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► **To cite this version:**

Veronique Trappe, Estelle Pitard, Laurence Ramos, Aymeric Robert, Hugo Bissig, et al.. X-Photon Correlation Spectroscopy investigation of q -dependent dynamical heterogeneity in a colloidal gel. 2007. hal-00133792v2

HAL Id: hal-00133792

<https://hal.science/hal-00133792v2>

Preprint submitted on 11 Apr 2007 (v2), last revised 16 Nov 2007 (v3)

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X-Photon Correlation Spectroscopy investigation of q -dependent dynamical heterogeneity in a colloidal gel

V. Trappe¹, E. Pitard², L. Ramos², A. Robert^{3,4}, H. Bissig¹, L. Cipelletti^{2,*}

¹ *Departement de Physique, Université de Fribourg, Chemin du Musée 3, 1700 Fribourg, Suisse*

² *Laboratoire des Colloïdes, Verres et Nanomatériaux (UMR CNRS-UM2 5587), CC26, Université Montpellier 2, 34095 Montpellier Cedex 5, France*

³ *European Synchrotron Radiation Facility - 6 rue Jules Horowitz BP 220, F-38043 Grenoble Cedex 9, France*

⁴ *Present address: Stanford Linear Accelerator Center 2575 Sand Hill Road, Menlo Park, CA 94025, USA **
(Dated: April 11, 2007)

We use time-resolved X-Photon Correlation Spectroscopy to investigate the slow dynamics of colloidal gels made of moderately attractive carbon black particles. We show that the slow dynamics is temporally heterogeneous and quantify its fluctuations by measuring the variance χ of the instantaneous intensity correlation function. The amplitude of dynamical fluctuations has a non-monotonic dependence on scattering vector q , in stark contrast with recent experiments on strongly attractive colloidal gels [Duri and Cipelletti, *Europhys. Lett.* **76**, 972 (2006)]. We propose a simple scaling argument that rationalize these findings.

PACS numbers: 64.70.Pf, 82.70.Gg, 82.70.Dd

Understanding the dramatic slowing down of the dynamics in systems undergoing a glass transition is one of the key problems in condensed matter and statistical physics [1]. In recent years, research efforts have focussed on the role of dynamical heterogeneity: as the glass transition is approached, the dynamics becomes increasingly correlated in space, since rearrangements are possible only through the cooperative motion of “clusters” of particles [2, 3, 4]. This cooperativity leads to strong temporal fluctuations of the dynamics. Indeed, because of dynamical correlations, the number of statistically independent objects in the system becomes smaller than the number of particles, thus leading to enhanced statistical fluctuations.

Numerical simulations have tested these features on a wide variety of systems [4]. Experimental work, by contrast, is much more scarce, because probing the dynamics with the spatial and temporal resolution needed to highlight their heterogeneous nature is an arduous task, especially for molecular glass formers [2, 3]. The slow dynamics of colloidal systems, foams and granular materials share intriguing similarities with those of glass formers [5], including dynamical heterogeneities. These are experimentally more accessible than in molecular systems, since the relevant time and length scales are larger. Various techniques have been used to characterize them, from direct space measurements [6, 7, 8] to novel scattering methods that probe the temporal fluctuations of the intensity correlation function [9, 10, 11, 12].

Valuable information on the physical origin of the average dynamics is generally obtained by studying its length scale dependence, e.g. the variation of the intensity correlation function with the scattering vector q in scattering experiments. Similarly, one expects to gain a better understanding of dynamical heterogeneities by analyz-

ing their behavior at different q 's. Unfortunately, experimental and numerical or theoretical determinations of dynamical fluctuations as a function of q are still very scarce [7, 12, 13, 14, 15, 16], leaving this issue an open question.

In this letter, we investigate dynamical fluctuations in colloidal gels made of moderately attractive carbon black (CB) particles, whose interaction potential at contact is of the order of few times the thermal energy, $k_B T$. We apply, to our knowledge for the first time, time-resolved scattering methods to X-Photon Correlation Spectroscopy (XPCS), thereby demonstrating that the dynamics of the CB gels are temporally heterogeneous. Dynamical fluctuations are quantified by means of a q -dependent dynamical susceptibility, χ , similar to the dynamical susceptibility χ_4 studied in simulations [15]. Surprisingly, χ is found to initially increase with q , but eventually to decrease at large scattering vectors. This non-monotonic behavior is in contrast with recent low- q measurements on diluted, strongly attractive colloidal gels [12], where dynamical fluctuations increased linearly with q . We propose a simple –yet general– scaling argument for the q -dependence of dynamical fluctuations in gels and glassy systems, which reconciles these contrasting findings.

