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Dynamical heterogeneities: from glasses to gels

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Abstract

One of the challenges in soft and condensed matter over the last few years has been understanding the phenomena of glass and jamming transitions. A recent advance in the field is the idea that the dynamical heterogeneities play here the same role as the critical fluctuations in ordinary critical phenomena. This is due to the fact that the decay of density fluctuations in glasses and jammed systems takes place thanks to the dynamically correlated motions of groups of particles. In this paper, after a brief review of the properties of the dynamical heterogeneities in glasses we analyze the cases of chemical and colloidal gels, which are still intensely debated.

1. Introduction

Glasses, colloidal and chemical gels, granular materials and foams are examples of systems which, by changing the control parameters, exhibit slow dynamics followed by a structural arrest, often called jamming. Understanding this jamming transition is still one of the major problems in soft and condensed matter physics. For example, the question whether the jamming or glass transitions are based or not on a true underlying phase transition is still open. Developments of the Adam and Gibbs' theory [1] and the analogy with the spin glass transition have suggested the idea that dynamical heterogeneities (DH) in the glass transition might play the same role as critical fluctuations in critical phenomena. Since then, the concept of DH seems very promising to distinguish between competing theories and understanding differences and universality in the jamming transition. Here we will exploit this idea to investigate the nature of structural arrest in chemical and colloidal gels. This question is also extremely interesting because of the many industrial applications of gels going from toothpaste to gelatins, paints and beauty products, just to mention a few of them relevant to our practical life.

In the following, we start by reviewing the main results of mode coupling theory (MCT) for the glass transition. We then introduce the concept of DH in glasses and hard sphere colloids and discuss the predictions of MCT. Then we analyze

the striking differences among DH in models of chemical gels, colloidal gels and glasses. This paper is based both on new results and on the elaboration of results previously published.

2. Mode coupling theory and the glass transition

Upon cooling a liquid, a melting temperature is reached below which the system shows a crystalline order. However, depending on the cooling procedure, the transition may be avoided and the system enters a supercooled metastable state until it gets out of equilibrium in a glassy state. The temperature where such a transition occurs depends on the cooling rate. With an infinitely slow cooling rate, one should reach the lowest glass transition temperature T_0 , often referred to as the ideal glass transition. Certainly, the striking feature of the glass transition is that the shear viscosity or the relaxation time varies by many orders of magnitude over a small range of temperatures, whereas no meaningful change is observed in the static structure factor of the system. The temperature dependence of the viscosity coefficient of the supercooled liquid can be fitted with an Arrhenius or Vogel–Fulcher law, which distinguishes a strong from a fragile glass according to Angel's classification [2].

An important advance in the understanding of these phenomena was obtained when Götze and his collaborators [3] proposed the MCT for the glass transition. Starting from first

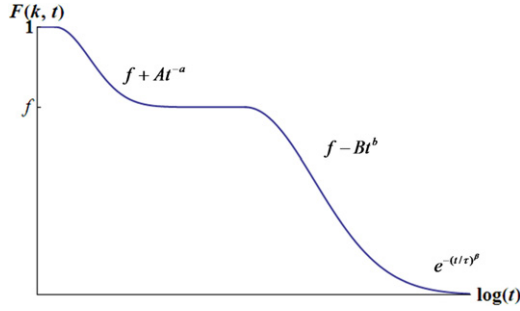


Figure 1. Schematic behavior of the intermediate scattering function, $F(k, t)$, in the mode coupling theory.

principles, they derived an equation for the time evolution of a typical autocorrelation function, e.g. the intermediate scattering function (ISF) $F(k, t)$, leading to a number of precise dynamical predictions. $F(k, t)$ is defined as

$$F(k, t) = \frac{\sum_{i,j=1}^N \langle e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(0))} \rangle}{S(k)}, \quad (1)$$

where $\vec{r}_i(t)$ is the position of the i th particle at time t , $\langle \dots \rangle$ is the ensemble average and $S(k) = \sum_{i,j=1}^N \langle e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \rangle$ is the static structure factor.

