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PAPER

Scaling between structural relaxation and particle caging in a model colloidal gel†

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In glassy dynamics, the rattling of particles in a cage formed by their neighbors is typically limited to a length scale of the order of the particle diameter but is nevertheless strongly coupled to the overall structural arrest of the system (solidification). Furthermore, the rattling amplitude and the structural relaxation time have been recently shown to follow the same scaling form in various polymer melts and supercooled liquids. In this paper we analyze from this perspective for the first time the glassy dynamics emerging from the formation of a persistent network in a model colloidal gel at very low density. The structural relaxation time of the gel network is compared with the mean squared displacement at short times, corresponding to the localization length associated to the presence of energetic bonds. Interestingly, we find that the same type of scaling as for the dense glassy systems holds. Our findings elucidate the strong coupling between the cooperative rearrangements of the gel network and the single particle localization in the structure, and support the general nature of the scaling proposed.

1. Introduction

Crowding and caging effects play major roles in the glass transition (GT) of molecular liquids of dense systems in soft matter.^{1–10} The strong localization of the particles in the cage formed by their neighbors typically shows up as a plateau in the time dependence of the particle mean square displacement (MSD). The value of the MSD plateau (u^2) yields the amplitude of the rattling motion inside the cage and hence the corresponding localization length. In spite of the extreme time-scale separation between the rattling motion ($\sim 10^{-12}$ s) and the structural relaxation ($\tau_\alpha \sim 10^2$ s at GT) strong correlations between them are present and have been investigated by several authors.^{11–30} In particular, it has been recently shown that the structural relaxation time τ_α and the rattling amplitude $\langle u^2 \rangle^{1/2}$ measured in different numerical models, including linear polymers, soft binary mixtures, prototypical glassformers like SiO₂ and o-terphenyl (OTP), and one icosahedral glassformer,^{26–28} can be related in a unique scaling form.

Remarkably, the same resulting master curve well fits to the experimental data from van der Waals and associating liquids,

polymers, metallic glasses, ionic liquids and network glass-formers over many decades in time.^{26–29} These results elucidate how the onset of a strong coupling between the overall relaxation, characterized by cooperative and heterogeneous processes, and the average localization at the level of a single particle, is a general, fundamental feature of glassy dynamics.

Structural arrest and glassy dynamics can be observed also in very dilute particle suspensions when gelation occurs, displaying significant hints of caging effects even at rather low volume fractions.^{31–40}

The similarities and differences with the dense glassy systems are still at the center of an intense debate: the caging takes place again over time scales well separated from the ones of structural relaxation, but it is much weaker than in dense systems and it has been associated to the particle bonding, rather than to the role of excluded volume interactions.^{41–43} In fact, in gels a somewhat more complex scenario for structural arrest takes place, with different localization processes over different length-scales, because particles get bonded into an interconnected network structure. A numerical study of a model colloidal gel has recently shown that the gel network indeed induces the same type of strong coupling in particle motion which is typically observed in dense glassy systems and that the glassy dynamics directly arises from the cooperative processes induced by the network.³⁹ With the motivation to further investigate the presence and nature of coupling between structural relaxation and particle localization in colloidal gelation, here we study for the first time the correlation between the structural relaxation time τ_α and $\langle u^2 \rangle$ in a model diluted colloidal gel and find the same type of scaling as in the dense system. This finding is remarkable because the

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caging mechanism and the origin of the slow dynamics are very different in this type of systems and gives indeed a new contribution to the understanding of glassy dynamics in diluted gel systems by indicating the presence of a complex *feedback* between the overall slow structural relaxation and the single particle localization.

The paper is organized as follows. In Section 2 we briefly recall the derivation of the scaling form subsequently discussed in the analysis, in Section 3 we briefly summarize the main features of the gel model as studied in Ref. 37–39 by molecular dynamics and of numerical simulations. In Section 4 we provide a simple protocol to test the universal scaling²⁶ for the gel system studied here. Finally in Section 5 we draw the conclusions of our analysis.

