X-ray Cross Correlation Analysis Uncovers Hidden Local Symmetries in Disordered Matter

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Recommended, with a commentary by Sunil Sinha, University of California San Diego.

The local structure of so-called "disordered solids" or glasses has always been fascinating to physicists and yet frustratingly difficult to characterize quantitatively. This is because commonly used tools such as x-ray and neutron scattering, which are capable of probing structure at atomic dimensions in bulk materials yield only orientationally averaged information embodied in the so-called " radial pair distribution function" which simply tells you the average number of particles at a certain distance from a given particle. Without a periodic crystal lattice, the elegant methods of conventional crystallography cannot be applied. Yet it is known from theory and computer simulations and indirect evidence such as spectroscopy that local order incorporating bond orientational order indeed exists. One example is the prediction, made decades ago, of the existence of icosahedral short range order in undercooled metallic liquids and Lennard-Jones systems [1-3]. Because of the five-fold symmetry, such local order cannot develop into long-range translational periodicity in 3 dimensions (a problem closely related to the formation of quasicrystals).

Of course if one could obtain a snapshot of the instantaneous positions of all the atoms in a particular sample, one could test for such local order. This is essentially what scattering of a coherent beam of x-rays does in Fourier or reciprocal space. Speckles are a ubiquitous phenomenon whenever a coherent beam of radiation, such as an ordinary laser beam, is scattered by matter possessing any kind of disorder. It arises from the (not completely)

random constructive and destructive interference of the wavelets scattered from the individual scattering centers, giving rise to bright and dark spots in the various directions of scattering. A speckle pattern in a sense represents a unique fingerprint via Fourier transform of the individual sample bathed in the coherent radiation, rather than the usual ensemble average accessed by scattering with incoherent radiation. The envelope of the fluctuating speckle intensities is in fact the ensemble-averaged S(Q) scattering function that is normally measured from a glass or liquid, so that the speckles tend to be clustered in rings as a function of wave vector transfer Q corresponding to the maxima of S(Q).While it is true that the observed speckle pattern yields only the intensities and not (directly) the phases of the Fourier transform*, this is sufficient to yield information about the bond-orientational order, as Wochner et al. have shown, applying an elegant cross-correlation technique to the scattering of a coherent x-ray beam from a colloidal glass. Coherent x-ray beams can be extracted from synchrotron undulator sources by placing a pinhole of the order of the transverse coherence length, typically a few microns in diameter, at a large distance (~30 m) for the source , allowing only the coherent fraction of the beam to go through.

Physics is full of examples of various types of "hidden" order being extracted from random-looking patterns. When the particles in a disordered sample move, the speckle pattern fluctuates in an apparently random manner with time for a particular wave vector transfer. Nevertheless, taking a time autocorrelation function of the intensities $\langle I(\mathbf{Q},t)I(\mathbf{Q},t+\tau)\rangle$, properly normalized and where the brackets represent an average over t, can be shown to yield a function of τ that is directly related to the intrinsic dynamical scattering function $S(\mathbf{Q},\tau)$ of the sample, limited only by the counting statistics of the experiment. This has been exploited for years in studying the diffusion of particles in liquids by laser scattering (known as dynamical light scattering or DLS) and more recently at shorter wavelengths to study slow dynamics in soft matter samples using coherent x-ray scattering (known as x-ray correlation spectroscopy or XPCS). What Wochner et al. have done is to use the same idea, but simply to autocorrelate instantaneous speckle intensities from a static sample in *angle* around various rings of constant Q in reciprocal space, or in other words to calculate $\langle I(Q,\theta)I(Q,\theta+\Delta)\rangle$, where θ,Δ are azimuthal angles around the ring and the average is over θ. Note that such a quantity is intrinsically a 4-point correlation function. (Normally, at least a 3-point correlation function is needed to establish bond-orientational order). Doing this, they find

remarkable five-fold, four-fold, six-fold and even 10-fold symmetries around the ring, depending on the magnitude of Q. They show that simulations of the coherent speckle pattern produced from a set of randomly oriented icosahedra show similar five-fold symmetries in the angular cross-correlation functions, although detailed comparisons of how such symmetries vary with the magnitude of Q are as yet missing. They also show that the bond-orientational order symmetries slowly relax as a function of time and switch from 5-fold to 6-fold at a given Q value in a manner which is not understood, but which they relate qualitatively to the structural rearrangements of the cages or so-called alpha relaxation. Clearly there is a wealth of detailed information about the kinetics of glass formation to be mined from such experiments.

One may ask, instead of colloidal glasses, could such experiments be done on actual monatomic metallic glasses and liquids? This would require scattering experiments at much shorter length scales and thus higher Q values, where even at the current high-brilliance synchrotron x-ray sources, one is fighting battles against both intensity and the degree of coherence of the X-ray beam, particularly for liquids where one would have to take fast snap-shot pictures of the speckle patterns. One may look to the new x-ray Free Electron Laser Sources to provide brilliant enough beams to carry out such experiments in the near future.

*Phase information and hence the individual particle positions can actually be accessed (at least down to length scales of a few nm) using various algorithms which have been developed recently based on the so-called over-sampling principle, but that is not our primary concern here and has been discussed in other commentaries in the journal club.

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