In a simple liquid, at high temperature, $F(k, t)$ decays exponentially. At low temperature, instead, deep in the supercooled regime, a two-step decay is found: a first decay to a plateau is followed by a second decay from the plateau to zero (figure 1). The decay to the plateau and the departure from it are characterized by power law behaviors. The exponent $0 < a < 0.5$ fixes the short-time behavior, $F(k, t) \sim f + At^{-a}$, whereas the departure from the plateau is characterized by the so-called von Schweidler law $F(k, t) \sim f - Bt^b$, where $0 < b \leq 1$. These exponents are related via the following equation:

$$\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)}, \quad (2)$$

and give the exponent $\gamma = \frac{1}{2a} + \frac{1}{2b}$ which governs the power law divergence of the structural relaxation time $\tau \sim (T - T_c)^{-\gamma}$.

At high temperature, the particle mean square displacement displays a diffusive behavior as in a simple liquid. In the supercooled regime of low temperatures, instead, it exhibits a sub-diffusive regime approaching a plateau, and eventually it crosses over, in the long-time regime, to a diffusive behavior. These features of the mean square displacement and $F(k, t)$ have led to the picture of a particle close to the glass transition being confined, due to the crowding, in a cage formed by its neighbors until the cage opening allows the particles to get out and eventually get trapped in another cage. The predictions of MCT are rather well verified experimentally and numerically for colloidal systems and at least on a short timescale for molecular liquids (see, for example, [4]). Although the assumptions underlying MCT are not easily controlled, it has been shown [5] that in the mean field version of the p -spin model the spin-spin autocorrelation function follows a time evolution equation which is identical to that obtained in the

simplified version of MCT. This has suggested that MCT corresponds in fact to a mean field approximation, and that the MCT critical temperature T_c is a temperature below which an infinite number of metastable states separated by infinite energy barriers appear where the system gets trapped with subsequent breakdown of ergodicity. However, in a real three-dimensional system, the barriers are not infinite and T_c should be considered as a crossover temperature towards a hopping regime where the relaxation time, albeit large, is still finite.

3. Dynamical heterogeneities

A somehow alternative theory, proposed by Adam and Gibbs [1], introduced the concept of cooperatively rearranging regions. The main idea is that, close to the glass transition, due to the crowding of particles, the decay towards equilibrium of a density fluctuation is due to a cooperative rearrangement of correlated regions. The theory has been revisited by Kirkpatrick *et al* [6]. Later these concepts have been further developed by Cicerone and Ediger [7] who introduced the concept of DH, further elaborated and quantified in [8, 9]. DH are associated with groups of particles whose motion is dynamically correlated both in space and time. The size of such groups of particles significantly grows as the glass transition is approached [10–19].

Other approaches based on facilitated models [20] suggest that the dynamics are governed by ‘mobility defects’. These also lead to DH characterized by bubbles in space and time, i.e. arrested domains in the trajectory space [21].

How to quantify the DH? A four-point correlation function has been introduced [8, 9], in analogy with spin glasses:

$$G_4(\vec{r}, t) = \langle \rho(0, 0) \rho(0, t) \rho(\vec{r}, 0) \rho(\vec{r}, t) \rangle - \langle \rho(0, 0) \rho(0, t) \rangle \langle \rho(\vec{r}, 0) \rho(\vec{r}, t) \rangle, \quad (3)$$

where $\rho(\vec{r}, t)$ is the density at position \vec{r} and time t . Since particles during the time t cannot be exactly in the same position, one usually introduces an overlap function $w(r) = 1$, if $r < a$ and 0 otherwise, and substitute $\rho(\vec{r}, 0) \rho(\vec{r}, t)$ with $\int w(r') \rho(\vec{r}, 0) \rho(\vec{r} + \vec{r}', t) d\vec{r}'$. This quantity is different from zero if a particle in \vec{r} has moved a distance less than a in the time interval t . On this basis, $G_4(\vec{r}, t)$ can be related to the probability that, if a particle at the origin has moved a distance less than a during time t , another particle at distance r has also moved a distance less than a in the same time t .