2. Universal scaling form

Upon approaching the glass transition, particles are longer and longer trapped into the cage formed by their neighbors. This caging phenomenon shows up as a plateau-like regime at short times in the MSD. The amplitude of the rattling motion $\langle u^2 \rangle^{1/2}$ during this caging regime, that occurs on very short time scales (e.g. picoseconds in molecular liquids), is the so-called Debye–Waller (DW) factor^{17,21} which is directly related to the short-time elastic properties of the system.²³ The DW factor is an experimentally accessible quantity¹⁶ that can be also measured by using the incoherent intermediate scattering function (ISF), evaluating at the short times the height of the plateau which signals the cage effects (see Ref. 27). We note that, as shown in Ref. 27 the DW factor extracted from MSD $\langle u^2 \rangle$ and the one defined from ISF are equivalent.

In spite of the fact that the DW factor is related to fast motion of particles occurring on time scales much shorter than the ones typical of structural relaxation, many studies evidence strong correlations between slow and fast degrees of freedom in glass-forming liquids.^{1,11,16,19–21,44–50}

In order to express the correlation between DW factor and structural relaxation time in a functional form, a classical argument estimating the height of the barrier between two potential energy minima from the curvature around the minima can be used. For glassy systems Hall and Wolynes¹⁴ applied this argument in their density functional theory where atomic motion is restricted to cells, picturing the GT as the freezing into an aperiodic crystal structure. In this approach the system relaxation towards equilibrium can be thought of as a series of activated jumps over energy barriers in its potential energy landscape.²² Following Ref. 22 we now give a derivation of an equation relating DW factor and structural relaxation, which is useful in the context of this paper.

For the sake of simplicity we restrict to the one-dimensional case where two minima are separated by a distance $2a$ (see Fig. 1). Referring to Fig. 1, we expand the potential $U(x)$ around the minimum on the left, whose position is labeled by x_1 :

$$U(x) = U_0 + \frac{\Lambda}{2}(x - x_1)^2 \quad (1)$$

Since system relaxation requires getting over the energy barrier ΔE , if τ_α is the system relaxation time and τ_0 the microscopic time:

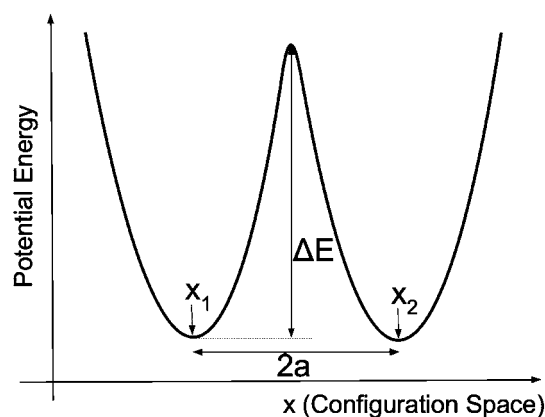


Fig. 1 Two level systems where structural relaxation is achieved through a jump from one minimum to the other one overcoming an energy barrier ΔE (see text for details).

$$\tau_\alpha = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (2)$$

From eqn (1) we can express ΔE as:

$$\Delta E = \frac{\Lambda}{2} a^2 \quad (3)$$

and from equipartition theorem:

$$k_B T = \Lambda \langle u^2 \rangle \quad (4)$$

where $\langle u^2 \rangle = \langle x^2 \rangle$. Inserting eqn (4) and (3) into eqn (2) one obtains finally:

$$\tau_\alpha = \tau_0 \exp\left(\frac{a^2}{2 \langle u^2 \rangle}\right) \quad (5)$$

It is important to note that eqn (5) is expected to fail if the amplitude of rattling motion $\langle u^2 \rangle$ becomes comparable to a^2 .

A natural generalization of eqn (5) can be achieved by adopting a proper distribution $p(a^2)$ of the squared displacement a^2 needed to overcome energy barriers, *i.e.* in our present study to break bonds. We note that the squared displacement a^2 is the cumulative displacement of the particles that move,¹⁴ hence according to Central Limit Theorem a suitable choice for $p(a^2)$ is a truncated Gaussian form, *i.e.*

$$p(a^2) = \begin{cases} A \exp\left[-\frac{(a^2 - \overline{a^2})^2}{2\sigma_{a^2}^2}\right] & \text{if } a > a_{\min} \\ 0 & \text{otherwise.} \end{cases} \quad (6)$$

where A is a normalization factor and a_{\min}^2 is the minimum displacement to reach the transition state. Averaging the eqn (5) over the distribution given by eqn (6), the following generalized HW equation is obtained:

$$\tau_\alpha = \tau_0 \exp\left[\frac{\overline{a^2}}{2 \langle u^2 \rangle} + \frac{\sigma_{a^2}^2}{8 \langle u^2 \rangle^2}\right] \quad (7)$$