Our gels are made of carbon black particles suspended in mineral oil at an effective volume fraction $\varphi \approx 6\%$. The CB particles are fused fractal aggregates with a primary particle diameter of ≈ 30 nm and an aggregate diameter of ≈ 500 nm. We study two gels with varying interparticle bonding energy, U , which we control by the addition of a double tail dispersant that grafts on the particle surface providing steric stabilization [17]. The samples are thoroughly mixed by direct sonication before being loaded in a 1 mm cylindrical capillary. The

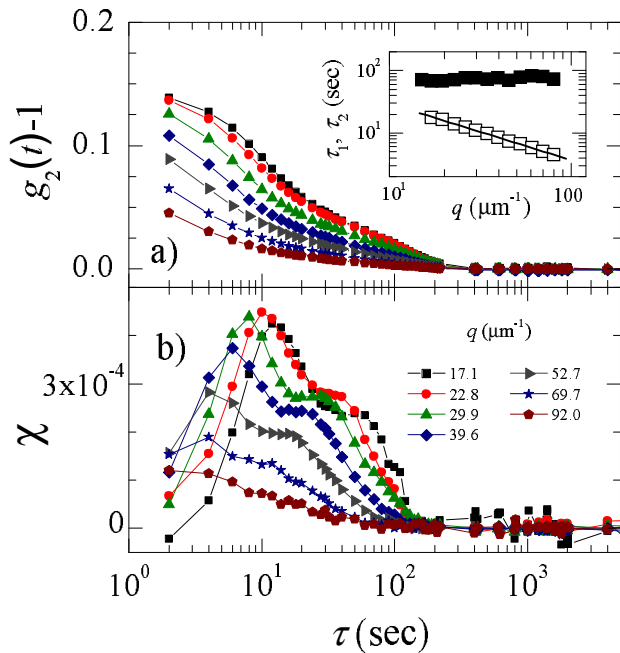


FIG. 1: (Color online) Top panel, main figure: intensity correlation functions at various q 's for a CB gel with 0.2% dispersant. From top to bottom, q ranges from $17.1 \mu\text{m}^{-1}$ to $92.0 \mu\text{m}^{-1}$ (see label in the bottom panel). Inset: fast (τ_1 , open squares) and slow (τ_2 , solid squares) relaxation times obtained from a scaling analysis of $g_2 - 1$. The line is a power law fit to $\tau_1(q)$ yielding an exponent -0.91 ± 0.1 . Bottom panel: dynamical susceptibility χ for the same q vectors as in the top panel. For the sake of clarity, not all available data have been plotted in the two main panels.

capillary is then indirectly sonicated for about half an hour and subsequently left at rest for 5 hours prior to measurement, each run lasting up to 10 hours. The dynamics of the CB gels are investigated by means of XPCS performed at the ID10 Troika beamline at the European Synchrotron Radiation Facility (ESRF), with X-rays of wavelength $\lambda = 1.55 \text{ \AA}$. The scattered intensity is recorded by a charge-coupled device (CCD) camera, covering about one decade in scattering vector: $15 \mu\text{m}^{-1} \lesssim q \lesssim 150 \mu\text{m}^{-1}$, corresponding to distances comparable to or smaller than the particle size. In order to measure the average dynamics and its fluctuations, we use the time-resolved correlation (TRC) method [9]. The instantaneous degree of correlation between X photons scattered at time t and $t + \tau$ is measured according to $c_I(q, t, \tau) = \langle I_p(t)I_p(t + \tau) \rangle_q / \left(\langle I_p(t) \rangle_q \langle I_p(t + \tau) \rangle_q \right) - 1$, where $I_p(t)$ is the scattered intensity at pixel p and time t and $\langle \dots \rangle_q$ is an average over a ring of pixels corresponding to approximately the same magnitude of \mathbf{q} but different azimuthal orientations. The usual intensity correlation function is $g_2(q, \tau) - 1 = \overline{c_I}$, where $\overline{\dots}$ indicates a time average.

