Structure and Relaxation Dynamics of a Colloidal Gel

Emanuela Del Gado¹ and Walter Kob²

¹ Dip. di Scienze Fisiche, Università di Napoli “Federico II”, 80125 Napoli, Italy
² Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier 2, 34095 Montpellier, France

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Abstract. – Using molecular dynamics computer simulations we investigate the structural and dynamical properties of a simple model for a colloidal gel at low volume fraction. We find that at low $T$ the system is forming an open percolating cluster, without any sign of a phase separation. The nature of the relaxation dynamics strongly depends on the length scale/wave-vector considered and can be directly related to the geometrical properties of the spanning cluster.

Gels are ubiquitous in daily life, biology, as well as technological applications. Like glass-forming systems, they are disordered and have slow and non-trivial relaxation |1, 2|. On the other hand, they are characterized by open spanning structures |3| and hence have a volume fraction $\phi$ that is significantly smaller than unity. To what extent the structural properties are related to the dynamical properties and what mechanism is responsible for the complex dynamics of these systems, are important questions to which so far no clear answer has been given. In particular, in view of the different nature of the various gels (colloidal gels, chemical gels, etc.), it is not evident at all that there are indeed unique answers.

In view of this variety it is not surprising that in the past various mechanisms for the complex dynamics of gels have been proposed, such as the occurrence of a percolation transition, the jamming of preformed clusters, the arrested dynamics of a phase separating system, and others |4|–|9|. Progress has also been hampered by the fact that there are so far very few microscopic realistic models for gels that allow to investigate these systems (in equilibrium!) by means of analytical methods or computer simulations. In this letter we present a simple model where the gel formation is entirely due to the interparticle interaction and that does indeed have the characteristics of (colloidal) gel-forming systems at a finite temperature. Subsequently we use the results on the structural and dynamical properties of this system to shed some light on the mechanism that is responsible for the slow dynamics in these systems.

The model investigated consists of identical particles of radius $\sigma$ that interact via an effective potential $V_{\text{eff}}$ that is the sum of a two- and three body terms. The two body potential is itself the sum of a hard core like interaction that is given by a generalized Lennard-Jones potential, $V_{\text{LJ}}(r)$, and a term $V_{\text{cp}}$ that depends on the relative orientation of the particles. For the radial term we have used $V_{\text{LJ}}(r) = 23\epsilon[(\sigma/r)^{18} - (\sigma/r)^{16}]$ where the prefactors and exponents have been chosen in such a way to give a relatively narrow well of depth $\epsilon = 1.0$ and width $0.2\sigma$. In the following we will measure length and energy in units such that $\sigma = 0.922$
and $\epsilon = 1$, respectively, and time in units of $\sqrt{m\sigma^2/\epsilon}$, where $m$ is the mass of a particle. A system with purely radial interaction is prone to undergo a phase separation [7]-[9] and is therefore not a good model for a gel forming system. In fact, colloidal particles are seldom uniform and smooth and in particular, their roughness can produce quite rigid links between them [10]. Actually the observation of equilibrium open structures [3] strongly suggests an effective three body potential that favors the creation of an open network structure, as also recently measured [11]. In our case we have introduced such an interaction by decorating each particle with 12 points that form a rigid icosahedron of radius $1.1\sigma$. The potential $V_{cp}$ between a particle #1 and a particle #2 is then set up in such a way that it is more favorable that the center of particle #1 approaches particle #2 in the direction of one of the points of the icosahedron that decorate particle #2. In addition we have also included an explicit (short range) three body potential $V_3$ in the form of a gaussian in the angle $\theta$ between three neighboring particles and which makes that values of $\theta$ smaller than $0.4\pi$ are unlikely. More details on these potentials will be given elsewhere [12]. In the proposed model the (meso) particles can form directional bonds that favor the formation of an open network structure, without, however, imposing a local symmetry or connectivity, in contrast to models that have been proposed before [6,13].

We have done microcanonical simulations of this model using constrained molecular dynamics with the SHAKE algorithm [14] with a step size of 0.002. The number of particles was 8000 and the size of the simulation box $L = 43.09$ which gives a volume fraction of 0.05. (This corresponds to a particle density of 0.1.) Before starting the production runs we carefully equilibrated the system by monitoring that the relevant time correlation functions have attained their asymptotic limit [12]. The temperatures investigated were 5.0, 2.0, 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, 0.09, 0.08, 0.06, and 0.05. In order to improve the statistics of the results we have averaged them over five independent runs.

