Cluster structure and dynamics in gels and glasses

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Received 4 February 2016
Accepted for publication 7 May 2016
Published 11 July 2016

Online at stacks.iop.org/JSTAT/2016/074011
doi:10.1088/1742-5468/2016/07/074011

Abstract. The dynamical arrest of gels is the consequence of a well defined structural phase transition, leading to the formation of a spanning cluster of bonded particles. The glass transition, instead, is not accompanied by any clear structural signature. Nevertheless, both transitions are characterized by the emergence of dynamical heterogeneities. Reviewing recent results from numerical simulations, we discuss the behavior of dynamical heterogeneities in different systems and show that a clear connection with the structure exists in the case of gels. The emerging picture may also be relevant for the more elusive case of glasses. We show, as an example, that the relaxation process of a simple glass-forming model can be related to a reverse percolation transition and discuss further perspective in this direction.

Keywords: dynamical heterogeneities (theory), percolation problems (theory), slow relaxation and glassy dynamics, supercooled liquids, glasses and gels
1. Introduction

Glasses and gels are disordered solids with an arrested dynamics. According to a gross classification, glasses are high density materials dominated by short range repulsion, hard sphere colloids being a paradigmatic case, whereas attractive interactions are necessary to form the low density and fractal structure characterizing gels. Polymeric suspensions represent a typical example of systems, where the inter-particle interaction can be finely tuned to obtain a glass or a gel. In the absence of cross-linkers or depletants, the system is well described as a hard sphere suspension: the dynamic slow down is driven by increasing the volume fraction $\phi$, with the glass transition occurring at a critical threshold, $\phi_{\text{glass}}$. This transition marks the arrest of the dynamics at all the relevant length-scales, for wave-vectors ranging from $k_{\text{min}} = 2\pi/L$ to $k_{\text{max}} = 2\pi/\sigma$, $L$ and $\sigma$; being the sizes of the system and of the particles, respectively. Surprisingly, this sharp dynamic transition is not accompanied by any clear structural signature [1]. Standard pair correlation functions, such as the structure factor or the radial distribution function, poorly change across the transition, whereas the possibility of finding a signature in more complex structural quantities remains a major and long standing open issue in condensed matter [2].

A polymeric suspension can also form a permanent gel, even at densities much smaller than $\phi_{\text{glass}}$, on increasing the cross-linker concentration, for instance, by radiation as in light induced polymerization processes (e.g. dental filling pastes) or by heat (e.g. cooking). In that way, the system is driven across a percolation transition, where a spanning cluster of connected monomers emerges. This also leads to a dynamical arrest transition, as the dynamics becomes frozen on the smallest wave-vector $k_{\text{min}}$, the spanning cluster being unable to diffuse. Thus, the dynamical transition of permanent gels originates from a well defined structural phase transition (percolation).

Despite the apparent differences between the glass and the gel transition, both of them are accompanied by the emergence of dynamical heterogeneities (DHs) [3],

doi:10.1088/1742-5468/2016/07/074011
groups of particles, spatially correlated over a time scale of the order of the relaxation time. DHs have been suggested to play a role similar to critical fluctuations in critical phenomena, and seem very promising to distinguish between competing theories and understanding differences and universality in the dynamical arrest transition.

In this paper, we review recent results on DHs in numerical models of chemical gels (permanent bonds), colloidal gels (temporary bonds) and colloidal glasses (no bonds), focusing on the connection with the structure. We start by discussing the case of chemical gels, where for $k \to 0$ and $t \to \infty$, the dynamic susceptibility $\chi_4(k, t)$ tends to the mean cluster size, which diverges at the gelation threshold [4]. Then, we consider to what extent this scenario holds on moving from chemical to colloidal gels [5, 7], and from colloidal gels to colloidal glasses [6], and the slow dynamics becomes progressively no longer due to the presence of bonds, but rather to particle crowding. While the framework of chemical gels cannot be trivially extended to glasses, it can still lead to novel approaches if the relevant clusters are suitably defined. As an example, we consider the case of a simple colloidal glass model, where the relaxation process and the emergence of DHs can be related to a reverse percolation transition. As a final perspective, we discuss which percolation model may describe the glass transition.

