diameter.

Although auto similarity is potentially present in the cluster model as a consequence of its generation algorithm, in the present case we have not considered a fractal description because the structure of target aerogels is not auto similar over more than one order of magnitude. In the future we will emulate the fractal structure of those aerogels that present a well-defined fractal dimension.

Cubic simulation boxes have been used for the characterizing applications that are boundary-dependent and finite size-dependent, to apply periodic boundary conditions. One of the main topics previously dealt with is the question regarding the finite size effect. To be absolutely certain that one is working under enough repetitive conditions from the point of view of the results, it is important to work always above the minimum representative size. To ensure that the results of the simulation are not determined by the size of the simulated system, one should work with what has been called the representative volume element [32]. To evaluate this feature, we tested the porosity, as this parameter is very easy and quick to calculate, and it presents a rapid convergence as the system size increases [33]. It was confirmed that, for models with a size above 8D, the values were within the statistical error. Therefore we always worked with systems larger than 8D.

2.2. Previous structural models

The starting point for this algorithm is the previous structural model for gels proposed by Rodríguez-Ortega and Esquivias [26,34]. These authors developed an algorithm for randomly-packed spheres and they characterise systems by geometrical considerations. The main advantage of this algorithm is that it always works with reduced units, so results are independent of particle-size. The most important objective is to obtain the pore size distribution. Each system yields a unique PSD, so this curve can be used to match real systems to their corresponding structural models.

2.3. Texture

The specific surface and volume, the porosity and the apparent density can be calculated by various simulation techniques or through geometrical considerations, as has been explained in a previous study [7]. This set of parameters is the main indicator used to match a cluster model to a real system. Thus, we built several cluster models varying the formative parameters in order to reproduce real values of texture, PSD, etc. We have applied the improved version of the pore volume calculation proposed by Gavalda [35] who explained that this value was being systematically underestimated. We took several real systems and built their respective cluster models, characterizing them through the usual simulation techniques previously cited. Most of the parameters are purely geometric, but others, like apparent density, needed the value of the skeleton density. We preferred to use the calculated value of the skeleton density of aerogels of 2.09 g/cm^3 [36] rather than the more usual value of 2.2 g/cm^3, from bulk silica, used in other simulations.

2.4. Pore size distribution

There are several possible methods for obtaining the PSD of any structural model built from elementary spheres. It is generally accepted that a pore can be understood as a spherical set of points, so the PSD is usually constructed by considering for each point of the pore space, the radius of the biggest sphere that can be placed in the pore volume, centred on the given point and without overlapping the solid phase [25].

An advance on this method was made by Gavalda and Gelb, who calculate the PSD by the technique known as MC integration [21,37]. For any given point in the pore space, they looked for the largest sphere that can be placed in that space without overlapping the solid phase, but now not restricted to being centred on the given point, merely containing that point. In this way, more irregularities and details of the pore shape are taken into consideration for the measurement, so pore space is more fully described.

Rodriguez-Ortega (RO) worked with another concept for obtaining the PSD, based on previous works by Finney and Wallace [38]. For each set of four elementary spheres in mutual contact, not necessarily tangentially, the largest sphere that the pore space between them can contain is obtained. Again, the pore shape description is improved when spheres are used as the basic tool.

In the triangulation method (TR) of Primera [16] no previous assumption is made in respect of the pore shape. This is a new technique that allows the pore size distribution to

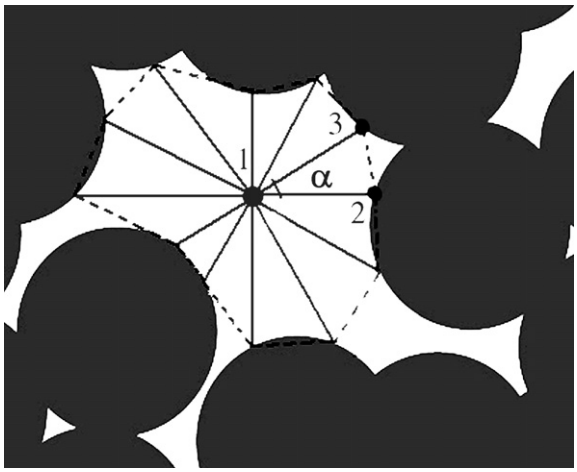

Fig. 2. Schematic illustration of the two-dimensional triangulation method applied to the pore space. Points 1, 2 and 3 correspond to the three vertices of one of the triangles.

