Length-Scale-Dependent Relaxation in Colloidal Gels

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We use molecular dynamics computer simulations to investigate the relaxation dynamics of a simple model for a colloidal gel at a low volume fraction. We find that due to the presence of the open spanning network this dynamics shows at low temperature a nontrivial dependence on the wave vector which is very different from the one observed in dense glass-forming liquids. At high wave vectors the relaxation is due to the fast cooperative motion of the branches of the gel network, whereas at low wave vectors the overall rearrangements of the heterogeneous structure produce the relaxation process.

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In gels, the deep connection existing between their unusual dynamics and the open network characterizing their structure is still not understood [1,2]. In the dramatic slowing down of the dynamics accompanying the gel formation, the relaxation functions are often stretched and/or, most remarkably, compressed; i.e., the time correlators decay faster than an exponential [3–7], showing a complex dependence on length scale. These findings suggest that different relaxation mechanisms interplay at a microscopic level, which have not been elucidated yet [8,9]. In the present Letter, we show that the formation of the gel network does induce a nontrivial length scale dependence of the dynamics in a simple model for colloidal gels. We use molecular dynamics computer simulations to study the gel formation from the equilibrium sol phase. Our results give evidence that in the incipient gel, the relaxation at high wave vectors is due to the fast cooperative motion of pieces of the gel structure, whereas at low wave vectors the overall rearrangements of the heterogeneous gel make the system relax via a stretched exponential decay of the time correlators. The coexistence of such diverse relaxation mechanisms is determined by the formation of the gel network (i.e., the onset of the elastic response of the system) and it is characterized by a typical crossover length which is of the order of the network mesh size. This is the first work where such a characterization of the gel dynamics in colloidal systems has been achieved, thus making important progress as compared to previous numerical studies [9–12].

In colloidal suspensions at low volume fractions gelation competes and/or interplays with phase separation. As a consequence, coarsening or ordering processes due to the underlying thermodynamics often interfere with the gel dynamics. Whereas in the experiments the time scale typical of the micro- or macrophase separation is often much longer than the observation time scales [3,4], this is not the case in numerical studies using traditional models for colloidal suspensions, where the investigation of the gel dynamics has been until now severely hindered [8–11]. To overcome this problem, we have developed a model in which directional interactions are able to produce a persistent gel network at relatively high temperatures, where phase separation does not occur. The model consists of identical particles of diameter σ, our unit of length, that interact via short-ranged two- and three-body terms. The two-body term gives rise to a narrow well of depth ϵ, our unit of energy, whereas the three-body term makes the angle between three neighboring particles unlikely to be smaller than 70°. As a consequence, at low temperatures there is a competition between local structures that are compact (due to the two-body terms) and open (due to the three-body terms). More details on the potential can be found in Refs. [13,14]. Differently from other recent models where a fixed connectivity is imposed with the same aim [10], here it is the balance between the two-body and three-body terms that will naturally limit the effective functionality of our particles at low temperatures, producing an open network with a certain local rigidity [15].

With these interactions we have done microcanonical simulations using the Verlet algorithm with a time step of 0.002, where time is measured in units of $\sqrt{m\sigma^2/\epsilon}$, with m as the mass of a particle. The number of particles is 8000 and the size of the simulation box is $L = 43.09$, which corresponds to a volume fraction of 0.05 (or a particle density of 0.1), and the temperatures T are 5.0, 2.0, 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.055, and 0.05. We carefully equilibrated the system and averaged the results over five independent runs. As shown in Ref. [13], there is no sign of a phase separation in this temperature range. At low T particles are linked by long-living bonds and, via a random percolation process, form an open network made of chains (particles with coordination number 2) connected by nodes (particles of coordination number 3). The mean value of the chain length distribution between two nodes of the network is 10, giving the typical mesh size. Such a simple structure of the gel network is a specific feature of this model, as compared to other recent studies [9–11], making it very useful to investigate the connection between dynamics and structural features. The static structure factor shows at intermediate and small wave vectors the increase typically found in network forming systems [1] (see inset in Fig. 1). In this T region the relaxation times measured from particle diffusion and density fluctuations increase with decreasing T quicker than an Arrhenius law. These static and dynamic properties are indeed very similar to the ones found in real colloidal gels [1,2,16].

