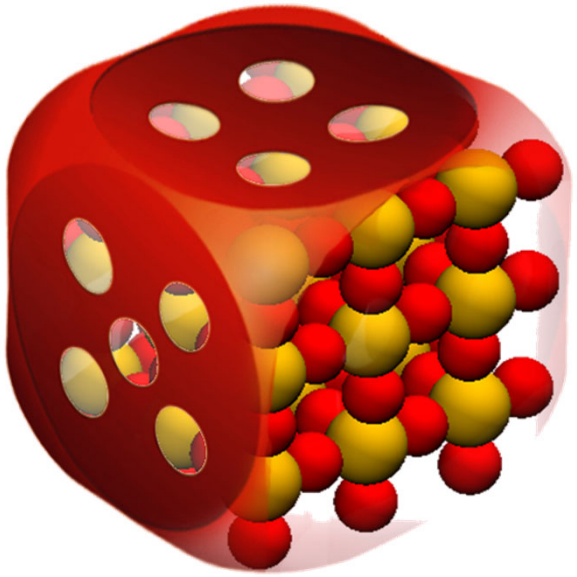
Reverse Monte Carlo simulations of EXAFS spectra



Janis Timoshenko

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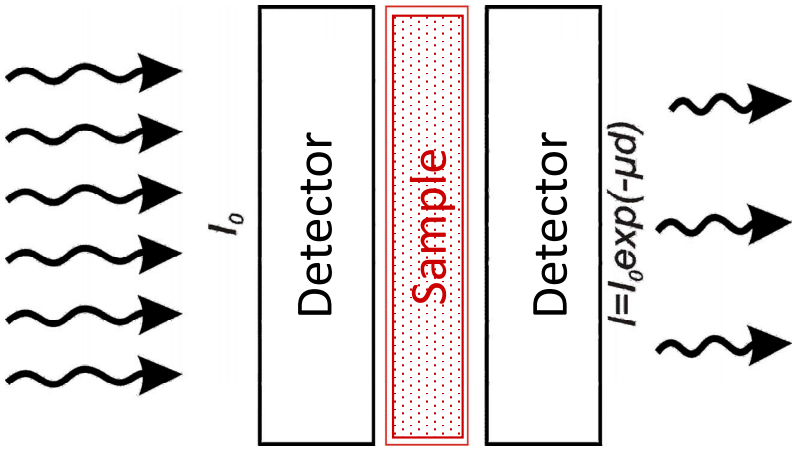
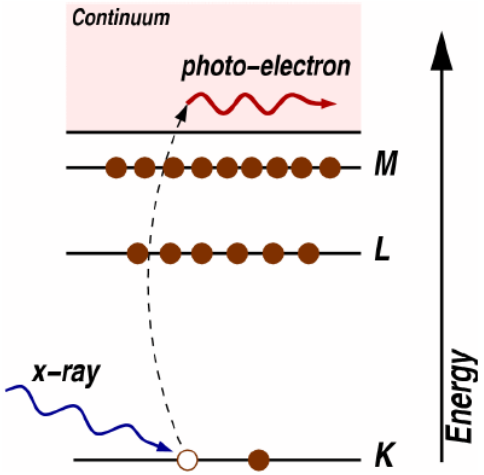
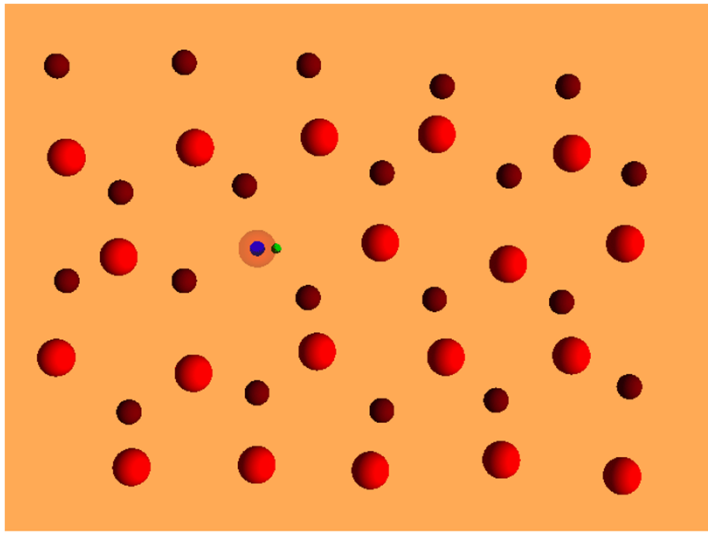
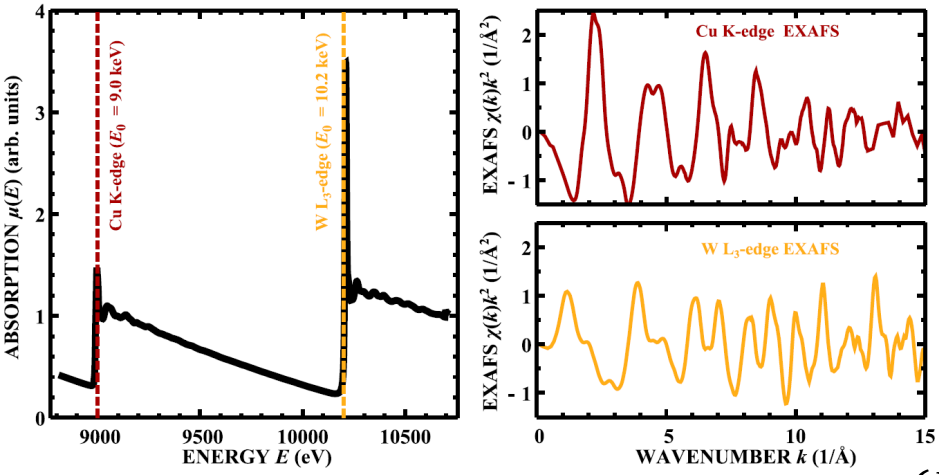
Fritz Haber Institute of Max Planck Society, Berlin, Germany
janis@fhi-berlin.mpg.de

XAS basics









J.Rehr et al, Rev. Mod. Phys 72 620 (2000)

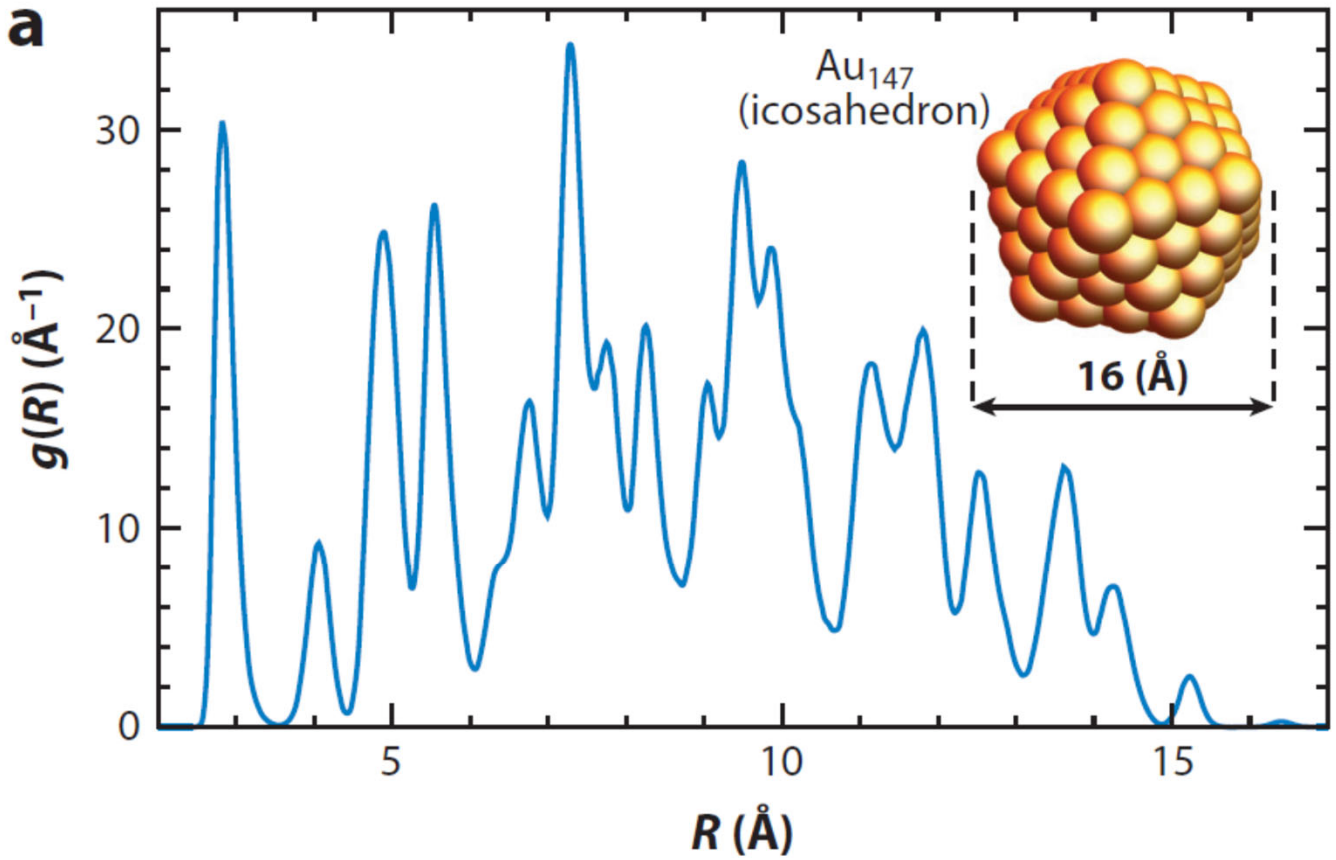
$$k = \sqrt{\frac{2m}{\hbar^2}\left(E_{photon} - E_0\right)}$$