In Fig. 1 we show the static structure factor for all temperatures investigated. We see that at high $T$ this function is relatively flat, thus showing that the system has a structure that is similar to the one of a gas of free particles. At around $T = 0.1$ $S(q)$ starts to show a peak at $q_0 = 7.7$, a wave-vector which corresponds to the distance between two nearest neighbor particles. In addition $S(q)$ shows at small $q$ an increase which indicates the formation of a disordered open network structure. In fact this increase is relatively moderate and does not strongly depend on $T$, giving evidence that the system does not undergo a phase separation even at the lowest temperatures considered. Furthermore $S(q)$ does not show any pronounced
Fig. 2 – Part of a configuration, a cube with side $L/2$, of the system at $T = 0.05$. The light and dark particles have coordination $n = 2$ and $n = 3$, respectively.

peak at these low wave-vectors and thus we can conclude that the network is disordered and does not have a well defined length scale. The appearance of the peak at $q_0 = 7.7$ is due to the fact that at intermediate and low $T$ the particles condensate into clusters that quickly grow and form at sufficiently low $T$ a percolating cluster. A snapshot of a configuration at low $T$ is shown in Fig. 2. This figure clearly demonstrates that at low temperatures the typical configurations are an open network in which most particles are forming chains (light spheres) that are connected in a relatively random way at points that have three or more neighbors (dark spheres).

The change of the topology of the structure with decreasing $T$ can be characterized by investigating the coordination number $c(n)$, which is shown in the inset of Fig. 1. We define $c(n)$ as the fraction of particles that have exactly $n$ neighbors. (Two particles are considered to be neighbors if their distance is less that $r_{\text{min}}=1.1$, the location of the first minimum in the radial distribution function.) We see that at high temperatures the vast majority of the particles are isolated, $n = 0$ (not shown), and that the fraction of dimers, $n = 1$, is around 30%. With decreasing $T$ this fraction increases, attains at around $T = 0.15$ a maximum, and then quickly decreases with decreasing $T$. Thus we can conclude that at low $T$ the number of free particles as well as the number of dimers (or chains ends) is very small. At the same time the number of particles that have exactly two nearest neighbors increases rapidly and these (local) configurations become by far the most prevalent ones at low $T$. Last not least also the number of particles with $n = 3$ neighbors increases quickly with decreasing $T$. From these curves we thus can conclude that with decreasing $T$ the system forms an open network in which most particles form chains that meet at points with coordination number three and which are important for the mechanical properties of the structure. Since on large length scales this structure is quite homogeneous, $S(q)$ does not show a very pronounced increase at small $q$, i.e. the compressibility of the system is relatively large but finite, in agreement with the experimental results of gel-forming systems [3]. Note that the curve for coordination $n = 3$ starts, at the lowest temperature, to become flat, i.e. the number of particles that are relevant for the size of the mesh of the network becomes independent of $T$. From this we can conclude that, at low $T$, this mesh size, and hence the overall structure, will only be a weak function of $T$, in agreement with the result shown in Fig. 1 (main panel) and experiments [3].
it must be expected that the asymptotic value of \( c(n = 3) \) depends on the concentration of the particles in that the concentration of points of connectivity three decreases with decreasing volume fraction.

