Fluctuation Microscopy in Scanning Electron Diffraction: New Analysis of Nanoscale Ordering in Disordered Materials

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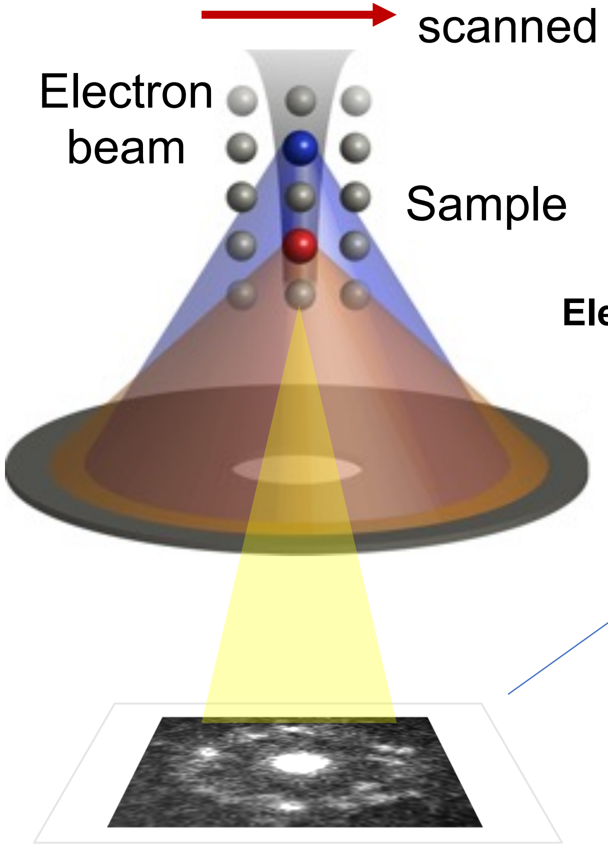
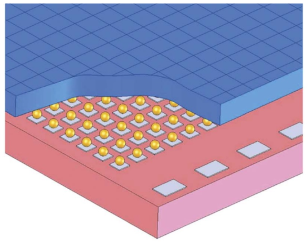
Overview

- Background
    - 4D-STEM (or scanning electron nanodiffraction)
    - Intensity variance analysis
    - Angular correlation function
    - 2D histogram of MRO size
- Medium range ordering in metallic glasses and their connection to mechanical properties
- Nanoscale ordering in semiconducting polymers
- Nanoscale intermediates in ALD-grown TiO_2 films for energy applications.

Electron Nanodiffraction with a Fast Pixelated Detector



Electro Microscopy Pixel Array Detector (EMPAD)



Tate et al., Microsc. Microanal. 22, 237 (2016)

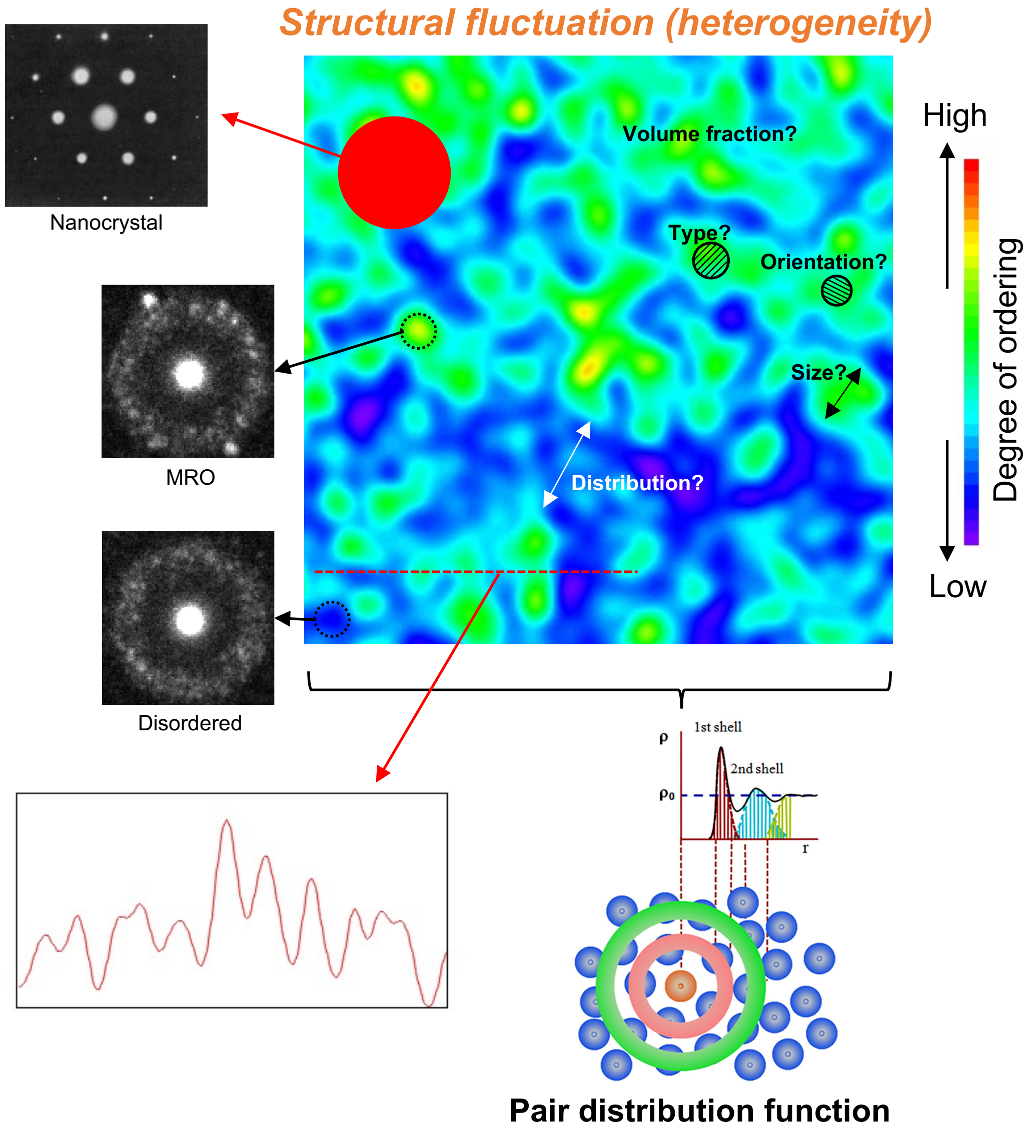
Variance (V) analysis

Angular correlation analysis

2D histogram of MRO size

- Small probe size (~ 1 to 5 nm) – nanoscale ordering can be detected.
- Medium range ordering (MRO).
- *k* space resolution and range are more limited.
- EMPAD provides new ways to determine the details of the nanoscale ordering (4D-STEM or scanning electron diffraction).

Medium Range Ordering

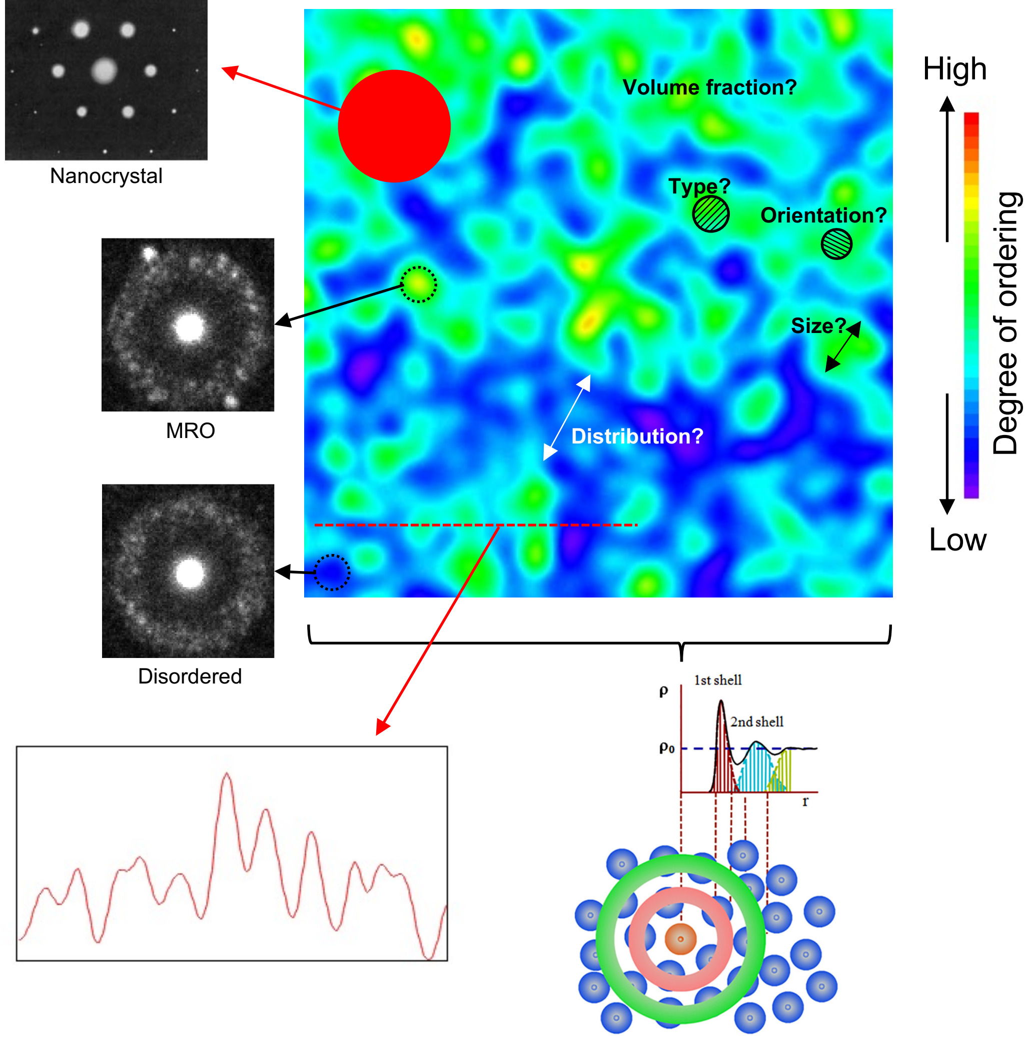


Yue et al., Mat. Res. (2017)

- Nanoscale medium range ordering (MRO) constitutes structural fluctuation (or heterogeneity) in disordered materials.
- MRO is different from nanocrystal – that would be a composite.

