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Sol–gel simulation—I: Scattering response

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ABSTRACT

Scattering of sol–gel structures is investigated computationally. Sol-gels are recreated through an aggregation algorithm incorporating Brownian motion and chemical reactions. Using the fractal character of sol–gels, the concept of recursion is introduced as a tool to perform multi scale computation of the response of sol–gels through the different scales from the molecular level to the macro scale. The concept is illustrated with the prediction of scattering intensity. The relationship between scattering intensity and functionality is investigated, noting that the latter is a function of the Brownian motion and chemical reactivity. Computational simulation tools are developed to predict scattering intensity as a function of density and reactivity, the former represented by the number of particles, or clusters, in the simulation box. Then, the results are correlated to an analytical model that reveals the critical wave number, or critical scale, at which percolation occurs.

1. Introduction

Advanced products such as dense films, Aerogels, super capacitors, and dense ceramics can be fabricated with sol–gel technology [1–9]. This technology uses colloidal aggregation [10–27], which after the removal of the liquid phase leaves a solid ceramic structure [28,12]. Extracting the liquid phase of the colloid gently, e.g. by supercritical drying, leaves a solid structure with unique physical properties [28,3,11,10,29].

The outstanding properties of gel-derived materials are the result of a) the physical properties of the base material and b) the unique structure of the resulting material [25,30]. To characterize the structure of gel-derived materials, Small Angle Neutron Scattering (SANS) and Small Angle X-Ray Scattering (SAXS) have been used extensively [31–35,12,29,36,37] revealing their fractal structure along several length scales [12].

In many cases, physical properties of the gel-derived structures can be explained by their fractal structure [25,30]. However, fractal theory is not always applicable, in particular when it becomes inadequate to associate a fractal range to the structure, or when within a proved fractal range the response is not explained by classical fractal theory [29,36].

In this work, it is proposed that some responses of gel-derived materials depend on the connectivity of the structure while other responses depend on the mass distribution of the structure. In this manuscript, density and scattering intensity are shown to depend on the mass distribution. For this, density and scattering intensity of computer generated structures that resemble gels and aerogels are evaluated. On the other hand, mechanical response of gels and aerogels and their relationship to scattering are investigated in Part II [38].

2. Computer-generated structures

The structures at scale $\lambda \in [1, \lambda_{max}]$ are generated by an aggregation algorithm explained in detail in [24]. Here λ_{max} stands for the maximum scale at the first generation of the multi scale algorithm, a scale that is given by the size of the simulation box $L = \lambda_{max}(2a_0)$, where $2a_0$ is the size of the primary particles. First, particles are randomly positioned at the sites of a cubic lattice inside the simulation box. Then, a particle is chosen randomly to move in the lattice, in order to reproduce the Brownian motion that occurs in a forming colloid satisfying Einstein–Smoluchowsky theory [39,40]. For two colliding particles, the probability of forming a bond is determined by the reactivity ω and their coordination numbers n_{cA} and n_{cB}. If the bond is formed, the clusters containing the colliding particles bond into a single, larger cluster. Periodic Boundary Conditions (PBC) are used to delimit the simulation box. The algorithm ends when all particles form a single cluster. At this point we say that all particles have aggregated, which is not the same as saying that all particles have bonded with their neighbors. For that one would have to age/sinter the structure. Typical structures are depicted in Fig. 1 for low and high reactivity w.

Reactivity is a measure of the increase or decrease of additional energy required to form a new bond as a function of the number of bonds already formed. Using this concept, the probability of reaction of two particles is calculated using the Metropolis algorithm [24]. In this way, different structures are formed by varying the reactivity. Longer branched structures are formed for lower reactivities, and more compact structures are formed for higher reactivities. The particular case of neutral Aerogels was found to correspond to a reactivity of $w = 1$.

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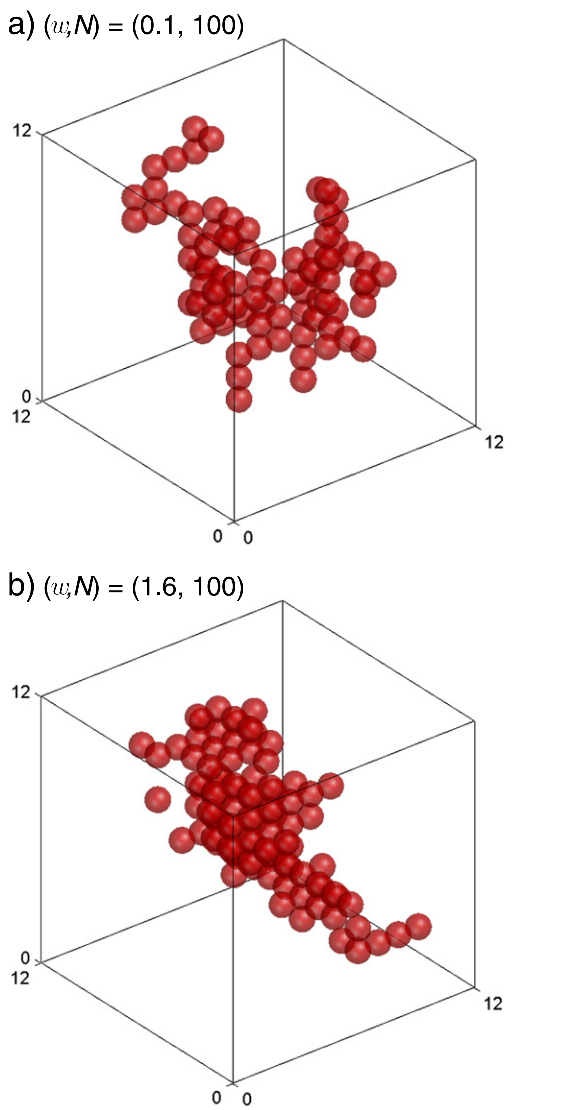

