Beyond simple exponential correlation functions and equilibrium dynamics in x-ray photon correlation spectroscopy

Anders Madsen\textsuperscript{1,4}, Robert L Leheny\textsuperscript{2,4}, Hongyu Guo\textsuperscript{2}, Michael Sprung\textsuperscript{3} and Orsolya Czakkel\textsuperscript{1}

\textsuperscript{1} European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France
\textsuperscript{2} Department of Physics and Astronomy, Johns Hopkins University, 3400 N Charles Street, Baltimore, MD 21218, USA
\textsuperscript{3} Hasylab at DESY, Notkestr. 85, 22607 Hamburg, Germany

E-mail: amadsen@esrf.fr and leheny@pha.jhu.edu

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Abstract. We discuss the complex dynamics in condensed matter studied with x-ray photon correlation spectroscopy (XPCS) in which non-exponential correlation functions and dispersion relations deviating from the simple diffusion law are observed. Results are presented for two systems whose dynamics are characterized by compressed, faster-than-exponential correlation functions associated with hyper-diffusive motion. In the first case, the microscopic response of an aerogel following sectioning is investigated. In the second, the out-of-equilibrium dynamics in a dense colloidal gel recovering from shear is analyzed. In both cases, the dynamics, which can be associated with relaxation of internal stress, exhibits ageing. Included in the analyses are calculations of two-time correlation functions and the variance of the instantaneous degree of correlation, yielding the dynamical susceptibility.

\textsuperscript{4} Authors to whom any correspondence should be addressed.
1. Introduction

In recent years, x-ray photon correlation spectroscopy (XPCS) has emerged as an important tool for investigating slow dynamics in materials at lengths approaching the nanometer scale. (For a thorough introduction to XPCS, see e.g. [1, 2].) In XPCS, like in dynamic light scattering (DLS) with visible light [3], fluctuations in the coherent scattering intensity from a material provide direct information about the material’s dynamics. However, due to the much shorter wavelength of x-rays, XPCS can probe motions over significantly smaller distances. In many cases, the primary quantity obtained in an XPCS measurement is the time-averaged temporal autocorrelation function of the scattered intensity,

\[ g^{(2)}(Q, t) = \frac{\langle I(Q, \tau) I(Q, \tau + t) \rangle}{\langle I(Q) \rangle^2} \]

where \( I(Q, \tau) \) is the intensity measured at wave vector \( Q \) at time \( \tau \). At small and large delay times \( t \), the numerator of \( g^{(2)}(Q, t) \) approaches the limits

\[ \lim_{t \to 0} \langle I(Q, \tau) I(Q, \tau + t) \rangle = \langle I^2(Q) \rangle \]

and

\[ \lim_{t \to \infty} \langle I(Q, \tau) I(Q, \tau + t) \rangle = \langle I(Q) \rangle^2, \]

respectively. Thus, \( g^{(2)}(Q, t) \) tends to unity for \( t \to \infty \), while for \( t \to 0 \) it approaches \( 1 + \beta \), where \( \beta \), known as the optical contrast, is the variance of the fluctuations in intensity divided by \( \langle I \rangle^2 \). For perfectly coherent chaotic light, \( \beta \) equals unity. If the scattering is incoherent (coherence volume \( \ll \) scattering volume) or if the spatial resolution of the detector is insufficient to provide discrimination at the angular scale of the intensity fluctuations (i.e. the speckles), one gets \( \beta \approx 0 \). For partially coherent radiation, which describes the usual situation in an XPCS experiment, the scattering geometry and the sample will typically affect the contrast. In such cases, measurement configurations that compromise between a reduced \( \beta \) in exchange for increased scattering intensity can optimize the signal-to-noise ratio [4].

