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The Cluster Model: A Simulation of the Aerogel Structure as a Hierarchically-Ordered Arrangement of Randomly Packed Spheres

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Abstract. A new structural model based on the premises widely used for describing the structure of aerogels has been introduced. These structures have been described as an assemblage of randomly-packed spheres in several hierarchically-ordered levels. A new algorithm has been developed for constructing our models from these premises using computer simulation. Subsequently, several applications have been simulated to characterize real systems, obtaining textural parameters such as the specific surface area, specific porous volume or the apparent density of the systems, based on the Monte Carlo technique and on geometrical considerations. The object of these is to test the ability of the models to explain the structure of some real aerogels. This Cluster Model has also been applied as an initial approach to the study of the mechanical properties of aerogels. Results support the general conclusion that these models are useful for explaining the structure of aerogels.

Keywords: aerogel, structural model, Cluster Model, mechanical properties, hierarchycal order, random packed spheres, Monte Carlo simulation

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], to avoid cracking. Using these methods silica aerogels are obtained; these are more porous materials than the conventionally-dried gels, also known as xerogels. The particular structure of these aerogels is responsible for their most interesting properties, such as low thermal conductivity or very high specific surface area, which can reach values exceeding 1000 m^2/g. Incidentally, an aerogel is currently considered the solid material with the lowest density ever synthesized [3], with a value of 1.9 mg/cm^3. Sonogels are obtained by exposing a mixture of alkoxide and water to intense ultrasound [4–6]. This method does not require adding a common solvent to achieve the homogeneous mixing of the alkoxide-water system. The density of these gels is higher and

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their structure is finer and more homogeneous than those of standard gels. This is because of the absence of a solvent to obtain the sol and, mainly, the initial cross-linked state of reticulation induced by ultrasound. Time required for gelation is measured in tens of second. Another special characteristic of these gels after drying (sono-aerogels) is that they have a particulate structure, in contrast to gels obtained by hydrolysis and polycondensation of metallorganic compounds under acid catalyst without the application of ultrasound. Sonogels have a very narrow pore size distribution, very high bulk density and their surface/volume ratio is two or three times higher than gels prepared in alcohol solutions. These gels do not fulfill the self-similarity condition for at least one order of magnitude [7].

The structure of the aerogels has been described as an assemblage of randomly-packed spherical particles in several hierarchically-ordered levels [8, 9]. Knowledge of the structure of aerogel has been acquired using computer simulation techniques that take inputs from several topics, like the understanding of the sol-gel process, the process of structure formation, and the relationship between the structure and the mechanical properties. The process of structure formation has been studied using the Molecular Dynamics Technique [10]. Since Garofalini first applied it to the sol-gel process in 1994 [11] using the Feuston-Garofalini potential [12], it has been concluded that the structure formation starts with a slow process while the clusters are growing, followed by the faster growth rate as the structure is formed by cluster-cluster aggregation. Hasmy has studied in greater depth the behaviour of the characteristic cluster size and the influence of the simulation box size [13]. Other authors like Gelb and Gubbins have mainly directed their research towards developing characterization applications based on the Monte Carlo technique for the porous structures generated by simulation [14]. They have worked with the Lennard-Jones potential for each element, and the Lorenz-Berthelot rules for mixing the inter-element potential.

Another topic of interest concerns reproducing the formation and growth processes of the aerogels by computer, using reaction- or diffusion-limited cluster aggregation (RLCA or DLCA) algorithms, or some modification of these [15], or the ballistic cluster-cluster aggregation [16]. Simulation techniques have even been used to test the validity of the BET [17] or the BJH [14] methods for analysing the adsorption/desorption isotherms.

Working on the relationship between structure and mechanical properties, Scherer et al. [18] have used structures generated with DLCA-modified algorithms, characterizing them by their fractal dimension, to achieve the power law exponent, and they have presented models to explain the structure-properties relationship [19, 20]. Like Woignier *et al.*, they have worked with DLCA-generated structures [21], introducing a new technique for characterizing this porous systems [22]. They conclude that the pore size distribution and the hydroxyl content are relevant for describing and understanding the mechanical properties of these materials [23]. In a previous study, Woignier and Phalippou proposed an approach starting from a cubic structural model [24] and using the Rumpf expression for the tensile strength of a rigid assembly of cohesive spheres [25]. Emmerlig and Fricke also studied the question of properties, in particular elasticity and thermal conductivity, through the scaling properties obtained by their simulated aerogel structures [15].