Note that $\langle q(t) \rangle = \langle \int w(r) \rho(0, 0) \rho(\vec{r}, t) d\vec{r} \rangle$ represents the time-dependent order parameter which decays to zero in the liquid and to a constant value different from zero in the glass. Therefore G_4 represents the fluctuations of the dynamical order parameter and it is a good candidate to describe the right correlation function.

3.1. Dynamical susceptibility

From the four-point correlation function in equation (3) one obtains the dynamical susceptibility [8, 9]

$$\chi_4(t) = \int G_4(\vec{r}, t) d\vec{r}. \quad (4)$$

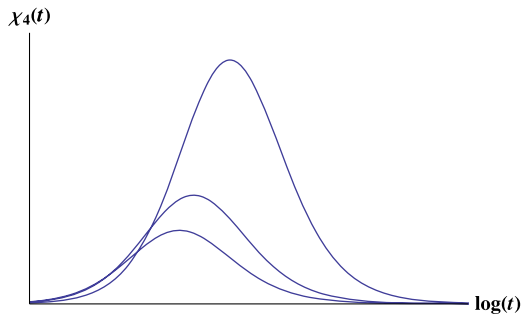


Figure 2. Schematic behavior of the dynamical susceptibility, $\chi_4(t)$, in a typical glass former for decreasing temperature (from bottom to top).

In the usual glassy systems $\chi_4(t)$ grows as a function of time, reaches a maximum and then decreases to a constant, consistent with the transient nature of DH (see figure 2). As the temperature decreases, the peak increases and shifts to longer times.

Evidence of DH is found in many numerical simulations [11, 12, 22–24] and experiments [7, 13, 19, 25–27]. Recently, DH have been detected in molecular supercooled liquids and more directly measured in granular materials, where the larger size of the particles makes the microscopic length more easily accessible [28, 29].

3.2. Non-Gaussian parameter

Another measure of DH is the non-Gaussian parameter α_2 [30] defined as

$$\alpha_2(t) = \frac{3\Delta r^4(t)}{5(\Delta r^2(t))^2} - 1, \quad (5)$$

where $\Delta r^2(t) = \frac{1}{N} \sum_{i=1}^N \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$ and $\Delta r^4(t) = \frac{1}{N} \sum_{i=1}^N \langle |\vec{r}_i(t) - \vec{r}_i(0)|^4 \rangle$. This is a measure of the departure from the Gaussian behavior of the probability distribution of particle displacements. In supercooled liquids, it has been shown to reflect the presence of DH [10]: upon entering the timescale typical of the caging, α_2 starts to increase, reaches a maximum at a time t^* and decreases to its long-time limit, 0, on the timescale of the cage opening. Its maximum value increases with decreasing T , due to the higher degree of heterogeneity of the dynamics, whereas t^* shifts to longer times.

3.3. Dynamical heterogeneities and mode coupling theory

The cage picture has generated the idea that the dynamical arrest described by MCT is governed by a short length scale phenomenon, and therefore in contrast with the picture emerging from the study of DH. However, DH in a glass transition have been recently derived also within MCT, leading to analytical predictions. Franz and Parisi [8] first introduced the dynamical susceptibility in the context of mean field p -spin glasses and showed that, within the schematic MCT, it becomes critical at the mode coupling temperature T_c . Connection with more standard MCT was later done in [15, 16] (for more developments see also [31, 32]). In this framework, detailed

predictions on the shape of the dynamical susceptibility are obtained. In particular, it is found that $\chi_4 \sim t^a$ in the early- β regime, i.e. when the intermediate scattering function approaches a plateau, and $\chi_4 \sim t^b$ on the timescales between the departure from the plateau and the peak of χ_4 . Finally, the value of the peak $\chi_4(t^*)$ is predicted to diverge at T_c with a power law, $\chi_4(t^*) \sim (T - T_c)^{-1}$. Due to the growth of χ_4 during the approach and the departure from the plateau, the cage picture needs to be modified: rattling in the cage is accompanied by a cooperative rearrangement of particles which actually leads to the opening of the cage.