be measured by means of a triangulation of the pore space. In this method numerous 2D cross-sections of the pore space are studied. For each cross-section, TR method is applied to the porous 'space'. A schematic illustration of this method is shown in Fig. 2. First, a large number of points are randomly located in the pore space and then the TR procedure is applied at each point.

This method of describing the pore space gives a more realistic result as it does not require any previous assumption of the shape of the pore, but considers all possible different shapes, not only the spherical.

3. Results

3.1. Emulating real systems

We have built several cluster models that represent the microstructure of various real systems. Initially, the aim of these models was to emulate the structure of the porous silica aerogels, but in fact, they can be used to emulate a variety of disordered particulate materials which could be described as randomly-packed spheres. Table 1 gives the characterization parameters of some real systems and their corresponding models. Systems #1 and #2 correspond to two different silica aerogels prepared from TEOS, and were characterized by the analysis of the N_2 adsorption/desorption isotherms [39]. System #3 corresponds to the porous TiO_2 usually used in solar cells. The object of this part of the work was to construct models corresponding as accurately as possible to the real systems. A very good correspondence can be seen between the real systems and their cluster models. Taking the experimental structural parameters, the models presented reproduce the textural values of the real systems.

As mentioned in the introduction, we have made use of our models to study mesoporous TiO_2 systems films for photovoltaic applications in dye sensitised solar cells.

Table 1
Structural parameters of several real systems and the geometric and structural parameters of their corresponding counterpart cluster models

System 1 *(pure silica aerogel)* Apparent density: 0.83 g/cm^3 Specific surface: 387–407 m^2/g Specific porous volume: 0.73–0.74 cm^3/g	*Model 1* Apparent density: 0.80 g/cm^3 Specific surface: 384 m^2/g Specific porous volume: 0.72 cm^3/g
System 2 *(pure silica aerogel)* Elemental sphere radius: 1.2 nm First aggregate radius: 4.5 nm Specific surface: 640 m^2/g	*Model 2* Elemental sphere radius: 1.1 nm First aggregate radius: 4.5 nm Specific surface: 612 m^2/g
System 3 (mesoporous TiO_2) Radius: 5–25 nm Apparent density: 1 g/cm^3 Specific surface: 20 m^2/g	*Model 3* (a) Radius: 15 nm Apparent density: 0.93 g/cm^3 Specific surface: 46 m^2/g (b) Radius: 20 nm Apparent density: 1.09 g/cm^3 Specific surface: 32 m^2/g

These films have apparent densities of around 1 g/cm^3 and porosities of around 50% [40]. Taking into account that usually the active surface in a solar cell is 1000 times the external surface of the cell, for a typical cell of around 1 cm^2 area and 50 μm thickness, a specific surface of 20 m^2/g is obtained.

A sketch of a cluster model can be seen in Fig. 3 rendered using the free software *POVRay* [41]. The system illustrated corresponds to the simulation box cropped from model #2, and has around 3000 particles.

