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Aggregation of model gels with directional interactions

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Abstract

We analyze connectivity and space-filling properties of colloidal gels obtained in a model with directional interactions. We compare gels formed upon slow cooling with the ones produced via quenching. The aggregation process is qualitatively different upon quenching: the cluster size distribution shows a percolation type of behavior but not the fully connected network achieved upon slow cooling. Because quenching favors the formation of defects, differently from systems where quenching tends to produce lower local connectivity and more open structures, here it favors instead more connected, but less space-filling, structures.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Disordered elastic solids (gels) can form via reversible aggregation in extremely diluted colloidal suspensions [1–5]. The idea that the arising of effective directional interactions is important for the formation of the network structure is finding, at present, more and more support: on the one hand, there are actually several possible sources of anisotropies, for example considering that often the building blocks of the gel are not the primary particles but larger aggregates of irregular shape [5]; on the other hand, the latest confocal microscopy images of these gel networks give evidence of a typical coordination number of 3–4, strongly supporting the scenario of locally rigid structures [6–8]. Another important issue is that, although obtained via reversible aggregation, gelation is usually the result of the overall arrest of the system due to the formation of the gel network and the gel morphology is found to strongly depend on the arrest conditions. In the case of more standard attractive effective interactions for colloidal systems, gelation can be obtained upon quenching the system in the spinodal region and the change in the morphology with the quenching protocol has been extensively investigated [9–11]. Sufficiently deep quenches are able, in these cases, to stabilize relatively open structures leading to gelation of the system. In general it is observed that deeper quenches are more effective in suppressing spatial correlations and therefore lead to thinner structures, more easily filling the space. Here we analyze the dependence on the arrest protocol in the case of directional interactions. We use the phenomenological model introduced in reference [12] for colloidal gels where the effective interaction potential contains, in addition to the usual attractive well of depth ϵ, a directional term which introduces a local rigidity. In [12, 13] the gelation has been studied via molecular dynamics simulations upon slow cooling samples of 8000 particles at temperatures from $T = 1.0$ down to $T = 0.05$ (in units of ϵ/k_B), at densities $0.05 \leqslant \rho \leqslant 0.15$. At low temperature the particles are linked by long-living bonds and form an open spanning network via a random percolation process which has a distinctive feature: once a percolating structure is formed, this rapidly evolves towards a persistent, fully connected open network. The structure of the gel network is relatively simple: it is made of interconnected chains of particles. Because of that, the connection between dynamics and structural features can be effectively investigated. The formation of the persistent network, in fact, produces the coexistence in the gel of very different relaxation processes at different length scales and the network nodes, i.e. the parts of the structure which are crucial to the mechanical stability, are involved in slow cooperative processes [13, 14]. We now investigate the case in which the gelation is obtained upon rapidly quenching the initial samples, equilibrated at high temperature, down to temperatures where gelation is observed in the case of slow cooling ($T < 0.05$). We find that quenching leads to gels whose structure is still made of chains connected by nodes, but it favors the formation of extended structures which are locally more connected and less efficient in space-filling. This effect is enhanced in deeper quenches.

2. Model and numerical simulations

The model consist of particles of radius σ, interacting via the potential V_{eff} [13], which includes three different terms.

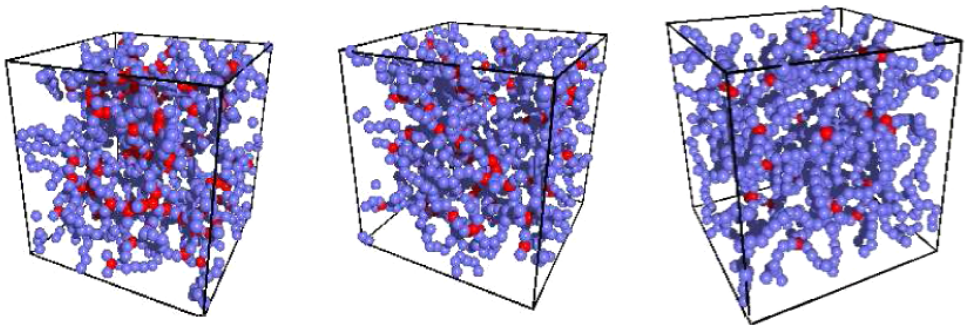

Figure 1. Snapshot of the system for $t_w = 10^6$ MD steps for the quenches at $T = 0.02$ and 0.04, and for the slow cooling (from left to right).