In this study we are proposing a new algorithm based on the premise of randomly-packed spheres in several hierarchically-ordered levels for building the Cluster Model, together with an approach to determining the mechanical properties of these materials based on these models. The aim of this technique is to build structural models of real systems. Its best performance feature 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 systems. The main structural parameters in this model are the elementary particle radius, the number of hierarchical levels and the contact distance and shells of each level. The density is merely a reference for estimating the number of levels in the hierarchy, since the density is strongly dependent of this parameter. However, systems made by this procedure are not intended to describe the growth process of real systems: they belong to what have been called static models [26] in the sense that these models describe the final state of the real systems, and provide a new tool for studying the structure.

2. Cluster Structural Model

From the premise that the aerogel structure can be described as an assemblage of randomly-packed spheres in several hierarchically-ordered levels, we developed an algorithm for building structural models. We have made use of an AMD Athlon 1700 (1.46 GHz) processor that required only a few seconds to construct such systems. In the course of this work, the particle diameter has been used as a reduced unit to describe the models.

We discounted the use of cubic simulation boxes for constructing these models, in spite of this being the most recommended technique, and instead constructed a spherical system. This is because, when we make the assumption of self-similarity in several hierarchically-ordered levels, the algorithm is easy to implement within a spherical symmetry, by simply substituting each sphere of the system for a spherical assembly of spheres. However, cubic simulation boxes have been used for those characterizing applications that are boundary-dependent and finite size-dependent, in order to permit periodic boundary conditions be applied. To obtain a cubic box for characterizing the system, we just cropped our spherical system to the largest size of internal cubic box it would accommodate.

2.1. *Algorithm*

The Cluster Model algorithm works as follows: first we place one *elementary* sphere of diameter 1 in the centre of our system. Then we place randomly other elementary spheres in contact with the first one's surface to construct the first random shell. Any sphere has to satisfy only one condition to be placed: it has to be in contact with at least one other sphere. The criterion of being in contact is understood as to be at a distance within the minimum and maximum contact distances previously defined, thus avoiding the existence of free-floating spheres. Within these limits, the actual distance between any two spheres within the contact range is chosen randomly. We let the system grow as many shells or layers of randomly-placed spheres as we consider necessary for constructing our desired model. Once this process is finished, this aggregate is taken as the *basic aggregate*. Its size is measured and another aggregate is built with *secondary* spheres of diameter equal to the diameter of the basic aggregate. After building this new aggregate, each secondary sphere is replaced by one basic aggregate obtaining a two-level hierarchically-ordered assemblage of randomly-packed spheres. Then, the system size is measured again and its size is taken as the diameter of one *tertiary* sphere. An aggregate of *tertiary* spheres is built then and, finally, each *tertiary* sphere is replaced by one two-level system, thus obtaining a three-level hierarchically-ordered system (Fig. 1). This process can be repeated as many times as required. Typical values of our models are 60.000 particles organised in 2 shells of randomly-packed spheres and three hierarchical levels; their contact distances, d, are set within the interval $(0.9D < d < 1.0D)$, D being the particle diameter (Fig. 2).

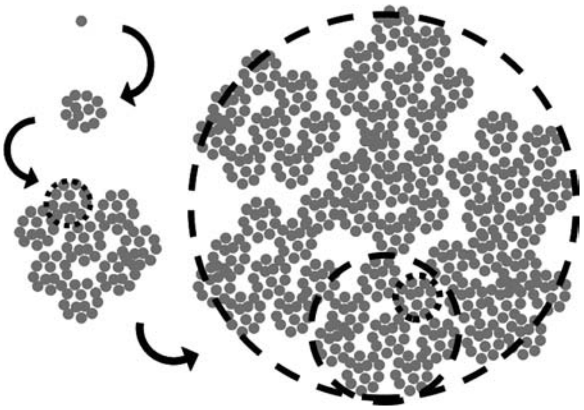


Figure 1. Diagram of Cluster Model algorithm.

Although self-similarity is potentially present in the Cluster Model as a consequence of the algorithm used to generate them, in the present case we have not adopted a fractal description because the structure of sonogels is not self-similar to one order of magnitude. In the future we will emulate the fractal structure of those aerogels that do present a well-defined fractal dimension.

