Glimpsing order within the disarray

M M J Treacy, D Kumar, A Rougée, G Zhao, P R Buseck, I McNulty, L Fan, C Rau and J M Gibson

1 Arizona State University, Dept. of Physics, Tempe, AZ 85287
2 Arizona State University, School of Earth and Space Exploration, Tempe, AZ 85287
3 Arizona State University, Dept. of Chemistry/Biochemistry, Tempe, AZ 85287
4 Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439

E-mail: treacy@asu.edu

Abstract. We describe some of the recent advances in the fluctuation microscopy technique for probing medium-range structural correlations in disordered materials. In particular we show that fluctuation microscopy is a surprisingly sensitive method for detecting trace quantities of C60 in a disordered graphite matrix. This surprising sensitivity arises because C60 does not have the same forbidden reflections as graphite. Modeling shows that the method should readily distinguish between C60, C70 and C72. This result indicates that the technique can be used to discern dilute distributions of macromolecules in an otherwise disordered matrix.

We also describe preliminary interferometric fluctuation microscopy studies using cross-correlations in diffraction between coherent double probes. This is a form of holography where the diffraction patterns from two neighboring regions are allowed to overlap and interfere. Young’s fringes appear wherever both regions scatter strongly. The cross-correlation can be examined as a function of probe separation to estimate a structure correlation length. At present, the method is being applied to x-ray and optical microscopies, but could also be applied to TEM. Since it isolates the essential four-body terms underpinning the fluctuation microscopy technique, this method holds much promise for studying medium-range order.

1. Introduction

Fluctuation microscopy is an imaging/diffraction technique that is especially sensitive to medium-range structural correlations in disordered materials. The ‘fluctuations’ are the differences in scattering between neighboring regions of the sample. The sensitivity to medium-range order comes from the fact that spatial scattering fluctuations depend on the higher-order atomic distribution functions within the sample [1–3]. Pure diffraction is a two-body signal that depends only on correlations between pairs of scatterers [4, 5]. The fluctuation microscopy method delivers information about pair-pair correlations (i.e. four-body correlations) [6, 7].

The higher-order correlations emerge because fluctuation microscopy is a spatially-resolved diffraction technique. Highly disordered samples tend to give tilted dark-field images that are speckled. Some of that speckle is due to random atom alignments, and some is due to local structural regularity. The statistics of the speckle depend on the higher-order correlations. The simplest statistical parameters are the mean and variance of the scattering, although these are by no means the only statistical moments available. Since the atomic scattering form factor tends to fall off with increasing Q, it is helpful to normalize the variance by dividing by the...
square of the mean intensity,

$$V_N(Q) = \frac{\langle I^2(r \cdot Q) \rangle}{\langle I(r \cdot Q) \rangle^2} - 1.$$  \hspace{1cm} (1)

\(r\) is the real space coordinate over the sample, and \(Q\) is the two-dimensional scattering vector. The subscript \(r\) indicates that the averaging is over the spatial coordinate. A random distribution of point scatterers will produce variance plots \(V_N(Q)\) vs \(Q\) that contain no special peaks in \(Q\)-space. If local ordering is present, such as small regions of cubic close packing, peaks appear at those \(Q\) vectors where non-random coherent scattering occurs. The peaks are broadened in part because the scattering region is small, and because of the angular width of the objective aperture.

The variance tends to be maximal when the image point spread function (resolution) is comparable to the characteristic width of the structural correlations in the sample. This offers a simple method for estimating the structural correlation length scale. In the TEM, it is difficult to vary the resolution continuously, although in principle a suite of discrete objective apertures could be employed. The flexibility of the probe-forming electron optics in the scanning transmission electron microscope allows the coherent probe width to be varied over a limited range without the need to change apertures.

In the TEM, fluctuation electron microscopy has been found useful for studying medium-range order in amorphous semiconductors [6–10], carbons [11–13] and intermetallic glasses [14–17]. Here, we outline some recent advances made in the fluctuation microscopy technique using not just electrons, but also for x-ray and visible light microscopies for studying structural correlations at a wide range of length scales.