The first is an interparticle attraction, given by a Lennard-Jones-like potential with a narrow well of depth ϵ. An additional soft-sphere repulsion is modulated by a geometric term, which reduces the attractive Lennard-Jones well unless particles are in specific relative configurations. To define such configurations the particles are decorated with *sticky* points: two bonded particles will be subjected to the full attraction if they touch in correspondence of such points and a reduced attraction (i.e. 20%ϵ) otherwise. The *sticky* points are 12 patches located on the vertices of the icosahedron inscribed in the sphere of diameter σ and centered on the particle position. Having 12 points allows us to define the favored bonding configurations without imposing a local maximum connectivity to the particles: for example, the choice of 3 or 4 points would anyway lead to the formation of an open network interfering with the effect of directionality which is more appropriate for the physics of these systems. This directional term alone is not able to effectively limit the functionality of the particles at the volume fraction and temperatures considered here [13]. Therefore the third term in $V_{\rm eff}$ is a three-body interaction which imposes an angular rigidity to bonds, making the angle among three neighboring particles unlikely to be smaller than 0.4π. This angular repulsion is sufficiently strong to limit, at low volume fractions, the effective functionality of the particles when the aggregation process starts at temperatures $T \approx 0.1\epsilon/k_B$. $V_{\rm eff}$ was implemented in a constrained molecular dynamics code to perform micro-canonical simulations, using a suitable combination of the algorithms RATTLE and SHAKE [15].

The analysis of the structures obtained upon slowly cooling systems at volume fractions $\phi \approx 0.025$–0.075 [12, 13] shows that the chains are locally stable structures, which optimize the interparticle interactions, whereas the formation of the nodes of the network is controlled by long-range correlations arising between the chain-like aggregates, and increasing with the volume fraction. Within this picture, the nodes could be seen as *defects* which form in the aggregation process at finite temperature and dilution: once a spanning network is formed, large scale rearrangements become too slow to allow for their annihilation. Here we want to investigate how the structural features of this type of gels can change when the gelation is the result of a rapid quench of the system. This might be, in fact, considered as closer to experimental conditions (for example, when the depletant is added to the suspension). For the work discussed here, we have therefore performed molecular dynamics simulations where the samples, initially equilibrated at $T = 1.0$, are then quenched at low temperature, i.e. below $T = 0.05$. The quench at the final temperature T_q is done by rescaling all the particle velocities to T_q; after that, the temperature is controlled by coupling the system to a heat bath throughout the simulation with a variant of Andersen's thermostat [15]: we assign all particles random velocities extracted from a Gaussian distribution of variance $\sqrt{k_B T/m}$ every Δ time steps. Δ has been varied and chosen so that the velocities reach thermal equilibrium before significant structural rearrangements take place. We have considered 5 independently generated samples of 8000 particles at density 0.1, i.e. in a simulation box of linear size $L = 43.09$ (in units of particle diameter), corresponding to an estimated volume fraction $\phi = 0.05$. As usual, in the simulations time is measured in units of $\sqrt{m\sigma^2/\epsilon}$, with σ the particle diameter and m the particle mass. At $t = 0$, we perform two different quenches from $T = 1$ to respectively $T_q = 0.02$ and $T_q = 0.04$; the evolution of the system at constant temperature is then monitored during 10^6 MD steps. For each sample, we have run different numerical experiments, starting respectively at $t_w = 0, 10^2, 10^3, 10^4, 10^5$ and 10^6 MD steps after the quench.