The Gaussian form for $p(a^2)$ is supported also by other considerations. For example if we substitute back $k_B T$ into eqn (7) using eqn (4) we end up with the following equation:

$$\tau_\alpha = \tau_0 \exp \left[\frac{\Lambda \overline{a^2}}{2k_B T} + \frac{\Lambda^2 \sigma_a^2}{8(k_B T)^2} \right] \quad (8)$$

Experimental data for both supercooled liquids⁵¹ and polymers⁵² together with theoretical approaches⁵³ and numerical simulations⁵⁴ support Gaussian form for $p(a^2)$ in eqn (8). Furthermore putting eqn (3) into eqn (6) to eliminate a^2 a Gaussian distribution for energy barriers is attained in accordance with other studies.⁵⁵

These ideas have been originally developed for the glassy dynamics of dense systems, where the caging occurs due to the high density. In the following we would like to try and apply them to the glassy dynamics of colloidal gels, where caging can take place at very low densities, because persistent bonds lead to an interconnected network structure.

3. Methods

3.1 Model

We refer to the studies carried out on in Ref. 37–39: the colloidal gel model considers identical particles of diameter σ interacting *via* a phenomenon-based potential V_{eff} , designed to account for the presence of directional interactions.

In gelling colloidal suspensions there are in fact several possible sources of anisotropic effective interactions, since the particle surface may not be smooth or the building blocks of the gel are not the primary particles but larger aggregates of irregular shape.⁵⁶ Confocal microscopy images obtained in recent experiments^{57–59} confirm this scenario: the distribution of the particle coordination number n in very diluted gel networks is strongly peaked around $n \approx 2,3$. In the chosen model, therefore, the interaction potential is given as the sum of three different contributions, $V_{\text{eff}} = V_{\text{LJ}} + V_{\text{d}} + V_3$, where V_{LJ} is a Lennard-Jones type of potential producing a narrow attractive well, and $V_{\text{d}} + V_3$ contains directionality and rigidity of inter-particle bonding.³⁹ Here we consider the same choice of parameters as in Ref. 37–39 and the range of volume fractions as investigated in Ref. 39.

As reported in the previous studies, in this model at low temperatures the system aggregates into an open persistent network of chains connected by a few bridging points (*nodes*). This takes place *via* a random percolation mechanism, but once a percolating structure is formed, it rapidly evolves towards a persistent, fully connected open network. The formation of the persistent network produces the coexistence, in the gel, of very different relaxation processes at different length scales: the relaxation at high wave vectors is due to the fast cooperative motion of pieces of the gel structure (*e.g.* the chains connecting two nodes), 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 characterized by a typical crossover length which is of the order of the network mesh size. The slow glassy dynamics at low wave vectors results in being directly connected to the presence of cooperative processes which can be recognized, for example, in the rearrangements of the network nodes along the complex structure of

the network itself.³⁹ This scenario is in agreement with the results of other recent studies on model colloidal gels.^{60,61}

3.2 Simulations details

We have used a MD code where the potential V_{eff} has been implemented *via* a suitable combination of the algorithms RATTLE and SHAKE.⁶² The unit of time is $\sqrt{m\sigma^2/\epsilon}$, with m the mass of a particle and the data reported here refer to a time step of 0.002. The data refers to micro-canonical simulations performed with 8000 particles in cubic boxes of size $L = 37.64, 43.09, 55.10$ in unit of σ , corresponding respectively to particle densities of $\rho = 0.15, 0.1, \text{ and } 0.05$, *i.e.* to approximately volume fractions $\phi \approx 0.075, 0.05, \text{ and } 0.025$. In the simulations 5 to 8 independent samples have been equilibrated starting from initial high temperature random configurations by replacing particle velocities with values extracted from a Maxwell-Boltzmann distribution every Δ time steps (where Δ varied with temperature from 10 to 10^3 MD steps). After equilibration the energy is constant, showing no significant drift over the simulation time window, and different one- and two- time autocorrelation functions display the equilibrium behavior, *i.e.* do not show any sign of aging. The data production starts from these equilibrated samples: the equilibration time grows with the relaxation time in the system and at the lowest temperatures equilibration required up to 2×10^7 MD steps.