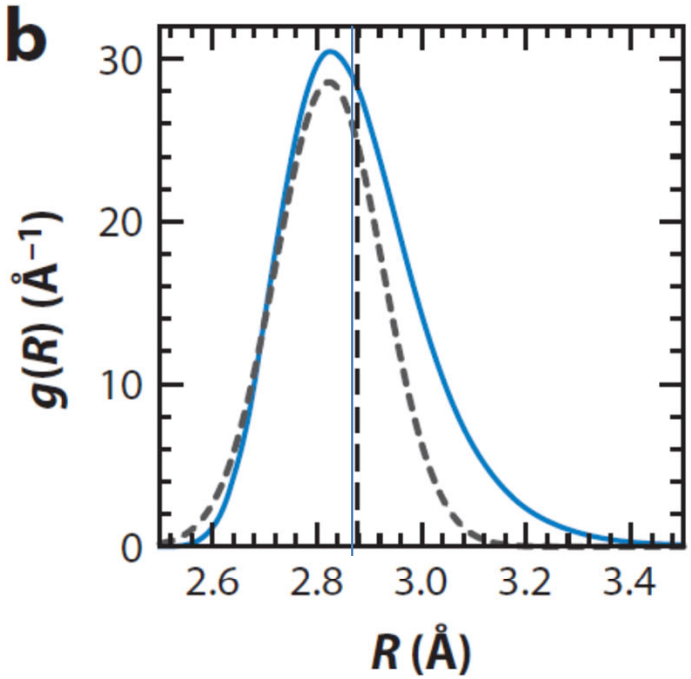
$$\chi(k) = \sum_p \chi_p(k)$$

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

Radial distribution function

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

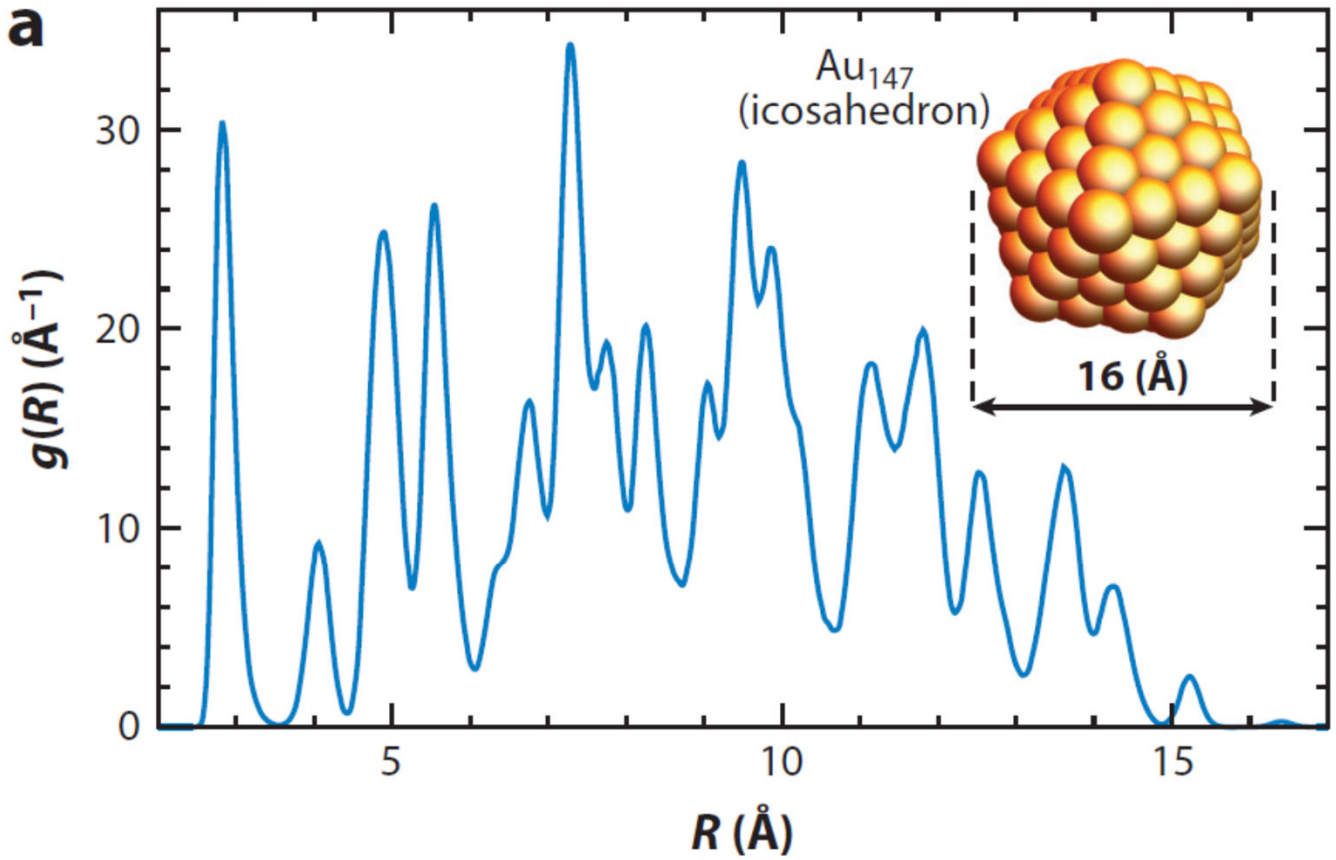


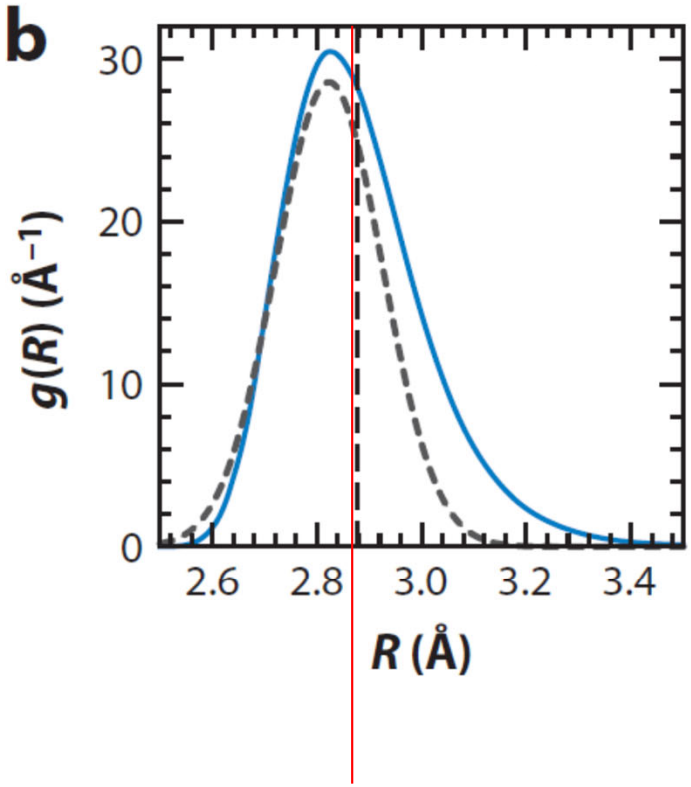


Timoshenko et al, Annu. Rev. Anal. Chem. 12 (2019)

Radial distribution function

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$



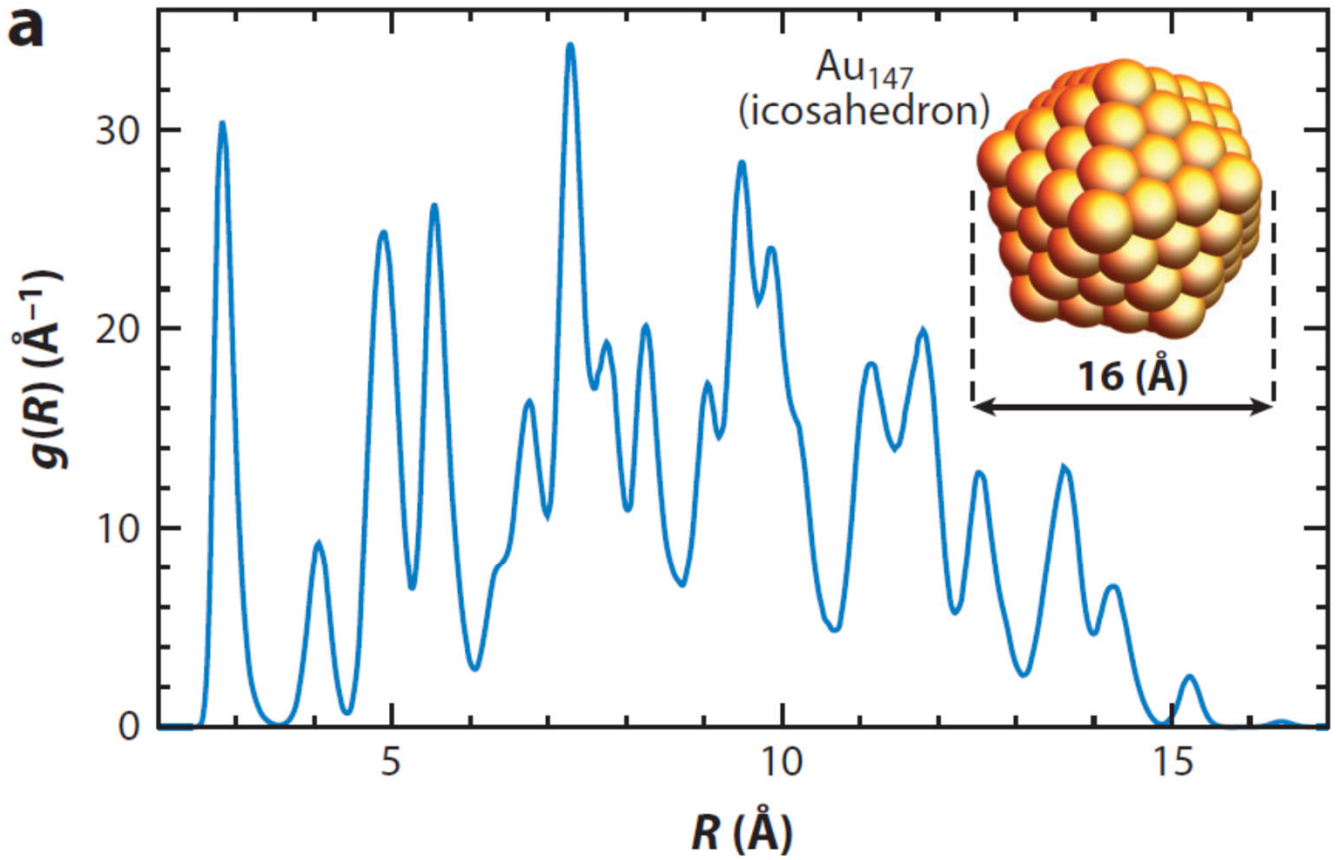


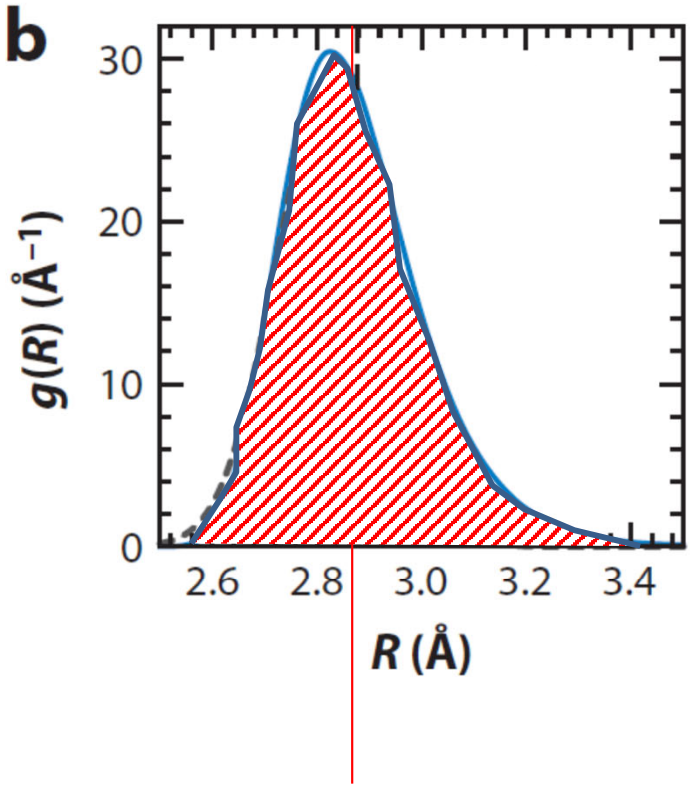
Average bond length

Timoshenko et al, Annu. Rev. Anal. Chem. 12 (2019)

