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Percolation of the organic phase in hybrid organic–inorganic aerogels

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Abstract The properties (texture, mechanical behaviour, etc.) of hybrid organic–inorganic silica aerogels change dramatically when the concentration of the organic additive is varied from a given value. It has been known for several years that this critical concentration is around 40% of the total weight of silica present in the sample. We have made use of a new structural model to conclude that this concentration of 40% by weight corresponds to the percolation threshold of the organic phase.

Keywords Aerogels · Hybrid organic–inorganic · Cluster model · Structural modelling · Computer simulation · Monte Carlo · Porous materials

1 Introduction

One of the routes proposed for making organic–inorganic hybrid materials (OIHM) incorporates the organic phase in the inorganic precursor sol under ultrasound assistance [1]. The two phases become chemically bonded after gelation and the resulting product is known as hard ormosil®, also called sono-ormosil. The aerogels resulting from drying these wet gels under supercritical conditions of the solvent [2] are nanostructured materials, since as they can be described as a coherent three-dimensional solid structure of particles and pores with sizes of several nanometres. These gels are denser and less porous, and present better thermal stability, than those prepared by the classic procedure [3]. By controlling the nature and morphology of the precursor molecules, it is possible to synthesize nanostructured hybrid aerogels with custom-tailored properties [4].

After researchers began in the 1980s to take an interest in hybrid organic–inorganic aerogels [2], studies appeared to focus on their mechanical properties from both the theoretical (e.g. scale laws for low density materials derived from percolation theory [5, 6]), and experimental perspectives [7–9]. During the 1990s the reinforcement effect due to the embedding of an organic phase within the nanostructure was studied in depth, mainly in order to avoid the high degree of brittleness of the inorganic aerogels [4, 10]. It was J. D. Mackenzie who definitively established that, as the organic content in the samples is increased, there is a property change from brittle material to elastomer; the critical concentration of organic polymer was found at around 40% of the total weight [11, 12]. This was first established for xerogels, and later similar results were obtained for aerogels [13]. Therefore, for low organic contents (less than 40%), their structure can be described as an inorganic matrix in which the organic phase is embedded; and for high organic contents, inorganic silica clusters are embedded within an organic matrix.

From a geometrical point of view, inorganic aerogels are commonly described as an assemblage of randomly packed spheres in several hierarchically-ordered levels [14–16]. This premise has been taken as the starting point for several simulation studies. For example the DLCA (Diffusion

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Limited Cluster–Cluster Aggregation) algorithm [17, 18] has been considered for building these nanostructures. Other simulated structures have also been proposed in which the presence of several typical sizes within the same structure is represented [19–21]. This article tries to explain and determine, starting from purely geometrical considerations, the critical concentration of relative organic content at which qualitative changes occur. This fact has been known for several years but, as far as we know, no explanation based on geometrical considerations has previously been proposed. We have developed a new structural model for hybrid porous random structures to illustrate this unusual topic of hybrid material science.

2 Experimental

Real aerogels were synthesized, as previously described [13], using tetraethyl orthosilicate (TEOS: $Si(OC_2H_5)_4$) (Merck, Germany; purity ≥99%) as the silica of the inorganic phase. TEOS was dissolved in 2 mL of EtOH in a molar ratio [TEOS]:[EtOH] = 0.66. A two-stage hydrolysis was performed as follows: TEOS was first partially hydrolysed (pH ~ 0) with HNO_3 catalyst in a molar ratio of [TEOS]:[H_2O] = 1:1.09. At this stage, 320 J cm^{-3} of ultrasound was applied to the mix from a device delivering 0.6 W cm^{-3} of ultrasound power energy to the system, giving a transparent and homogeneous solution as the result. Silanol-terminated poly-dimethyl-siloxane (PDMS) with quoted average molecular weight of 400-700 g/mol (ABCR, USA; 99.5%) was used as the polymer component [22–24]. This organic polymer was added (drop by drop, under the action of 320 J cm^{-3} of ultrasound) in a molar ratio [TEOS]:[DMS] = 1:0.014, 1:0.028, 1:0.043, 1:0.057, 1:0.071 and 1:0.085, respectively (representing 10, 20, 30, 40, 50 and 60%, respectively, by weight of PDMS with respect to the final amount of silica), where the organic fraction has been expressed as a function of the dimethylsiloxane monomer, DMS. Then the sols were left in an oven for 24 h at 50° C. The mixes were hydrolysed (pH ~ 1) with HNO_3 catalyst (Panreac, Spain; 60%) in a molar ratio [TEOS]:[H_2O] = 1:4.08, applying again 320 J cm^{-3} of ultrasound energy. The mixtures were poured into polyethylene containers and kept until gelation took place. These containers were then left in an oven at 50° C for 24 h.

