High Contrast X-ray Speckle from Atomic-Scale Order in Liquids and Glasses

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The availability of ultrafast pulses of coherent hard x rays from the Linac Coherent Light Source opens new opportunities for studies of atomic-scale dynamics in amorphous materials. Here, we show that single ultrafast coherent x-ray pulses can be used to observe the speckle contrast in the high-angle diffraction from liquid Ga and glassy Ni$_2$Pd$_2$P and B$_2$O$_3$. We determine the thresholds above which the x-ray pulses disturb the atomic arrangements. Furthermore, high contrast speckle is observed in scattering patterns from the glasses integrated over many pulses, demonstrating that the source and optics are sufficiently stable for x-ray photon correlation spectroscopy studies of dynamics over a wide range of time scales.

Since the initial observation of speckle in the diffraction of coherent short-wavelength x rays [1], it has been recognized that coherent x-ray techniques have the potential to provide powerful new probes of atomic scale structure and dynamics in noncrystalline systems, analogous to the techniques developed to study disorder at much larger length scales using coherent visible light [2]. In particular, x-ray photon correlation spectroscopy (XPCS) has been developed using high-brightness synchrotron x-ray sources to observe equilibrium and nonequilibrium dynamics in diverse systems [3,4]. A limiting factor in the development of XPCS for atomic scale studies has been the signal level that can be obtained. Almost all XPCS studies to date probe relatively large length scale (> 10 nm) structures, for example, via small-angle scattering from colloids and polymers [5–9] or diffuse scattering near Bragg peaks of crystals [10–12], because of their larger scattering cross sections compared with atomic-scale fluctuations, and the limited coherent x-ray power available. The first XPCS observation of truly atomic-scale dynamics was obtained only recently [13] in a study of diffusion in Cu-Au on relatively slow time scales (> 10 s).

One of the scientific drivers for the new generation of intense, coherent hard x-ray free electron laser sources, such as the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory, has been their potential for XPCS studies to open a new frontier at the natural time scales of even the fastest condensed matter systems, e.g., atomic diffusion in liquids [14,15]. The combination of femtosecond pulses and atomic resolution speckle provides unprecedented opportunities to test theories of liquid structure and dynamics, such as the intriguing predictions that have recently emerged regarding the complex dynamics of both diffusive [16] and vibrational [17] modes in liquids and glasses. Ultrafast XPCS provides a time-domain probe complementary to inelastic scattering, capable of studies of submicron volumes and nonequilibrium dynamics. To reach femtosecond time scales, which are much faster than the time resolution of imaging detectors, a pulse split-and-delay technique has been proposed [14,15,18–20] in which the correlation time is determined from the change in contrast of the sum of two speckle patterns, as a function of the delay time between the patterns. Although LCLS provides a huge leap in available coherent flux and accessible time scales, the high number of photons delivered in a single pulse poses challenges in avoiding x-ray effects on the sample during a dynamics measurement [14,15]. A primary issue is whether accurate contrast values can be extracted from the relatively weak speckle patterns expected in optimized XPCS studies. Likewise, the variations in pulse energy and position pose potential challenges for speckle measurements. Here, we report the first observation of high contrast x-ray speckle from the atomic scale structure in both liquid and glass samples. These were obtained using femtosecond hard x-ray pulses from the LCLS. We present an effective analysis procedure to extract contrast, show the dependence of contrast on experimental conditions, report the observed perturbation thresholds of various samples, and discuss the design of an optimized atomic resolution XPCS experiment.