Radial distribution function

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$



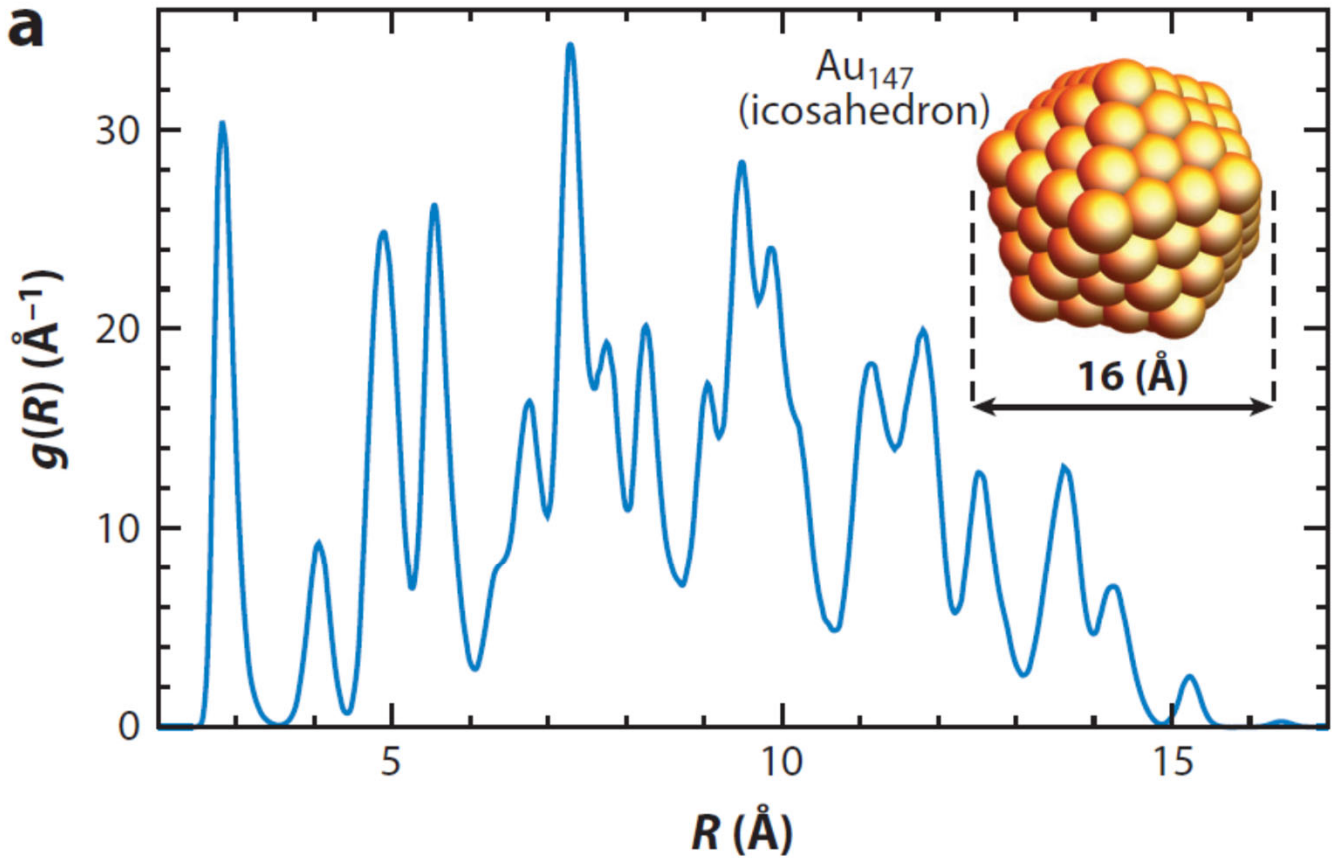


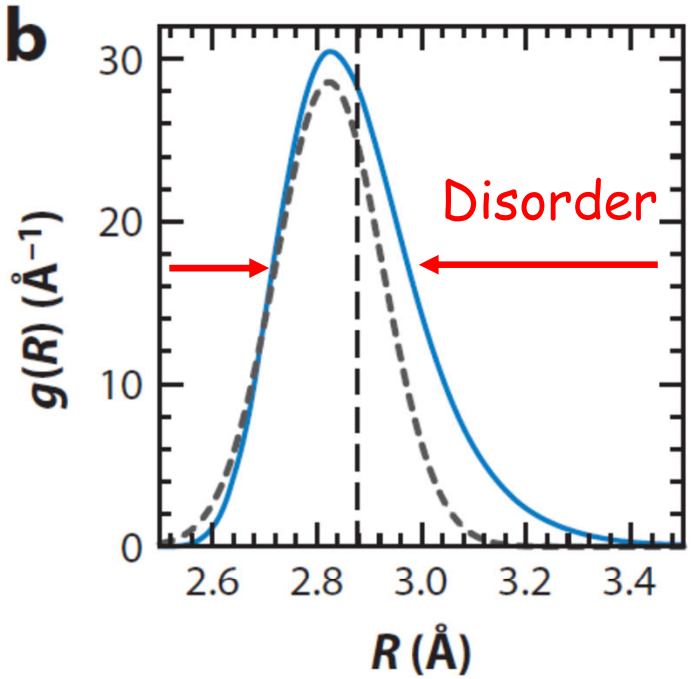
Coordination number

Timoshenko et al, Annu. Rev. Anal. Chem. 12 (2019)

Radial distribution function

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

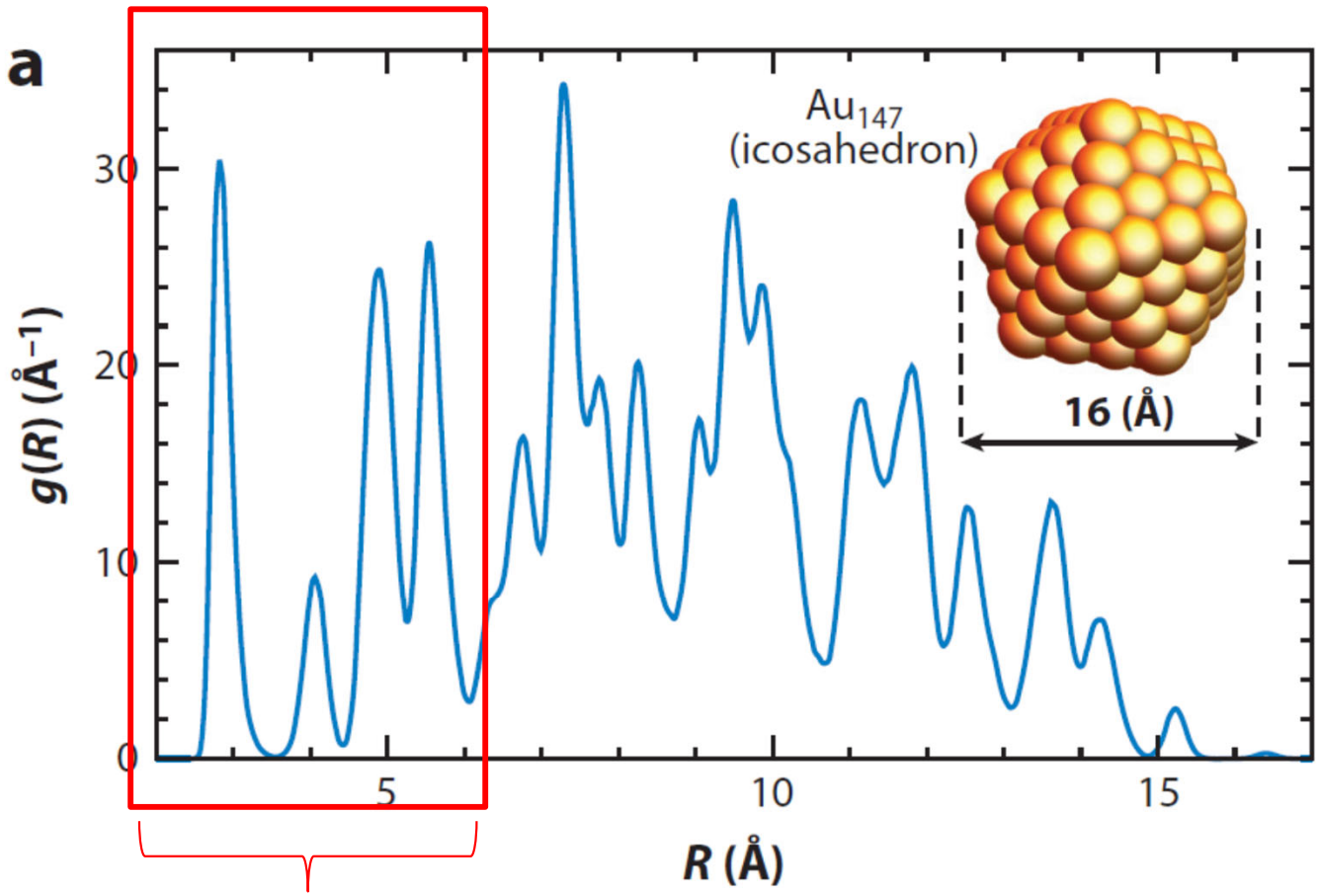


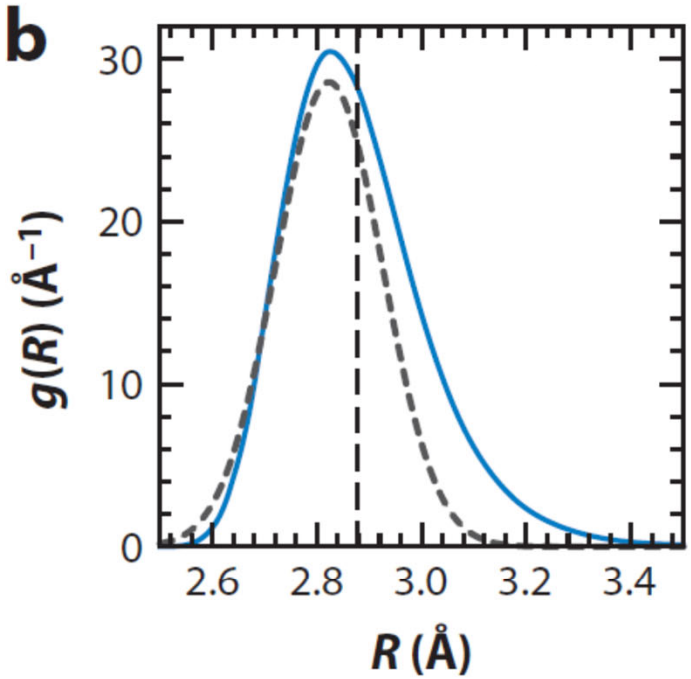


Timoshenko et al, Annu. Rev. Anal. Chem. 12 (2019)

Radial distribution function

$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$



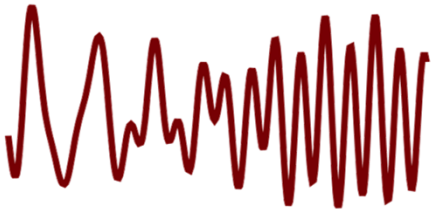


RDF accessible by EXAFS

Timoshenko et al, Annu. Rev. Anal. Chem. 12 (2019)

Conventional EXAFS analysis

Experimental EXAFS



$$\chi_p(k) = S_0^2 \int_0^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

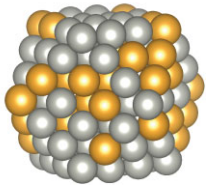
- Some a-priori shape for bond length distribution (e.g., Gaussian) needs to be assumed: may be unreliable for disordered materials;
- Challenging to analyze contributions beyond the first coordination shell;

Structure parameters

N, R, σ^2

$$\chi_p(k) = S_0^2 N_p \frac{f_p(k)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

