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# **Development of ultra-small-angle X-ray scattering–X-ray** photon correlation spectroscopy

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# 1. Introduction

Compared with earlier X-ray sources, third-generation synchrotron sources produce partially coherent X-rays that are several orders of magnitude more intense. This characteristic has led to major progress in structural physics and X-ray science. The development of new static probes such as X-ray phase contrast imaging (Davis *et al.*, 1995), X-ray holography (Faigel & Tegze, 1999) and coherent X-ray diffraction imaging (Miao *et al.*, 1999) has enabled structural determination of objects with low X-ray scattering/imaging contrast, as well as high-resolution imaging of noncrystalline nanoscale structures. Meanwhile, the development of temporal probes such as X-ray photon correlation spectroscopy (XPCS) has enabled the direct measurement of longtime-scale equilibrium and non-equilibrium dynamics in disordered systems.

In many aspects, XPCS can be regarded as an extension into the X-ray regime of long-wavelength laser photon correlation spectroscopy (also known as dynamic light scattering, DLS), which probes the dynamics of a material by employing the spatial and temporal coherence of laser light and analyzing the temporal correlations of photons scattered by the material (Prasad *et al.*, 2007). Many similarities are shared between these two techniques. For example, both techniques exploit the coherence of the radiation by restricting the dimensions of the scattering sample volume to within the coherence volume of the beam. Either the beam may be intrinsically coherent

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This paper describes the development of ultra-small-angle X-ray scattering– X-ray photon correlation spectroscopy (USAXS–XPCS). This technique takes advantage of Bonse–Hart crystal optics and is capable of probing the long-timescale equilibrium and non-equilibrium dynamics of optically opaque materials with prominent features in a scattering vector range between those of dynamic light scattering and conventional XPCS. Instrumental parameters for optimal coherent-scattering operation are described. Two examples are offered to illustrate the applicability and capability of USAXS–XPCS. The first example concerns the equilibrium dynamics of colloidal dispersions of polystyrene microspheres in glycerol at 10, 15 and 20% volume concentrations. The temporal intensity autocorrelation analysis shows that the relaxation time of the microspheres decays monotonically as the scattering vector increases. The second example concerns the non-equilibrium dynamics of a polymer nanocomposite, for which it is demonstrated that USAXS–XPCS can reveal incipient dynamical changes not observable by other techniques.

> (laser or X-ray free-electron laser) or it can be spatially filtered using an aperture smaller than the coherence area of the beam (partially coherent X-ray beam from a thirdgeneration X-ray source). For a disordered system, the summation of complex amplitudes from the coherent scattering gives rise to a 'speckle' pattern, which contains information on the specific spatial configurations of scatterers within the scattering volume. It has been shown that, when the spatial sampling frequency exceeds twice the Nyquist frequency (Miao et al., 1998), the two-dimensional projection of the scattering object can be reliably reconstructed based on a static speckle pattern. The time-varying configuration of scatterers is also reflected in the coherent scattering pattern, as illustrated by the intensity fluctuation of a speckle at a given scattering vector. This fluctuation forms the basis of both XPCS and DLS.

> There also exist major differences between XPCS and DLS, mostly due to the difference in radiation wavelength. Visiblelight DLS has proved to be a powerful technique for studying the long-wavelength dynamics of simple fluids, liquid crystals and colloids, yet DLS suffers from two limitations. The wavelength of visible light ranges from 400 to 700 nm, which restricts the scattering to a small scattering vector,  $\mathbf{q}$  $[q = (4\pi/\lambda) \sin \theta, q$  is the magnitude of the scattering vector,  $\lambda$ is the wavelength and  $\theta$  is one-half of the scattering angle  $2\theta$ ]. More significantly, it is difficult, if not impossible, for visiblelight DLS to probe the dynamics of optically opaque or highly absorbing media because of strong absorption and/or multiple

scattering effects. Meanwhile, XPCS, being an X-ray technique, is not hindered by these limitations and offers an unprecedented capability to measure low-frequency  $(10^{-3}-10^{6} \text{ Hz})$  dynamics of structures in the range 1–1000 Å. Here we note that a novel technique based on *near-field* coherent X-ray scattering is also capable of revealing structural and dynamical information of materials (Cerbino *et al.*, 2008), albeit in a *q* range largely considered to be part of the range of DLS  $(10^{-5}-10^{-4} \text{ Å}^{-1})$ .

XPCS, which was introduced less than two decades ago (Brauer et al., 1995; Dierker et al., 1995; Sutton et al., 1991), has greatly impacted on many aspects of statistical physics and provided access to a wide range of physical events with slow dynamics. Depending on the scattering geometry, XPCS can be divided into two categories. In transmission mode, XPCS has been successfully employed to study equilibrium dynamics of colloidal dispersions (Dierker et al., 1995; ThurnAlbrecht et al., 1996; Lurio et al., 2000; Banchio et al., 2006; Gapinski et al., 2009), nanoparticles in a polymer melt (Guo et al., 2009) and a supercooled glass-forming liquid (Caronna et al., 2008), block copolymer micelles (Mochrie et al., 1997), and vesicles (Falus et al., 2005); critical fluctuations of liquid crystals (Poniewierski et al., 1998; Madsen et al., 2003); non-equilibrium slowvarying dynamics such as coarsening fluctuation in alloys (Livet et al., 2001) and weakly disturbed soft condensed matter systems (Chung et al., 2006; Bandyopadhyay et al., 2004; Robert et al., 2006; Lu et al., 2008); and most recently, atomic diffusion in intermetallic alloys (Leitner et al., 2009). An alternative XPCS approach is to use a reflection geometry with the grazing incidence angle of the incoming X-ray beam well below the critical angle for total external reflection. Under such a grazing incidence condition, the X-ray penetration is limited to a thin layer ( $\sim 10$  nm) below the surface. Thus, the resultant scattering is surface sensitive and free from bulk contamination. This technique has been successfully employed to study the surface dynamics of various systems, including capillary waves on the surface of viscoelastic films (Seydel et al., 2001; Madsen et al., 2004; Jiang et al., 2007; Mukhopadhyay et al., 2008), nanoparticles moving on the surface of thin polymer films (Narayanan et al., 2007; Streit et al., 2007; Duri et al., 2009) and plane-displacement fluctuations in smectic liquid-crystal membranes (Sikharulidze et al., 2002, 2003).

While XPCS has enjoyed great success, it is important to recognize that a gap exists between its currently accessible q range and that of DLS, especially for optically nontransparent samples. This gap lies between  $10^{-4}$  and  $10^{-3} \text{ Å}^{-1}$ . The dynamics of a wide variety of microstructures in the size range from 100 nm to several micrometres (Zhang & Ilavsky, 2010), including various polymer gels and solutions, nanocomposites, and other colloidal suspensions and gels, are best studied in this q range since this is the regime where  $qD \simeq 1$ , where D is a representative microstructure dimension. A new technique, therefore, is needed to bridge the gap between DLS and XPCS – a gap that largely corresponds to that between light scattering and small-angle X-ray scattering (SAXS) (Allen *et al.*, 1994).

In this paper, we introduce ultra-small-angle X-ray scattering-X-ray photon correlation spectroscopy (USAXS-XPCS), which aims to bridge this gap. USAXS-XPCS has been developed from the technique of ultra-small-angle X-ray scattering (USAXS) (Ilavsky et al., 2009), which utilizes multiple reflections from single-crystal optics to approach qvalues that are normally inaccessible in small-angle X-ray scattering experiments. The single-crystal optics, when used in a nondispersive configuration, maintain the coherence property of the X-ray beam and therefore preserve the intensity fluctuations that are associated with the sample dynamics in XPCS experiments. In §2, we introduce the instrumental configuration of USAXS-XPCS, especially that relevant to coherent scattering. Experimental details and sample preparation are discussed in §3. In §§4 and 5, we present results for our two sample systems in order to demonstrate the performance and capability of USAXS-XPCS. Finally, concluding remarks are offered in §6.

