Effect of Container Size on Gelation Time: Experiments and Simulations

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The gelation time t_g of silica gels has been determined experimentally in containers of different sizes. It is found that t_g is almost independent of the container size for gels prepared without a catalyst while it increases with the container size for gels prepared under basic catalysis. These results are explained by numerical simulations based on the recently developed fluctuating bond aggregation model which considers a possible cluster flexibility during the sol-gel process. Gelation under basic catalysis or without catalysis corresponds to small and large flexibility, respectively, in agreement with what is known on the corresponding aerogel structures.

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Gelation is an irreversible phenomenon which occurs when, due to the coagulation of some component up to macroscopic scale, a solution loses, at a given time, its flowing property. It is now well admitted that this is due to the appearence of an "infinite cluster" which starts to span the container from side to side [1]. Such an is apparent in a wide range of scientific areas such as physics, chemistry, biology, medicine, etc., and it may have some important technological applications. In particular, the "sol-gel" process, based on hydrolysis and polycondensation of metal alkoxides, is widely used to design aerogels, glasses, and ceramics [2]. If the chemistry of such a process is quite well understood, the fundamental physical mechanisms are still not completely known. Several complementary theories have been introduced, based either on the Smoluchowski equation [3] or on percolation concepts [1,4] and restricted to the kinetical or geometrical aspects, respectively. In the 1980s, the development of computer models, such as the diffusion-limited cluster-cluster aggregation (DLCA) model [5,6] which directly simulates the Brownian diffusive motion and irreversible sticking of rigid clusters, was able to conciliate these two approaches. The DLCA model, which was originally designed to describe the aggregation mechanism of colloidal particles, was shown to quantitatively account for the structural properties of silica aerogels prepared under basic catalysis [7]. The more tenuous and flexible polymeric structure of aerogels prepared without a catalyst was only recently accounted for by the fluctuating bond aggregation model (FBA) [8] which can be considered as an extension of the DLCA model including possible deformations of the clusters during the aggregation process. One fundamental aspect of the FBA model is that there exists a nonzero concentration threshold c_g below which the satisfaction of all intracluster bonding possibilities prevents the formation of a gelling network. Correlatively, for $c > c_g$, the gelation time (i.e., the time at which the infinite cluster is formed) t_g is well defined and does not depend on the size of the box used in the numerical simulation, in contrast with the original DLCA model where c_g vanishes and t_g diverges as the box size increases, as it was already pointed out ten years ago [9]. In other words the sol-gel transition in the FBA model is well defined in the thermodynamic limit while it is not in the DLCA model.

In this Letter, we show that these tricky theoretical predictions concerning the box size dependence of t_g are well observed in real sol-gel experiments performed with silicon alkoxides in containers of different sizes. While for base-catalyzed gels we find that t_g increases unambiguously with the container size, for neutrally reacted gels we find that t_g is almost independent of the container size. These experimental results are qualitatively well accounted for by numerical calculations performed on the FBA model by using a small, or large flexibility parameter in the basic or neutral cases, respectively, in reasonable agreement with what is known on the structures of these gels.

The gels were prepared by hydrolysis of tetramethoxysilane (TMOS) in ethyl-alcohol without using any catalyzer, or using a 0.05N ammonia-water solution, hereafter referred to as N or B cases, respectively. We used four moles of water solution per mole of TMOS and various amounts of alcohol. Each gel was prepared simultaneously in different glassy cylindrical containers of diameters 10, 14, and 32 mm. The containers were then hermetically closed and the gels were allowed to form either at room temperature in the B case, or at 45 °C in the N case (in order to reduce the reaction times). The criterion to determine t_g was the nonflow of the solution when the container was tilted. It might be argued that such an experimental procedure to estimate t_g is quite rough and empirical and could produce systematical errors (tilting the container may break the gel). However we have used, for all TMOS concentrations, the same procedure, systematically, and we have verified that the results were reproducible. We think that this method allows us to estimate t_g with a relative error $\Delta t_g/t_g \leq 0.1$, which includes both the difference between two successive measurements and the incertitude on the visual determination of the threshold. The amount of solution in each container was large enough so that the ratio volume/surface was rather independent of the height of solution. We checked that, in these conditions, t_g was independent of the height of solution within the experimental uncertainties. The experimental results are summarized in Fig. 1 where t_g has been plotted as a function of the TMOS volumic fraction ϕ for the different container sizes. While in case N the different curves are almost superimposed, in case B their differences are larger than the error bars and correspond to a net increase of t_g with the container size for all ϕ values.