In order to characterize the structure of the system on a large length scale it is useful to investigate \( n(s) \), the number of clusters that have exactly \( s \) particles. (We define that a particle belongs to a cluster if its distance from at least one member of the cluster is less than \( r_{\text{min}} \).) This distribution is shown in Fig. 3 for all temperature investigated. For \( T \geq 0.3 \) the distribution nicely follows an exponential law (see inset), a behavior that corresponds to the random formation of transient clusters of non-bonded particles at low densities. For the system size considered the largest of such clusters found is around 15 particles, i.e. relatively small. At \( T = 0.1 \) the shape of the distribution has strongly changed in that now the most probable clusters have size \( s = 2 \). At the same time \( n(s) \) has grown a tail at large \( s \) in that the largest clusters found have now \( O(100) \) particles. At lower temperatures, \( n(s) \) crosses over to a power law regime for high values of \( s \), with a crossover point that moves to larger \( s \) with decreasing \( T \). At \( T = 0.06 \) this regime is apparently compatible with an exponent around \(-2.2\) (main plot in Fig. 3), corresponding to random percolation [15]. At the lowest temperatures, \( T \leq 0.06 \), the distribution shows a gap at large \( s \) in that the system can form one big cluster that contains a substantial fraction (more than 70%) of the particles in the system. Finally at \( T = 0.05 \) we have only very few particles that are members of small clusters, with an \( n(s) \) that is basically a constant, whereas the overwhelming majority of the particles belongs to one large percolating cluster. Hence, at very low temperatures the distribution \( n(s) \) is basically a constant since it is energetically very unfavorable to have small free clusters. (Note that the value of this “constant” decreases very rapidly with decreasing \( T \), see Fig. 3.) These distributions show that for this system the formation of the gel is intimately connected to the formation of a percolating cluster [5, 6].

Having characterized the structure of the system, we now turn our attention to its dynamical properties. In view of the open network structure of the system at low temperatures, it is of interest to investigate the lifetime of a bond between two neighboring particles [12] at intermediate and low temperatures. For this we have determined \( C_b(t) \), the probability that
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Fig. 4 – Arrhenius plot of the diffusion constant $D$ and of the relaxation time $\tau_s(q,T)$ as determined from the self-intermediate scattering function $F_s(q,t)$. The solid line is a fit to the high $T$ data for $q = 3.0$ of the form $\tau \propto T$.

a bond that exists at time zero is still present at time $t$. We have found that the resulting $C_b(t)$ are well described by an exponential with a relaxation time that shows an Arrhenius dependence. At low $T$ ($T < 0.1$) this is the longest relaxation time in the system. As in Fig. 2 we make the distinction of bonds that are connected to particles that have a coordination number of three (let’s call them “anchor particles”) from the bonds that are connected to particles that have a coordination number of two (“bridging particles”), and find that the lifetime of the former bonds is around a factor of 20 smaller than the one of the latter, but the $T^{-dependence}$ is the same. This result is reasonable since the anchor particles experience on average more mechanical stress than the bridging particles and, due to their higher coordination, have less possibilities to yield to this stress. Hence it is more likely that their bonds are broken. Therefore one can envision the relaxation process in this system that the connecting branches of the network detach from the anchor particles, the branch reorients and attaches itself to a different branch, thus creating a new anchor point. (However, the possibility that a branch breaks at a bridging particle can not be neglected completely since there are significantly more bridging particles than anchor particles. Thus this type of motion will contribute to the relaxation dynamics as well.)

In order to understand the role of the diffusive behavior of the particles, we have determined the mean-squared displacement of a tagged particle, $\langle r^2(t) \rangle = \langle |r_j(t) - r_j(0)|^2 \rangle$, which for high $T$ shows at early times a ballistic behavior and at long times a diffusive one [12]. From this function we used the Einstein relation to obtain the diffusion constant $D(T)$. Furthermore we have calculated the self-intermediate scattering function $F_s(q,t)$ for wave-vector $q$, $F_s(q,t) = N^{-1} \sum_{j=1}^{N} \langle \exp[iq \cdot (r_j(t) - r_j(0))] \rangle$. The discussion of the quite complex $q$ and $T$ dependence of $\langle r^2(t) \rangle$ and $F_s(q,t)$, characteristic for a gel-forming system, will be presented elsewhere [12] and here we focus only on the $T$–dependence of $D$ and the relaxation time $\tau$. The latter quantity has been obtained by calculating the area under $F_s(q,t)$. Figure 4 is an Arrhenius plot of $\tau_s(q,T)$ for intermediate and small wave-vectors. From the figure we recognize that at high $T$ the relaxation time follows for all $q$ a $T^{-0.5}$–dependence which can be easily understood from the ballistic motion of the free particles and the small clusters. (Recall that in this $T$–range the distribution of the cluster size is independent of $T$, see Fig. 3). For wave-vectors that are large, $q \geq 2.0$, the $T$–dependence of $\tau$ at low temperatures is relatively weak but still somewhat...
stronger than $T^{-0.5}$. This can be understood by realizing that on the corresponding length scales the particles can still undergo an (almost) ballistic motion, despite the fact that they are, at low $T$, connected to other particles, since the whole local structure is moving ballistically. This type of motion is no longer possible if one considers length scales that become comparable to the size of the mesh of the network which is around 10 and thus corresponds to a $q$ smaller than 1.0. For $q = 0.55$ we find at low temperatures a $T$-dependence of $\tau$ that is close to an Arrhenius law whereas for smaller wave-vectors we find an even stronger $T$-dependence. On length scales that are thus comparable or larger than the typical mesh size of the network the $T$-dependence is thus very similar to the one characterizing the slow dynamics of dense glasses. Finally we mention that wave-vectors around or larger than $q_0$ are not very relevant for the slow dynamics of this system [7], in strong contrast to usual glass-forming systems that are at much higher volume fraction.