## 2. Experimental configuration

The experiments described here were carried out at beamline XOR-32-ID of the Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL, USA, where the APS USAXS instrument is located. Details of the USAXS instrument setup are presented elsewhere (Ilavsky *et al.*, 2009). In this section, we focus on elements of the beamline that are relevant to coherent scattering as used in the case of USAXS–XPCS.

A schematic of the beamline is shown in Fig. 1. The undulator source is a 2.4 m-long APS undulator A insertion device with 72 magnetic poles (Lai *et al.*, 1993). The X-ray energy can be continuously tuned by adjusting the gap of the magnetic poles, and the accessible energy range extends from 3.2 keV to more than 80 keV. For an undulator, the spatially coherent X-ray flux is directly proportional to the X-ray brilliance, which makes an undulator beamline more desirable for coherent X-ray scattering than a bending-magnet beamline. Furthermore, an undulator produces an X-ray beam with a much smaller source size. The spatial coherence length of a beam with a Gaussian intensity profile is related to the source size according to

$$\xi_{x,y} = \frac{\lambda R}{2\pi\sigma_{x,y}},\tag{1}$$

where  $\xi_x$  and  $\xi_y$  are the transverse coherence lengths in the **x** and **y** directions;  $\lambda$  is the X-ray wavelength, *R* is the distance between the effective X-ray source and the coherencedefining aperture (secondary source), and  $\sigma_x$  and  $\sigma_y$  are the electron source size in the **x** (horizontal) and **y** (vertical) directions (Paterson *et al.*, 2001). Here, the source size is determined primarily by the APS storage ring emittances,  $\varepsilon_x$  and  $\varepsilon_y$ , respectively, and the  $\beta$  functions  $\beta_x^U$  and  $\beta_y^U$ , which are properties of the undulator (Borland *et al.*, 2010). The source sizes are given approximately by  $\sigma_x = (\varepsilon_x \beta_x^U)^{1/2}$  and  $\sigma_y = (\varepsilon_y \beta_y^U)^{1/2}$ . Here small effects such as dispersion in the synchrotron ring straight section and small variations in  $\beta^U$  are neglected. For most current operating modes of the synchrotron (including the continuous top-up mode),  $\varepsilon_x = 3.1$  nm rad and  $\varepsilon_y = C\varepsilon_x = 3.1 \times 10^{-2}$  nm rad, where C = 0.01 is the coupling constant. For an undulator A device,  $\beta_x^U = 14.2$  m and  $\beta_y^U = 10.0$  m (Borland *et al.*, 2010). Therefore, typical source sizes are given by  $\sigma_x = 210$  µm and  $\sigma_y = 21$  µm. For 10 keV X-rays, and with the USAXS instrument located 37 m downstream from the undulator (R = 37 m), equation (1) gives  $\xi_x =$ 3.5 µm and  $\xi_y = 34.5$  µm. We note that a special operating mode (reduced beam size mode) is available for 32-ID at the APS, where the nominal horizontal beam size is reduced to 120 µm with the coupling constant *C* unchanged at 0.01. Under this operating mode, the horizontal and vertical coherence lengths for 10 keV X-rays are given by  $\xi_x = 6.1$  µm and  $\xi_y =$ 60.9 µm, respectively.

Upstream from the USAXS instrument, the undulator X-ray beam passes through a fixed-offset Si(111) monochromator, which is capable of tuning the X-ray energy to any value between 8 and 35 keV. The monochromator also serves to define the longitudinal coherence length of the X-ray beam following (Goodman, 1985)

$$\xi_1 = \frac{\lambda^2}{2\Delta\lambda},\tag{2}$$

where  $\Delta\lambda$  is the full width at half-maximum of the wavelength spread function for X-rays passing through the monochromator. For Si(111) crystal optics, a typical longitudinal coherence length  $\xi_1$  for 10 keV X-rays is ~1.3 µm. In order to satisfy the conditions for coherent scattering, the maximum optical path-length difference cannot be greater than  $\xi_1$ . For a sample with thickness  $t_s$ , at a scattering angle  $2\theta$ , and transverse beam size d, the maximum path-length difference  $\Delta L$ can be approximated by  $\Delta L = 2t_s \sin^2(\theta) + d \sin(2\theta)$  when  $\theta$  is small (Grubel & Zontone, 2004). On setting  $\Delta L = \xi_1$ , we have

$$t_{\rm s} \simeq \frac{\xi_{\rm l} - d\sin(2\theta)}{2\sin^2(\theta)}.$$
 (3)

For  $q = 1 \times 10^{-2} \text{ Å}^{-1}$ , with  $\xi_1 \simeq 1.3 \,\mu\text{m}$  and  $d = 15 \,\mu\text{m}$ , we find that  $t_s \simeq 65 \,\text{cm}$ , which is significantly larger than any sample thickness encountered in USAXS–XPCS measurements. In real experiments, we do not expect this simple calculation based solely on the path-length difference to hold because other effects, such as X-ray absorption, multiple scattering and X-ray energy dispersion, will also play a role. Nonetheless, we

believe that the longitudinal coherence condition is always satisfied in our measurements, in which the maximum sample thickness is  $\sim 1$  mm. In principle (*e.g.* when beam damage is minimal), it is possible to use a 'pink' beam (with a spread of X-ray energies) instead of a monochromatic beam in XPCS measurements because of its larger incident flux (Abernathy *et al.*, 1998; Sandy *et al.*, 1999). This is not applicable in the case of USAXS–XPCS because the technique relies on crystal optics to obtain the small *q* values not accessible in 'conventional' XPCS.

A pair of flat vertically reflecting mirrors is used to reject X-ray photons with higher-order harmonic energies. The beam size is controlled by two-dimensional beam-defining high-resolution (10 nm resolution in slit positioning) slits. In USAXS–XPCS measurements, these slits also serve as the coherence-defining aperture, and here they were set to a slit opening of  $15 \times 15 \mu$ m. This slit size was optimized to give the best visibility for a static speckle while maintaining a high level of incident flux because the coherent scattering intensity lies on top of a background composed of incoherent scattering from the sample and from air. The speckle contrast needs to be optimized to prevent the coherent scattering intensity from being buried in this background.

The USAXS instrument in its two-dimensional collimated USAXS mode (Ilavsky et al., 2009) is placed after the beamdefining slits. All of the crystal pairs in this setup are in a nondispersive configuration, which is known to best preserve the coherence of monochromatic X-rays (Petrascheck, 1988). The horizontal and vertical collimating crystals not only collimate the incident X-ray beam, but also serve as crystal guard apertures to remove the unwanted parasitic scattering from the coherence/beam-defining aperture, thus eliminating the need for guard slits commonly present in XPCS measurements (Abernathy et al., 1998; Sandy et al., 1999). These Si(220) collimating crystals, whose Darwin curve has a full width at half-maximum of 15.36 µrad at 10 keV, provide the best energy resolution of the crystal optics and further improve the already very good longitudinal coherence of the beam. A similar one-dimensional application of a crystal guard aperture can be found in coherent diffraction imaging (Xiao et al., 2006).