2.1 Drying and characterization

The wet gels were dried using a supercritical drying process. They were placed in an autoclave (capacity: 500 mL) and covered with an amount of ethanol sufficient for the critical pressure of ethanol to be exceeded at the critical temperature. Then the temperature was slowly raised by 1° C/min until T = 252° C, which resulted in an increase in pressure to 78 atm. These conditions were maintained for half an hour. The full experimental details have been reported elsewhere [3].

Nitrogen physisorption experiments at constant temperature of 77 K were conducted in a Sorptomatic 1990 automated device from Fisons Instruments. The curves were studied in accordance with the usual theories [25, 26] to obtain the various textural features (specific surface, porosity, pore radius, etc.). Bulk (apparent) density measurements were made directly by weighing the samples and measuring their size. During this study, we have worked with several samples of increasing organic content, ranging from a pure silica aerogel to a gel with an organic content of 60%.

3 Structural approach

This study considers a new algorithm for building models of the structure of hybrid organic–inorganic nanoporous aerogels. This has involved improving our previous Cluster Model algorithm for inorganic structures [27]. This initial Cluster Model algorithm is based on the premises of Random Close Packing of spheres [28] and on previous studies of structural models for gels [29, 30]. Our Cluster Model can be classified as a static model [31], in the sense that it is not intended to reproduce the actual process of formation of the structure but only its final state.

The algorithm takes 2.09 g/cm^3 for the density of the inorganic skeleton formed by silica spherical elementary particles as reported [32] for this kind of system; this is slightly lower than the typical silica density of 2.2 g/cm^3 due to the existence of longer Si–O bonds [33].

The simulation work began with the construction of the inorganic structure. We proceeded by packing the elementary particles to form an aggregate. Then these aggregates are randomly packed with themselves, thus forming a two-level aggregate. This new two-level aggregate can also be randomly packed with itself, yielding a system of three hierarchical levels. This aggregating and packing process can be continued indefinitely, as desired. This algorithm has been fully explained in the previous articles [27, 34].

To answer the question: "Where is the organic polymer?" from a structural point of view, we have made use of our small angle scattering results [35]. These permit the main premise of this algorithm to be established, namely, that the organic polymer chains (the coils of thin black lines seen in the diagram of Fig. 1) take the form of shells around the first aggregates (dashed circles also in Fig. 1). Firstly, an inorganic skeleton that matches the nanostructure of a real inorganic aerogel (the small particles shown as grey spheres in Fig. 1) is built. Then we envisage an

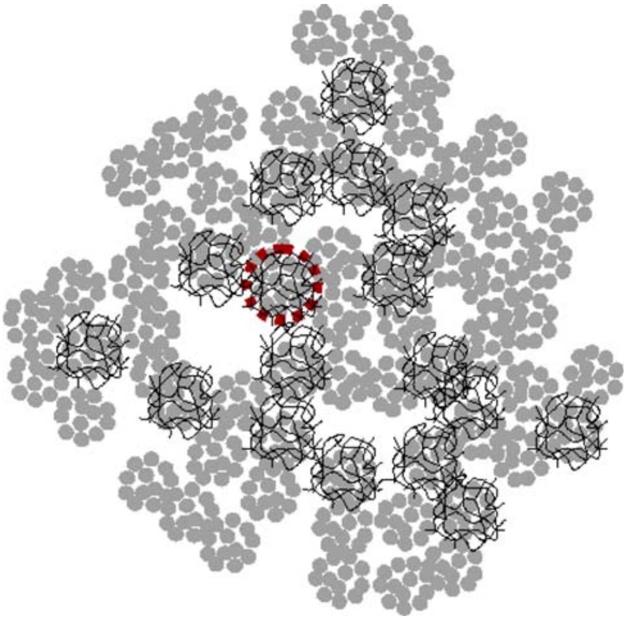

Fig. 1 Two-dimensional diagram of the hybrid structure: the inorganic skeleton is formed by silica spheres (small grey spheres). The organic chains are placed as random coils (thin entangled black lines) forming a shell around the first level aggregates (dashed circles)