2. Dynamical heterogeneities in chemical gels

The transition from solutions (sol) to chemical gels is due to the onset of a permanent spanning cluster, which gives rise to the divergence of the viscosity as the transition is approached from the sol phase, and to an elastic modulus vanishing as the transition is approached from the gel phase. Since the pioneering work of Flory [8, 9], chemical gelation has been explained in terms of percolation models (for a review see [10]).

Here, we consider a model for chemical gels extensively studied in [4, 11] using molecular dynamics (MD) simulations. Briefly, after equilibrating a system of $N$ particles, interacting via the Weeks–Chandler–Andersen (WCA) potential [12], permanent bonds between particles at a distance smaller than $1.5\sigma$ are introduced, by adding a finitely extendable nonlinear elastic potential (FENE) [13, 14]. The numerical simulations have shown a percolation transition at volume fraction $\phi_c \approx 0.1$, with critical exponents in agreement with random percolation. For further details on the MD simulations see [4, 11]. Alternatives models have been described in [15, 16], and more recently, in [17, 18].

The emergence of DHs is characterized by the dynamical susceptibility, $\chi_4(k, t)$ defined as the fluctuations of the self intermediate scattering function (ISF), $\Phi(k, t)$: $\chi_4(k, t) = N[\langle |\Phi(k, t)|^2 \rangle - \langle \Phi(k, t) \rangle^2]$, where $\langle \ldots \rangle$ is the thermal average for a fixed bond configuration, $[\ldots]$ is the average over the bond configurations, and $\Phi(k, t) = \frac{1}{N} \sum_{i=1}^{N} e^{iK \cdot (\vec{r}_i(t) - \vec{r}_i(0))}$. The wave-vector $k$ allows DHs to be probed at different length scales.

In the main frame of figure 1, $\chi_4(k, t)$ is plotted as a function of time for $k_{\text{min}} = 2\pi/L$ and different $\phi$. In this case, for each value of the volume fraction, $\chi_4(k_{\text{min}}, t)$ reaches a plateau after a characteristic time of the order of the relaxation time. It was theoretically shown [4], and numerically verified, that, in the limit of small $k$, the asymptotic
value of $\chi_4(k, t)$ coincides with the mean cluster size (see inset of figure 1), defined as $S = \sum s^2 n(s)/\sum s n(s)$, where $n(s)$ is the number of clusters of size $s$, which diverges at the gelation threshold with the random percolation exponent $\gamma$. Thus, in chemical gels, DHs are due to the presence of clusters of bonded particles. This result also indicates that the percolation exponents can be measured by means of the asymptotic dynamic susceptibility, and that the asymptotic value of the dynamical susceptibility plays the same role as the static scattering function near a liquid-gas critical point. We note that the dynamical susceptibility shown in figure 1 is qualitatively different from that observed in glasses. In glasses, $\chi_4$ does not asymptotically reach a plateau, but has a maximum and then decays to zero [3].

3. Dynamical heterogeneities in colloidal gels

In chemical gels, where the structural arrest is related to the formation of clusters of bonded particles, the dynamical susceptibility can be directly connected to the clusters. This clarifies the nature of the slow dynamics/structural arrest in these gels as compared to hard sphere glasses [19], where bonds do not exist at all. Very intriguing is the case of gels formed in attractive colloids [20], which are in between these two extremes. In these systems, upon tuning the strength of the attractive interactions, one can go from an irreversible gel, very similar to the chemical gel just described, to a non-permanent colloidal gel and, finally, to a hard sphere glass. For example, the addition of non-adsorbing polymers to the suspension induces effective attractive interactions between the colloidal particles due to depletion [21]. In this case, in the temperature-volume fraction plane, the structural arrest line, where jamming transition occurs, typically interferes with the coexistence curve [22]. Gelation may occur, due
to an interrupted phase separation, which has been accurately studied in a combined experimental and numerical effort [23]. The presence of a long range repulsion between particles, due for example to the presence of residual charges, may suppress phase separation and avoid its interference with gelation. A DLVO-type potential can be used to model this kind of effective interaction, as often seen in the literature [24, 25]. Actually, it was shown that the competing attraction and repulsion favors ordered columnar and lamellar phases at low temperatures [26, 27], therefore limiting the possibility to study the metastable states associated to slow dynamics and structural arrest. However, upon adding a small degree of polydispersity, it is possible to avoid the ordered phases and study the arrested line without such interference [5].

Since the study of DHs in these systems might unveil new behaviors arising in intermediate situations and shed new light on the nature of the structural arrest, we now review some findings on a DLVO-type model from [5] and refer to this paper for further details on the MD simulations.