Medium Range Ordering

Structural fluctuation (heterogeneity)

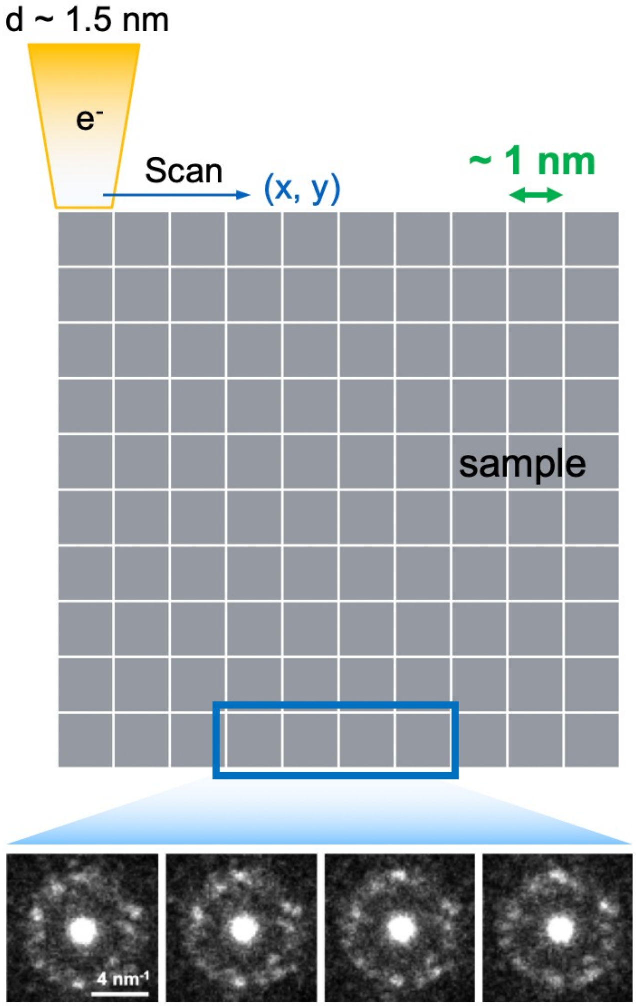


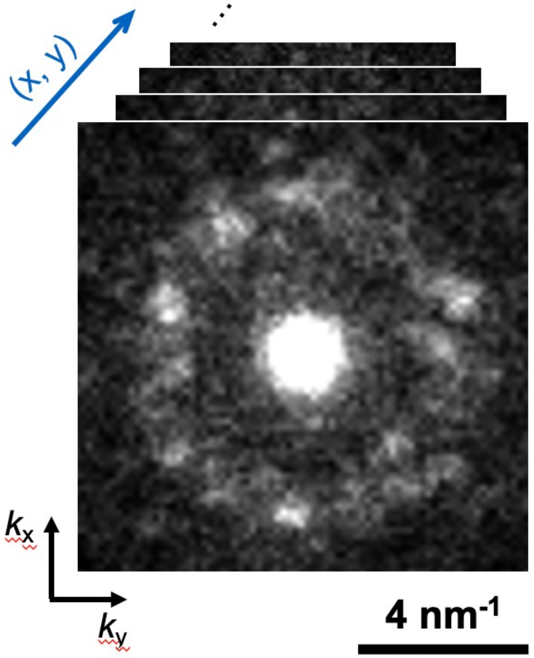
Pair distribution function

`Yue et al., Mat. Res. (2017)`

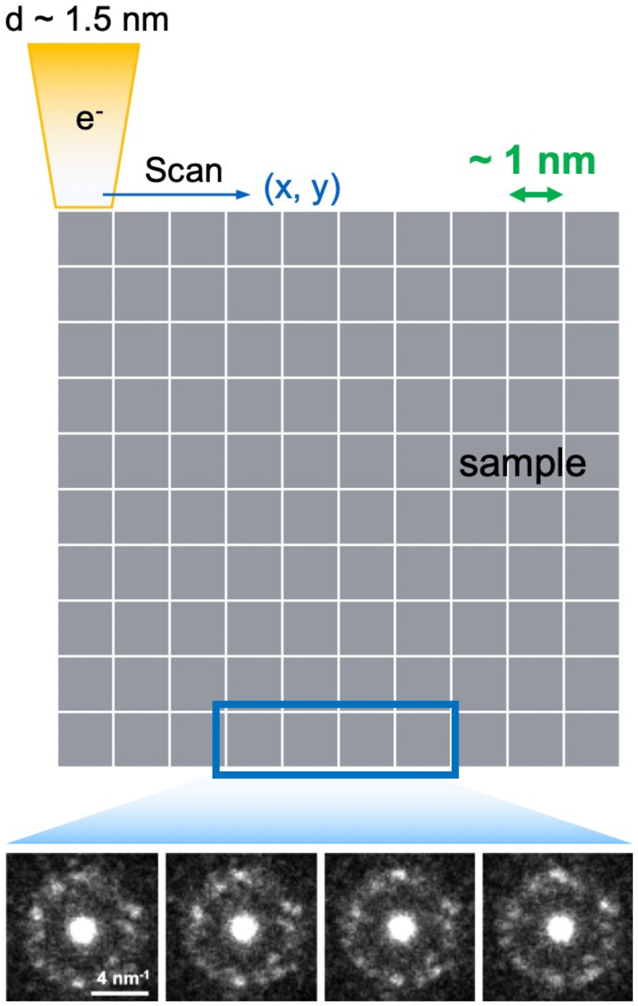
- Many unknowns about MRO because it's difficult to measure. e.g. Pair distribution function only shows information averaged over a large area, and the heterogeneity is typically not resolved.
- What kind of aspect MRO is important in general?
- *Type, size, distribution, orientation, and volume fraction of MRO.*
- They can be separate parameters and important to understand.