We recorded speckle patterns from three samples: Ga heated into the liquid phase at 35 °C, and two glasses at room temperature, Ni$_2$Pd$_2$P and B$_2$O$_3$. The average
structure factors of these systems have all been previously characterized using standard scattering methods [21–23]. Experiments were carried out with the X-ray Pump-Probe instrument at LCLS, using a Si (111) monochromator with $1.4 \times 10^{-4}$ bandwidth set to 7.99 keV photon energy, and a 70 fs electron pulse width [24]. The average unattenuated x-ray pulse energy was typically $\sim 1 \times 10^{10}$ and $\sim 4 \times 10^{10}$ photons per pulse for single-pulse or multipulse images, respectively [24], although there was a very broad distribution of pulse energies with a maximum typically 5 times the mean. The scattering geometries were chosen to provide coherent illumination conditions that would fulfill the requirements to produce high-contrast speckle patterns [25,26] and to resolve this pattern at the detector. Measurements were made with a beam focused to 1.7 $\mu$m FWHM at the sample using Be compound refractive lenses. Diffraction patterns were recorded using a direct-x-ray-detection CCD with 20 $\mu$m square pixels at a distance from the sample of $L = 18$ to 142 cm, positioned at an average scattering angle corresponding to the peak in the strongest amorphous scattering ring. For Ga and Ni$_2$Pd$_2$P, we employed bulk samples in reflection geometry at $Q = 2.60$ and 2.95 Å$^{-1}$, respectively; for B$_2$O$_3$, we employed a fiber of 18 $\mu$m thickness in transmission geometry at $Q = 1.62$ Å$^{-1}$. Unattenuated single-pulse speckle patterns were recorded from all samples. To investigate the stability of the experimental setup and perturbation of the sample by the x-ray beam, we also recorded speckle patterns from the glass samples that were sums of multiple attenuated pulses.

Figure 1(a) shows a typical region of amorphous scattering viewed by the detector at $L = 37$ cm for liquid Ga.

This image of the average scattering was obtained by summing many single-pulse patterns and binning the pixels to smooth out the photon statistics. Figure 1(c) gives a small region of one of the single-pulse patterns, showing the individual photon hits. Since the width of the x-ray pulses is expected to be shorter than the time scale of equilibrium diffusive and vibrational motions of the atoms in the liquid, such single-pulse diffraction patterns should exhibit high speckle contrast if the x-ray optics are sufficiently free of aberrations, the detector resolution and noise characteristics are adequate, and the x-ray pulse does not disturb the atomic positions in the sample on the time scale of the measurement. A critical issue is to understand the accuracy with which the contrast can be determined from such weak speckle patterns.

Recent studies have obtained the contrast in speckle patterns from the normalized variance of the signal distribution on the detector [27,28]. When the photon density is low, the variance contains a large contribution from the counting statistics of individual photons in addition to the contrast [3,18,24]. Our approach to extracting the contrast is to compare the observed probability for $k$ photons arriving in a single detector pixel to the negative binomial distribution expected for a speckle pattern of a given contrast [29].

$$P(k) = \frac{\Gamma(k + M)}{\Gamma(M)\Gamma(k + 1)} \left(1 + \frac{M}{k}\right)^{-1} \left(1 + \frac{k}{\tilde{k}}\right)^{-M},$$

where $\tilde{k}$ is the mean photon density (counts per pixel), $M$ is the number of modes in the speckle pattern, and $\Gamma$ is the gamma function. The speckle contrast factor $\beta = M^{-1}$ has a maximum value of unity for a single-mode distribution, and it drops to zero as $M$ increases. For $M \rightarrow \infty$, Eq. (1) approaches the familiar Poisson distribution for uncorrelated photon positions, $P(k) = \tilde{k}^k \exp(-\tilde{k})/k!$. The contrast factor will be less than unity if the conditions are not met for the required transverse or longitudinal coherence of the incident beam [25,26], if the detector pixels are too large to fully resolve the speckle, or if the sample is not static on the time scale over which the pattern is recorded. It is this latter effect that allows the sample dynamics to be extracted from measurements of speckle contrast. In particular, if we record the sum of two speckle patterns of contrast factor $\beta_0$ from two equal-energy x-ray pulses separated by a time $\tau$, the contrast factor of the sum will drop from $\beta_0$ to $\beta_0/2$ as $\tau$ is varied from much less than to much more than the correlation time of the sample dynamics [15,29].

