Structural Relaxation of a Gel Modeled by Three Body Interactions

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We report a molecular dynamics simulation study of a model gel whose interaction potential is obtained by modifying the three body Stillinger-Weber model potential for silicon. The modification reduces the average coordination number, and suppresses the liquid-gas phase coexistence curve. The low density, low temperature equilibrium gel that can thus form exhibits interesting dynamical behavior, including compressed exponential relaxation of density correlations. We show that motion responsible for such relaxation has ballistic character, and arises from the motion of chain segments in the gel without the restructuring of the gel network.

Gels are low density disordered networks of interacting molecules that are structurally arrested and capable of sustaining weak stresses. They are ubiquitous in nature and among man-made materials and are composed of a diverse range of materials such as polymers, silica, or colloidal particles. Depending on the life time of the bonds between the basic units of the network, they can either be chemical gels, or reversible, physical gels, the latter displaying complex dynamics. In particular, colloidal gel formers exhibit intricate dynamic behavior in equilibrium, as well as in nonequilibrium aging conditions, can form arrested states, and have been the subject of a considerable number of experimental, theoretical and simulation studies \cite{ref1, ref2, ref3, ref4, ref5, ref6, ref7, ref8, ref9, ref10, ref11, ref12, ref13, ref14, ref15, ref16, ref17, ref18, ref19, ref20}.

One reason for the interest in colloidal gels is that these systems permit access to the glassy state via several mechanisms: Cluster aggregation \cite{ref3, ref19}, structural arrest in the dense phase following phase separation \cite{ref11, ref14}, or crossing of a glass transition line from an equilibrium fluid to an arrested state \cite{ref8, ref15}. For the occurrence of this latter scenario it is necessary that upon cooling the system does not enter the liquid-gas coexistence region \cite{ref8, ref10, ref11, ref13, ref21}, i.e. one seeks systems for which the coexistence region is at low temperatures, $T$, and densities, $\rho$. One possibility to achieve this is to choose a “maximum valency" interaction, in which each particle can interact only with a restricted (small) number of particles \cite{ref8, ref10, ref11}. In the following we will show that a very simple model involving three body interactions is also able to generate a coexistence region that is located at low $T$ and $\rho$ and which therefore allows one to probe easily the interplay of phase transformations and dynamics in molecular dynamics simulations in such systems.

A further intriguing property of colloidal gels is the fact that their relaxation dynamics can be compressed \cite{ref4, ref6}, i.e. the time correlation functions decay faster than an exponential, in stark contrast to structural glasses at higher densities for which one usually finds a stretched exponential relaxation. The microscopic origin of this fast relaxation is not well understood, and various mechanisms have been proposed to explain it \cite{ref2, ref17, ref20}. We present analysis that shows that for our model, compressed exponential relaxation arises from the ballistic motion of chain segments in the gel without restructuring the gel network.

The model we consider is a modification of the potential proposed by Stillinger and Weber (SW) for the description of silicon \cite{ref22}. Particles interact via a sum of two and three body interaction terms, $v = v_2(r) + \lambda v_3(r, \theta)$ \cite{ref23}, where $r$ denotes interparticle distances and $\theta$ the angle formed by three particles. $\lambda$ determines the strength of the three body interaction which depends on the angle $\theta$ via a term proportional to $(\cos \theta + \alpha)^2$ with $\alpha$ determining the most preferred angle. Thus by varying $\lambda$ \cite{ref24} and $\alpha$ we can tune the locally preferred arrangement of the particles.

We have performed constant temperature, volume molecular dynamics (MD) simulations (using a constraint that conserves kinetic energy) with 4000 particles, using the method proposed in \cite{ref25, ref26, ref27} to efficiently compute three body interactions. Gibbs-Ensemble-Monte-Carlo (GEMC) simulations \cite{ref28} are performed to obtain liquid-gas coexistence curves have been performed with 2000 particles. All results are reported in reduced units for the Stillinger-Weber potential \cite{ref22}.