MCT also predicts a specific behavior for the non-Gaussian parameter for a hard-sphere system [33], characterized by a maximum at a time t^* . The value of the maximum of α_2 slowly increases as the volume fraction approaches the critical value, whereas the time t^* shifts to longer times.

4. Dynamical heterogeneities in gels

The nature of slow dynamics and structural arrest phenomena in gelling systems has been strongly debated in the rich literature of the last few years. This is certainly due to the relevance of understanding their rheological and mechanical features in a number of technological applications but also to the connection that these phenomena show with the glassy dynamics observed in molecular liquids. In particular, one of the most debated points is how intimate is the connection between the slow dynamics/structural arrest and the structuring typical of gelation. This question is particularly intriguing in the case of attractive colloidal suspensions, where the gelation results from nonpermanent bonding of the particles in a transient network, making the understanding of the role of gelation in the structural arrest even more elusive. A striking feature is that in gels a growing structural length scale (e.g. the one related to the growth of connectivity due to gelation) can be readily identified, different from supercooled molecular liquids where no structural length scale corresponding to the growing size of DH could ever be found. That is why it is extremely interesting to compare the complex relaxation dynamics and the DH of these systems to the one of supercooled liquids.

In the following, we start from the case, relatively simpler, of chemical gels where gelation is due to permanent bonds. After analyzing the DH in these systems, we go to the case of colloidal gels and we finally consider the crossover from colloidal gelation to the hard-sphere colloidal glasses.

4.1. Dynamical heterogeneities in chemical gels

The transition from sol to gel is due to the onset of a spanning cluster, giving 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 [34, 35] chemical gelation has been explained in terms of percolation models (for a review see [36]). However, it is important to remark that, different from the case of the liquid–gas transition, in this percolation description of the gelation transition, the clusters could never be associated with density fluctuations or to any other directly detectable quantity.

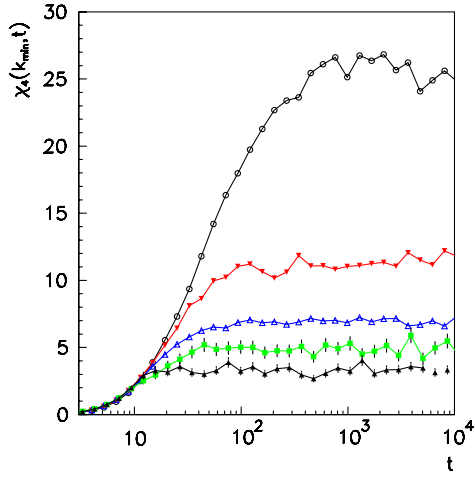


Figure 3. Dynamical susceptibility, $\chi_4(k, t)$, in the FENE model, as a function of time for $k = k_{\min} \simeq 0.35$ and different volume fractions, $\phi = 0.05, 0.06, 0.07, 0.08$ and 0.09 (from bottom to top).

We have recently investigated the problem with a suitable model to study chemical gels by means of molecular dynamics [37]. The model is a 3d system of N particles interacting with a soft potential given by a Weeks–Chandler–Andersen (WCA) potential [38]. After the equilibration, particles spacing less than R_0 are linked by adding an attractive potential representing a finitely extendible nonlinear elastic (FENE), first introduced in [39] and widely used to study linear polymeric systems [40]. The introduction of the FENE potential leads to the formation of permanent bonds among all the particles whose distance at that time is lower than R_0 . For alternatives models see also [41, 42] and more recently [43]. Our numerical simulations have shown a percolation transition at volume fraction $\phi_c \simeq 0.1$, with critical exponents in agreement with random percolation. In particular, the cluster size distribution, $n(s) \sim s^{-\tau}$, at ϕ_c with $\tau = 2.1 \pm 0.2$, the mean cluster size $S(\phi) = \sum s^2 n(s) / \sum s n(s) \sim (\phi_c - \phi)^{-\gamma}$ with $\gamma = 1.8 \pm 0.1$, and the connectedness length $\xi \sim (\phi_c - \phi)^{-\nu}$ with $\nu = 0.88 \pm 0.01$.