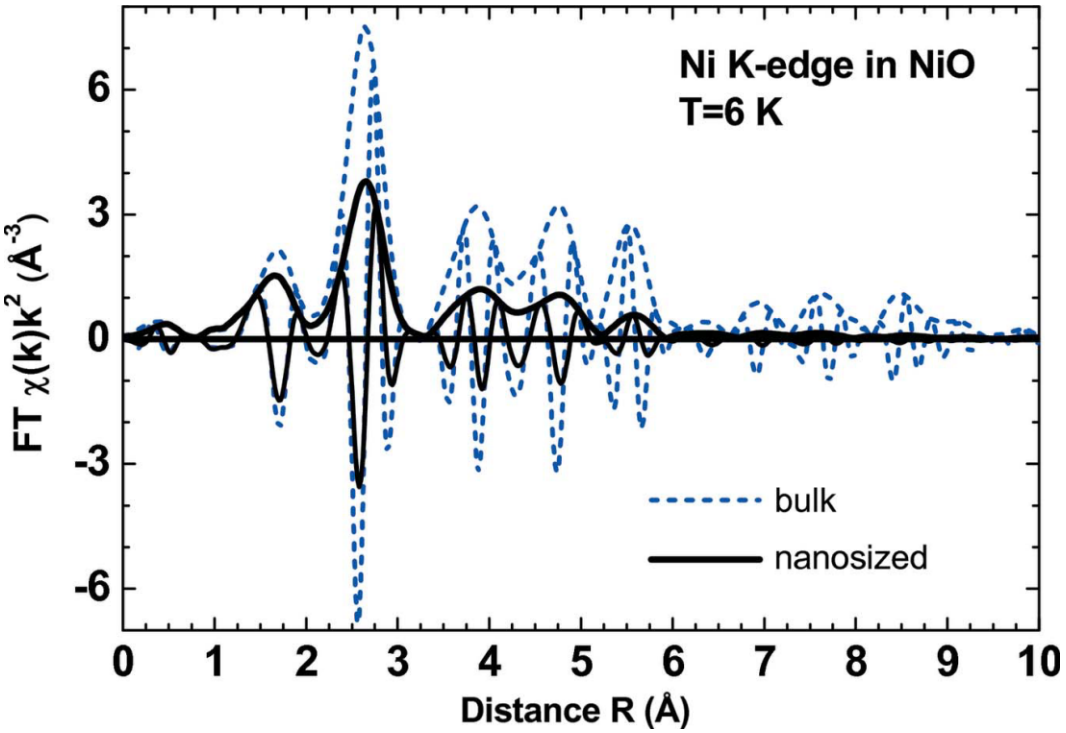
3D structure model

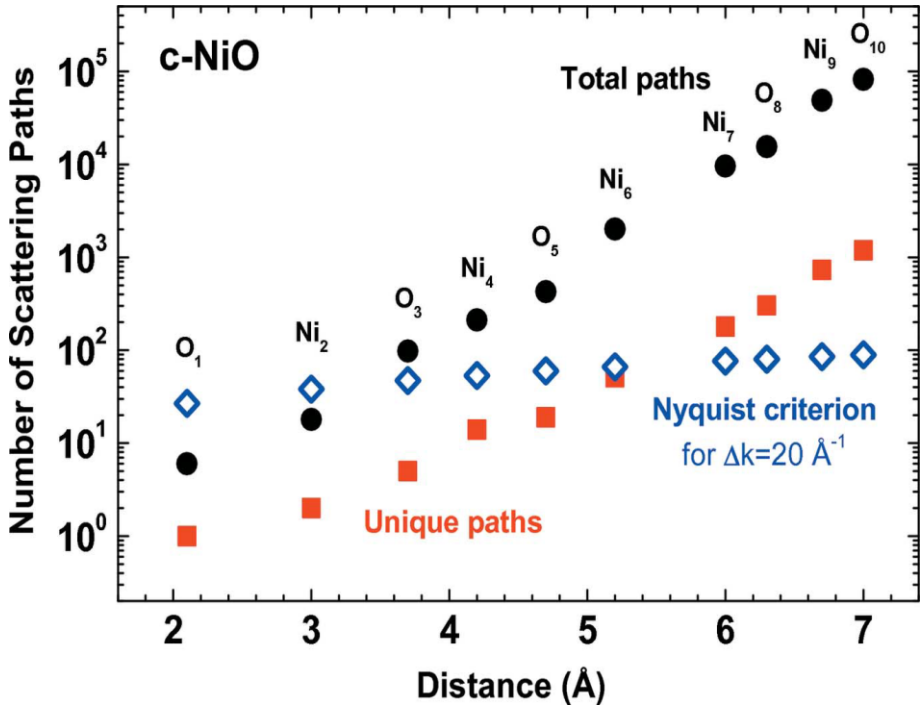


- Not a straightforward procedure
- No unique solution
- Gets very complicated, if different species are present in the sample

Challenges I

Information from atoms at distances up to 10 Å can sometimes be encoded in experimental EXAFS. Our ability to access this information, however, is very limited.





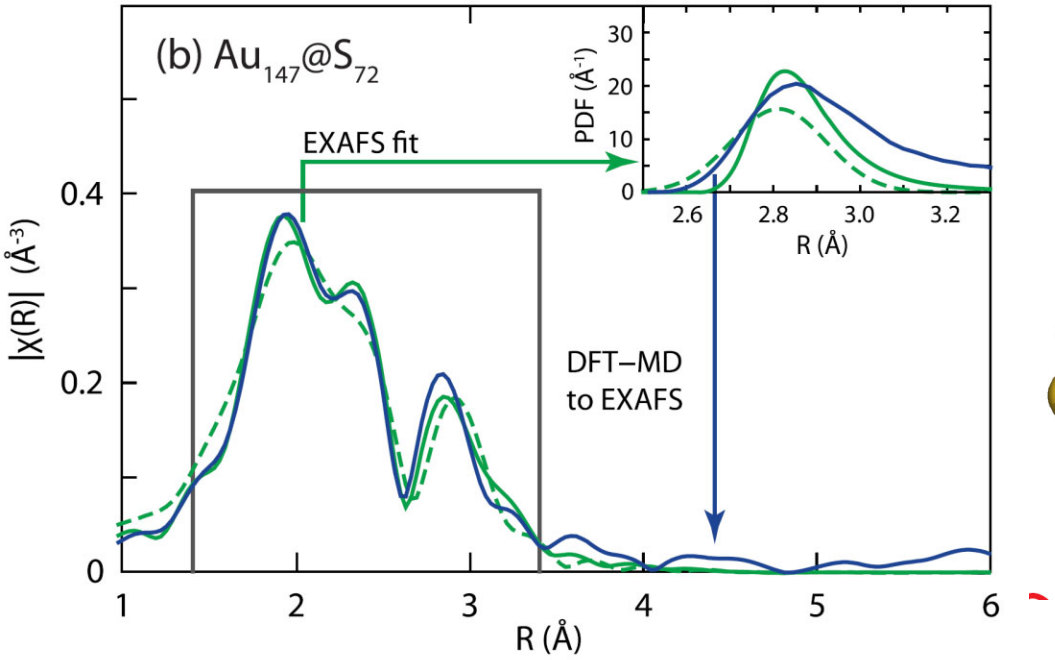
A. Kuzmin and J. Chaboy, IUCrJ 1 (2014) 571-589.

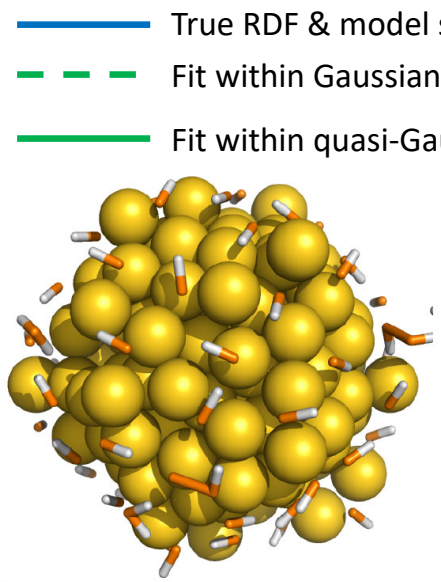
List of paths, included in the analysis, should be very carefully considered

Challenges II

Additional parameters needs to be included in EXAFS equation to account for deviations from Gaussian distributions (skewness (C_3), flatness (C_4), …)

$$\chi_p(k) = S_0^2 \frac{1}{k} F(k) \exp\left(C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 - \frac{4}{45}C_6k^6\right) \times \sin\left(2kC_1 - \frac{4}{3}C_3k^3 + \frac{4}{15}C_5k^5 + \phi(k)\right)$$





True RDF & model spectrum

Fit within Gaussian approximation

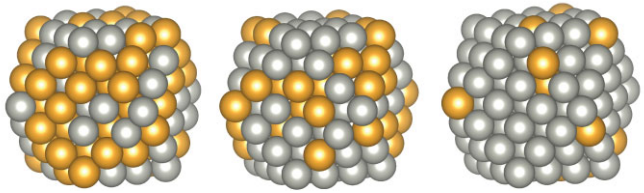
Fit within quasi-Gaussian approximation (with C_3)

Chill et al, ACS Nano 9 4036 (2015)

However, for very distorted materials cumulant expansion does not converge!

Simulations-based EXAFS analysis

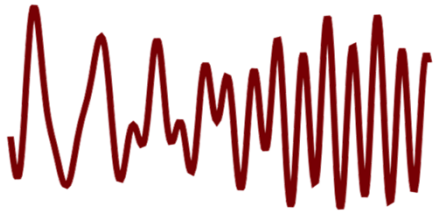
3D structure models



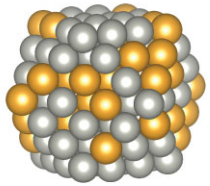
- Classical molecular dynamics
- Ab-initio molecular dynamics
- Monte-Carlo simulations
- Reverse Monte Carlo simulations

Time- and configuration-averaged theoretical EXAFS data

Experimental EXAFS



Best structure model



Structure parameters

N, R, σ^2

Reverse Monte Carlo simulations

- RMC procedure fits the experimental EXAFS spectra, but the variables are now the atomic coordinates in the 3D structure model of the material (rather than R, σ^2, N)
- Stabilizes solution by using geometrical constraints
- No additional information is required (but may be used, if available)
- Allows analysis of distant coordination shell and MS effects
- No assumptions of the shape of bond length dsitribution is required

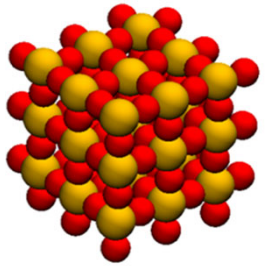
Outline

- Monte Carlo, Reverse Monte Carlo, Hill Climbing and Simulated Annealing
- Evolutionary algorithm
- Examples of RMC/EA-EXAFS applications

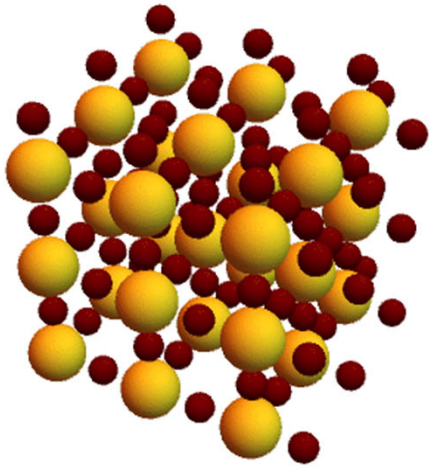
Reverse Monte Carlo simulations

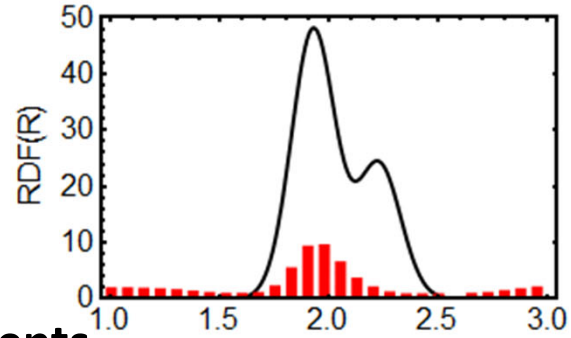
R.L. McGreevy and L. Pusztai. Mol. Simul, 1988