To accurately extract the contrast in these weak speckle patterns, we first employ a “droplet algorithm” [24,30] to locate the positions of each detected photon by fitting each recorded pattern. Typical results for extracted photon positions are shown in Fig. 1(c). Experimental probabilities $P(k)$ are obtained by choosing a region of pixels that has nearly uniform $\tilde{k}$ and $Q$, i.e., along the peak of the

![FIG. 1 (color online).](image-url)

(a) Average scattering of liquid Ga integrated over 309 pulses from LCLS. The detector at $L = 37$ cm from the sample subtends scattering angles including the main amorphous scattering ring at $Q = 2.60$ Å$^{-1}$. Dashed box shows region of pixels used in contrast analysis. (b) Average photon density vs scattering angle. (c) Expansion of small region of a single-pulse scattering pattern showing signal in analog-to-digital units (ADUs) from individual photons, and assignment of photon positions.
amorphous scattering ring as shown in Fig. 1(a), binning
the photon positions into the detector pixels, and determin-
ing the fraction of pixels that have k photons. Figure 2
shows the experimental probabilities for k = 1 to 4 for 309
speckle patterns having various mean count densities k. We
obtained a contrast factor β for each speckle pattern by
analyzing the P(k) as described in the Supplemental
Material [24]. The weighted average of these values gives
〈β〉 = 0.276 ± 0.004 for liquid Ga and L = 37 cm. While
the speckle patterns with highest k provide the highest
accuracy contrast values, the full distribution of weaker
and stronger speckle patterns obtained (due to the wide
incident pulse energy variation characteristic of monochro-
matic hard x-ray experiments at LCLS) verifies the pre-
dicted k dependencies given by the negative binomial
distribution. These measurements on liquid Ga represent
the first observation of speckle from the atomic-scale order
in a liquid.

To investigate whether the stability of the source and
experiment will affect the contrast in multipulse XPCS
experiments, and to understand the thresholds for irrevers-
ible perturbation of the sample structure by the incident
x-ray pulses, we studied two glasses where the liquidlike
atomic arrangement should be static over the time range of
a pulse sequence, unlike the case for liquid Ga. For the
metallic glass Ni2Pd2P, we collected not only single-pulse
speckle patterns without attenuation of the incident beam,
but also sums of 500 consecutive attenuated pulses. The
values of 〈β〉 extracted for both single-pulse and attenuated
500-pulse speckle patterns at three different values of
sample-to-detector distance L are given in Table I. Scat-
ttering from the low-atomic-number glass B2O3 was
too weak to obtain values of 〈β〉 from single pulses under
the available experimental conditions; Table I gives results
for multiple-pulse patterns with various L.

The observed 〈β〉 values can be compared with those
calculated for a static sample using an incident beam with
full transverse coherence but nonzero photon energy band-
width, and a detector with nonzero pixel size. These reso-
lution effects reduce the calculated static contrast factor
β_{\text{calc}} from unity depending upon the size of the illuminated
volume, the scattering angle, and the sample-to-detector
distance L [24]. Table I gives β_{\text{calc}} values for each of the
samples and experimental conditions. The observed 〈β〉
value for liquid Ga is 90% of the corresponding β_{\text{calc}},
indicating that the x-ray optics are almost free of aberr-
tions and that the ultrafast x-ray pulses have effectively
frozen the motion of the atoms, giving a coherent diffraction
snapshot of their arrangement in the liquid. It also
indicates that the unattenuated, focused x-ray beam does
not significantly alter the atomic arrangements in liquid Ga
during the time of the pulse, even though the energy
deposited in the illuminated sample volume (~ 30 eV
per atom per average pulse) is typically enough to vaporize
it on a longer time scale [24]. If the atomic positions were
completely rearranged on time scales much shorter than
the pulse, the contrast would approach zero.

