Advances in Nanoparticle Structure Characterization by XAS

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A Neural Network Approach:
1) Inverting XANES spectra to obtain coordination numbers in nanoparticles
   J. Timoshenko, D. Lu, Y. Lin, A. I. Frenkel
2) Inverting EXAFS spectra to obtain Pair Distribution Function
   J. Timoshenko, A. Anspokas, A. Cintins, A. Kuzmin, J. Purans, A. I. Frenkel

Size is a property descriptor… But not only size.

Finite size effects in nanoparticles

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<th>Property Type</th>
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<td>Structural properties</td>
<td>$\Delta \sigma \propto \frac{1}{d}$</td>
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<td>Thermal properties</td>
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<td>Electronic properties</td>
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<td>Phase Diagrams</td>
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Finite size effects:

- **Laplace’s Law (~18th century)**
  
  \[ \frac{\sigma}{\sigma_0} = \left( \frac{R}{R + d} \right)^2 \]

- **Gibbs-Thomson relation**
  
  \[ \frac{\sigma}{\sigma_0} = \left( \frac{R}{R + d} \right)^2 \]

- **Kubo gap**
  
  \[ \Delta \sigma = \frac{1}{d} \]

- **Hall-Petch relationship**
  
  \[ \sigma = \sigma_0 + C_d \cdot d^{1/2} \]

- **Miscibility vs segregation**

Size, shape, strain of NPs: Important for reactivity

- Coordination numbers:
  - N1, N2, N3, N4: Indices of size, shape, morphology
- Interatomic distances:
  - Bond strain

Theory of EXAFS and XANES

EXAFS is caused by the interference of the outgoing and back-scattering photoelectron waves:

\[ E = E_0 + \frac{p^2}{2\mu} \]

EXAFS function:

\[ \mu(E) = \sum \frac{|F_{\text{int}}|^2}{|F_{\text{is}}|^2} \delta(E - E_i + E) \]

Fermi’s Golden Rule in one-electron approximation:

\[ \mu(E) \sim k^2 f(E) \]

Transmission mode

Absorption in the isolated atom

Fluorescence mode

Absorption in the atom with neighbors
In situ / operando transformations

- Size, shape and structure of nanoparticles may change in reaction conditions
- Coordination numbers (C1…C4) are difficult to obtain reliably in harsh reaction conditions
- Low metal loading reduces EXAFS data quality

Extracting the architecture of metal catalysts from XAS data using Neural Network approach

Forward problem

\[ \rho(E) \propto \sum_{i=1}^{S} \| f(H_{xi}) \| \delta(E - E_{i} + E_{0}) \]

Inverse problem:
- No analytical eq. exists!
- Should be model-independent

Objective: given experimental XANES spectrum, determine 3D structure for the nanomaterial

Machine learning guided interpretation of X-ray absorption data
Size and shape effect in XANES

Particles of different sizes and shapes have different ratios of distinct sites: XANES should be sensitive to NPs size/shape.

Averaging

Trends in theoretical XANES data agree qualitatively with the trends in experimental data: there is information on particle size/shape!

But how can we extract it?

Supervised machine learning methods can help here!

Validation with theoretical data

For validation we use theoretical, particle-averaged XANES data (for particle models, used to generate training data, as well as for some other particle models). True particle-averaged coord. numbers are, of course, known.

A very good correlation was obtained between the true values of coord. number, and coord. numbers, predicted by NN trained on 200 000 – 600 000 examples!

Coordination numbers extracted from XANES using NN method correlate well with the results of EXAFS analysis.

Obtained coordination numbers agree well with what is expected for close-packed metallic particles with fcc-type structure.

Application to experimental data

Training data

Performance of SVM methods depends critically on the size of training data set. Hundreds of thousands examples (XANES spectra with known corresponding average coordination numbers) may be required. Where to get them from?

- First thought – let’s use theoretical XANES data, calculated for model particles of different sizes and shapes (and, hence, different average coord. numbers)...

- Still, the number of such spectra is very limited (XANES calculations are computationally demanding)

New opportunities for ML-XAS

- **In situ/operando and high throughput studies:**
  - On the fly analysis
  - Reaction on demand

- **Bimetallic NPs:**
  - Partial CNs, including elements with overlapping edges: Pt-Au, Pt-Ir etc.

