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Decoding Order evolution in Disordered Materials with Scanning Nano-structure Electron Microscopy (SNEM)

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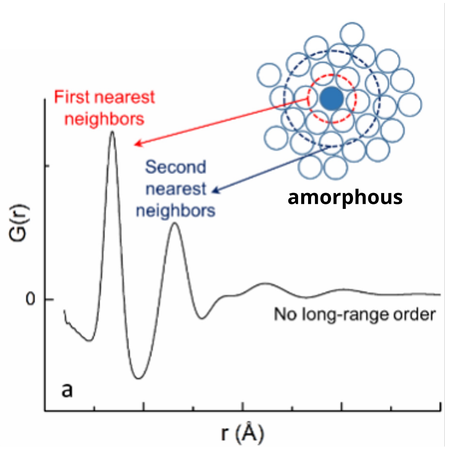
Based on REF [1]: Y. Rakita et al, Mapping structural heterogeneity at the nanoscale with scanning nano-structure electron microscopy (SNEM), Acta Materialia, 242, 118426 (2023)

Background and Motivation: Disorder in materials refer to the lack of inter-atomic correlations. And yet, besides in an ideal gas, locally-ordered metastable structures will occur in all materials, even in glasses. Glasses, for example, are technologically important (e.g., IR opto-electronics, neuromorphic computation, energy conversion and storage), but our comprehension of their local structural organization and evolution, especially at the nano-scale, is very limited. Understanding these structural features is a key for understand their local chemical potential landscape, and properties.

While capturing and controlling the formation of metastable phases is, both scientifically and technologically, critical, our mental picture about ordering in disordered materials is based on measurement tools that lack the proper spatial resolution. Classically, the local structural order (order correlations and correlation lengths) of glasses is studied in synchrotron facilities, partly by **total-scattering and pair-distribution function (PDF) analysis**. Due to spatial averaging, x-ray-based PDF, as well as other local-order probes, e.g., Raman, NMR, EXAFS, lack the required spatial resolution for detecting possible differences in the local ordering at the nano-scale. The resolution problem is a potential origin for a critical misconception in the mental-picture of the ordering in metastable materials. Glasses, for example, are often addressed as continuous and homogeneous, but as we will show here, once resolving their structural order with a *nm*-resolution probe[1], we see that this is not necessarily the case.



Pair Distribution Function of amorphous materials

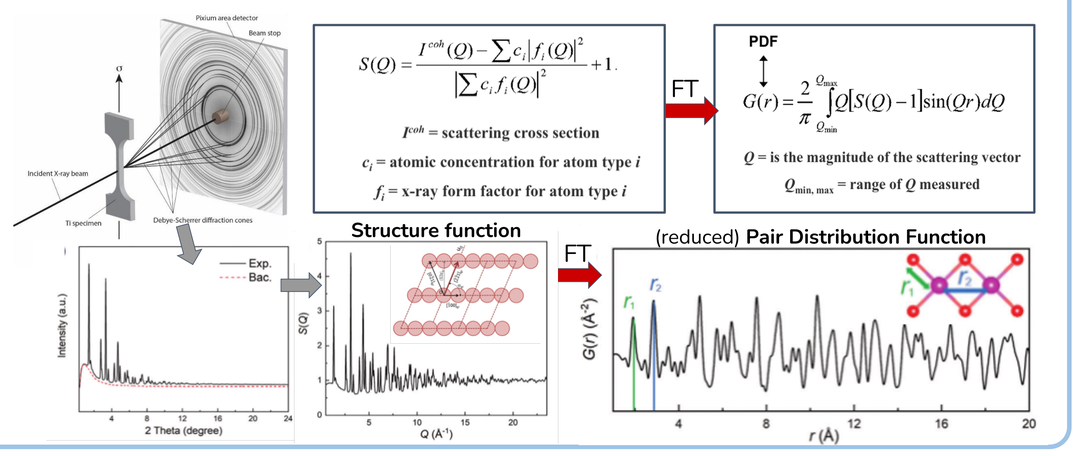
Pair Distribution Function (PDF) is a histogram of two particle correlation function weighted by the particles' scattering factors.

