Questioning the relationship between the $\chi^4$ susceptibility and the dynamical correlation length in a glass former

Rémy Colin, Ahmed Alsayed, Cyprien Gay, Bérengère Abou

To cite this version:

Rémy Colin, Ahmed Alsayed, Cyprien Gay, Bérengère Abou. Questioning the relationship between the $\chi^4$ susceptibility and the dynamical correlation length in a glass former. 2015. hal-01098350v3

HAL Id: hal-01098350
https://hal.archives-ouvertes.fr/hal-01098350v3
Submitted on 10 Sep 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Revealing the relationship between the $\chi_4$ susceptibility and the dynamical correlation length in a glass former

Rémy Colin **a**, Ahmed M. Alsayed b, Cyprien Gay a and Bérengère Abou **a**

**a** Laboratoire Matière et Systèmes Complexes, UMR CNRS 7057 & Université Paris Diderot, 10 rue A. Domon et L. Duquet, 75205 Paris Cedex 13, France.

E-mail: remy.colin@univ-paris-diderot.fr; berengere.abou@univ-paris-diderot.fr;

b Complex Assemblies of Soft Matter Laboratory, UMI CNRS 3254,
Rhodia INC., 350 G. Patterson Bld, Bristol PA 19007, USA.

(Dated: September 10, 2015)

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, and used in various experimental works to probe DHs. Here, we investigate DHs in dense microgel suspensions using image correlation analysis, 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.

The present version was accepted for publication in [Soft Matter](https://soft-matter-journal.org). PACS numbers: 05.40.-a, 05.20.-y, 05.70.-a

Introduction

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 [7–9]. 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 – representing the clusters size – 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 dynamical susceptibilities $\chi_4$ which have recently been proposed as easy-to-compute indirect tools [11][24].

Here, we investigate DHs with both a four-point correlation function $G_4$ and its associated dynamical sus-
with a dominant dynamical correlation length scale $\xi_4(\tau)$, the correlation function decays at large $r$ as:

$$G_4(r, \tau) \sim \frac{1}{r^p} \exp(-r/\xi_4(\tau))$$  (2)

where exponent $p$ is defined as the dynamical correlation length $\xi_4$.

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

$$\chi_4(\tau) = N \langle (Q_i^2(\tau))_t - \langle Q_i(\tau) \rangle_t^2 \rangle$$  (3)

with $N$ the number of points in space under consideration. Let us see how $\chi_4$ is indirectly connected to $\xi_4$. Since $Q_i(\tau) \equiv \langle g_i(\tau) \rangle$, it can be shown that $\chi_4$ is related to $G_4$ by $\chi_4(\tau) = \sum_r G_4(\tau)$ which can be expressed in the continuous limit as:

$$\chi_4(\tau) = \rho \int d^2r G_4(|r|, \tau)$$  (4)

with $\rho$ the average density of points in space. It was recently proposed to use $G_4(r, \tau) \sim A(\tau)/r^p \exp(-r/\xi_4(\tau))$ and Eq. (1) to clarify the link between $\chi_4(\tau)$ and $\xi_4(\tau)$. In two dimensions, $\chi_4(\tau)$ is then:

$$\chi_4(\tau) \sim A(\tau) 2\pi \rho \xi_4^{-p}(\tau)$$  (5)

The peak of $\chi_4(\tau)$ was proposed and used widely in numerical simulations and experiments [21, 25, 27, 34, 35] to determine the time for which the dynamics is the most heterogeneous and indirectly, the correlation length value $\xi_4$. Here, the exponent $p$ can be related to the clusters fractal dimension or, if the clusters are all compact, to the cluster size distribution. 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 fulfilled.