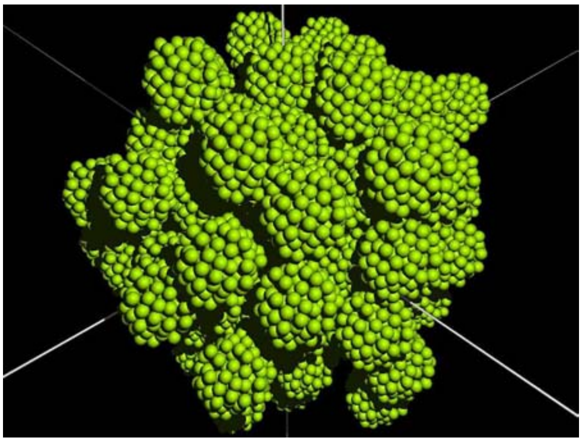
2.2. *Characterization Techniques*

Several applications for characterizing the models have been developed to calculate textural parameters of the simulated structures. The comparison of the calculated values with their actual counterparts checks the validity of the models. In this work we try to construct cluster models with the same structural parameters as selected real aerogels. We take a real system as a target and we fine-tune the geometric parameters as the algorithm is being constructed in order to obtain a model corresponding to the target, that is, the model with exactly the same texture as the real system.

In this paper we present results from this strategy applied to real systems used in previous studies.

The parameters that we have tried to reproduce are:

Density: our system is considered to be formed by an assemblage of pure silica spheres of density 2.2 g/cm^3, so given the number of spheres, the specific mass of the



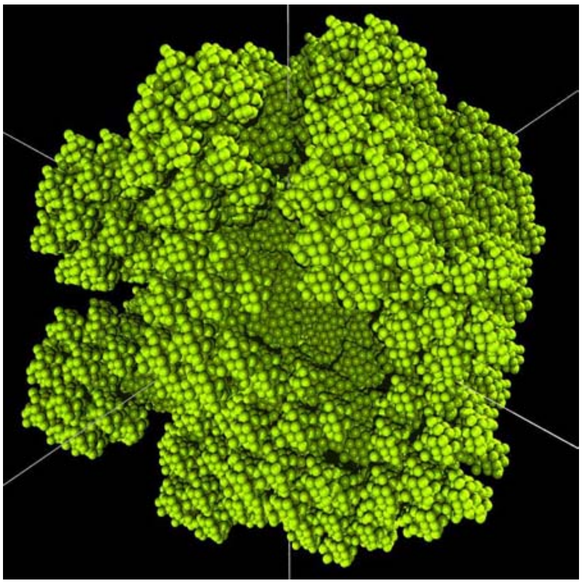


Figure 2. Two examples of Cluster Models with 3 shells of randomly-packed spheres and 2 hierarchical levels (up), and with 2 shells of randomly-packed spheres and three hierarchical levels (down).

system is known. In some identified cases, when we are trying to emulate a system comprising elemental particles described as having a certain density [24, 27] we take the density of our elemental spheres to be this particular value (2.09, 1.85 g/cm^3) instead of the recorded density for the bulk silica. This difference may be due to longer Si-O bond distances [28] or to the failure to detect some kind of microporosity by the characterization method used. On the other hand, we consider the volume overlapped between spheres as counted twice in the mass calculation (volume shared by three spheres is negligible). Consequently we subtract the overlapped mass corresponding to one of the two spheres.

Specific Surface Area: the theory describes the real physisorption experiment starting with the formation of a nitrogen monolayer on the surface of the system to be characterized. This monolayer does not cover the whole external surface of the material, but only the parts of the surface accessible to the nitrogen. Taking this into account, among the different definitions of surface area [17], the one calculated in this study is called the accessible surface area. We considered a spherical model of the nitrogen molecule of 16.2 Å^2 of cross section that gives a radius of 0.227 nm, and we defined the reduced radius of the elemental silica sphere by reference to this. Then, we obtained by Monte Carlo method the external surface accessible to the nitrogen molecule in our system. This method is widely used [14, 17, 29, 30] for characterizing structural models for porous materials.

Specific Porous Volume and Porosity: we calculated by Monte Carlo method the volume accessible to a nitrogen sphere inside our system. On this point we had to consider the finite volume correction presented by Sandra Gavalda [31]: The volume obtained by this technique is lower than the expected accessible volume due to the omission of the volume between the centre of the nitrogen spheres and the surface of our system. To fix this, Sandra Gavalda proposed adding the volume calculated conventionally by Monte Carlo to the volume resulting from multiplying the specific surface by the nitrogen sphere radius. Porosity is obtained automatically along with this parameter, by reducing the values and expressing them as the percentage not occupied by the system.

Apparent Density: Since our system is defined in several hierarchical levels, we know the number of spheres involved in building any of the levels and the volume occupied by those spheres that comprise it. Consequently, we obtain the density at the different levels, from the lowest—the elementary particle—to the highest, also called the apparent density.

3. Results and Discussion

We applied this simulation technique for the construction of several systems to explain the structure of various real systems. As an initial application, we took from a previous study [27] the texture parameters of two aerogels and constructed their corresponding hierarchical models. As a second application, we tried to determine the relationship between the structure and mechanical properties, similar to the study done by Woignier [24].

