TITLE:

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 aerogels structure has been introduced. These structures have been described as an assembly of random-packed spheres in several hierarchically-ordered levels. A new algorithm for building our models by Computer simulation have been developed from these premises. Subsequently, some characterizing applications for obtaining the textural parameters as the specific surface, specific porous volume or the apparent density of the systems, based on the Monte Carlo technique and in geometrical considerations have been simulated for testing the ability of the models in explaining the structure of some real TMOS and TEOS aerogels. As a first approach to the study of the mechanical properties of the aerogels these models have been applied as well. Results support the idea that these models are a good way for explaining the structure of the aerogels.

I. 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

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conceived by S. Kistler [2] for avoiding cracking. This way we obtain the silica aerogels, more porous materials than the conventionally-dried gels, also known as xerogels. Its particular structure is responsible for the most interesting properties of the aerogels, such as low thermal conductivity or very high specific surface area what can reach values like 1000 m^2/g or more. By the way, nowadays an aerogel is the solid with the lowest density ever synthesized [3], with a value of 1.9 mg/cm^3. Sonogels are obtained exposing a mixture of alkoxide and water to intense ultrasound [4,5,6]. This method does not require adding a common solvent (generally, methyl or ethyl alcohol) to mix homogeneously the system alkoxide-water. These gels are dense and their structure is fine and homogeneous, because of the absence of solvent for the sol obtaining and, mainly, by the initial cross-linked state of reticulation induced by ultrasound. Gelation occurs in tenths of seconds. Other special characteristic of these gels after drying is that sonogels result in a particulate structure, contrary to gels obtained by hydrolysis of metallorganic compounds under acid catalyst without applying ultrasound. Sonogels have a very narrow pore size distribution, very high bulk density and surface/volume ratio, two or three times higher than gels prepared in alcohol solutions. These gels, do not fulfill the autosimilarity condition along one order of magnitude [7].

The structure of the aerogels has been described as an assembly of random-packed spherical particles in several hierarchically-ordered levels [8,9]. The knowledge about the aerogel structure has been approached using computer simulation techniques that take inputs from several topics, like the understanding of the sol-gel process, the structure formation process or the relationship between the structure and the mechanical properties. The structure formation process has been studied by Molecular Dynamics Technique [10] since Garofalini first applied it to the sol-gel process in 1994 [11] using the Feuston-Garofalini potential [12], concluding that the structure formation starts with a

slow growing process of the clusters, followed by the faster growing of the structure due to the cluster-cluster aggregation. A. Hasmy has gone deeper in this aspect studying the behaviour of the characteristic cluster size and the influence of the simulation box size [13]. Other authors as Gelb and Gubbins mainly have addressed their work to develop 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.

Other topic of interest consists of reproducing the formation and growing processes of the aerogels by computer, using the reaction or diffusion limited cluster aggregation (RLCA or DLCA) algorithms, or some modification of them [15], or the ballistic cluster-cluster aggregation [16]. Even simulation techniques have been used to test the validity of the BET [17] or the BJH [7] methods for analysing the adsorption/desorption isotherms.

Working in the structure-mechanical properties relationship, Scherer [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 some models to explain the structure-properties relationship [19,20]. As for Woignier et col., 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 work, Woignier and Phallipou proposed one 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 studied this problem, exactly elasticity and conductivity, through the scaling properties obtained by their simulated aerogel structures [8].

In this we are proposing a new algorithm based on the premise of random-packed spheres in several hierarchically-ordered levels for building the Cluster Models, together with an approach to the mechanical properties of these materials based on these models. The aim of this technique is to build structural models of the real systems. Its best performance is its versatility: tuning the geometric parameters of the model we can obtain very different assemblies of random-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 just a reference to estimate the number of hierarchic levels since the density is strongly dependent of this parameter. However, systems made by this procedure are not supposed to describe the growing process of real systems, but they belong to what has been called static models [26] in the sense that these models describe the final state of the real systems, providing a new tool for the structural studies.