When the scattering volume contains a large number of independent scattering sites undergoing thermally excited motion in equilibrium, the central limit theorem guarantees that the temporal fluctuations in the coherent scattering intensity obey Gaussian statistics, so that
$g^{(2)}(Q, t)$ fully describes the correlation spectrum. In this case, $g^{(2)}(Q, t)$ can be directly related to the normalized intermediate scattering function, $f(Q, t) = S(Q, t)/S(Q, 0)$, of the scattering system through the Siegert relation,

$$g^{(2)}(Q, t) - 1 = \beta |f(Q, t)|^2. \quad (4)$$

The intermediate scattering function, which is equivalent to the dynamic structure factor in the time domain, is given by

$$S(Q, t) = \sum_{n=1}^{N} \sum_{m=1}^{N} \langle b_n(Q) b_m(Q) \exp(iQ \cdot [r_n(t) - r_m(0)]) \rangle, \quad (5)$$

where $r_n(t)$ is the position of the $n$th scatterer at time $t$, and the angular brackets $\langle \rangle$ indicate the ensemble averaging over the scattering volume. The pre-factor $b_n$ is the scattering length, which for x-rays equals the Thomson scattering length. $S(Q, t)$ is fundamental in the description of the dynamical behavior of condensed matter and is often the key quantity through which a detailed comparison between theory and experiment can be achieved. Hence, a major strength of XPCS is its access to this important material property.

If the scatterers undergo free diffusion, i.e. their mean-square displacement is proportional to time, then the correlation function assumes a simple exponential form,

$$g^{(2)}(Q, t) - 1 = \beta \exp(-2\Gamma t), \quad (6)$$

where $\Gamma(Q)$ is the relaxation rate, or $1/\Gamma = \tau_c$ is the relaxation time. The factor 2 accounts for the homodyne detection scheme in which the scattered intensity is not mixed with a reference wave (heterodyne detection). For free diffusion one finds $\Gamma = D_0 Q^2$, where $D_0$ is the scatterers’ Stokes–Einstein diffusion coefficient. In polydisperse systems, one can have a distribution on $D_0$, which leads to a smearing of the exponential line shape [5]. In the frequency domain, accessed in inelastic scattering techniques where the energy difference between the incoming and outgoing photons is related to frequency by $\Delta E = h\omega$, a simple diffusive process leads to a quasi-elastic Lorentzian line shape for the dynamical structure factor, $S(Q, \omega) \propto 1/(\Gamma^2 + \omega^2)$. This result is consistent with equation (6) since $S(Q, \omega) \approx \omega^2$ and $f(Q, t)$ are Fourier pairs.

Such a characterization of diffusion with coherent scattering is an important capability [3] and indeed the ability to track diffusion at the atomic scale with XPCS has recently been demonstrated [6], thereby opening a unique window into the fundamental collective motions in materials. However, for complex dynamics in condensed matter, diffusive motion obeying equation (6) is often the exception rather than the rule. In this paper, we discuss cases of material dynamics probed with XPCS that deviate from simple diffusive behavior. We begin in section 2 with a brief review of several examples, including capillary wave motion, collective diffusion near the colloidal glass transition and the dynamics in disordered soft solids such as gels and emulsions. For such disordered soft solids, recent XPCS and DLS experiments have observed a process of slow, hyper-diffusive motion characterized by compressed, faster-than-exponential correlation functions. A related, important feature of these materials is their out-of-equilibrium behavior. As described below, for out-of-equilibrium dynamics the correspondence between $g^{(2)}(Q, t)$ and $f(Q, t)$ can break down, and characterization of the coherent scattering fluctuations beyond $g^{(2)}(Q, t)$ then provides significant new insights. As a way of illustration, we present in sections 3 and 4 new results and analysis of two different systems displaying compressed-exponential correlation functions: an aerogel following sectioning and a dense colloidal gel recovering from a strong shear.
2. Examples of XPCS studies of non-diffusive dynamics

2.1. Inelastic measurements in the time domain: capillary waves

One class of dynamics that, when probed in the frequency domain, is characterized by line shapes that deviate from simple quasi-elastic Lorentzians is collective phenomena where Stokes/anti-Stokes satellites are present. Prominent examples include phonon modes in ordered and disordered materials as well as molecular excitations. Equivalent behavior in the time domain has been observed for capillary wave dynamics studied by photon correlation spectroscopy, both with DLS [7] and XPCS in the ms–µs range [8]. Capillary waves are thermally excited waves that decorate liquid surfaces and interfaces thanks to the surface tension that acts as a restoring force to surface disturbances. Below a certain viscosity, the capillary waves display a transition from quasi-elastic, overdamped modes to propagating modes [9]. In this case, the correlation function becomes

\[ g^{(2)}(Q,t) - 1 \propto \cos^2(\omega_0 t) \exp(-2\Gamma t), \] (7)

which in the frequency domain corresponds to a Lorentzian line shape centered at \( \omega = \omega_0 \).