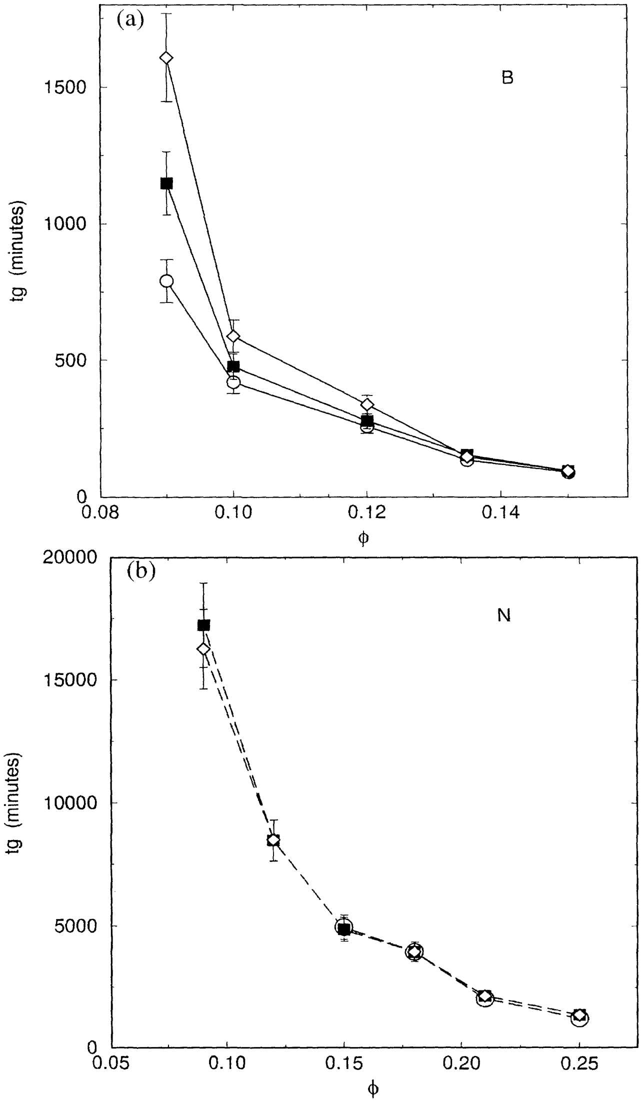

FIG. 1. Experimental dependence of the gel time t_g with the TMOS volumic fraction ϕ for different container sizes. Circles, squares, and diamonds correspond to container diameters of 10, 14, and 32 mm and cases (a) and (b) correspond to B and N gels, respectively.