At small wavevectors, the self-intermediate scattering function $\langle \Phi_s(k, t) \rangle = \langle \frac{1}{N} \sum_{i=1}^N e^{i\mathbf{k} \cdot (\vec{r}_i(t) - \vec{r}_i(0))} \rangle$ shows a stretched exponential decay as a function of time before the percolation threshold and a dynamical transition at the threshold, characterized by the onset of a power law decay. The relaxation time diverges as a power law as the threshold is approached. These findings are consistent with the experimental results [44] and other numerical simulations [41, 42].

We have studied the dynamical susceptibility by calculating the fluctuations of the self-intermediate scattering function $\chi_4(k, t) = N[\langle |\Phi_s(k, t)|^2 \rangle - \langle \Phi_s(k, t) \rangle^2]$, where $\langle \dots \rangle$ is the thermal average for a fixed bond configuration and $[\dots]$ is the average over the bond configurations. The wavelength k allows us to probe DH at different length scales. We have calculated χ_4 for fixed k and different volume fraction ϕ . In figure 3 $\chi_4(k, t)$ is plotted for $k = k_{\min} = 2\pi/L$ and different ϕ , and in figure 4 $\chi_4(k, t)$ is plotted at the percolation threshold for different k . These figures show the

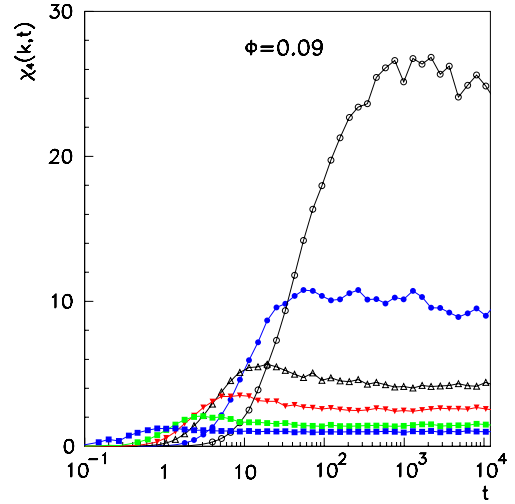


Figure 4. Dynamical susceptibility, $\chi_4(k, t)$, in the FENE model, as a function of time for $\phi = 0.09$ and different wavevectors, $k = 0.35, 0.6, 1, 1.4, 1.9$ and 3.9 (from top to bottom).

striking difference of the dynamical susceptibility in chemical gels from the one in glasses. For each value of the volume fraction, $\chi_4(k, t)$ reaches a plateau after a characteristic time of the order of the relaxation time. We have been able to show in [37] that in the limit of small k the asymptotic value of $\chi_4(k, t)$ coincides with the mean cluster size and verified it numerically. Our results indicate that in permanent gels DH are due to the presence of clusters of bonded particles. We could also show, more generally, that $\chi_{as}(k, \phi) = k^{\eta-2} f(k\xi)$ where $2 - \eta = \gamma/\nu$. This remarkable result demonstrates that it is possible to connect the percolation clusters to the asymptotic value of the dynamical susceptibility. Not only does this indicate that the percolation exponents can also be measured by means of the asymptotic dynamical susceptibility, but it also states that the asymptotic value of the dynamical susceptibility plays the same role as the static scattering function near a liquid–gas critical point.