Resolution effects need to be included for a proper modeling of such correlation functions observed for propagating modes [10, 11]. Pronounced viscoelastic behavior may affect the dispersion relations of capillary waves, and behavior of this kind has been studied with XPCS in a variety of systems ranging from viscous free surfaces to thin polymer films and liquid-crystalline membranes [12]-[17].

2.2. Cooperative relaxations near the colloidal glass transition

Another prominent example of deviations from simple exponential correlation functions occurs with glass-forming liquids, where diffusion becomes increasingly anomalous as the glass transition is approached. Near the transition, \( g^{(2)}(Q,t) \) acquires a two-step line shape with a partial decay, known as the beta relaxation, followed by a terminal decay known as the alpha relaxation. The decay time of the rapid beta relaxation is relatively insensitive to the proximity of the glass transition, while the decay time of the alpha relaxation time grows dramatically and freezes out on approaching the transition. Microscopically, the beta relaxation is identified with localized motion of molecules within the potential-energy ‘cage’ defined by interactions with their neighbors, while the alpha relaxation corresponds to structural re-arrangements that are thought to become increasingly cooperative on approaching the transition. Near the transition, the alpha relaxation typically acquires a non-exponential shape that is approximated by the Kohlrausch–Williams–Watts (KWW) form,

\[ g^{(2)}(Q,t) - 1 = \beta \exp(-2[\Gamma t]^\gamma), \] (8)

where the value of the KWW exponent \( \gamma \) implies that the decay is faster (\( \gamma > 1 \)) or slower (\( \gamma < 1 \)) than exponential. For liquids near the glass transition, the correlation function is stretched, \( \gamma < 1 \). While equation (8) is empirical, a connection to continuous time Lévy flights, which are common in nature and give rise to anomalous diffusion [18], has been suggested. In particular, recent molecular dynamics simulations have shown that continuous time Lévy flight models can be derived numerically from the dynamics of a glass-forming liquid [19].

While the scattering intensity from atomic and molecular glass formers is so weak that XPCS measurements of their structural dynamics are almost impossible using existing x-ray sources, coherent scattering experiments have explored the related dynamics associated...
with glass transitions in colloidal suspensions. For colloids interacting through a hard-sphere potential, DLS studies have investigated the slowing dynamics as a function of colloid volume fraction $\phi$ on approaching the hard-sphere glass transition, $\phi_{hs} \approx 0.58$ [20]. This work has been complemented by XPCS experiments that have tracked the initial deviations from simple exponential correlation functions with increasing $\phi$ at lower concentration [21]. The collective nature of the structural dynamics near the hard-sphere glass transition was further captured in a recent coherent x-ray scattering study that investigated cross correlations in the time-dependent scattered intensity along different wave vector transfer directions. Temporal correlations between intensity patterns with different azimuthal symmetries indicated the prevalence of certain transitions between different preferred forms of local order and particularly the long persistence of icosahedral-symmetry (five-fold-symmetry) packings [22].

Another area of recent interest in colloidal glass transitions has concerned the evolution in colloidal dynamics as a short-range attraction between particles is introduced in addition to the hard-core repulsion. Weak short-range attractions cause suspensions above $\phi_{hs}$ to transform from the hard-sphere repulsive glass to a liquid, while stronger attractions drive suspensions from the liquid state to a reentrant, ‘attractive glass’ phase [23]. This process has been monitored in a recent XPCS study, which also observed logarithmic line shapes for $g^{(2)}(Q, t)$ like those predicted to occur near a higher-order glass transition singularity in the phase diagram of colloidal suspensions with short-range attraction [24]. At lower volume fraction and stronger attraction, colloidal suspensions can form gels [23], and stretched correlation functions approximated by equation (8) have also been observed with XPCS on approaching this gel transition [25].