II. CLUSTER STRUCTURAL MODEL

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

We discarded using cubic simulation boxes for building the models in spite of being the most recommended technique, but we built a spherical system. This is because the algorithm premise of self-similarity in several hierarchically-ordered levels is easy to implement within a spherical symmetry simply substituting each sphere of the system for a spherical assembly of spheres. Cubic simulation boxes do have been used for those

characterizing applications that are boundary-dependent and finite size-dependent to permit periodic boundary conditions be applied. To obtain a cubic box for characterizing the system, we just cropped the biggest cubic box inside our spherical system.

1. Algorithm

The Cluster model algorithm works this way: first we place one *elementary* sphere of diameter 1 in the centre of our system. Then we place randomly other elementary spheres coating the first one's surface so the first random shell is built. Any sphere has to satisfy one condition to be placed: it has to be in contact at least with another one. The criterion to be in contact is understood as to be at a distance between the minimum and maximum contact distances previously defined, thus avoiding the existence of free spheres. With this purpose, the distance within the contact range is chosen randomly. We let it grow as many shells of random placed spheres as we consider necessary for building our wished model. Once finished this process, 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 assembly of random-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, obtaining this way a three-level hierarchically-ordered system (Figure 1). This process can be repeated as many times as necessary. Typical values of our models are 60.000 particles organised in 2 shells of random-packed spheres and three hierarchical levels; their contact distances, d, are found in the interval ($0.9D < d < 1.0D$), D being the particle diameter (Figure 2).

Although autosimilarity is potentially present in the Cluster Models as a consequence of its generation algorithm, in the present case we have not gone in a fractal description because the structure of sonogels is not autosimilar along on order of magnitude. In the future we will emulate fractal structure of those aerogels that does present a fractal dimension well defined.

2. Characterization techniques

Some 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. Along this work we try to build Cluster models with the same structural parameters than the real aerogels. We take a real system as a target and we work tuning the geometric parameters in the building algorithm in order to obtain its corresponding model, that is, the model with the same texture than the real system.

In this work we present results from this strategy applied to real systems from previous works.

The parameters that we tried to reproduce are:

Density: we consider our system formed by an assembly of pure silica spheres of density 2.2 g/cm^3, so once known the number of spheres, it is known the system specific mass. In some identified cases, when we are trying to emulate a system whose elemental particles are described to have a determined density [20, 27] we consider the mass of our elemental sphere with this particular value (2.09 g/cm^3, 1.85 g/cm^3) instead of the registered density for the bulk silica. This difference may be caused by longer Si-O bond distances [28] or not having detected 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 once the overlapped mass.

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

Specific porous volume and porosity: we calculated by Monte Carlo the volume accessible to a nitrogen sphere inside our system. In 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. For fixing this, Sandra Gavalda proposed adding the volume calculated conventionally by Monte Carlo to the resulting volume from multiplying the specific surface by the nitrogen sphere radius. Porosity is obtained automatically next to this parameter, reducing the values and expressing them in 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 are forming it. Consequently, we obtain the density at the different

levels, from the lowest – the elementary particle – to the highest, also called apparent density.

III. RESULTS AND DISCUSSION

We applied this simulation technique to build several systems for explaining the structure of some real systems. As a first application, we took from a previous work [27] the texture parameters of two aerogels and we built their corresponding hierarchical models. As a second application, we face the problem between the structure and mechanical properties, similar to what has been done by Woignier [20].

1. Simulation of structures

In [24] the studied items were two aerogels prepared from TEOS. Different cluster models for describing those aerogels' structures were generated. Both sets of data are shown in Table 1. The models corresponding to the first aerogel was a three hierarchical level arrangement 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 considered these values for defining our system, so the resulting models were based on the real data.