A windowless ionization chamber is placed after the collimating crystals to monitor the incident X-ray beam intensity on the sample. The coherent scattering intensity from the



#### Figure 1

Schematic of the USAXS–XPCS instrument. The undulator beam enters from the right, and passes through a high-heat-load monochromator and harmonic rejection mirrors before reaching the two-dimensional coherence-defining slits. The X-ray beam divergence is collimated in both transverse directions in this two-dimensional collimated configuration. After passing through the sample, the coherently scattered X-ray is analyzed by the analyzing crystals in both transverse directions before reaching the detector.

sample is selected point-wise by the analyzing crystal pair, which offers an angular resolution of  $1 \times 10^{-4} \text{ Å}^{-1}$  in both transverse directions. The scattering intensity is collected with either a photodiode detector, having a linear response of more than ten decades of intensity (Jemian & Long, 1990; Ilavsky et al., 2009), or a low-noise scintillation detector. The time resolutions of these two detectors differ: the photodiode detector has a time resolution of 0.1 s and the scintillation detector  $1 \times 10^{-3}$  s. The photodiode detector, despite its poorer time resolution and higher noise, is easier to set up with USAXS than the scintillation detector. Additionally, we show in Appendix A that the random readout noise from the detector alone does not affect the measured dynamics as determined by the time-dependent intensity autocorrelation function. Therefore, unless better time resolution is required, we have performed USAXS-XPCS measurements with the photodiode detector.

We established two data-collection modes for USAXS-XPCS measurements. In the first mode, the instrument is set to a given fixed q, and the coherent scattering intensity is monitored as a function of time. This mode, similar to the standard XPCS operation, is suitable for relatively fast dynamics that require better time resolution. In the second mode, q is scanned in the vertical  $(\mathbf{y})$  direction within a suitable q range while maintaining  $q_x = 0$ . This mode is best suited to systems with slowly evolving non-equilibrium dynamics where more information about the transformation of the speckle patterns is desired. Although the same instrument setup is used, data collected using the scan mode require a different analysis method because of the non-equilibrium nature of the dynamics. This analysis, described in detail in §5, does not involve the calculation of the intensity autocorrelation function, and marks the most significant difference from the standard and well established XPCS analysis procedure. Currently, with a 50-point 1 s (data-collection time) per point scan, the time resolution of the scan mode is approximately 100 s. This data-collection mode benefits from the recent addition of a robust and highly reproducible rotational stage that controls the rotational motion of the analyzer crystals. The variation of the analyzer angular position of the beam



#### Figure 2

Consecutive USAXS-XPCS curves show identical speckle patterns when the sample is in a static condition.

center for multiple (5+) consecutive scans is negligible (0.0072 arcseconds). This feature eliminates the need of retuning the optics between scans and therefore greatly improves the time resolution of the scan mode. We note that, in a static condition, consecutive scans acquire identical speckle patterns, as illustrated in Fig. 2, which shows two scans taken  $\sim 10$  min apart on a polymer composite sample. This figure confirms that, without external perturbation to the sample, the USAXS–XPCS pattern reflects the static microstructure and its signal level is significantly above any noise that either the storage ring or the instrument introduces. Therefore, any observed change in the speckle pattern is attributed to the sample dynamics, which consequently offers the feasibility of monitoring equilibrium or non-equilibrium dynamics of the sample with USAXS–XPCS.

#### 3. Experimental methods

#### 3.1. Material systems

Two material systems were studied in our measurements to explore the applicability and demonstrate the capability of USAXS–XPCS. The first sample system was prepared from an aqueous colloidal suspension of polystyrene (PS) microspheres with 10% solid mass fraction (Thermo Scientific Inc.,<sup>1</sup> Fremont, CA, USA). The mean manufacturer-specified diameter of these microspheres was 1  $\mu$ m, with a stated size uniformity smaller than 3%. Suspensions with a narrow size distribution simplify interpretation of the measured dynamics from a distribution of particle diameters. The refractive index of the PS microspheres was 1.59 at a radiation wavelength of 589 nm. As a result, the as-acquired suspension appeared milky, which makes it a non-ideal sample for dynamical light scattering. The density of the PS microspheres was 1.05 g cm<sup>-3</sup>.

The aqueous PS suspension was mixed with a pre-determined amount of reagent-grade glycerol to prepare a PS suspension. The main motivation for this transfer was that the viscosity of glycerol (1.5 Pa s at 298 K) is about three orders of magnitude greater than that of water  $(8.9 \times 10^{-4} \text{ Pa s} \text{ at} 298 \text{ K})$ . Thus, on transfer to glycerol, the dynamics of the suspension are slowed significantly, enabling dynamic measurements with point detectors. Additionally, the difference in scattering length density between glycerol and PS  $(2.04 \times 10^{10} \text{ cm}^{-2})$  is significantly greater than that between water and PS  $(0.16 \times 10^{10} \text{ cm}^{-2})$ , which results in a 160-fold increase in the scattering intensity.

The mixtures were placed in an evacuated desiccation chamber for >600 h. Four samples with different volume concentrations of PS microspheres (1, 10, 15 and 20%) were prepared. The desiccation process did not completely remove the water from these mixtures. The final physical states of the

<sup>&</sup>lt;sup>1</sup> Certain trade names and company products are mentioned in the text or identified in illustrations in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

samples are listed in Table 1. A 15 s sonication was performed on the samples occasionally to avoid particle aggregation. The PS suspension remained well dispersed throughout the sample preparation process, and the final suspensions remained milky under visible light.

Polymer composites of amorphous calcium phosphate (ACP) and amorphous silicon dioxide filled bisphenol A diglycidyl methacrylate (Bis-GMA) constitute the other material system that was investigated with USAXS–XPCS. Details of the sample synthesis procedure can be found in earlier articles on these materials (Skrtic & Antonucci, 2003; Skrtic *et al.*, 2004). The composites were molded to form disc-shaped specimens by filling circular openings of flat Teflon molds. The filled molds were covered with mylar films and glass slides, and then clamped tightly with spring clips. The composite discs were cured by means of a 120 s photo-polymerization procedure (Skrtic & Antonucci, 2003).

### 3.2. Ultra-small-angle X-ray scattering measurements

USAXS measurements were made with beam-defining slits at  $0.5 \times 0.5$  mm. The X-ray energy was 10.5 keV ( $\lambda = 1.18 \text{ Å}$ ). USAXS measurements were performed in the q range from  $10^{-4}$  to  $10^{-1} \text{ Å}^{-1}$ . Data were collected at 150 points logarithmically distributed throughout the q range and the datacollection time for each data point was 1 s. Radiation damage was minimal, as shown by the well defined oscillations in the high-q region characteristic of scattering from monodisperse spheres.

The samples were loaded into a custom-made sample cell with polyamide entrance and exit windows and a 1 mm X-ray scattering path. The temperature of the sample cell was controlled with a Linkam TH600 thermal stage (Linkam Scientific Instruments Ltd, Tadworth, UK) assisted with liquid nitrogen circulation for rapid heating and cooling. The heating/cooling rate was set at 50 K min<sup>-1</sup>. We estimate that the temperature deviation from the thermocouple readout was less than 1 K, and the temperature gradient in the sample was negligible.

## 3.3. USAXS-XPCS measurements

USAXS–XPCS measurements were made with the beamdefining slits set at  $15 \times 15 \,\mu\text{m}$  and an X-ray energy of 10.5 keV. The APS storage ring was used in both a conventional operating mode and the special reduced horizontal beam size operation mode that provides greater coherence. We found that the operating modes of the storage ring affect the quality of the beam coherence but not the observed sample dynamics.

For the two material systems discussed in this article, different data-collection modes were chosen to address the different natures of their dynamics. For the stable colloidal suspensions, equilibrium dynamics applies and the dynamical behavior is independent of the starting time. A point-detection data-collection mode was used for these dispersions to give the best possible time resolution. The suspension was cooled to 278 K to slow the dynamics and the intensity fluc-

## Table 1

Physical parameters	of PS/glycerol	suspensions.
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PS % volume fraction in suspension	Glycerol % mass fraction in solvent	Solvent scat- tering length density $(10^{14} \text{ m}^{-2})$	PS scattering length density (10 <sup>14</sup> m <sup>-2</sup> )	Scattering contrast (10 <sup>28</sup> m <sup>-4</sup> )
1	0.988	11.587	9.581	4.024
10	0.974	11.563	9.581	3.929
15	0.967	11.547	9.581	3.863
20	0.958	11.529	9.581	3.793

tuations were recorded at q values of 0.00015, 0.0003, 0.0004, 0.0005, 0.0006 and 0.0007 Å<sup>-1</sup>. At each q, 1200 intensity data points were measured, giving a total data-collection time of ~1400 s (1 s data-collection time for each data point with ~0.2 s readout delay).