4. Results and discussion

4.1 Relaxation and transport properties

We use the static structure factor $S(q)$, defined as follows:

$$S(q) = \frac{1}{N} \sum_{i,j} \langle e^{iq \cdot [r_i - r_j]} \rangle \quad (9)$$

to quantify the extent of spatial correlation in the system and obtain informations on the gel structure. In Fig. 2 (from the data in Ref. 39) $S(q)$ of the gel network (*i.e.* at the lowest temperature considered) displays a peak around $q_{\text{max}} \approx 8$ corresponding

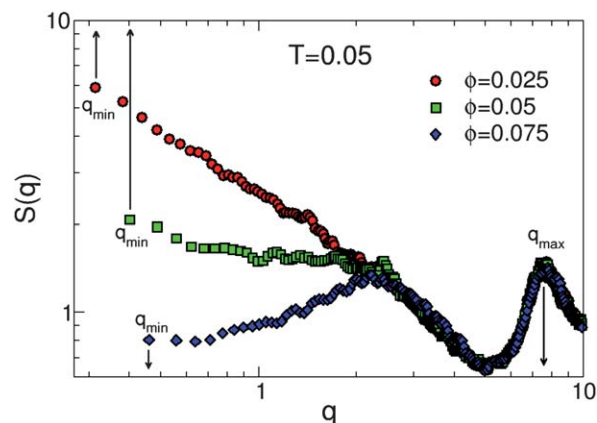


Fig. 2 Static structure factor at lowest temperatures investigated for all volume fractions. q_{min} and q_{max} are also pointed out where q_{min} is the minimum wave vector allowed by finite size of simulation box and q_{max} is the wave vector corresponding to the maximum of $S(q)$ at length scales comparable to particles diameter.

roughly to the particle diameter. This peak basically arises from excluded volume interactions between particles, *i.e.* it approximately corresponds to the first peak of radial distribution function. In glassy systems the slow relaxation arises first, and has its strongest signature, at these wave vectors. It is clear from the figure that in the gel significant spatial correlations are present also at smaller wave vectors. In Ref. 39 $S(q)$ has been compared to the static structure factor of a polymer chain solution⁶³: length scales matching smaller wave vectors $2.0 < q < 7.0$ can be interpreted as an *intra-molecular* regime for spatial correlations of the aggregates (*i.e.* chains). Mesoscopic and macroscopic length scales $q \leq 2.0$ can instead be thought of as corresponding to *inter-molecular* regime, due to the long-range interactions induced by the formation of the persistent gel network. Correlations in the particle motion over different length scales can be effectively quantified in terms of ISF:

$$F_s(q, t) = \frac{1}{N} \sum_j^N \langle e^{iq[\mathbf{r}_i(t) - \mathbf{r}_j(0)]} \rangle \quad (10)$$

The analysis of its behavior^{37–39} indicates that in the gel the slowest modes correspond to the *inter-molecular* regime of wave vectors. In Fig. 3 $F_s(q, t)$ is plotted as a function of the time, rescaled by the relaxation time $\tau_\alpha(q)$, at the lowest temperature $T = 0.05$ for different wave vectors. $\tau_\alpha(q)$ has been calculated from $F_s(q, \tau_\alpha(q)) = 1/e$. The figure shows that the stretched exponential decay $\exp\{-[t/\tau_\alpha(q)]^\beta\}$ with $\beta < 1$, typical of glassy dynamics, arises only at low wave vectors ($q \leq 1.0$). In other words, the slow structural relaxation modes of the gel structure can be detected only at low q . In contrast, at higher wave vectors, the time decay of correlations is faster than exponential ($\beta \approx 1.4$): in Ref. 38, 64 these processes have been carefully analyzed and it has been shown that they are due to fast coherent motion of pieces of the gel network (*i.e.* the chains between two bridging point or *nodes*).

The overall scenario of relaxation modes in the gel is therefore rather different from the one discussed in Ref. 26 and 27 for glassy systems at high densities. It is interesting to note that here the particle bonding is the basic ingredient of the structural arrest, since the persistence of the gel network certainly relies