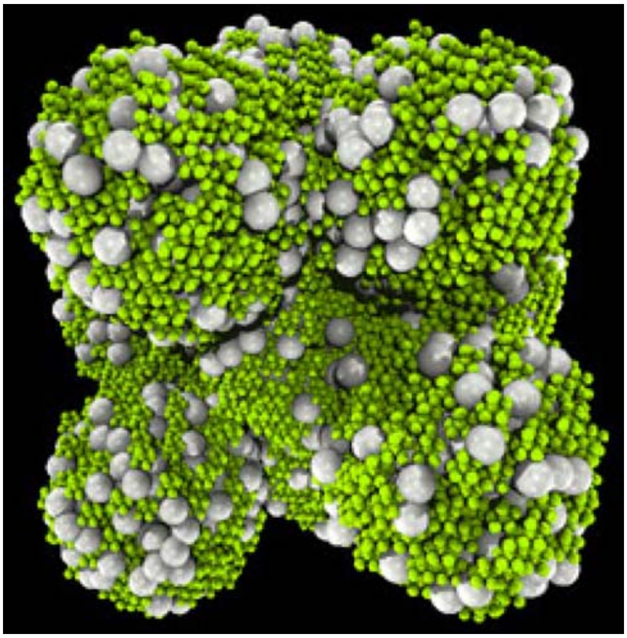

Fig. 2 A picture of a hybrid cluster model. The inorganic skeleton is formed by small spheres (grey spheres, green in online version) and larger white organic shells randomly placed. This system corresponds to an organic content of 50% by weight

organic spherical hollow shell being formed at random around a number of the first level aggregates. It was confirmed that the thickness of these shells is not a critical parameter, but a value of around 2 nm has been taken. The shells of PDMS were considered to have an apparent density [36] of 0.98 g/cm^3 and, obviously, the total number of shells depends on the content of PDMS with respect to the silica present in the simulated aerogel. Figure 2 shows a hybrid system constructed using the POVRay software [37]; several light-coloured shells are shown randomly placed within the inorganic skeleton comprising the smaller grey (green in the online Fig. 2) spheres.

For the applications to characterize the models, we have worked on cubic systems larger than the minimum representative size. In order to avoid the finite volume effect, we have included the periodic boundary conditions [38]. In addition, for the pore volume and porosity, we have applied the correction for the finite volume of the test particle [39]. The models were generated with an AMD Athlon processor of 1.5 GHz, and with a Pentium IV 3.5 GHz that permits up to several hundreds and thousands of spheres to be managed. For statistical accuracy, results were averaged over five different replicates of each system. These applications allow us to evaluate the ability of our models to represent real systems. Thus, the different textural features measured in real aerogels were checked against those of the models. For the application that emulates the physisorption results, we have taken the N_2 molecule as a sphere of 0.227 nm radius, as this corresponds to the typical value of 16.2 Å^2 usually given to the N_2 molecule cross-section in the BET calculations.

4 Results and discussion

From the plots shown in Fig. 3 the dependence of both porosity and bulk density on the increasing organic content, as obtained in our simulations, is evident. This can be compared with the values obtained experimentally (Table 1). A very good correspondence between experimental and theoretical values can be observed from the porosity values. The simulated values reproduce the experimental trend of density for PDMS content higher than 10% by weight, thus endorsing the capacity of these hybrid models to represent the structure of the samples. It should be noted that the only model that had previously been generated to match a priori real texture values was the totally inorganic model [27]. The values obtained for specific surface area (Fig. 4) reproduce, from 20% PDMS content, the decrease of this experimental parameter with the increasing PDMS content. However, the experimental values show a sharp step down starting at around a PDMS content of 40%, which is almost certainly related to the change of role that each phase plays in the structure when the organic polymer concentration is at or near this critical percentage value. This step down is not reproduced at all by the hybrid model, as could be expected due to the nature of its algorithm.