Here we also investigate the behavior of the non-Gaussian parameter. As shown in figure 5, in this case the difference in the behavior observed in the chemical gel is also striking: instead of displaying a maximum, α_2 grows with time to a plateau value. This behavior is qualitatively similar to the one of $\chi_4(k_{\min}, t)$ reported above. However, even if α_2 also tends to a plateau, the value of the plateau does not diverge as a function of $(\phi_c - \phi)$. This indicates that α_2 is not related to the mean cluster size, which instead controls the asymptotic behavior of $\chi_4(k_{\min}, t)$ [45].

4.2. Dynamical heterogeneities in colloidal gels

We have found that 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 has clarified the nature of the slow dynamics/structural arrest in these gels as compared to hard-sphere glasses, where bonds play no role. Very intriguing is the case of gels formed in attractive colloids which are in between

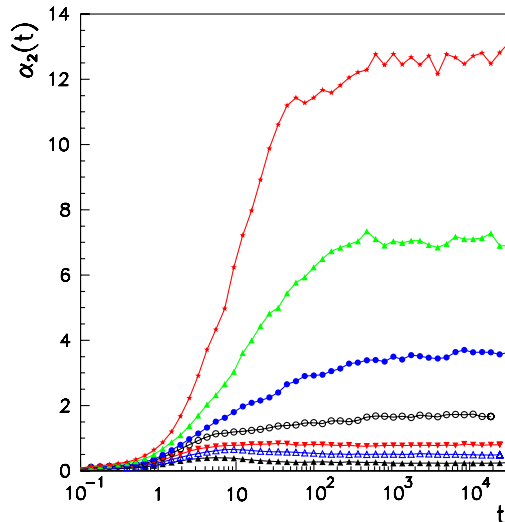


Figure 5. Non-Gaussian parameter, $\alpha_2(t)$, in the FENE model, as a function of time t for $\phi = 0.05, 0.07, 0.08, 0.09, 0.10, 0.11$ and 0.12 (from bottom to top).

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 nonpermanent colloidal gel and finally to a hard-sphere glass. Therefore, the study of DH in these systems might unveil new behaviors arising in intermediate situations and shed new light on the nature of the structural arrest transition. A numerical study of the dynamical susceptibility in the attractive glass region [23] has already shown a marked difference in the k dependence of the maximum of χ_4 as compared to the hard-sphere glass. In the following, we discuss the behavior of the dynamical susceptibility at low volume fractions, i.e. at the crossover between the irreversible and the nonpermanent colloidal gelation, and upon approaching the glassy region.

Colloids consist of suspensions of solid particles, whose size may range from ~ 5 nm and ~ 0.2 μm . The suspension being usually density- and index-matched, the particles behave as hard spheres. Therefore at small volume fraction the colloidal suspension will display the features of a normal liquid. By increasing the volume fraction if one avoids crystallization, the system undergoes a jamming transition due to the crowding of the particles (for a classical paper on the experimental study of colloidal hard spheres see [46]). The addition of non-adsorbing polymers to the suspension induces effective attractive interactions between the colloidal particles due to depletion [47]. In this case, in the temperature–volume fraction plane, the structural arrest line, i.e. where the jamming transition occurs, typically interferes with the coexistence curve [48]. Gelation may occur, due to an interrupted phase separation which recently has been accurately studied in a combined experimental and numerical effort [49] (for a review on different roots to colloidal gelation see also [50]).

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 potential can be used to model this kind

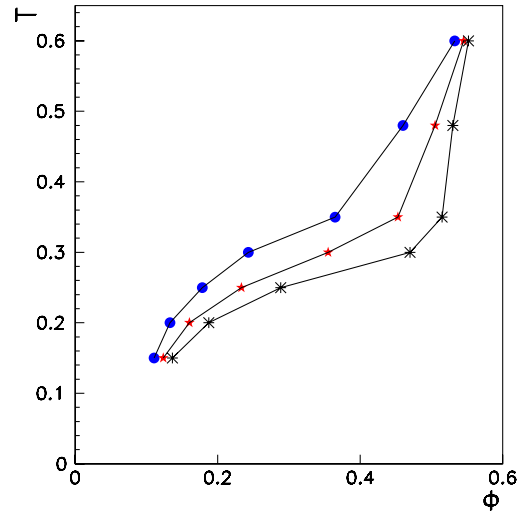


Figure 6. Iso-diffusivity curves obtained in the DLVO model, in the temperature–volume fraction plane, respectively, for $D = 10^{-3}, 10^{-4}$ and 10^{-5} (from top to bottom).