Fig. 1. Cross-section of an aggregated structure inside the simulation box, at scale $\lambda \in [1, \lambda_{max}]$.

The resulting structure has a functionality[1] distribution which not always coincides with the coordination number[2] distribution. However, both distributions can be modified as follows. When sintering and/or aging a sol, the coordination number distribution approaches the functionality distribution, as bonds appear between the particles that are next to each other. Also, as the initial density is lowered, the functionality distribution approaches the coordination number distribution (since all particles that are neighbors tend to bond when the density is low). Thus, responses such as stiffness, which are associated to the connectivity of the structure, are expected to be related to the coordination number rather than to the mass distribution, which is measured by the functionality. On the other hand, responses such as scattering intensity, which are associated to mass distribution, are expected to be related to functionality.

In this paper, scattering intensity (as a measure of mass distribution) is investigated for sol–gels. Mechanical properties (as a measure of the connectivity of the structure) and their relationship to scattering, are investigated in Part II [38].

[1] The functionality counts how many particles are next to a particle.

[2] The coordination number counts how many particles are bonded to a particle.

3. Correlation length

The correlation length ξ is a measure of the size of the clusters that have aggregated during the gelation process. The relation between correlation length and density of the cluster is developed in this section for structures with constant fractal dimension. In a simulation box of size L, the aggregation process initially consists of N_0 primary particles of size $2a_0$ that aggregate. The primary particles may be molecules like SiO_2, or cluster of molecules with a known size and density. In this study SiO_2 is chosen in order to use the structures assembled in [24], which happen to be build on the basis of SiO_2. Structures based on other precursors are not readily available but could be used if they were available. The effective density is $\rho_{ef}^0 = N_0/L^3$, where N_0 is the number of particles in the simulation box. Conservation of mass implies that the effective density is constant through the aggregation process. However, during aggregation, gaps are created as the clusters bond without perfect match. Therefore, the density of the forming clusters decreases due to the incorporation of vacancies, the size of the clusters ξ increases, and the number of clusters N_C decreases. Due to the decrease in the number of clusters in the simulation box, the average distance between clusters d increases. In this way, the density of the cluster can be calculated as

$$\rho_C = \frac{N_C}{L^3} = \frac{1}{d^3} \tag{1}$$

Note that the number of particles N_0 can be calculated as

$$N_0 = N_C \; N_{k/C} \tag{2}$$

where $N_{k/C}$ is the number of particles per cluster. Furthermore, assuming that the aggregation process leads to a fractal structure, $N_{k/C}$ follows a power law as

$$N_{k/C} = \left(\frac{\xi}{2a_0}\right)^{\mathcal{D}} \tag{3}$$

where $\mathcal{D}$ is the fractal dimension of the of the clusters.

At the end of the aggregation process, when only one cluster is found inside the simulation box, $N_C = 1$. Therefore, Eq. (3) can be rewritten as

$$\frac{\xi}{2a_0} = N_0^{1/\mathcal{D}} \tag{4}$$

From Eq. (1), it is concluded that the mean free path d becomes equal to the size of the simulation box, i.e. $d = L$.

Note that if $\xi < L$, the structure will not percolate and the effective density N_0/L^3 would be lower than the density of the cluster N_0/ξ^3.

Since ξ is limited by d, the system percolates for $L = \xi = d$, thus defining the critical percolation density

$$\rho_{crit} = \frac{L^{\mathcal{D}-3}}{(2a_0)^{\mathcal{D}}} \tag{5}$$

In other words, if ξ is chosen to be at least d, the cluster spans the entire simulation box, connecting opposite faces of the simulation box. Using a dimensionless system, we have $2a_0 = 1$, $L' = L/(2a_0)$, and $\rho' = (2a_0)^3\rho$. Then, $\rho'_{crit} = L'^{\mathcal{D}-3}$.

4. Percolation kinematics

In this section, the evolution of a cluster during the aggregation process is described in terms of the number of particles per cluster $N_{k/C}$ and the number of clusters N_C in the simulation box.