Dynamical heterogeneities in attractive colloids

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Abstract. We study the formation of a colloidal gel by means of molecular dynamics simulations of a model for colloidal suspensions. A slowing down with gel-like features is observed at low temperatures and low volume fractions, due to the formation of persistent structures. We show that at low volume fraction the dynamical susceptibility, which describes dynamical heterogeneities, exhibits a large plateau, dominated by clusters of long living bonds. At higher volume fraction, where the effect of the crowding of the particles starts to be present, it crosses over towards a regime characterized by a peak. We introduce a suitable mean cluster size of clusters of monomers connected by ‘persistent’ bonds which well describes the dynamical susceptibility.

Keywords: percolation problems (theory), dynamical heterogeneities (theory), structural colloidal and polymer glasses (theory), colloids, bio-colloids and nanocolloids
Recent advances in colloidal science allow us to obtain colloidal particles or nanoparticles with specific functional properties, of electronic, chemical, biological or mechanical nature. Hence the packing and aggregation of colloidal particles are important for a wide variety of applications, including biological arrays, sensors, paints, ceramics, and photonic crystals. In particular, by adding polymers to a colloidal solution, it is possible to induce an effective short range attraction between colloidal particles, known as the depletion effect. Attractive colloids exhibit a rich phenomenology in the temperature–volume fraction plane [1]–[7]: at high temperature, by increasing the volume fraction, if crystallization is avoided, a hard sphere glass transition occurs. By decreasing the temperature, the effect of the short range attraction induces an attractive glass line which is strongly temperature dependent, as predicted by mode coupling theory (MCT) [8], and by mean field theory [9]. Finally, at low temperature and low volume fraction, the attractive glass line turns into a colloidal gelation line, where structural arrest exhibits properties similar to the sol–gel transition [3], [10]–[13].

In this letter we are interested in the study of this low temperature and low volume fraction region. In particular, in order to further understand the connections and differences between colloidal gelation, chemical gelation and glass transition, we propose an analysis based on the behavior of dynamical heterogeneities, which have been successfully introduced in glasses [14]–[24]. The dynamical heterogeneities describe the correlated motion of particle clusters and can be quantitatively studied via the so-called dynamical susceptibility [16]. In a Lennard-Jones binary mixture, a typical model for glass transition [25], the dynamical susceptibility grows as a function of time, reaches a maximum and then decreases to a constant [26], consistently with the transient nature of the dynamical heterogeneities. Recent developments of MCT [27] allow us to predict in detail the shape of the dynamical susceptibility in supercooled liquids.

Dynamical heterogeneities have also been observed in attractive colloidal systems in both experiments [28,29] and numerical simulations [31,30,32]. In particular, in [32] a systematic study of the dynamical susceptibility was done along the attractive glassy line. Typically, the dynamical susceptibility displays a well pronounced peak, but in the attraction-dominated limit, the dependence on both time and wavevector differs markedly from that in standard repulsion-dominated systems (the hard sphere limit).

Here we study the dynamical susceptibility in a Derjaguin, Landau, Verwey and Overbeek (DLVO) type of model for colloidal gelation [34,35], at very low volume fraction
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and temperature, where the system exhibits gelation properties more markedly. Using MD simulations we find an interesting and completely unusual behavior. The dynamical susceptibility, defined as the fluctuations of the self intermediate scattering function (ISF) [27], for low wavevectors, increases with time until it reaches a large plateau, and only for very long time does it decay to 1. This finding can be compared with the behavior in a model for irreversible gels [33], where monomers are bonded via permanent chemical bonds. In this model the dynamical susceptibility, in the limit of low wavevector, is found to tend for long times to a plateau, whose value coincides with the mean cluster size. We propose to describe the dynamical heterogeneities in the colloidal gelation model presented here, in terms of clusters made of ‘mobile’ particles connected by ‘persistent’ bonds. We find that the mean cluster size of such clusters reproduces the observed behavior of the dynamical susceptibility at low temperature and low volume fraction. At higher volume fractions, the dynamical susceptibility starts instead to display a peak and shows a discrepancy with the time-dependent mean cluster size, indicating a crossover towards a new regime where, besides the clusters, also the crowding of the particles starts to play a role in the slowing down of the dynamics [42]. Although we have considered a DLVO type of model, we expect that the main results of our paper should be valid also for other model systems exhibiting colloidal gelation [36,37].

1. The model

The DLVO model, considered here, has been previously studied using molecular dynamics (MD) [12,13,38]. In agreement with experimental findings [35], this model displays a structural arrest very close to the percolation threshold at low temperature, where clusters are made of particles connected by long living bonds.