For a CB gel with 0.2% dispersant (estimated inter-

particle bonding energy $U \approx 12 k_B T$) we find $g_2 - 1$ to exhibit a two-step decay, as shown for various q 's in the upper panel of fig. 1 (data are corrected for stray light). Given the limited number of data points covering the initial relaxation, we scale the data at different q 's onto a master curve to determine its shape with a reasonable accuracy. Fitting the initial decay of the master curve to a stretched exponential, $A \exp[-(\tau/\tau_1)^{p_1}]$, yields $p_1 = 1.2 \pm 0.2$ and allows us to extract the initial relaxation time, $\tau_1(q)$, and amplitude, $A(q)$, on an absolute scale. We find $\tau_1 \sim q^{-0.91 \pm 0.1}$, as shown in the inset of fig. 1. We can exclude the origin of the initial relaxation of g_2 to be due to the thermally induced fluctuations of the gel branches [18], which we expect to exhibit characteristic times at least three orders of magnitude smaller than τ_1 . Thus, it is likely that an additional, faster decay is present at short time lags, although it is not accessible using a CCD detector. The nearly q^{-1} dependence of τ_1 and $p_1 > 1$ hint to rearrangement dynamics driven by the relaxation of internal stress, similar to those in other glassy soft materials (see [5, 19] and references therein). The final decay of the correlation function is approximately exponential, with a decay time τ_2 that is q -independent, as obtained both by a scaling analysis and a direct fit of g_2 . We point out that this final relaxation is not an artifact due to setup mechanical instability, as checked using a static scatterer (Vycor glass). This behavior most probably stems from random rare rearrangements occurring in the gel when bonds are broken, leading to particle displacements larger than $1/q$. Indeed, in this case one single rearrangement would be sufficient to fully decorrelate the contribution to $g_2 - 1$ of the displaced scatterers. The only time scale for the final relaxation of g_2 is then the average time between rearrangements, regardless of q . Assuming uncorrelated events with Poissonian statistics, one expects an exponential decay of g_2 , in agreement with our measurements.

To quantify dynamical heterogeneity we calculate $\chi(\tau, q) = \text{var}(c_I(q, t, \tau))$, the temporal variance of the instantaneous degree of correlation, $c_I(q, t, \tau)$ [20]. The data are corrected for the measurement noise as described in [21]. The bottom panel of fig. 1 shows the τ -dependent amplitude of the fluctuations: at all q 's, χ exhibits a peaked shape similar to that observed in other glassy systems [7, 10, 11, 12, 13, 14, 15], the largest fluctuations occurring on the time scale of τ_1 . A similar behavior is also observed for CB gels with no dispersant (data not shown).

Figure 2 displays the q -dependence of the height of the peak of $\chi(\tau, q)$, $\chi^*(q)$, for the two samples. For both gels, $\chi^*(q)$ has a peaked shape, first increasing with q but eventually decreasing at large scattering vectors. Dynamical fluctuations are more pronounced when no dispersant is added, i.e. for the gel with stronger interparticle bonds, for which the estimated U is 2 to 3 times larger than for the sample with 0.2% dispersant. This is

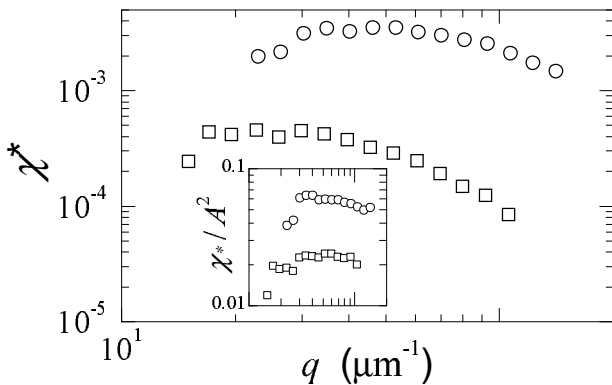


FIG. 2: Peak of the dynamic susceptibility, χ^* , vs q for a CB gel with 0.2% dispersant (squares) and no dispersant (circles). Inset: same data normalized by the squared amplitude of $g_2 - 1$.

consistent with the intuitive picture that dynamical heterogeneity grows as the sample is increasingly jammed. Indeed, we expect the size of regions that rearrange cooperatively to be larger in gels with stronger interparticle interactions, yielding larger fluctuations. Additionally, it is conceivable that the relaxation process itself is more heterogeneous in time for stronger gels, where internal stress build-up and release is likely to be more important, further contributing to enhanced fluctuations. In ref. [12], χ was normalized by the (q -dependent) squared amplitude of the relaxation of $g_2 - 1$, in order to compare data obtained at different q 's. [22]. Here, such a correction is affected by a large uncertainty, since the short-time behavior of g_2 is not accessible to the CCD. The height of the peak of the variance normalized using the amplitude estimated via the scaling procedure, χ^*/A^2 , is shown in the inset of fig. 2. Although the data are more noisy, the peaked shape observed in the main plot is preserved.