The configurations quenched at the final temperature T_q are compared here to the ones obtained by slowly cooling the system down to $T = 0.05$ [12]: starting from initial high temperature random configurations, the system was equilibrated at several intermediate temperatures using the same type of thermostat, where Δ was suitably varied with temperature from 10 to 10^3 MD steps. In this case we checked that after equilibration the energy was constant, showing no significant drift over the simulation time window. We monitored independently translational and rotational contributions to kinetic energy. Finally, we verified that different one- and two-time autocorrelation functions had reached the equilibrium behavior, i.e. did not age. The slow cooling down to $T = 0.05$ leads to a fully developed gel network involving more than 97% of the particles. In this model at $\phi = 0.05$ gelation takes place at temperatures at which phase separation does not occur: large scale spatial correlations (measured via the static structure factor) do not show the strong intensity peak at the lowest wavevectors which is typical of phase separation, in the whole range of temperatures investigated [13].

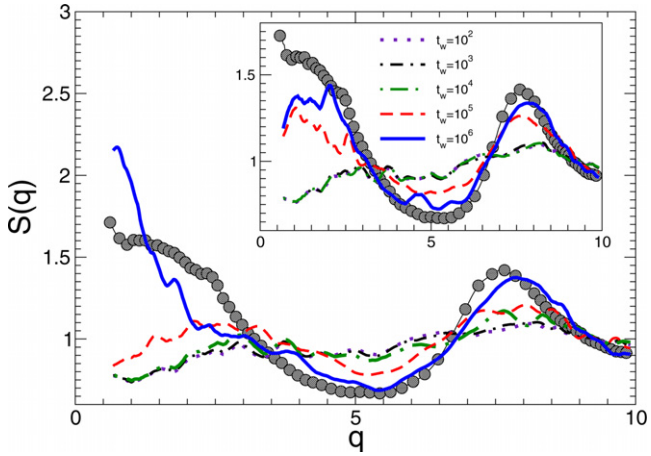

Figure 2. Structure factor calculated at different waiting times for the quench at $T = 0.02$ (main frame) and $T = 0.04$ (inset). The dark circles correspond to $S(q)$ obtained by slow cooling at $T = 0.05$.

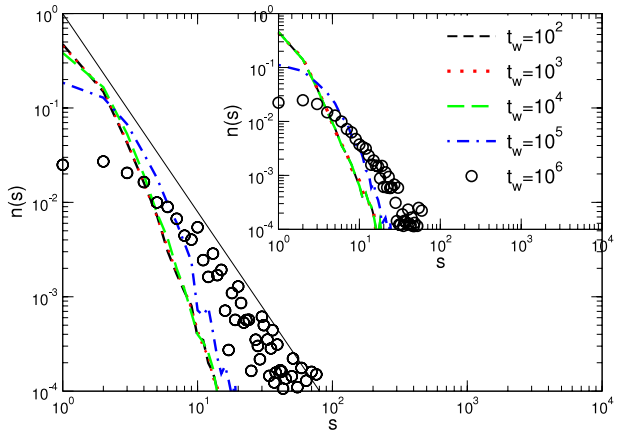

Figure 3. Cluster size distribution for the systems obtained via quenching at $T = 0.02$ (main frame) and $T = 0.04$ (inset). The continuum line is the random percolation behavior $s^{-2.2}$.

Figure 1 shows three snapshots obtained at the end of a simulation run, respectively in the cases ($T_q = 0.02$, $t_w = 10^6$ MD steps), ($T_q = 0.04$, $t_w = 10^6$ MD steps) and slow cooling, which show qualitative differences. In the following, we quantitatively characterize them and discuss the dependence of the structures obtained on t_w and T_q.