3.1. *Simulation of structures*

In [27] the items studied were two aerogels prepared from TEOS. Different cluster models were generated to describe the structures of those aerogels. Both sets of data are shown in Table 1. The models corresponding to the first aerogel presented an arrangement of three hierarchical levels of packing spheres. The elementary particles of this system were described in the original work as spheres of radius of 1.1 nm with a density of 2.09 g/cm^3. We took these values to define our system, so the resulting models were based on the real data.

The goal of this part of the work was to construct models corresponding accurately to the real system, starting from the experimental structural parameters. The presented models reproduce the textural values of the real systems, as was expected. We can see how models built as an assemblage of randomly packed spheres of hierarchically arranged levels can reproduce quite well the texture of the real aerogels. Parameters of the resulting models are also shown in Table 1.

Table 1. Structural parameters of the real aerogels and of their corresponding Cluster Model.

Real system	Models
System 1	
Apparent density: 0.83 g/cm^3	Apparent density (g/cm^3)
Specific surface: 387–407 m^2/g	Specific surface (m^2/g)
Specific porous volume:	Porous volume (cm^3/g)
0.73–0.74 cm^3/g	Model A
	0.80
	384
	0.72
	Model B
	0.81
	376
	0.88
System 2	
Elemental sphere radius: 1.2 nm	Aggregate radius (nm)
First aggregate radius: 4.5 nm	Specific surface (m^2/g)
Specific surface: 640 m^2/g	Model C
	4.5
	612
	Model D
	4.4
	669

3.2. *Mechanical Properties*

In [24], a simple structural model was applied to explain the mechanical properties of these materials. A study of the relationship between the normalized strength and the porosity was presented.

The normalized strength of aerogels from TMOS as silica precursor was obtained by three-point flexural tests and diametral compression tests (also known as "Brazilian test", ASTM #D3967 [32]). To explain the behaviour of this parameter and its dependence on the porosity, Woignier and Phalippou used a structural model of cubic cells in which the edges are formed by spherical silica beads. The cohesion of the systems is explained as a function of the overlapping volume between neighbouring spheres, taking into account the expression of Rumpf for the tensile strength of a rigid assembly of cohesive spheres of radius R [25]:

$$\sigma = \frac{9\phi K F}{32\pi R^2} \tag{1}$$

where ϕ is the volume fraction of the solid, related to the porosity P as $(1 - P)$, and K is the mean coordination number. The factor F, given by Eq. (2), is the bonding force between two overlapped spheres of dense silica with an overlapping neck radius a:

$$F = \sigma_0 \pi a^2 \tag{2}$$

where σ_0 is the mechanical strength of dense silica glass. Thus, the tensile strength is normalized as follows:

$$\frac{\sigma}{\sigma_0} = \frac{9}{32}(1 - P)K\left(\frac{a}{R}\right)^2 \tag{3}$$

Figure 3 represents the results for the experimental values of the reduced modulus, based on the structural models applied in [24], together with those resulting from applying our Cluster Model. As can be seen, in spite of the simplicity of the model, Woignier *et al.* successfully describe qualitatively the behaviour of the normalized strength of the aerogels.

With the aim of improving on this result in quantitative terms, we modified the final expression of the normalized strength of the aerogels (Eq. (3)). In this equation, it is shown that this parameter is directly proportional to the relative area of the maximum circle

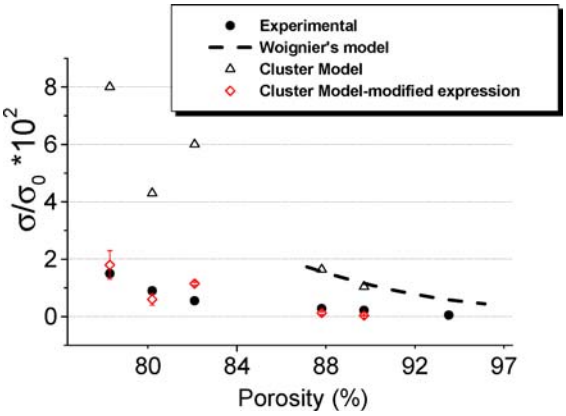


Figure 3. Comparative results of the normalized strength from experimental tests, Woignier's theoretical model, Cluster Model with the original Rumpf's expression and the modified expression. Values and their error bars in Cluster Model data are the result of the average of at least 5 repeats of the same system.