Figure 1 shows the coexistence curves obtained for various combinations of $\lambda$ and $\alpha$. We see that with increasing $\lambda$ or $\alpha$, liquid-gas phase coexistence gets shifted to smaller temperature and density ranges, analogous to the observations in \cite{ref8, ref10, ref11}. In the following we will fix $\lambda = 10.0$ and $\alpha = 1.49$. For this choice the structure of the system at low $T$ and $\rho$ is given by quasi-one-dimensional chains of particles, interconnected by three coordinated junctions. At low $T$ bond breaking becomes extremely difficult and consequently a reliable estimate of the coexistence curve via GEMC is no longer possible. Based on MD runs where we observe signatures of phase separation, we indicate in Fig. 1 the region where we expect phase separation (shaded area). Also included
in the graph is the percolation line which indicates the density and temperature range (to the lower right of the percolation line) where we may expect gel-like structural arrested states. (The bend in the percolation line at low temperature is due to phase separation [27].) In the following we will study the relaxation dynamics of the system for \( \rho = 0.06 \) and from Fig. 1 it is clear that at this density phase separation will not play a role.

In order to characterize the relaxation dynamics of the system we consider the normalized collective, and self intermediate scattering functions, defined as \( F(k, t) = S(k)^{-1} \sum_j \langle \exp[-i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \rangle \), where \( S(k) \) is the static structure factor, and \( F_s(k, T) = N^{-1} \sum_j \langle \exp[-i\mathbf{k} \cdot \mathbf{r}_j(0)] \rangle \), respectively. The time dependence of these correlators is shown, in semi-log plots, in Fig. 2 for the low temperature \( T = 0.03 \), i.e. well below the percolation line, and various values of the wave-vector \( k \). At this \( T \) the relaxation dynamics of the system is already very sluggish and hence we deal here indeed with a glass-forming system (see Fig. 4 in which one observes a strong change of the relaxation times with temperature, and Ref. 27 for a detailed discussion). Since we look for compressed exponentials, we plot the data as a function of \( t/\tau \) and \( t/\tau_s \), where \( \tau \) and \( \tau_s \) are the relaxation times defined by requiring that the correlator has decayed to \( \varepsilon^{-1} \) of its initial value. We see that the two time correlation functions display remarkably different behavior: For intermediate wave-vectors \( F(k, t) \) curves downward and can be fitted well by the Kohlrausch-Williams-Watts (KWW) function \( A \exp(-(t/\tau)^\beta) \) with \( \beta \approx 3/2 \), the so-called compressed exponential (CE). If \( k \) is very small or very large the decay is even faster, i.e. \( \beta \geq 1.5 \) (not shown). Such a behavior (\( \beta \approx 3/2 \)) has been observed in experiments of slowly relaxing gels [4, 6], and analyzed theoretically using a stress relaxation model [20]. On the other hand \( F_s(k, t) \) shows, like most other glass-forming systems, a stretched exponential, i.e. \( \beta \leq 1.0 \) for small and intermediate wave-vector, and a compressed exponential at large wave-vectors. Such a behavior has also been observed in [10], and interpreted as arising from the averaging of ballistic motion of particles which form a part of chain segments of varying lengths in the disordered percolating network.

To analyze further the nature of the relaxation, we determined the KWW-exponent \( \beta \) by fitting the correlators to a KWW-function. Since the time correlators exhibit different regimes of decay, it is necessary to choose a meaningful and consistent procedure for obtaining \( \beta \) and we choose to fit the curve in the time window in which the correlator is between 0.9 and 0.1. This choice

\[
\begin{align*}
\beta_s(\mathbf{k}) & = 2, \\
\beta_s(\mathbf{k}) & = 3, \\
\beta_s(\mathbf{k}) & = 4, \\
\beta_s(\mathbf{k}) & = 5.
\end{align*}
\]

FIG. 2: The collective intermediate scattering function \( F(k, t) \) (left panel) and self intermediate scattering function \( F_s(k, t) \) (right panel) at \( T = 0.03 \), for a range of wave-vectors \( k \).