The details of the FBA model were described earlier [8]. We recall that it is an extension (including aggregation) of the bond fluctuation algorithm which was first introduced to describe the equilibrium kinetics of linear polymers [10,11]. On a cubic lattice of unit length, limited to a cubic box of edge length L, "particles," assumed to be hard cubes of edge length 2, can move by successive unit jumps on the lattice (periodic boundary conditions are considered at the box edges). A bond is formed permanently as soon as two particles try to overlap and, after that, the bond length is limited between 2 and $\sqrt{10}$ (forbidding $\sqrt{8}$ to avoid bond crossings). As in the DLCA model, the numerical simulation starts with a collection of N randomly positioned particles in the box and, as time goes on, clusters of particles are irreversibly grown. In addition to L and N, two extra parameters are considered compared to DLCA, which are the cluster flexibility F and the particle connectivity f. For $F = 0$ the DLCA model (rigid clusters) is recovered while for $F = \infty$ the motion of a cluster is due to only a combination of the random movements of its particles. The parameter f fixes the total possible number of bonds per particles. Here we have taken $f = 4$ in agreement with the silicon coordinate. The procedure consists in choosing, at each Monte Carlo step, a cluster of n particles with probability P_n proportional to $[(1 + Fn)/(1 + F)]n^{\alpha}$ and deciding either to move it rigidly by one unit in a random direction, or to move one of its particles (chosen at random), with probabilities $Q_n = 1/(1 + Fn)$ and $1 - Q_n$, respectively. Such a choice ensures, for all F, a cluster mobility proportional to n^{α}, as in DLCA. Also we have taken $\alpha = -0.5$, in agreement with the resulting fractal dimension, of order 2, of the clusters. The physical time t is calculated by adding $\delta t = 1/\sum[(1 + Fn)/(1 + F)]n^{\alpha}$ at each iteration. The gel time t_g is reached when a "true" infinite cluster appears, i.e., a cluster which is self-connected through the periodic boundary conditions. In Fig. 2 we give the results for t_g, averaged over a large number of independent runs, as a function of the particle volumic fraction $c = 8N/L^3$, for three different box sizes $L = 30, 60, 120$. Cases (a) and (b) correspond to $F = 0.5$ and 125, respectively. While t_g increases with L for the small F value, it is almost L independent for the large F value. When analyzing more intensely the numerical results as a function of the parameter F, it turns out that the size effects do not appear suddenly after a threshold value of F. More likely there exists some crossover length L_c for the box size, above which the size effects disappear gradually and L_c tends to infinity as F tends to zero.

When comparing Figs. 1 and 2, the qualitative agreement between experiments and simulations turns out to be extremely good if one assigns the B and N cases to small and large flexibility, respectively. The experimental

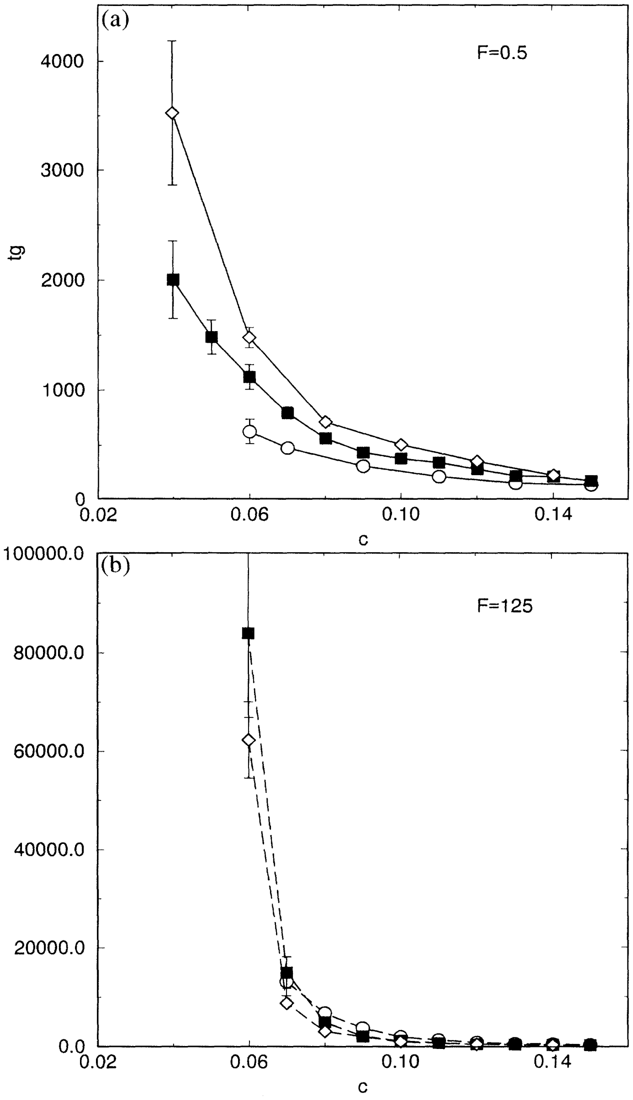

FIG. 2. Theoretical dependence of the gel time t_g with the volumic fraction of particles c calculated with the FBA model with $f = 4$ and different box sizes L. Circles, squares, and diamonds correspond to $L = 30, 60,$ and 120 and cases (a) and (b) correspond to $F = 0.5$ and 125, respectively. In case (a), t_g results from an average over 400, 250, and 80 runs and in case (b), over 400, 80 and 20 runs for $L = 30, 60,$ and 120, respectively.