II. MATERIALS AND METHODS

Microgel suspension preparation. Our model glass 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 with an external parameter [36, 37]. The suspension was prepared by mixing small and large microgels with a diameter ratio 1:1.8, constant over the investigated temperature range 20–30 °C (number fraction of large particles: 18%). The bidispersity was used to suppress crystallisation. Figure 1 shows the microgel diameters as a function of temperature, measured with Dynamic Light Scattering. The diameters decrease by ~20% over the investigated temperature range. Within the 20–30 °C range, the pNIPAm particles behave as hydrophilic repulsive soft spheres (the transition to hydrophobic attractive spheres occurs at 32–33 °C and is easily identified by microscopy).

Effective volume fraction of the suspension. At temperature $T = 30$ °C, an effective volume fraction was assigned to the microgel suspension. For this purpose, latex probes (radius $R = 0.5 \mu m$ comparable to the microgel radius) were added to the suspension and their mean-squared displacement (MSD) measured. The MSD was found to increase linearly with time, which defines a diffusion coefficient $D(\tau) \sim \langle \Delta r^2(\tau) \rangle_{t} = 4D_\tau$. A suspension viscosity $\eta = 45$ mPa.s was deduced from the Stokes-Einstein relation in this case.

Sample preparation and video recording. The microgel suspension was injected in a 3 × 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 to avoid evaporation and contamination. The samples were observed using standard
Figure 2: Images of the microgel suspension at various volume fractions, (0.49, 0.55, 0.60, 0.64 and 0.66) in bright field microscopy at \( \times 100 \) magnification (oil immersion objective, \( \text{NA}=1.3 \)); the subsets dimension is \( 187 \times 187 \) pixel\(^2\). The white bar is 96 pixel long (7 \( \mu \text{m} \)). Images have been processed (see details in the appendix) to filter out the noise before image correlation analysis. The histogram of pixel intensities of these processed images is shown. The condenser aperture stop was set to the same setting for each experiment (condenser \( \text{NA}=0.55 \)).

Bright field microscopy on a inverted Leica DM IRB microscope at \( \times 100 \) magnification (oil immersion objective, \( \text{NA}=1.3 \)), depth of focus: \( \sim 200 \) nm. Typical images of the suspension at various volume fractions can be seen in Figure 2. The objective temperature was adjusted with a Biophtechs objective heater within \( \pm 0.1 \) °C. The sample temperature was maintained through the immersion oil in contact. A CCD camera (FOcules 124B) coupled to the microscope, was recording films of the microgel suspension. The camera 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 \( \mu \text{m} \) away from the sample edges to avoid boundary effects.

**Image correlation analysis.** Films of the microgel suspension were analyzed with image correlation analysis, a suitable technique when particle trajectories cannot be resolved individually. Films consist of successive video frames (640 \( \times \) 480 pixel\(^2\)). Frames are first pre-processed following a procedure described in appendix. Image correlation analysis was then performed on \( 187 \times 187 \) pixel\(^2\) subsets of the pre-processed frames using home-made ImageJ plugin (subset dimension: \( 13.6 \times 13.6 \mu \text{m}^2 \), 1 px = 72.75 nm). Each frame subset is 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 time position of the frame in the film. Possible global variations of illumination and contrast along the film were wiped out using the normalised frame intensity \( i_p(t) \) at pixel \( p \):

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

with \( \delta I_p(t) = I_p(t) - \langle I_p(t) \rangle_p \), and \( \langle \cdot \rangle_p \) the average over all the pixels in the frame. The subsets are divided into non-overlapping squared Regions Of Interest, ROI, of dimension equivalent to a particle size, 11 \( \times \) 11 pixel\(^2\) (289 ROIs in a subset). The subset intensity \( i_p(t) \) is now denoted as \( i_{p,j}(t) = \langle I_{p,j}(t) \rangle_p \), with \( j \) the center of ROI\([j]\) and \( j' \in \text{ROI}[j] \). (ROI\([j]\) is centered around pixel \( j \).) For each subset, following [40], a local order parameter, \( q_{j,t}(\tau) \), was defined as,

\[
q_{j,t}(\tau) = \langle \langle I_{j,t}(t + \tau) - I_{j',t}(t + \tau) \rangle \rangle_{j' \in \text{ROI}[j]},
\]

The functions \( Q(\tau) = \langle q_{j,t}(\tau) \rangle_{j,t} \), \( \chi_4(\tau) \) and \( G_4(\tau) \) were then derived from \( q_{j,t}(\tau) \) using our home-made ImageJ plugin.