FIG. 3: Wave-vector dependence of the KWW exponent \( \beta \) for \( F(k, t) \) and \( \beta_s \) for \( F_s(k, t) \) for four different temperatures.
avoids the (trivial) ballistic regime at very short times and instead focuses on the relaxation regime seen at intermediate times. The wave-vector dependence of the so obtained KWW-exponents is shown in Fig. 4 for four different temperatures. The $\beta$ values for $F(k,t)$, shown in the top panel, are seen to be always 2.0 for $T = 5.0$, indicating that ballistic motion dominates the decay (as discussed in the context of gels in [14]) at all wavelengths. While this is expected for large $k$, we note that the behavior at small $k$ is a result of the low density of our system which leads to significant decay of collective density fluctuations even on large wavelengths through non-diffusive motion of particles. If $T$ is decreased $\beta$ shows a minimum at intermediate values of $k$ and the width of this minimum broadens with decreasing $T$, suggesting that on intermediate length scales the decay mechanism is distinct. The typical values of $\beta$ in this minimum are around 1.3 $-$ 1.6, i.e. similar to the values that have been found in the experimental systems or in the theoretical calculations.

The $\beta_s$ values for $F_s(k, t)$, shown in the bottom panel, are found, for the highest temperature $T = 5.0$, to change from 2.0 at large $k$ towards 1.0 at small $k$, which we interpret as the expected crossover from ballistic to diffusive decay. Again, for low temperatures, we find superposed on this overall trend an intermediate regime, in which the dynamics becomes “stretched”, i.e., the decay of the self motion becomes slower than exponential. Thus from this figure we can conclude that the self and collective density correlation functions exhibit complex behavior, that is non-trivial, and different from dense fluids.

The relaxation times, $\tau_A(k)$ and $\tau_s^A(k)$, obtained from calculating the area under $F(k,t)$ and $F_s(k,t)$, are shown in Fig. 4 as a function of $k$ for different temperatures. Since for ballistic motion one expects the relaxation time to be proportional to $k^{-1}$, we show $\tau_A(k)$ and $\tau_s^A(k)$ multiplied by $k$. From the figure we recognize that at high and intermediate $T$ this scaling gives indeed horizontal line, showing that the motion can be interpreted as ballistic. Furthermore we see that the self and collective relaxation times track each other for all $k$. At low $T$ and small $k$ the curves are no longer horizontal, indicating that there is a significant non-ballistic component. As we shall see below, at these low temperatures, $F(k,t)$ has a significant long time relaxation that is clearly distinguishable from an intermediate relaxation process which we shall identify with CE behavior. Furthermore there is a strong decoupling at low $k$ in that $\tau_s^A$ exceeds $\tau_A^s$ by a large factor.

![FIG. 4: The wave-vector dependence of relaxation time from the area of $F(k,t)$ and $F_s(k,t)$ for temperature 0.028, 0.06, 0.30 and 5.00 at density 0.06. The filled symbols are for $\tau_s$ and opaque symbols indicates $\tau$.](image)

![FIG. 5: (a) The $F(k,t)$ from molecular dynamics (MD), and Langevin dynamics (LD) for different damping constants $\gamma$. Also shown is $F(k,t)$ from constrained MD simulation described in the text, and the KWW fit to the MD curve for intermediate times. (b) $\tau_0 k$ vs wave-vector, $k$ for a range of temperatures, showing that at low $k$, $\tau \sim 1/k$.](image)

We now investigate the nature of the compressed exponential relaxation of $F(k,t)$ (shown for $T = 0.04, k = 0.15$ in Figure 5(a)), which we observe on intermediate time scales. At low temperatures, CE relaxation accounts for a substantial part of the decay of $F(k,t)$ for a wide range of intermediate $k$ values. Since at these low temperatures the average life time of the bonds is longer than the decay time of $F(k,t)$ in the CE regime [27],
we expect the CE to be associated with the floppy dynamics of chain segments in the transient gel network, without network restructuring playing any role. In order to analyze the motions that are relevant, we therefore compare the $F(k, T)$ obtained in MD simulations to: (a) MD simulations with the imposition of a constraint that prevents bond breaking and formation of new bonds. This is accomplished by identifying bonded neighbors in the initial configuration we consider, and adding a suitably parametrized barrier potential of gaussian form to the two body part of the S-W potential. (b) Langevin dynamics simulations, to study the role of microscopic dynamics. For the Langevin dynamics we have used a predictor-corrector integrator [23], and the damping coefficient is tuned to span the range from very small damping, $\gamma = 0.004$ (corresponding to MD) to strong damping, $\gamma = 0.4$. In Fig. 5 (a) we show $F(k, t)$ from these different simulations.