In [38], we found that, at low temperatures, on increasing the volume fraction, the system undergoes a transition from a disordered cluster phase to an ordered hexagonal lattice of tubular structures and, at higher volume fraction, to an ordered lamellar phase. If this ordered state is avoided, the system enters a ‘supercooled’ metastable liquid phase until structural arrest (gelation) occurs [12,39] very close to the percolation threshold. For this reason we introduce here a small degree of polydispersity, which actually hinders the formation of the ordered phases. In this way we are able to fully investigate and characterize the gel formation at different temperatures and volume fractions. The interaction potential between two particles $i$ and $j$ is

$$V_{ij}(r) = \epsilon \left[ A \left( \frac{\sigma_{ij}}{r} \right)^{36} - B \left( \frac{\sigma_{ij}}{r} \right)^6 + C e^{-r/\xi} \right], \tag{1}$$

where $A = 3.56$, $B = 7.67$, $C = 75.08$, $\xi = 0.49$, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. In the following we consider the diameters $\sigma_i$ randomly distributed in the interval $\sigma - \delta/2 < \sigma_i < \sigma + \delta/2$ with $\delta = 0.05\sigma$. The potential is truncated and shifted to zero at a distance of 3.5$\sigma$. The temperature $T$ is in units of $\epsilon/k_B$, where $k_B$ is the Boltzmann constant, wavevectors are in units of $\sigma^{-1}$, and times in units of $\sqrt{m\sigma^2/\epsilon}$, where $m$ is the mass of the particles.

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6 Two particles are considered linked if their relative distance is smaller than the local maximum of the potential.

7 In [12,38], particles interact via a formally slightly different potential but, with the present choice of parameters, practically coinciding with equation (1) in the monodisperse case.
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Figure 1. The self ISF, \( F_s(k,t) \), for \( T = 0.15 \), \( k = k_0 \simeq 0.36 \), and \( \phi = 0.01, 0.05, 0.08, 0.10, 0.11, 0.12, 0.13 \) (from left to right).

The volume of the simulation box is kept constant, \( V = 5000\pi\sigma^3/3 \), and different volume fractions are obtained by varying the number of particles \( N \), so that \( \phi = \pi\sigma^3 N/6L^3 \). We have performed Newtonian MD at constant \( NVT \) using the velocity Verlet algorithm and the Nosé–Hoover thermostat with time step \( \Delta t = 0.01 \).

At low temperatures and low volume fractions, we find a first regime characterized by a cluster phase, followed by a second regime where a percolation transition in the same universality as random percolation occurs. As a consequence we find two different regimes in the connectivity properties. For example, for \( T = 0.15 \) the mean cluster size in the first regime seems to diverge at an effective percolation threshold \( \phi_p \simeq 0.14 \), followed by a crossover to a new regime in which the data extrapolate towards a higher threshold [40].

2. Self intermediate scattering functions

In order to study the dynamical behavior of the model, we measure the self ISF, \( F_s(k,t) = 1/N\langle \Phi_s(k,t) \rangle \), where \( \Phi_s(k,t) = \sum_{i=1}^{N} e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_i(0))} \), \( \langle \cdots \rangle \) is the thermal average, and \( \vec{r}_i(t) \) is the position of the \( i \)th particle at the time \( t \). In figure 1 \( F_s(k,t) \) is plotted for \( T = 0.15 \) and for a small wavevector \( k_0 \) (here chosen to be the minimum value \( k_0 = 2\pi/L \simeq 0.36 \)). On increasing the volume fraction, the relaxation functions show a two-step decay, with a plateau value decreasing with the wavevector.

From the self ISF we calculate the structural relaxation time, \( \tau_\alpha(k) \), defined as \( F_s(k, \tau_\alpha(k)) \simeq 0.1 \). In figure 2, \( \tau_\alpha(k_0) \) is plotted as a function of the volume fraction for two values of temperature, \( T = 0.15 \) and 0.25. In the same figure for the sake of
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Figure 2. The structural relaxation time, $\tau_\alpha(k_0)$ (circles), compared with the bond relaxation time, $\tau_b$ (stars), for $T = 0.15$ and 0.25 (from bottom to top). The continuous line is a power law fit $(0.14 - \phi)^{-3.8}$.

The non-monotonic behavior of $\tau_b$ is essentially due to the presence of competitive interactions. After the formation of the cluster phase, where all particles essentially feel only the attractive interaction, the bond strength of further particles decreases due to the effect of the long range repulsion.