The dynamics of the polymer composites upon temperature change, on the other hand, are inherently non-equilibrium in nature. Owing to its ability to capture dynamics through a q range, the use of USAXS–XPCS in the scan mode was clearly advantageous compared with the point-detection mode. The measurements followed the procedure described below, which offered the best time resolution while maintaining the optimal alignment of the instrument.

In each case, once the sample temperature had reached the set point (378, 388 or 398 K), a full 100-point USAXS–XPCS scan was started, which covered a q range from  $-1.3 \times 10^{-4}$  to  $1 \times 10^{-3}$  Å<sup>-1</sup>. The data-acquisition time for each data point was 1 s. We denote this as a 'long' scan, which took ~5 min to complete. Because long scans included the rocking curve section of the scattering profile, they provided an accurate definition of the forward scattering (q = 0) direction, from which the q values of all the subsequent data points were deduced. Additionally, the long scans were used to determine the amount of sample attenuation of the X-ray beam, which served as a sensitive measure of any rare, abrupt, change in the beamline configuration.

Five 'short' scans whose scanning q range was from  $1 \times 10^{-4}$  to  $1 \times 10^{-3}$  Å<sup>-1</sup> were taken after each long scan. Each short scan contained 50 data points and took ~2 min to complete (including the time for the USAXS stages to return to their starting positions). After one long scan and five short scans, the optics were retuned to verify that the instrument was still in optimal alignment before starting another set of long and short scans. The total measurement time was based on the amount of time required for the material system to reach equilibrium, *i.e.* until the scanning profiles (speckle patterns) no longer changed significantly, scan to scan. Depending on the temperature, the total measurement time was as long as 6 h before an equilibrium state was achieved.

# 4. Results and discussion of XPCS studies of colloidal suspensions

### 4.1. USAXS results

The two-dimensional collimated USAXS data reduction and analysis were performed using the standard SAXS data analysis package *Irena* (Ilavsky & Jemian, 2009) developed at the Argonne National Laboratory. USAXS profiles from three samples were measured. The volume concentrations of PS microspheres were 10, 15 and 20%, respectively. For the purpose of exhibiting the applicability of USAXS–XPCS, we show the results from 10% PS microspheres in glycerol only.

The calibrated scattering intensity, I(q) or  $d\Sigma/d\Omega$ , data obtained from 10, 15 and 20% volume PS microsphere suspensions are shown in Fig. 3. The intensity oscillations in the high-q region indicate that the sizes of the PS microspheres are very narrowly distributed. To extract the exact size distribution of the PS microspheres, we analyzed the scattering profile assuming the scattering form factor for spheres, and a consequent scattering intensity, I(q), from a monodispersed population with sample volume fraction,  $\varphi$ , given by

$$I(q) = \varphi(\Delta\rho)^2 V \left[ 3 \frac{\sin(qr) - qr\cos(qr)}{(qr)^3} \right]^2, \tag{4}$$

where V and r are the volume and radius of the sphere, respectively, and  $\Delta \rho$  is the difference between the scattering length densities of the solute and solvent. To avoid complications introduced by the unknown form of the scattering structure factor, the high-q region of the scattering profile was modeled using a least-squares analysis method based on integrating equation (4) over a Gaussian volume fraction size distribution. In this region the particle interference can be regarded as negligible. The result from the sample containing 10% volume PS microspheres in glycerol is shown in Fig. 4. The size distribution can be approximated with a Gaussian function with mean diameter 10 168 Å and Gaussian width 264 Å. Both of these parameters are close to the manufacturer-specified values, and they confirm that the PS microspheres have a very narrow size distribution. In addition, no upturn was observed at the very low q range of the USAXS



Figure 3

Absolute-calibrated USAXS profile of 10, 15 and 20% volume PS microsphere suspensions in glycerol. The standard deviation uncertainties are smaller than the symbols for the points.

profile, which indicates that the PS microspheres do not aggregate.

The scattering structure factor was found by dividing the USAXS data by the particle scattering form factor, which was obtained by convolving the single-particle scattering form factor with the particle size distribution. The scattering structure factor is shown in Fig. 5(a). We observed that the magnitude of the pronounced peak in the scattering structure factor increases as the volume fraction of PS microspheres increases. This corresponds to the increased interparticle interaction between the microspheres. The structure factor can be approximately described with the Percus-Yevick pairdistribution function (Kotlarchyk & Chen, 1983), which applies to monodisperse particles with a hard-sphere interaction potential. The theoretical Percus-Yevick structure factor functions corresponding to our samples are plotted in Fig. 5(b). We attribute the difference between Figs. 5(a) and 5(b) to the polydispersity of the PS spheres and the charged sulfate groups that are on the surface of the PS spheres; these factors violate some of the underlying assumptions of the Percus-Yevick derivation. Our result is in good agreement with a previous SAXS study of PS suspensions in glycerol, albeit the nominal size of PS microspheres was much smaller (66 nm; Lurio et al., 2000). The fact that the hard-sphere potential fits the scattering structure factor confirms that no significant aggregation of PS microspheres exists in the suspension. Moreover, even at the highest PS concentration of all three samples, no diffraction peak was observed in the structure factor, indicating that the PS microspheres are still in a fluid state.

#### 4.2. USAXS-XPCS results

XPCS probes the dynamic properties of matter by measuring the temporal correlation of the scattering intensity. The intensity–intensity time correlation function is defined by Grubel & Zontone (2004) as



#### Figure 4

Fitted size distribution for the PS microspheres. This size distribution can be approximated as Gaussian, with mean diameter at  $10\,168$  Å and Gaussian width at 264 Å.



#### Figure 5

(a) Experimental structure factor for 10, 15 and 20% volume PS microspheres in glycerol. The corresponding number densities for the polystyrene spheres in all three dispersions are  $1.91 \times 10^{17}$ ,  $2.87 \times 10^{17}$  and  $3.82 \times 10^{17}$  m<sup>-3</sup>, respectively. (b) Theoretical Percus–Yevick structure factor for 1 µm-diameter monodisperse hard spheres at 10, 15 and 20% volume fraction.

$$g_2(t) = \frac{\left\langle I(t+t')I(t')\right\rangle_{\rm E}}{\left\langle I(t')\right\rangle_{\rm E}^2},\tag{5}$$

where I(t) is the integrated scattering intensity in an interval  $\Delta t$  around a time t, and the angular brackets in equation (5) denote an ensemble average. This autocorrelation function can be related to the intermediate scattering function of the sample, following

$$g_2(t) = 1 + \beta |f(q, t)|^2,$$
 (6)

where f(q, t) = S(q, t)/S(q) is the normalized intermediate scattering function with S(q) and S(q, t) the initial structure factor and that after time, t, respectively;  $\beta$  is the optical contrast, which under ideal experimental conditions (*e.g.* fully coherent radiation and no readout noise) would be equal to unity. In XPCS experiments,  $\beta$  takes a lower value as a result of the incoherent averaging introduced by the partially coherent X-ray beam, the geometrical configuration of the beamline and readout noise. In Appendix A, we discuss in detail the impact of random readout noise of the detector and show that this noise does not change the form of the intermediate scattering function, although it does decrease the optical contrast obtained from the temporal intensity autocorrelation function.

