Advanced Photon Source Activity Report 2003: Characterization of medium-range order in noncrystalline systems by fluctuation x-ray microscopy

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Introduction

In recent years, materials research has increasingly focused on developing a better understanding of the disordered state of matter. Much of our understanding amorphous materials has depended upon the atomic pair distribution function (PDF) obtained from diffraction experiments. However, the PDF method has poor sensitivity to medium-range order (MRO), the characterization of which is a long standing problem. Recently, fluctuation electron microscopy (FEM) was developed and successfully used for probing MRO in amorphous materials [1-3]. This technique gains its sensitivity to MRO by examining fluctuations in coherently scattered (speckle) intensity patterns from very small sample volumes, on a length scale determined by the illuminated radius or associated imaging resolution. The speckle variance depends on two-, three- and four-body atomic correlation functions, whereas the average, which is just the diffracted intensity, depends only on the two-body PDF. Higher order correlation functions are more sensitive to MRO [4].

In the x-ray regime, many techniques exist to probe long- and short- range order in matter, in real space by imaging and in reciprocal space by diffraction and scattering. The average intensity obtained from scattering and diffraction experiments is routinely inverted to give the atomic PDF. At present, no x-ray technique effectively probes MRO. By comparison to electrons, x-rays provide access to longer length scales due to their longer wavelengths and offer greater sample penetration with less radiation damage, as well as elemental and chemical sensitivity through resonant effects. Consequently, we are developing fluctuation x-ray microscopy (FXM) at the 2-ID-B soft x-ray beamline to study MRO in bulk samples, solutions and films at nanometer and larger length scales [5]. Compared to FEM, FXM is better suited to materials with larger characteristic length scales such as polymers, biological macromolecules and their complexes, as well as other nanostructured materials, nanocomposites and hybrids.

Methods and Materials

Working definition of MRO

It is helpful here to consider a working definition of MRO [5]. As shown in Fig. 1, consider a unit (an atom or other extended object). Suppose the distance between the units is d and correlation length of these units (the distance over which they reveal orientational or other correlated ordering) is L. Then a working definition of medium-range order is $5 \le L/d \le 50$. At short length scales, $L/d \le 5$, we have short-range order that is readily detected from the PDF. At $L/d \ge 50$ we have well-established long-range order that can be examined by Bragg diffraction.

FXM method

Fluctuation microscopy is closely related to photon correlation spectroscopy (PCS), but it examines fluctuations in space rather than in time. FXM examines variations in coherent x-ray speckle patterns measured as a function of illumination

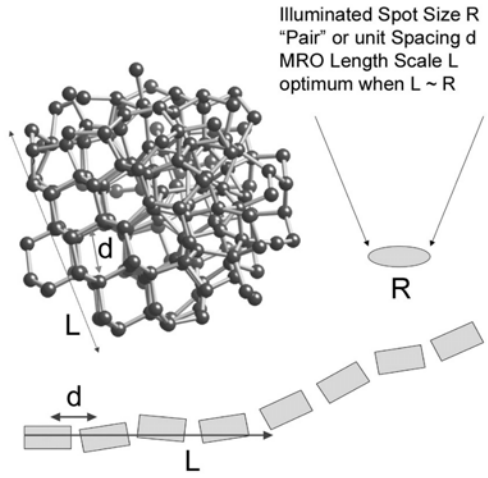

Fig. 1. *Medium-range order definitions*

radius R_0 and sample position $\{\vec{r}_n\}_{n=1}^{N}$, where *N* is the number of the sample scan points [6]. The speckle variance can be expressed as

$$V(R_0,\vec{q}) = \frac{\left\langle I^2(\vec{r}_n,R_0,\vec{q})\right\rangle}{\left\langle I(\vec{r}_n,R_0,\vec{q})\right\rangle^2} - 1 \quad , \qquad (1)$$

where $\vec{q}$ is the momentum transfer with magnitude $|\vec{q}| = 4\pi\sin(\theta)/\lambda$, and < > indicates averaging over all speckle patterns obtained from the sample scan area. The variance V($\vec{q}$) gives information about the degree and distribution of MRO in the sample. The variance $V(R_0)$ yields the correlation length. Systematically measuring V($\vec{q}$, R_0) produces a fluctuation map that contains quantitative information about MRO within the sample.

Materials

To demonstrate the method we performed FXM measurements on disordered films of polystyrene latex spheres that could serve as a model for a dense random packed glass. The films were made by drying an aqueous suspension of sonicated, highly mono-disperse, 277 nm diameter latex spheres (Duke Scientific) onto silicon nitride membranes.

Experimental results

We chose the 2-ID-B beamline [7] at the Advanced Photon Source to develop FXM. The 2-ID-B beamline is optimized for high coherent flux and coherent scattering experiments, with a unique ability to deliver tunable, highly coherent 1-4 keV x-rays. X-ray energies of a few keV are well suited for studying these latex samples, which were typically 7 μm thick.