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

2. Mechanical properties

In [24], a simple structural model was applied to explain the mechanical properties of these materials. A study about 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]). For explaining the behaviour of this parameter and its dependence with the porosity, they 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 neighbour spheres, taking into account the Rumpf's expression for the tensile strength of a rigid assembly of cohesive spheres of radius *R* [25]:

$$\sigma = \frac{9\phi KF}{32\pi R^2}$$

Equation 1

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

$$F = \sigma_0 \pi a^2$$

Equation 2

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

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

Equation 3

In Figure 3 are represented results of the experimental values of the reduced modulus based on the structural models applied in [24] besides those resulting from applying our Cluster models. As it can be seen, in spite of the simplicity of the model, Woignier et col. describe qualitatively the behaviour of the normalized strength of the aerogels.

With the aim of improve quantitatively this result, we modified the final expression of the normalized strength of the aerogels (**¡Error! No se encuentra el origen de la referencia.**). It shows that this parameter is directly proportional to the relative area of the maximum circle of the overlapped zone, i.e., $\sigma/\sigma_0 \propto (a/R)^2$. Instead of this, we have assumed that the normalized strength should be shared volume dependent. From the expression of a spherical cap (

Figure 4),

$$V(h) = \pi R h^2 - \pi h^3/3$$

Equation 4

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

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

Equation 5

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

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

Equation 6

Considering this way, the factor $(a/R)^2$ has been substituted by this new one that accounts for the relative overlapped volume in the whole system φ.

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

Equation 7

and this expression has been used for explaining the mechanical behaviour working with the Cluster Models. Structural Cluster models have been developed corresponding to the samples studied, and applied the modified expression similar to that used in [24] (Figure 3). This assumption was only considered in order to find an expression that improves the Woignier's results that took the cohesive force between two overlapping spheres as to be neck-area dependent (Equation 2). We consider replacing this assumption in the final expression of the reduced force by the assumption of shared-volume dependent.

The values obtained for the Woignier's systems are shown in Table 2. The result for the last system (94% porosity) cannot be reproduced due to the size of the needed system. For obtaining models with porosities greater than 90%, systems of several hundreds of thousands particles has to be considered. Several months of computing time in our

facilities should be employed only for the preliminary studies, so we could not afford this problem presently.

As it can be seen in Figure 3, when using Rumpf's expression the Cluster model and the Woignier's model results are quite alike, even both models describe roughly qualitatively the influence of the porosity in this normalized strength. However, their values are deviated above the experimental data. For improving this, the proposed modified expression has been tested using the Cluster models. Results confirm the improvement of the data: not only is the behaviour of the strength described qualitatively but also quantitatively. Cluster models plus modified expression give very good values, close to the experimental data.

IV. CONCLUSSION

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

The generated Cluster Models reproduce satisfactorily both structural and textural parameters of real systems. The performance of this approach can be improved finely tuning the geometrical parameters of the building algorithm and spending more computing time in this work.

Regarding the application of these models to relate structure and mechanical properties, the overlapped volume between neighbouring spheres is responsible of the bonding force and consequently of the system cohesion. A modified expression from that proposed [24] was applied to the Cluster Models. Results describe perfectly the dependence of the strength with porosity, from a qualitative point of view. Quantitatively these models

describe better the actual behaviour than previously published results. These results support the idea of considering the Cluster Models as a good tool to explain the aerogels structure.

More characterization techniques of these models are needed for a more completely comparison with the real systems, as the pore size distribution curves or the pair correlation function in order to simulate small-angle scattering experiments. Works in these topics are in progress.

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FIGURES

Figure 1: Cluster model algorithm diagram.