The intensity I(t) in equation (5) is the detected intensity normalized by the ion-chamber readout, which is proportional to the incident flux of partially coherent X-rays on the sample. The ion-chamber readout, as a parameter, accounts for all of the front-beam optics, as well as fluctuations in the undulator beam, provided that the coherent X-ray fraction of the incident beam remains constant for a given experiment. The goal of XPCS measurements is to measure the dynamics in the sample. Therefore, it is necessary to examine the dynamics of the X-ray beam to ascertain that the origin of the observed dynamics is within the sample itself. The ion-chamber readout provides a measure for this purpose. The beam dynamics were studied using the 10% volume PS suspension in glycerol at 278 K. The XPCS data were taken at  $q = 0.0005 \text{ Å}^{-1}$  and the normalized intensity is shown in Fig. 6(*a*). Dynamical intensity fluctuations are clearly visible in these data. The temporal behavior of these fluctuations is approximately constant, which is characteristic of equilibrium dynamics. Fig. 6(*b*) shows the intensity autocorrelation functions of the normalized and unnormalized intensities, whose maximum value is around 1.04. These two autocorrelation functions overlap through the entire range of time delays, which suggests that the impact of normalization is minimal. Furthermore, the intensity autocorrelation function of the ion-chamber readout is shown in Fig. 6(*c*). We note that this autocorrelation function displays a slight departure from



#### Figure 6

(a) Normalized scattering intensity as a function of time for 10% volume PS microspheres in glycerol at  $q = 0.0005 \text{ Å}^{-1}$ . (b) Intensity autocorrelation functions for the un-normalized intensity (circle symbols) and normalized intensity (line). (c) Intensity autocorrelation function of the ion-chamber readout. For the data shown in this figure, the temperature of the sample was 278 K.

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Figure 7

Normalized intensity autocorrelation functions (symbols) measured at q = 0.00015, 0.0003, 0.0004, 0.0005, 0.0006 and 0.0007 Å<sup>-1</sup> for 10% volume PS microspheres in glycerol. The temperature of the colloidal dispersion was 278 K.

unity. The autocorrelation function also decays as a function of time delay, and indicates that instrument dynamics on the scale of a few hundred seconds do exist. However, the deviation of the magnitude of the instrument dynamics from unity is consistently two orders of magnitude smaller than that of the autocorrelation function of the scattering intensity from the sample. This leads us to conclude that the effect of instrument dynamics is negligible in USAXS–XPCS experiments.

Similarly, we examined the time autocorrelation function of the dark current of the photodiode detector, which also shows a very small deviation from unity and confirms that the dark current does not interfere with the results from sample dynamics.

Representative intensity autocorrelation functions of the sample comprising 10% volume PS microspheres in glycerol after normalization by optical contrast are shown in Fig. 7 for time delays from 1 to 100 s and at q = 0.00015, 0.0003, 0.0004, 0.0005, 0.0006 and 0.0007 Å<sup>-1</sup>. It is apparent that, with increasing q value, the dynamics become faster. For a colloidal dispersion with hard-sphere interactions, it is expected that short-range fluctuations (high q, small length scale) occur more rapidly than long-range fluctuations (low q, large length scale). The small fluctuations in the normalized autocorrelation functions at long time delay in our data are similar to the effects caused by the partial coherence and detector resolution as shown by Gutt *et al.* (2008).

We further analyzed the intensity autocorrelation functions with a stretched exponential decay model to extract the relaxation time constant of the particle diffusion and hyperdiffusion process. A stretched exponential model has been successfully employed in many dynamical studies of colloidal dispersions and gels (Pontoni *et al.*, 2003; Duri *et al.*, 2009; Bandyopadhyay *et al.*, 2004; Bellour *et al.*, 2003; Cipelletti & Ramos, 2005; Fluerasu *et al.*, 2007). The stretched exponential function [also known as the Kohlrausch–Williams–Watts (KWW) function (Caronna *et al.*, 2008)] is defined as

$$g_2(t) = \beta \exp[-2(t/\tau)^{\gamma}] + 1.$$
 (7)

Here,  $\tau$  is the characteristic relaxation time, and  $\gamma$  is an exponent (the Kohlrausch exponent) which, when greater than 1, indicates a decay that is compressed and faster than that expected from particles under Brownian motion ( $\gamma = 1$ ).

The characteristic relaxation time from all three samples as a function of q is plotted in Fig. 8(a). For each sample, a

monotonic decrease of the relaxation time was observed as q increases, which reflects the slower dynamics associated with larger dimensions. This behavior is consistent with the results found in a study of the dynamics of silica nanoparticles in 1,2propanediol in a temperature range from 205 to 240 K, where a monotonic decrease was also observed (Caronna et al., 2008). Slower dynamics also occur at higher concentrations of PS microspheres, which suggests that particle motion is suppressed with increasing interparticle interaction, as shown in Fig. 5.

A simple scaling of the relaxation data in Fig. 8(a) causes all three curves to collapse onto a single curve (see inset plot in Fig. 8a), thus



#### Figure 8

(a) Relaxation time,  $\tau$ , obtained from fits of equation (7) to the USAXS-XPCS data from 10% volume (circles), 15% volume (triangles) and 20% volume (squares) PS microspheres in glycerol suspensions as a function of q. Scaling each curve by a constant factor causes them to collapse onto a single curve (inset plot). Averaging these scaled plots gives the filled circles in (b). The corresponding curve is a  $q^{-2}$  fit to all but the lowest-q data point and the dashed vertical line is the inverse of the radius of gyration of the PS particles. The uncertainty bars indicate one standard deviation.

demonstrating that the functional dependencies of  $\tau$  on q and the particle volume concentration,  $V_{\rm f}$ , are approximately separable within this concentration range. Thus, we can write

$$\tau(q, V_{\rm f}) = F(q) G(V_{\rm f}). \tag{8}$$

At higher concentrations, the simple behavior described by equation (8) is expected to fail as interparticle interactions impact significantly on the q behavior. This separability puts a strong constraint on our understanding of the underlying physics. Since the q dependence is largely independent of  $V_f$ , F(q) describes the single-particle behavior of this dynamic system. Averaging all three scaled curves in the inset figure gives the data plotted in Fig. 8(b). Across the measured q range these data exhibit an approximate  $q^{-2}$  behavior (albeit with the addition of a constant), which is not inconsistent with Brownian-type motion in a dilute system. The lowest-q data point occurs below the inverse of the radius of gyration of the PS spheres,  $1/R_g$ , which roughly separates the Porod (high-q) and Guinier (low-q) scattering regimes. Clearly, the  $q^{-2}$ behavior breaks down in this regime.

The dependence of relaxation time on concentration described by  $G(V_f)$  is qualitatively predicted by a many-body theory of mobile spheres in suspension, where it is shown that the many-body hydrodynamic interaction (HI) in mobile spheres leads to an increase in the effective viscosity of the suspension and thus slows down the particle dynamics (Beenakker & Mazur, 1984). The concentration scaling in our data appears to be exponential, but since only three concentrations were examined, this result must be considered preliminary.

The exponent  $\gamma$  is greater than 1 in every case. This indicates that the motion of the PS microspheres is at least partially collective in nature, and thus deviates from the simple diffusion process expected in a dilute colloidal dispersion. Also, the optical contrast parameter,  $\beta$ , shows a monotonic decline from q = 0.0003 to  $0.0007 \text{ Å}^{-1}$  (data not shown). This behavior is caused by the decreasing magnitude of the scattering intensity with increasing q, which decreases the signal-to-noise level. According to the discussion in Appendix A, a higher noise level acts to reduce the optical contrast. On the other hand,  $\beta$  increases from q = 0.00015 to  $0.0003 \text{ Å}^{-1}$ . This occurs because the presence of unscattered (partially coherent) X-rays in the  $q = 0.00015 \text{ Å}^{-1}$  data complicates the detection of intensity by adding a background, which in turn leads to a lower optical contrast.