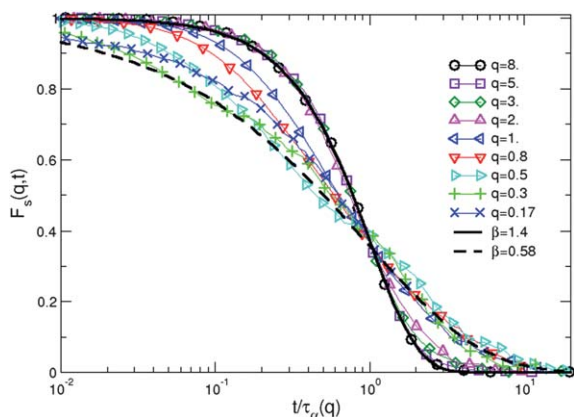


Fig. 3 Self part of the intermediate scattering function for different q from q_{\min} to values around q_{\max} . Solid and dashed black lines are fits to a stretched exponential with $\beta = 0.58$ (dashed) and $\beta = 1.4$ (solid) respectively for minimum and maximum wave vectors.

upon the long living bonds. On the other hand, the analysis of the relaxation modes well elucidate that formation of single bonds cannot be responsible, on its own, for the cooperative glassy dynamics which instead arises from the long-range correlations between them induced by the network.³⁹ Within this picture, the question of the existence and nature of a direct correlation between the single particle average localization and the structural arrest, as discussed in Section 4.2, becomes particularly intriguing and is the main focus of this work.

To this aim, we have calculated the relaxation time τ_α associated to the structural relaxation of the gel as $\tau_\alpha = \tau_\alpha(q_{\min})$, where q_{\min} is the smallest wave vector compatible with periodic boundary conditions in our simulations boxes, *i.e.* it corresponds to length scales of the order of the box size.

For evaluating the rattling amplitude of the particle motion corresponding to caging, we consider the MSD:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_i^N \langle \|\mathbf{r}_i(t) - \mathbf{r}_i(0)\|^2 \rangle. \quad (11)$$

Fig. 4 shows MSD divided by time for all temperatures at volume fraction $\phi = 0.05$ (from Ref. 37). Since the system is very diluted, localization phenomena can be very weak and this type of plot helps to better recognize different regimes. At very short

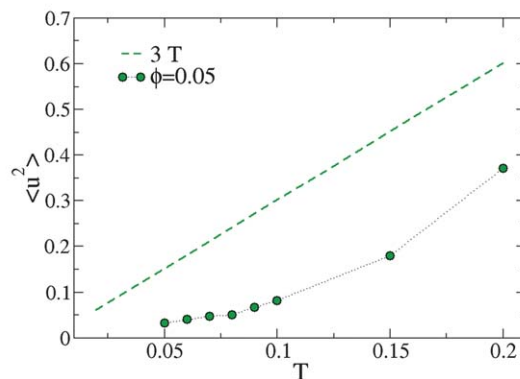
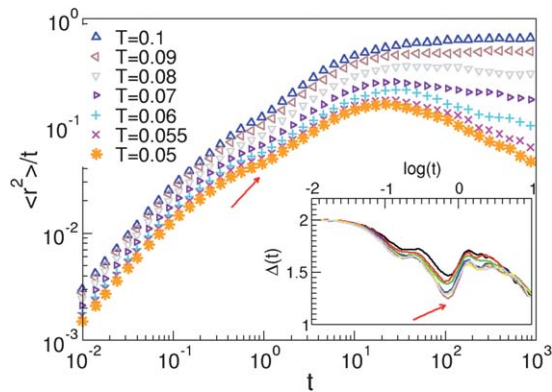


Fig. 4 Top: $\langle r^2(t) \rangle / t$ as a function of time at $\phi = 0.05$. Inset: Logarithmic derivative showing the minimum corresponding to caging. The arrows indicate the regime chosen for the evaluation of the DW factor. Bottom: DW factor for $\phi = 0.05$ as a function of T . Dashed line shows the purely ballistic behavior of $\langle u^2 \rangle(T)$ for $t^* \approx 1$, where the slope, according to eqn (14) is $3k_B t^{*2}/m \approx 3$ in reduced units.

times a ballistic regime is found where MSD increases according to $\langle r^2(t) \rangle \approx (3k_B T/m)t^2$ (*i.e.* $\langle r^2(t) \rangle/t \propto t$). Formation of bonds with other particles slows down the displacement and $\langle r^2(t) \rangle/t$ shows an inflection point. At high temperatures, bonds break within a time interval much smaller than τ_α and particle starts diffusing, *i.e.* $\langle r^2(t) \rangle/t$ eventually reaches a plateau. At $T < 0.1$ bond lifetime sets instead the longest relaxation time-scale in the system and in this regime the formation of the gel network starts, with the MSD becoming increasingly sub-diffusive over times much longer than the localization process related to the rattling of the particle within the bonding length scale. Therefore we evaluate the caging from this first localization process as explained in the following.