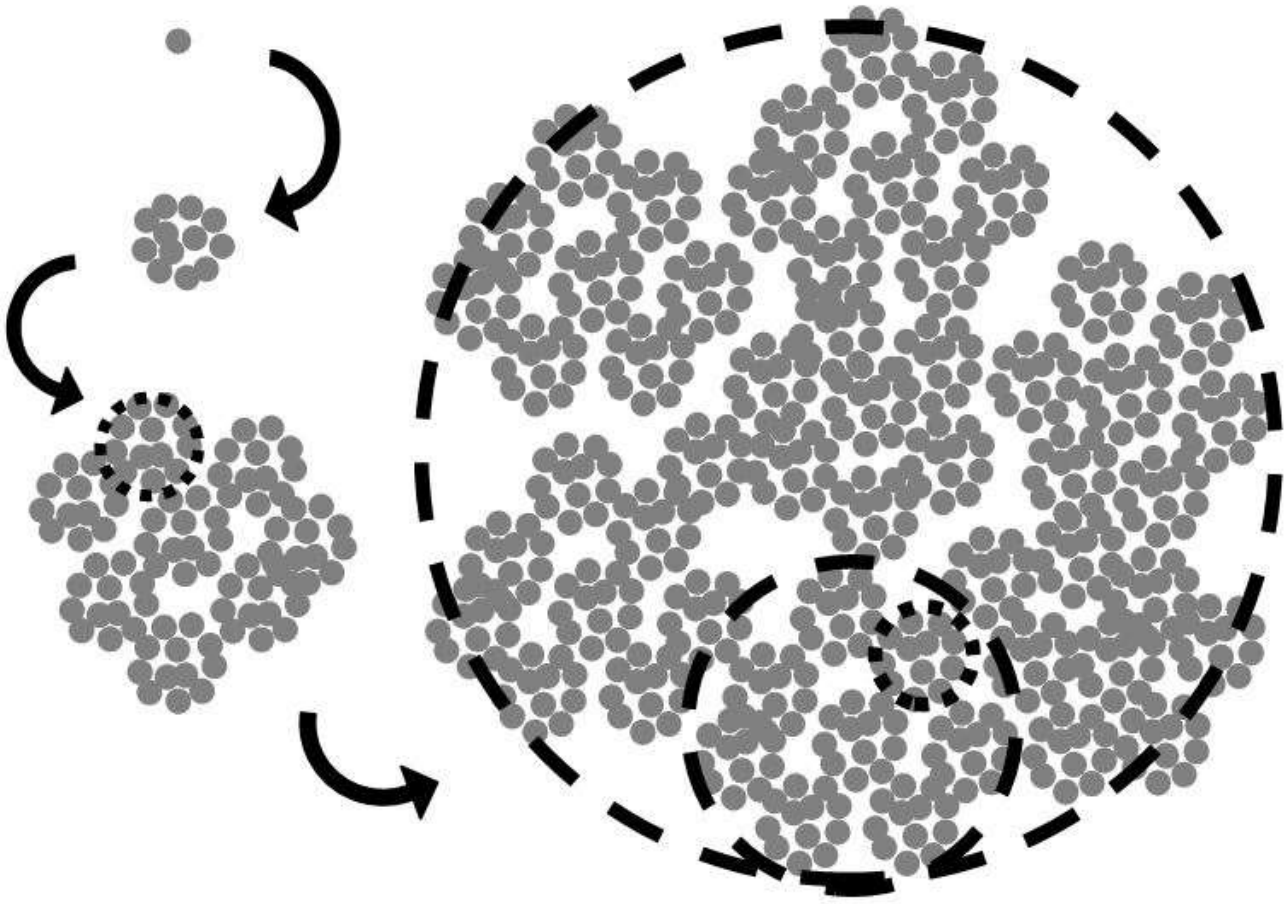