3. Spatial correlations

At the end of each run we calculate the static structure factor averaged over the different samples prepared in the same conditions:

$$S(q) = \frac{1}{N} \sum_{ij} \left(e^{i\mathbf{q}\cdot(\mathbf{r}_i - \mathbf{r}_j)} \right) \quad (1)$$

where the values of the modulus of the wavevector q considered are the ones compatible with the periodic boundary conditions. In figure 2 $S(q)$ is plotted as a function of q for different waiting times t_w for the quench at $T_q = 0.02$ (main frame) and $T = 0.04$ (inset). $S(q)$ for the gel obtained by slow cooling at $T = 0.05$ is also shown for comparison. Upon increasing the waiting time, for $t_w \geqslant 10^5$ MD steps the structure factor displays an enhancement of spatial correlations at low wavevectors, indicating the presence of important structuring, but without the typical features of phase separation (i.e. a much faster growing peak at the lowest wavevectors). The patterns obtained for $S(q)$ differ qualitatively from the ones observed with the slow cooling and, at sufficiently long t_w, show a strong dependence on T_q. In particular, for a deeper quench the peak at low q moves to lower values and the signal is stronger, indicating that such correlations involve a larger number of particles. This tendency is the opposite of what is usually found in the arrested phase separation of attractive systems with isotropic interactions, where a deeper quench will interfere more with the phase separation and reduce instead the extent of the associated density fluctuations [10].

4. Clusters and connectivity

We define clusters of particles which are neighbors within the range of the attractive well and, at the end of each run, we calculate the cluster size distribution $n(s)$ (with s the cluster size). The results are plotted in figure 3: for both T_q considered here, $n(s)$ does change with t_w, although a qualitative change is only observed for $t_w > 10^5$ MD steps. Here the cluster size distribution significantly widens and starts to display a power law tail, indicating the presence of a percolating regime [16]. It is interesting to notice that, although a random percolation process characterizes the gelation upon slow cooling as well, this aggregation process is quantitatively different. In the case of the slow cooling, in fact, the percolation process rapidly evolves toward large structures in which all the particles are connected. In the quenched gelation, instead, the percolation regime, at least in the time window investigated in the simulations, does not produce clusters of size larger than 100 particles. These findings suggest the presence of structures which are locally denser and less efficient in filling the space. Let us now investigate more the local features of the quenched structures, via the fraction $c(n)$ of particles that have n neighbors: this quantity gives information on the topology of the structures formed. In figure 4 (left) we plot $c(n)$ for $n = 0, 1, 2, 3$ at the start of the simulation as a function of the waiting time. As in the study performed via slow cooling, at this volume fraction there are no particles with $n = 4$. In the right panel we have plotted, for comparison, $c(n)$ obtained in the slow cooling study as a function of the inverse temperature $1/T$. The change of the topology upon increasing the waiting time, in fact, has some interesting analogies with the aggregation upon slowly lowering the temperature: the fraction of free particles ($n = 0$) strongly decreases, whereas the fraction of particles with $n = 2$ neighbors (*chains*) and $n = 3$ (*nodes*) increase. Therefore the structuring of the quenched system with t_w leads to a structure with the same basic ingredients, although qualitatively different, as the snapshots in figure 1 show. In fact, figure 3 also indicates that the structuring upon quench is