2. Detection of dilute random distributions of fullerenes in shungite

In a recent study we found that fluctuation microscopy can detect low concentrations of \(C_{60}\) molecules within a disordered partially graphitized matrix [13]. It was known that crystalline \(C_{60}\) (fullerite) can occur in shungite, which is a natural carbonaceous rock that can be almost 100% pure carbon [18]. Diffraction and high resolution bright-field imaging studies show that shungite is essentially a highly defective form of graphite [19]. On rare occasions, small crystals of \(C_{60}\) can be found [18]. The occurrence of \(C_{60}\) and \(C_{72}\) was confirmed by time-of-flight mass spectroscopy [18].

A fullerene molecule, within an otherwise disordered carbon matrix, is equivalent to medium-range order on the length scale of about 0.8 nm – the diameter of the \(C_{60}\) molecule measured carbon center to carbon center. Figure 1 compares a fragment of graphite with a \(C_{60}\) molecule. Although both are 3-coordinated carbon networks, with similar C-C bond distances, their diffraction patterns are distinct. Figure 2a shows profiles of the calculated mean diffraction

![Figure 1](image_url)

**Figure 1.** Comparison of a graphite fragment (left) and a \(C_{60}\) molecule (right). The graphite sheet is viewed down the 6-fold axis, and the \(C_{60}\) is viewed down a 2-fold axis.
patterns for graphite and C\textsubscript{60}. The calculations assume a resolution of 1.5 nm, which contributes to the peak broadening. These plots are radial line traces of the powder pattern created by incoherently adding the diffracted intensities from a large ensemble of randomly oriented fragments. Figure 2b shows the normalized variance of the ensemble of diffraction patterns.

C\textsubscript{60} has a peak near 7.1 nm\textsuperscript{-1} that does not appear in graphite. There is a dip in this region in the mean diffraction profile for both C\textsubscript{60} and graphite. \( Q \approx 7.1 \text{ nm}^{-1} \) corresponds to a spacing of \( \sim 0.14 \text{ nm} \), which is close to the C-C bond distance in graphite and C\textsubscript{60}. In graphite, reflections from this spacing (equivalent to \( \{3/2 0 0\} \) planes) are forbidden because adjacent C-C pairs are staggered by half a C-C bond distance, ensuring destructive interference. However, in C\textsubscript{60}, some orientations can generate significant intensity at this scattering vector. In a randomly oriented ensemble of C\textsubscript{60}, some molecules will be oriented correctly for strong scattering into this reflection, enhancing the speckle near \( Q \approx 7.1 \text{ nm}^{-1} \). Experimental FEM data (see Figure 3) confirm that samples of pure C\textsubscript{60} and shungite both exhibit pronounced peaks at the special \( Q \approx 7.1 \text{ nm}^{-1} \) diffraction vector, whereas textured graphite (not shown) and graphitic carbon black (shown) do not. High resolution bright-field images of shungite
Figure 3. Experimental normalized variance plots for a pure sample of C$_{60}$, a shungite sample, and a sample of carbon black. Both the shungite and C$_{60}$ samples show the same peak near $Q \approx 7.1$ nm$^{-1}$. The carbon black sample, which is a form of disordered graphite, shows only graphite peaks and no peak at $Q \approx 7.1$ nm$^{-1}$.

occasionally reveal isolated fullerenes with diameters less than 1 nm. Although those sightings are rare, they affirm the claims based on FEM data. We find that the $Q \approx 7.1$ nm$^{-1}$ peak can vary significantly over the shungite sample, indicating a heterogeneous distribution of C$_{60}$.

At present we do not know how to quantify the concentration of C$_{60}$ based on the FEM data alone. We do not know yet how to invert the variance data to obtain a structure. Our simulations show that the $Q \approx 7.1$ nm$^{-1}$ peak is essentially unique to C$_{60}$, or fragments thereof. For larger fullerenes, such as C$_{70}$ and C$_{72}$ etc, the peak moves significantly to higher $Q$, and can even vanish. The simulations indicate that the $Q \approx 7.1$ nm$^{-1}$ peak is associated with the curvature of the graphene.

Figure 4. Illustration of a thin disordered sample being scanned by a coherent double probe.