In the low temperature and low volume fraction phase, particles tend to form strong bonds, with a lifetime many magnitude orders larger than the structural relaxation time, $\tau \gg \tau_v$ (see figure 2(a)). In this region, the dynamical susceptibility, $\chi_d(k_{\text{min}}, t)$ (plotted in figure 2(b)), reaches a plateau, roughly coinciding with the mean cluster size. After a time of the order of the bond lifetime, $\chi_d(k_{\text{min}}, t)$ decreases, due to the breaking of the clusters. This plateau disappears at higher volume fractions, where the bond lifetime is comparable to the structural relaxation time. In this case, $\chi_d(k_{\text{min}}, t)$ eventually exhibits a maximum, as found in hard sphere glasses. These results clearly demonstrate that, when the bond lifetime is long enough, as compared to the relaxation time, the behavior of the dynamical susceptibility is akin to that measured in chemical gels, on time scales for which the bonds can be considered as permanent. At longer times, the breaking of the clusters causes the final decay to zero. A geometrical interpretation of $\chi_d(k_{\text{min}}, t)$ in this system can be given by considering the time dependent mean cluster size $S_m(t)$ of mobile particles [5]. Here two particles are considered as part of the same cluster if they are bonded both at time zero and at time $t$. In the inset of figure 2(b), $S_m(t)$ is plotted for volume fraction $\phi = 0.05$ and $\phi = 0.12$. At low volume fraction the coincidence of $\chi_d(k_{\text{min}}, t)$ and $S_m(t)$ is excellent. At higher volume fraction the maximum of $\chi_d(k_{\text{min}}, t)$ is larger than the maximum of $S_m(t)$, denoting that the contribution to the peak comes not only from the cluster formation, but also from the crowding of the particles, as usually observed in glassy systems. The figure exemplifies that there are two different mechanisms underlying the presence of significant DHs at different volume fractions. It also shows the crossover from the cluster dominated regime to the crowding dominated regime.

4. Dynamical heterogeneities in structural glasses

We now discuss how arguments from percolation and gels can be useful to characterize the relaxation process and DHs in glasses, where particles interact via a hard core repulsion, and the dynamics slows down at high density due to crowding. To this aim, we review recent results [6, 28] from numerical simulations of the KA lattice model [29].
The KA is a kinetically constrained model [30], in which a lattice of volume \( V \) is randomly occupied by a number \( V \rho \) of non overlapping particles, and each particle is allowed to move in a near empty site if it has less than \( m = 4 \) neighbors before and after the move. Previous studies have shown that this model reproduces many aspects of glass forming systems, as the dynamics slows down on increasing the density, and suggests the existence of a transition of structural arrest at \( \rho_{KA} = 0.881 \) [29]. Even though, it has been demonstrated that in the thermodynamic limit the transition of dynamical arrest only occurs at \( \rho = 1 \) [31].

After introducing an occupation number \( n_i(t) = 1(0) \), if site \( i \) is (is not) persistently occupied by the same particle in the time interval \([0, t]\), we monitor the relaxation process through the density of persistent particles, \( p(t) = \frac{1}{V} \sum_{i=1}^{V} n_i(t) \), which is related to the high wave-vector limit of the self ISF [32]. Accordingly, we define the structural relaxation time from the relation \( p(t)/\rho = e^{-\tau_{\rho}} \). The decay in time of the ensemble average, \( p(t)/\rho \), for a high density value is illustrated in figure 3.

Similarly, we quantify the emergence of DHs focusing on the spatial correlation function between persistent particles at time \( t \) [28],

\[
g_s(r, t) = \langle n_i(t)n_j(t) \rangle - \langle n_i(t) \rangle \langle n_j(t) \rangle, \quad r = |i - j|.
\]

and, from its spatial decay, we extract a dynamical correlation length \( \xi(t) \).