4.2 Scaling between relaxation and caging dynamics

Following the discussion in Ref. 27, we evaluate the DW factor in our gel system in order to provide a suitable characteristic length scale for the particle temporarily trapped into the cage over length scales typical of the energetic bonds. DW factor can be defined picking a suitable value of MSD within a time window that begins just after ballistic regime and that ends just before structural relaxation sets in. First we have to identify such time window and to do that we consider the slope $\Delta(t)$ of MSD in a log-log plot, *i.e.*:

$$\Delta(t) = \frac{\partial \log \langle r^2 \rangle}{\partial \log t} \quad (12)$$

Representative plots of $\Delta(t)$ for our gel system can be found in the inset of Fig. 4 (top). The short-time ballistic regime corresponds to $\Delta(t) \approx 2$ while the long time diffusive regime corresponds to $\Delta(t) \approx 1$. Between these two regimes an intermediate regime is present where caging of particles gives rise to a clear minimum of $\Delta(t)$ (see Fig. 4). We thus define the DW factor $\langle u^2 \rangle$ as follows:

$$\langle u^2 \rangle = \langle r^2(t = t^*) \rangle \quad (13)$$

where t^* is the time corresponding to the minimum of $\Delta(t)$ within this intermediate regime.

As evidenced in Fig. 4 (top) t^* is independent of temperature, hence one could be tempted to ascribe the decrease of $\langle u^2 \rangle$ with temperature to a “ballistic slowing down” rather than to an increasing localization (caging) of particles. If the motion of a particle up to t^* can be approximately considered ballistic one has that:

$$\langle u^2 \rangle \approx \frac{3k_B T}{m} t^{*2} \quad (14)$$

and being t^* independent of temperature $\langle u^2 \rangle$ should exhibit a linear dependence on T . Anyway Fig. 4 (bottom) shows that $\langle u^2 \rangle$ is not linearly dependent on T indicating that the decrease in $\langle u^2 \rangle$ with T cannot be ascribed to the ballistic slowing down and is instead due to the particle caging.

We are now in a position to establish a correlation between structural relaxation and caging dynamics. In Fig. 5, $\log(\tau_\alpha)$ is plotted against the inverse of DW factor $1/\langle u^2 \rangle$ for the three volume fractions investigated. The figure clearly shows that τ_α is strongly correlated to the DW factor. Furthermore, the

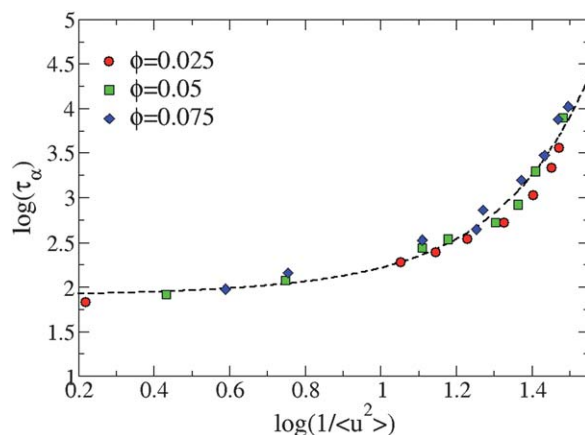


Fig. 5 Scaling of gel data for all densities investigated, *i.e.* $\phi = 0.025, 0.05, 0.075$. Dashed line is a fit of all data to the function $\log \tau_\alpha = \alpha' + \beta \langle u^2 \rangle^{-1} + \gamma \langle u^2 \rangle^{-2}$ with $\alpha' = 1.893$, $\beta = 0.0177$ and $\gamma = 0.00144$.

correlation has a very specific form (see the fitting curve in the figure) agreeing well with the prediction of eqn (7). This is far from being obvious because here the structural relaxation is related to length scales of the order of the simulation box (*i.e.* $2\pi/q_{\min}$) whereas the DW factor corresponds to caging phenomena occurring on much smaller length scales of the order of first neighbor distance, *i.e.* $q \approx 2\pi/\sigma \approx q_{\max}$ (see Fig. 2), where the relaxation is rather dominated by other mechanisms (see Fig. 3). It is also remarkable that the all data for different volume fractions collapse onto the same scaling curve, because the structure, as described by spatial correlations in Fig. 2, changes significantly with ϕ at small q ($S(q_{\min})$ increases in fact by almost an order of magnitude from $\phi = 0.075$ to $\phi = 0.025$), whereas it is not affected by changes in ϕ at large wave vectors q .

