Susceptibility $\chi_4$ fails to capture significant increase of dynamic correlation length near glass transition
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Clusters of fast and slow correlated particles, identified as dynamical heterogeneities (DHs), constitute a central aspect of glassy dynamics. A key ingredient of the glass transition scenario is a significant increase of the cluster size $\xi_4$ as the transition is approached. In need of easy-to-compute tools to measure $\xi_4$, the dynamical susceptibility $\chi_4$ was introduced recently. Here, we investigate DHs in dense microgel suspensions using image correlation, and compute both $\chi_4$ and the four-point correlation function $G_4$. The spatial decrease of $G_4$ provides a direct access to $\xi_4$, which is found to grow significantly with increasing volume fraction. However, this increase is not captured by $\chi_4$. We show that the assumptions that validate the connection between $\chi_4$ and $\xi_4$ are not fulfilled in our experiments. Our findings question the relevance of the broadly used $\chi_4$ in describing DHs.

Understanding the glass transition and the out-of-equilibrium glassy dynamics remains a challenge in condensed matter physics. In practice, glass transitions are observed in various systems, such as molecular liquids, colloids or granular materials [1-3]. Among all, dense colloids are model systems with a glass transition at ambient temperature upon increasing volume fraction [4]. They display slow but accessible timescales and can be probed with simple optical techniques such as microscopy and dynamic light scattering [5, 6].

Over the last 15 years, dynamical heterogeneities (DHs) have been recognized as a promising feature in understanding slow relaxation processes in glass-forming systems [7-9]. DHs consist of fast and slow clusters of dynamically correlated particles, coexisting in the material, with the idea that a dynamical correlation length $\xi_4$ diverges when approaching the glass transition [10-16]. Dynamical heterogeneities are predicted by theories and have been observed in numerical simulations [11, 17-23] and experimental works [24-32]. They can mainly be quantified with tools such as four-point correlation functions $G_4$, whose spatial dependence gives a direct access to the dynamical correlation length $\xi_4$, or with a dynamical susceptibility $\chi_4$ which has recently been proposed as an easy-to-compute indirect tool [11, 24].

Here, we investigate DHs with both a four-point correlation function $G_4$ and its associated dynamical susceptibility $\chi_4$ in dense suspensions of soft microgel particles, by performing image correlation. With the direct tool $G_4$, we measure a significant growth of the dynamical correlation length $\xi_4$ with increasing volume fraction. We then investigate the validity of the dynamical susceptibility $\chi_4$ as a tool to extract the dynamical correlation length $\xi_4$, and analyze the reason why it fails to quantify the growth of $\xi_4$.

From a theoretical point of view, let us consider a system described by a local order parameter $q_{4,t}(\tau)$, here defined as the time correlation of the observable quantity between time $t$ and $t + \tau$ at point $j$. A space-averaged and a space-time-averaged order parameters, $Q_t(\tau) = \langle q_{4,t}(\tau) \rangle_j$ and $Q(\tau) = \langle Q_t(\tau) \rangle$, respectively, are constructed so that the averaged time-correlation function $Q(\tau)$ measures the relaxation dynamics of the system. This quantity decays from 1 to 0 as particles move a characteristic distance between $t$ and $t + \tau$ [33].

A direct route to the correlation length $\xi_4$ is the 4-point correlator $G_4^{\text{vct}}(r, \tau)$ which reflects how $q_{4,t}(\tau)$ is correlated between points separated by $r$:

$$G_4^{\text{vct}}(r, \tau) = \langle (q_{4+t, \tau}(r) - q_{4+t}(\tau))(q_{4,t}(\tau) - q_{4}(\tau)) \rangle_{j,t}$$

where $q_{4}(\tau) = \langle q_{4,t}(\tau) \rangle_j$. The corresponding 4-point correlation function $G_4(r, \tau)$ is defined as,

$$G_4(r, \tau) = (G_4^{\text{vct}}(r, \tau))_{r < |r| < r + \delta r},$$

with $\delta r$ chosen such that the average runs over a sufficient number of points. In a system with a dominant correlation length scale $\xi_4(\tau)$, the correlation function decays at large $r$ as:

$$G_4(r, \tau) \sim \frac{1}{r^{4\xi_4(\tau)}} \exp(-r/\xi_4(\tau))$$

Equation (3) defines the dynamical correlation length $\xi_4$.