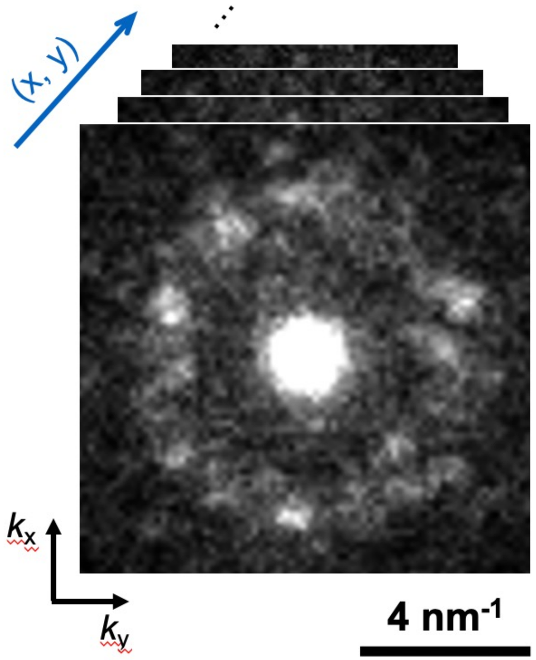
4D-STEM + Fluctuation Microscopy

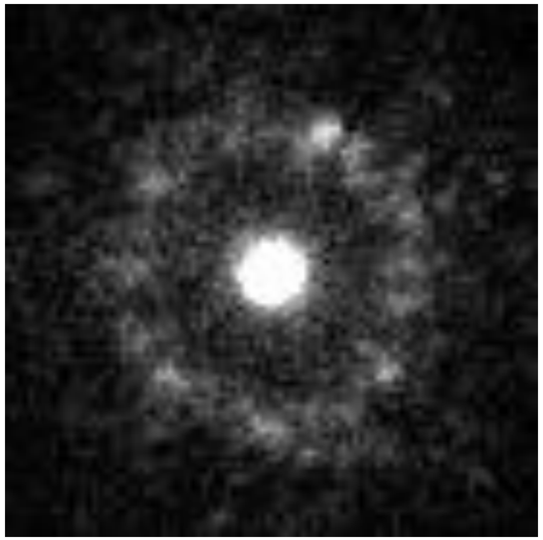




4D-STEM + Fluctuation Microscopy

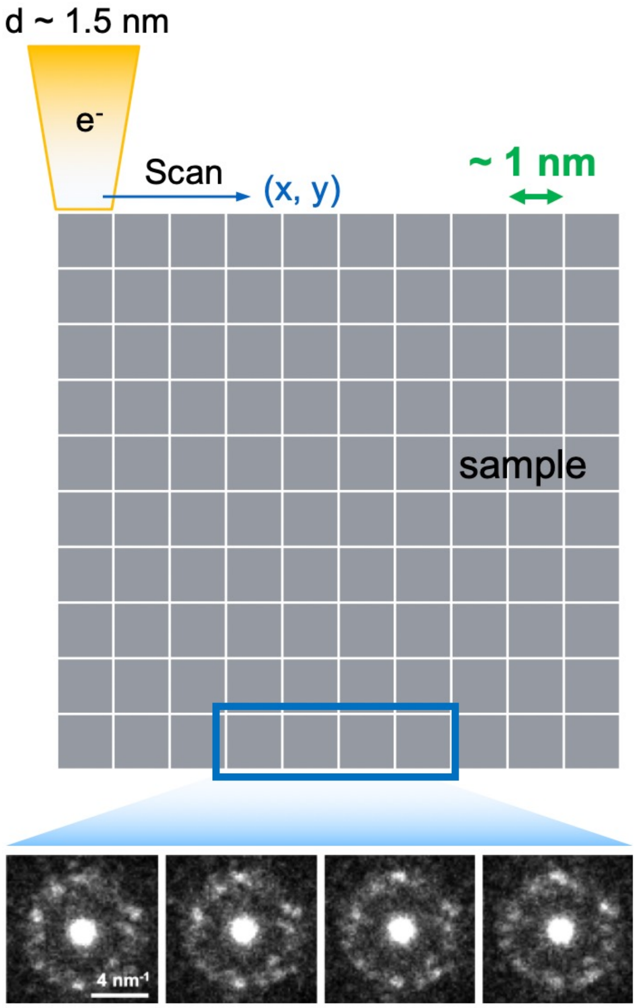


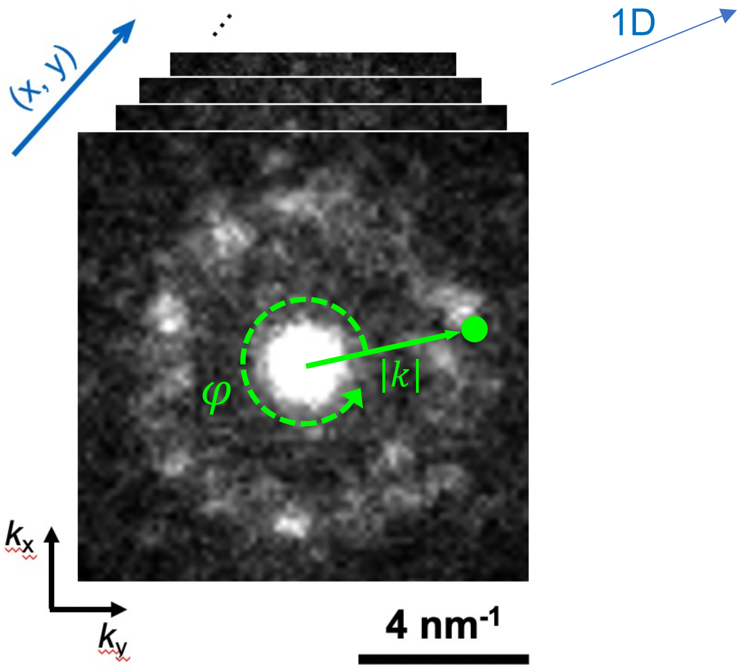


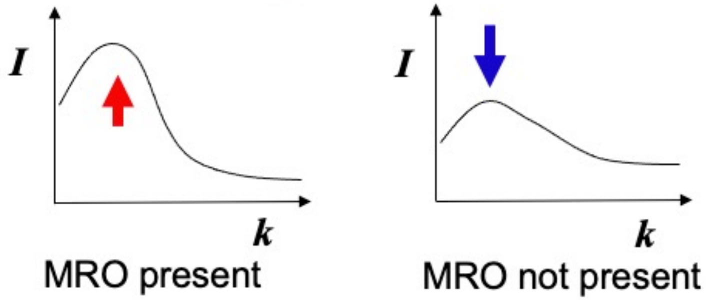


$I(x, y)$

Variance Analysis







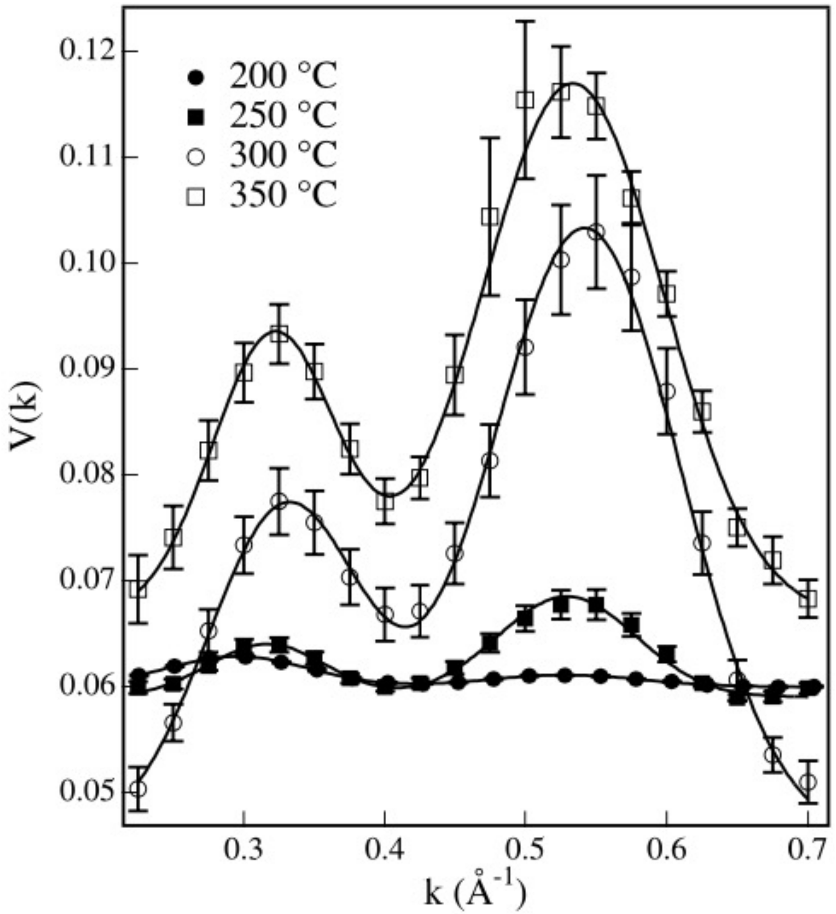
$$V(k,R)=\frac{\langle I^2(k,R,\mathbf{r})\rangle_{\mathbf{r}}}{\langle I(k,R,\mathbf{r})\rangle_{\mathbf{r}}^2}-1$$

V : Variance
I : Diffraction Intensity
k : Scattering vector magnitude
R : Probe size (resolution)
r : Position on the sample area

V shows the degree of the MRO with a certain structure (k)

Variance Analysis

$$V(k,R)=\frac{\langle I^2(k,R,\mathbf{r})\rangle_{\mathbf{r}}}{\langle I(k,R,\mathbf{r})\rangle_{\mathbf{r}}^2}-1$$



Amorphous silicon

Voyles et al., Journal of Non-Crystalline Solids 293, 45 (2001)

What can the intensity variance (*V*) show?

- *V*, typically as a function of *k*.
- *V* relates to 3 and 4 body correlation function (g_3, g_4).
- High *V* means high degree of MRO.
- *k* peak position relates to the type of MRO.

Average dark-field image intensity

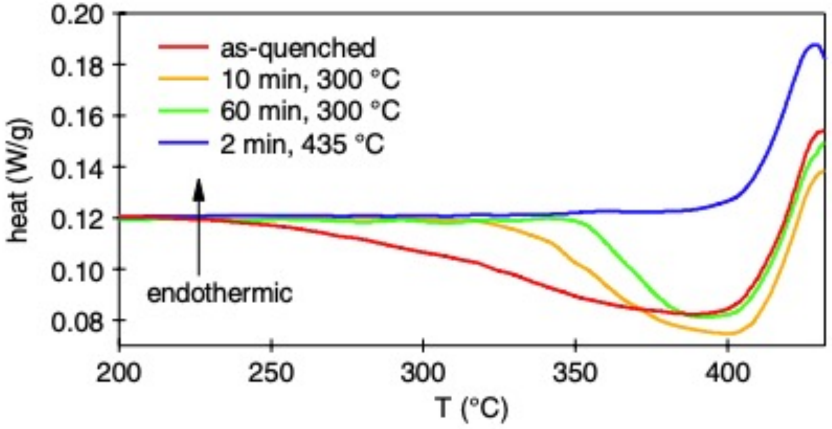
$$\langle I(k,Q)\rangle=\pi^2Q^2f^2(k)\lambda^2\rho_0t\left(1+\rho_0\int d^3r\cdot g_2(r)F_k(r)A_Q(r)\right)$$

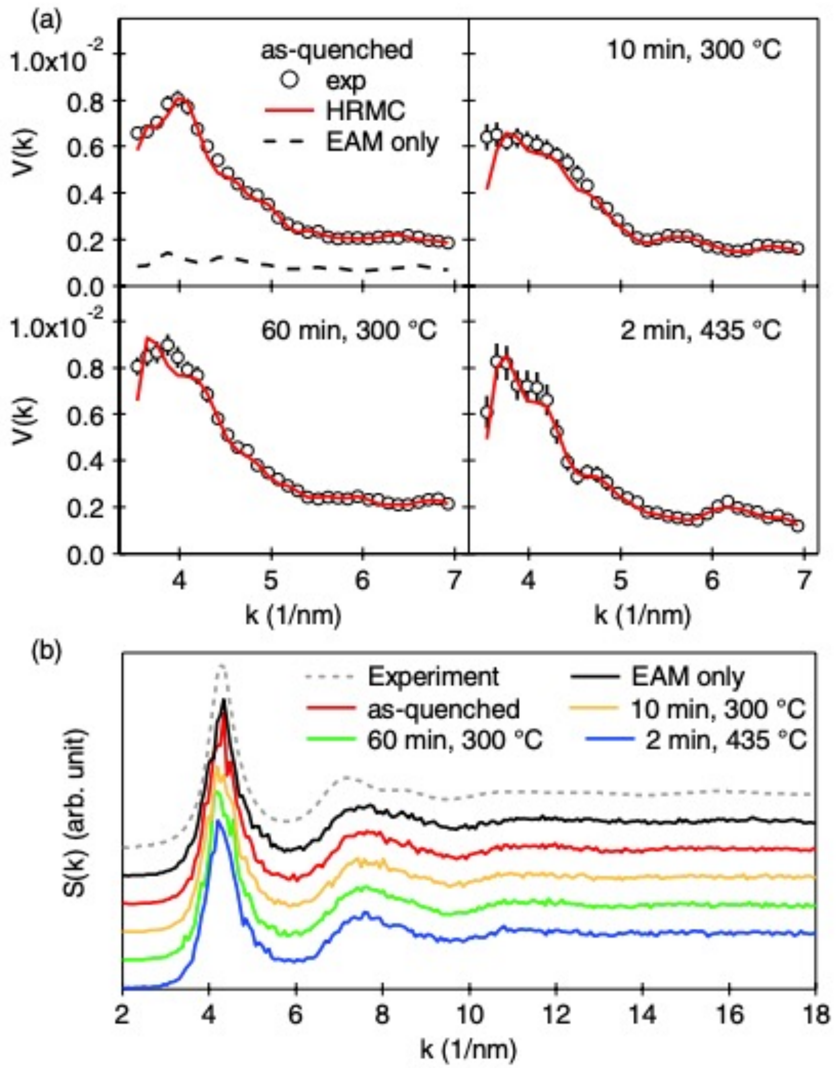
DF image intensity 2nd moment:

$$\langle I^2(k,Q)\rangle=C_1\rho_0t+C_2\rho_0^2t\Gamma_1\left[g_2(r_1)\right]+C_3\Gamma_2\left[g_3(r_1,r_2)\right]$$
$$+\frac{128f^4(k)\rho_0^4t}{\pi^3\lambda^2Q^6}\int d^3r_1d^3r_2d^3r_3\cdot g_4(r_1,r_2,r_3)F_k(r_1)F_k(r_2)$$
$$\times A_Q(\sigma_1)A_Q(\sigma_2)A_Q(\sigma_3)A_Q(\sigma_1-\sigma_2)A_Q(\sigma_1-\sigma_3)A_Q(\sigma_2-\sigma_3)$$

(F_k : coherence volume; A_Q : microscope point spread function)

Variance Analysis

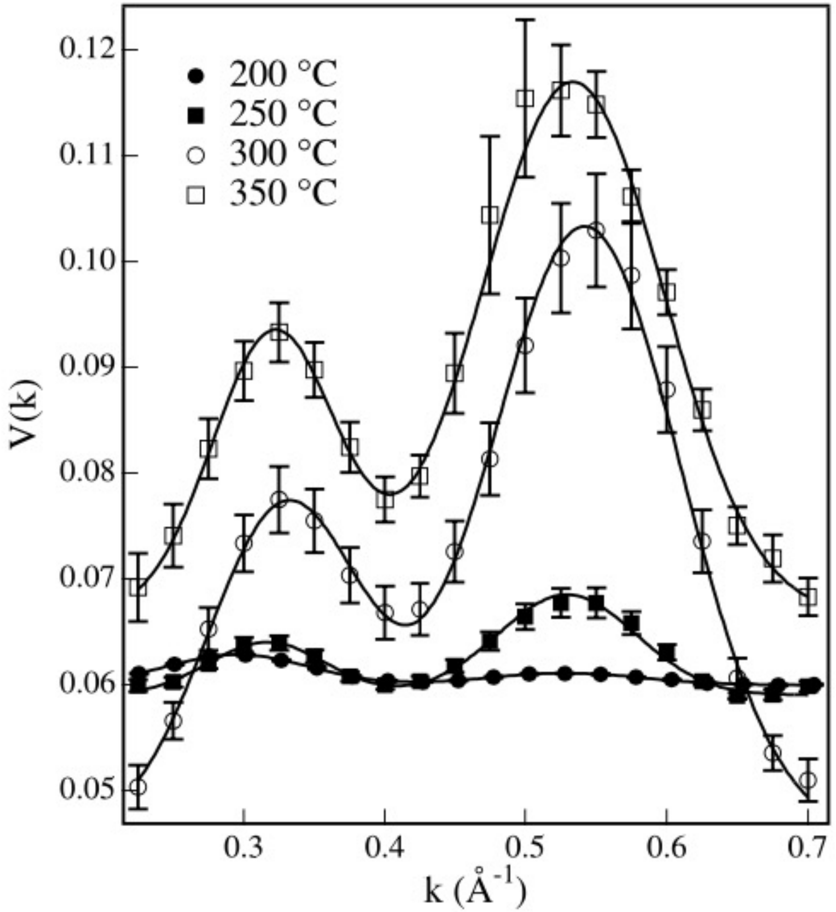




- Structural relaxation in $Zr_{50}Cu_{45}Al_5$ metallic glass.
- DSC shows the relaxation by annealing.
- Changes are detected in V(k), but not in PDF.