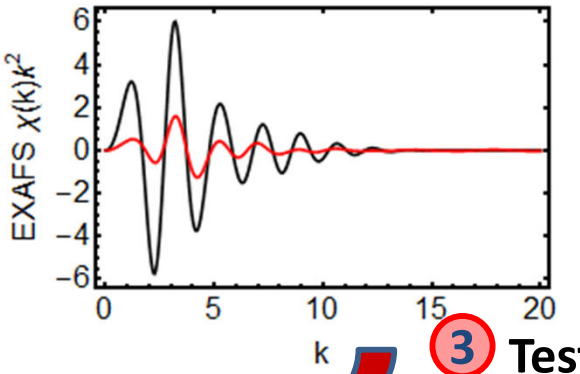
1 **Initial structure model**



2 **Calculations of EXAFS data**







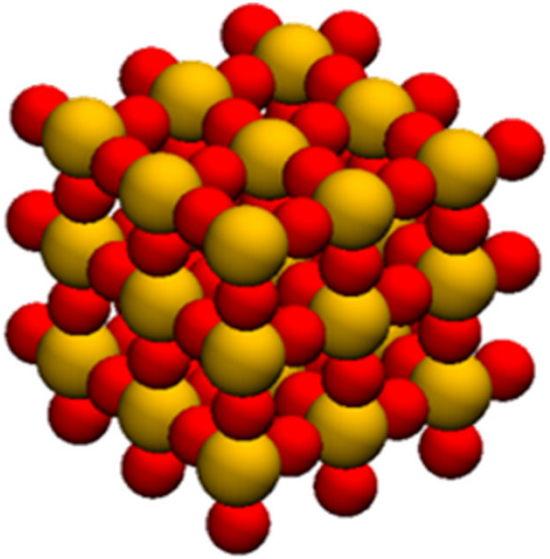
3 **Testing agreement of theoretical data with experimental**

4 **Random displacements of atoms (or some other update of 3D structure)**

5 **Analysis of final structure**

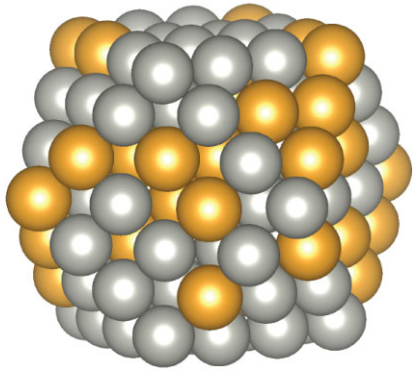
N, R, σ^2

Initial structure model



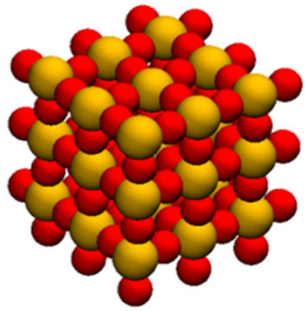
- For crystals - equilibrium structure from XRD
- For disordered materials – random mixture of atoms (with specified density)

- For nanomaterials – stable structures, DFT predictions, MD results, something derived from bulk structure motiffs...



Calculations of EXAFS spectra

- Codes like FEFF allow one to obtain EXAFS spectra, knowing atomic coordinates



A. Ankudinov A, B. Ravel , J. Rehr, Phys. Rev. B 1998

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PRINT     1      0     0     0     0       0

*         r_scf    [ l_scf  n_scf  ca ]
SCF       4.128968281384   0       30      0.100000000000     1

*         ixc   [ Vr  Vi ]
EXCHANGE  0       0   0

EXAFS 20.0
RPATH     6.000000000000
NLEGS     8
CRITERIA  0.0  1.500000000000
CFAVERAGE 1 1 6.000000000000


POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
      0   28    Ni     -1      -1       0
      1   28    Ni     -1      -1       1

ATOMS
7.101266483000 7.157770981000 7.012750102000 1 Ni
8.774130656000 7.075883002000 5.310066029000 1 Ni
5.373045190000 6.990703735000 5.344682688000 1 Ni
8.837089280000 8.859356899000 7.034820065000 1 Ni
7.030365631000 8.808748666000 8.811565053000 1 Ni
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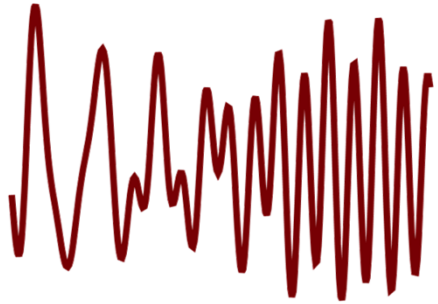
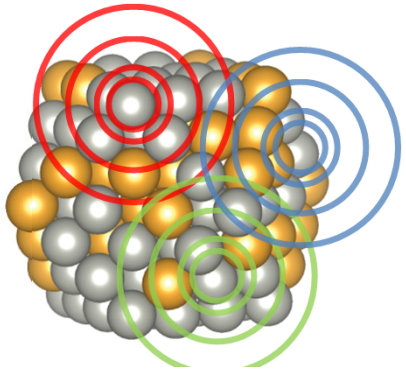


- Unlike conventional EXAFS fitting**, inclusion of additional scattering paths in the analysis does not increase the number of variables**: one can (and should) include **all** relevant scattering paths: contributions form distant coordination shells, multiple scattering effects

- Spectra should be calculated **for all absorbing atoms in the model**, and then averaged



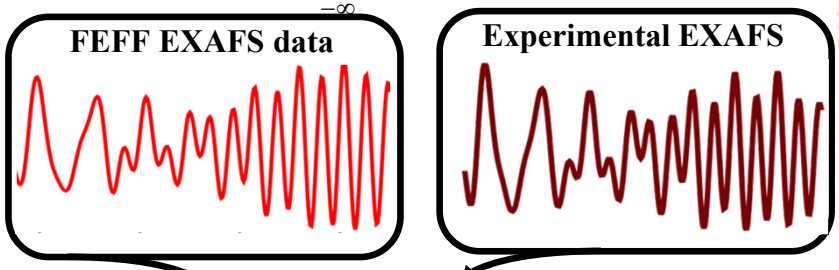
For bulk materials special attention needs to be paid to boundary conditions

Comparison of EXAFS spectra

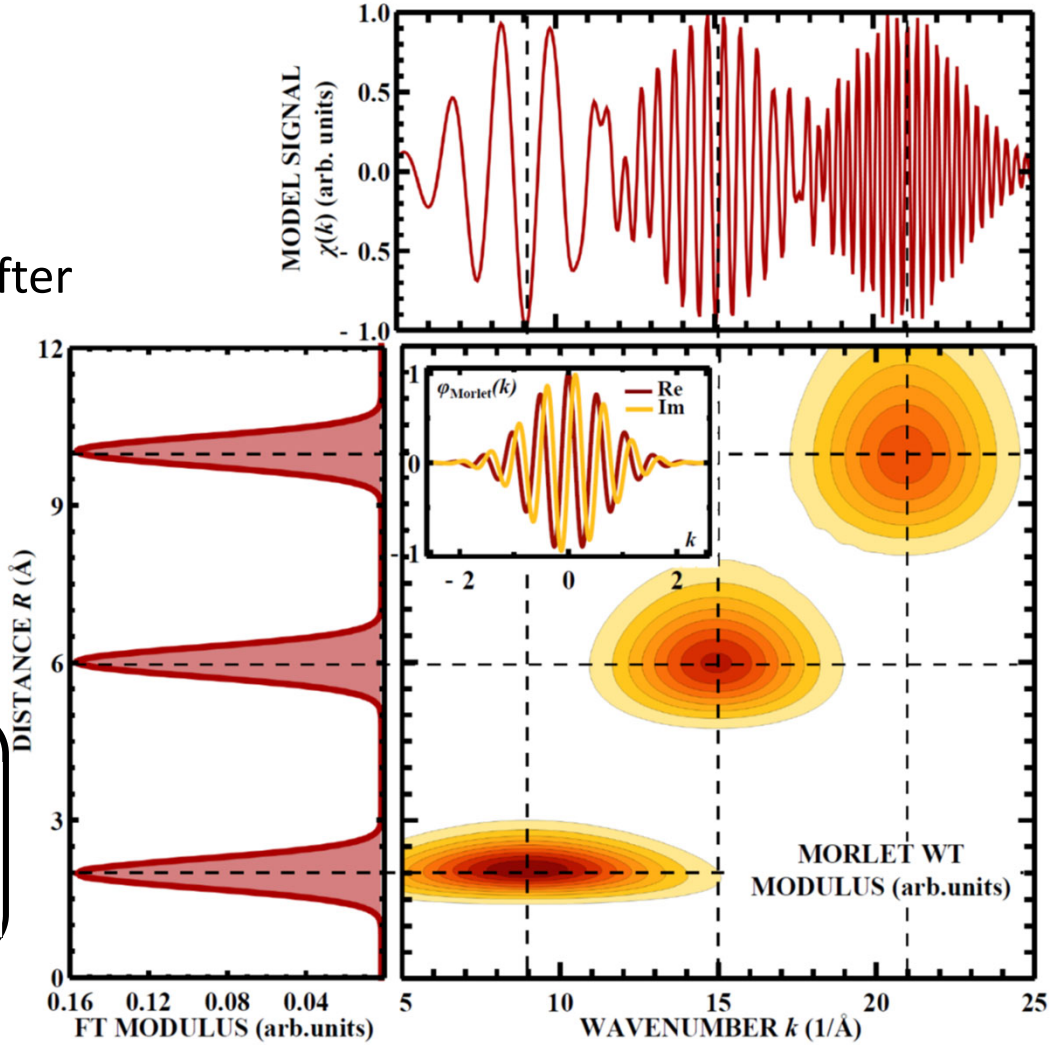
Comparison of theoretical and experimental spectra can be done in

- *k*-space
- in *R*-space (after Fourier trasform)
- in *q*-space (after Fourier filtering)
- in k- and R- spaces simultaneously (after wavelet transform)

$$w(R,k) = \sqrt{R/R_0}\int_{-\infty}^{+\infty} \chi(k')\phi\big((R/R_0)(k'-k)\big)dk'$$



$$\xi_{k,R} = \frac{\left\| w_{tot}(R,k) - w_{\exp}(R,k) \right\|_2}{\left\| w_{\exp}(R,k) \right\|_2}$$

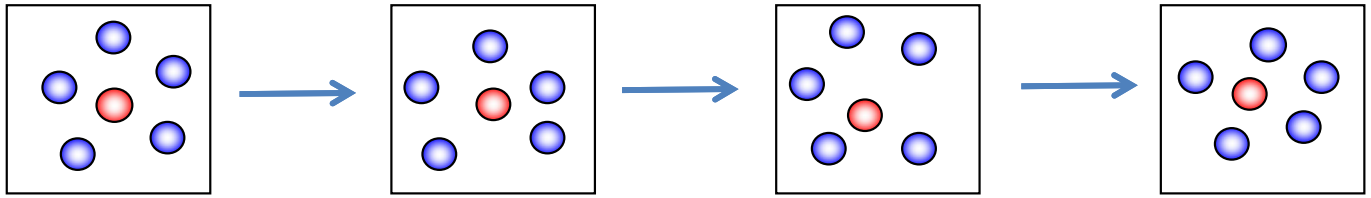


M. Munoz *et al,* Am. Min., 2003
H. Funke, *et al*, Phys. Rev. B, 2005.

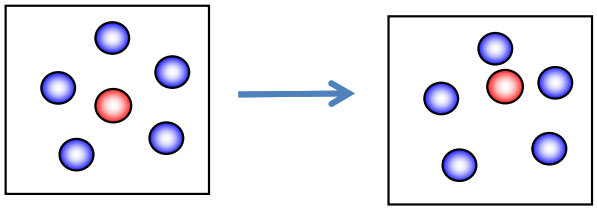
Update of structure model

1) Dispalcements of all atoms:

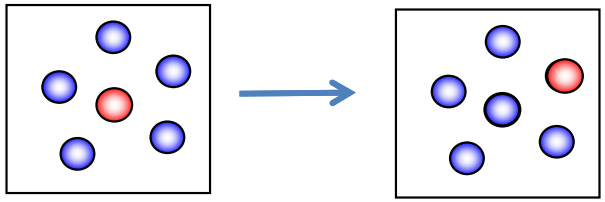
$$\boldsymbol{r}_i(t + \Delta t) = \boldsymbol{r}_i(t) + \boldsymbol{\delta}_i$$



