Fluctuation Microscopy: What is it?

Michael M. J. Treacy

Dept. of Physics and Astronomy, Arizona State University, Tempe

mike_treacy@mac.com

Fluctuation microscopy is the enigmatic name given to an otherwise straightforward technique for studying medium range order in highly disordered materials. By medium range, we mean atomic ordering at length scales within the range 0.5 ~ 2.0 nm, where traditional imaging and diffraction techniques have the most difficulty detecting structural correlations in amorphous materials. Puzzlement over fluctuation microscopy generally arises not because of the "microscopy" part of the name, but because of the "fluctuation" part. What, exactly, is fluctuating? And, why does it fluctuate?

The fluctuations are simply the variations in scattering between small sub-volumes within a thin sample. These are usually not time-varying fluctuations (although they could be), but instead they are the position-varying fluctuations in local diffraction.

The next question might be; how do we distinguish between the scatterings from one sub-volume relative to another sub-volume at a different location in the sample? That is where the "microscopy" part comes in, the ability to resolve the scattering between different sample regions.

Perhaps the simplest way to explain the principles underpinning fluctuation microscopy is to consider an idealized experiment, as it would be conducted in a scanning transmission electron microscope (STEM). Figure 1 depicts such an idealized experiment. When the electron probe is focused onto a thin sample, centered at location (x, y), a sample volume is being explored, defined by the area of the probe's illumination disk times the thickness. The probe width is related to the microscope resolution, which in turn is governed by the objective aperture width (the smaller the aperture, the wider the probe) and the objective lens aberrations. We assume that the illumination across the probe is coherent, but it does not need to be uniform. Atoms within the probed volume scatter electrons. We are interested in the elastic coherent scattering from the volume. If the sample is crystalline, coherent diffraction disks emerge from the volume and a microdiffraction pattern can be collected revealing the underlying symmetry (ordering) of the diffracting volume. If the probe is significantly wider than the unit cell, the diffraction disks do not overlap, and the microdiffraction pattern does not change as the probe is scanned across the sample (assuming uniform sample thickness, and no strain and no defects etc.). If the sample is polycrystalline however, the diffraction pattern remains unchanged only as long as the probe stays on a given microcrystalline grain. When the probe moves onto a new grain, the microdiffraction pattern changes accordingly. During a typical scan of the sample, the probe will encounter many different grains, and the microdiffraction pattern will be observed to *fluctuate* as the probe progresses. Individual microdiffraction patterns from each sample location (x, y) will exhibit a pattern of disks or spots, with intensity distribution $I_{x,y}(q_x, q_y)$. The *mean* diffraction pattern over many grains is just

$$\langle I(q_x, q_y)\rangle = \frac{\sum_{x,y} I_{x,y}(q_x, q_y)}{N}$$

where N is the number of probed sample volumes. The mean will tend to show continuous rings similar to a powder pattern. Fluctuations between diffraction patterns are best revealed by computing the normalized *variance* of the patterns, which is found from

$$V(q_x, q_y) = \frac{\langle I^2(q_x, q_y)\rangle}{\langle I(q_x, q_y)\rangle^2} - 1 \,.$$

$\langle I^2(q_x, q_y)\rangle$ is the mean of the *square of the intensity*. In this digital age, the mean and the normalized variance are easily computed. The reason for the normalization is to eliminate the scattering intensity fall-off with increasing angle due to the atomic scattering factors.

The normalized variance pattern of a polycrystalline material looks like a high-contrast diffraction pattern, with rings exactly where the diffraction rings occur. However, this is deceptive. The variance pattern is not a diffraction pattern. It would be essentially featureless if the sample were a perfect single crystal. The normalized variance pattern is a remarkably sensitive indicator of those diffraction vectors whose intensity is fluctuating the most.