Figure 4 suggests that, as time advances and the number of persistent particles decreases, spatial correlations first grow and then decay. Accordingly, figure 5(a) shows that \( \xi(t) \) exhibits, at short times, a power-law increase, and then decreases after reaching its maximum value \( \xi^* \) at time \( t_{\xi}^* \). Both \( \xi^* \) and \( t_{\xi}^* \) increase as power laws of \( \rho_{KA} - \rho \). Figure 5(b)

Figure 2. (a) The structural relaxation time, \( \tau_{\rho}(k_{\min}) \) (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 \((0.14 - \phi)^{-3.8}\). Adapted from [5]; (b) Main frame: the fluctuations of the self ISF, \( \chi_4(k_{\min}, t) \), obtained in the DLVO model, for \( T = 0.15 \) and \( \phi = 0.01, 0.05, 0.08, 0.10, 0.11, 0.12 \) (from left to right). Inset: \( \chi_4(k_{\min}, t) \) (circles) compared with the time dependent mean cluster size, \( S_m(t) \), of mobile particles (open circles), for \( T = 0.15 \) and \( \phi = 0.01, 0.12 \). Adapted from [5].
shows that the dynamical susceptibility, $\chi_4(t) = \frac{V}{\rho}(\langle p(t)^2 \rangle - \langle p(t) \rangle^2) = \frac{1}{\rho^2} \int_V g_4(r, t) \, d^3r$ has a behavior qualitatively similar to $\xi_4(t)$ [6] and allows the difference to be appreciated with the gel case, as discussed before. We also found [6] that the relation between the behavior of $\langle p(t) \rangle$, $\xi_4(t)$ and $\chi_4(t)$ can be rationalized within the diffusing defect paradigm [33, 34], which ascribes the relaxation of the system to the diffusion of possibly extended defects.

To provide a geometrical characterization of this scenario, we consider that the glass former may be thought as rigid on time-scales smaller than the relaxation time $\tau$, and as liquid at larger times. In that sense, we expect that, as long as the system behaves as a solid, a percolating cluster of persistent particles plays the role of the physical backbone in gels, and that a reverse dynamical percolation transition occurs for time-scales of the order of the relaxation time. Indeed, the absence
of the percolating cluster should lead to the loss of rigidity. In order to investigate whether this supposed transition was related to the relaxation process, we define a dynamical kind of bond, similarly to the case of colloidal gels: two particles $i$ and $j$ are bonded in the interval $[0, t]$ if they are nearest neighbors and persistent in this time interval.

In figure 3, we show $P(t)$, the density of persistent particles belonging to the spanning cluster. $P(t)$ vanishes at a time $t_{\text{per}}$, which is found to scale with the relaxation times, $\tau$, as the density increases (figure 3, inset). The figure also reveals that the cluster strength overlaps with the total density of persistent particles, $P(t) \approx \langle P(t) \rangle$, up to large times. This means that the percolating cluster is the only cluster present during this time interval. At larger time, $P(t)$ slowly decays, while $P(t)$ vanishes, because of the emergence of finite clusters, with a broad size distribution, which give contributions to $\langle P(t) \rangle$, but not to $P(t)$. This circumstance may explain the crossover from power-law to stretched exponential observed for $\langle P(t) \rangle$ [6]: indeed the short time decay is characterized by a single relaxation time, whereas the long time decay results from a broad spectra of finite cluster lifetime.

To better understand the geometrical properties of this process, we investigate the correlation length, $\xi_{\text{per}}(t)$, which is defined by the percolative correlation function $g_{\text{per}}(r, t)$:

$$g_{\text{per}}(r, t) = P_{ij}(r, t) + P_{ij}(r, t) - \langle P(t) \rangle^2$$

(2)

where $P_{ij}(r, t)$ and $P_{ij}(r, t)$ are the probabilities that two sites $i$ and $j$, in the configuration of persistent particles at time $t$, belong to the same finite cluster, or to the percolating cluster respectively. Accordingly, if the percolating cluster is absent, $g_{\text{per}}(r, t) = P_{ij}(r, t)$.
and $\xi_{\text{per}}(t)$ measures the typical size of finite clusters. Conversely, if finite clusters are negligible, then

$$g_{\text{per}}(r, t) = P^\infty_{i,j}(r, t) - \langle P(t) \rangle^2$$

measures the extension of the density fluctuations within the percolating cluster. In our case, at short time, $\langle P(t) \rangle \simeq \langle p(t) \rangle$ and $P^\infty_{i,j}(r, t) \simeq \langle n_i(t)n_j(t) \rangle_{-|j|=r}$ because almost all persistent particles belong to the percolating cluster, making the connectedness condition negligible [35]. Inserting these equalities into equation (3) and comparing it with the definition of the four point correlation function, $g_4(r, t)$, equation (1), we find that $g_{\text{per}}(r, t) \simeq g_4(r, t)$, and consequently $\xi_{\text{per}}(t) \simeq \xi_4(t)$. Indeed, figure 3 confirms that the dynamical correlation length coincides with the percolative length, as long as finite clusters are negligible.