Another tool was introduced recently to characterize dynamical heterogeneities [18], namely the dynamical susceptibility $\chi_4$.
susceptibility $\chi_4(\tau)$. It can be measured as the variance of the temporal fluctuations of $Q_4(\tau)$:

$$\chi_4(\tau) = N((Q_4^2(\tau))_t - \langle Q_4^2(\tau) \rangle_t^2)$$  \hspace{1cm} (4)

with $N$ the number of points in space under consideration. Let us see how $\chi_4$ is indirectly connected to $\xi_4$. Since $Q_4(\tau) \equiv \langle q_{4,t}(\tau) \rangle_j$, it can be shown that $\chi_4$ is related to $G_4$ by:

$$\chi_4(\tau) = \sum_r G_4^{\text{rect}}(r, \tau)$$  \hspace{1cm} (5)

which can be expressed in the continuous limit as :

$$\chi_4(\tau) = \rho \int d^2 r G_4(|r|, \tau)$$  \hspace{1cm} (6)

with $\rho$ the average density of points in space. It was recently proposed [18] to use $G_4(r, \tau) \sim A(\tau)/r^p \exp(-r/\xi_4(\tau))$ and Eq. (6) to clarify the link between $\chi_4(\tau)$ and $\xi_4(\tau)$. In two dimensions, $\chi_4(\tau)$ is then :

$$\chi_4(\tau) \sim A(\tau) 2\pi \rho \xi_4^2 - p(\tau)$$  \hspace{1cm} (7)

The peak of $\chi_4(\tau)$ was proposed and used widely in numerical simulations and experiments [24, 25, 27, 34, 35] to determine the time for which the dynamics is the most heterogeneous and indirectly, the correlation length value $\xi_4$. As stated in [18], the growing peak in $\chi_4$ upon increasing volume fraction reveals the growth of a dynamical correlation length if the assumptions made for the scaling of $G_4$ are correct.

Our experimental system consists of a suspension of thermosensitive microgels, made of pNIPAm (poly-N-isopropylacrylamide) crosslinked with BIS (N,N'-methylenebisacrylamide), whose synthesis is described in [14]. The microgel diameter decreases with temperature, which provides a unique way of tuning volume fraction $\Phi$. In the inset, $\Phi$ increases in a quasistatic way, allowing the system to relax between each step and reach an equilibrium state. A weak polydispersity was used to suppress crystallisation occurring at high volume fraction (see Materials and Methods for sample preparation).

A local order parameter, $q_{j,t}$, defined from the normalised frame intensity $i_{j,t}$ as,

$$q_{j,t}(\tau) = \langle i_{j,t}(t + \tau) i_{j,t}(t) \rangle_{t\in \text{ROI}[j]},$$  \hspace{1cm} (8)

was measured to perform image correlation analysis (see Materials and Methods for image correlation), a suitable technique when particle trajectories cannot be resolved individually.

Figure 1-a shows the ensemble-averaged order parameter $Q(\tau) = \langle q_{j,t}(\tau) \rangle_{j,t}$, similar to the one in [25, 38, 39] in the microgel suspension at various volume fractions. It decreases from its maximal value – ideally 1 at $\tau = 0$ – to 0 at the largest lag times, with a typical decay time $\tau^*$. It is intuitive that $\tau^*$ is related to the particles dynamics : as the particles get farther from their initial positions with increasing lag time $\tau$, the time correlation function $Q(\tau)$ between two frames separated by $\tau$ gets smaller on average. With increasing volume fraction, the relaxation time $\tau^*$, defined by $Q(\tau^*) = 0.25$ [43], increases by three orders of magnitude, revealing the suspension dynamics slowing down.

The dynamical susceptibility $\chi_4(\tau)$ is shown in Figure 1-b. It exhibits a maximum whose value increases with volume fraction. In the inset, $\chi_4(\tau)$ is plotted as a function of $Q(\tau)$, giving evidence that its maximum is reached for approximately the same value of $Q(\tau)$, corresponding to the suspension relaxation time $\tau^*$. Under the assumptions detailed in [18], the increase of the peak...
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tion function 4-point correlation function with a normalized correlation length [see Eq. (7)].