**III. DYNAMICAL SUSCEPTIBILITY \( \chi_4 \)**

The microgel suspension was investigated at various volume fractions in the supercooled states, at volume fractions below the glass transition [14]. The volume fraction was increased in a quasistatic way, allowing the system to relax between each step and reach an equilibrium state. Figure 3a shows the ensemble-averaged order parameter \( Q(\tau) = \langle q_{j,t}(\tau) \rangle_{j,t} \), similar to the one in [25, 40, 41] 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 \( Q(\tau^*) = 0.25 \) [40], increases by three orders of magnitude, revealing the suspension dynamics slowing down.

The dynamical susceptibility \( \chi_4(\tau) \) is shown in Figure 3b. It exhibits a maximum whose value increases with volume fraction. In the inset, \( \chi_4(\tau) \) is plotted as a function of \( Q(\tau) \). Its maximum is reached for approximately...
FIG. 3: Mean correlation function $Q(\tau)$ and dynamical susceptibility $\chi_4(\tau)$ measured in the micropel suspension with increasing volume fraction. In (a), the values of the typical decay time $\tau^*$ of $Q(\tau)$, denoted by large empty circles, are: 0.88, 1.7, 4.3, 36 and 5.310^2 s. In (b), the peak value of $\chi_4$ increases with volume fraction, suggesting the increase of a spatial correlation length. The inset reveals that the peak value is reached approximately for $Q(\tau) = 0.25$ (vertical line), the value chosen to estimate the typical decay time $\tau^*$.

the same value of $Q(\tau)$, corresponding to the suspension relaxation time $\tau^*$. Under the assumptions detailed in [18], the increase of the peak value $\chi_4(\tau^*)$ with volume fraction suggests an increase of the spatial correlation length $\xi_4(\tau^*)$ with volume fraction, see Eq. (5). In the following, we measure $\xi_4(\tau^*)$ from $G_4(r, \tau^*)$ and test the reliability of Eq. (5).

IV. DIRECT MEASUREMENT OF THE SPATIAL CORRELATION LENGTH $\xi_4$

Let us first focus on the direct measurement of dynamical heterogeneities with a normalised 4-point correlation function $G_4(r, \tau)/G_4(0, \tau)$ [11][19]. Figure 4a shows $G_4(r, \tau^*)/G_4(0, \tau^*)$ in the micropel suspension with increasing volume fraction at time $\tau^*$, consistent with the peak value of $\chi_4$ (see inset of Figure 4b), 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 $a = 0.31 \mu m$ which we will hereafter name “effective particle radius” as it corresponds approximately to the radius of the most abundant micropel $0.42 \mu m$ at $T = 30^\circ C$. For the two highest volume fractions $\Phi_{eff} = 0.64$ and $\Phi_{eff} = 0.66$, the same exponential decay at small $r$ is followed by a second decay at large $r$. This decay becomes weaker with increasing volume fraction, directly suggesting the increase of spatial correlations as the glass transition is approached. The normalised spatial correlation then reaches the noise floor, which is around $10^{-3}$ for all volume fractions.