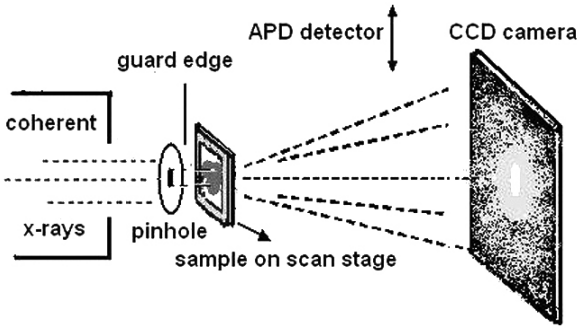

Fig. 2. *Schematic of the FXM setup at 2-ID-B.*

A schematic of the setup is shown in Fig. 2. In these experiments we used 1.83 keV x-rays and a modified scanning transmission x-ray microscope configuration. The illumination radius was controlled by selecting pinholes of 0.8, 1.6, 5.5, and 10 µm in diameter; the pinhole sizes were measured from their diffraction patterns. An avalanche photodiode was inserted downstream of the sample to locate regions of good uniformity by measuring the transmission as the samples were scanned. A CCD camera mounted on a two-circle goniometer was used to record the speckle patterns. The sample-CCD distance was 1 m, which gave sufficient resolution to resolve individual speckles and provided sufficient Q range to determine the characteristic length scale of the samples. By scanning the sample and exchanging pinholes, we obtained speckle patterns over a range of sample positions with various illumination radii.

Fig. 3 shows the mean and variance obtained from the speckle data. The mean image is equivalent to the small-angle scattering pattern from the sample, consistent with a disordered assembly of spherical balls. In contrast, the variance, shown on the right of Fig. 3, reveals sharp spots indicative of MRO. As can be seen, FXM is far more sensitive to MRO than conventional small-angle scattering.

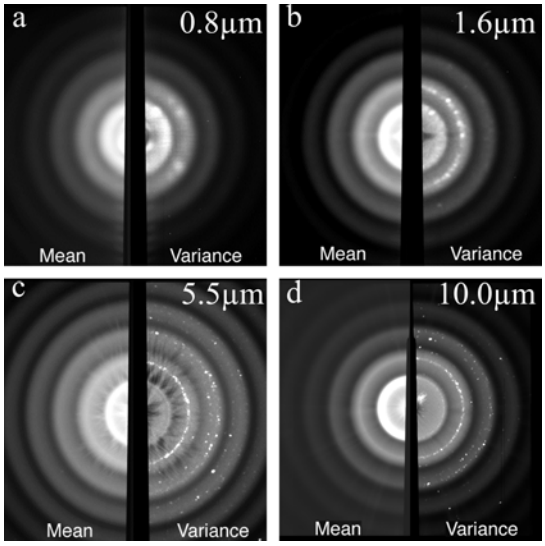

Fig. 3. *Mean (left) and variance (right) data from ~4000 speckle patterns obtained from a latex sphere sample.*

For a completely random sample, the variance is zero. For a heterogeneous structure with local ordering, such as randomly oriented ordered clusters, the variance is non-zero and depends on the sampling conditions. When the illumination size is comparable to the size of the ordered cluster, the variance is maximized. If the illumination size is smaller or larger, the structures included within each volume are similar, leading to a decrease of the variance. Use of a range in illumination sizes allows extraction of the correlation length.

As shown in Fig. 4, the variance grows with increasing illumination size until 5 µm then decreases using the 10 µm pinhole, implying a correlation length on the order of ~5 µm (~18 sphere diameters) for this latex sphere "glass". The correlation length can be more accurately obtained using the quantitative theory developed by Gibson *et al.* for FEM [8].

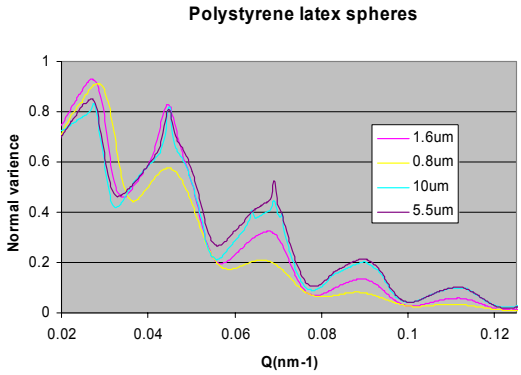

Fig. 4. *Azimuthally-integrated $V(q, R_0)$ for the latex spheres.*

Conclusions and discussions

Our experiments demonstrate that FXM is valuable for studying MRO in disordered materials and is more sensitive than small-angle scattering to partial ordering in the materials. We would like to point out that this technique is still under development. Our current FXM pinhole setup at 2-ID-B allows us to study ordering in systems with structural units of sizes ~100 nm–2 µm. With future development of nanofocusing optics, we will be able to study length scales of 10 nm–100 nm and correlation lengths of 50 nm–500 nm. This length-scale range is particularly interesting for a wide range of materials, such as polymers, biological systems, self-assembled nanostructures, nanocomposite and hybrid materials. X-ray optics improvements for focusing hard-x-rays into the nanometer range would make this a very exciting frontier for the study of inorganic glasses and disordered materials.

Acknowledgments

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References

[1] M.M.J. Treacy, J.M. Gibson, Acta Cryst. **A52,** 212 (1996).
[2] J.M. Gibson, M.M.J. Treacy, Phys. Rev. Lett. **78,** 1074 (1997).
[3] P.M. Voyles., J.E. Gerbi, J.M. Gibson, J.R. Abelson, Phys. Rev. Lett. **86,** 5514 (2001).
[4] M.M.J. Treacy, P.M. Voyles, J.M. Gibson, J. Non-Cryst. Sol. **150,** 266 (1999).
[5] L. Fan, I. McNulty, D. Paterson, M.M.J. Treacy, J. M. Gibson, Nucl. Instrum. Methods B, accepted
[6] L. Fan, I. McNulty, D. Paterson, M.M.J. Treacy, J. M. Gibson, Mat. Res. Soc. Symp. Proc., accepted
[7] I. McNulty, et al., Rev. Sci. Instrum. **9**, 67 (1996), CD-ROM.
[8] J.M. Gibson, M.M.J. Treacy, P.M. Voyles, Ultramicroscopy, **83,** 169, (2000).