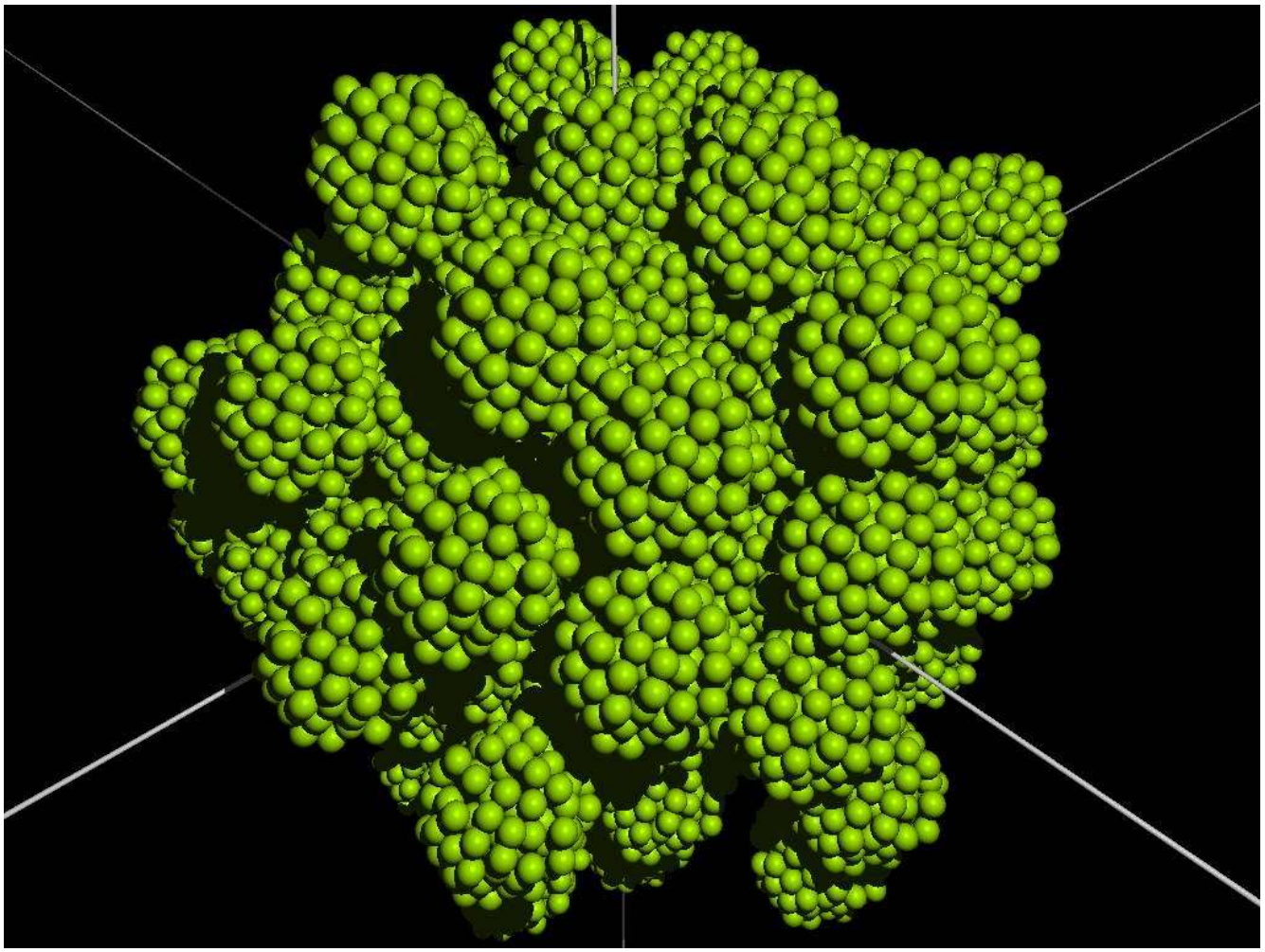