In Fig. 1 we show the time dependence of $\langle r^2(t)\rangle$, the mean squared displacement (MSD) of the particles for all temperatures investigated. For high T, due to the Newtonian dynamics, one finds at short times the ballistic behavior $\langle r^2(t)\rangle \propto t^2$ followed at $t \approx 1.0$ by a crossover to a diffusive behavior, i.e., $\langle r^2(t)\rangle \propto t$. At low T, apart from the ballistic regime at short t, we see at $t \approx 1$ a weak shoulder at around $\langle r^2\rangle \approx 0.05$, i.e., a localization length around 0.2, due to the onset of the caging regime in which a particle is trapped by its nearest neighbors. At $T = 0.05$, more than 97% of the particles belong to the percolating network. We have separately analyzed the motion of particles with different connectivity within the network and found that the motion of particles which are weakly connected to the nodes (i.e., particles in the middle of a chain connecting two nodes or particles belonging to dangling ends) is less affected by this localization process. This indicates that the gel has a very flexible structure since the chains can still perform an oscillatory motion without breaking. Thus, the movement of the overall local structure makes that the MSD shows only a weak sign of this trapping, in contrast to dense glass-forming systems [17]. Most remarkably the MSD at low T shows at times $t \approx 10^2$ a second shoulder with a height of around 10^2, corresponding to a localization distance of around 10. This localization process appears when the spanning network is formed and the lifetime not only of the bonds but also of the nodes becomes comparable to the longest relaxation time [14]. It indicates that the system is now viscoelastic over the observation time scale and its typical length scale is comparable to the mesh size of the disordered network [18].

Relevant information on the relaxation dynamics over different length scales can be obtained from the self-intermediate scattering function $F_s(\vec{q}, t) = N^{-1}\sum_{j=1}^{N}\langle\exp[i\vec{q}\cdot[\vec{r}_j(t) - \vec{r}_j(0)]]\rangle$, where $\vec{q}$ is the wave vector. In Fig. 2 we show the q dependence of τ_s for all temperatures investigated. Since at high T the relaxation dynamics at short distances, i.e., large q, can be expected to be of ballistic nature, it can be approximated by the function $F_s(q, t) = \exp[-Tq^2t^2/(2m)]$ and therefore the relaxation time, defined as the time integral of the correlator, should be given by $\tau_s = (\sqrt{\pi m/2T})/q$. The excellent agreement with our data at high T and large q is shown by the plot of the quantity $\tau_s q\sqrt{T}$ in Fig. 2. At lower T (but $T > 0.1$) the rescaled data lie higher than the ones for high T. At these T the bond lifetime becomes comparable to the typical relaxation time for q values that correspond to distances of the order of a few interparticle diameters. Therefore the small aggregates signaled by the cluster size distribution [13] will have a lifetime longer than the relaxation time on this length scale. Finally, both at high and intermediate T the data deviate at the lowest q, where one expects a crossover to the hydrodynamic dependence $\tau_s(q, T) \propto q^{-2}$ (see Fig. 2). At even lower T, the data for large q appear to follow a different nearly-ballistic regime, in that the curves at large q are also almost horizontal. We recall that as we lower the temperature the bond lifetime is longer than the longest relaxation time in the system and that the cluster size distribution significantly widens [13]. E.g., at $T \leq 0.055$ most of the particles (more than 97% at $T = 0.05$) belong to one percolating cluster [14]. This nearly-ballistic regime at high q thus corre-

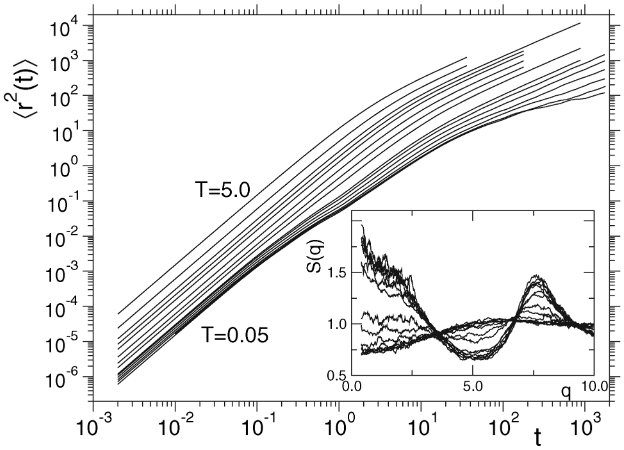

FIG. 1. Time dependence of the mean squared displacement of a tagged particle for all T investigated. Note the presence of a shoulder in the curves at low T at $t \approx 1.0$ and $t \approx 10^2$. Inset: Static structure factor of the system at $T = 5.0$, 0.3, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.05.

