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Demonstration of 3D photon correlation spectroscopy in the hard X-ray regime

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Three-dimensional photon correlation spectroscopy (3D PCS) is a well-known technique developed to suppress multiple scattering contributions in correlation functions, which are inevitably involved when an optical laser is employed to investigate dynamics in a turbid system. Here, we demonstrate a proof-of-principle study of 3D PCS in the hard X-ray regime. We employ an X-ray optical cross-correlator to measure the dynamics of silica colloidal nanoparticles dispersed in polypropylene glycol. The obtained cross correlation functions show very good agreement with auto-correlation measurements. This demonstration provides the foundation for X-ray speckle-based studies of very densely packed soft matter systems.

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Investigations of the structural and dynamic properties of a sample system based on speckle correlation techniques have played a key role in understanding various complex systems in condensed matter physics, such as colloids [1–4], polymers [5,6], capillary waves [7], metallic glasses [8,9], molecular glasses [10], and water [11–13]. The main assumption in the speckle analysis is that photons interact within the sample weakly, i.e., the single scattering approximation is valid [14]. However, more than one scattering event may be involved in the measured intensity when the light propagates through concentrated samples [15,16]. Multiply scattered photons are capable of affecting the speckle patterns, owing to their path length differences [17], and might give rise to an inaccuracy in the obtained sample dynamics from photon correlation spectroscopy (PCS) [18–20]. PCS has been well established as a versatile speckle-based technique for decades to investigate the dynamics of disordered systems. By correlating a time series of speckle intensities generated by a coherent light source, the correlation function decays as a function of delay time, with a relaxation rate governed by the sample dynamics. Faster dynamics lead to rapid decorrelations of scattered intensity traces because the speckle pattern reflects the spatial arrangement of the sample. Optical lasers are

widely employed, thanks to their high flexibility and accessibility at the laboratory experiment scale. However, the visible light scattering techniques are affected by multiple scattering contributions during investigations of optically opaque systems. To suppress the multiple scattering events, the sample has to be diluted so that the sample transmission is above 0.95 [21]. However, for important cases, studying concentrated or strongly interacting suspensions and glasses, a few measurement techniques have been developed, e.g., by reducing the scattering volume along the beam path using a flat cell [21,22] or by measuring backscattering with fiber optics [23,24]. Another two essential techniques are based on the cross correlation of two simultaneously performed PCS experiments. The first one, two-color dynamic light scattering (TC-DLS) involves using two different incident photon energies [25,26]. The second one is 3D PCS, which employs two nonparallel incidence beams with a certain angular offset [26–32]. The speckle patterns from the same scattering volume are collected by two spatially separated detectors placed at positions corresponding to the same scattering wave vector. Single-scattered photons are correlated and can be extracted by cross correlation of two signals of the detectors. Multiple scattering is uncorrelated; therefore, it is suppressed.

The PCS technique was extended by employing X-rays as a probe, i.e., to X-ray photon correlation spectroscopy (XPCS), providing a wide range of accessible scattering vectors with a spatial resolution down to the atomic length scale (typically from 10^{-3} to a few $\text{\AA}^{-1}$). Moreover, the development of synchrotron-based X-ray sources and detection schemes enables measurement at a wide range of time scales, from nanoseconds to minutes [4,11,33,34]. In particular, the wave vector transfer range of XPCS allows the study of hydrodynamic interactions in colloidal suspensions [35,36] mediated by a solvent. These studies require access to length scales of the order of inter-particle distances and have to be taken into account as the concentration of colloidal particles increases. Furthermore, XPCS investigations on atomic length scales have been reported [8,37]. Despite the expectation that multiple scattering could be negligible in X-ray measurements, owing to the small scattering cross-sections, recently, it was reported that multiple scattering events could be observed in small-angle X-ray scattering

(SAXS) experiments [14,38]. Up to now, no extensive study has been undertaken to verify the significance of multiple scattering in XPCS measurements. The main hindrance is the special kind of optics for X-ray cross correlation required for radiation with wavelengths shorter than 1 nm.

In this Letter, we demonstrate the feasibility of 3D PCS in the hard X-ray regime. This was accomplished by employing an X-ray optical cross-correlator [39] and two area detectors. Our result shows a very good agreement with the relaxation rates of both auto- and cross correlation functions, which indicates a successful proof-of-principle demonstration for 3D XPCS at a third-generation storage ring source.

