Dynamical and correlated disorder at nanoscale in complex materials

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Complex and inhomogeneous materials

Complex materials are characterized by variations in the atomic and electronic structure on different length scales.

- Atomic scale
- Molecular scale
- Nanoscale
- Mesoscale
- Microscale

Time

Energy

CDW, SDW, orbitals
electronic clumpy patterns

Perovskites

Myelin
Fluctuations at nanoscale

Bone tissue
Mixture at nanoscale

Cements
Packing at nanoscale

Steel
GB at micron scale
Inhomogeneity at atomic scale: X-ray diffuse scattering

......from point to topological defects: heterogeneous matter

Modulations

Striped atomic G and GB

Order  Correlated disorder  Disorder

superlattice peaks  streaks
Disorder and complexity in matter

**Correlated disorder**

La$_2$CuO$_{4.1}$  HgBa$_2$CuO$_{4.12}$

**Pattern formation**

Conformation n  Conformation m

ΔE ≈ meV

ΔE ≈ meV

ΔE ≈ meV

**Complexity**

The spontaneous emergence of spatial patterns and correlated disorder is due to many competing states, as in soft materials and biological systems.

Different spatial patterns produce an energy landscape where transitions between different conformations involve similar energy values down to few meV.

Several materials have inhomogeneous phases. This occurs when several physical interactions such as spin, charge, strain, orbital are simultaneously active.
(i) high intensity and brilliance (20 orders of magnitude higher); 
(ii) broad and continuous spectral range from the infrared to the X-ray; 
(iii) narrow angular divergence; 
(iv) high degree of polarization; 
(v) pulsed time structure.
High Precision X-ray Measurements
1. Crystal orientation and peaks indexing

Correlated disorder in atomic structure

4 circle K-diffractometer
High Precision X-ray Measurements

2. Scanning micro/nano XRD

Scanning X-Ray Diffraction

FOCUSING OPTICS

- NFL refractive
- K-B reflective
- ZONE PLATES: diffractive

Mesh: 100x100 µm

Step: 1 µm; 10000 frames

Step: 100 nm; 1000000 frames
Methods

3. Big datasets analysis: Statistical Physics

X-ray microdiffraction analysis

**Mapping**
(domain size, population of coexisting soft-like phases)

Spatial Statistical analysis
Spatial Probability Distributions

**Correlations in space and time**
Continuous/Discrete patterns

**Clustering**
Aggregation/dispersion
Spatial tessellation

**Connectivity**
Percolation
APPLICATIONS

1. HTCS cuprates

- Lattice inhomogeneity
- Electronic inhomogeneity

Layers at atomic scale

2. Myelin

Layers at nanometric scale
Scale-free structural organization of oxygen interstitials in La$_2$CuO$_{4+y}$

Evolution and control of oxygen order in a cuprate superconductor

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Layered structure + i-O dopants

i-O ordering + CDW ordering

Thermal cycling + X ray illumination
Two different sample preparation with the same oxygen content but different Tc and configurations due to oxygen distribution.
The CDW crystalline puddles form inhomogeneous spatial patterns giving rise to a new non-Euclidean geometry in the interstitial space left by the crystals of electrons. The free electrons, which do not crystallize, form Cooper pairs flowing along paths in the interstitial space at low temperatures.
Order and correlated disorder in biology

Structural Fluctuations at nano/mesoscale
Myelin X-ray Diffraction and E-D profiles

Myelin structural unit with the four principal myelin protein. The PMP22 protein is located in the lpg membrane. The PO protein helps to build the myelin layers stacking. The cytoplasmic layer, cyt, (yellow), is the location of the structured protein P2 and the intrinsically disordered protein MBP.

2-D diffraction pattern of myelin shows the expected arc-rings corresponding to the Bragg diffraction orders \( h = 2, 3, 4, 5 \). The exposure time was 300ms.

From the differences between two adjacent maxima \( d_{\text{cyt}} \), \( d_{\text{ex}} \), \( d_{\text{lpg}} \) and \( d_\lambda = 2d_{\text{lpg}} + d_{\text{ex}} + d_{\text{cyt}} \) were obtained.
Myelin
Spatial statistics of fluctuations

Functional state  Aged state

PERIOD

CYT

EXT

LPG

\[ \xi = \frac{d_{\text{ext}} + d_{\text{cyt}}}{2d_{\text{lpg}}} \]

Larger correlated fluctuations in the functional state
Levi correlated disorder in functional state

The PDF of $\xi$ shows a skewed Levy distribution in the functional state. The Levy distributions provide a statistical description of complex systems out of thermodynamic equilibrium.
Correlated disorder and IDP

Myelin basic protein dynamics from out-of-equilibrium functional state to degraded state in myelin

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SAXS profiles measured at room temperature of the MBP in aqueous solution alongside the curve fit (green line) obtained by Ensemble Optimization Method (EOM)

A 3D representation of some possible conformations of MBP extracted by EOM, used to fit the SAXS data. Large combinations of network interactions allow to organize the disorder

A 3D representation of P2 folded structure
Conclusions

Functional disorder control for Multiscale Material Engineering

above 10 microns are a classical issue of Material Engineering to optimize material properties.

from 10 microns to 0.1 nm structural fluctuations represent a new field of fundamental science for developing innovative material functionality.
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Thanks