Also included in Fig. 4 is the inverse of the diffusion constant $D$, scaled by a factor $A = 49.2$ in order to make it coincide with the value of $\tau_s(q = 0.14, T = 1.0)$. We find that in the whole $T$-range investigated this quantity follows very closely the $T$-dependence of $\tau_s(q, T)$ for small $q$, which is evidence that in this system the relaxation of the structure is closely linked to the diffusive motion of the particles, in contrast to the behavior found in dense glass-forming systems in which the $T$-dependence of $D$ is weaker than the one of $\tau_s$ [16]. This is due to the fact that here at the lowest temperatures nearly all the particles belong to the network, as discussed above. It is also interesting to notice that at low temperatures the mean-squared displacement $\langle r^2(t) \rangle$ shows at intermediate times a small shoulder which is the signature of a (weak) caging effect with a localization length around 0.2 [12], that is similar to the value found in dense glasses. In contrast to these systems we find that at later times $\langle r^2(t) \rangle$ shows a pronounced second plateau with a localization length around 10, a value which is comparable to the mesh size. Thus we see that in this system the effective cages for the particles are significantly larger than the interparticle distances, a characteristics of a “soft matter” system.

In summary we have presented a new realistic model for gel forming systems. In particular this model has the advantage to allow the investigation of such systems even at very low volume fractions and in equilibrium. The presented results show that the dynamics become already glassy before the phase separation starts, i.e. the occurrence of the gel is not necessarily connected to the presence of an impeded phase separation [8,9]. Here the gel is related to the formation of ramified clusters that grow with decreasing $T$ and therefore connect to each other to form a percolating network in which the anchor points are connected by flexible branches. Since these clusters form and dissociate quite easily, it is not clear whether a description of the gel-forming process in terms of a jamming of clusters [4] is appropriate, since the clusters completely integrate into the network and thus loose their identity faster than the time scale of the relaxation time of the system.

It is evident that the anchor points are very important for the mechanical stability of the structure. On length scales of the order of the interparticle distance the structure is quite flexible whereas on the scale of the mesh size of the network, which is given by the typical distance between the anchor points, the structure becomes somewhat more rigid due to the constrains imposed by the enhanced connectivity. However, even on that length scale the system is relatively soft as compared to the one found in dense glasses. With decreasing temperature the connecting chains will become stiffer and hence give rise to an increased effective interaction between the anchor points. The mode-coupling theory of the glass transition [17] proposes a mechanism that is able to rationalize why a small change in the coupling strength, in our case the effective interaction between the anchor points due to the connecting chains, gives rise to a very strong change in the relaxation time and non-exponential relaxation. Note
that in our case the mechanism which produces the coupling enhancement of the effective interaction is due to the presence of the percolating open network, which connects the particles over different length scales. Thus it is reasonable to assume that the super-Arrhenius dependence of $\tau_s(q,T)$ for wave-vectors corresponding to the length scale of the mesh size, see Fig. 4, is related to the increased coupling between the anchor points, an interaction that is transmitted by the connecting chains of the network through its structure, and that this mechanism is also the explanation for the strongly non-exponential relaxation dynamics [12].

Last not least we mention that since the lifetime of the bonds shows only an Arrhenius dependence, it can be expected that at sufficiently low temperatures the relaxation times of the system will also show an Arrhenius dependence. This suggests that the system does not show a real dynamical arrest at any finite temperature, in agreement with the experimental findings [2] and in strong contrast to the more dense glasses for which an apparent dynamical singularity is found at a finite temperature.

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