Hwang et al., Physical Review Letters 108, 195505 (2012)

Variance Analysis



Amorphous silicon

Voyles et al., Journal of Non-Crystalline Solids 293, 45 (2001)

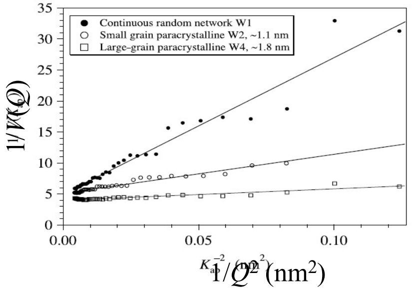
Limitations:

- *V* combines many MRO aspects: size, degree of ordering (i.e. how much ordering is close to that of crystals), and number density.
- Reduced to 1 dimension – rotational symmetry information lost. Detailed structure may be difficult.
- In electron diffraction, V tends to include experimental artifacts, such as from the sample thickness, surface roughness, voids, and etc.

Models to Interpret V(k) data

Pair persistent model

Gibson et al., *Ultramicroscopy* (2000)

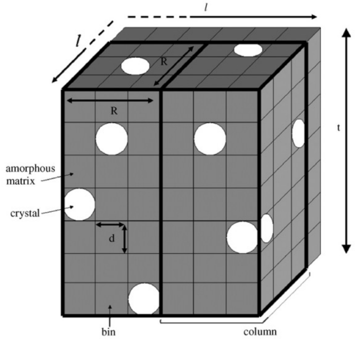


- Correlation length, *Λ*.
- Assumes g_4 as Gaussian with width *Λ*. (*Λ* ≈ radius of MRO).
- Predicts $1/V(Q)$ vs. $1/Q^2$ to be linear → *Λ* can be calculated.

Amorphous / nanocrystal analytical model

Assumes $R > d$.

$I \approx$ (# of atoms in nanocrystal) at Bragg cond.



$$V \approx \left\{ \frac{\frac{\pi}{6} C_{hkl} \Phi d^2 \left(d^3 \rho\pi/6\right)^2}{t\left[C_{hkl}\Phi\left(d^2\rho\pi/6\right)+1\right]^2} \right\} \frac{1}{R^2}$$

R = FEM resolution (probe size)

C_{hkl} = Bragg active fraction

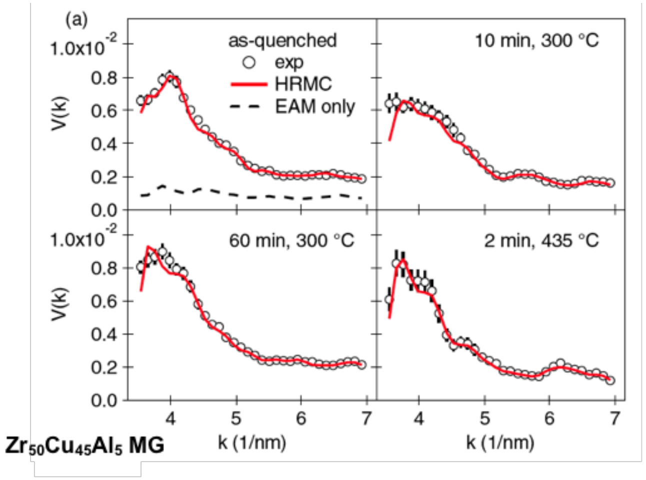
d = Diameter of MRO

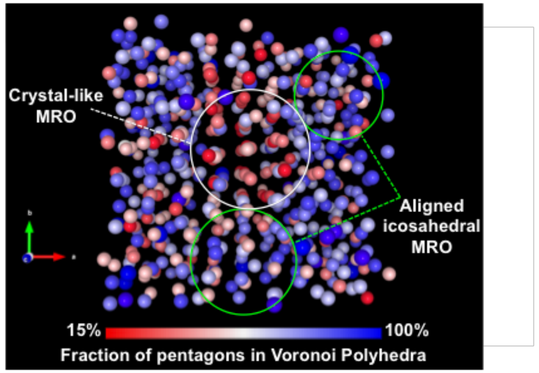
Φ = Volume fraction of MRO

Stratton et al., *Ultramicroscopy* (2008)

Reverse Monte Carlo (RMC) simulation

Generates an atomic model that gives the best agreement with the FEM data, by minimizing the mean square deviation.

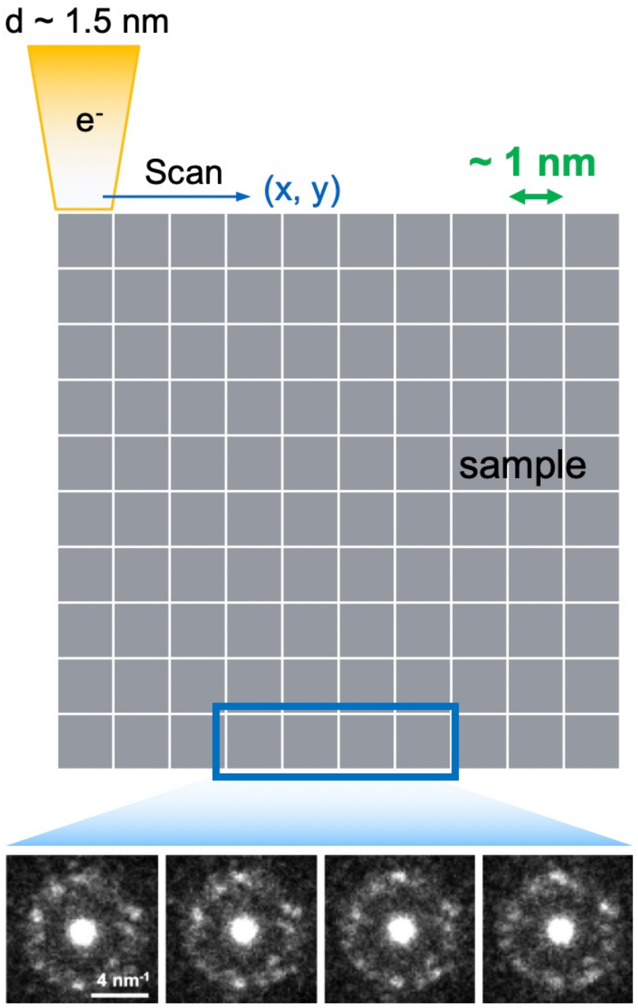


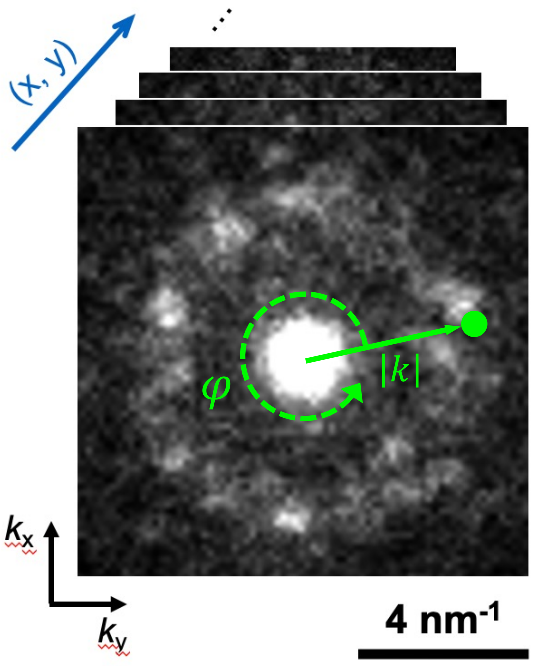


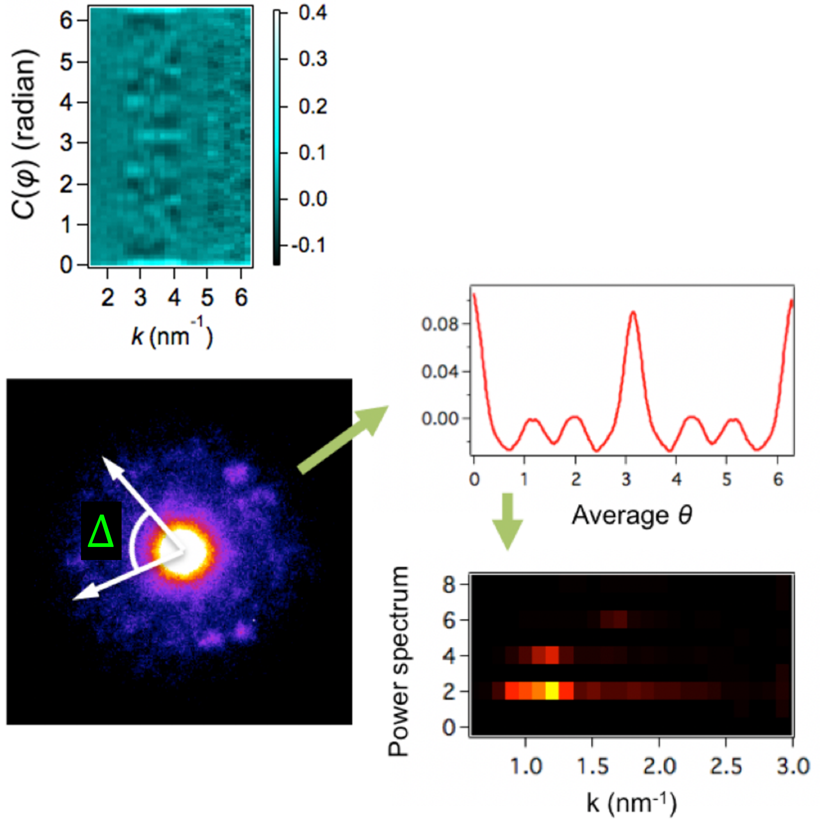
Hwang et al., Phys. Rev. Lett (2012)

- Still, it is challenging to directly determine or separate the structural parameters of MRO.
- Ongoing effort to direct determination of individual MRO parameters (type, size, distribution, orientation, and volume fraction) separately.