The q dependence of χ^* found here is very different from the one measured in low- q light scattering experiments on strongly attractive gels [12], where $\chi^* \sim q$. A growing trend in the low q regime, although with $\chi^* \sim q^2$, is also predicted for dynamically facilitated models, for which χ^* saturates in the opposite limit $q \rightarrow \infty$ [13]. For a 2-D granular system [7] and a Lennard-Jones glass former [15], a non-monotonic behavior has been reported, with χ^* initially growing with q but then decreasing after peaking at a length scale comparable to the inter-particle distance. The high- q regime has been explored for hard spheres within the mode coupling theory in [14], where the amplitude of χ_ϕ , a lower bound for χ_4 , was reported to decrease with q around the peak of the static structure factor.

In order to provide a general framework for these observations, we propose a simple scaling argument for the length-scale dependence of dynamical fluctuations in

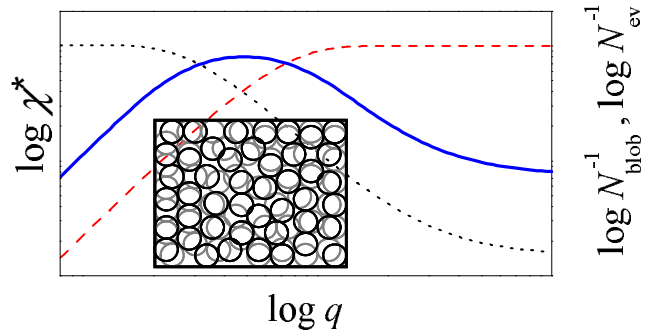


FIG. 3: (Color online) Inset: schematic representation of the rearrangement events within the scattering volume. Successive events at the same location are indicated by circles of different grey level. Main figure: qualitative double logarithmic plot of the proposed q -dependence of dynamical fluctuations. Left axis: χ^* (continuous line, blue); right axis: N_{blob}^{-1} (dashed line, red), and $N_{\text{blob}}^{-1} \sim V_b$ (dotted line, black).

glassy systems. We assume the dynamics to be due to random rearrangement events each affecting a “blob” of volume V_b . The fluctuations of c_I then stem from fluctuations of N_{tot} , the total number of events needed to decorrelate the scattered light. In determining N_{tot} , one has to take into account that one single event may not displace particles far enough to fully suppress the local contribution to the scattered light; additionally, one single event may affect only a portion of the whole scattering volume. Thus, $N_{\text{tot}} \sim N_{\text{blob}} N_{\text{ev}}$, where $N_{\text{blob}} \sim V_{\text{sc}}/V_b$ is the number of blobs of volume V_b contained in the scattering volume V_{sc} , and N_{ev} is the number of rearrangement events that are needed, at any given location, to relax the local contribution to the correlation function. The inset of fig. 3 is a schematic representation of this concept for $N_{\text{blob}} \sim 50$ and $N_{\text{ev}} = 2$: in this case, $g_2 - 1$ decays to zero when at least two rearrangement events have occurred at every location in the system. Given the random nature of the events, N_{tot} fluctuates, and so does c_I , with $\text{var}(c_I) \sim \text{var}(N_{\text{tot}})$. According to the central limit theorem, the relative variance of N_{tot} —and thus χ —is expected to scale as $N_{\text{tot}}^{-1} \sim (N_{\text{blob}} N_{\text{ev}})^{-1}$.