The high volume fraction data in Figure 4-a for $G_4(r)$ were fit in the range $r = 3\times10^2 \mu m$, corresponding to the large-$r$ regime, with the following family of functions,
following Eq. [2]:
\[ G_4(r, \tau^*)/G_4(0, \tau^*) \propto K_\Phi \left( \frac{a}{\xi_4(\tau^*)} \right)^p \exp \left( -\frac{r}{\xi_4(\tau^*)} \right) \]
(8)
where the exponent \( p \), the correlation length \( \xi_4 \), and the coefficient \( K_\Phi \) are adjustable parameters [50]. Values of \( p \) close to zero were found to provide the best adjustments and we set \( p = 0 \). In order to check the robustness of the \( \xi_4 \) values obtained from the \( G_4 \) measurements, we added extra noise to the film images purposefully, and it showed that the measurement of \( \xi_4 \) is fairly robust against noise. [51]

The correlation length \( \xi_4(\tau^*) \), shown in Figure 4-b and extracted from the fit, increases significantly with volume fraction, and reaches a value (29 ± 19 microns) that exceeds the size of the observed field (13.6 × 13.6 microns) for the highest volume fraction investigated.

V. BAD ESTIMATE OF THE SPATIAL CORRELATION LENGTH FROM THE SUSCEPTIBILITY \( \chi_4 \)

Let us estimate the growth of the correlation length that would be derived from \( \chi_4 \) if one were to use
\[ 2\pi \rho \xi_4^2(\tau^*) A = \chi_4(\tau^*) \]
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 effective particle radius, \( \xi_4 = a \). This also sets the value of the prefactor \( A \). At higher volume fraction, keeping the same value of \( A \) for the whole set of data yields \( \xi_4^{\Phi_{\text{eff}}=0.64} = 1.16a \) and \( \xi_4^{\Phi_{\text{eff}}=0.66} = 1.41a \). The growth of this estimate of \( \xi_4 \) is widely underestimated as compared to the direct measurement (see Fig. 3-b).

Given our experimental data for \( G_4 \), let us investigate the possible sources of error and assess how reliably the growth of \( \xi_4 \) with volume fraction can be inferred from the growing peak in \( \chi_4 \). Since \( \chi_4 \) and \( G_4 \) are related through Eq. [4], let us investigate \( G_4 \) in more detail. As shown in Fig. 3-a, \( G_4 \) displays two spatial regimes for the highest volume fractions, with a crossover radius \( r_c \) corresponding to approximately 5 effective particle radii \( a = 0.31 \mu \text{m}, r_c = 1.4 \mu \text{m} \) for \( \Phi_{\text{eff}} = 0.66 \) and \( r_c = 1.7 \mu \text{m} \) for \( \Phi_{\text{eff}} = 0.64 \). We now estimate both parts of the integral in Eq. [4], \( r < r_c \) and \( r > r_c \), as
\[ J_0^r 2\pi r \exp(-\frac{r}{\xi_4}) dr \quad \text{and} \quad J_r^\infty 2\pi r K_\Phi \exp(-\frac{r}{\xi_4}) dr \]
The quantity \( K_\Phi \) was found to depend on volume fraction, as \( K_\Phi = 0.66 = 0.0105 \pm 0.0016 \) and \( K_\Phi = 0.66 = 0.0063 \pm 0.0015 \). For \( \Phi_{\text{eff}} = 0.66 \), we calculate that the \( r < r_c \) part of the integral in Eq. [4] contributes about 1% to the entire integral, while for \( \Phi_{\text{eff}} = 0.64 \), it represents more than 25% of the entire integral. Even though this short distance contribution which pollutes \( \chi_4 \) vanishes at large volume fraction, it makes it risky to use \( \chi_4 \) for processing experimental results. Indeed, in an experiment, the importance of this contribution cannot be estimated without measuring \( G_4 \) explicitly.