3. Interferometric fluctuation microscopy
In its original form, fluctuation microscopy uses a spatially coherent broadened probe to examine many sample volumes to obtain a signal that depends on atom pair-pair correlations. Another approach is to illuminate the sample with two smaller mutually coherent probes. Each probed region generates a microdiffraction pattern. The two diffraction patterns exhibit a Young’s
fringe intensity modulation wherever both patterns scatter significantly at the same scattering vector. If the diffracted wavefunctions under each probe are $\psi_A(Q)$ and $\psi_B(Q)$, and the probe separation is $R$, then the resultant diffraction intensity is

$$I = |\psi_A|^2 + |\psi_B|^2 + \psi_A^* \psi_B \exp(-2\pi i Q \cdot R) + \psi_A \psi_B^* \exp(2\pi i Q \cdot R).$$

(2)

The first two terms are the incoherent sum of the separate diffraction patterns from each probe. The second two terms are the interference terms due to the mutual coherence of the displaced probes. Figure 4 illustrates the concept of coherent double probes on a thin disordered sample.

Figure 5. Proof-of-principle optical data from a sample comprising a disordered (polycrystalline) monolayer of 20 $\mu$m diameter latex beads on glass. Two pinholes, of diameter 100 $\mu$m and vertical separation 400 $\mu$m, were scanned across the sample to collect 1600 diffraction patterns. (a) The mean diffraction pattern shows finely-spaced horizontal Young’s fringes. (b) The Fourier transform of the mean diffraction pattern shows the $\pm R$ satellite spots corresponding to the interference fringes.

We have conducted trial experiments with double probes using both x-rays and laser light. Figure 5a shows the mean diffraction pattern obtained with He-Ne laser light at 632.8 nm from a test sample comprising a monolayer of 20 $\mu$m diameter latex spheres on a glass slide. The sample was scanned across a coherently-illuminated vertically separated double pinhole, where each pinhole had diameter 100 $\mu$m and they were separated by 400 $\mu$m. The sample was about 200 $\mu$m from the pinholes, so propagation broadening effects are small. Optical microscopy shows that the typical ordered region in the sample was about 500 $\mu$m across. About 1600 diffraction patterns were obtained using step sizes of 50 $\mu$m along perpendicular x and y directions – this being the nominal Nyquist sampling rate for a single 100 $\mu$m pinhole. The mean pattern shows finely spaced horizontal interference fringes due to the approximately vertical separation of the two pinholes. Figure 5b shows the Fourier transform of this diffraction pattern. As expected, satellite patterns corresponding to the Fourier transforms of the cross terms $\psi_A^* \psi_B$ and $\psi_A \psi_B^*$ are centered at the $\pm R$ positions. In addition, satellite spots appear at the $\pm 2R$ harmonics. These are caused by non-linearity in the detected signal such as saturated pixels in the CCD camera, and shot noise, which has a non-linear dependence on intensity.

If one of the first-order satellite spots in the Fourier transform is masked by a circular aperture of radius less than $R$, and then back-transformed into $Q$-space, we obtain a filtered version of the diffraction cross terms $\Re\{\psi_A^* \psi_B\}$. The resultant interference patterns represent the cross correlation of the diffraction patterns under the two spatially separated probes. If the two diffracted signals have no features in common, then there is only a central spot. If the two
patterns have scattering features in common, then those features will persist in the interference pattern. For example, a perfectly ordered crystal will produce similar diffraction amplitudes under the two probes at all separations, provided the two probes are mutually coherent. The interference patterns will resemble the diffraction pattern from a single probe.

Figure 6 shows optical interference patterns for He-Ne laser light ($\lambda = 632.8$ nm) for two test samples made from monolayers of 20 µm latex spheres on a glass slide, similar to that used in Figure 5. The double pinholes used were 100 µm diameter and separated by $R = 100$ µm, 200 µm, 400 µm, 600 µm and 1000 µm. The pinholes were $\sim 200$ µm from the sample to minimize the beam dispersion at the sample due to pinhole diffraction. The top row is for a sample that has a characteristic polycrystalline domain size of about 500 µm. The bottom row is for a similar sample that had a domain size of about 300 µm. The five columns correspond to the five probe separations, increasing in $R$ from left to right. The patterns at $R = 100$ µm (left) lack circular symmetry because the masking aperture does not fully isolate the contributions from the cross terms. As expected, the cross-correlated patterns for the more disordered sample (lower row) decay faster with probe separation than do the patterns for the more ordered sample (top row). The decay rate appears to be faster at the higher $Q$ values. The zero order intensity remains approximately constant, indicating that the two probes remain mutually coherent.