Angular Correlation Analysis



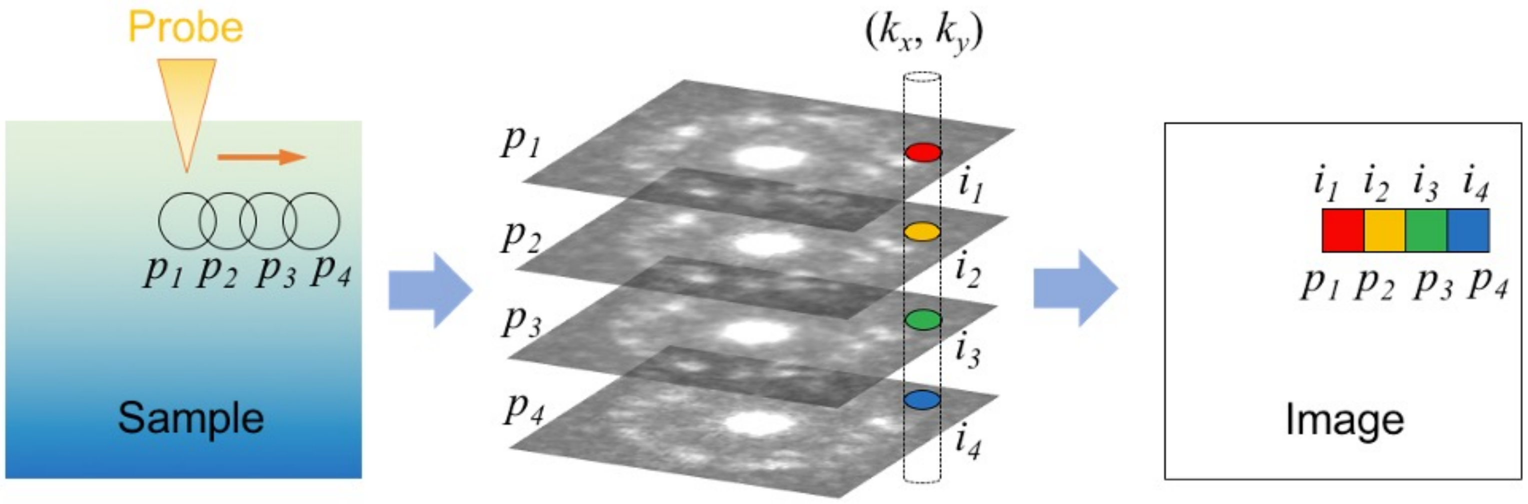


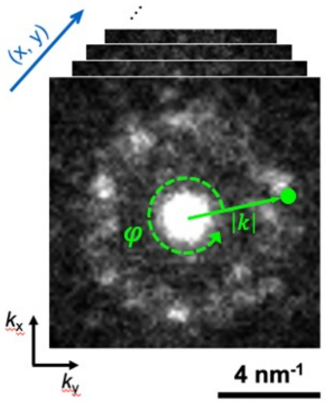


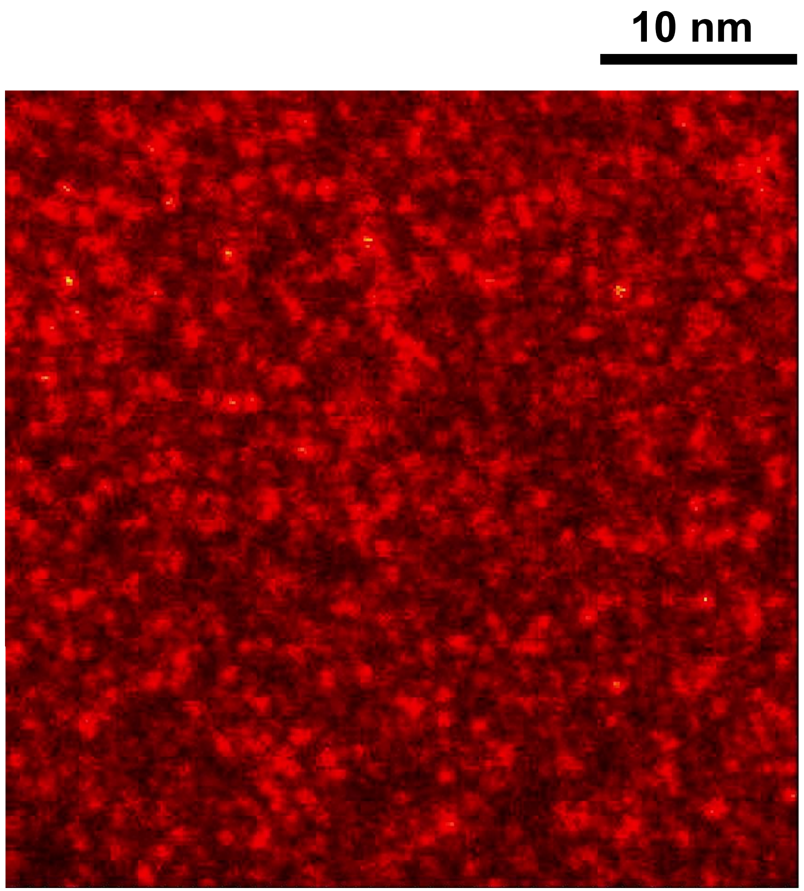
$$C_Q(\Delta) = \frac{\langle I(Q,\varphi) I(Q,\varphi+\Delta)\rangle_\varphi - \langle I(Q,\varphi)\rangle_\varphi^2}{\langle I(Q,\varphi)\rangle_\varphi^2}$$

Angular correlation

Direct Imaging of Diffracting Domains

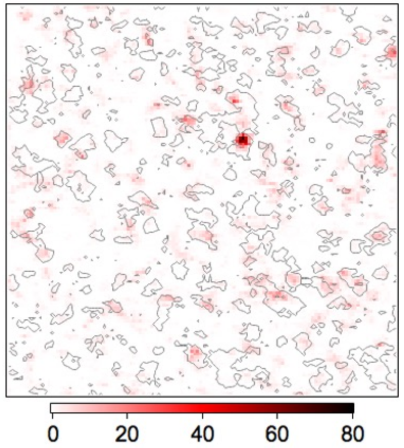




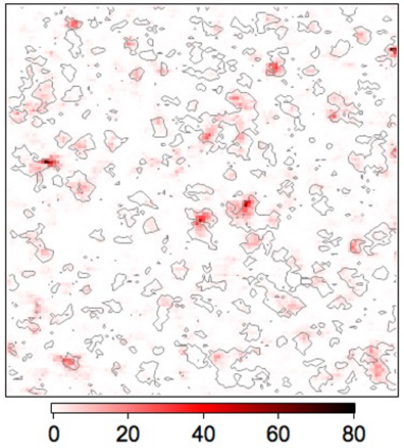


$$I_k(\varphi)$$

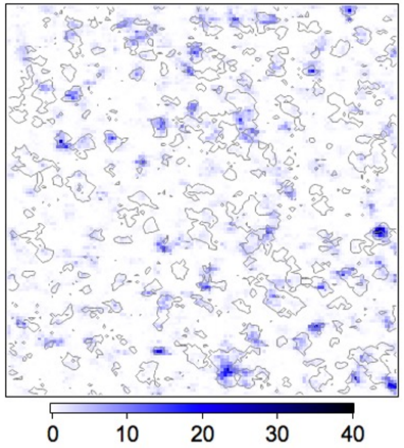
MRO Map of $Zr_{55}Co_{25}Al_{20}$ Metallic Glass



2 fold

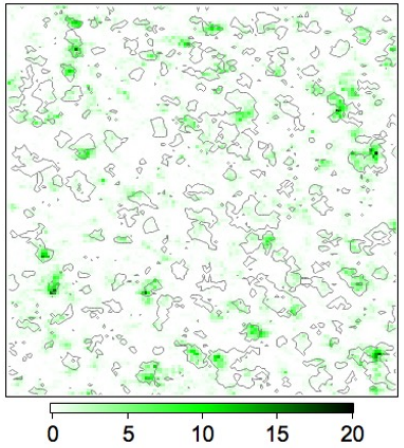


4 fold

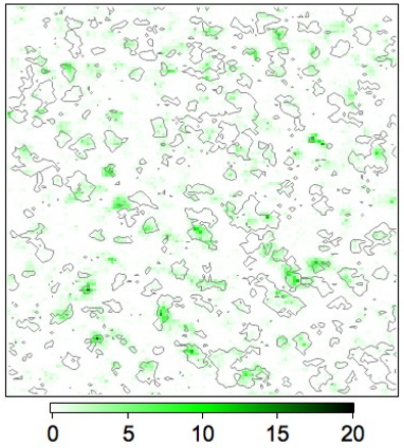


6 fold

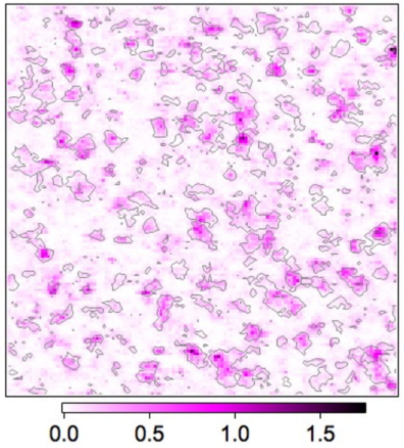
10 nm



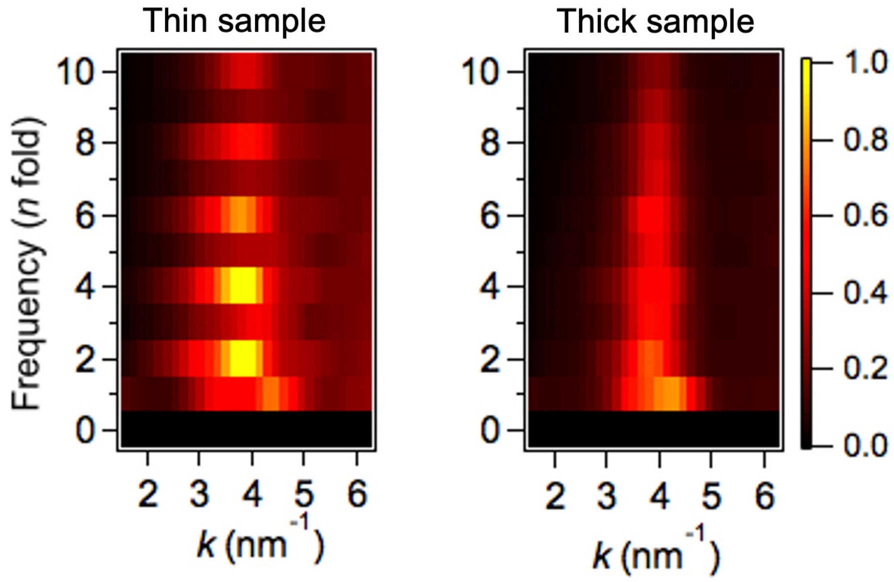
8 fold



10 fold



Sum

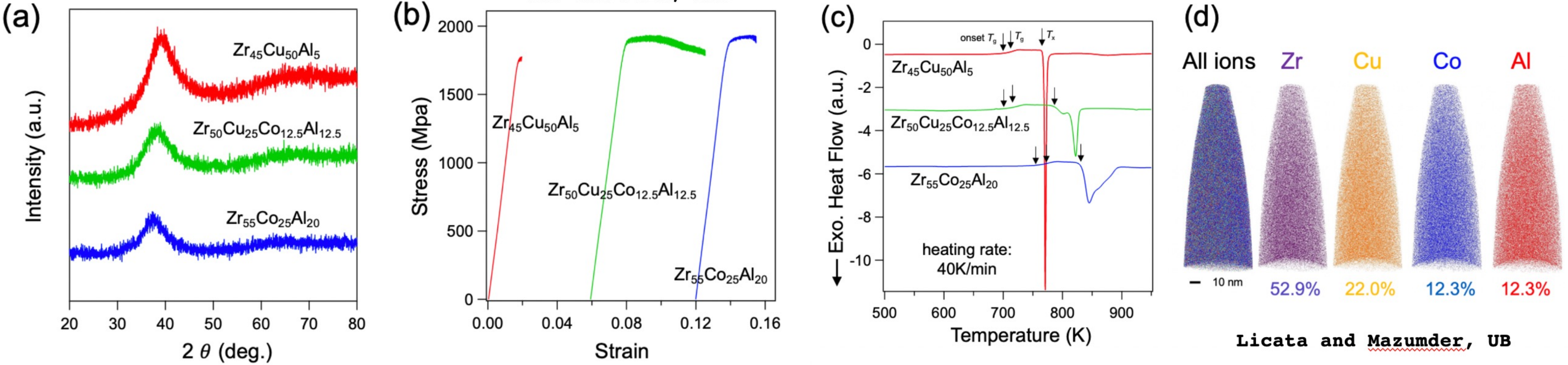


- Different rotational symmetry calculated using angular correlation per probe position provides a detailed *n*-fold spatial map for each *n*.
- Sample must be thin so that kinematic condition is dominant. Artifacts arise otherwise.
- FT also induces artifact in the powerspectrum.