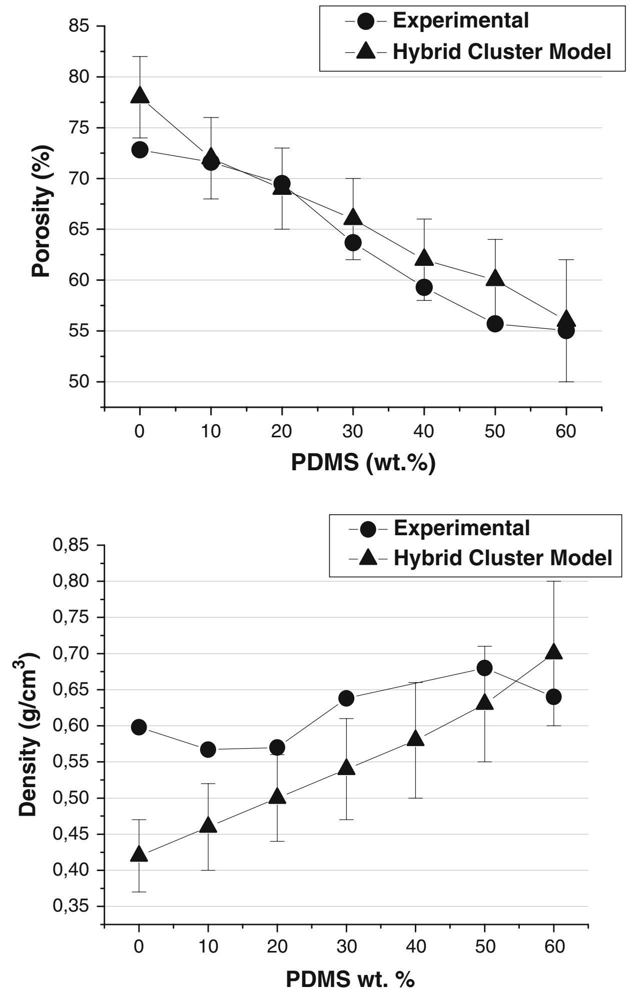

Fig. 3 Upper: Porosity of the hybrid aerogels with increasing organic content, measured by nitrogen physisorption, and simulation values of the hybrid models. Simulation values are averaged over five different replicates of each system. Lower: Apparent density of the samples and their corresponding simulation values

Table 1 Experimental values: Textural values of the hybrid aerogels obtained from N_2 isothermal nitrogen adsorption–desorption at 77 K. Theoretical values: The number of organic shells needed to emulate the relative organic content (% PDMS) in each hybrid sample, and the corresponding fraction φ of the space occupied, apart from the inorganic skeleton

% PDMS	Experimental values			Theoretical values	
	S_{BET} (m^2/g)	P (%)	ρ (g/cm^3)	No of organic shells	φ
0	800	73	0.598	–	–
10	800	72	0.567	148	0.065
20	900	69	0.570	296	0.130
30	880	64	0.638	444	0.194
40	420	59	0.680	593	0.259
50	516	56	0.640		
60	142	55	–		

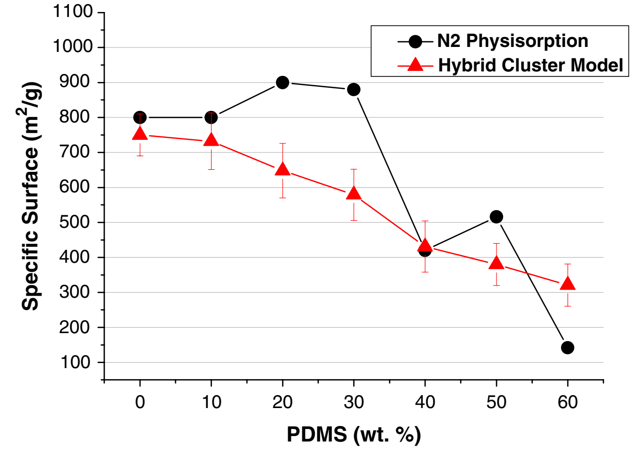

Fig. 4 Specific surface area of the hybrid aerogels with increasing organic content, measured by nitrogen physisorption, and simulation values of the hybrid models. Simulation values are averaged over five different replicates of each system

Although the hybrid Cluster Models can reproduce, with more or less successfully, the textural values of the hybrid aerogels, when working with the complete set of samples of increasing organic content, two important aspects of this algorithm should be discussed. Firstly, for all of the samples tested, we are working with the same inorganic skeleton, so implicitly we are assuming that the arrangement of this inorganic phase does not depend on the addition of the organic precursor. This premise may not be completely realistic, as these structures are very sensitive to small changes of the conditions of synthesis. Secondly, this algorithm works in the same way for all the values of organic content: it takes the inorganic phase as the matrix within which the organic phase becomes embedded. Therefore, it does not take into account the qualitative change of the role of the phases that is found for organic contents greater than 40%, when the organic phase constitutes the matrix of the structure. Despite these reservations, the experimental trends of the textural parameters are reproduced in a realistic way.