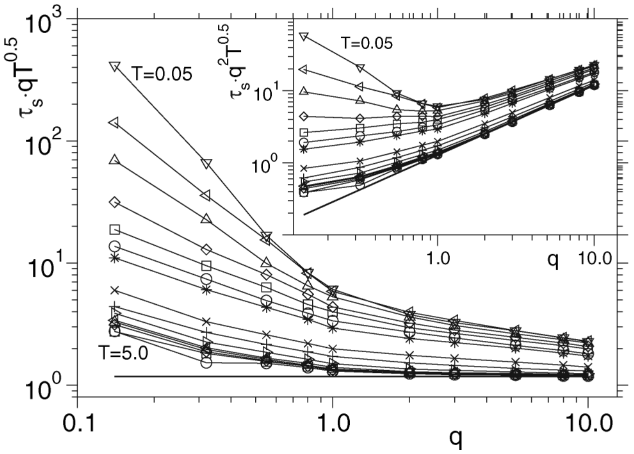

FIG. 2. Wave vector dependence of the relaxation time for all T. Main figure: $\tau_s q\sqrt{T}$ vs q showing the ballistic motion at high T and large q. The bold line is the theoretical expectation for a ballistic motion. Inset: $\tau_s q^2\sqrt{T}$ vs q to check for the onset of the hydrodynamic regime at small q.

sponds to time and length scales where the MSD is strongly dominated by the motion of the particles connected only weakly to the nodes; i.e., it is due to the fast motion of the branches of the gel network.

The length scale $q \simeq 1.0$ marks the crossover to a different dynamic regime. In fact, for wave vectors less than 1.0, i.e., distances that are comparable or larger than the length scale of the mesh size, we find strong deviations from the previous q dependence in that τ_s increases rapidly with decreasing q. This strong q dependence, which resembles the one found in dense glass-forming liquids, is here observed at wave vectors that correspond not to an interparticle distance, but to the mesh size of the network. Note that the formation of the gel network induces a correlation length rapidly increasing with decreasing T, and in fact the hydrodynamic regime at the lowest T sets in only at length scales that are larger than the size of the simulation box (see inset of Fig. 2).

We now discuss in more detail the T- and q dependence of $F_s(q, t)$, which give us further insight in the dynamics. In Fig. 3 we show $F_s(q, t)$ as a function of $t/\tau_s(q, T)$ for $q = 0.55$. At high temperatures this wave vector corresponds to the crossover from the trivial ballistic regime to the hydrodynamic one; i.e., isolated particles have a significant probability to collide before making a displacement of the order of $2\pi/q$ (leading to an exponential decay of the correlation function). The cluster size distribution indicates the presence of small aggregates [13] but the bond lifetime is smaller than the relaxation time on this length scale. Therefore, the small clusters that move ballistically break up before they have made a displacement of the order of $2\pi/q$ (which would lead to a Gaussian decay). Hence the overall relaxation on this length scale is faster than exponential and basically follows a compressed exponential (CE). With decreasing T this exponent diminishes monotonously to around 0.58 at $T = 0.05$, giving a stretched exponential (SE) decay. This is due to the change of the bond lifetime and of the cluster size distribution: If the bond lifetime is comparable to $\tau_s(q, T)$ but the size of the aggregates is still small, one expects a nearly exponential relaxation. With decreasing T, the particles aggregate in long-living structures and form a percolating network. Therefore the relaxation curves become more stretched and, at the lowest temperature considered, can be well approximated by a stretched exponential. This pronounced stretching can be understood from the very heterogeneous structure of the network on the length scale of the size of the mesh.

Let us now analyze $F_s(q, t)$ at the lowest temperature $T = 0.05$, for different values of q, as a function of $t/\tau_s(q, T)$; see Fig. 4. For large q the curves fall all on a master curve and in the inset we show that the latter is well described by a CE with an exponent around 1.5. At this T, finite clusters and free particles are extremely rare and the main contribution to the particles MSD comes from the particles of the network which are less connected to the nodes. This indicates that, for wave vectors q corresponding to a few interparticle distances and smaller, the motion of the branches of the percolating cluster leads to a complete decay of $F_s(q, t)$. Hence their mean free path is larger or comparable than $2\pi/q$ and for these intermediate and large wave vectors the motion can be considered as nearly ballistic. Note that these moving entities do have different masses and therefore different thermal velocities. Since $F_s(q, t)$ is the average over the different local relaxation functions, assuming that each of them is of the Gaussian form given above, it must be expected that $F_s(q, t)$ decays more slowly than a Gaussian in time, i.e., that the exponent in the CE is less than 2.0, in agreement with our results, see Fig. 4.