The correlation between DW factor and structural relaxation time τ_α points to a strong correlation between the long-range correlations established by the network and the localization within the structure at the level of the single particle.

To better elucidate the nature of the scaling found, we have also investigated the existence of correlations at different wave vectors. In the gel network, $\tau_\alpha(q)$ displays a complex dependence on q as discussed in Ref. 38 and 39. In particular, $\tau_\alpha(q) \propto q^{-1.4}$ at large q , corresponding to the regime where relaxation is dominated by fast collective motion of pieces of the structures (*i.e.* chains between two nodes). Therefore in Fig. 6 we have used the same type of plot as in Fig. 5 where $\tau_\alpha(q)$ has been rescaled with $q^{1.4}$. The data refer to different q at $\phi = 0.075$. At the largest q the data well collapse on top of each other and display a very different dependence on $1/\langle u^2 \rangle$. Upon decreasing q the data depart from the $q^{1.4}$ scaling in q and also approach the scaling form of Fig.5. This analysis further demonstrates that the scaling found specifically relates the average localization at the level of the single particle (as quantified by $\langle u^2 \rangle$) to the relaxation modes associated to the arising of glassy, cooperative dynamics.

4.2.1 Comparison with other MD Studies. In Ref. 27 it has been shown that, for several model glassformers and experimental systems, by plotting $\log(\tau_\alpha)$ versus $\langle u_g^2 \rangle / \langle u^2 \rangle$ (where $\langle u_g^2 \rangle$ is the DW factor at the GT) all data scale onto the same master curve, *i.e.*:

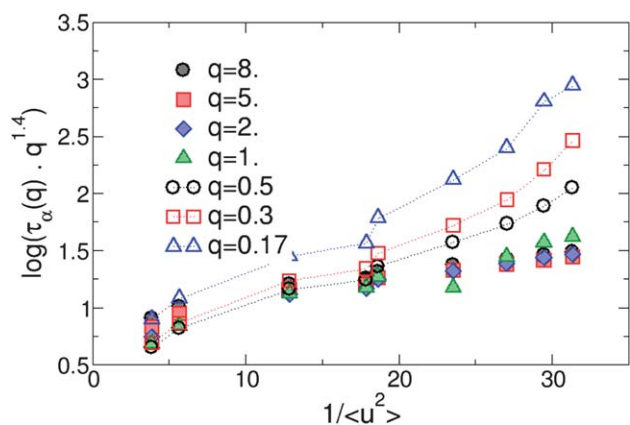


Fig. 6 Plot of $\log(\tau_\alpha(q) \cdot q^{1.4})$ versus $1/\langle u^2 \rangle$ for different q at $\phi = 0.075$. Upon increasing the wave vector from q_{\min} , the data strongly depart from the scaling form of eqn (7).

$$\log \tau_\alpha = \alpha + \tilde{\beta} \frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} + \tilde{\gamma} \left(\frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} \right)^2 \quad (15)$$

where:

$$\alpha = -0.424(1) \quad (16)$$

$$\tilde{\beta} = \frac{\overline{a^2}}{2 \ln 10 \langle u_g^2 \rangle} = 1.62(6) \quad (17)$$

$$\tilde{\gamma} = \frac{\sigma_{a^2}^2}{8 \ln 10 \langle u_g^2 \rangle^2} = 12.3(1) \quad (18)$$

The scaling form obtained in Fig. 5 for the colloidal gel is superimposed on the universal curve of eqn (15) with the vertical shift $\alpha - \alpha' = -2.32$ and upon using the scaled variable $\langle u^2 \rangle / \langle u_g^2 \rangle$ with $\langle u_g^2 \rangle = 0.104$ on the x -axis. It is found that $\langle u_g^2 \rangle^{1/2} = 0.104$ of the colloidal gel is close to $\langle u_g^2 \rangle^{1/2} = 0.129$ of polymer melts and binary mixtures.^{26,27}

It is worth noting that the Lindemann ratio $f \equiv \langle u_g^2 \rangle^{1/2} / d$ ($d \sim 1$ being the average next-neighbour distance of the particles) has been proposed to be, as in crystals,⁶⁵ a quasi-universal number close to the glass transition ($f \sim 0.1$).⁶⁶ Although our scaling procedure does not rely on this criterion, our results are consistent with it.