An explanation for the qualitative change of these properties observed in these hybrid materials can be found in the percolation theory [40]. As already explained, the organic phase is constructed by randomly selecting several aggregates within the inorganic skeleton. These selected aggregates had also been constructed in a random way, and they were forced to be separated from each other by a distance very close to their shell diameter (D), typically 0.97 D, so they form a set of non-overlapping spheres. Each selected aggregate is then surrounded by a spherical shell formed by the organic phase. Therefore, in principle, each point in the interior space of the aerogel has the same probability of being occupied by an organic-shell sphere, and once an organic-shell sphere occupies particular points

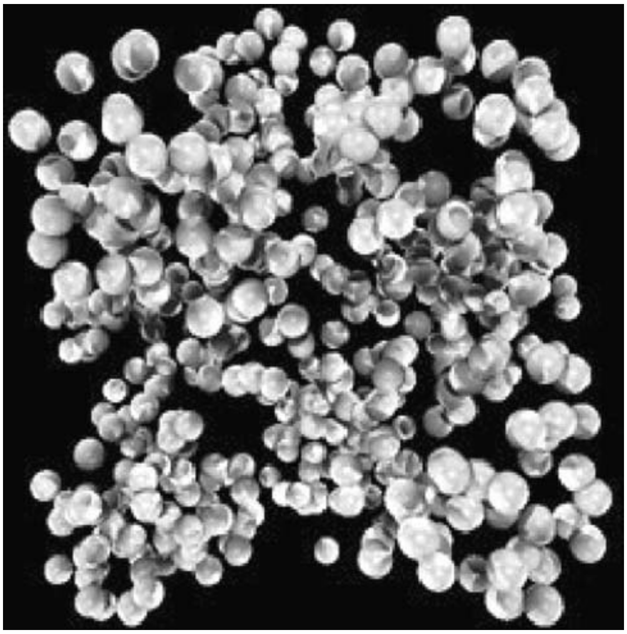

Fig. 5 Picture of the set of organic spheres, shown apart from the inorganic skeleton, for the sample with an organic content of 10%

of the space, they are no longer accessible to the rest of the spheres. Hence, the organic phase, that is, the set of organic spherical shells (Fig. 5), can be considered as a set of hard spheres randomly positioned within the total space.

For a set of hard spheres, it is known that the percolation threshold is around $f\phi = 0.16$, f being the packing fraction of the construction algorithm: in our case, for the random close packing of hard spheres, $f = 0.637$; and ϕ is the occupation fraction, which is directly related to the porosity P, with $\phi = 1 - P$. Thus, the percolation threshold for these systems is reached when, $\phi = 0.25$. The values of the occupation fraction ϕ of the set of organic spheres were calculated. Table 1 shows these values for the increasing organic content. As can be checked, for the 40% by weight gel, the organic phase reaches the percolation threshold, and this explains the qualitative change in the properties of the hybrid materials. Moreover, this result also supports the idea that, for high organic contents, the structure can be understood as an organic skeleton within which the inorganic porous silica clusters are embedded. Consequently, the hybrid cluster model algorithm for constructing structural models of aerogels with high organic content needs to be improved.

5 Conclusions

1. The new model reproduces the experimental trends of the textural parameters in a realistic way.
2. An explanation for the qualitative change of these properties observed in these hybrid materials can be found in the percolation theory.
3. The hybrid cluster model algorithm for constructing valid structural models of aerogels with high organic content needs to be improved.

