Molecular Dynamics approach of sol–gel transition: Comparison with experiments

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Abstract

A new aggregation model by a Molecular Dynamics approach at constant temperature was compared with experimental results on a zirconia precursor gelling process. The evolution of the distribution of the experimental scattered intensities (small angle X-ray scattering curves), during gelling, was compared with the results of our Molecular Dynamics method, via the computation of structure factors of the numerical structure for different times: a very good agreement was found. Our numerical model allows one to understand the evolution as a function of time of the size and quantity of matter corresponding to the upper limit of the fractal domain.

1. Introduction

Different models exist to represent aggregation and gelation in colloidal systems. Up to now, the three main methods used to analyze gelation were, first, the

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Smoluchowsky equation [1–4], which gave the evolution in time of the number of particles inside clusters, but did not give an exact view of the internal structure of the studied material. And second, the other method was the Diffusion Limited Cluster Cluster Aggregation (DLCA) model [5–9] which, for given materials gave an exact view of the internal structure but did not give, at least directly, the evolution in real physical time as it was a Monte Carlo approach. The third approach, was the computation of gelling and aggregation by a Brownian dynamics approach [10–12]. In this last case, evolution and structure can be analyzed almost directly but the particles and clusters trajectories correspond to a probability density function and not to deterministic trajectories like in Molecular Dynamics.

In this article, we will present a new Molecular Dynamics model for aggregation at a constant temperature (Section 2). Section 3 corresponds to the experimental set up description. In Section 4, the numerical results as well as experimental data are shown. In Section 5, results are discussed and a comparison is made between numerical and experimental data. And we conclude in Section 6.

2. Numerical model

The model system consisted of N spherical particles of diameter 1, contained in a cubic simulation box of edge length L with periodic boundary conditions. The volume fraction, c, for this system is:

$$c = \frac{\pi}{6} \frac{N}{L^3} . \tag{1}$$

The trajectories of the particles are computed using a Molecular Dynamics algorithm at constant temperature. To solve Newton's equations we use a Verlet list algorithm [13,14] and a predictor–corrector algorithm [15]. At each time step, all particles receive a random force and have their velocities lowered using a constant friction. It is equivalent to say that the particles are in contact with a thermostat maintained at a constant temperature. The average magnitude of the random forces and the friction are related in a particular way: called the Langevin thermostat formalism. In this formalism, the particle i equation of motion becomes

$$m\mathbf{a_i} = -m\gamma\mathbf{v_i} + W_i(t) , \tag{2}$$

where $\mathbf{a_i}$ (resp. $\mathbf{v_i}$) is the acceleration (resp. velocity) of particle i which has a mass m, γ is a friction coefficient with units of s^{-1} and $W_i(t)$ is a Gaussian random force with a mean given by

$$\langle W_i(t), W_j(t) \rangle = \delta_{ij}\delta(t - t')6k_B mT\gamma , \tag{3}$$

where T is the temperature, k_B is Boltzmann constant and t corresponds to time. By this definition, this Gaussian random force is not correlated in space and time. Moreover, the momentum $\mathbf{p} = \mathbf{mv}$ is not conserved.

No long range interactions have been used in our model. Moreover, gravity has been neglected as we assume that our particles are small and that the effect of weight is negligible with respect to the thermal agitation.

When two or more particles touch each other, they stick definitively. Then the mean acceleration and velocity resulting from all independent accelerations and velocities of the particles inside the cluster are computed. And, in order to conserve the relative positions of the particles inside the cluster, the mean acceleration and velocity are used for all particles of the corresponding cluster. This allows the cluster to move as a whole, in translation. By this method the friction coefficient and the random force $W_i(t)$ act individually on each particle of the cluster and are not renormalized with respect of the new size of the cluster: indeed, physically the liquid surrounding the cluster acts on each particle individually as does the random force $W_i(t)$.

We use this method and not attractive potentials between particles for a computing time reason: with attractive potentials, the Molecular Dynamics time step has to be very small (down to 10^{-5} s and less) in order for the cluster to remain stable and with irreversible sticking. Our method allows us to use up to 10^{-2} s Molecular Dynamics time step, hence taking less computing time. Furthermore, with this method of irreversible aggregation, there is no aging of the structure and no restructuration.