| Sample | Pulses | n_{\text{patt}} (ct/pulse) | n_{\text{pix}} (ct/pix) | 〈I_0〉 | 〈k〉 | Average contrast factor 〈β〉 | β_{\text{calc}} |
|--------|--------|--------------------------|-----------------------|--------|------|--------------------------|---------|
| Ga     | 37     | 1 004 1.1 × 10^{10}      | 0.019                 | 0.276 ± 0.004 | 0.307 |
|        | 18     | 1 005 1.5 × 10^{10}      | 0.072                 | 0.245 ± 0.006 | 0.349 |
|        | 18     | 500 60 1.7 × 10^{7}      | 0.065                 | 0.276 ± 0.005 | 0.349 |
|        | 18     | 500 47 8.4 × 10^{7}      | 0.184                 | 0.156 ± 0.002 | 0.349 |
|        | 35     | 1 490 1.2 × 10^{10}      | 0.016                 | 0.360 ± 0.010 | 0.645 |
|        | 35     | 500 40 1.8 × 10^{7}      | 0.014                 | 0.492 ± 0.022 | 0.645 |
|        | 35     | 500 60 8.7 × 10^{7}      | 0.041                 | 0.319 ± 0.006 | 0.645 |
|        | 142    | 500 20 4.4 × 10^{8}      | 0.016                 | 0.408 ± 0.019 | 0.713 |
| B2O3   | 37     | 1 005 9.6 × 10^{9}       | 0.007                 | 0.291 ± 0.057 | 0.446 |
|        | 37     | 100 20 1.9 × 10^{10}     | 0.056                 | 0.195 ± 0.005 | 0.446 |
|        | 37     | 500 61 3.6 × 10^{8}      | 0.017                 | 0.356 ± 0.014 | 0.446 |
atom absorbed energy. The dataset for \(B_2O_3\) ple disturbance effects occurs at about 1 eV per illuminated mum incident pulse energies in the attenuated 500-pulse absorption length, which agrees with the observed higher atom per average pulse) than for Ga owing to its shorter maximum temperature rise of \(0^\circ C\). Measurements is the signal-to-noise ratio for \(\beta\) of \(Ni_2Pd_2P\) incident beam. For the single-pulse data, the energy density deposited is higher for \(Ni_2Pd_2P\) or single pulse patterns with no attenuation, consistent with some disturbance of the sample structure by the incident beam. For the single-pulse data, the energy density deposited is higher for \(Ni_2Pd_2P\) than for Ga owing to its shorter absorption length, which agrees with the observed higher disturbance during single pulses [24]. Based on the maximum incident pulse energies in the attenuated 500-pulse sequences, the threshold for longer time (interpulse) sample disturbance effects occurs at about 1 eV per illuminated atom absorbed energy. The dataset for \(B_2O_3\) indicates that this threshold is also about 1 eV per atom in this “light” material, corresponding to a higher incident flux because of its longer absorption length. Based on the observed melting threshold for \(Ni_2Pd_2P\), we estimate that the deposited pulse energy is thermalized in a volume 50 times larger than the illuminated volume, consistent with the expected spread of the electron, photon, or phonon cascade generated by x-ray absorption [24], resulting in a maximum temperature rise of 0.02 eV/3\(k_B\) = 80 K.

These measurements allow an analysis of the feasibility of femtosecond XPCS experiments using the split-pulse technique [14,15,18]. The figure of merit for such measurements is the signal-to-noise ratio for \(\beta\), which for low \(\kappa\) is determined by fluctuations in the small number of \(k = 2\) events and can be expressed as [24] \(\beta/\sigma_\beta = \beta k [n_{pix}h_{patt}/2(1 + \beta)]^{1/2}\). This expression agrees well with the observed accuracy of \(\langle \beta \rangle\) given in Table I, indicating that other potential experimental contributions to the uncertainty are negligible. If we use a detector capable of recording \(n_{pix} = 10^6\) pixels at the full LCLS repetition rate of 120 Hz, to give \(n_{patt} = 4 \times 10^4\) in six minutes per delay time, and extrapolate the measured relationships between \(\kappa\) and \(I_0\) [24], the pulse energies needed to give a signal-to-noise ratio of 5 sufficient for XPCS are \(I_0 = 6, 0.3, \) or \(0.13 \times 10^8\) photons per pulse, corresponding to sample temperature rises of 3 to 7 K, for \(B_2O_3\), Ga, or \(Ni_2Pd_2P\), respectively. These temperature rises are significantly below the 80 K threshold for structural disturbance by diffusive atomic rearrangement that we observed for the glass samples, indicating that even more sensitive samples and processes can be studied.

The new analysis technique presented here will allow the accurate determination of speckle contrast using the weak patterns that will be generated in experiments done under conditions in which the x-ray pulses from a free electron laser do not disturb the sample dynamics. We observe high contrast factors in x-ray speckle patterns from liquids and glasses obtained with ultrafast pulses, indicating that XPCS studies of their atomic-scale dynamics on time scales down to the femtosecond range are likely to be feasible. We find that the atomic motions associated with x-ray damage occur on time scales shorter than the x-ray pulse width used here for deposited energy densities greater than about 50 eV per illuminated atom [24]. This provides guidance for the design of studies in which single-pulse speckle patterns are analyzed to obtain atomic-scale structural information.

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