2.3. Non-equilibrium and jammed dynamics

A particular focus of recent XPCS research has been the microscopic dynamics in disordered soft solids, such as colloidal gels and concentrated emulsions, where again pronounced deviations from simple exponential correlation functions are observed. Specifically, a surprising finding of this work, and of related DLS experiments, has been the observation of compressed, faster-than-exponential correlation functions that are well approximated by equation (8) with $\gamma > 1$ [24], [26]–[39]. An accompanying feature of these dynamics is a relaxation rate that varies approximately linearly with wave vector, $\Gamma \sim Q$, implying hyper-diffusive, convective-like motion. The wide assortment of disordered soft materials displaying these dynamics, as well as their observation with XPCS in a variety of polymeric systems [40]–[47] and in colloidal motion in glassy solvents [46, 48, 49], suggests a generic underlying mechanism; however, no clear consensus about their microscopic origin has emerged. As mentioned above, the continuous time Lévy flight model with a power-law distribution of waiting times can account for equation (8) with either $\gamma < 1$ or $\gamma > 1$. Support for this model in describing the observed hyper-diffusive motion comes from several systems for which $\gamma$ has a $Q$-dependence that is accurately captured by the model [31, 48]. Another explanation for the hyper-diffusive dynamics invokes a process of stress relaxation in which point-dipole stress fields create a distribution of strain velocities [27]. Support for this scenario comes from several systems for which $\gamma \approx 1.5$, a value predicted by models of such stress relaxation [27, 50].

An important feature of these disordered soft solids is their out-of-equilibrium behavior, which can complicate the analysis of XPCS measurements. Specifically, an implicit assumption in the calculation of $g^{(2)}(Q, t)$ through equation (1) is that the dynamics is stationary over the
duration of the measurement; that is, no information is lost by performing a time-averaging of the quantities (indicated by the angular brackets $\langle \rangle$). This assumption breaks down if the dynamics changes during the measurement, such as can occur with systems that are out of equilibrium. In this case, the correlation analysis must be performed explicitly as a function of time, or ‘age’, and the time average in equation (1) must be replaced by an ensemble average taken over equivalent scattering wave vectors. This approach necessitates the use of an area detector with high spatial resolution where symmetries in the scattering pattern, such as the azimuthal symmetry of scattering from an isotropic system, can be exploited to collect intensity measurements simultaneously at many equivalent wave vectors.

In a multi-speckle time-correlation scheme [51, 52], the age dependence of the dynamics can be captured by replacing the time-averaged correlation function with a two-time correlation function,

$$G(Q, t_1, t_2) = \frac{\langle I(Q, t_1)I(Q, t_2)\rangle_{\phi}}{\langle I(Q, t_1)\rangle_{\phi}\langle I(Q, t_2)\rangle_{\phi}},$$

where the subscript $\phi$ indicates that the averaging is performed on the ensemble of pixels corresponding to a range of wave vectors, $|Q| = Q \pm \Delta Q$, over which the correlations are expected to show negligible variation. This two-time approach was pioneered for XPCS by Sutton and co-workers [53, 54] in a series of experiments on materials with non-stationary dynamics, such as alloys undergoing phase separation. In particular, this work demonstrated how plotting the instantaneous correlations provides an effective method for identifying and characterizing rapidly evolving dynamics, for example enabling tests of critical scaling [53]–[56].

In the cases where time averaging is valid, $g^{(2)}(Q, t)$ can be obtained by averaging values of $G(Q, t_1, t_2)$ at fixed delay time, $t = t_2 - t_1$,

$$g^{(2)}(Q, t) = \langle G(Q, t_1, t)\rangle_{t_1}.$$

Examples are shown in sections 3 and 4 below. However, even for out-of-equilibrium systems with dynamics that are nominally stationary or that evolve sufficiently slowly so that time averaging over the measurement to obtain $g^{(2)}(Q, t)$ is not obviously problematic, the temporal variations of the correlations can still contain important information. For instance, fluctuations could signal dynamic heterogeneity that would not be noticed in the average $g^{(2)}(Q, t)$. Specifically, for equilibrium, diffusive motion the values of $G(Q, t_1, t)$ at different $t_1$ follow a Gaussian probability distribution with a Gaussian width dictated by the intrinsic statistical noise of the measurement. In this case, the average of $G(Q, t_1, t)$, and hence $g^{(2)}(Q, t)$, contains all the pertinent information regarding the system’s dynamics. Conversely, larger fluctuations in the value of $G(Q, t_1, t)$ or a probability distribution deviating from Gaussian statistics can be indicative of collective motion or non-equilibrium behavior that an analysis focused simply on the shape of $g_2(Q, t)$ would fail to identify. Examples of such dynamics have been nicely demonstrated in a series of recent DLS experiments on soft glassy materials by Cipelletti and co-workers [31, 51, 57, 58]. In other examples, theoretical models of glassy systems both with and without quenched disorder have revealed temporal auto-correlations with an asymmetric distribution that resembles the Gumbel form prevalent in extreme value statistics [59]–[62]; by analyzing the fluctuations in the degree of correlation, such behavior could possibly be experimentally demonstrated.
A useful measure of the fluctuations in $G(Q, t_1, t)$ is provided by its normalized variance [31]:

$$\chi(Q, t) = \frac{\langle G^2(Q, t_1, t) \rangle_{t_1} - \langle G(Q, t_1, t) \rangle_{t_1}^2}{(g_2(Q, 0) - 1)^2}. \quad (11)$$