3. Experiments

As described elsewhere [16], the zirconia precursor gels were prepared in the zirconium *n*-propoxide, *n*-propanol, acetylacetone (acacH) and water system. In an air dried glove-box, the zirconium *n*-propoxide was diluted with *n*-propanol and chelated by acetylacetone. The complexing ligands are not easily hydrolyzed and lead to obtain a chemical control of reactions [16,17] by avoiding precipitation and slowing down condensation effects. Then, a water-alcohol mixture was added under vigorous mechanical stirring and the glass container was hermetically closed until gelling occurred.

The small angle X-ray scattering (SAXS) experimental set up was an original one adapted to a rotating anode X-ray generator. For time-dependent investigation, a small amount of the solution was placed in a cell with two kapton windows, spaced at about 0.5 mm, and studied in situ at room temperature. The scattered intensity was measured for successive aging times with an exposure time of 2 h. From time to time, SAXS curves were collected on new samples from the "mother" solution to check that no volume effect was involved.

4. Results

Numerically, we used a concentration of $c = 0.05$ for a box edge length of $L = 35$, this corresponds to $N = 4094$ particles. The diameter of the particles was equal to

$d = 1$. Numerical results have been averaged over three different realizations. The friction coefficient was chosen equal to $\gamma = 0.9$.

Experimentally, the chemical parameters for the sol are the concentration in zirconium $C = [Zr] = 0.25 \, \text{mol/l}$ the hydrolysis rate $W = [H_2O]/[Zr] = 10$ and the complexation rate $R = [acacH]/[Zr] = 0.7$.

In Fig. 1a and b, there are two snapshots of the internal numerical structure of the forming gel at respectively time $t = 1$ and $4563 \, \text{s}$.

Numerical structure factors have been computed as in Ref. [18]: the local structure was examined in real space using the radial distribution function $g(r)$. The pair distribution functions are a measure of the probability of finding a particle at a distance r from another particle, and a fractal structure shows up as a power law region in $g(r)$ for the distance over which the fractal structure holds,

$$g(r) \propto r^{D_f - 3} \, . \tag{4}$$

By plotting the pair distribution functions on a log–log scale, any fractal region will appear as a straight line, the slope of the line giving a value for the fractal dimension D_f.

The long range structure can also be analyzed via the structure factor $S(q)$ which is derived from the pair distribution function, $g(r)$ by the following Fourier transform:

$$S(q) = 1 + \frac{6c}{\pi} \int_0^\infty (g(r) - 1) 4\pi r^2 \frac{\sin(qr)}{qr} \, dr \, . \tag{5}$$

In Fig. 2a, we plotted the numerical structure factors of the forming gel $S(q)$ as a function of $q = 2\pi/r$, at different times, starting from $t = 1$ to $4563 \, \text{s}$. Fig. 2b corresponds to the SAXS intensity curves of the corresponding zirconia gelling sol, at different times.

We analyzed the preceding numerical structure factors. For each structure factor, the point where the fractal slope was lost: $S_{cut\text{-}off}(q_{cut\text{-}off})$ was saved for each time t. We deduced from Fig. 3a, where were plotted $S_{cut\text{-}off}$ and $q_{cut\text{-}off}$ as a function of time t.

As a comparison, we saved the corresponding experimental points where the fractal slope was lost on the SAXS curves. Each of these points has three coordinates: $I_{cut\text{-}off}$, $q_{cut\text{-}off}$ and t. From these points we plotted $I_{cut\text{-}off}$ and $q_{cut\text{-}off}$ as a function of time t in the same figure (Fig. 3b).