Comparing MD with the constrained MD results, we see that the regime of CE dynamics is essentially unaltered by the imposition of the constraint not to break or form bonds. This shows clearly that the CE dynamics arises from the dynamics of the non-restructuring gel network. However, at longer times the relaxation dynamics of the constrained MD is essentially frozen, indicating that long time relaxation in the MD, cleanly separated from the compressed exponential decay, arises from network restructuring, a result that is also confirmed by the time dependence of the mean squared displacement of the particles (not shown) [27].

In Fig. 5 (b) we show $\tau \times k$ where $\tau(k)$ is obtained by fitting $F(k, t)$ by a KWW function in the intermediate time window displaying CE relaxation, as shown in Figure 5 (a) (note that these $\tau$ values are different from those shown in Fig. 4 which are obtained from the area under $F(k, t)/S(k)$). The near constant value of $\tau \times k$ for small $k$ corroborates the ballistic origin of the compressed exponential relaxation, consistent with predictions [1, 20].

For the Langevin dynamics we see that for small and intermediate values of the damping coefficient $\gamma$, the correlator tracks the one from the MD and thus a CE will be observed. However, for large damping the shape of the curve is very different from the one of the MD and no CE is seen anymore. Thus we see that the dissipative dynamics, relevant for example for real colloidal gels, will not show a CE dynamics. Therefore we can conclude that the CE seen in those systems is likely due to the aging dynamics.

In conclusion, we have proposed a model system which allows the simulation and study of gel forming fluids under equilibrium conditions, by suppressing the liquid-gas phase coexistence curve to an arbitrarily small temperature and density window. At low densities and temperatures the structural and dynamical features show many similarities to the one of experimental systems. In particular we find an intricate behavior of the density correlation functions, including compressed exponential relaxation of the collective intermediate scattering function with a compressing exponent that depends on temperature and wave-vector considered. The motion responsible for the compressed relaxation is found to have ballistic character and to arise due to the motion of chain segments in the gel without the restructuring of the gel network.

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[22] P.H.Stillinger and T.A. Weber, Phys. Rev. B 31, 5262 (1985).
[23] The SW potential is written as $u_{SW} = \sum_{i<j} u^{(2)}(r_{ij}) + \sum_{i<j<k} u^{(3)}(r_{ij}, r_{jk}, r_{ik})$. The two-body potential is short-
ranged and has the form \( u^{(2)}(r_{ij}) = \epsilon f^{(2)}(r_{ij}/\sigma) \), with

\[
f^{(2)}(r) = \begin{cases} 
A(Br^{-4} - 1)e^{\left(-\frac{r}{a}\right)} & r < a \\
0 & r \geq a
\end{cases}
\]

where \( A = 7.049\,556\,277, \) \( B = 0.602\,224\,558 \), and \( a = 1.8 \). The repulsive three-body potential is also short-ranged, and has the form \( u^{(3)}(r_i, r_j, r_k) = \epsilon f^{(3)}(r_i/\sigma, r_j/\sigma, r_k/\sigma) \) with \( f^{(3)} \) given by

\[f^{(3)}(r_i, r_j, r_k) \equiv h(r_{ij}, r_{ik}, \theta_{ijk}) + h(r_{ij}, r_{jk}, \theta_{ijk}) + h(r_{ik}, r_{jk}, \theta_{ikj}),\]

where \( \theta_{ijk} \) is the angle formed by the vectors \( r_{ij} \) and \( r_{ik} \) and

\[h(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda e^{\left(-\frac{\gamma}{r_{ij} - a} + \frac{\gamma}{r_{ik} - a}\right)} (\cos \theta_{ijk} + \alpha)^2 \times H(a - r_{ij})H(a - r_{ik})\]

where \( \gamma = 1.20, \ \lambda = 21.0, \ \alpha = \frac{4}{3} \) in the original parametrization\[22\], and \( H(r) \) is the Heaviside function. Reduced units for computations are specified in terms of potential parameters \( \epsilon, \sigma \) and the mass \( m \) of particles.

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