decrease of the gel time with concentration in both B and N cases is recovered in the simulation and, even if one cannot compare quantitatively the simulation times to the real times, their relative values are larger in the N case compared to the B case in both simulations and experiments. But the main conclusion is that in both simulations and experiments the t_g vs concentration curves are almost independent of size in the N case while they correspond to an increase of t_g with the box (container) size in the B case. Moreover, the conclusion that the N and B cases would correspond to large and small flexibility, respectively, is in agreement with what is known from small angle neutron scattering experiments on the corresponding aerogels [12]: the aerogels formed under basic conditions are made of strongly bonded mesoscopic silica particles and are therefore certainly much more rigid than the ones prepared under neutral conditions which rather exhibit a tenuous and flexible polymeric structure [2,7]. However, due to the crudeness of the FBA model, it is excluded to go further and to try to obtain any quantitative fit. Neither the correspondence between ϕ and c nor the one between the container size and L is explicit. In particular, the experimental size ratio between the container and particle sizes is considerably larger than L. But one can understand that, as soon as it exists, the box size effect should persist on all lengths scales. The best quantitative way to compare the size effects would have been to perform a systematic finite size scaling analysis of both experimental and theoretical results. Unfortunately we do not have enough data available and the error bars are too large to be able to do it properly. Also to relate ϕ and c, one should assign some value to the "particle" size in the simulation. In real neutrally reacted gels, the cluster deformations are certainly not due to bond length variations but rather to free rotations around Si-O-Si bonds and bond angle deformations. As already argued in the case of linear polymers [11] the particles of the FBA model should be viewed, in a coarse-graining framework, as an ensemble of connected monomers whose precise size is difficult to estimate [13]. Another consequence is that the simulation time, whose unit corresponds to a time step of these particles Brownian motion, cannot be estimated either.

In conclusion, we have reported, for the first time, on an experimental dependence of gel time with the container size, at least for "rigid" gels. The important additional information contained in the present Letter is the striking similarity of the experimental results with computer simulations performed in the framework of a newly developed theoretical model. Moreover, these results are in agreement with previous conclusions [8] that the sol-gel transition of silica gels prepared without catalyst, whose characteristics are size independent, appears to be a "true" phase transition (well defined in the thermodynamic limit of an infinite system) in contrast with the case of base-catalyzed gels which are more rigid. A theoretical explanation might be that the rigidity of the bonds in the basic case inhibits configurations' fluctuations and therefore prevents the occurrence of a phase transition. But, even if the similitudes between experiments and simulations are strong enough, this physical explanation should not be considered as definitive unless all other possible explanations are not completely ruled out. For example, due to the mechanical contact between the weak gel and the container wall, some fractures might be created which can affect our experimental gel time value. Even if it is quite hard to understand why such an effect should depend so drastically on the pH of the solution during the gel preparation, we have planned further experiments to clarify this point. Another quite serious argument involves the chemical reactivity of the silica gel at the glass surface which is more important for basic aerogels and therefore might induce some size effects in that case [14]. This hypothesis has been tested by performing similar experiments in plastic containers (which are known to be less reactive) and we have also clearly seen a size effect for basic aerogels of the same order of magnitude as in glass containers. Many other arguments might be proposed and we are convinced that this Letter opens interesting perspectives for the future. Further experimental checks will be done to test our interpretation based on the FBA model. In particular, we intend to study the effect of temperature which should be more important when the flexibility is large. Also, there should exist a considerably larger well-defined nonzero concentration threshold c_g in the neutral case than in the basic case. But such an experimental test will be hard to be made convincingly since basic gels recover a quasipolymeric structure for very low TMOS concentrations.

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[13] In any case the particle size should be larger than the monomer size and this might explain why the same qualitative size effect is seen for a parameter L smaller than the actual container/monomer size ratio.
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