3.2. Pore size distribution

In order to ensure the consistency required between the RO [26] and cluster models, we performed some simple simulated experiments, obtaining the PSD by the MC

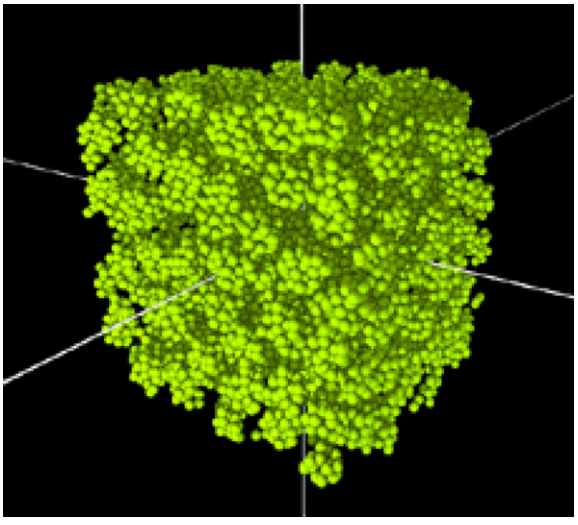

Fig. 3. Sketch of a cluster model, corresponding to the simulation box cropped from Model #2 of Table 1.

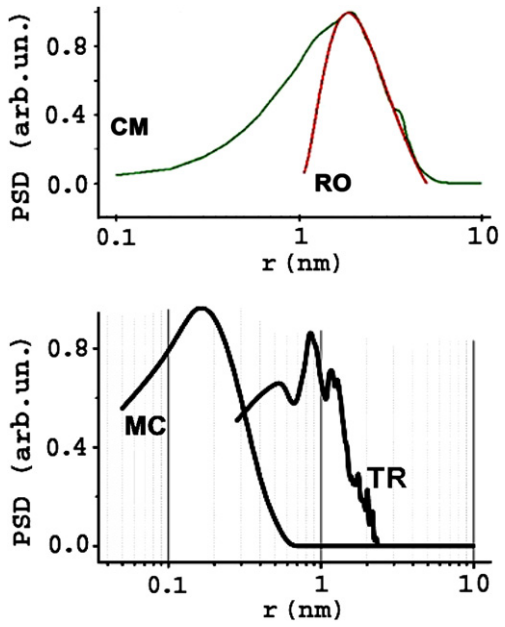

Fig. 4. Upper: pore size distributions (PSD) of a cluster model (CM) and the corresponding fitted model of Rodríguez-Ortega (RO). The CM curve was averaged over at least five replicas. Lower: comparison of the PSD of a system constructed by the cluster model algorithm, calculated using two different techniques: the Monte Carlo (MC) Integration and the triangulation method (TR).

Integration of a cluster model as if it were a real system, and using it to look for the matching RO model. Then, the parameters of the two models were compared. The resulting curves and the geometrical parameters are shown in Fig. 4, Upper and Table 2, respectively.

With regard to the different techniques for calculating the Pore Size Distribution, we have compared the resulting curves obtained by two different methods: the widely used MC Integration, and the TR method. For a given cluster model, we applied the two methods to obtain the two PSD curves, which are shown in Fig. 4, Lower. The TR curve was taken from 25 2D cross-sections of the system. Both curves were obtained by averaging over at least 5 replicas.

Results show that the curve obtained by TR presents more noise, whereas MC gives a smoother PSD. Moreover, TR yields larger pore sizes and a size distribution centred on around 0.8D. It also indicates the presence of pores of around 0.5D and 1.1D, whereas MC gives just one typical size for the pore space of around 0.16D.

Table 2
Textural parameters of both models: the cluster model and the model of Rodríguez-Ortega

Cluster model	Model of Rodriguez–Ortega
Apparent density: 1.11 ± 0.06 g/cm^3	Apparent density: 1.06 g/cm^3
Porosity: $54 \pm 3\%$	Porosity: 52%
Specific porous volume: 0.49 ± 0.06 cm^3/g	Specific porous volume: 0.48 cm^3/g

4. Discussion

4.1. Emulating real systems

Geometrical parameters of selected models reproduce quite well those values reported from experimental measurements. There is a good agreement on the particle size of 1.1 nm for elementary particles reported in the literature [36,39] and that obtained through modelling. The apparent densities and specific surface data obtained for TiO_2 are close to the values determined experimentally for this type of system. In fact, roughness factors (ratio of the surface to the volume) ranging between 57 and 149 μm^{-1} are found by gas sorption experiments [30]. Our predictions are 43 and 35 μm^{-1} for the models of 15 and 20 nm particle radius, respectively. Furthermore, the theoretical results predict a decrease of the roughness factor with the size of the particle, in complete agreement with the experimental findings [30].