Another important source of error arises from the volume fraction dependence of the prefactor \( A \) in Eq. [5]. Using Eq. [8] with \( p = 0 \), Eq. [5] writes:
\[ 2\pi \rho \xi_4^2(\tau^*) \sim \frac{\chi_4(\tau^*)}{K_\Phi G_4(0, \tau^*)} \]
(9)
with \( K_\Phi G_4(0, \tau^*(\Phi)) = A(\tau^*) \). The quantity \( G_4(0, \tau) \), displayed in Figure 5 is found to decrease with the lag time \( \tau \) and to depend on volume fraction. We find that \( K_{0.64} G_4(0, \tau^*(0.64)) = 0.0011 \) at \( \Phi_{\text{eff}} = 0.64 \) and \( K_{0.66} G_4(0, \tau^*(0.66)) = 0.0020 \) at \( \Phi_{\text{eff}} = 0.66 \). Since the prefactor \( A(\tau^*) \) depends significantly on volume fraction, we can not obviously estimate the growth of \( \xi_4 \) with volume fraction, using \( \chi_4(\tau^*) \) alone.

Conclusion

In conclusion, with the standard direct tool \( G_4 \), we measure the growth of a dynamical correlation length \( \xi_4 \) from 1 to 93 ± 63 effective 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 [42]. Recently, various experimental studies have focused on the dynamical susceptibility \( \chi_4 \) as a convenient indirect tool to quantify DHs, mainly because the correlation function \( G_4 \) requires finer measurements and data processing. Meanwhile, in various theoretical works, \( \chi_4 \) was understood to be not necessarily reliable [18, 23, 49, 51].

Our results provide the first quantitative experimental evidence that there is a significant error in estimating the dynamic correlation length \( \xi_4 \) through \( \chi_4 \). 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. [5] varies with volume fraction. It implies that \( \chi_4 \) should \textit{a priori never} be used as a quantitative indicator of the increase of the spatial correlations, before having first performed a direct measurement of \( G_4 \) to estimate its validity. Nevertheless, as it is the variance of the time correlation function \( Q_4(\tau) \), 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 \( \tau^* \) defined by \( Q(\tau^*) = 0.25 \), see Fig. 3.

The two sources of error highlighted in this work should be kept in mind when trying to relate the dynamic heterogeneities with other features of the glass transition, such as e.g. the local structure [45] or the soft modes of vibration [17, 25]. They should be investigated in other glass forming materials and using other observable quantities.
Acknowledgements

We thank E. Bertin, L. Cipelletti, O. Dauchot, J.-B. Fournier, F. van Wijland and L. Wilson for fruitful discussions, and A. Callan-Jones for a critical reading of the manuscript. We acknowledge support from PICS-CNRS SoftTher (B.A. (P.I.), R.C. and A.A.).

VI. APPENDIX

Image pre-processing: The images are preprocessed in 4 steps. We divide first the images by an average blank image taken with a water only sample to account for heterogeneities in illumination coming from out-of-focus beads, and a Savitzky and Golay filter (local polynomial interpolation, width=5 px, order=4) is applied to reduce the effect of the camera shot noise.

of the drift of the sample relative to the objective. We use the beads embedded in the suspension, which primarily are used for computing the volume fraction at 30°C, to record the motion of the sample. Usually 2 to 3 beads are visible in the entire field of view of the CCD camera. We compute the average velocity of the centre of mass of the beads, smoothed over 1000 frames using a temporal sliding window. A subset of the image, as large as possible to fit in the field of view while being advected is extracted by advecting the subframe at the drift speed, using a bilinear pixel interpolation to extract pixel values. Further preprocessing consists in applying 2 filters. A rolling ball background subtraction (radius 60 px) to eliminate heterogeneities in illumination coming from out-of-focus beads, and a Savitzky and Golay filter (local polynomial interpolation, width=5 px, order=4) is applied to reduce the effect of the camera shot noise.

D. A. Weitz, 2011.


[49] 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 $Q$.

[50] 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 × 17 ROIs), see Eq. (1).

[51] Noise levels equal to 0.3, 1 and 3 standard deviation of the original pixel intensity distribution were added. At 0.3 and 1 standard deviations, the resulting normalised $G_4(r, \tau^*)$ profiles (not shown) were unnoticeably altered and the value of $\xi_4$ was correspondingly unaffected. Only at a noise level of 3 standard deviations was the first spatial decay of $G_4$ substantially stronger.