Fluctuation electron microscopy (FEM) did not originate as a STEM technique. In fact most FEM experiments are conducted in the TEM by collecting dark-field images of the sample (see Figure 2). It turns out that, thanks to the reciprocity principle, the data collected in the TEM is equivalent to that in the STEM. In essence, the STEM experiment described above collects microdiffraction intensity data $I(q_x, q_y)$, each pattern being at a fixed location x, y. Microdiffraction patterns are collected over all sample locations x, y to reveal the fluctuation map (normalized variance). In the TEM on the other hand, speckly dark-field image intensity information $I(x, y)$ is collected at fixed q_x, q_y beam tilt. Images are collected

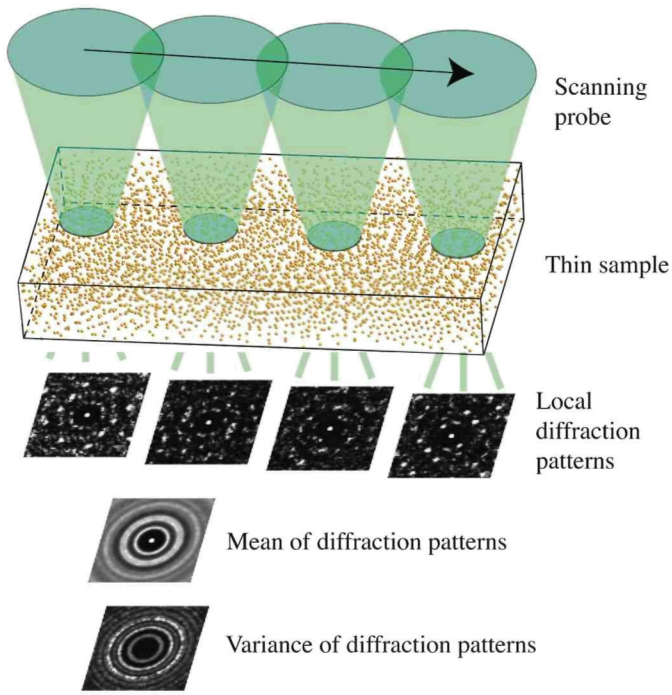

Figure 1. Depiction of an idealized STEM experiment on a disordered material. As the probe is scanned across the sample, the microdiffraction pattern (which is speckly) changes. A measure of the speckliness is the intensity variance of all the microdiffraction patterns collected from the sample. The variance reveals those diffraction vectors (structural length scales) that fluctuate the most.