4.2. Pore size distribution

Regarding the consistence between the cluster models and their predecessors, the RO models, good agreement can be found between the two sets of textural parameters (Table 2), those of the 'real' system obtained from the cluster model via MC and those from the fitted RO model. The corresponding RO model was found by fitting the peak and the shape of the curve (Fig. 4, upper). As each RO model describes just one hierarchical level, the absence of fit on the left side of the PSD, regarded as the microporosity, reveals the existence of two hierarchical levels. The selected model satisfactorily describes the mesoporous structure (~2 nm pore radii), so in order to make a complete description of the PSD, another RO model should be considered for describing the microporous structure. Therefore, on the one hand, this result is consistent with the real structure, thus supporting the consistence between the two models, but on the other hand, this fact implies that reported RO textural values are relatively underestimated.

Considering the comparison between MC and the TR curves of the PSD obtained from the same cluster model (Fig. 4, lower), it can be seen that TR finds larger pores than MC. The lack of constraints of the TR method enables it to give a more realistic description of the pore space. Fig. 5 illustrates diagrammatically a 2D pore between 4 spheres. In the pore *space* (white) several test points have been positioned in the form of a grid. It can be clearly seen that all the 13 test points belong to the same connected pore space. However, a technique that considers the pore as the largest test sphere that can be centred on a test point without overlapping the solid phase will yield 4 different pore sizes. If movements of the centre of the growing test sphere are allowed as in MC Integration, we will obtain a bimodal PSD, one size corresponding to the radius of the circle containing, for example, point 2 in the diagram, and the other size corresponding to the radius

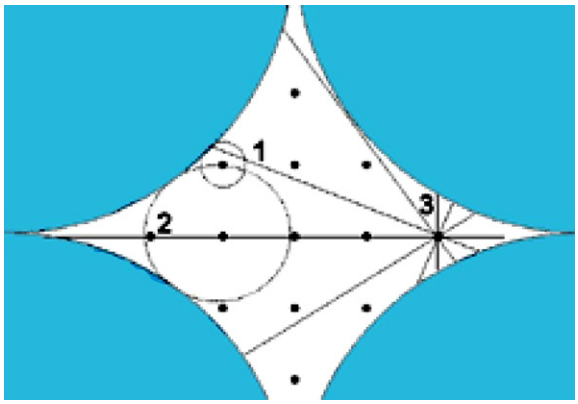

Fig. 5. 2D diagram of a grid in the pore space between 4 spheres.

of the maximum circle tangential to the four circles representing the solid phase, which contains the remaining 9 points. In contrast, the RO and TR methods will yield a monomodal PSD for this connected pore space. RO will find the same four spheres in mutual contact, and thereby the largest sphere that the pore space between them can contain for all the 13 points will be the same, and with TR, because even the most 'interstitial' points like #3 in Fig. 5 almost 'sees' the whole pore space, the 13 points will also yield the same pore radius.

5. Conclusions

The new algorithm that has been introduced is a very useful tool for modelling the microstructure of random materials. The parameters of these models can be easily tuned to match the values of a variety of porous systems, as it has a very versatile geometrical construction. Cluster models have been used to model very different porous systems, to give an interesting illustration of the microstructure.

The models provide a straightforward and precise computation of the internal surface of titania mesoporous films, a parameter of great importance in the performance of dye sensitised solar cells.

These new models are consistent with their predecessors, as can be deduced from the comparative study performed. Different models, giving a similar texture, have the same pore size distribution curve.

Several techniques for obtaining the pore size distribution have been compared and the different concepts of what constitutes a pore are also discussed. The triangulation algorithm yields a more realistic pore space description, especially in comparison with the Monte Carlo integration technique. Hence the consideration of the pore as a sphere may not be adequate for describing the real pore space.

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