PDF is derived directly from **total scatting** measurements.

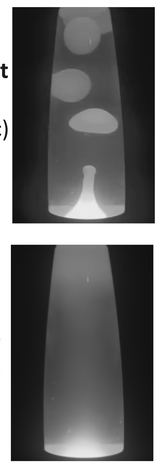
Absolute structures can be derived by fitting a PDF to a structure-based simulated PDF. However, since amorphous structures are defined by the distribution of local structural motifs, **we use relational-PDF to follow the changes (evolution) in local structural correlations and correlation lengths.**

Tracking changes between relational-PDF data allows us to track, most reliably, the structural evolution of disordered materials.

Typical analysis pipeline for generating PDF data



The resolution problem

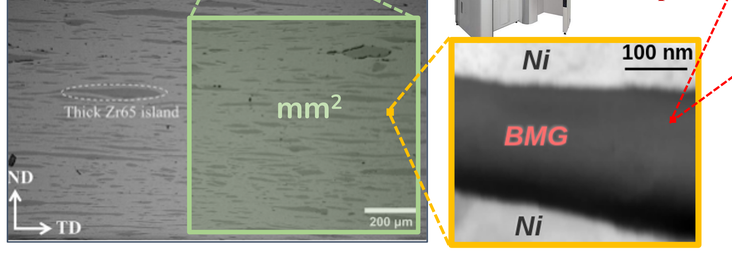


Studying disordered materials with a synchrotron-like spatial resolution will be as if one is avaraging 20,000 frames of a "lava-lamp" movie into a single frame. No "bubbles" will be evident, which will lead to misconcetion abot the strucutral order of the the laba-lamp.

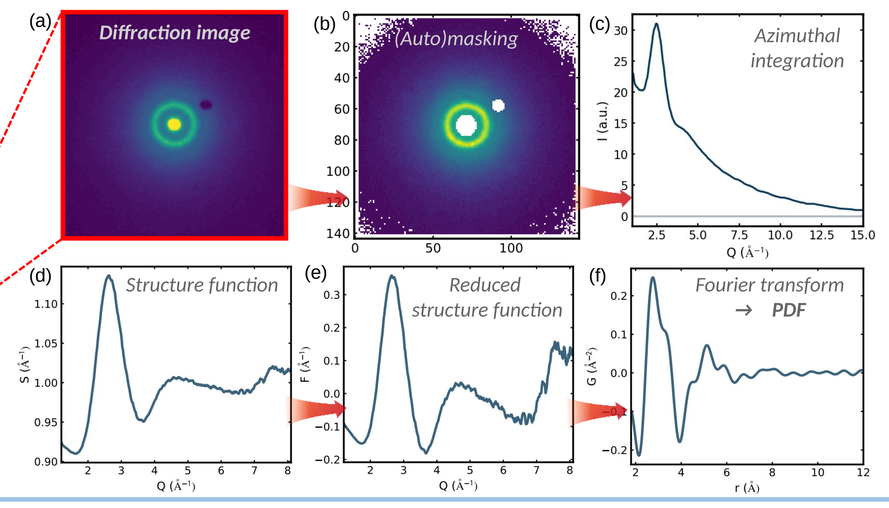
Given the fact that what we know about glasses is based on synchrotron-based experiemtns: does our concenption about uniformity in glasses represents reality?

Typical spatial resolution from synchrotron-based x-ray diffraction:
mm x mm x mm

Spatial resolution from a nano-beam electron diffraction
nm x nm x (10-100) nm



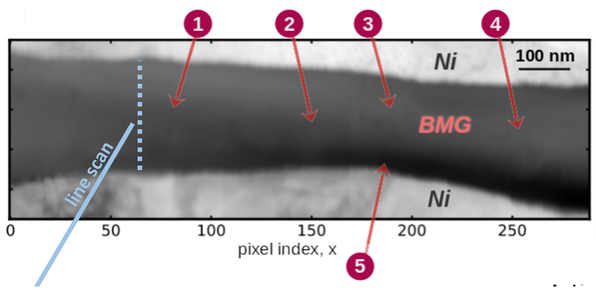
Data-reduction pipeline to get ePDFs in a 4D-STEM experiment