2) Displacements of one, randomly selected atom



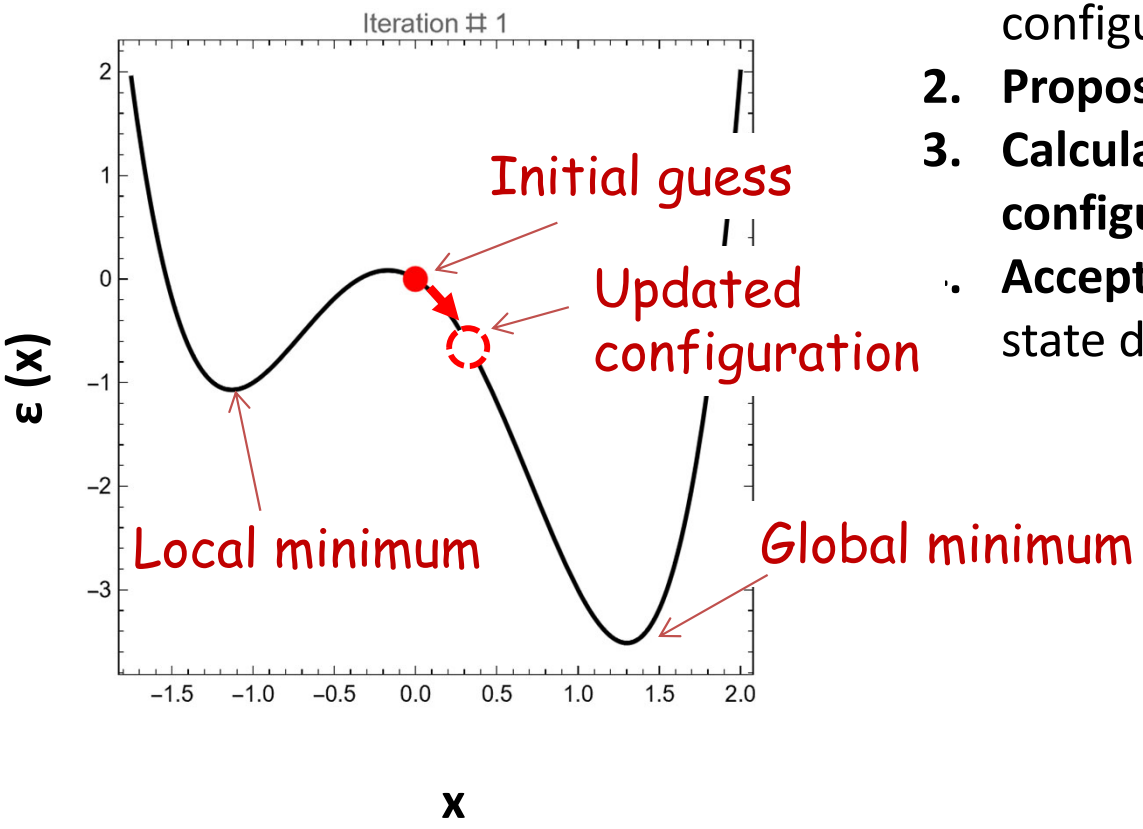
3) Swapping two atoms



4) ....

M. Munoz *et al,* Am. Min., 2003
H. Funke, *et al*, Phys. Rev. B, 2005.

Structure model optimization: Hill Climbing

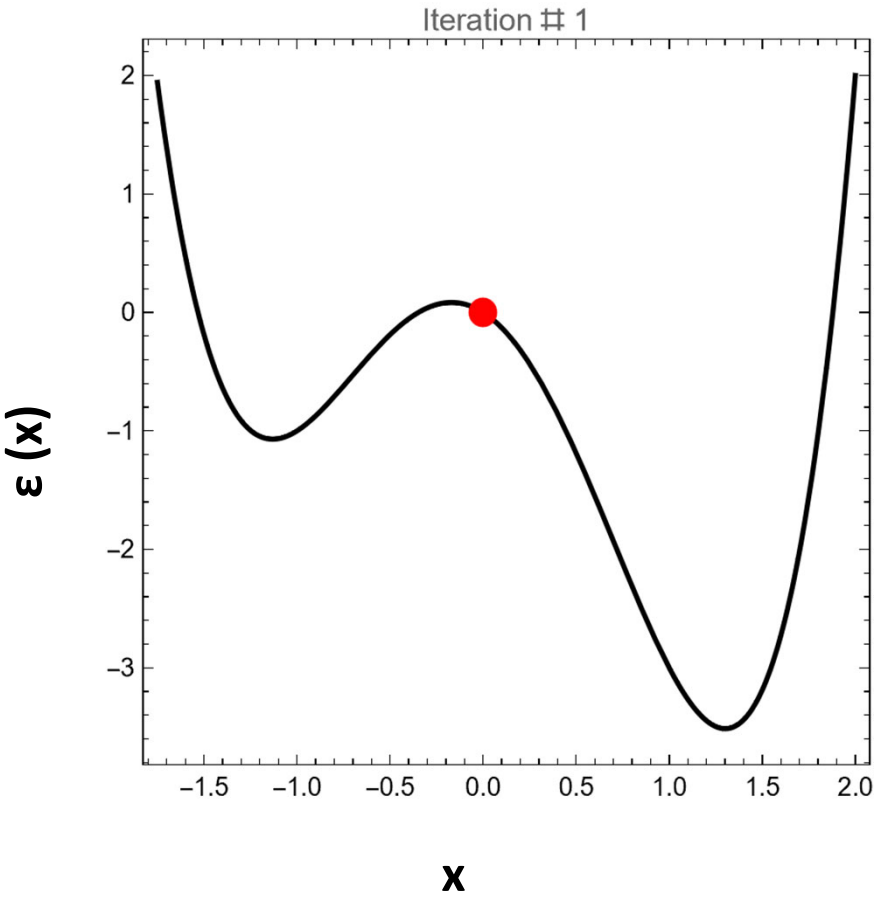


1. **Calculate** property ε (e.g., EXAFS) for given configuration x.
2. **Propose** a **random** update of configuration
3. **Calculate** property (e.g., EXAFS) for **updated configuration**
4. **Accept** the update **or return** to the previous state dependently on the new and old values of ε

Hill Climbing algorithm:

- $\varepsilon < \varepsilon_{old}$: configuration is accepted

Structure model optimization: Hill Climbing



1. **Calculate** property ε (e.g., EXAFS) for given configuration x.
2. **Propose** a **random** update of configuration
3. **Calculate** property (e.g., EXAFS) for **updated configuration**
4. **Accept** the update **or return** to the previous state dependently on the new and old values of ε

Hill Climbing algorithm:

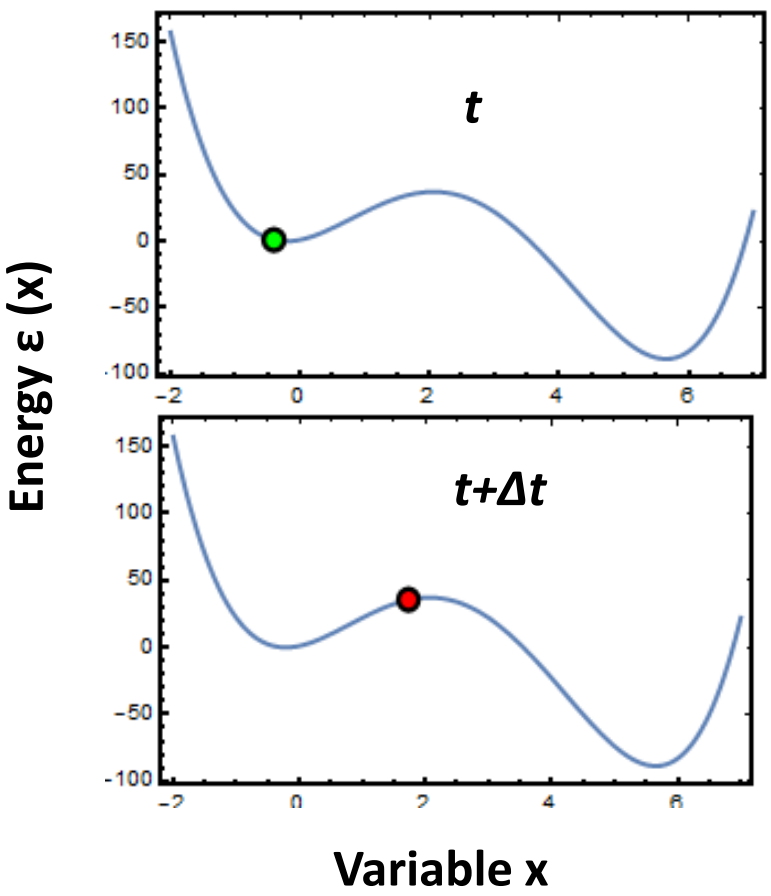
- $\varepsilon < \varepsilon_{old}$: configuration is accepted

- **HC is very simple and works well in many cases, where the good initial structure model is known**
- **For more complicated cases it can stuck in the local minimum**

(Metropolis) Monte Carlo

A method for configurations sampling according to desired distribution:

1. **Calculate** property ε (e.g., energy) for given configuration x.
2. **Propose** a random update of configuration
3. **Calculate** property (e.g., energy) for **updated configuration**



4. Accept the update **or return** to the previous state dependently on the new and old values of ε

Typical application: sampling configurations, so that their energies follow Gibbs' distribution

Metropolis algorithm:

- $\varepsilon < \varepsilon_{old}$: configuration is accepted
- $\varepsilon > \varepsilon_{old}$: configuration is accepted, if

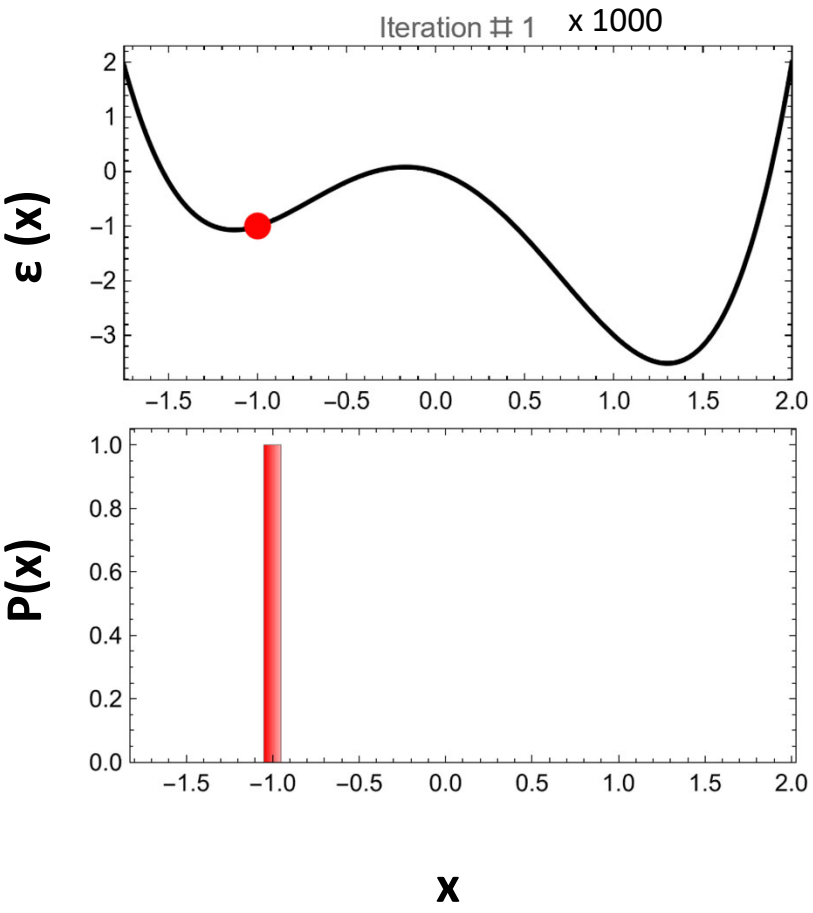
$$\exp[-(\varepsilon - \varepsilon_{old}) / T] > \rho$$

***T* – scaling parameter**
***ρ* – random number (0..1)**

Metropolis, Rosenbluth, Rosenbluth, Teller, Teller 1953 J.Chem. Phys. 21 1087

Reverse Monte Carlo

After sufficient number of iterations the probability to find system in a given state x will be proportional to exp[-ε(x)/*T*]



«Direct» Monte Carlo:
Energy function → correctly sampled configurations → properties (e.g., heat capacity, average interatomic distance, averaged spectra, etc.)

