Theory of cross-correlation analysis in disordered systems

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In a recent experiment [1], partially coherent x-rays with a wavelength of 0.154 nm were used to investigate a colloidal glass composed of PMMA spheres of 117 nm radius, with particle suspensions of concentration exceeding the glass formation value. The scattering pattern on a 2D detector has the concentric ring structure characteristic of disordered systems, and the speckled appearance results from the partial coherence of the undulator x-rays at the European Synchrotron Radiation Facility (ESRF). The authors of Ref. [1] have introduced the 4-point angular cross-correlation function (CCF) $C_q(\Delta)$ defined as

$$C_q(\Delta) = \frac{\langle I(q,\varphi) I(q,\varphi+\Delta)\rangle_\varphi - \langle I(q,\varphi)\rangle_\varphi^2}{\langle I(q,\varphi)\rangle_\varphi^2},$$

where $I(q, \varphi)$ is the scattered intensity, q is the magnitude of the scattering vector $\boldsymbol{q}$, φ is an angular coordinate around a diffraction ring of radius q, and $\langle\ldots\rangle_\varphi$ denotes an angular average around the ring. One of the important results of the Ref. [1] is that, at least for some q values, $C_q(\Delta)$ is well approximated by a cosine function of an integer multiple of the angle Δ, i.e., $C_q(\Delta) \sim \cos(n\Delta)$; different values of n are observed for different q. In particular, the experiment on PMMA spheres, for $q \approx 0.04$ nm^{-1}, showed a very pronounced cosine behavior with n=5.

Here, we give a general theoretical treatment [2] of the problem of the x-ray cross-correlation analysis (XCCA) in a partially disordered system. We derive analytical expressions for the Fourier series expansion of the correlation function $C_q(\Delta)$ in the $0 \leq \Delta < 2\pi$ interval, from which the cosine-like behavior of the angular correlation function is related to the arrangement and orientation of bond angles and interatomic distances in the system in a completely general way. We limit ourselves to the kinematical diffraction case here. We show that Fourier coefficients of the CCF C^n_q can be presented as a product of Fourier coefficients of intensity $I^n(q)$ indicating that cross-correlation analysis does not contain any additional information with respect to the Fourier analysis of the φ dependence of the intensity. One additional aspect of this phenomenon is that it is essentially two-dimensional in character; in a disordered three-dimensional (3D) system, it appears that among randomly oriented local bond arrangements, the largest effects are expected from local bond arrangements where n-fold symmetry axes are (at least approximately) lined up with the direction of the incident x-

rays. This leads us to investigate the relationship to pure two-dimensional (2D) systems. In fact, extremely marked effects, unveiled by previous x-ray studies performed with x-ray beams with the limited degree of coherence of bond-orientational order in liquid crystals [3] (especially hexatic ones) and dynamical light scattering experiments [4] performed with coherent laser beams on ordered 2D colloid systems, are strongly related to the recent results of Ref. [1]. Our aim is to provide a sound basis to the statement that the angular intensity correlations deliver information on local bond arrangements in a disordered (or partially ordered) system. In the dilute limit (where local entities containing specific bond angles are separated by distances much larger than the bond lengths) the angular correlation function can be explicitly related to a bond-orientational order parameter, which generalizes the order parameter proposed for hexatic liquid crystals by Bruinsma and Nelson [5].

We also consider correlations in 3D systems, when the effect of the Ewald sphere curvature becomes important. Conditions, at which the angular CCF shows cos($n\Delta$) behavior with odd n-numbers are analysed.

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