The fact that finite clusters are essentially absent until a spanning cluster exists, suggests that this percolation is different from the random percolation, which drives instead the chemical gelation. Thus, what is the type of percolation relevant to describe the relaxation process in the KA model? The scenario emerging from the related mean field case could be useful to tackle this issue. In a recent paper [36], the dynamical behavior of the Fredrickson and Andersen (FA) facilitated model [37], which is a spin version of the KA model, was indeed studied on the Bethe lattice. In the infinite time limit, this model reproduces [38] the bootstrap percolation (BP) model [39–41]. In BP, the lattice sites are occupied randomly with density $\rho$. Then each particle, which has less than a fixed number $m$ of neighbors, is removed, until a stable configuration is reached. This configuration is made of clusters of particles, where each particle has less than $m$ neighbors. BP on the Bethe lattice of coordination number $z$ has a mixed order transition when $m > 2$. Below the percolation threshold, there are no occupied sites, while above the threshold there are no finite clusters, but only an infinite cluster which is called $m$-cluster. The percolation order parameter, $P_c$, jumps discontinuously at the threshold from 0 to $P_c$, and the approach to $P_c$ from the percolating phase is characterized by a critical exponent $\beta = 1/2$ [39], while the fluctuation of the order parameter and the associated length diverge with exponents $\gamma = 1$ and $\nu = 1/4$ [36], respectively.

Summarizing, in the FA model, the infinite time limit of the dynamical order parameter, its fluctuation and the dynamical length are given by the corresponding static quantities of BP. Consequently, these static quantities are different from zero only in the glassy phase, and become critical at the threshold. Nevertheless, in the liquid phase, the time dependent dynamical quantities $\langle p(t) \rangle$, $\xi_4(t)$ and $\chi_4(t)$ of the FA model, although tend to zero in the infinite time limit, reflect at finite time the behavior of the BP static quantities [36]. The picture is similar to that found in the liquid phase of colloidal gels, in the particular case in which the bond lifetime and the relaxation time become comparable, with the difference that random percolation drives the dynamical transition in gel models, whereas bootstrap percolation drives the glass transition in the FA model. Interestingly enough there is strong evidence [36, 38, 42–44] that the dynamical behavior of the FA model on the Bethe lattice and of gel systems in the mean field are related [46] to the ones predicted by the discontinuous and the continuous mode coupling theory (MCT) [45], respectively.
5. Conclusions

The study of DHs contributes to the clarification of the nature of slow dynamics and structural arrest in gels and glasses. The behavior of the dynamical susceptibility in chemical gelation is quite different from that found in hard sphere glasses. It grows steadily and reaches a plateau, whose value, in the low wave-vector limit, coincides with the mean cluster size. In colloidal gelation, at low temperature, DHs are associated to clusters made of long living bonds and the dynamical susceptibility reaches a plateau, as found in chemical gels, except that it decays to zero at long times, due to the finite lifetime of the clusters. DHs in physical gels are also analyzed in [17], where a FENE model with finite bond lifetime is studied using molecular dynamics simulations. However, the dynamical susceptibility, evaluated only at large wave-vectors, displays the behavior usually found in glassy systems. We expect that also in that case, when the bond lifetime is long enough, the dynamical susceptibility in the gel phase displays, at small wave-vectors, a plateau at intermediate times, signaling the presence of persistent clusters. At higher volume fraction, DHs crossover to a different behavior, where crowding starts to play a role, which becomes dominant for glasses. In this case, the bootstrap percolation model seems to provide a geometrical characterization of DHs. Finally, we suggest that the use of very recent optical techniques, such as the digital differential microscopy [47, 48], might provide new experimental insights on DHs of colloidal systems in a wide range of wavelengths.

Acknowledgments

We acknowledge financial support from MIUR-FIRB RBFR081IUK, from the SPIN SEED 2014 project Charge separation and charge transport in hybrid solar cells, and from the CNR-NTU joint laboratory Amorphous materials for energy harvesting applications.

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doi:10.1088/1742-5468/2016/07/074011
doi:10.1088/1742-5468/2016/07/074011