The experiment was performed at the P10 beamline of PETRA III using 8 keV X-rays monochromatized by a cryogenically cooled Si (111) crystal monochromator [40]. The X-ray beam was focused down to a size d_b of $20 \times 10 \mu\text{m}$ ($h \times v$), vertically divided into two equal parts and propagated to the sample with an angular offset α defined by the X-ray optical cross-correlator device. The optical cross-correlator consists of two single Si crystals. The first Si (111) crystal splits the beam by wavefront division, and the second Si (220) crystal defines the angular offset $\alpha = 19^\circ$ [39]. The sample was located at the spatial overlap position of the two beams. The position was verified using a high-magnification microscope with a depth of field of $100 \mu\text{m}$. Colloidal silica particles were dispersed in PPG4000 (polypropylene glycol, 4000 g/mol) and placed in a quartz capillary with a diameter of 0.7 mm. The capillary was aligned to the overlap position by scanning the sample along one of the beam directions. The sample was prepared with a volume fraction $\phi = 0.019$. Two X-ray area detectors (EIGER 4M: D_1 and EIGER 500K: D_2) were employed to measure each speckle pattern separately. Owing to experimental constraints, the sample-to-detector distances L_1 and L_2 were set at 5050 and 4362 mm, respectively. The expected speckle sizes are 78.2 and $67.6 \mu\text{m}$ and are comparable to the pixel size of the detectors ($75 \mu\text{m}$). In total, 80 time series of speckle patterns were collected. Each series contained 10 000 frames with 2 ms exposure time, so that the total measurement time was sufficient to capture the overall decay curves of the correlation functions. To avoid sample damage, each series was measured at a fresh sample spot by changing the capillary position.

Figure 1 shows the setup geometry with the cross-correlator and the two detectors, as well as the scattering geometry with the two incoming and outgoing wave vectors $\mathbf{k}_{i1}$, $\mathbf{k}_{i2}$ and $\mathbf{k}_{f1}$, $\mathbf{k}_{f2}$, respectively. In the single scattering regime, the scattering vector $\mathbf{Q}$ is defined as $\mathbf{Q} = \mathbf{k}_{i1} - \mathbf{k}_{f1} = \mathbf{k}_{i2} - \mathbf{k}_{f2}$, as well as $Q = |\mathbf{Q}| = 4\pi/\lambda \sin(2\theta/2)$, where λ and 2θ are the X-ray wavelength and the scattering angle, respectively. The intensity fluctuations, including the normalized field correlation function $g^{(1)}(Q, \tau)$, can be expressed with auto-correlation $g_a^{(2)}(Q, \tau)$ and cross correlation $g_c^{(2)}(Q, \tau)$ via the Siegert relation [41]:

$$g_{a,1(2)}^{(2)}(Q, \tau) = \frac{\langle I_{1(2)}(Q, t) I_{1(2)}(Q, t + \tau) \rangle}{\langle I_{1(2)}(Q, t) \rangle^2} = 1 + \beta |g^{(1)}(Q, \tau)|^2, \quad (1a)$$

$$g_c^{(2)}(Q, \tau) = \frac{\langle I_{1(2)}(Q, t) I_{2(1)}(Q, t + \tau) \rangle}{\langle I_1(Q, t) \rangle \langle I_2(Q, t) \rangle} = 1 + \beta_{ov} |g^{(1)}(Q, \tau)|^2, \quad (1b)$$

where $I_1(Q, t)$ and $I_2(Q, t)$ are the scattered intensities measured at the scattering vector Q and time t collected by D_1 and D_2 , respectively. The time delay τ denotes the temporal separation

between recorded scattering patterns. The brackets $\langle \rangle$ stand for time averaging. The overlap factor β_{ov} denotes the maximum contrast of the cross correlation and is given by [29]

$$\beta_{ov} = \beta A = \beta \exp(-\delta Q^2 d_b^2/4) \exp(-\delta x^2/d_b^2), \quad (2)$$

where β is the contrast of the auto-correlation function and A is a reduction factor. While β is mainly related to the source coherence and speckle size at the detector [3], A takes into account the scattering vector mismatch δQ and scattering volume mismatch δx . The contribution of the multiple scattering component is accounted for by the factor δQ originating from the difference between the outgoing wave vectors of multiply scattered photons.

Conversely, the factor δQ , also taking into account the scattering geometry (e.g., the sample-to-detector distance), was corrected to retrieve the contrast value. To achieve this, the sample-to-detector distance correction was applied to the data after the measurement. We accurately extracted L_1 and L_2 using a reference sample, e.g., dried silica nanoparticles of $R = 252 \text{ nm}$ on a SiN membrane. Subsequently, the difference $\Delta L = |L_1 - L_2|$ was extracted by matching the scattered intensity profiles from both detectors (see Supplement 1, Fig. S1).