`Im et al, Ultramicroscopy 195, 189 (2018)`

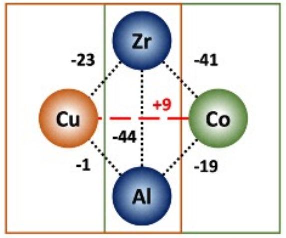
Structure, Ductility, and Glass Forming Ability of Zr-Cu-Co-Al MGs

Yoo and Park, SNU



Licata and Mazumder, UB

- Zr-Cu-Co-Al MGs – a mixture of two glass forming systems, Zr-Cu-Al and Zr-Co-Al.
- Substantial increase in ductility at 50:50 mixture, $Zr_{50}Cu_{25}Co_{12.5}Al_{20}$.
- No detectable phase separation.



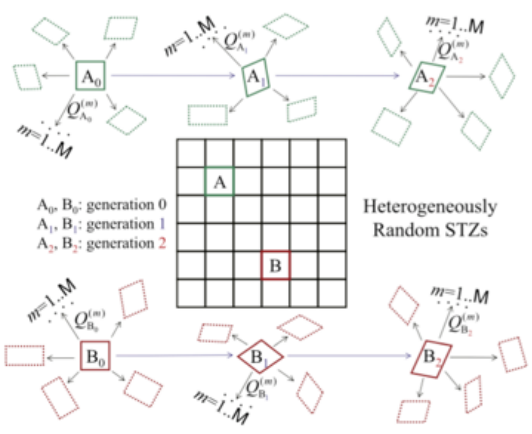
$(Zr_{45}Cu_{50}Al_5)_{1-x}(Zr_{55}Co_{25}Al_{20})_x$

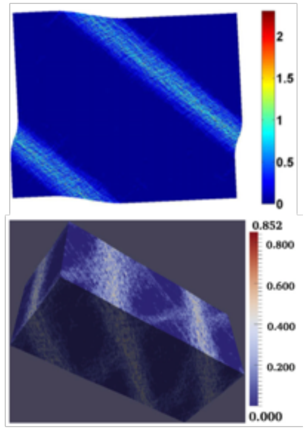
Im et al., (in review)
J. Park et al., Metal. Mater. Trans.43A, 2598 (2002)

2D histogram of MRO Sizes vs. *k*

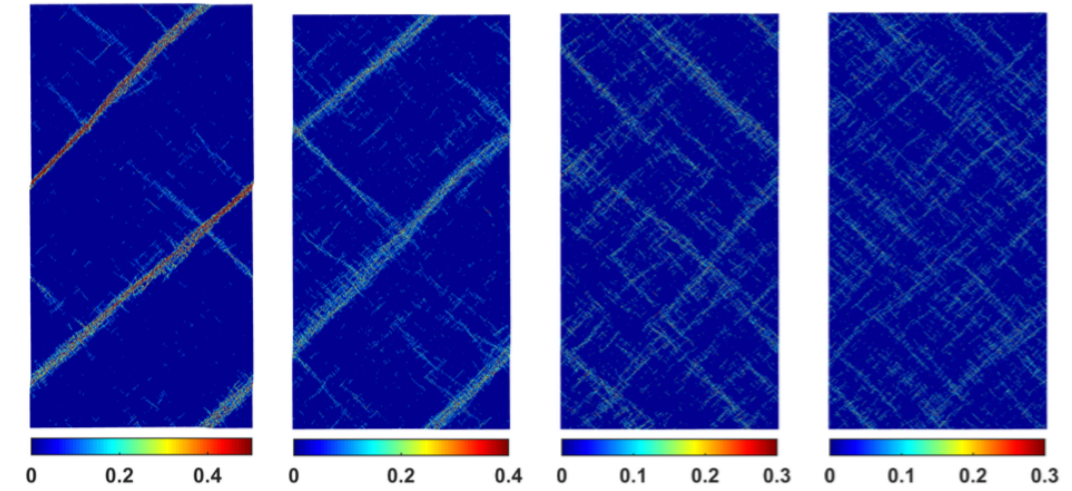
2D histogram of MRO Sizes vs. *k*

Deformation Simulation Incorporating MRO





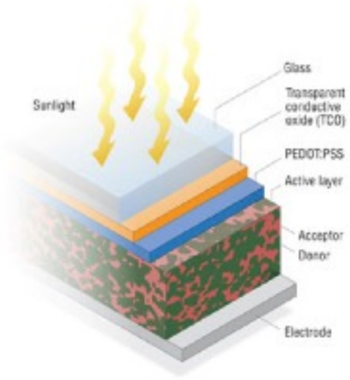
Yunzhi Wang, OSU



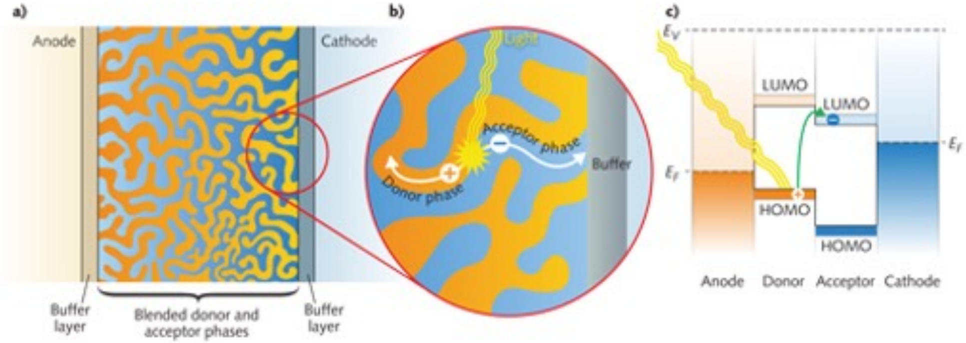
0 % **10 %** **20 %** **30 %**

P. Zhao, J. Hwang, and Y. Wang Acta Materialia 134, 104 (2017)

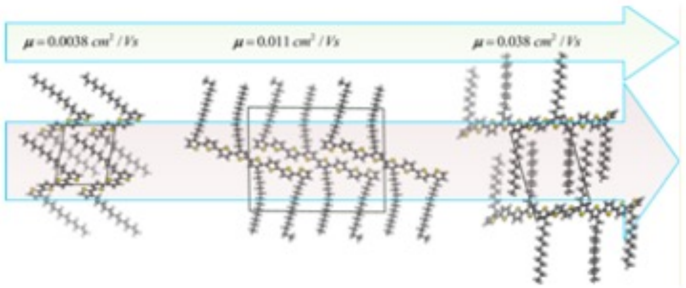
Molecular Ordering in Semiconducting Polymers



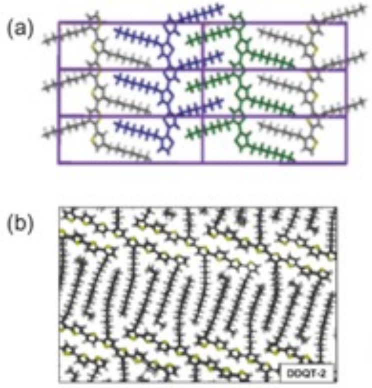
www.energy.gov



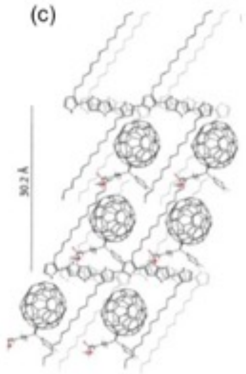
www.laserfocusworld.com/



Yavuz et al., J. Phys. Chem. C119, 158 (2015)



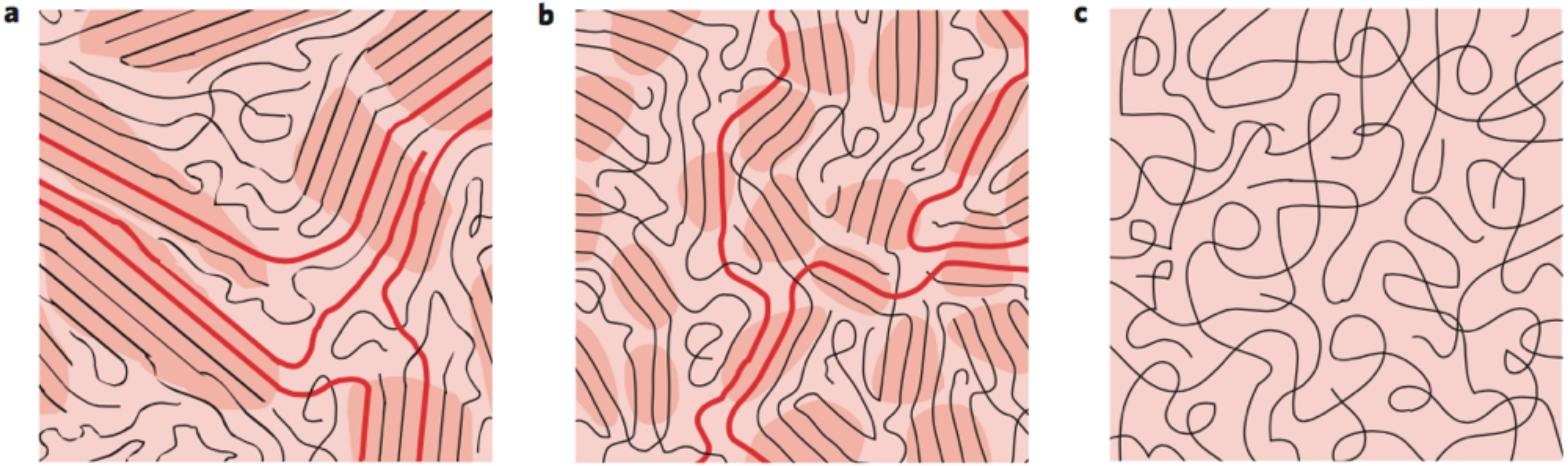
Mayer et al.