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References

1. Mackenzie JD (1994) J Sol-Gel Sci Tech 2:81
2. Phalippou J (2008). http: www.solgel.com/articles/june00/phalip/introsolgel.htm. Accessed 5 Sept 2008
3. de la Rosa-Fox N, Esquivias L, Piñero M (2003) Organic–inorganic hybrid materials from sonogels. In: Nalwa SH (ed) Handbook of organic–inorganic hybrid materials and nanocomposites, vol 1. American Scientific Publishers, CA, pp 241–270
4. Pekala RW, Alviso CT, Kong FM, Hulsey SS (1992) J Non-Cryst Solids 145(1–3):90
5. Ma H, Roberts AP, Prévost J, Jullien R, Scherer GW (2000) J Non-Cryst Solids 277:127
6. Woignier T, Reynes J, Alaoui A, Beurroies I, Phallipou J (1998) J Non-Cryst Solids 241:45
7. Roberts AP, Garboczi EJ (2001) Acta Mater 49:189–197
8. Pirard R, Pirard JP (1997) J Non-Cryst Solids 212:262
9. Emmerling A, Fricke J (1997) J Sol-Gel Sci Technol 8:781
10. Pekala RW, Alviso CT, LeMay JD (1990) J Non-Cryst Solids 125:67
11. Mackenzie JD, Huang Q, Iwamoto T (1996) J Sol-Gel Sci Technol 7:151
12. Hu Y, Mackenzie JD (1992) Mater Res Soc Symp Proc 271:681
13. Piñero M, Morales-Florez V, de la Rosa-Fox N, Esquivias L (2005) Bol Soc Esp Ceram V 44(5):291
14. Zarzycki J (1992) In: Hench L, West JK (eds) Chemical processing of advanced materials. Wiley & Sons Inc., New York, p 84
15. Esquivias L, Rodríguez-Ortega J, Barrera-Solano MC, de la Rosa-Fox N (1998) J Non-Cryst Solids 225:239
16. Leventis N, Sotiriou-Leventis C, Zhang G, Rawashdeh A (2002) Nano Lett 2(9):957
17. Ma H, Prévost J, Jullien R, Scherer GW (2001) J Non-Cryst Solids 285:216
18. Ma H, Prévost J, Scherer GW (2002) Int J Solids Struct 39:4605
19. Lours T, Zarzycki J, Craievich AF, Aegerter MA (1990) J Non-Cryst Solids 121:216
20. Posselt D, Pedersen JS, Mortensen K (1992) J Non-Cryst Solids 145:128
21. Schaefer DW (1994) MRS Bull XIX(4):49
22. Clarson SJ, Rabolt JF (1993) Macromolecules 26:2621
23. Arrighi V, Gagliardi S, Zhang CH, Ganazzoli F, Higgins JS, Ocone R, Telling MTF (2003) Macromolecules 36(23):8738
24. http://www.mtas.es/insht/plastico/FT_14_0.htm. Accessed 16 March 2008
25. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T (1985) (IUPAC Subcommittee on Reporting Gas Adsorption Data) Pure Appl Chem 57(4):603

26. Brunauer S (1944) The adsorption of gases and vapours. Oxford University Press, Oxford, p 150
27. Morales-Flórez V, de la Rosa-Fox N, Piñero M, Esquivias L (2005) J Sol-Gel Sci Technol 35:203
28. Zinchenko A (1994) J Comput Phys 114:298
29. Zarzycki J (1990) J Non-Cryst Solids 121:110
30. Rodríguez-Ortega J, Esquivias L (1997) J Sol-Gel Sci Technol 8:117
31. To LT, Stachurski ZH (2004) J Non-Cryst Solids 333:161
32. Barrera-Solano MC, de la Rosa-Fox N, Esquivias L (1992) J Non-Cryst Solids 147 & 148:194
33. Esquivias L, Barrera-Solano MC, de la Rosa-Fox N, Cumbrera FL, Zarzycki J (1992) In: Uhlmann DR, Ulrich DR (eds) Ultrastructure processing of advanced materials. John Wiley and Sons Inc., New York, pp 315–325
34. Morales-Flórez V, Piñero M, de la Rosa-Fox N, Esquivias L, Anta JA, Primera J (2008) J Non-Cryst Solids 354:193
35. de la Rosa-Fox N, Morales-Flórez V, Toledo-Fernández JA, Piñero M, Esquivias L, Keiderling U (2008) J Sol-Gel Sci Technol 45(3):245
36. Yaworski HG, Craig G, Roberts D (1996) Proceedings of the transmission and distribution conference (IEEE, 1996), pp 396–401, 15–20 Sept 1996
37. Persistence of vision (2008). http://www.povray.org. Accessed 19 Sept 2008
38. Blonsky S, Garofalini S (1996) J Chem Phys 100:2201
39. Gavalda S, Kaneko K, Thomson KT, Gubbins KE (2001) Colloids Surf A 187:531–538
40. Efros A (1994) Física y Geometría del Desorden. Editorial URSS, Moscow