# 5. Results and discussion of USAX-XPCS studies of dental composites

Notwithstanding the successes that XPCS has achieved in the study of low-frequency dynamics, the application of conventional XPCS is mostly focused on studies of equilibrium dynamics or near-equilibrium dynamics of soft materials. Non-equilibrium dynamics of hard materials, an area that is equally important, remains largely unexplored. In this section, we introduce briefly the capability of USAXS–XPCS in the study of non-equilibrium dynamics of polymer composites. Detailed

discussion will be presented in a subsequent paper that focuses on this application.

ACP particle reinforced Bis-GMA polymer composites are synthesized as advanced dental materials, which are capable of releasing supersaturating levels of bioactive mineral ions to promote remineralization of early enamel lesions. These materials undergo irreversible amorphous-to-crystalline phase transformation of the ACP upon heating. Because of an associated increase in the particle density, this transformation results in changes in the local arrangements of the reinforcement particles due to creep in the surrounding polymer matrix. Polymer matrix creep also arises from the thermal mismatch between the particles and the matrix on heating or cooling. The subtle changes in local particle arrangements are not detectable by bulk sampling techniques such as SAXS or USAXS, X-ray diffraction (XRD) or Fourier transform infrared spectroscopy (FTIR). For example, USAXS measurements of silanized ACP/Bis-GMA composite, shown in Fig. 9, do not show any effect.

Fig. 9 shows USAXS data from the same sample volume before heating, after heating and after cooling (the heating/ cooling procedure is detailed in §3). It is notable that all three data curves overlap, which would normally suggest that no microstructural change has occurred during the thermal annealing and that the sample structure is thermally stable. However, in USAXS-XPCS measurements, the coherent X-ray scattering component is extremely sensitive to the precise spatial arrangement of the particles within the small sample volume probed; this provides the required measurement sensitivity to detect incipient local structural changes. Fig. 10 shows the reduced USAXS–XPCS data, using a 15  $\times$ 15 µm partially coherent beam, collected at 0, 18, 36, 54 and 73 min after the start of the heating process to 388 K. Here, coherent speckles are identified in every data curve, and the five data sets no longer overlap. This result shows directly that



#### Figure 9

A comparison of USAXS data for silanized ACP/Bis-GMA composite collected at room temperature (RT) before heating, after heating at 388 K and after cooling to room temperature. Statistical uncertainties for the individual data points are smaller than the size of the symbols plotted.

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USAXS–XPCS is more sensitive to local structural variation than static scattering techniques such as USAXS, in which scattering from the overall scattering volume is incoherently summed.

To analyze quantitatively the USAXS–XPCS data, we established the following procedure.

(1) We normalize the USAXS and USAXS–XPCS profiles with their respective small-angle scattering invariant. Here, the small-angle scattering invariant, A, is defined as

$$A = \int I(q) q^2 \,\mathrm{d}q,\tag{9}$$

where I(q) is the scattering intensity.

(2) At each q, we calculate the ratio between the difference of normalized USAXS–XPCS and USAXS intensities and the normalized USAXS intensity.

$$I''_{\rm XPCS}(q) = \frac{I'_{\rm XPCS}(q) - I'_{\rm USAXS}(q)}{I'_{\rm USAXS}(q)},$$
(10)

where  $I'_{XPCS}(q)$  and  $I'_{USAXS}(q)$  are the normalized USAXS-XPCS and USAXS intensities according to equation (9). The normalization with  $I'_{USAXS}(q)$  in equation (10) is necessary because the intensity of USAXS-XPCS ranges over two orders of magnitude. This normalization gives intensities at different q values equal weight.

(3) We define the correlation coefficient  $\varphi(i, j)$ , a statistical parameter that describes the degree of resemblance between two data sets, following

$$\varphi(i,j) = \frac{C(i,j)}{\left[C(i,i) C(j,j)\right]^{1/2}}.$$
(11)

In equation (11), i and j represent the *i*th and *j*th data set; C(i, j) is the covariance of variables i and j, and follows the standard statistical definition,

$$C(i,j) = \langle (i - \langle i \rangle) (j - \langle j \rangle) \rangle, \tag{12}$$



Figure 10

Reduced USAXS–XPCS data for silanized ACP/Bis-GMA composite collected at 388 K at 0, 18, 36, 54 and 73 min after the start of heating. The standard deviation uncertainties are smaller than the symbols for the data points.

where  $\langle \ldots \rangle$  represents the statistical mean.

(4) We calculate the correlation coefficient between every pair of normalized USAXS-XPCS data sets,  $I''_{XPCS}(q)$ , and draw conclusions from the evolution of the correlation coefficients.

This analysis, which is based on the time-dependent coherent scattering curves, is different from the conventional time-autocorrelation analysis routinely used for XPCS studies of equilibrium systems, as detailed in the previous section. An example of this correlation coefficient analysis is shown in Fig. 11. The measurements were made on a silanized ACP/Bis-GMA composite during the cooling process after it had been exposed to a temperature of 388 K for  $\sim$ 200 min. The horizontal axis shows the starting time of the first component of the correlation coefficient  $\varphi(i, j)$ . The vertical axis shows the time difference between the second component and the first component of  $\varphi(i, j)$ . The correlation coefficient is displayed with a color scale, with values close to unity indicating that two XPCS profiles are highly correlated. Fig. 11 clearly shows that, after a short period ( $\sim 10 \text{ min}$ ) in which the system undergoes rapid cooling with associated structural relaxation, the local structure of the XPCS becomes stable. A detailed study of dental composites using XPCS will be described in a forthcoming publication.

### 6. Concluding remarks and discussion

The USAXS–XPCS technique has been developed to bridge the gap in accessible q values  $(10^{-4}-10^{-3} \text{ Å}^{-1})$  between conventional XPCS and DLS. USAXS–XPCS utilizes multiple reflections from single-crystal optics to reach low q values not normally accessible in XPCS experiments. We determined the operating parameters for optimizing the coherent scattering



#### Figure 11

Correlation coefficient map of silanized ACP/Bis-GMA composite during the cooling process after a  $\sim 200$  min heating procedure at 388 K. For each pixel on the map, the *x* coordinate is the starting time of a scan; the *y* coordinate shows the forward time difference of this scan with a later scan. The correlation coefficient is represented using the color scale shown in the sidebar. The higher the correlation coefficient (highest = red/brown), the more similar are the speckle patterns in the two USAXS– XPCS scans compared. conditions for the scattering volume and established measurement routines for XPCS experiments. We measured the equilibrium dynamics of PS microsphere suspensions in glycerol at 10, 15 and 20% volume concentrations in the point detection mode. The relaxation time shows a monotonic decline with increasing q and decreasing volume concentration of the PS microspheres. These results show good agreement with earlier XPCS measurements on similar systems by others and confirm the robustness of USAXS–XPCS. The expansion of the q range by USAXS–XPCS opens up the possibility of probing slowly evolving equilibrium dynamics of large structures, as well as the large-scale collective dynamics that are of great interest for fundamental problems such as gelation and jamming.

In a previous XPCS study of a similar system (PS spheres with nominal radius 66.5 nm in glycerol at 268 K) (Lumma et al., 2000), the authors found that the intensity autocorrelation function follows a simple exponential decay for suspensions with PS volume concentration as high as 28%, which indicates that the particles still follow Brownian, thus individual, motion. Our results are different in this respect - the Kohlrausch exponent,  $\gamma$ , is greater than one for every concentration at every q, which suggests hyperdiffusive behavior of the PS microspheres. Interestingly, this type of dependence of the Kohlrausch exponent on q is observed in a study of nanoparticle motion in polymer melts, where the nanoparticles follow Brownian-type diffusive motion in a high-q region and KWW-form hyperdiffusive motion in a low-q region (Guo et al., 2009). We speculate that this phenomenon may relate to the dependence of HI on the wavenumber q in many-body colloidal systems (Banchio et al., 2006). Given that the dynamics of such systems are determined by both direct interactions of the colloids and the solvent-flow-mediated HIs, by expanding the *q* range, USAXS-XPCS offers a distinctive opportunity to probe the q-dependent part of the hydrodynamic function. In addition, owing to its scattering q range, USAXS-XPCS in point-detection mode is primed to reveal equilibrium dynamics of complex fluids with suitable sizes, such as that of the nanoparticle haloing effect (Zhang et al., 2008).