5. Discussion

As one can see in Fig. 2a and b, for early stages of the gelling process, the computed structure factor and the SAXS curve do not present a real power law in a log–log graphic, i.e., the slope at high q is not constant. In these two figures and for later stages of the gelling process, this slope grows, being included between the Guinier regime and the Porod regime: we call it the fractal slope because it is the
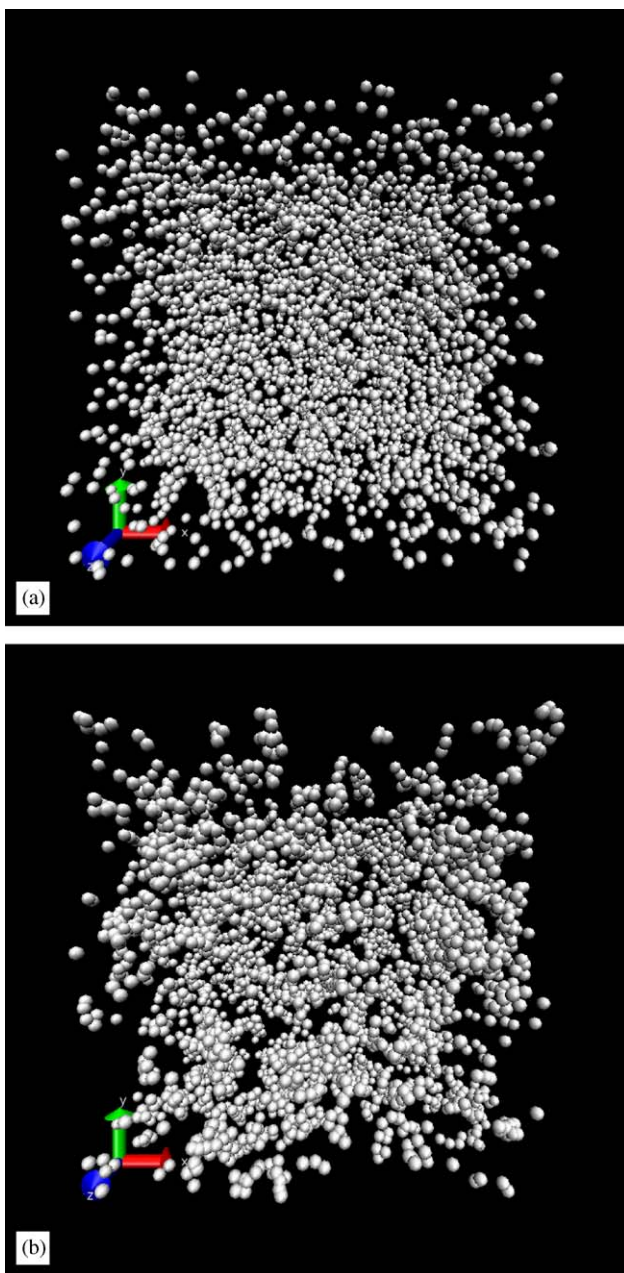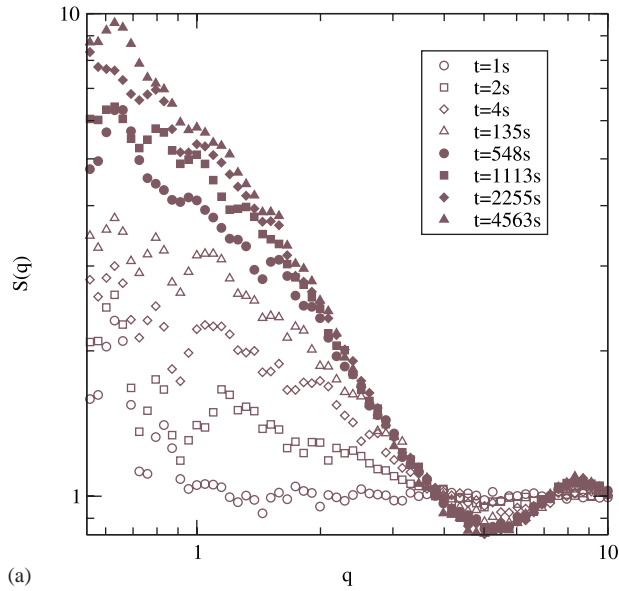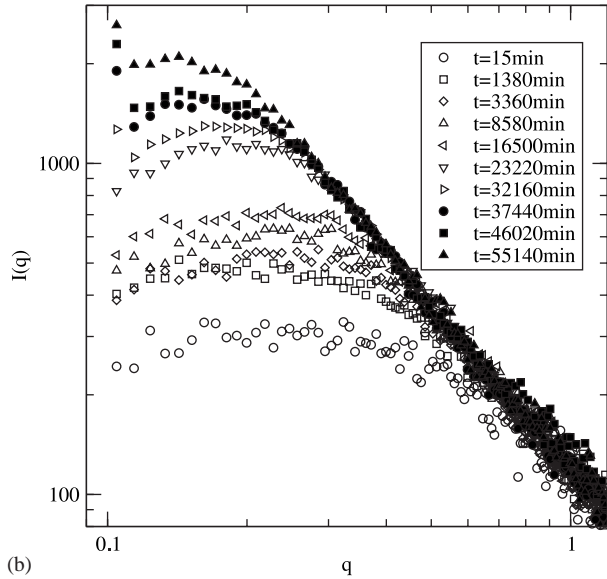
Fig. 1. (a) Snapshot of the internal structure of the numerical sol at time $t = 1$ s, (b) snapshot of the internal structure of the numerical gelling sol at time $t = 4563$ s.

