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X-ray cross correlation analysis uncovers hidden local symmetries in disordered matter

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We explore the different local symmetries in colloidal glasses beyond the standard pair correlation analysis. Using our newly developed X-ray cross correlation analysis (XCCA) concept together with brilliant coherent X-ray sources, we have been able to access and classify the otherwise hidden local order within disorder. The emerging local symmetries are coupled to distinct momentum transfer \( Q \) values, which do not coincide with the maxima of the amorphous structure factor. Four-, 6-, 10-, and most prevalently, 5-fold symmetries are observed. The observation of dynamical evolution of these symmetries forms a connection to dynamical heterogeneities in glasses, which is far beyond conventional diffraction analysis. The XCCA concept opens up a fascinating view into the world of disorder and will definitely allow, with the advent of free electron X-ray lasers, an accurate and systematic experimental characterization of the structure of the liquid and glass states.

Disordered matter, such as glasses and liquids, does not exhibit translational symmetry and in turn is able to accommodate different local symmetries in the same system, among them the icosahedral local order, which belongs to the forbidden motifs in periodic structures. This mysterious and so far experimentally inaccessible localized order within disorder has been fascinating scientists for many decades (1–5), because it is held responsible for the undercooling of liquids and the existence of the glass state. Similarly, nonperiodic materials have always attracted the attention of materials scientists, because they do carry—through these structural degrees of freedom—a unique potential to display novel smart functions (6–8).

The microscopic understanding of the structure and properties of crystals has advanced rapidly during the last decades. The translational invariance of the crystalline state allowed the introduction of the Brillouin Zone concept, thus enabling an elegant and powerful theoretical description of the thermal, electronic and magnetic properties. At the same time, crystal diffraction has continuously been developed to such a fine art that even complex biological structures can be solved today with the advent of free electron X-ray lasers, an accurate and systematic experimental characterization of the structure of the liquid and glass states.

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A typical dataset displays the expected isotropic granular “intensity rings” that are mediated by the random local order within the system (Fig. 1A). The deduced angular averaged structure factor shows the standard radial intensity distribution (Fig. 1B).

To transcend this information, we must unravel correlations in the angular distribution of the X-ray speckles. At first sight this is not evident at all, because the angular variation of the intensity exhibits an isotropic distribution as anticipated for amorphous systems (Fig. 1A). However, as we shall show, this is possible by considering the generic intensity-intensity cross correlation.

Fig. 1. Experimental data and XCCA results. (A) CCD image showing a typical intensity spectrum with speckle structure. (B) Angular averaged structure factor of the image in A, which is the standard radial intensity distribution. (C) Experimental results after applying the cross-correlator $C_Q(\Delta)$ to the data in A at different $Q$ values. Solid lines are guide to the eyes.

Fig. 2. Temporal relaxation behavior of $C_Q(\Delta)$ and $\langle I(Q,t)I(Q,t')\rangle$. (A) Normalized temporal intensity autocorrelation function $\langle I(Q,t)I(Q,t')\rangle$ for different $Q$ values (black squares: $Q = 0.020$ nm$^{-1}$; blue triangles: $Q = 0.032$ nm$^{-1}$; red dots: $Q = 0.054$ nm$^{-1}$). $\Delta t - t' \rightarrow t$. Solid lines are guide to the eyes. (B) The cross-correlation function $C_Q(\Delta)$ at $Q = 0.04$ nm$^{-1}$ evolves from an initially 6-fold to a 5-fold symmetry. The curves at 600 s and 300 s are averaged over the subsequent 100-s interval; the one at 100 s is averaged over a 50-s interval.
The normalized angular 4-point cross-correlation function \( g \) and the associated 4-point correlation function. Here, we introduce a first angular cross-correlation function. We define the normalized angular 4-point cross-correlation function as

\[
C_{\phi}(\Delta) = \frac{\langle I(Q, \phi) I(Q, \varphi + \Delta) \rangle_\phi - \langle I(Q, \phi) \rangle_\phi^2}{\langle I(Q, \phi) \rangle_\phi^2} \tag{3}
\]

with

\[
\langle I(Q, \phi) I(Q, \varphi + \Delta) \rangle_\phi \sim \langle \rho_0(\phi) \rho_0^*(\phi + \Delta) \rangle_\phi \tag{4}
\]

where \( \langle \ldots \rangle \) denotes an angular average.

**Angular Cross Correlation Function.** Here, we introduce a first simple subset of these new types of higher-order correlations, i.e., the instantaneous local angular correlations with respect to a given azimuth. They are found by performing the average in Eq. 1 over \( \phi \) with the vectors \( Q \) and \( Q' \) separated by \( \Delta \) on the intensity ring of modulus \( Q \) (see Fig. 3B) at \( t = t' \). We define the normalized angular 4-point cross-correlation function

\[
\langle I(Q, \phi) I(Q', \phi') \rangle = \int \int \int e^{-iQr - iQ'r'} \, g_4(r, \phi, t, r', \phi', t') \, dr \, ds \, dr' \, ds' \tag{1}
\]

and the associated 4-point correlation function

\[
g_4(r, \phi, t, r', \phi', t') = n_0^{-4} \langle \rho(r, t) \rho(s, t) \rho(r', t') \rho(s', t') \rangle \tag{2}
\]

where \( \langle \ldots \rangle \) means a statistical average.