The spatial correlation length \( \xi \) with volume fraction increases significantly with volume fraction, indicating that the spatial correlations increase. We define the critical radius \( r_c \) as the intersection of both asymptotes. The solid lines correspond to fits according to Eq. (9) with \( p = 0 \).

(b): The correlation length \( \xi_4 \) extracted from the fits increases significantly with volume fraction. The highest value of \( \xi_4 \) is slightly larger than the image size (horizontal line) and must be considered with caution. Values: \( \xi_4/a = 93 \pm 63 \) at \( \Phi_{\text{eff}} = 0.66 \); \( \xi_4/a = 22 \pm 5 \) at \( \Phi_{\text{eff}} = 0.64 \); At \( \Phi_{\text{eff}} = 0.60, 0.55 \) and 0.49, the second decay cannot be quantified and we identify the correlation length with the particle radius, \( \xi_4 = a \). The values of the correlation length derived from the peak value of \( \chi_4 \) (denoted as stars) are significantly lower.

value \( \chi_4(\tau^*) \) with volume fraction suggests an increase of the spatial correlation length \( \xi_4(\tau^*) \) with volume fraction (see Eq. (7)).

Let us now focus on the direct measurement of dynamical heterogeneities with a normalized 4-point correlation function \( G_4(r, \tau)/G_4(0, \tau) \) [11, 19]. Figure 2-a shows \( G_4(r, \tau^*)/G_4(0, \tau^*) \) measured in the microgel suspension with increasing volume fraction at time \( \tau^* \), consistent with the peak value of \( \chi_4 \) (see inset of Figure 2-b), where dynamical heterogeneities are expected to be at their maximum. At low volume fraction, \( G_4(r, \tau^*)/G_4(0, \tau^*) \) exhibits an exponential decay on a length scale \( a = 0.31 \mu m \) corresponding approximately to the microgel radius, with which it will hereafter be identified [44]. This suggests that \( \xi_4 = a \) at low volume fraction.

For the two highest volume fractions \( \Phi_{\text{eff}} = 0.64 \) and \( \Phi_{\text{eff}} = 0.66 \), the same exponential decay at small \( r \) is followed by a second decay at large \( r \). This decay becomes slower with increasing volume fraction, directly suggesting the increase of spatial correlations as the glass transition is approached. The high volume fraction data in Figure 2-a for \( G_4(r) \) were fit in the range \( r = 3 - 10 \mu m \), corresponding to the large \( r \)-regime, with the following family of functions, following Eq. (3):

\[
G_4(r, \tau^*)/G_4(0, \tau^*) \propto K_\Phi \left( \frac{a}{r} \right)^p \exp \left( - \frac{r}{\xi_4(\tau^*)} \right)
\]

where the exponent \( p \), the correlation length \( \xi_4 \), and coefficient \( K_\Phi \) are adjustable parameters [45]. The value of \( p \sim 0 \) was found to provide the best adjustment. The correlation length \( \xi_4(\tau^*) \), shown in Figure 2-b and extracted from the fit, increases significantly with volume fraction, and reaches a value (29 \( \pm \) 19 microns) that exceeds the size of the observed field (13.6 \( \times \) 13.6 microns) for the highest volume fraction investigated.

Given our experimental data for \( G_4 \), let us investigate if the growth of \( \xi_4 \) can be reliably inferred from the growing peak in \( \chi_4 \). As shown in Fig. 2-a, \( G_4 \) displays two spatial regimes for the highest volume fractions, with a crossover radius corresponding to approximately 5 particle radii (\( r_c = 1.4 \mu m \) for \( \Phi_{\text{eff}} = 0.66 \) and \( r_c = 1.7 \mu m \) for \( \Phi_{\text{eff}} = 0.64 \)). We now estimate both parts of the integral in Eq. (6), \( \int_0^{r_c} 2\pi r \exp(-r/a)dr \) and \( \int_{r_c}^{\infty} 2\pi r K_\Phi \exp(-r/\xi_4)dr \). The quantity \( K_\Phi \) was found to depend on volume fraction, as \( K_{\Phi=0.66} = 0.0105 \pm 0.0016 \) and \( K_{\Phi=0.64} = 0.0063 \pm 0.0015 \). For \( \Phi_{\text{eff}} = 0.66 \), we calculate that the \( r < r_c \) part of the integral in Eq. (6) contributes about 1% to the entire integral, while for \( \Phi_{\text{eff}} = 0.64 \), it represents more than 25% of the entire integral. Thus, at \( \Phi_{\text{eff}} = 0.64 \), the short distance contribution to the integral pollutes the quantity \( \chi_4 \), deviding it of any reliable information on collective behaviour.
The quantity $G_4(0, \tau)$, displayed in Figure 3, was found to decrease with the lag time $\tau$ and slightly depend on volume fraction. We find that $K_{\Phi=0.64} G_4(0, \tau^*) = 0.0011$ at $\Phi_{\text{eff}} = 0.64$ and $K_{\Phi=0.66} G_4(0, \tau^*) = 0.0020$ at $\Phi_{\text{eff}} = 0.66$. Since the prefactor $A(\tau^*) = K_{\Phi} G_4(0, \tau^*(\Phi))$ depends on volume fraction, we can not obviously estimate the growth of $\xi_4$ with volume fraction, using $\chi_4(\tau^*)$ alone.