In some respects, $\chi(Q, t)$ is similar to the dynamical four-point susceptibility $\chi_4$ that has been widely studied in glassy materials to characterize spatial heterogeneity in their dynamics. Specifically, an increase in $\chi_4$ has been identified as a key signature of a growing dynamical correlation length in a range of disordered systems approaching arrest, such as supercooled liquids near the glass transition and granular materials near the jamming transition [63]–[69].

While $\chi$ defined in equation (11) characterizes temporal heterogeneity and $\chi_4$ characterizes spatial heterogeneity, so that the quantities measure different dynamical properties, one can potentially relate the two by noting that an increasing length over which dynamics are cooperative would imply fewer dynamically independent scattering sites in the scattering volume and a concomitant increase in temporal fluctuations. Indeed, a power-law scaling relation between $\chi_4$ and a corresponding temporal quantity similar to $\chi$ has been advanced to connect the spatial and temporal heterogeneity of collective dynamics in granular materials [63, 65]. This connection thus opens up an opportunity with XPCS to make contact with recent key advances in the study of disordered, glassy and out-of-equilibrium materials through analysis of $\chi(Q, t)$, and several recent XPCS studies [37]–[39] of glassy colloidal systems have considered the behavior of $\chi(Q, t)$.

3. Analysis of stress relaxation in an aerogel

A notable consequence of the hyper-diffusive motion in disordered soft solids is that it restores ergodicity, in the sense that intensity fluctuations decorrelate fully on experimental time scales, whereas the jammed states of these materials would suggest dynamical arrest. Here we report XPCS measurements on an aerogel, which is a chemically bonded organic polymer gel, which illustrate this feature vividly. To fabricate the sample, a resorcinol-formaldehyde (RF) polymer hydrogel, free of any metal ions or colloidal particles, was synthesized to produce a fractal polymer matrix [70, 71]. Solvent removal was ensured by extraction with supercritical CO$_2$. XPCS data on a piece of RF polymer aerogel were taken on the ID10A (Troika) beamline of the European Synchrotron Radiation Facility. A well-defined wavelength ($\lambda = 0.1557$ nm) with a narrow bandwidth was selected using an Si(111) Bragg reflection and an Si mirror to reflect the beam. Coherent illumination of the sample was ensured by a small aperture ($10 \times 10 \mu m^2$) intersecting the x-ray beam to limit the scattering volume to the coherence volume of the beam, as described in [2]. By the use of a scalpel, a sample slice of 1 mm thickness was sectioned out from a larger piece of aerogel, thereby introducing internal stress in the structure.

A direct illumination CCD detector was used to record the speckle pattern, and the multi-speckle technique was employed to calculate the two-time correlation functions according to equation (9). Examples of graphical representations of $G(Q, t_1, t_2)$ are shown in the upper left and upper right panels of figure 1, which correspond to data acquired starting approximately 5 and 180 min after the sectioning, respectively. In the two panels, the color represents the value of $G$ in the point $(t_1, t_2)$ with red being the largest ($G \approx 1.2$) and blue the smallest ($G \approx 1$) (this range is retrieved on the graphs showing the time-averaged correlation functions in the lower panels of figure 1). A delay time and a sample age can be defined as $t = t_1 - t_2$ and
Figure 1. Top left: $G(Q = 3.25 \times 10^{-2} \text{ nm}^{-1}, t_1, t_2)$ for the $\tau + 5$ min old sample. Top right: $G(Q = 3.25 \times 10^{-2} \text{ nm}^{-1}, t_1, t_2)$ for the $\tau + 180$ min old sample. The lower panels show the time-averaged correlation functions $g^{(2)}(Q, t)$ over the investigated $Q$-range for the two ages, and the fits with the KWW expression. 