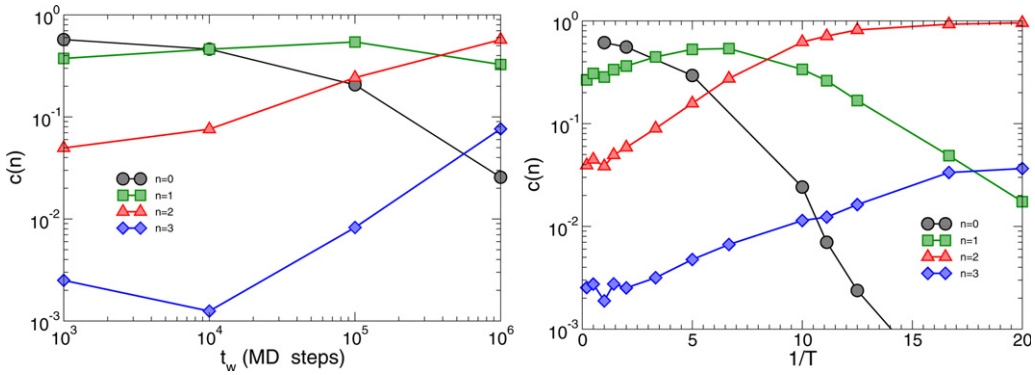

Figure 4. Left: coordination number $c(n)$ as a function of t_w obtained upon quenching to $T = 0.02$. Right: $c(n)$ calculated in the study where the gelation is obtained upon slow cooling.

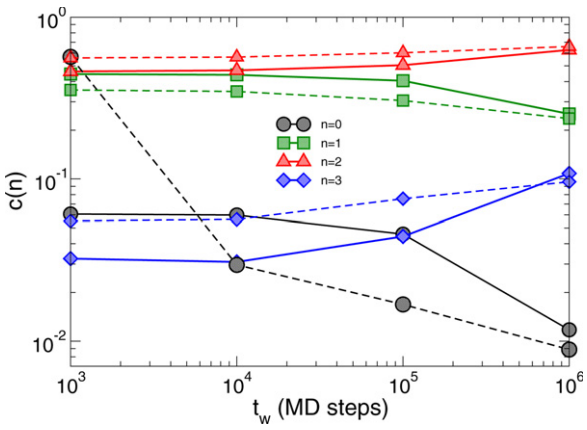

Figure 5. Coordination number $c(n)$ as a function of t_w. Data points connected by continuum and dashed lines respectively refer to $T_q = 0.02$ and $T = 0.04$.

less efficient: it corresponds to a comparatively larger fraction of free particles and does not lead, at least within the timescale of the numerical experiment, to a fully connected network to which all the particles belong. Interestingly, this corresponds, in this case, to structures which are locally more connected: the fraction of nodes is comparatively higher. For $t_w > 10^6$ MD steps, i.e. beyond our simulation time window, we would expect, in principle, the topology to slowly evolve towards the one obtained upon slow cooling. For the longest waiting time considered here, hardly any bond-breaking is observed over the simulation time window and the decay of time correlations at low wavevectors is much slower than exponential. Finally, in figure 5 we plot $c(n)$ calculated instead at the end of the run as a function of t_w: here we compare the case of $T_q = 0.02$ (continuum line) to the case $T_q = 0.04$ (dashed line): the data indicate that the deeper the quench, the less efficient the structuring is in recruiting particles. The quench at $T = 0.04$ indicate values of $c(n)$ closer to the structure obtained upon slow cooling. For $t_w = 10^6$ MD steps, anyway, the topology as described by $c(n)$ does not significantly change with T_q, the main difference being the larger amount of free particles and of nodes for a deeper quench. Both can be seen as *defects* as compared to the aggregation process upon slow cooling.

5. Conclusions

We have studied the structuring after quench in a model for colloidal gels where directional effective interactions introduce a local rigidity. This limits the effective functionality of the particles in the gelation process. The results obtained show that the topology change of the system upon structuring produces the formation of chains connected by nodes, similar to the structuring obtained upon slow cooling. On the other hand, the structuring after quench is much less effective in recruiting particles in the structure. The cluster size distribution shows a significant widening and a percolation regime, but for comparatively smaller clusters. Interestingly, these features correspond to structures which are locally more connected, due to a higher presence of nodes. The space filling of the structures obtained upon quenching is therefore reduced. This is the opposite of what is typically observed in quenched isotropic systems. The observations reported here should also have a relevance for the mechanical response of the system and a separate study is currently in progress.

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