Furthermore, USAXS-XPCS is based on the coherent interference of short-wavelength X-ray radiation, which leads to its high sensitivity to microscopic structural variations. Using an ACP/Bis-GMA polymer composite system as an example, we demonstrated the unique capability of USAXS-XPCS in identifying non-equilibrium dynamics that cannot be identified with other techniques such as XRD and FTIR. It is a fundamental challenge to characterize matter away from equilibrium where static approaches often do not apply. To understand non-equilibrium behaviors, we must address the difficulties associated with connecting theories with measurements across many length and time scales. While the applicable time and size range of USAXS-XPCS is limited, it is a unique tool for following slow dynamics in disordered materials. We envision its application in understanding the dynamic evolution of a wide variety of perturbed material systems as they evolve towards steady states and equilibriums.

# APPENDIX A

# The effect of detector noise on the autocorrelation function

The presence of noise is very common among X-ray detectors. The effect of noise is magnified when the signal-to-noise level is low. This situation is often encountered in XPCS studies when the coherent photon flux is limited. In this appendix, we present an analysis of the effect of detector noise on the autocorrelation function, which will help elucidate the role of noise in the detected dynamics.

We use a photodiode detector for the purpose of this discussion. For a photodiode detector, besides a signal that is linearly proportional to the incident intensity, a random noise exists. The total readout intensity can be written as

$$I = I_{\rm N} + I_{\rm R},\tag{13}$$

where  $I_{\rm N}$  is the readout noise and  $I_{\rm R}$  is the real signal.

The time-correlation function is defined as

$$g_2(t) = \frac{\langle I I(t) \rangle}{\langle I \rangle^2}.$$
 (14)

Here, for simplicity, the time variable t' and the ensemble average E are omitted compared with equation (5).

After inserting equation (13) into (14), we have

$$g_{2}(t) = \frac{\langle (I_{\rm N} + I_{\rm R}) [I_{\rm N}(t) + I_{\rm R}(t)] \rangle}{\langle I_{\rm N} + I_{\rm R} \rangle^{2}}$$
$$= 1 + \frac{\langle I_{\rm R} I_{\rm R}(t) \rangle - \langle I_{\rm R} \rangle^{2}}{\langle I_{\rm N} \rangle^{2} + 2 \langle I_{\rm N} \rangle \langle I_{\rm R} \rangle + \langle I_{\rm R} \rangle^{2}}.$$
(15)

The 'real' time-correlation function for the signal alone is defined as

$$G_2(t) = \frac{\left\langle I_{\rm R} I_{\rm R}(t) \right\rangle}{\left\langle I_{\rm R} \right\rangle^2} = 1 + \beta \left| f(q, t) \right|^2.$$
(16)

Comparing equations (16) and (15), we have

$$g_{2}(t) = 1 + \beta \frac{\langle I_{R} \rangle^{2}}{\langle I_{N} \rangle^{2} + 2 \langle I_{N} \rangle \langle I_{R} \rangle + \langle I_{R} \rangle^{2}} \left| f(q, t) \right|^{2}.$$
 (17)

If we define the effective optical contrast  $\beta' = \beta \langle I_R \rangle^2 / (\langle I_N \rangle^2 + 2 \langle I_N \rangle \langle I_R \rangle + \langle I_R \rangle^2)$ , equation (17) can be simplified to

$$g_2(t) = 1 + \beta' |f(q, t)|^2.$$
 (18)

Equations (17) and (18) show that the form of the intermediate scattering function  $|f(q, t)|^2$  obtained from the autocorrelation of noisy data is identical to that from the autocorrelation of no-noise data, although the scattering contrast is modified because of the existence of detector noise. When the signal-to-noise ratio is high, the effective optical contrast from  $g_2(t)$  analysis is close to the real value of the optical contrast.

If we assume that the detector has a fixed level of readout noise that is independent of the incoming X-ray flux, from equation (17), it is straightforward to show that, as the scat-

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tering intensity becomes smaller, the observed optical contrast becomes smaller. We have observed this effect in our analysis of colloidal dispersions in glycerol, as detailed in §4.

In summary, this analysis shows that readout noise in the detector will decrease the value of the optical contrast obtained in a time-correlation analysis. The line shape of the cross-correlation curve, however, is not affected. The extracted dynamical parameters, therefore, are not affected by this readout noise.

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#### References

- Abernathy, D. L., Grübel, G., Brauer, S., McNulty, I., Stephenson, G. B., Mochrie, S. G. J., Sandy, A. R., Mulders, N. & Sutton, M. (1998). J. Synchrotron Rad. 5, 37–47.
- Allen, A. J., Jemian, P. R., Black, D. R., Burdette, H. E., Spal, R. D., Krueger, S. & Long, G. G. (1994). Nucl. Instrum. Methods Phys. Res. Sect. A, 347, 487–490.
- Banchio, A. J., Gapinski, J., Patkowski, A., Häussler, W., Fluerasu, A., Sacanna, S., Holmqvist, P., Meier, G., Lettinga, M. P. & Nägele, G. (2006). *Phys. Rev. Lett.* **96**, 138303.
- Bandyopadhyay, R., Liang, D., Yardimci, H., Sessoms, D. A., Borthwick, M. A., Mochrie, S. G., Harden, J. L. & Leheny, R. L. (2004). *Phys. Rev. Lett.* **93**, 228302.
- Beenakker, C. W. J. & Mazur, P. (1984). Physica A, 126, 349-370.
- Bellour, M., Knaebel, A., Harden, J. L., Lequeux, F. & Munch, J. P. (2003). *Phys. Rev. E*, **67**, 031405.
- Borland, M., Decker, G., Emery, L., Guo, W., Harkay, K., Sajaev, V. & Yao, C. Y. (2010). APS Storage Ring Parameters, http://www.aps. anl.gov/Facility/Storage\_Ring\_Parameters/SRparameters.html.
- Brauer, S., Stephenson, G. B., Sutton, M., Bruning, R., Dufresne, E., Mochrie, S. G. J., Grubel, G., Alsnielsen, J. & Abernathy, D. L. (1995). *Phys. Rev. Lett.* **74**, 2010–2013.
- Caronna, C., Chushkin, Y., Madsen, A. & Cupane, A. (2008). Phys. Rev. Lett. 100, 055702.
- Cerbino, R., Peverini, L., Potenza, M. A. C., Robert, A., Bosecke, P. & Giglio, M. (2008). *Nat. Phys.* **4**, 238–243.
- Chung, B., Ramakrishnan, S., Bandyopadhyay, R., Liang, D., Zukoski, C. F., Harden, J. L. & Leheny, R. L. (2006). *Phys. Rev. Lett.* 96, 228301.
- Cipelletti, L. & Ramos, L. (2005). J. Phys. Condens. Matter, 17, R253– R285.
- Davis, T. J., Gao, D., Gureyev, T. E., Stevenson, A. W. & Wilkins, S. W. (1995). *Nature (London)*, **373**, 595–598.
- Dierker, S. B., Pindak, R., Fleming, R. M., Robinson, I. K. & Berman, L. (1995). Phys. Rev. Lett. 75, 449–452.
- Duri, A., Autenrieth, T., Stadler, L. M., Leupold, O., Chushkin, Y., Grübel, G. & Gutt, C. (2009). *Phys. Rev. Lett.* **102**, 145701.
   Faigel, G. & Tegze, M. (1999). *Rep. Prog. Phys.* **62**, 355–393.