We stress that in general both N_{blob} and N_{ev} are q -dependent quantities. Indeed, N_{ev} decreases as q increases, because fewer events are needed to displace the particles over the smaller distances corresponding to larger scattering vectors. More specifically, we expect $N_{\text{ev}} \sim q^{-2}$ if the particle displacements due to successive events are uncorrelated (“Brownian-like” rearrangements), in which case the system’s average relaxation time scales as $\tau_r \sim q^{-2}$, since in our model the average number of events is proportional to time. By contrast, $N_{\text{ev}} \sim q^{-1}$ if the displacement direction persists over several events (“ballistic-like” rearrangements, for which $\tau_r \sim q^{-1}$), as found for internal stress-driven dynamics [5, 12, 19]. Therefore, the q -dependence of N_{ev} may be di-

rectly inferred from the average dynamics: $N_{\text{ev}} \sim \tau_r(q)$. Note that at very large q N_{ev} should saturate to one, when the particles' displacement due to one single event exceeds $1/q$, the length scale probed in a scattering experiment. By contrast, there are no *a priori* prescriptions on the q -dependence of N_{blob} . However, it is reasonable to assume that the latter be an increasing function of q , since in glassy systems rearrangements involving displacements over large distances (probed at low q) are likely to require the highly cooperative motion of many particles, whereas smaller displacements (probed at high q) may be achieved independently by clusters containing just a few particles. Thus, for $q \rightarrow 0$, N_{blob} is expected to saturate at a lower bound, which may be as low as 1 when V_b is larger than the scattering volume, as observed in [12]. In the opposite limit, $q \rightarrow \infty$, N_{blob} should saturate to N_p , the number of particles in the system.

The main panel of fig. 3 illustrates schematically the q -dependence of N_{blob}^{-1} and N_{ev}^{-1} (right axis) and that of $\chi^* \sim (N_{\text{blob}}N_{\text{ev}})^{-1}$ (left axis). At low q , χ^* increases with q , since N_{blob}^{-1} saturates to one whereas N_{ev}^{-1} is an increasing function of q , as discussed above. This is the regime observed for the strongly attractive gels of ref. [12] (for which $N_{\text{blob}} = 1$ and $\chi^* \sim N_{\text{ev}}^{-1} \sim \tau_r(q)^{-1} \sim q$) and discussed, in the diffusive limit, in [13, 14]. At very large q , χ^* tends to a constant value, because N_{blob}^{-1} and N_{ev}^{-1} saturate to N_p^{-1} and one, respectively. The behavior of the dynamical susceptibility for intermediate q 's depends on the detailed interplay between N_{blob} and N_{ev} . In fig. 3 we have sketched the case where N_{blob}^{-1} decreases faster than N_{ev}^{-1} grows, yielding a peaked shape of χ^* , as observed in the experiments presented here.

Simulations of glass formers and experiments on 2D granular materials suggest that χ^* is maximum on the length scale of the particle size. Colloidal gels present an additional characteristic length, the size of the (fractal) clusters that compose them. For the gels of ref. [12], χ^* was shown to grow with q for length scales intermediate between the cluster and the particle size. For the CB gels studied here, χ^* peaks at $q \approx 20 - 50 \mu\text{m}^{-1}$ (see fig. 2), corresponding to a length scale $2\pi/q \approx 125 - 300 \text{ nm}$ slightly smaller than the particle size. Collectively, these observations suggest that the crossover length scale for dynamical heterogeneity in colloidal gels is of the order of the particle size, similarly to molecular glass formers and granular materials, rather than the cluster size.

Our measurements demonstrate that XPCS may be used to obtain quantitative information not only on the average dynamics, but also on its heterogenous behavior. This opens a new way to investigate dynamical heterogeneity in a wide variety of materials, possibly including molecular glass formers, whose characteristic length scales match those probed by XPCS. For the CB gels, dynamical fluctuations increase with q , peak around the inverse particle size, and decrease at larger scattering vectors. This behavior and that of other systems can be

rationalized by a simple scaling argument, providing a general framework for understanding temporal fluctuations of the dynamics in glassy systems.

We thank ESRF for provision of synchrotron radiation facilities and financial support. We are indebted to P. Clegg for generously providing us with some of his beam time at ESRF for control experiments. We thank L. Berthier, W. Kob and A. Duri for many useful discussions. This work was supported in part by the European MCRTN ‘‘Arrested matter’’ (MRTN-CT-2003-504712), the NoE ‘‘SoftComp’’ (NMP3-CT-2004-502235), the Swiss National Science Foundation, the French CNRS (PICS no. 2410), and ACI JC2076 and ANR JCJC-CHEF grants. L.C. is a junior member of the Institut Universitaire de France, whose support is gratefully acknowledged.

* Electronic address: lucacip@lcvn.univ-montp2.fr

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