Fig. 2. (a) Structure factors $S(q)$ as a function of q in a log–log plot for times ranging from $t = 1$ to 4563 s, (b) SAXS intensity $I(q)$ as a function of q in a log–log plot for times ranging from $t = 15$ to 55140 min.

signature of a fractal structure between two cut-off lengths. The cut-off at large q corresponds to the beginning of the Porod regime: i.e., in the experimental SAXS curves, it corresponds to the apparition of a -4 linear slope in a log–log plot, while in the numerical curves it corresponds to the apparition of oscillations. The cut-off at
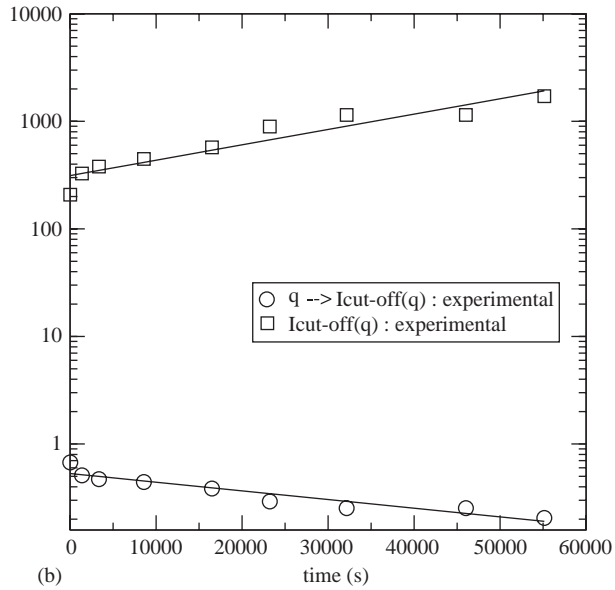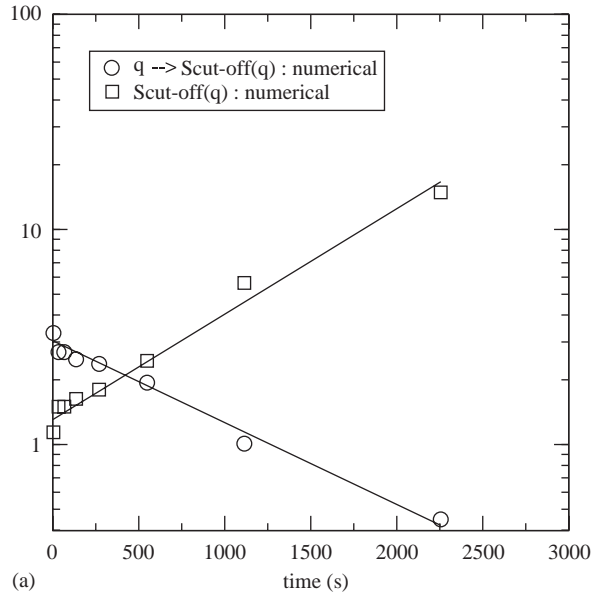
Fig. 3. (a) Evolution of $S_{cut\text{-}off}$ (squares) and $q_{cut\text{-}off}$ (circles) as a function of time t in a linear-log plot: numerical results, (b) evolution of $I_{cut\text{-}off}$ (squares) and $q_{cut\text{-}off}$ (circles) as a function of time t in a linear-log plot: experimental results.

small q corresponds to the locations on the curves (experimental and numerical) where the fractal slope is lost. Let us call $q_{cut-off} = 2\pi/\xi$ this location: ξ is the size of the smallest fractal cluster in the solution. For smaller q (i.e., larger sizes) the space distribution of matter loses its mean fractal characteristic causing the slope of the SAXS curves or of the structure factors to lose their power law behavior. When the different fractal clusters or domains in the simulation box or in the experimental gelling sol have a narrow distribution in sizes, the maximum of the small angle scattering curve is smooth and can be interpreted as the inverse of the mean size of the clusters. The largest cluster corresponds to a value of q for which the small angle scattering intensity decreases for $q \rightarrow 0$.