High energy resolution:
- Better contrast of XANES features

**Bench-top XAS**
G. Seidel, et al
RSI 85, 119906 (2014)

**Conventional EXAFS analysis (inverse modelling)**

\[ \chi_c(\ell) = \sum_{n} \frac{N_{n}}{R_{n}^{2}} \exp \left[-\frac{2\pi}{\ell} \right] \sin \left[2\pi R_{n} \ell + \phi_{n}(\ell) \right] \]

- Some a priori shape for bond length distribution (e.g., Gaussian) is assumed: may be unreliable for disordered and/or nanoscale materials;

- It is challenging to analyze contributions beyond the first coordination shell;

- Gets very complicated if the distribution of compositions is broad
- No unique solution
- Multiple scattering contributions are very difficult to analyse reliably

**Extracting the architecture of metal catalysts from EXAFS data**

**Inverse modeling:**

**Forward modeling:**

Kuzmin, Purans, Ansapsa, Cintins (ISSP, Riga)
EXAFS data: Synchrotron: ELETTRA, Italy

**Coordination numbers approach: Does not describe transitional phenomena**
(either a cat or a "no cat" but not a hybrid)

BCC to FCC (α→γ) transition in Fe at 1190 K


JVST A 32, 020801 (2014)
PRB 85, 075409 (2012)
Regularization approach

phys. stat. sol. (b) 104, 747 (1981)

Subject classification: D0

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A New Interpretation of EXAFS Spectra in Real Space

1. General Formalism

By

Yu. A. Barashov (a), V. V. Vas'kin (b), A. L. Agerov (b), and N. V. Kuzinov (a)

It is shown that the problem of determining the function of radial atomic distribution around an absorbing atom by oscillations of the X-ray absorption coefficient belongs to a family of inverse problems. A regularization algorithm is proposed for the problem considered. Computational schemes realized involving the use of computers are described. Some results of model calculations are given.

\[ \chi(k) = 4 \pi g \left[ \frac{f(k, n)}{k} \right] \int_0^\infty \int_0^\infty \sin(2\pi r + 2\theta) \, d\theta \, dr \]

ML for EXAFS analysis

More detailed information of bond-length distribution can be extracted from EXAFS data: as a descriptor of materials structure we can use entire Radial Distribution Function:

ML for EXAFS analysis

BCC to FCC (α→γ) transition in Fe at 1190 K

Challenge: disorder effects need to be included in the training data set

For this purpose we can rely on molecular dynamics simulations

Experimental Fe K-edge EXAFS (ELETTRA)

Reconstructed RDF

Bimetallic NPs can be analyzed by NN approach

ML-EXAFS method is useful for studies of structural changes in bulk and nanomaterials (phase transitions, particle shape transformations, etc.)

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ML for EXAFS analysis

Stony Brook University
Solving "Inverse problem" (Spectrum → Structure)

Data point:
Experimental XANES or EXAFS spectrum

Grid node:
Theoretical XANES or EXAFS spectrum

Descriptors:
CN (e.g., N1, N2, N3, N4), R, Bin of the g(r)

NN for XANES analysis
NN for EXAFS analysis

Development of ML-based methods for structural characterization of nanocatalysts

NN-XANES of ultra-small clusters
NN-XANES of bimetallic catalysts
NN EXAFS of mono- & bimetallic catalysts

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https://www.bnl.gov/chemistry/SDAN/
http://you.stonybrook.edu/frenkel
"Complex Systems are systems that comprise many interacting parts with the ability to generate a new quality of macroscopic collective behavior the manifestations of which are the spontaneous formation of distinctive temporal, spatial or functional structures."

**Disordered**

**Ordered**

**Dynamic structure**

**Heterogeneity**

**Attrbutes of Complexity**
**An Incomplete List of Unsolved Problems**

**Extended X-ray Absorption Fine Structure**

**Interatomic distances**

1. Expansion due to anharmonic effects
2. Contraction due to surface tension

**Disorder**

1. Static disorder
2. Thermal disorder

**Coordination numbers**

1. Crystalllographic structure
2. Size, shape of monometallic NPs
3. Local ordering of atoms of different types in heterometallic NPs

**Surface energy**

**Mischibility, phase diagrams on nanoscale**

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In a synchrotron electrons are accelerated and stored at a certain energy. At NSLS-II the energy is 3 GeV and the current is 500 mA.