Figure 2**:** *Two examples of Cluster models with 3 shells of random-packed spheres and 2 hierarchical levels (left), and with 2 shells of random-packed spheres and three hierarchical levels (right).*



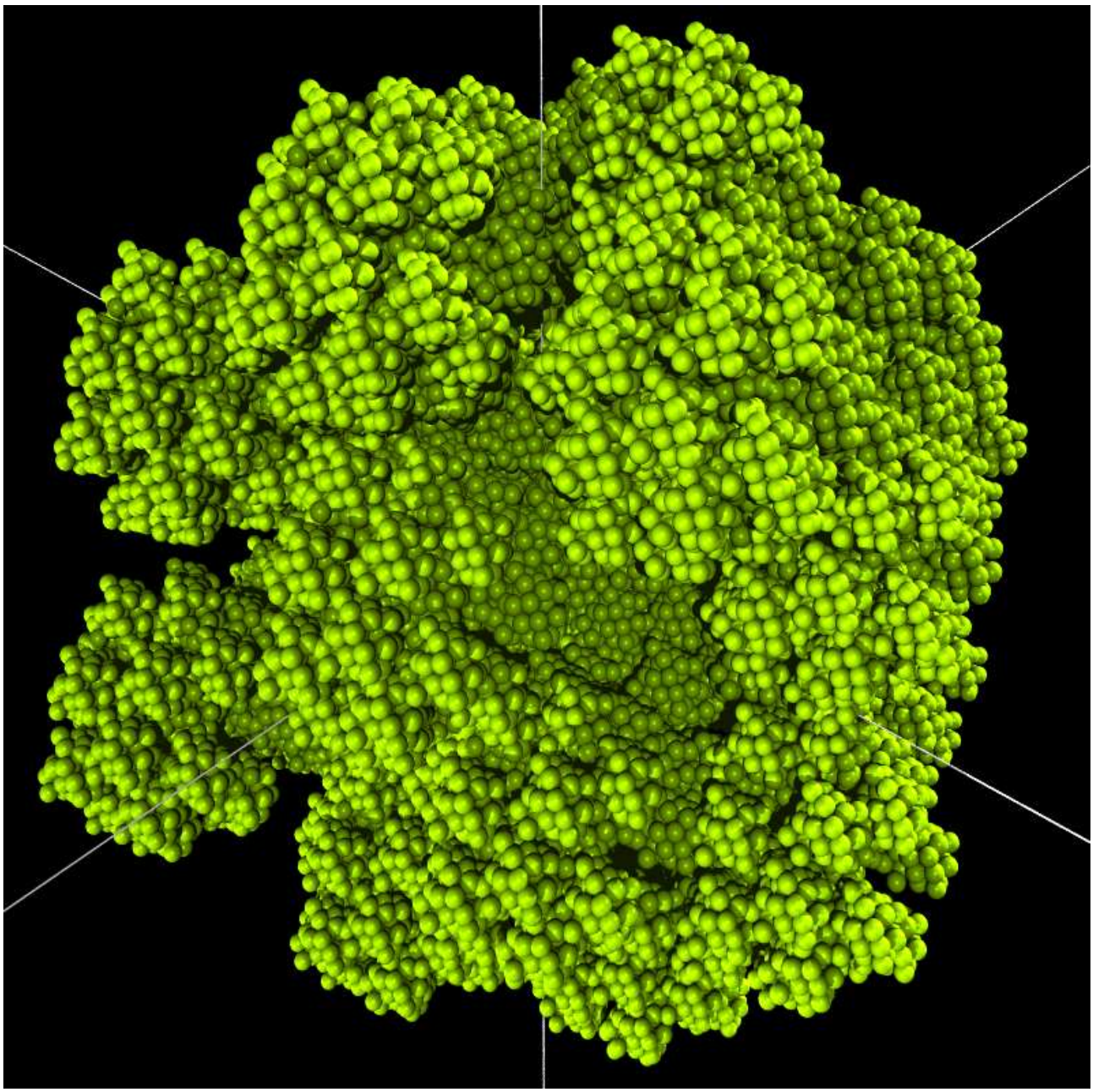


Figure 3: Comparative results of the normalized strength from experimental tests, Woignier's theoretical model, Cluster model with the original Rumpf's expression and the modified expression. Values and their error bars in Cluster model data are the result of the average of at least 5 repeats of the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