As to the vertical shift to superimpose the colloidal data with the ones of polymer melts and binary mixtures, we note that, according to our simplified treatment of the system relaxation as activated jumps over energy barriers in the potential energy landscape, $\alpha = \log \tau_0$ where τ_0 is the infinite temperature limit of eqn (2), *i.e.* $\tau_0(\phi)$ can be interpreted as the relaxation time of a system with only excluded volume interactions. The colloidal gel volume fractions are almost two orders of magnitude smaller than typical volume fractions of polymers and soft binary mixtures, which are around 0.50–0.60. This huge difference in volume fraction between gel and glasses should reflect in a significantly different τ_0 , *i.e.* in a significant vertical shift of the curve $\log \tau_\alpha$ vs. $1/\langle u^2 \rangle$.

Using such vertical shift and such value for $\langle u_g^2 \rangle$ to adjust gel data we can compare them to the results obtained from soft

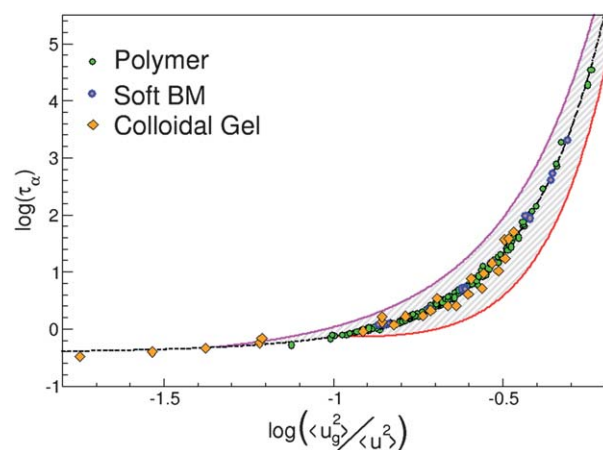


Fig. 7 Scaling of the structural relaxation time vs. the reduced DW factor of polymers,²⁶ soft binary mixtures (Soft BM)²⁷ and colloidal gel (present work). For the colloidal gel $\langle u_g^2 \rangle^{1/2} = 0.104$ and data have been shifted vertically by -2.32 in log scale. Dashed line is the universal curve defined in eqn (15). Solid lines bound the accuracy of eqn (7) obtained fitting data from polymer models studied in Ref. 26 and correspond to the two definitions $\langle u^2 \rangle \equiv \langle r^2(t=0.6) \rangle$ (magenta) and $\langle u^2 \rangle \equiv \langle r^2(t=1.4) \rangle$ (red) (see Ref. 27 for more details).

binary mixtures²⁷ and polymer systems²⁶ as shown in Fig. 7. It is clear from this figure that within the accuracy (marked by solid lines) the scaling procedure also works well for the colloidal gel model considered in the present paper.

5. Conclusions

We have investigated possible correlations between the localization at the level of the single particle and the structural relaxation in a model colloidal gel at very low volume fractions, with directional effective interactions and local rigidity. We have found that strong correlations are present over different length scales. In this type of systems, the localization of particles due to persistent bonding is of course the initiator of the process that leads to gelation, but cannot be responsible, on its own, for structural arrest, which arises thanks to the formation, eventually, of an interconnected network structure. Remarkably, we have found that relaxation modes at the lowest wave vectors, *i.e.* over length scale much larger than the bond localization length, strongly correlate to the localization of single particles within the typical bonding length. We think that these findings indicate a type of *feedback* mechanism between dynamical processes at different length-scales: particle bonding leads to the network formation and long range correlations induced by the presence of the network actually transforms the particle bonding into a glassy caging, coupling eventually the particle localization to the glassy structural arrest. This complex structural arrest scenario is consistent with the observed mechanical/rheological behaviour of this type of systems,⁶⁷ where the role of energetic bonds and of the network topology explicitly manifests. Moreover, we have shown that the gel data display the same scaling form found for a large class of dense glassy systems in experiments and simulations (molecular glasses, polymers, *etc.*): this result strongly suggests that the scaling captures the essential, basic ingredients in the physics of glassy structural arrest. Future

work will try to test these conclusions against different experimental results and compare the behavior of attractive colloidal gels (diluted and dense) and dense colloidal glasses.

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