of effective interaction, as often seen in the literature [51, 52]. Actually, it has been shown that the competing attraction and repulsion will favor ordered columnar and lamellar phases at low temperatures [53, 54], therefore limiting the possibility to study the metastable states associated with 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 [55]. Figure 6 shows the iso-diffusivity curves in the temperature–volume fraction plane, giving an estimate of the shape of the structural arrest line. At high temperature the line of structural arrest approaches the hard-sphere glass transition. In the low temperature phase, particles tend to form strong bonds which give rise to a macroscopic network, able to bear stress. The arrested state exhibits a gel behavior (see [56] for experiments and [53, 57] for numerical simulations; see also [50] and references therein). However, if the temperature is not low enough the bonds have a finite lifetime and particles can only form a transient network. In this case, the structural arrest will move towards higher volume fractions and display features typical of attractive and hard-sphere glasses [55].

Figure 7 shows the relaxation time, calculated from the self-intermediate scattering function at small wavevector, together with the lifetime of the bonds τ_b . It indicates that at low volume fraction the lifetime of the bonds is much longer than the relaxation time. In fact, the relaxation time exhibits a power law with an apparent divergence at the percolation threshold, as in chemical gelation, i.e. as if the clusters were due to permanent bonds. Consistently, such power law divergence is not observed at higher temperatures where the lifetime of the bonds and relaxation time are of the same order of magnitude [41, 51].

The dynamical susceptibility, $\chi_4(k, t)$, for the lowest value of k is shown in figure 8: for small values of the volume fraction, after a timescale of the order of τ , $\chi_4(k_{\min}, t)$ reaches a plateau whose value is given roughly by the mean cluster size. However, after a time of the order of the bond

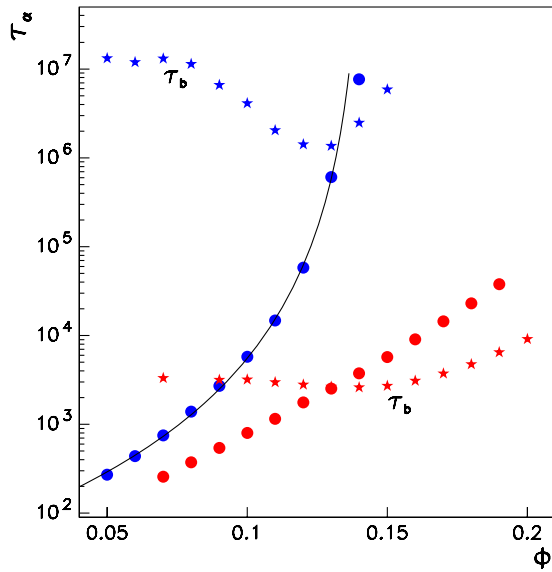


Figure 7. The structural relaxation time, $\tau_\alpha(k_{\min})$ (circles), compared with the bond relaxation time, τ_b (stars), for $T = 0.15$ and 0.25 (from bottom to top). The continuous line is a power law fit $(0.14 - \phi)^{-3.8}$.