$\tau = (t_1 + t_2)/2$, respectively. Hence, the diagonals from the lower left to the upper right of the figures correspond to $t = 0$, and lines parallel to the diagonal are iso-$t$ lines. Along an iso-$t$ line the age $\tau$ increases linearly from the lower left to the upper right. In the direction perpendicular to these diagonals, $t$ varies, while $\tau$ remains constant. For stationary dynamics, the contour lines in plots of $G(Q, t_1, t_2)$ are parallel to the diagonal (as in figure 1) and in this case a $\tau$-averaging can be performed to yield the regular $g^{(2)}(Q, t)$ through equation (10). The upper panels of figure 1 meet this criterion to good approximation, indicating the dynamics was rather stationary over the duration of the runs (1000 CCD frames acquired in about 20 min and 580 frames in 12 min). The two-time correlation functions were therefore time averaged to provide the usual $g^{(2)}(Q, t)$, as shown in the bottom panels of figure 1. (A counterexample displaying non-stationary dynamics in $G(Q, t_1, t_2)$ can be seen in figure 3 below.) The solid lines in the lower panels of figure 1 are the results of fits to the KWW form, which remains empiric but models the short time decay of the correlation functions very well. The fit parameters $\Gamma$ and $\gamma$ are shown in figure 2. One observes that relaxation rates have decreased by more than a factor of five when the sample is older compared to when it is younger. However, the strongly non-exponential character of the relaxations persists as characterized by highly compressed decays.
Figure 2. The results of the fits with equation (8) for the young sample (left) and the old sample (right). The top panels show the approximate linear relation between $\Gamma$ and $Q$, while the lower panels present $\gamma(Q)$, which is almost constant and approximately equal to two.

and an approximately linear relationship between $Q$ and $\Gamma$ (figure 2). This is rather similar to the observations in [48], where non-exponential relaxations and $Q \propto \Gamma$ behavior were observed in a system (nano-particles in a supercooled glass-forming solvent) without any visible ageing of the dynamics. In contrast to [48], here we observe almost no dispersion of $\gamma$, which remains very close to 2 in the investigated $Q$-range for this aerogel. This points towards a length scale $\delta$ of characteristic jumps that would be very small (upper limit: $\delta \lesssim 0.1/Q_{\text{max}} = 0.5 \text{ nm}$) if these data were to be modeled within the continuous time random walk (CTRW) model assuming Gaussian jumps to account for $\gamma = 2$. We may speculate that this behavior could be connected with the nature of the aerogels where a characteristic length scale is given by the typical molecular size. Another line of explanation assumes that correlated traction regions exist in the sample, causing deviations from the simple picture of ‘micro-collapses’ that give rise to the randomly distributed point-like stress dipoles leading to $\gamma = 1.5$ in the stress-relaxation models [50]. Obviously, additional theoretical work is required to determine the microscopic picture of the dynamics observed here and explain the $\gamma = 2$ behavior. Finally, we note that the dynamics of the sample
is totally arrested, up to 10 000 s timescales, for old samples (after a few days of waiting time). An investigation of the static averaged small angle scattering showed very isotropic patterns and almost no differences between samples at different ages, thus indicating that the average fractal structure of the aerogel is preserved during the relaxation. Further studies will elucidate this remarkable dynamic behavior and also focus on the second decay (visible in the lower left panel of figure 1) that is not captured by the KWW expression. This large-time tail of the correlation function could provide another indication of the nature of the dynamics and may point towards a distribution of velocities in the sample with large static regions.

4. Dynamical heterogeneity in an ageing colloidal gel

To illustrate the non-Gaussian nature of the hyper-diffusive dynamics in a disordered soft solid undergoing ageing, we have applied the analysis described in section 2.3 to obtain $\chi(Q, t)$ from XPCS measurements on a concentrated suspension of nanoparticles that forms a gel through a depletion interaction [33]. The gel was composed of octadecyl-grafted silica colloids (radius = 22 nm) at a volume fraction $\phi = 0.33$ in decalin with non-absorbing polystyrene (radius of gyration $= 3.5$ nm) at a concentration of $c/c^* = 0.18$, where $c^*$ is the overlap concentration. Like many soft glassy materials, the gel displays a thixotropic response to stress [72], and the recovery of the gel from a fluidizing shear is characterized by an evolution in microscopic dynamics that is revealed with XPCS [33].