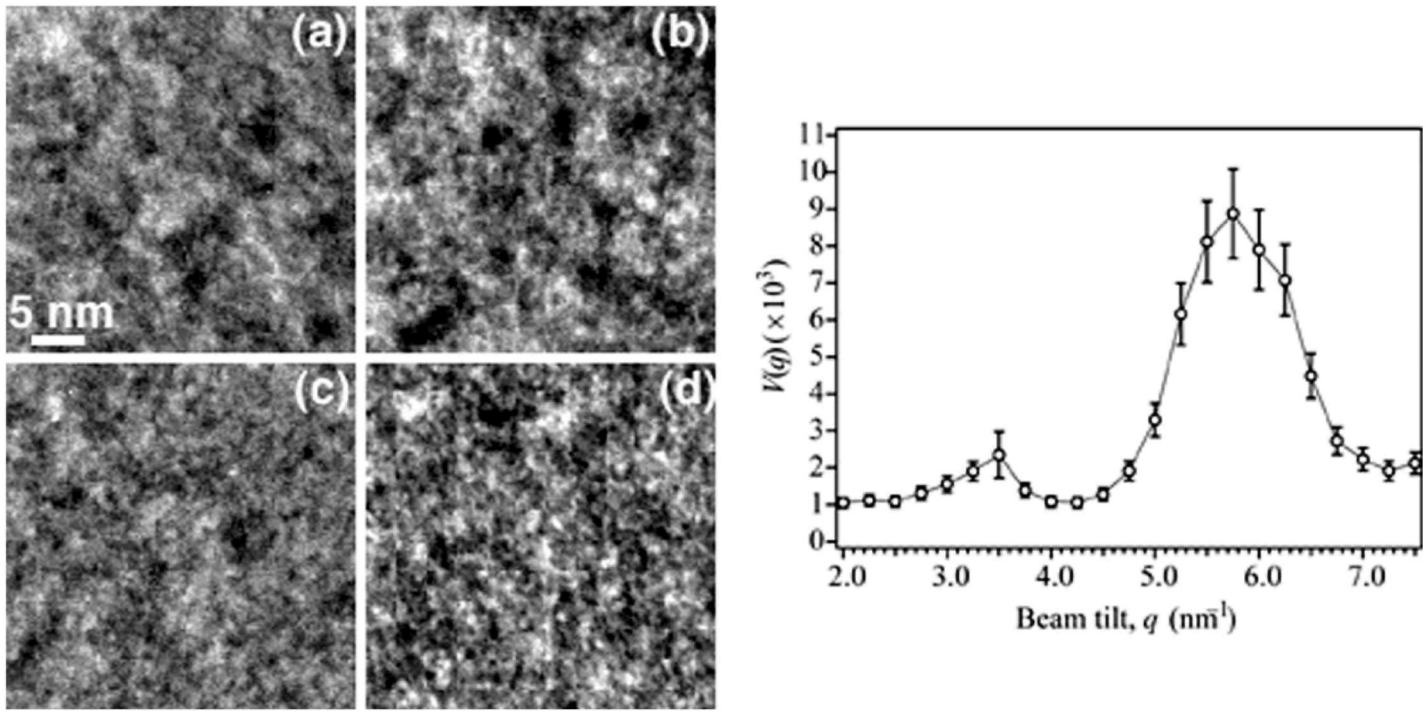

Figure 2. Left: Series of TEM dark-field images of 23 nm thick amorphous Ge. The illumination tilt angle q increases from (a) to (d). The speckliness of the images changes with q. Speckliness can be estimated by the image intensity variance, which is plotted on the right as a function of q. The two prominent peak locations indicate that cubic Ge 111 reflections are contributing to the first peak, and cubic Ge 220 and 311 reflections are contributing strongly to the second peak. The peaks indicate the presence of medium range order in this sample.

over a range of q_x, q_y beam tilts to sample all diffraction vectors. The sampling volume in the TEM dark-field images is defined by the microscope resolution, which is equivalent to the STEM probe width. Thus, in principle, both TEM and STEM approaches collect a 4-dimensional data set of intensities $I\left(x, y, q_x, q_y\right)$. The plot shown in Figure 2, of normalized variance V versus q, is equivalent to a line trace through the variance image depicted in Figure 1.

The power of FEM does not come from its ability to study polycrystalline materials – those can be studied well by conventional imaging and diffraction methods. FEM excels in studies of disordered materials where the ordering length scale is in the 0.5 – 2.0 nm range. Topologically ordered regions tend to be strained, and are referred to as paracrystallites. Paracrystallites rarely show up unambiguously in images, and are generally diffraction amorphous. However, FEM speckle statistics can reveal their presence, as in Figure 2.

FEM is being applied by a number of groups to a wide range of materials problems, including amorphous tetrahedral semiconductors, disordered carbons, metallic glasses, amorphous mineral phases, amorphous oxides (*e.g.* SiO_2) and phase change memory alloys (*e.g.* $Ge_2Sb_2Te_5$).

Fluctuation microscopy is not unique to electrons. In principle, the technique can be applied to optical microscopy for studying ordering at longer length scales (> 5μm). An X-ray version, appropriately termed fluctuation X-ray microscopy (FXM), is currently being developed at the Advanced Photon Source synchrotron facility at the Argonne National Laboratory for studying medium range ordering in self-assembled nanoscale materials at 50 nm – 1 μm length scales. ■

References:

(1) M.M. J. Treacy and J. M. Gibson, Variable Coherence Microscopy: A Rich Source of Structural Information from Disordered Materials, Acta Cryst. A52 212–220 (1996).

(2) M. M. J. Treacy, J. M. Gibson and P. J. Keblinski, Paracrystallites found in evaporated amorphous tetrahedral semiconductors, J. Non-Cryst. Solids, 231 99–110 (1998).