lifetime, $\chi_4(k_{\min}, t)$ decreases. For higher volume fraction the difference between $\tau(k_{\min})$ and τ_b decreases and the persistence of the plateau in time decreases until $\tau(k_{\min})$ and τ_b are of the same order of magnitude and the plateau disappears. In this case, $\chi_4(k_{\min}, t)$ eventually exhibits a maximum like the one of hard-sphere glasses. These results demonstrate well that, when the bond lifetime is long enough, as compared to the relaxation time, the behavior of χ_4 is the same as the one measured in chemical gels, on timescales for which the bonds can be considered as permanent. At longer times the breaking of the clusters causes the final decay to zero. In fact, a geometrical interpretation of $\chi_4(k_{\min}, t)$ in this system can be given by considering a new cluster definition made of ‘mobile’ monomers, connected by bonds which are present at both time zero and time t . The mobile monomers are particles which have moved at least a suitable small distance r_0 .⁶ The mean cluster size of such mobile clusters $S_m(t)$ is a time-dependent function which will decrease in the limit of large t when the bonds starts to break. At $t = 0$, $S_m(t) = 0$ since particles have not moved. In the inset of figure 8 $S_m(t)$ is plotted for volume fractions $\phi = 0.01$ and 0.12 . At low volume fraction the coincidence of $\chi_4(k_{\min}, t)$ and $S_m(t)$ is excellent. At higher volume fraction the maximum of $\chi_4(k_{\min}, t)$ 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, typical of the hard-sphere glasses. The figure well exemplifies that there are two different mechanisms underlying the presence of significant DH at different volume fractions. It also shows clear evidence of the crossover from the cluster-dominated regime to a crowding-dominated regime.

⁶ For each volume fraction, we fix r_0 so that $S_m(t)$ and $\chi_4(k_{\min}, t)$ start to grow at the same time.

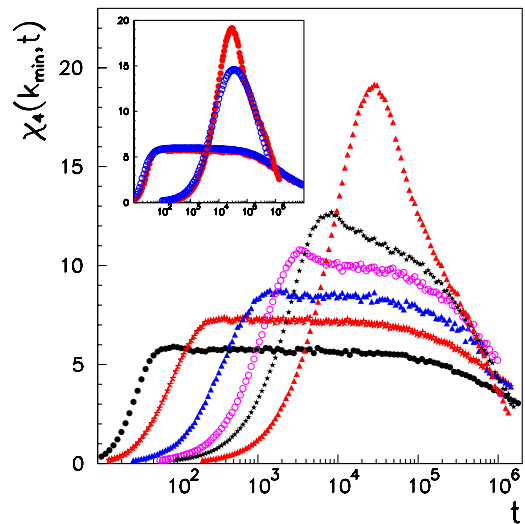


Figure 8. Main frame: the fluctuations of the self-ISF, $\chi_4(k_{\min}, t)$, obtained in the DLVO model, for $T = 0.15$ and $\phi = 0.01, 0.05, 0.08, 0.10, 0.11$ and 0.12 (from left to right). Inset: $\chi_4(k_{\min}, t)$ (circles) compared with the time-dependent mean cluster size $S_m(t)$ of mobile particles (void circles), for $T = 0.15$ and $\phi = 0.01$ and 0.12 .

5. Conclusions

The study of DH allows us to clarify the nature of slow dynamics and structural arrest observed in gels and glasses. The behavior of the dynamical susceptibility, which describes the DH, in chemical gelation is quite different from that found in hard-sphere glasses. It grows steadily and reaches a plateau whose value coincides with the mean cluster size in the low wavevector limit. In particular, the low wavevector signal is able to detect the critical behavior of the system at the gelation transition. The large wavevector signal, as well as measures of DH based on single-particle diffusion, is dominated by finite clusters and is not sensitive enough to the gelation. In colloidal gelation at low T , DH are associated with clusters made of long living bonds and the dynamical susceptibility reaches a plateau as found in chemical gels, except that, at long time, it decays to zero due to the finite lifetime of the clusters. At higher volume fraction the DH cross over to a different behavior where crowding effects start to dominate. This difference actually gives rise to the different dynamical behaviors found in gels and glasses. Whether and how it is possible to also geometrically characterize the type of DH typical of glasses is still an open question.

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