The experiment was conducted at Sector 8-ID in the Advanced Photon Source using the procedures described in [33]. Briefly, fluidization of the quiescent gel was accomplished by extrusion through a needle of length 38 mm and inner diameter 0.255 mm at a controlled rate of 0.67 ml min$^{-1}$, corresponding to an average shear rate of approximately 4300 s$^{-1}$ [33]. The recovery time, or waiting time, $t_d$ was measured from the cessation of shear. For the XPCS measurements, the suspension was extruded directly into a sealable, stainless-steel sample holder with thin polyimide windows for transmission scattering and sample thickness 0.5 mm. The measurements were performed with 7.66 keV x-rays, and the temperature of the sample was held at 25 °C. The scattering intensity was recorded by a direct-illuminated CCD area detector 3.4 m after the sample to cover a wave vector range $0.04$ nm$^{-1} < Q < 0.39$ nm$^{-1}$.

The evolution in microscopic dynamics following the application of shear is captured in the two-time correlation function calculated from the scattering images, as shown in figure 3 for $Q = 0.16$ nm$^{-1}$, a wave vector near the first peak in the structure factor of the suspension. The measurement was initiated at a beginning waiting time $t_d = 700$ s, so that the age of the sample at any point in figure 3 can be taken as $t_d = 700 + (t_1 + t_2)/2$ s. The steady slowing of the microscopic motion characterizing the recovery from shear is illustrated by the increasingly broad span of large $G$ values along the diagonal from the lower left (small $t_d$) to the upper right (large $t_d$). Figure 4 displays $g_2(Q, t)$ at this wave vector at several waiting times. To prevent the evolution in the dynamics from influencing the calculation of $g_2(Q, t)$, the correlations at each $t_d$ were averaged over a time window of size $t_d/10$ in an effort to capture a ‘snapshot’ of the dynamics at a given waiting time. By varying this time window, we found that the choice $t_d/10$ was large enough to observe most of the decorrelation of $g_2(Q, t)$ but still small enough that the shape of $g_2(Q, t)$ was not noticeably distorted by the evolution in the dynamics within the window.

In figure 4, the solid lines through the data depict the results of fits to equation (8). The wave vector dependence of the correlation time, $\tau_c = \Gamma^{-1}$, shown in figure 5, follows an inverse
Figure 3. Two-time correlation function $G(Q = 0.16 \text{nm}^{-1}, t_1, t_2)$ for a concentrated depletion gel after the application of strong shear [33]. The measurement was initiated approximately 700 s after the application of the shear, so that the waiting time $t_d$ can be taken as $t_d = 700 + (t_1 + t_2)/2$ s.

Figure 4. Intensity autocorrelation function for the concentrated gel at $Q = 0.16 \text{nm}^{-1}$ and at different waiting times: $t_d = 1400$ s (red circles), 3400 s (blue squares), 7000 s (green triangles) and 14 000 s (black diamonds). The solid lines display the results of fits to a compressed exponential form (equation (8)) with $\gamma \approx 1.5$.

relation, $\tau_c \sim Q^{-1}$, indicating the dynamics are representative of the hyper-diffusive motion described above. The KWW exponent $\gamma$ is approximately 1.5, independent of $Q$, consistent with a stress-relaxation model of the motion [27, 33, 50]. The correlation times scale roughly linearly with the waiting time, as shown in figure 6. Such a linear scaling is common to many ageing systems.

Figure 7 shows $\chi(Q, t)$ as a function of delay time $t$ at the same waiting times and the same $Q$ as in figure 4. In the calculation of $\chi(Q, t)$, the contribution from the measurement noise due to the finite number of pixels has been removed by following established procedures [58]. At each waiting time, $\chi(Q, t)$ displays a peak at a delay time that tracks the time scale of the decay in $g_2(Q, t)$. The positions of the peak $\tau^*$ as a function of $Q$ and as a function of waiting time...
are shown in figures 5 and 6, respectively, illustrating this close correspondence between the maximum of the temporal heterogeneity and the correlation time. Similar correspondence has been observed for \( \chi(Q, t) \) for several systems [31], [37]–[39], [49, 73] and also for \( \chi_4 \), where the peak position is considered a measure of the persistence of spatial heterogeneities [63]–[66].