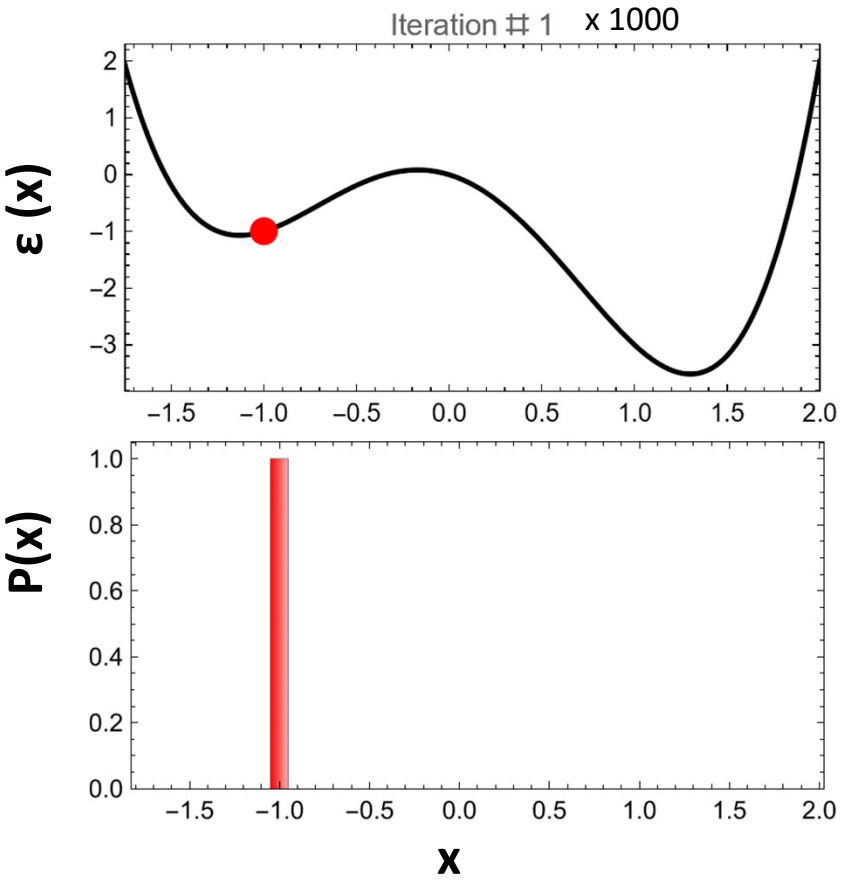
Reverse Monte Carlo: ε(x) will be the difference between experimental and theoretical data

Properties (e.g., EXAFS spectra) → atomic configurations

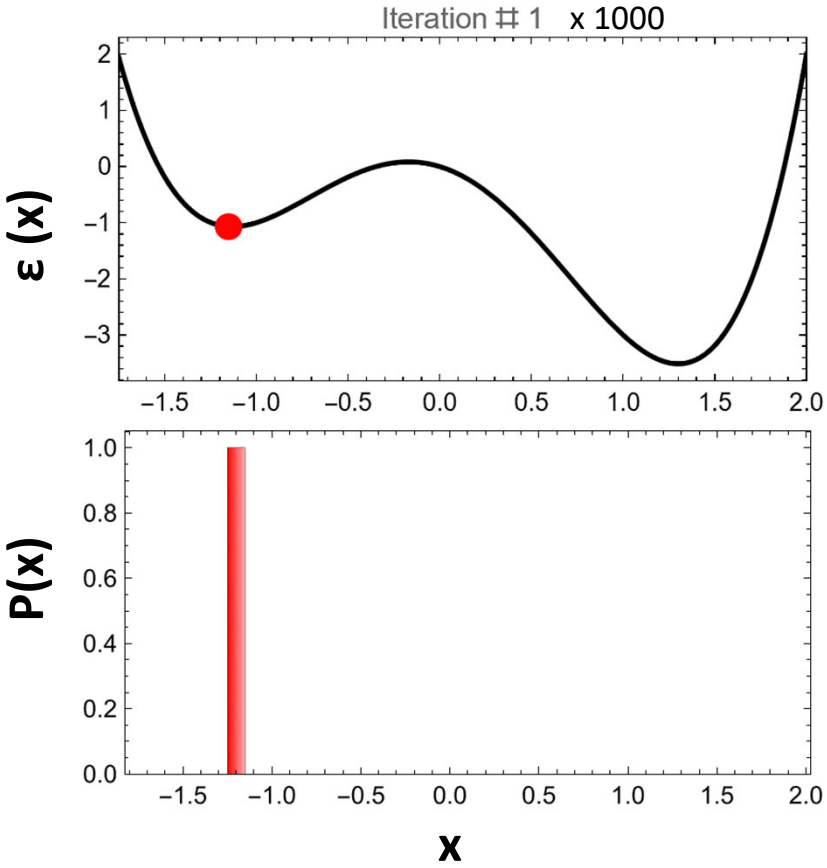
R.L. McGreevy and L. Pusztai. Mol. Simul, 1988

Influence of *T*

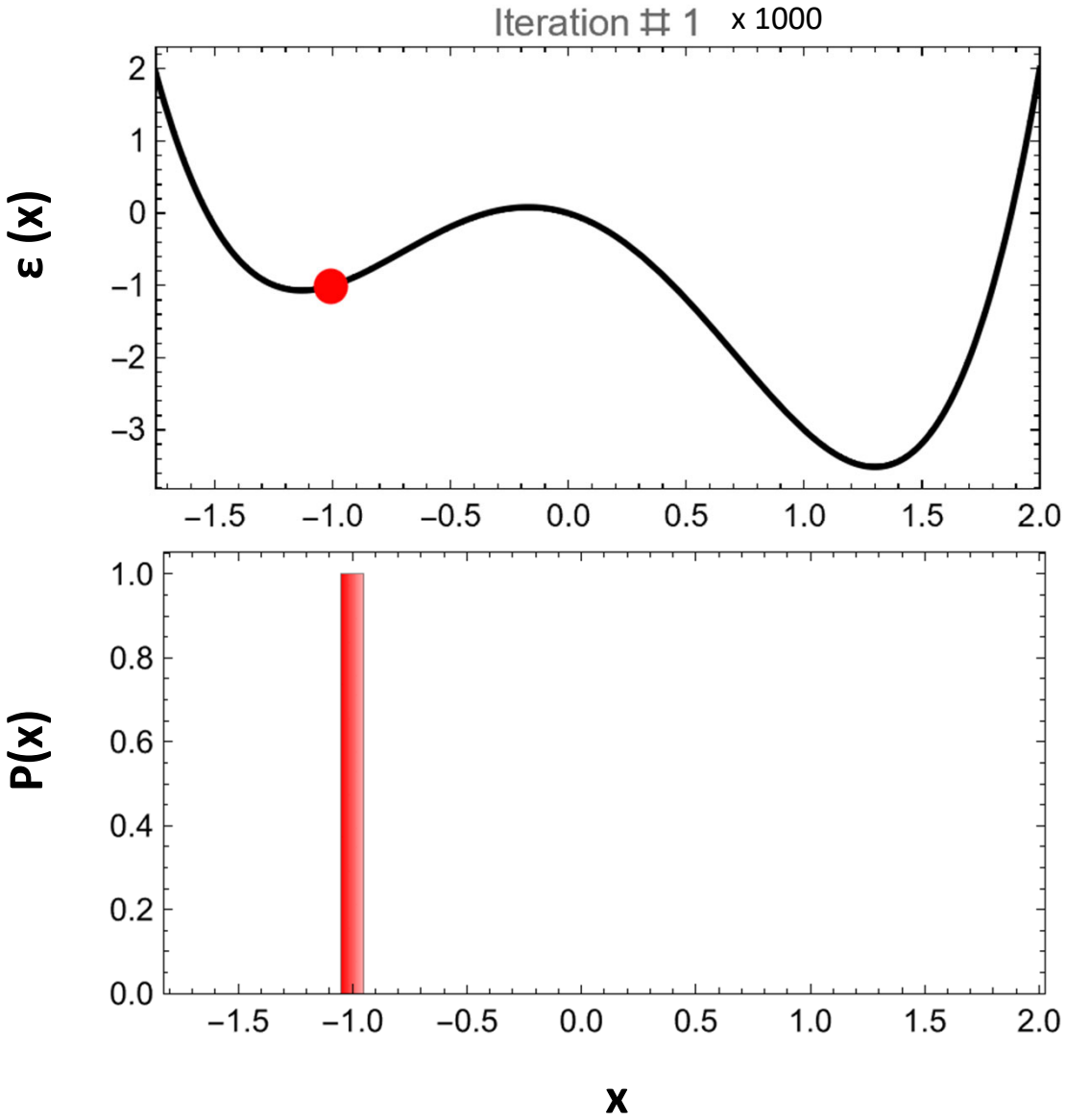
Too low *T*: system never leaves the local minimum



Too high *T*: all *x* are almost equally probable



Simulated annealing



Large *T* at the beginning of simulations

to facilitate quick exploration of configuration space

Low *T* at the end of simulations

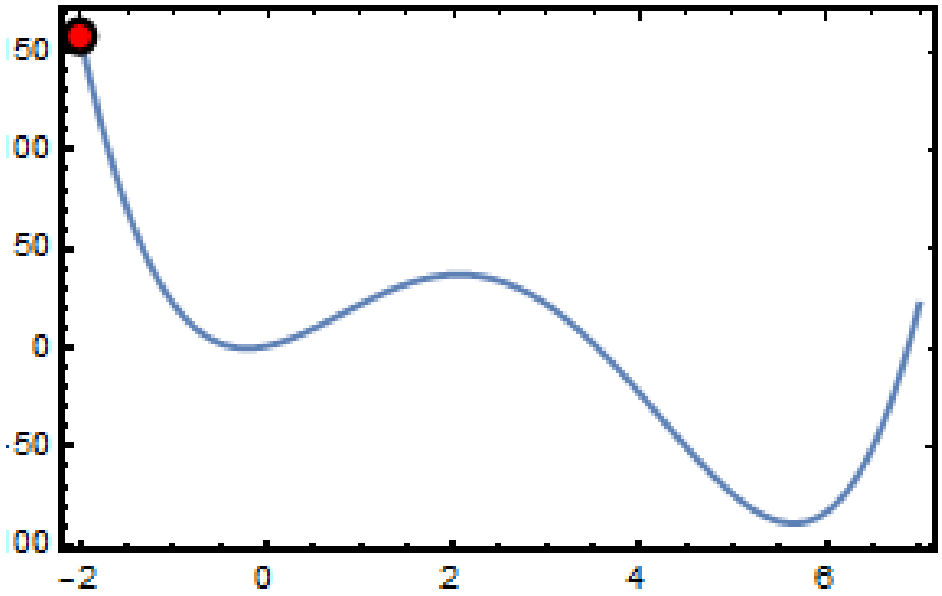
to end up with a single, «globally» optimal configuration

Kirkpatrick S, Gelatt C D and Vecchi M P 1983 Science 220 671

Constraints

are important, because reduce significantly the size of configurational space

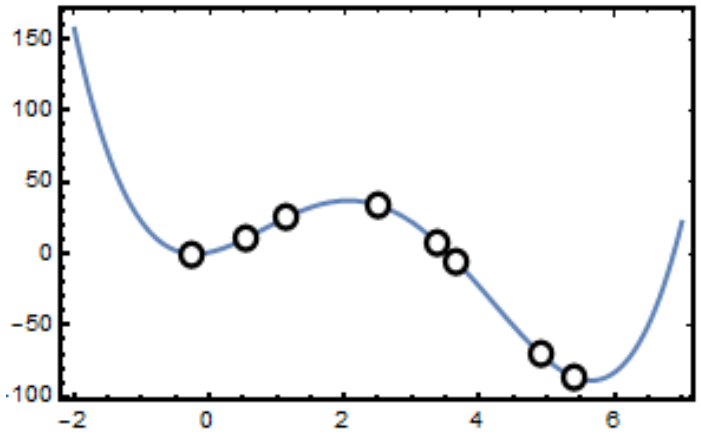
In RMC method constraints are very easy to implement, by **adding some penalty** to ε(x) function, when x gets unacceptable.