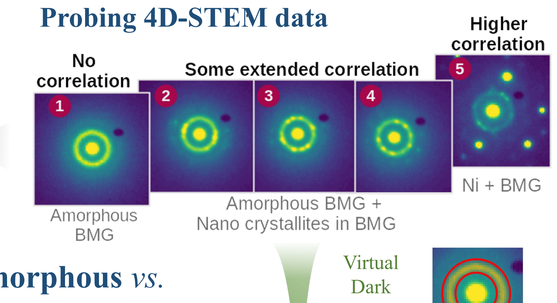
Scanning Nano-structure Electron Microscopy (SNEM) [1] methodology, which was developed specifically for this purpose. SNEM uses electron-diffraction relational-data from scanning transmission electron diffraction (4D-STEM) measurements, which is integrated with routine synchrotron-based total-scattering analysis pipelines (corrected for electrons). Using both typical feature-extraction methods or more advance machine-learning tools, we show how one can spatially map, and potentially follow, the formation of structural and chemical-order in disordered materials. For example, as it was shown for Ni-encapsulated, $Zr_{65}Cu_{17.5}Ni_{10}A_{17.5}$ bulk metallic glass (BMG), it was possible to learn about pre-nucleation events, and learn how emergence of local chemical ordering is correlated with the emergence of nano-sized nuclei [1].

SNEM

Polycrystalline Ni-encapsulated, **$Zr_{65}Cu_{17.5}Ni_{10}A_{17.5}$** bulk metallic glass (BMG)

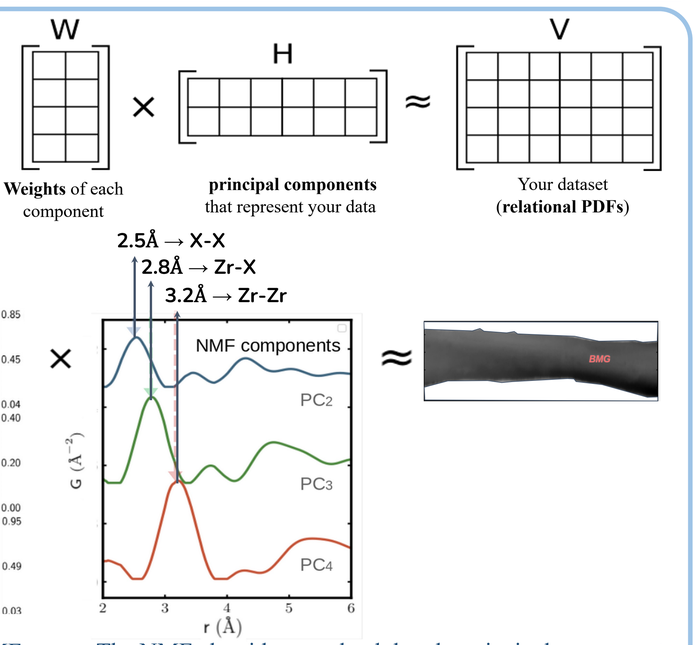


Probing 4D-STD data



Non-Negative Matrix Factorization (NMF)

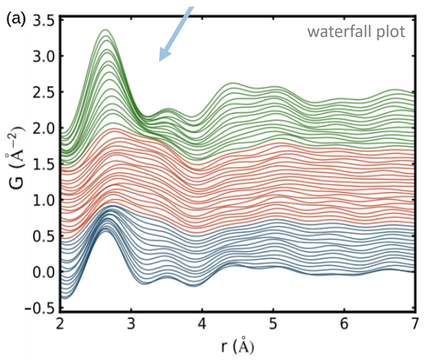
(principal component analysis)



The weight matrix of the NMF components represents the partial occupancy of each of the three pairs.