While the position of the peak in \( \chi(Q, t) \) unsurprisingly follows this common trend, the magnitude of \( \chi(Q, t) \) for the sheared depletion gel is significantly smaller than the variance characterizing the hyper-diffusive dynamics in dilute gels measured with DLS [31], reflecting the relatively smooth evolution in dynamics observed in figure 3. However, the magnitude of \( \chi(Q, t) \) in figure 7 is similar to the magnitudes seen for other dense colloidal systems with XPCS [37]–[39]. Given this small magnitude, we note that the results should be viewed with caution, particularly since the ageing of the system will lead to a variance in the instantaneous correlations irrespective of any dynamic heterogeneity. Specifically, calculation of the variance resulting from a linear increase in correlation time during the duration of each measurement,
Figure 7. Normalized variance of the instantaneous correlations for the same gel as in figure 3 as a function of delay time for waiting times $t_d = 1400\text{ s}$ (red circles), $3400\text{ s}$ (blue squares), $7000\text{ s}$ (green triangles) and $14\ 000\text{ s}$ (black diamonds).

Figure 8. Magnitude of the peak in the variance of the instantaneous correlations for the same gel as in figure 4 at $Q = 0.16\text{ nm}^{-1}$ as a function of waiting time.

$0 < t < t_d/10$, indicates that the ageing contributes as much as half of the total variance shown in figure 7. While protocols to correct $\chi(Q, t)$ for such contributions from ageing have been implemented in other cases [39], here we are interested in observing how the variance evolves with waiting time. Therefore, at each waiting time we simply calculate $\chi(Q, t)$ over measurements spanning a time window that is the same small fraction of the waiting time, $t_d/10$, with the assumption that the resulting contribution to the variance from ageing at all waiting times is consequently also the same.

Figure 8 shows the resulting magnitude of the peak in the variance $\chi^*$ as a function of $t_d$. As the figure illustrates, the magnitude shows no systematic variation with waiting time, suggesting that the degree of heterogeneity of the dynamics remains largely unchanged as the system ages despite the dramatically slowing dynamics. In terms of the microscopic picture that associates the hyper-diffusive motion with strain in response to local heterogeneous stress, this observation appears to constrain the processes underlying the ageing. Specifically, within this picture the increase in $\tau_c$ with increasing $t_d$ corresponds to a decrease in the characteristic strain velocity [33]. One interpretation for a decreasing velocity would be a decrease in the population
density of local sites actively undergoing stress relaxation. An explanation like this has been advanced in a model of the stress relaxation developed by Bouchaud and Pitard in which the activation energy for new ‘micro-collapses’, which are the local processes generating stress in the model, increases with the amount of accumulated strain, thereby causing ageing [50]. However, one would expect that such a decrease in the density of sites of growing stress would imply a larger range over which the strain motion is correlated, thereby leading to a more strongly non-Gaussian character to the dynamics that should be reflected in an increasing rather than a constant variance. An alternative explanation for the decreasing characteristic velocity with age is a decrease in the growth rates of the stress and hence the strain rates associated with a nominally fixed population density of actively relaxing stress dipoles. In this case, one should expect that the variance would change little with waiting time, consistent with the observed trend. Additional experimental investigations into the evolution in dynamic heterogeneity during ageing and further development of microscopic models for the hyper-diffusive motion that can account for this evolution would be valuable.

5. Conclusions

As this paper has attempted to highlight, the scientific content in XPCS measurements often derives from the deviations of the intensity correlation functions from simple exponential line shapes. Indeed, precise and reliable line shape analysis is often key to making rigorous contacts with theory. Looking to the future of the technique, the prospect of higher coherent flux at upgraded existing facilities, particularly the ESRF and the APS, and at new low-emittance facilities, such as Petra III and NSLS-II, suggests a highly promising outlook. While much of the excitement surrounding these expected improvements focuses on the ways they will expand the reach of XPCS, for example by enabling measurements at shorter delay times and on more weakly scattering materials, another important benefit will be improvement in the signal-to-noise ratio that will permit more precise determination of the shapes of intensity correlations. Such an improved signal-to-noise ratio will be particularly germane to studies of out-of-equilibrium systems where time averaging cannot be exploited to build statistics and where higher-order moments in the intensity fluctuations, such as $\chi(Q, t)$, which require more demanding statistics, are important. Given the unique insight into material dynamics that these higher moments can provide, we expect that analysis including their calculation will become a standard aspect of XPCS.

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