Going back to Fig 1, the growth of the correlation length that would be derived from $\chi_4$ if one were to use $2\pi \xi_4^2(\tau^*) A = \chi_4(\tau^*)$ while ignoring the two sources of error described above, is estimated. At low volume fraction $\Phi_{\text{eff}} = 0.49, 0.55$ and 0.6, the peak value of $\chi_4$ is a constant. Since no correlations are expected, the correlation length is set equal to the particle size, $\xi_4 = a$. This also sets the value of the prefactor $A$. At higher volume fraction, keeping the same value $A$ for the whole set of data yields $\xi_4^2(\Phi_{\text{eff}}=0.64) = 1.16a$ and $\xi_4^2(\Phi_{\text{eff}}=0.66) = 1.41a$. As can be seen in Fig. 2-b, the growth of this estimate of $\xi_4$ is widely underestimated as compared to the direct measurement.

In conclusion, with the standard direct tool $G_4$, we measure the growth of a dynamical correlation length $\xi_4$ from 1 to 93 $\pm$ 36 particle radii with increasing volume fraction in our soft microgel suspension. This shows that the dynamics become highly heterogeneous in space when approaching the glass transition, consistent with the broad theoretical picture [40]. Recently, most studies have focused on the dynamical susceptibility $\chi_4$ as a convenient and indirect tool to quantify DHs. Here, we show that the significant increase of $\xi_4$ with volume fraction is not properly captured by $\chi_4$. Our results suggest that $\chi_4$ should be a priori never be used as a quantitative indicator of the increase of the spatial correlations, before having performed a direct measurement of $G_4$ to estimate its validity. However, as it is the variance of the time correlation function $Q_1(\tau)$, the susceptibility $\chi_4$ is expected to remain an indicator of the lag time for which the dynamics is the most heterogeneous. In our experiments, the peak occurs approximately at the suspension relaxation time $\tau^*$. The origin of the failure of $\chi_4$ is related to the fact that (i) it contains the correlations at the scale of the particle radius and (ii) the prefactor $A(\tau^*)$ in Eq. (7) varies with volume fraction. This result suggests investigating other glass forming materials and using techniques other than image correlation to understand which physical properties generate this predominance of small distance correlations and impair the relevance of $\chi_4$.

Materials and methods

Microgel suspension volume fraction. The microgel suspension is prepared by mixing two suspensions of microgel particles with a diameter ratio 1:1.8, constant over the range of temperature we used. The numerical fraction of large particles is 18%. The smaller particle diameter is $1.03 \pm 0.01 \mu m$ at $20^\circ C$ and decreases down to $0.862 \pm 0.006 \mu m$ at $30^\circ C$. An effective volume fraction was assigned to the microgel suspension at $T = 30^\circ C$ in the following way. Latex probes of radius $R = 0.5 \mu m$ comparable to that of the microgels, were added to the suspension. Their mean-squared displacement (MSD) was measured and found to increase linearly with time, which defines a diffusion coefficient $D \sim (\Delta t^2(\tau))/\tau = 4D\tau$. A suspension viscosity was defined as $\eta = \eta_0 T/6\pi R D$. The viscosity was between 8 and 74 mPa.s, at $T = 30^\circ C$. It was shown that for pNIPam suspensions similar to ours, $\eta/\eta_0$ can be used to estimate the volume fraction [41]. In our case, the volume fraction at $T = 30^\circ C$ was approximately $\Phi_{30} = 0.45$. The volume fraction for all bath temperatures $T$ was derived using the relation $\Phi_{\text{eff}}(T) = (d(T)/d_{30})^3 \Phi_{30}$, where $d$ is the diameter of the microgels at temperature $T$, measured with Dynamic Light Scattering experiments, and $d_{30}$ refers to their diameter at $T = 30^\circ C$.