---

**Materials and Method.** We have made several systematic observations in all colloidal glass systems. The emerging local symmetries are coupled to distinct \( Q \) values, which do not coincide with the maxima of the amorphous structure factor. The most fascinating is \( C_{\phi}(\Delta) \) is a superposition of the angular intensity-autocorrelation function of individual local structures, each contributing an intensity pattern \( |\rho_0(\phi)|^2 \) as the one in Fig. 4B. In the coherent speckle pattern produced by the random ensemble of such clusters, this pattern becomes completely obscured. Only the application of XCCA recovers its symmetries.

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*The observation of odd symmetries appears to be in conflict with Friedel’s law \((I(-Q)) = I(Q))\), which holds for any plane in reciprocal space that intersects the origin. The observation of odd symmetries in our scheme is due to the deviation from the far-field (Fraunhofer) limit (13), because the sample is located as close as 20 cm to the 10-μm entrance slit, thereby adding an imaginary part to the phase factor of each particle.
In the SI we present a straightforward discussion of the $Q$-dependence of $C_\alpha(\Delta)$ based on an analytical derivation of the structure factor of icosahedral clusters (20–22). We note that angular correlations between local clusters, so called medium-range correlations, are also accessible by XCCA. This requires a different 4-point correlator in Eq. (3), which takes $Q$-vectors with $|Q| \neq |Q|$ into account.

We have performed calculations of the full expression (Eq. 3) for 8000 randomly oriented icosahedra (Fig. 4C) on a cubic lattice. The resulting correlation patterns confirm very nicely the local angular symmetries of our experiment (Fig. 4A) and show that the sprinkle of the data points is due to the coherent scattering process (speckles).

**Dynamical Heterogeneity.** A further most fascinating observation is associated with the temporal relaxation behavior of $C_\alpha(\Delta)$ (Fig. 2B). Our new 4-point correlator unveils a continuous change of the locally-favored structures within the first 600 s from initially 6-fold symmetry to 5-fold symmetry, with no obvious symmetry in between. Apparently, icosahedral clusters reorganize in different orientations, form either out of local nanocrystals (hexagonal/fcc) or disorder, all of which involves a breaking and forming of bonds. Such behavior is known from molecular dynamics simulations as “dynamical heterogeneity” (19). Within the observed time frame, the temporal autocorrelation drops below 30% (see Fig. 2A). This new X-ray cross-correlation analysis concept reveals now that the processes, which are responsible for these relaxations, are accompanied by distinct changes of the local structures. These cooperative processes are the $\beta$-relaxation at shorter and $\alpha$-relaxation at longer time scales (23), where the $\beta$-relaxation describes the rattling of individual particles trapped in transient cages formed by their neighbors and the $\alpha$-relaxation the structural rearrangement of these cages (24). In future, this technique can be interrogated to see the time dependence of the local structures in glassy and supercooled states and new local structural motifs in strong and fragile glass formers by employing even more sophisticated cross-correlators between intensities at different times.

**Conclusions**

We have introduced and applied a particularly simple 4-point cross correlator that enables us to unveil otherwise hidden symmetries in a colloidal glass. Our approach is general enough to accommodate many more complex cross correlators derived from Eq. 1. In particular, the orientational pair-pair correlations will allow access to midrange order. Preliminary yet promising calculations employing a mode-coupling ansatz and an appropriate atomic potential (25) show a dominant instability for 6- and 5-atomic potential (associated with close-packed structures) and a multitude of incommensurate wave vector instabilities (associated with random arrangements). This should enable to extract in the future the relevant interaction potentials from experimental datasets.

The availability of short-pulse XFEL radiation in the 0.1-nm regime and with 100-fs pulse length will open up the fascinating option to analyze the local structure of liquids (in particular also water) by applying the new concept of X-ray cross correlation analysis (XCCA) to single laser shot speckle diffraction pattern. The combination of short-pulse XFEL radiation and large 2D-detector arrays will also open up the window for the study of nano-powders and transient complex molecular structures in solution.

**Materials and Methods**

**Samples.** The colloidal particles were synthesized via a polymerization method for preparing lattices of poly(methylmethacrylate) (PMMA) with a covalently surface linked stabilizer of poly(12-hydroxy-stearic-acid) (PHSA) following the method of Antl et al. (26). These fluorescent PMMA particles are obtained by copolymerization of methyl methacrylate, methacrylic acid and the fluorescent monomer, 7-nitrobenzo-2-oxa-1,3-diazole-methyl methacrylate (NBD-dyed) (27). To obtain highly concentrated, glassy systems, particle suspensions of ~20–30% in volume were filled into quartz-glass capillaries of 1 mm and centrifuged at 1,360 × g for ~2 days. The supernatant decalin has been removed and the capillaries sealed.

**Data Treatment.** The dark images were averaged and subtracted from the data. The colloidal form factor $f(Q)$ has been obtained from a diluted PMMA sample. The form factor allowed to deduce the static structure factor $S(Q)$ of the concentrated sample presented in this work. A multispeckle temporal intensity autocorrelation analysis yielded the dynamic correlation function of the sample. The dynamical correlation function, which relates to the diffusive motion of the colloidal particles, shows no decay within the first 100 s. Therefore, for the XCCA analysis we averaged 50–100 CCD images. Ranges of intensity with constant $Q$ and 1 to 2-pixel widths have been extracted and an unbiased cross correlation function according to Eq. 3 has been calculated.

Note also that a diffraction pattern obtained via a 2D detector (i.e., mapping an Ewald sphere) will not satisfiably fit Friedel’s law at higher momentum transfers (see SI).

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