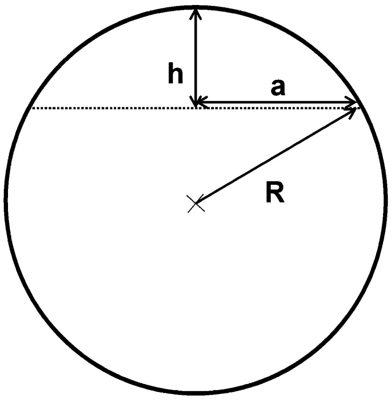


Figure 4. Two-dimensional diagram of the spherical cap, with height h, and the base radius or overlapping neck radius a, and sphere radius R.

of the overlapped zone, i.e., $\sigma/\sigma_0 \propto (a/R)^2$. But instead of this, we assume that the normalized strength should be shared in a volume-dependent way. From the expression of a spherical cap (Fig. 4),

$$V(h) = \pi R h^2 - \frac{\pi h^3}{3} \tag{4}$$

the reduced volume shared by two overlapped spheres φ, at a distance d, can be calculated by

$$\varphi = \frac{\frac{R}{4}(2R-d)^2 - \frac{1}{24}(2R-d)^3}{\frac{4}{3}R^3} \tag{5}$$

Table 2. Structural parameters of the Woignier's aerogels (left) and of their corresponding Cluster Model. Errors in results of models reflect the standard error from at least 10 iterations.

Experimental			Models		
Porosity (%)	Specific surface (m^2/g)	Density (g/cm^3)	Porosity (%)	Specific surface (m^2/g)	Density (g/cm^3)
78	450	0.41	77 ± 1	459 ± 5	0.41 ± 0.02
80	400	0.36	81 ± 3	404 ± 2	0.36 ± 0.02
82	250	0.33	83 ± 2	253 ± 9	0.34 ± 0.02
88	350	0.23	88 ± 2	340 ± 3	0.20 ± 0.01
90	300	0.19	90 ± 5	307 ± 4	0.19 ± 0.02

which gives, in reduced units, the final expression for the introduced parameter φ

$$\varphi = \frac{3}{4}(1-d)^2 - \frac{1}{4}(1-d)^3 \tag{6}$$

In our approach, the factor $(a/R)^2$ has been substituted by this new factor accounting for the relative overlapped volume in the whole system φ.

$$\frac{\sigma}{\sigma_0} = \frac{9}{32}(1-P)K\varphi \tag{7}$$

and this expression has been used to explain the mechanical behaviour when working with the Cluster Model. Structural cluster models have been developed corresponding to the samples studied, and the modified expression similar to that used in [24] (Fig. 3) has been applied. It should be noted that this assumption was only considered in order to find an expression that improves on Woignier's results that assumed the cohesive force between two overlapping spheres to be neck-area dependent (Eq. (2)), and we therefore replace this assumption in the final expression of the reduced force by that of shared-volume dependence.

The values obtained for the systems according to Woignier are shown in Table 2. The result for the last system (94% porosity) cannot be reproduced due to the size of the system needed. To obtain models with porosities greater than 90%, systems of several hundred thousand particles must be considered. Several months of computing time in our facilities would be required merely for the preliminary studies, and this could not be afforded at present to resolve this particular problem.

As can be seen in Fig. 3, when using the expression of Rumpf, the results from the Cluster Model and that of Woignier are quite similar, with both models describing qualitatively and in approximate terms the influence of the porosity on this normalized strength. However, the values deviate from the experimental data, and are considerably higher. To improve on this, the proposed modified expression has been tested using the Cluster Model. Results confirm the improvement of the model: not only is the behaviour of the strength described qualitatively but also quantitatively. The Cluster Model plus the modified expression gives very good values, close to the experimental data.

4. Conclusion

An algorithm for a new structural model for aerogels has been developed by describing the aerogels as an assembly of randomly-packed silica spheres arranged in several hierarchically-ordered levels. These new models have been named Cluster Model.

The Cluster Models generated reproduce satisfactorily both the structural and textural parameters of real systems. The performance of this approach can be improved by finely tuning the geometrical parameters of the algorithm as it is being constructed, and devoting more computing time to this work.

Regarding the application of these models for determining the relationship between structure and mechanical properties, the overlapped volume between neighbouring spheres is responsible for the bonding force and consequently for the cohesion of the system. An expression modified from that proposed in [24] was applied to the Cluster Model. Results describe perfectly the dependence of the strength on porosity, from a qualitative point of view. Quantitatively these models describe the actual behaviour better than previously published results. These results support the view that the Cluster Model can be considered a useful tool for explaining the structure of aerogels.

More characterization techniques of these models are needed for a more complete comparison with real systems, particularly in respect of pore size distribution curves and the pair correlation function, in order to simulate small-angle scattering experiments. Research work on these topics is in progress.

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