For values of $q \leq 1.0$ the data for $F_s(q, t)$ no longer fall onto a master curve and the shape of the correlator be-

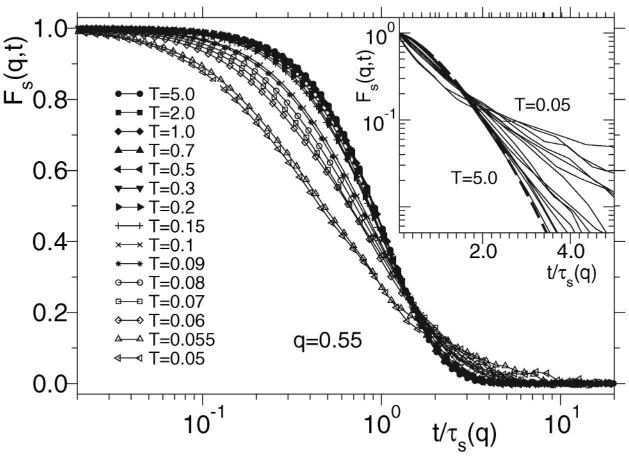

FIG. 3. $F_s(q, t)$ vs $t/\tau_s(q, T)$ for $q = 0.55$ and the indicated temperatures. Inset: The same data in a log-lin representation. The bold dashed line is a compressed exponential with exponent 1.5.

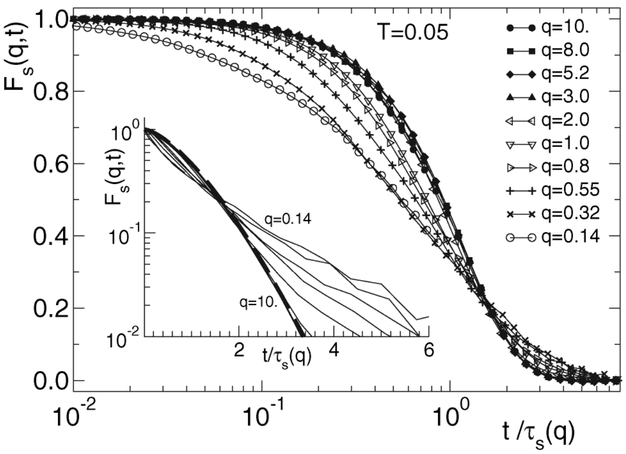

FIG. 4. $F_s(q, t)$ vs $t/\tau_s(q, T)$ for $T = 0.05$ and the indicated wave vectors. Inset: The same data in a log-lin representation. The bold dashed line is a compressed exponential with exponent 1.45.

comes a stretched exponential (inset of Fig. 4). Thus only for these intermediate and large length scales the system shows a relaxation dynamics similar to the one found in dense glass-forming liquids; i.e., the presence of the disordered structure on this length scales leads to a heterogeneous dynamics characterized by a stretched exponential. We emphasize that the inset of Fig. 2 well illustrates this peculiar length scale dependence of the relaxation dynamics at $T = 0.05$, which is crucially determined by the network. Once the nodes are persistent enough as compared to the relaxation times at small wave vectors (i.e., over distances larger than the network mesh size), this network induced relaxation regime sets in: The network determines the coexistence of such diverse relaxation mechanisms on different length scales.

Finally, an interesting point which deserves further investigation is the relation between the compressed exponential decay of the time correlators with the experimental observations [3,4,6,7]. Although this issue is far beyond the aim of the present Letter, it is worth to recalling that here we have approached the gel formation from the equilibrium sol. As a consequence, even at the lowest temperature the distribution of the thermal velocities of the moving entities is the equilibrium one and hence each contribution to the average $F_s(q, t)$ is a Gaussian function of the time. In contrast to this, in experiments which study far from equilibrium gels, dipolar forces due to frozen-in stresses might produce a power law distribution of velocities of the moving entities. Hence such forces might be responsible for the nearly-ballistic dependence of the relaxation time on the wave vector and of CE decay of time correlators with an exponent ~ 1.5 [3–5]. Similarly, if the system is sheared and the perturbation gives (at least locally) rise to a linear displacement in time, one can again expect this type of relaxation [4,19]. Interestingly, in the nonergodic gels just mentioned the relaxation is supposed to occur via the motion of the connecting branches of the gel network and formation or breaking of network nodes, see Ref. [5], as we actually find here. These considerations suggest that an analogous analysis of the length scale dependence of the dynamics in this model in the far from equilibrium gel, obtained by deeply quenching the system, would significantly contribute to the understanding of the experimental findings.

In conclusion, our study shows that in colloidal gels at low volume fractions the formation of the gel network corresponds to the coexistence of very different microscopic relaxation mechanisms. Once that the network is formed, fast collective motions of subentities (branches, etc.) of the incipient gel drive the relaxation on small length scales, whereas the relaxation on large length scales is due to the overall rearrangements of the disordered structure. In our model this corresponds to decays of time correlators as diverse as CE at high wave vectors vs stretched exponential decays at low q. The mechanisms discussed here are likely to affect the stress transmission within the gel network and might therefore play a role also in the nonergodic phase investigated in the experiments [3,4,6,7]. We suggest the relaxation mechanisms elucidated here and the length scale dependence of dynamics to be a general feature in gels, coupling the complex slow dynamics of glassy systems to the structural variety and tunability of gelling materials.

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