One can see that there is a very good qualitative agreement between experimental SAXS curves and numerical structure factors as a function of time. This allows us to say that our Molecular Dynamics model at constant temperature used adequate hypothesis to model the sol–gel transition of our zirconia precursor.

Let us now compare the evolution of $q_{cut-off}$ as a function of time numerically (squares in Fig. 3a) and experimentally (squares in Fig. 3b). We plotted their evolution in a linear-log plot. We plotted also in Fig. 3a (resp. Fig. 3b) the evolution of $S_{cut-off}(q_{cut-off})$ (resp. $I_{cut-off}(q_{cut-off})$), represented both by circles, as a function of time. All the data of Figs. 3a and b follow an exponential law. To explain that feature, report on Eq. (2). If we neglect the very first stages of aggregation in the numerical model and if we take into account that we averaged all forces acting on the clusters (see Section 2), we can say that the random force acting on each cluster tends to zero (see, Eq. (3)) as the cluster grows. So for medium and large clusters, Eq. (2) reduces to

$$m\mathbf{a_i} = -m\gamma\mathbf{v_i} \,. \tag{6}$$

We call $\xi(t)$ the characteristic length which the clusters have to go before encountering another cluster at each time t: we suppose that for an interval of time Δt the size of the cluster grows of the value $\Delta\xi$. With a dimensional analysis of the preceding equation and thus taking the absolute values of each side of Eq. (6), we obtain

$$m\frac{\mathrm{d}\xi(t)/t}{\mathrm{d}t} = m\gamma\xi(t)/t \,. \tag{7}$$

We obtain

$$\xi(t) = \exp(A\gamma t + B) \,, \tag{8}$$

where $A > 0$ and B are integration constants. Hence

$$q_{cut-off} = \frac{2\pi}{\xi(t)} = \exp(-C\gamma t + D) \,, \tag{9}$$

where $C > 0$ and D are integration constants.

As ξ is the size of fractal clusters, we can apply the following equation:

$$M \propto \xi^{D_f} \,, \tag{10}$$

where M is the mass corresponding to a cluster of size ξ. Moreover, as $q_{cut-off}$ and $I_{cut-off}$ (experimental SAXS intensity) or $S_{cut-off}$ (computational structure factor)

are related by

$$q_{cut\text{-}off} = \frac{2\pi}{\xi} \propto M^{-1/D_f} \propto I_{cut\text{-}off}^{-1/D_f} \qquad (11)$$

because the SAXS intensity or the structure factor intensity are proportional to the mass at the corresponding length (i.e., ξ). Hence

$$I_{cut\text{-}off} = \exp E \frac{\gamma}{D_f} t + F, \qquad (12)$$

where $E > 0$ and F are constants. Qualitatively and with the same reasoning, $S_{cut\text{-}off}(q_{cut\text{-}off})$ has also an exponential behavior as a function of time.

Finally, we can say that the fractal dimensions D_f given by the linear slope of the SAXS curves and the structure factors agree very well: each slope in a log–log plot is equal to $D_f = 1.6$. Let us remark that, even if the probability of aggregation is equal to one (irreversible aggregation), our model does not give the same fractal dimension as a stochastic method like the DLCA method for which the resulting fractal dimension is equal to 1.8.

6. Conclusion

We showed here a new Molecular Dynamics method modelling the gelation of an assembly of small particles. The parameters that we took for our numerical model lead to results that fit very well with the experimental results. Comparison between the numerical structure factors and the SAXS curves are qualitatively very good, leading to the conclusion that the size of the fractal domains and the mass distribution during gelation follows an exponential law as a function of time.

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