The NMF algorithm resolved that the principal components that build the ePDF relational dataset contains a component for each one of the three pairs :
|| X—X || Zr--Zr || Zr--X ||

Quantitative evidence for local chemical order evolution



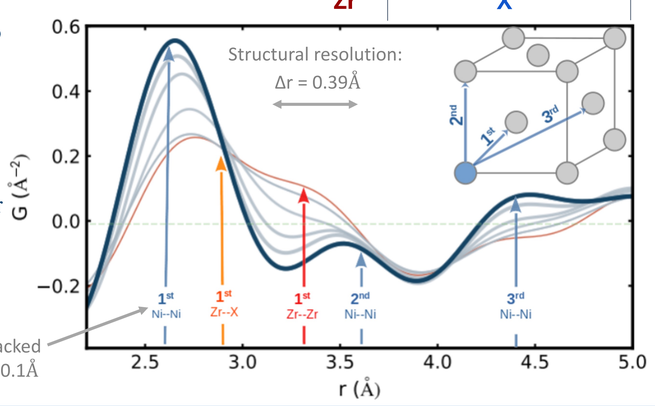
Structural evolution with relational-ePDFs every 3 nm. Blue/green – strongly varying edges that are close to the Ni interface, and red a weakly-varying core.

Atomic radii (metallic)→Zr-X structure

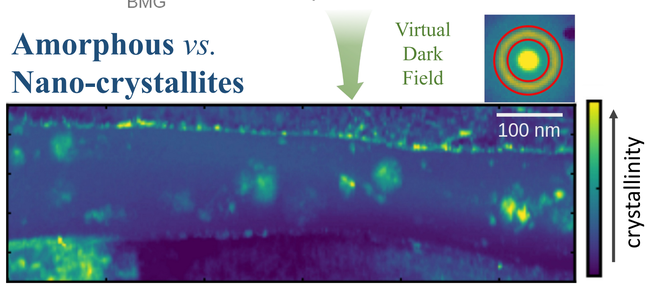
Zr	Cu	Ni	Al
1.60Å	1.28Å	1.24Å	1.43Å
Zr	X		

From edge to center:

- X-X pair density decrease
- Zr-Zr pair density increase

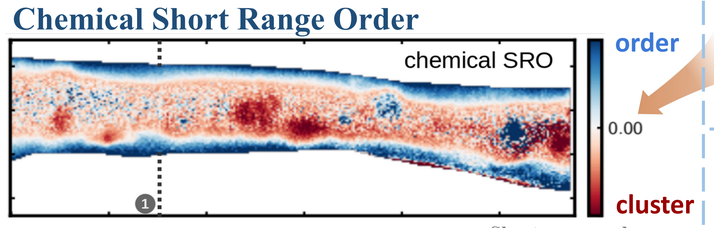


Amorphous *vs.* Nano-crystallites



The bright regions inside the BMG represent regions with nano-particle nuclei

Chemical Short Range Order



$$\alpha = SRO_{[Zr-X]} \equiv \frac{P_{[Zr-X]} - P_{random}}{P_{max} - P_{random}}$$

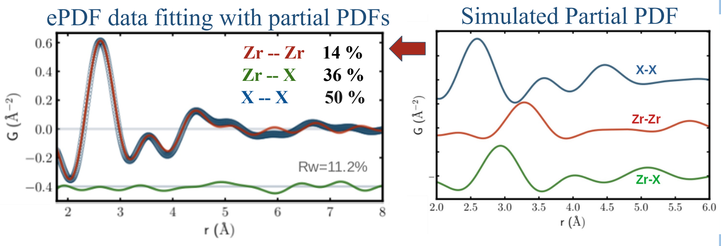
Short range order parameter: Computes the distance of a distribution from a random chemical order.

Blue regions refer to preference to form Zr--X bonds

Red regions refer to preference to form Zr--Zr or X--X bonds

White area shows regions with a random chemical distribution

Validation that the ePDF data can be represented by a combination of Zr-X pairs.



Future work: Develop an in-situ SNEM for order evolution studies in glass-forming materials for Neuromorphic computation applications and bio-mineralization control.