3. Dynamical heterogeneities

According to the above interpretation of the dynamics, we would expect, for time windows comparable to or larger than $\tau_b$, a deviation from the dynamics of irreversible gels even for $T = 0.15$. This crossover in the dynamics can be better investigated by looking at the dynamical susceptibility, defined as $\chi_4(k, t) = 1/N[(|\Phi_s(k, t)|^2) - (|\Phi_s(k, t)|^2)]$.

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In the main frame of figure 3, $\chi_4(k_0, t)$ is plotted as a function of $t$, for $T = 0.15$ and different $\phi$. For low volume fractions, after a time roughly of the order $\tau_\alpha$, $\chi_4(k_0, t)$ reaches a plateau and decays after a time roughly of the order $\tau_\beta$. As the volume fraction increases, a small peak appears at a time roughly of the order $\tau_\alpha$. On further increasing the volume fraction, when $\tau_\beta$ and $\tau_\alpha$ become of the same order of magnitude, the plateau disappears and $\chi_4(k_0, t)$ exhibits a well defined peak similar to those of glassy systems. We have also checked that for temperature $T = 0.25$, $\chi_4(k_0, t)$ exhibits a small peak and no plateau.

To characterize the dynamical heterogeneities geometrically, we introduce a time-dependent mean cluster size, $S(t)$, defined by ‘persistent bonds’, that is, bonds that are present at both time 0 and time $t$ (see the inset of figure 3). This quantity coincides with the usual mean cluster size, $\sum_s s^2 n_s / \sum_s n_s$, at $t = 0$. At low volume fractions, $S(t)$ quantitatively describes the plateau region and the long time decay of $\chi_4(k_0, t)$, suggesting that in this system at low volume fraction the dynamical heterogeneities can be described in terms of clusters made of persistent bonds. Interestingly, the plateau value roughly coincides with the usual mean cluster size, $S(0)$, as in the case of irreversible gels [33].

As the volume fraction increases, the dynamical susceptibility starts to display a peak not representable in terms of clusters, indicating a crossover towards a new regime, where, besides the clusters, the crowding of the particles also starts to play a role in the slowing down of the dynamics. This crossover can be better viewed in terms of a new quantity,

\footnote{A similar definition of a time-dependent cluster, in the context of water, was proposed in [41].}
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Figure 4. Main frame: The dynamical susceptibility, $\chi_4(k_0, t)$ (circles), compared with the time-dependent mean cluster size of mobile particles, $S_m(t)$ (stars) for $T = 0.15$ and $\phi = 0.01, 0.12$. Inset: the maximum of $S_m(t)$ (stars), as a function of $\phi$, compared with the maximum of the dynamical susceptibility, $\chi_4(k_0, t^*)$ (circles).

the mean cluster size for ‘mobile’ particles, $S_m(t)$, where the clusters are made as before by particles connected by persistent bonds, but restricted to particles that in the time interval $[0, t]$ have moved at least a distance $r_0$. As we see in the main frame of figure 4, at very low volume fractions, $S_m(t)$ and $\chi_4(k_0, t)$ agree surprisingly well. A peak higher than the one of $S_m(t)$ appears on further increasing the volume fraction, signaling the crossover to the different regime (see also the inset of figure 4).

Conclusions

We have reported new results regarding dynamical heterogeneities in a colloidal system at low volume fraction: their behavior is shown to be dramatically different from the one typically found at high volume fraction. In addition, most importantly, we are able here to geometrically characterize the dynamical heterogeneities at low and intermediate volume fractions. This may also provide a good starting point for a generalization to the glassy regime, shedding new light on the nature of the transition.

These results are, on the one hand, amenable to experimental verification, and on the other hand, they could also be a test for theory. In particular, in the context of the

10 The distinction between mobile and quasi-frozen particles has been discussed in the literature; see, for example, [15, 31].

11 For each volume fraction, we fix $r_0$ so that the time at which $S_m(t)$ and $\chi_4(k_0, t)$ start to grow is the same. The values chosen were $r_0 = 4.5$ for $\phi = 0.05$, $r_0 = 4$ for $\phi = 0.10$, and $r_0 = 3.5$ for $\phi = 0.12$. At a first analysis, the relevant value of $r_0$ seems to depend roughly on $\phi^{-1/3}$, and be related to the mean distance between clusters.
MCT, the calculations which allow us to predict the shape of dynamical susceptibility in supercooled liquids [27] can be extended to colloidal gels at low volume fraction, and the theoretical predictions compared with the results presented here, offering an optimal test for the validity of the MCT in this regime.

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