- Falus, P., Borthwick, M. A. & Mochrie, S. G. (2005). *Phys. Rev. Lett.* **94**, 016105.
- Fluerasu, A., Moussaid, A., Madsen, A. & Schofield, A. (2007). Phys. Rev. E, 76, 010401.
- Gapinski, J., Patkowski, A., Banchio, A. J., Buitenhuis, J., Holmqvist, P., Lettinga, M. P., Meier, G. & Nägele, G. (2009). J. Chem. Phys. 130, 084503.
- Goodman, J. W. (1985). *Statistical Optics*. New York: Wiley-Interscience.
- Grubel, G. & Zontone, F. (2004). J. Alloys Compd. 362, 3-11.
- Guo, H., Bourret, G., Corbierre, M. K., Rucareanu, S., Lennox, R. B., Laaziri, K., Piche, L., Sutton, M., Harden, J. L. & Leheny, R. L. (2009). *Phys. Rev. Lett.* **102**, 075702.
- Gutt, C., Ghaderi, T., Tolan, M., Sinha, S. K. & Grubel, G. (2008). *Phys. Rev. B*, **77**, 094133.
- Ilavsky, J. & Jemian, P. R. (2009). J. Appl. Cryst. 42, 347-353.
- Ilavsky, J., Jemian, P. R., Allen, A. J., Zhang, F., Levine, L. E. & Long, G. G. (2009). J. Appl. Cryst. 42, 469–479.
- Jemian, P. R. & Long, G. G. (1990). J. Appl. Cryst. 23, 430-432.
- Jiang, Z., Kim, H., Jiao, X., Lee, H., Lee, Y. J., Byun, Y., Song, S., Eom, D., Li, C., Rafailovich, M. H., Lurio, L. B. & Sinha, S. K. (2007). *Phys. Rev. Lett.* **98**, 227801.
- Kotlarchyk, M. & Chen, S. H. (1983). J. Chem. Phys. 79, 2461-2469.
- Lai, B., Khounsary, A., Savoy, R., Moog, L. & Gluskin, E. (1993). Undulator A Characteristics and Specifications. Advanced Photon Source, Argonne National Laboratory, Illinois, USA.
- Leitner, M., Sepiol, B., Stadler, L. M., Pfau, B. & Vogl, G. (2009). *Nat. Mater.* **8**, 717–720.
- Livet, F., Bley, F., Caudron, R., Geissler, E., Abernathy, D., Detlefs, C., Grubel, G. & Sutton, M. (2001). *Phys. Rev. E*, **63**, 036108.
- Lu, X., Mochrie, S. G., Narayanan, S., Sandy, A. R. & Sprung, M. (2008). *Phys. Rev. Lett.* **100**, 045701.
- Lumma, D., Lurio, L. B., Borthwick, M. A., Falus, P. & Mochrie, S. G. J. (2000). *Phys. Rev. E*, **62**, 8258–8269.
- Lurio, L. B., Lumma, D., Sandy, A. R., Borthwick, M. A., Falus, P., Mochrie, S. G., Pelletier, J. F., Sutton, M., Regan, L., Malik, A. & Stephenson, G. B. (2000). *Phys. Rev. Lett.* 84, 785–788.
- Madsen, A., Als-Nielsen, J. & Grübel, G. (2003). Phys. Rev. Lett. 90, 085701.
- Madsen, A., Seydel, T., Sprung, M., Gutt, C., Tolan, M. & Grübel, G. (2004). Phys. Rev. Lett. 92, 096104.
- Miao, J., Sayre, D. & Chapman, H. N. (1998). J. Opt. Soc. Am. A, 15, 1662–1669.
- Miao, J. W., Charalambous, P., Kirz, J. & Sayre, D. (1999). *Nature* (*London*), **400**, 342–344.
- Mochrie, S. G. J., Mayes, A. M., Sandy, A. R., Sutton, M., Brauer, S., Stephenson, G. B., Abernathy, D. L. & Grubel, G. (1997). *Phys. Rev. Lett.* 78, 1275–1278.
- Mukhopadhyay, M. K., Jiao, X., Lurio, L. B., Jiang, Z., Stark, J., Sprung, M., Narayanan, S., Sandy, A. R. & Sinha, S. K. (2008). *Phys. Rev. Lett.* **101**, 115501.
- Narayanan, S., Lee, D. R., Hagman, A., Li, X. & Wang, J. (2007). *Phys. Rev. Lett.* **98**, 185506.
- Paterson, D., Allman, B. E., McMahon, P. J., Lin, J., Moldovan, N., Nugent, K. A., McNulty, I., Chantler, C. T., Retsch, C. C., Irving, T. H. K. & Mancini, D. C. (2001). *Opt. Commun.* **195**, 79–84.
- Petrascheck, D. (1988). Physica B+C, 151, 171-175.
- Poniewierski, A., Holyst, R., Price, A. C., Sorensen, L. B., Kevan, S. D. & Toner, J. (1998). *Phys. Rev. E*, 58, 2027–2040.
- Pontoni, D., Narayanan, T., Petit, J. M., Grübel, G. & Beysens, D. (2003). Phys. Rev. Lett. 90, 188301.
- Prasad, V., Semwogerere, D. & Weeks, E. R. (2007). J. Phys. Condens. Matter, 19, 113102.
- Robert, A., Wandersman, E., Dubois, E., Dupuis, V. & Perzynski, R. (2006). *Europhys. Lett.* **75**, 764–770.
- Sandy, A. R., Lurio, L. B., Mochrie, S. G. J., Malik, A., Stephenson, G. B., Pelletier, J. F. & Sutton, M. (1999). *J. Synchrotron Rad.* 6, 1174–1184.

- Seydel, T., Madsen, A., Tolan, M., Grubel, G. & Press, W. (2001). *Phys. Rev. B*, **63**, 073409.
- Sikharulidze, I., Dolbnya, I. P., Fera, A., Madsen, A., Ostrovskii, B. I. & de Jeu, W. H. (2002). *Phys. Rev. Lett.* **88**, 115503.
- Sikharulidze, I., Farago, B., Dolbnya, I. P., Madsen, A. & de Jeu, W. H. (2003). *Phys. Rev. Lett.* **91**, 165504.
- Skrtic, D. & Antonucci, J. M. (2003). Biomaterials, 24, 2881-2888.
- Skrtic, D., Antonucci, J. M., Eanes, E. D. & Eldelman, N. (2004). *Biomaterials*, 25, 1141–1150.
- Streit, S., Gutt, C., Chamard, V., Robert, A., Sprung, M., Sternemann, H. & Tolan, M. (2007). *Phys. Rev. Lett.* **98**, 047801.
- Sutton, M., Mochrie, S. G. J., Greytak, T., Nagler, S. E., Berman, L. E., Held, G. A. & Stephenson, G. B. (1991). *Nature (London)*, 352, 608–610.
- ThurnAlbrecht, T., Steffen, W., Patkowski, A., Meier, G., Fischer, E. W., Grubel, G. & Abernathy, D. L. (1996). *Phys. Rev. Lett.* 77, 5437–5440.
- Xiao, X., de Jonge, M. D., Zhong, Y., Chu, Y. S. & Shen, Q. (2006). *Opt. Lett.* **31**, 3194–3196.
- Zhang, F. & Ilavsky, J. (2010). Polym. Rev. 50, 59-90.
- Zhang, F., Long, G. G., Jemian, P. R., Ilavsky, J., Milam, V. T. & Lewis, J. A. (2008). *Langmuir*, **24**, 6504–6508.