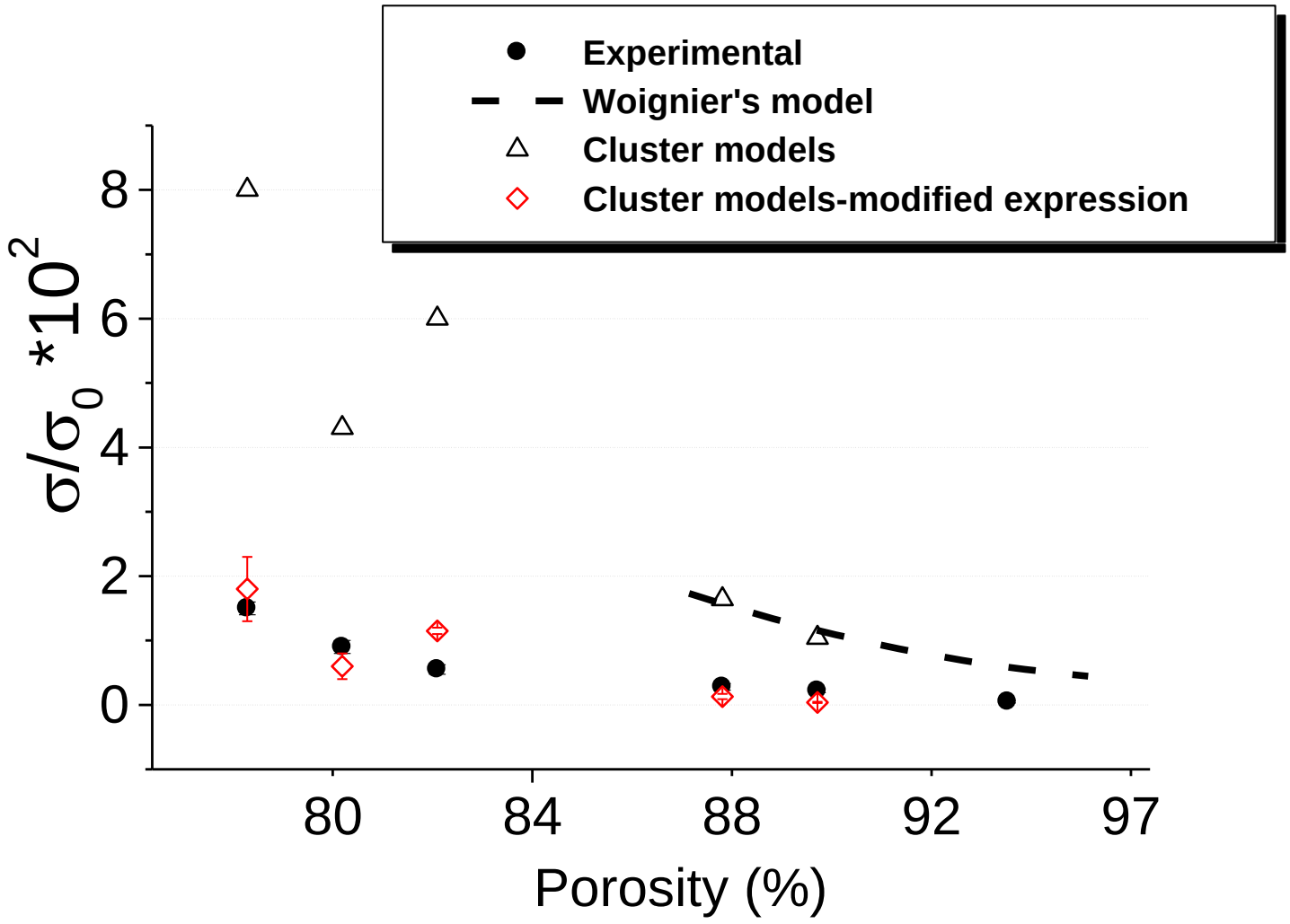
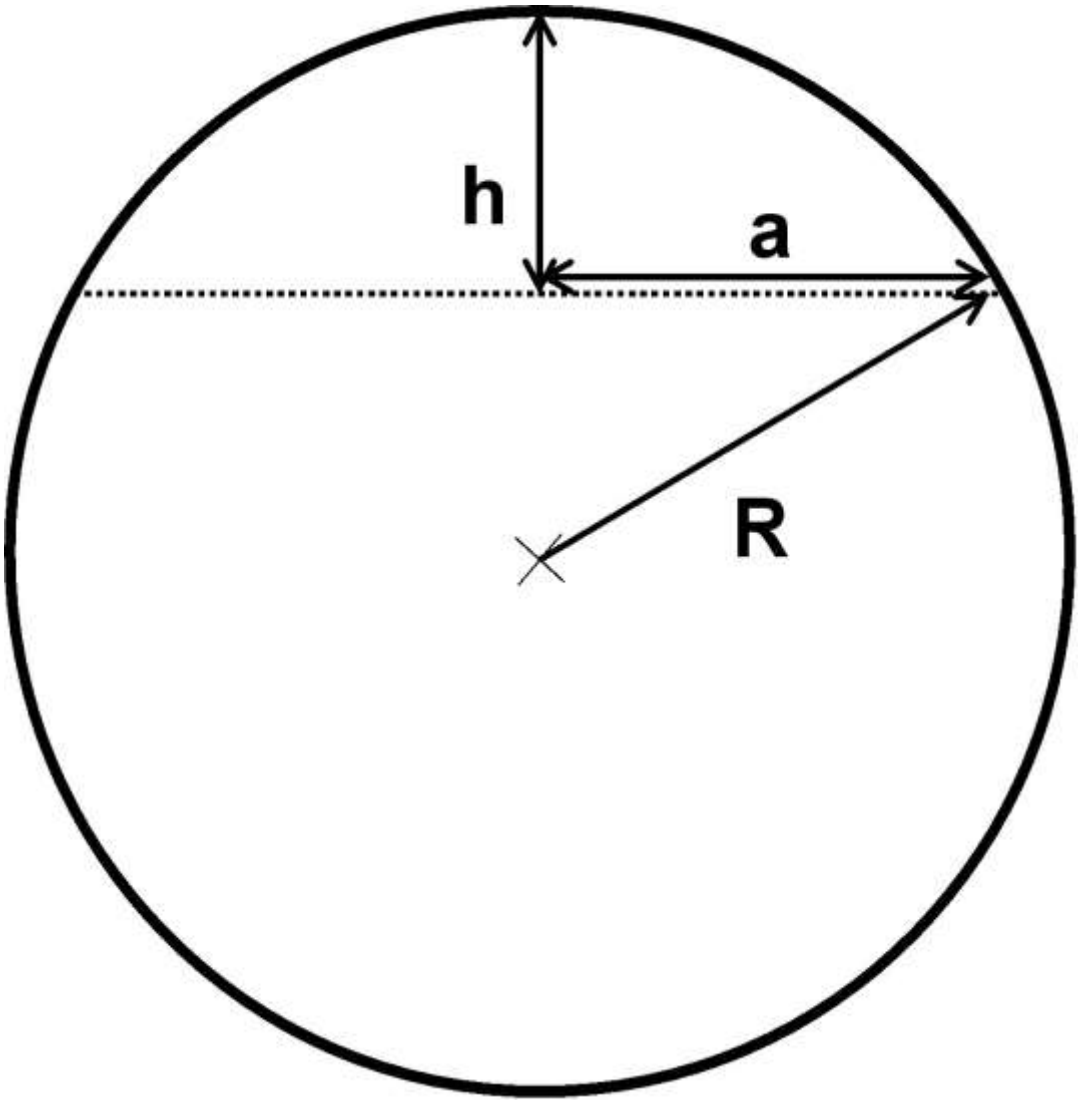


Figure 4: *Two-dimensional diagram of the spherical cap, with height* h*, and the base radius or overlapping neck radius* a*, and sphere radius* R*.*



TABLES

Table 1. Structural parameters of the real aerogels and of its corresponding cluster models.

REAL SYSTEM	**MODELS**		
Apparent density: 0,83 g/cm^3	Apparent density (g/cm^3)	Specific surface (m^2/g)	Porous volume (cm^3/g)
Specific surface: 387-407 m^2/g	0,80	384	0,72
Specific porous volume: 0,73-0,74 cm^3/g	0,81	376	0,88

REAL SYSTEM	**MODELS**	
Elemental sphere radius: 1,2 nm	Aggregate radius (nm)	Specific surface (m^2/g)
First aggregate radius: 4,5 nm	4,5	612
Specific surface: 640 m^2/g	4,4	669

Table 2. Structural parameters of the Woignier's aerogels (left) and of their corresponding cluster models. Errors in models' results concern to 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	.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

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