Figure 2 shows the detector frames of D_1 [Figs. 2(b) and 2(d)] and D_2 [Figs. 2(a) and 2(c)] with single acquisition scattering patterns [Figs. 2(a) and 2(b)] and average patterns [Figs. 2(c) and 2(d)], respectively, after applying the sample-to-detector distance correction. In the single-shot images, grainy interference scattering patterns, i.e., speckle patterns, are presented. The averaged image of 10^4 frames shows smooth concentric ring patterns, but the speckle features are smeared out owing to the decorrelations of the sample dynamics during that time. The azimuthally integrated scattering intensity of the sample is shown in Fig. 3, together with a single-sphere form factor fit of $R = 102 \text{ nm}$. The intensity profile and form factor fit of a highly diluted sample are shown in Supplement 1, Fig. S3.

Figure 4(a) shows the auto- and cross correlation results for selected values of Q . The cross correlation curves have lower zero-time intercepts than the auto-correlation curves at the same values of Q , owing to the reduction factor A [see Eq. (2)]. Our results show that $A = 0.13 \pm 0.017$, based on the value of β obtained from the correlation results in Fig. 4(a). We attribute

Fig. 1. Schematic view of the 3D XPCS experiment using the X-ray optical cross-correlator. Two area detectors (D_1 and D_2) were located in the SAXS geometry to collect speckle patterns generated by the two beams. Bottom left: Corresponding scattering wave vectors.

Fig. 2. (a) Single-frame and (c) average images of D_2 . (b) Single-frame and (d) average images of D_1 after applying the sample-to-detector distance corrections. The beam stops are shown in black.

Fig. 3. Azimuthally integrated intensity profiles of D_1 (solid line) and D_2 (dotted line) as a function of Q . The dashed line represents the form factor fit, taking into account the polydispersity ($\Delta R/R$).

this low value of A to the value of δQ , corresponding to about 0.45 pixel mismatches when $\delta x = 1 \mu\text{m}$.

Assuming Brownian motions of the colloidal particles in PPG4000 simplifies the case of the normalized field correlation function in Eq. (1) to [19]

$$g^{(1)}(Q, \tau) = \exp(-D_0 Q^2 \tau) = \exp(-\Gamma \tau), \quad (3)$$

where Γ is the relaxation rate of the system and D_0 is the particle diffusion coefficient defined by the Stokes–Einstein relation, $D_0 = k_b T / 6\pi\eta R$, where η , T , k_b , and R denote the medium viscosity, temperature, Boltzmann constant, and particle radius, respectively. The dashed lines in Fig. 4(a) represent fits of the model given by Eq. (3) to the data, and the fitting

Fig. 4. (a) Intensity correlation results of auto- and cross correlation functions. The dashed lines are the fit result using Eq. (3). (b) Corresponding value of Γ from the fits, with $\phi = 0.019$. The dashed lines represent the fitting curves of each dataset.

parameters (Γ) are shown in Fig. 4(b). We obtained very good agreement between the diffusion coefficients from auto- and cross correlation functions (D_a and D_c) to 1640.3 ± 29.6 and $1675.5 \pm 101.1 \text{ nm}^2/\text{s}$ by fitting with $\Gamma = D_0 Q^2$. This result indicates that there were no contributions of multiple scattering to the XPCS data at volume fractions up to $\phi = 0.019$ in 0.7 mm of sample thickness. Based on the Stokes–Einstein relation, we obtained PPG4000 viscosities of 1.28 and 1.32 Pa·s in the auto- and cross correlation schemes, respectively.

In conclusion, we have proved the principle of employing the 3D PCS technique in the hard X-ray regime. The speckle patterns were measured using an X-ray optical cross-correlator and two separate area detectors. The relaxation rates and diffusion coefficients obtained from both auto- and cross correlation functions show very good agreement for silica nanoparticles dispersed in PPG4000 at $\phi = 0.019$. The 3D XPCS studies can be applied to more concentrated and strongly interacting colloidal systems to suppress multiple scattering contributions in XPCS-based measurements. Moreover, for more X-ray sources offering a high coherent photon flux, such as an X-ray free-electron laser [42] or diffraction-limited storage rings [43], which would be capable of collecting speckle patterns at wide-angle X-ray scattering configurations, this capability will be essential for investigating bulk atomic dynamics, where the probability of multiple scattering is higher. The 3D XPCS configuration using two separate detectors is an alternative solution

in performing split-pulse XPCS to mitigate speckle contrast reduction owing to the δQ mismatches [44] inevitably involved when the two speckle patterns fall onto the same detector.

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors on reasonable request.

Supplemental document. See Supplement 1 for supporting content.

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