Oliveira et al.

Ordering among molecules can directly affect charge transport and solar cell efficiency

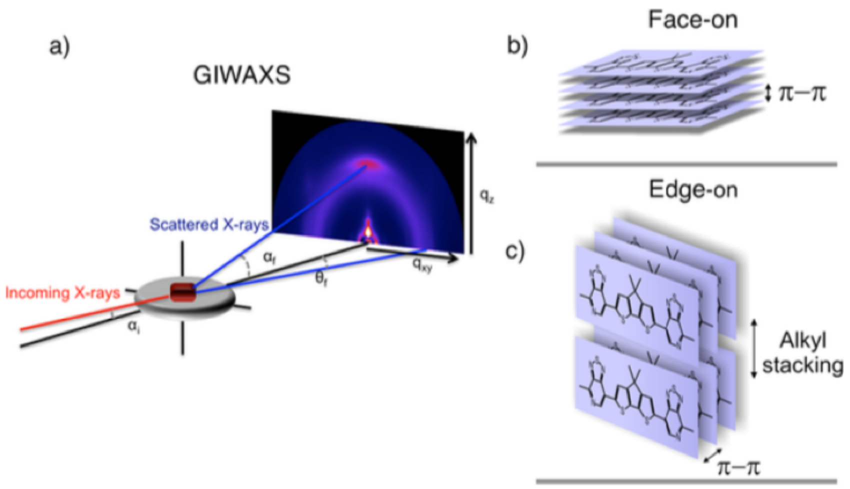
Molecular Ordering in Semiconducting Polymers



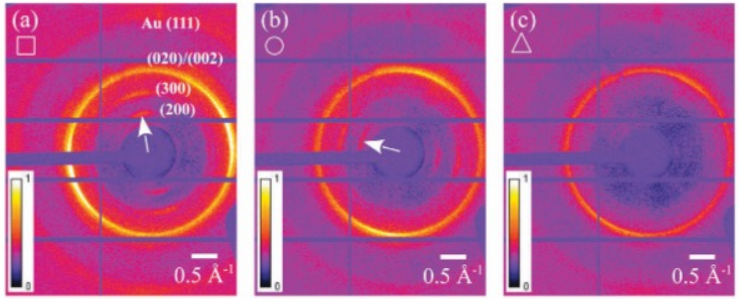
Noriega et al., Nat. Mater, 12, 1038 (2013)

- Structure always incorporates at least some degree of disorder.
- Ordering is small, and typically embedded in disorder.
- Scattering from organic molecules is usually small.
- Susceptible to radiation damage.

Molecular Ordering in Semiconducting Polymers



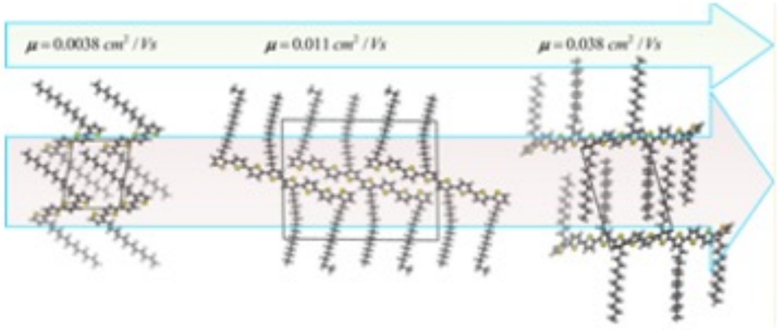
Perez et al., Macromolecules (2014)



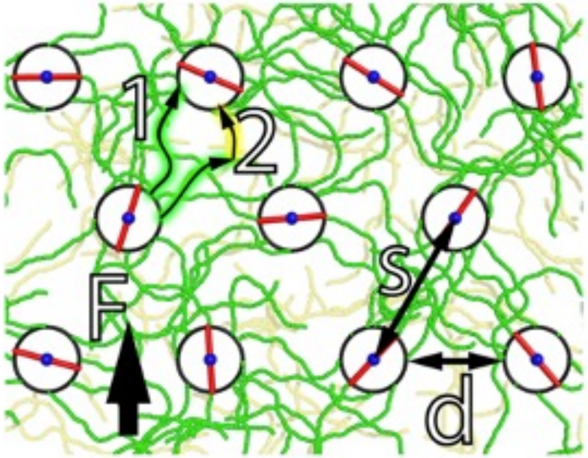
Kurta et al., PCCP 17. 7404 (2015)

- Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS).
- Overall degree and type of the ordering.
- Uses large probe; spatially resolved information unobtainable.
- We are interested in ordering at the nanometer scale (1 to a few nm).

Molecular Ordering in Semiconducting Polymers



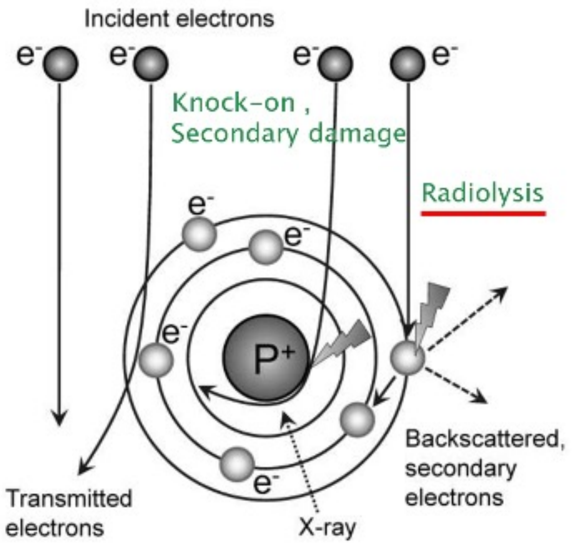
Yavuz et al., J. Phys. Chem. C119, 158 (2015)



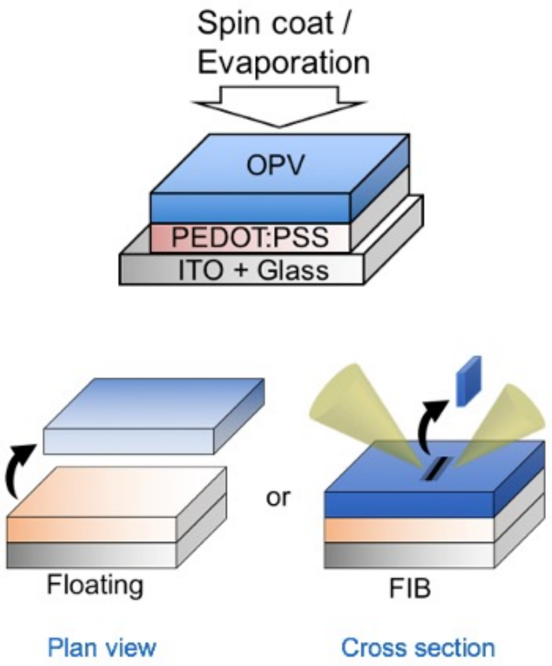
Mollinger et al., ACS Macro Letters 4, 708 (2015)

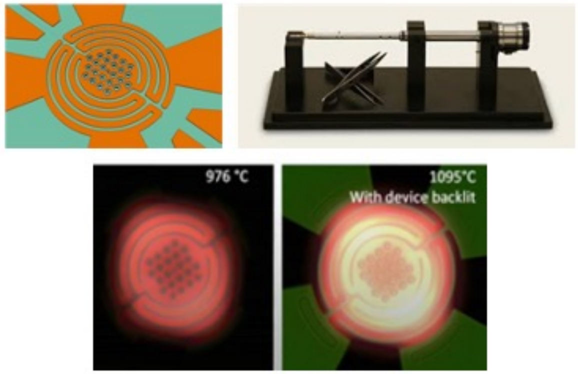
- Transport models show how the ordering may affect charge transport.
- Important framework to connect the ordering to properties.
- Need input parameters – *type, size, volume fraction, spatial and orientation distribution, connection and percolation of ordering.*
- Must be *experimentally determined*.