The optical experiments were conducted as proof-of-principle experiments for synchrotron x-ray experiments. In addition, we have conducted simulations using models of disorder, such as that shown in Figure 4. Both the optical experiments and the modeling indicate that this interferometric fluctuation microscopy method holds much promise for obtaining quantitative details about the order length scales in a sample.

For optical and electron experiments, focused double-probes can be formed using optical devices such as Fresnel biprisms. Biprism wires are already used for electron holography experiments [20]. In fact, interferometric fluctuation microscopy as described here is a form of holography. However, unlike normal holography, the reference beam is not an unscattered
beam, but a reference scattered beam from another area of the sample. At present, it is difficult to get two coherent probes close enough together using a Fresnel biprism wire. To probe medium-range order, the probes need to be as close as 0.5 nm, or even closer. With improved electron optics, it may be possible to overcome this practical limitation.

Figure 7. Calculations of the mean diffraction pattern obtained when a coherent double electron probe is scanned across a model of disordered silicon. Young’s interference fringes appear wherever there is significant overlap in diffraction amplitude from both probes. In this model the probe diameter (resolution) was 0.5 nm. The probe separations were $R = 0.1$ nm, 0.3 nm, 0.5 nm, 1.0 nm, 1.5 nm and 2.0 nm.

Figure 7 presents simulations of the mean kinematical diffraction pattern obtained when a focused electron probe pair are scanned across a model of disordered silicon. In the simulation, the probe widths are 0.5 nm. Six separations are shown, corresponding to $R = 0.1$ nm, 0.3 nm, 0.5 nm, 1.0 nm, 1.5 nm and 2.0 nm. The model is for amorphous silicon containing 4096 disordered atoms in a cubic cell 4.52 nm wide that is periodically repeated. When $R \geq 0.5$ nm, the central diffraction disks show strong interference fringes because both probes have strong zero-order beams. Interference fringes persist in the diffraction rings because there is significant structural correlation between the material under each probe. As the probe separation increases, the fringe spacing decreases, and the fringe modulation in the diffraction rings diminishes due to the fact that the two probes tend to be exploring inherently different structures more often. However, the fringes do not disappear completely since both probes can scatter into the same diffraction vector because of random structural correlations.

Double probe electron experiments have not yet been conducted because of the difficulty in getting the probes close enough together using existing Fresnel biprism wires and associated optics. Experiments have been done using both optical probes with He-Ne lasers, and with coherent synchrotron x-rays. For x-ray experiments, double pinholes have been constructed with diameters as small as 0.1 µm. Alternatively, two zone plates can be placed in close proximity and the lateral separation can be varied continuously. X-ray zone plates tend to be transparent,
and thus they both can produce well-focused beams at the sample. The zone plates can be slid over one another, making them almost coplanar. Their separation can easily lie well within the depth of focus of each zone plate so that both probes can be considered sufficiently well focused on the sample. At present, the x-ray experiments are not capable of studying structures at the atomic scale. However, interferometric x-ray fluctuation microscopy is potentially useful for studying ordering in nanoscale materials.

There are still important details to be worked out in these experiments. For example, poor signal-to-noise in the scattering generates higher order harmonics in the Fourier transform that will complicate the analysis. However, it is clear that this interferometric approach can provide important additional information about pair-pair structural correlations.

4. Conclusions

Fluctuation microscopy is an evolving technique. We have shown that it is a sensitive method for detecting and identifying dilute distributions of macromolecules within a matrix. The matrix need not be disordered. In shungite, trace amounts of C\textsubscript{60} were detected in a disordered graphitic carbon matrix. Modeling studies show that for best sensitivity, the macromolecule should be capable of scattering strongly into scattering vectors that have weak intensity from the matrix.

The sensitivity to medium-range order arises from the fact that the normalized variance depends on higher order correlations, up to 4-body terms. Theory shows that the 4-body terms appear as pair-pair correlations. Here we show that the use of coherent double-probes in interferometric fluctuation microscopy may allow us to explore the pair-pair correlations more systematically. However, to do this in the TEM, the optics associated with the Fresnel biprism wires will need modification to get the probes close enough together.

Interferometric fluctuation microscopy potentially increases the information obtainable from disordered samples, and will help make the technique more accessible to theoretical modeling.

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