Sample preparation and video recording. The microgel suspension was injected in a $3 \times 3$ mm² chamber made of a microscope plate and a coverslip separated by a 250 µm thick adhesive spacer. The chamber was sealed with araldite glue oil immersion objective. The objective temperature was adjusted with a Biophtechs objective heater within ±0.1°C. A CCD camera (FOculus 124B), coupled to the microscope, was recording the microgel suspension dynamics. It was running at a frame rate from 30 down to 0.375 fps for a few minutes to several hours, depending on the suspension dynamics. The region of observation was chosen at least 100 µm away from the sample edges to avoid boundary effects.

Image correlation analysis. Films consist of successive video frames, each described by a matrix of pixels $p$ of intensity $I_p(t)$, where $p$ is the two-dimensional index of the pixel position and $t$ the temporal position of the frame in the film. The normalized frame intensity $i_p(t)$ at pixel $p$ reads:

$$i_p(t) = \frac{I_p(t) - \langle I_p(t) \rangle_p}{\sqrt{\langle \delta I_p(t)^2 \rangle_p}}$$

with $\delta I_p(t) = I_p(t) - \langle I_p(t) \rangle_p$, and $\langle \rangle_p$ the average over all the pixels in the frame. The normalization wipes out the possible global variations of illumination and contrast along the film.

Each frame was divided into non-overlapping squared Regions Of Interest, ROI, of dimension equivalent to a particle size, ROI[j] is centered around pixel $j$. The normalized frame intensity $i_p(t)$ at pixel $p$ is now denoted as $i_{j,p}(t) \equiv i_p(t)$, with $j$ the center of ROI[j] and $p \in$ ROI[j]. For each frame, following [39], the local order parameter, $q_{j,\tau}(\tau)$, was defined as:

$$q_{j,\tau}(\tau) \equiv \langle i_{j,p}(t + \tau) i_{j,p}(t) \rangle_{j \in \text{ROI}[j]}$$

Image correlation was performed on regions of dimension $187 \times 187$ pixels², corresponding to $13.6 \times 13.6 \mu m^2$ i.e. and around 200 particles in the field. The dimension of the ROIs

This is even more pronounced at lower volume fractions.

Since the effect of the small scale contribution is only of 25% at $\Phi_{\text{eff}} = 0.64$, let us now assume it can be neglected at first order. Using Eq. (9) with $p = 0$, Eq. (7) writes:

$$2\pi \rho \xi_4^2(\tau^*) \sim \frac{\chi_4(\tau^*)}{K_{\Phi} G_4(0, \tau^*)}$$

The quantity $G_4(0, \tau)$, from 1 to 93 $\pm$ 36 particle radii with increasing volume fraction, we can not obviously estimate the growth of $\xi_4$ with volume fraction, using $\chi_4(\tau^*)$ alone.
sets the spatial resolution. It was chosen as 11px, i.e., equivalent to the particle size. A home-made ImageJ [42] plugin was used to calculate the quantities $Q(\tau), G_2(0, \tau), \chi_4(\tau)$ for each film.

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[40] L. Berthier, G. Biroli, J.-P. Bouchaud, and R. L.
The decay time $\tau^*$ can be arbitrarily defined as

$$Q(\tau^*) = 0.25.$$  

In the range $0.2 < Q(\tau) < 0.4$, the curves of $Q$ are parallel to each other and the increase in $\tau^*$ with volume fraction does not depend much on the value of $Q$.

The microgel radius, measured with Dynamic light scattering experiments, depends on temperature. It is $0.43 \mu m$ at $T = 30^\circ C$.

To perform the fits, the weight for each $G_4(r, \tau^*)$ data point was chosen as the number of pairs of ROIs involved in the average over the whole sample ($17 \times 17$ ROIs) in Eq. (1) and in the average over an annular region in Eq. (2).