Molecular Ordering in Semiconducting Polymers

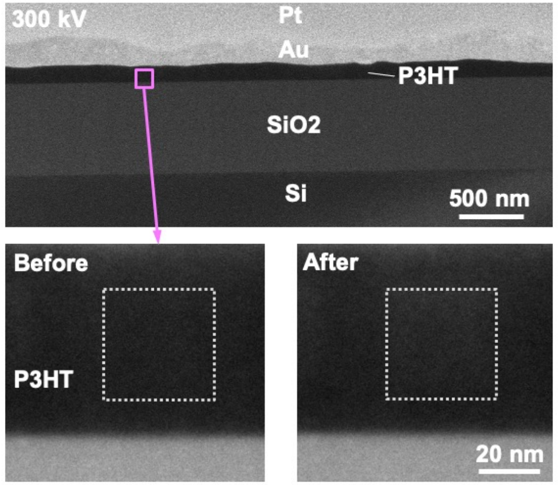


www.hic.ch.ntu.edu.tw



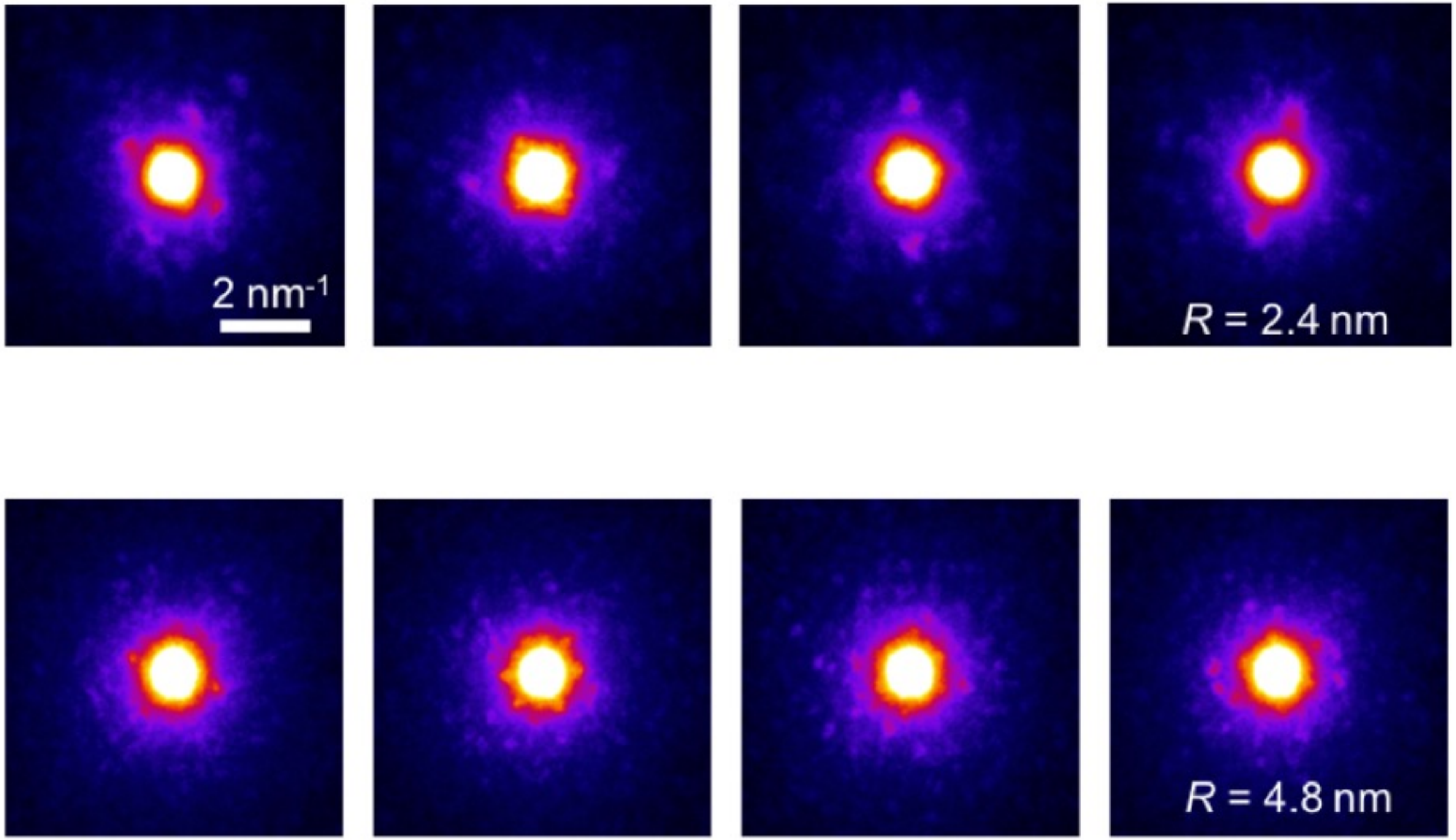


In situ annealing in TEM
130˚C for an hour

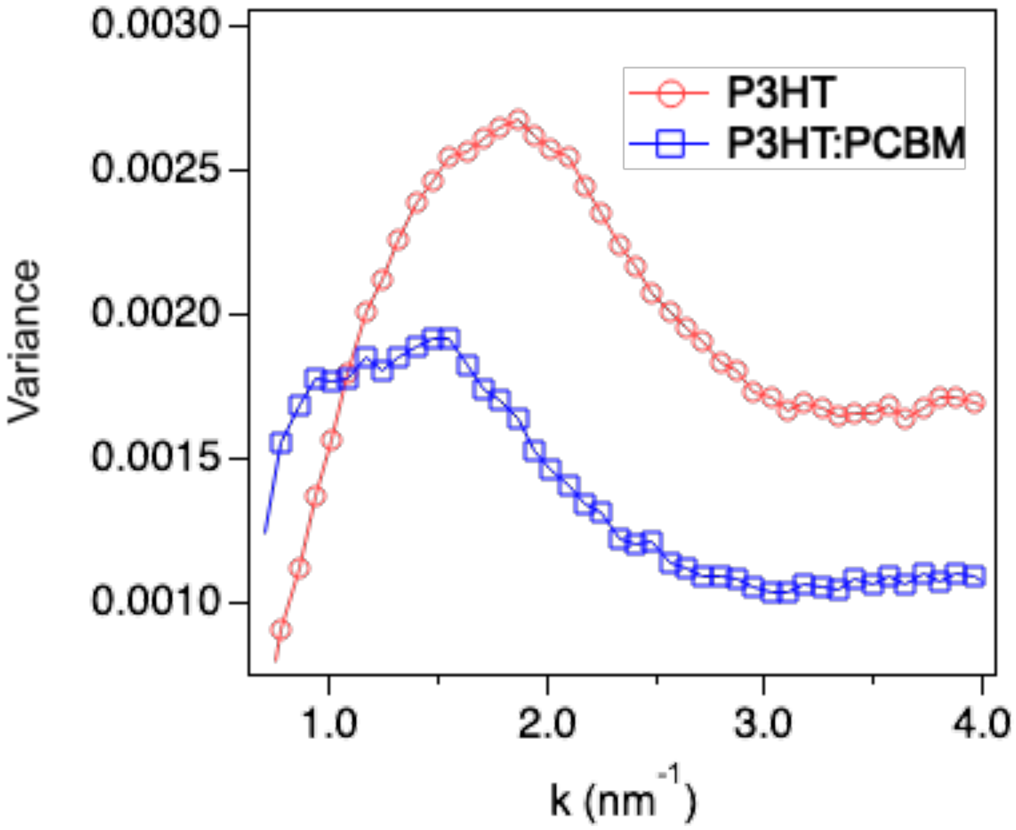


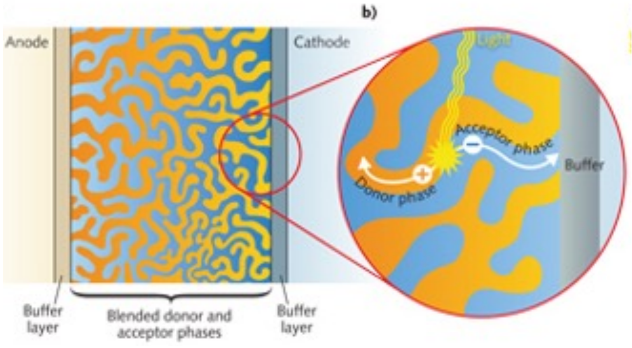
- Radiolosys increases with increasing scattering cross section – *higher voltage* may be more beneficial.
- Short beam exposure.
- Plasma clean *cannot be used* because it damages the molecule.
- In situ annealing to remove residual solvent

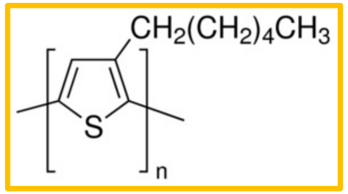
Molecular Ordering in Semiconducting Polymers (P3HT)



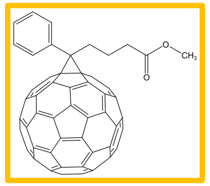
Molecular Ordering in Semiconducting Polymers







Donor: P3HT



Acceptor: PCBM

- V shows peaks at certain k, which indicates the major peak positions that represent the ordering type (intermolecular spacing).
- Mixing PCBM changes the type of the ordering.
- But peaks are broad, so more details are unclear.
- V combines the information about many different aspects of the ordering, such as size, volume fraction, and etc. So we need to separate those parameters using different analysis of the data.

Molecular Ordering in Semiconducting Polymers

Molecular Ordering in Semiconducting Polymers

Molecular Ordering in Semiconducting Polymers

Molecular Ordering in Semiconducting Polymers

Nanoscale Intermediates in ALD-grown Amorphous TiO_2 Films

Summary

- 4D-STEM demonstrates the correlation between detailed MRO parameters and important properties, including ductility and glass forming ability.
- Mesoscale simulation based on the experimentally determined MRO information confirms that the diverse types and sizes of MRO domains can significantly influence the MGs’ mechanical behavior.
- Detailed ordering at the nanometer scale in semiconducting polymers that connects directly to charge transport and solar cell efficiency.
- Provides important quantitative details of the structural heterogeneity in disordered materials and how it connects to their properties.

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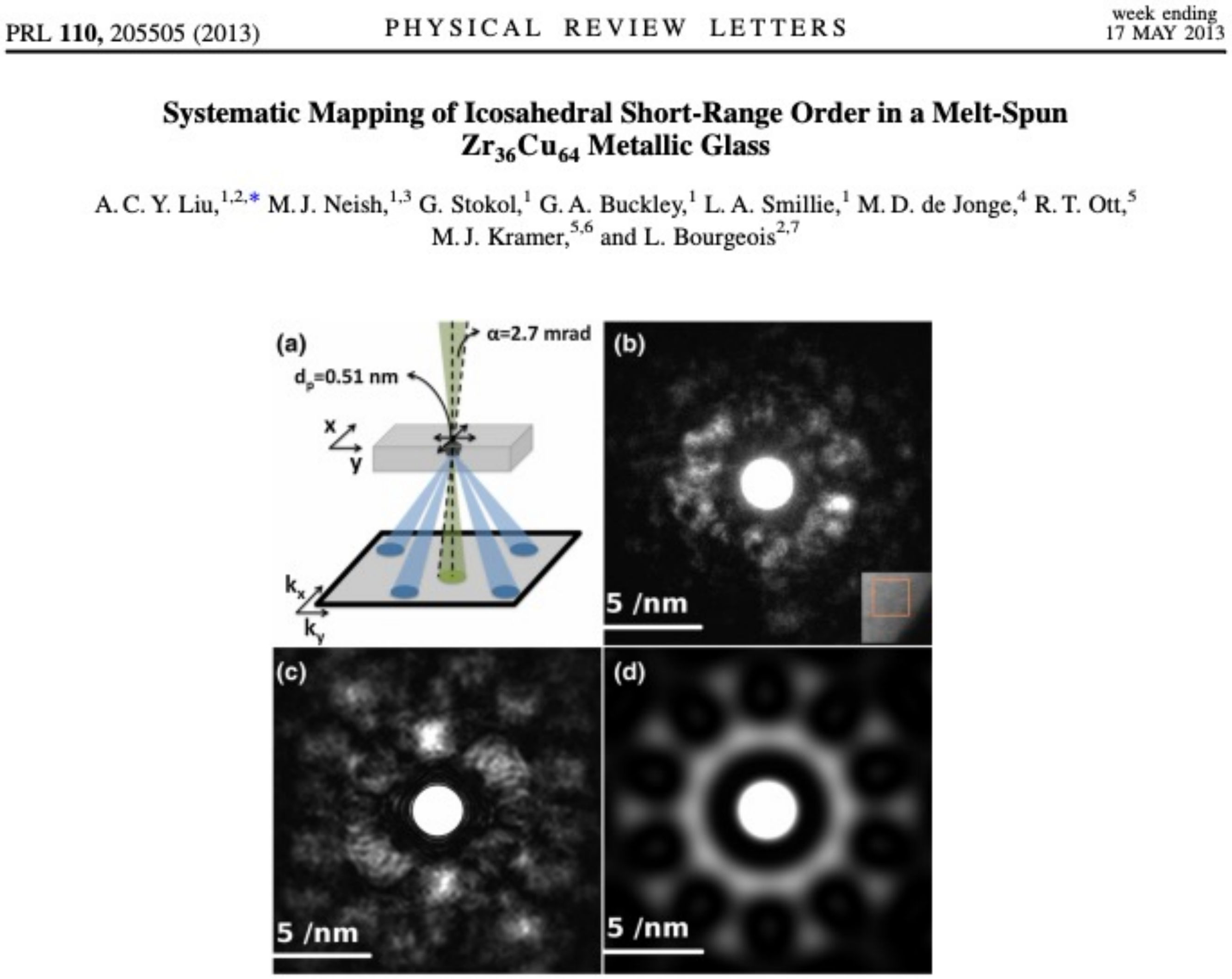
Angular Correlation Analysis



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Systematic Mapping of Icosahedral Short-Range Order in a Melt-Spun $Zr_{36}Cu_{64}$ Metallic Glass

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