Useful constraints for atomistic simulations:

minimal allowed interatomic distance
maximal allowed displacement from initial position
...

Evolutionary algorithm

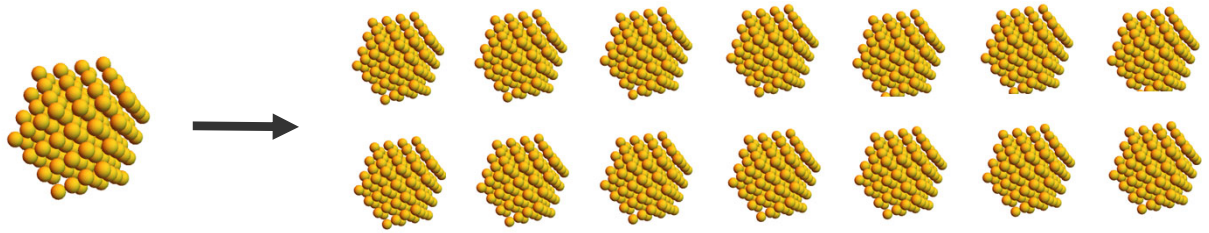


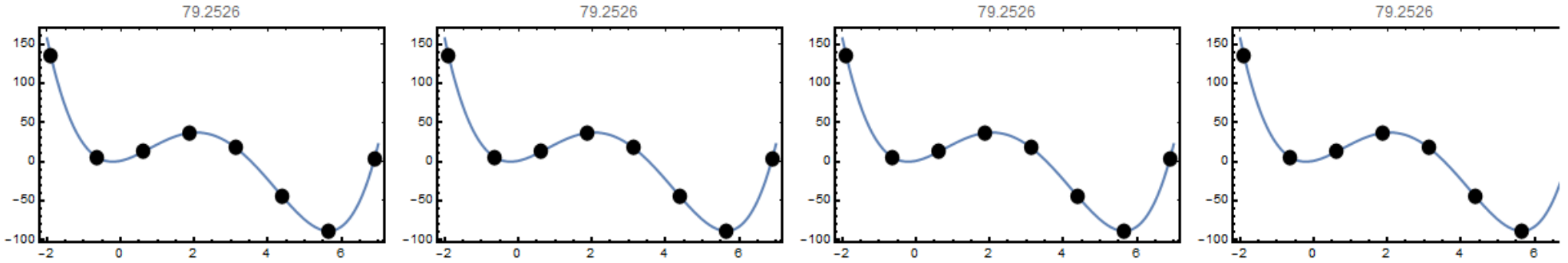
More realistic situation: **many variables** need to be optimized.

The more variables (dimensions) the harder it is to find a good solution **("dimensionality curse").**

Some of the many-dimensional problems can be solved more efficiently with so called **evolutionary algorithms** (genetic algorithms)

Several copies of the model that needs to be optimized



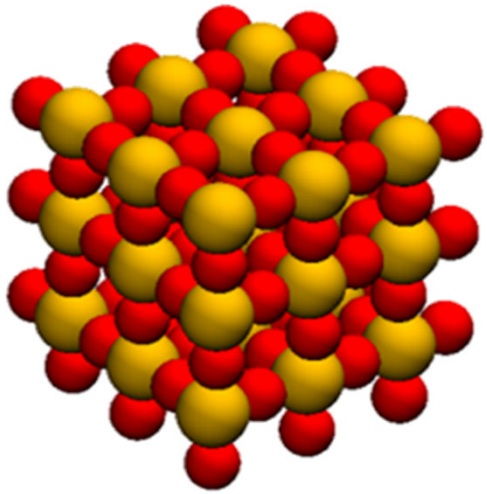


J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.

Interpretation of results

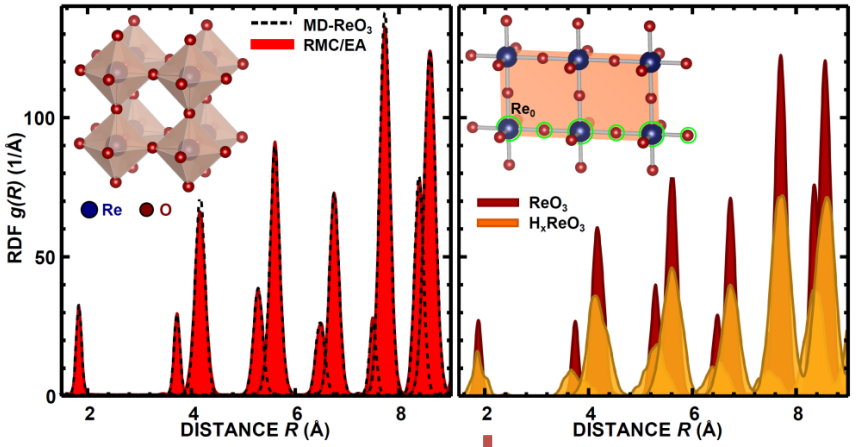
Final results of RMC simulations – **set of atomic coordinates.**
It is **not unique** and **not meaningful**.

Statistical analysis of coordinates is necessary: calculations of average distances, angles, construction of bond-length histograms, etc.



3D structure model from RMC

Bond-length distributions

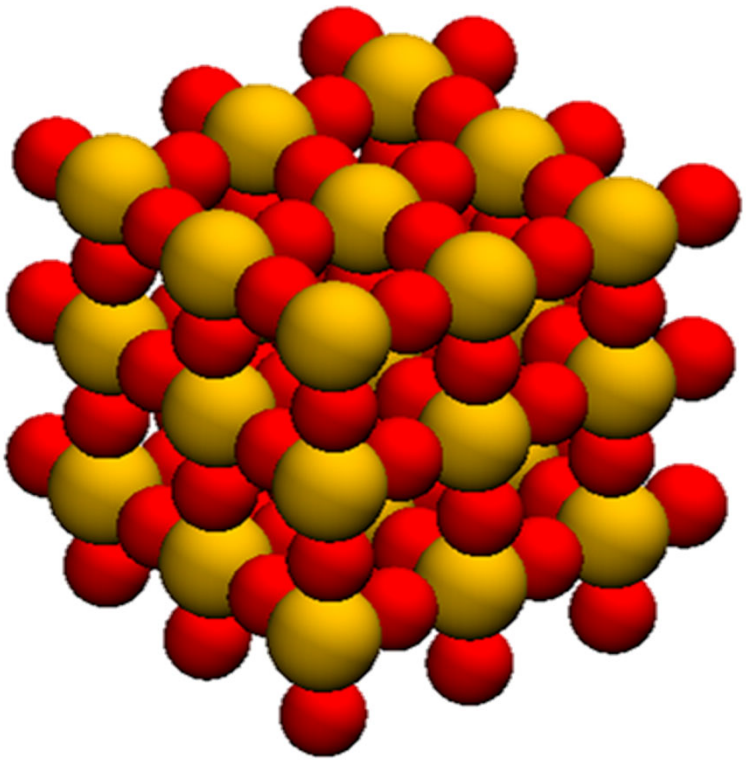


Structure parameters

$$R_{EXAFS} = \langle R \rangle = \frac{1}{N}\int_{-\infty}^{+\infty} \boldsymbol{g_p(R)} R \; dR$$

$$\sigma^2 = \frac{1}{N}\int_{-\infty}^{+\infty} g_p(R)(R - R_{EXAFS})^2 \, dR$$

ReO_3



ReO_3: crystalline material with cubic, perovskite-type structure (Pm-3m)

Metallic conduction (delocalized 5*d* electron of rhenium), bet also a good ionic conductor (hydrogen ions easily intercalate into the lattice)

Very strong correlations of atomic motion: Re-O bonds are very strong and their length is weakly dependent on temperature, “rigid” ReO_6 octahedra

Model material for negative thermal expansion studies

Focusing effect: very strong influence of multiple scattering effects

N Alberding *et al*, Le Journal de Physique Colloques, 1986;
A Ferretti *et al,* J. Phys. Chem. Solids, 1965;
T. Chatterji *et al,* Appl. Phys. Lett, 2009.
E. Cazzanelli *et al*, J. Appl. Phys, 2009

Examples

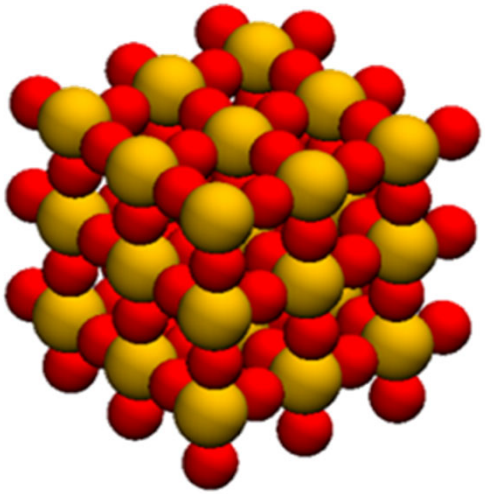
- **RMC for crystalline materials (ReO_3 and W)**
  - EXAFS analysis beyond the 1st coordination shell in the presence of strong multiple-scattering effects
  - Disorder in a crystalline material
  - Anisotropy of atomic motion
  - Correlations in atomic motion

- **Structure of disordered materials (Zn and Au_{147} particles):**
  - EXAFS analysis of non-periodic systems
  - Probing non-Gaussian bond-length distributions

- **Structure of multielement nanoparticles ($CuWO_4$ and $CoWO_4$):**
  - Simultaneous analysis of EXAFS data from multiple edges
  - RMC-EXAFS for validation of structure models

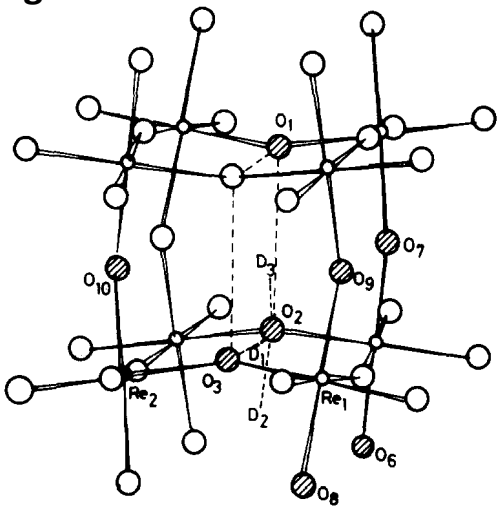
Hydrogen intercalation into ReO_3

Perovskite-type structure of ReO_3

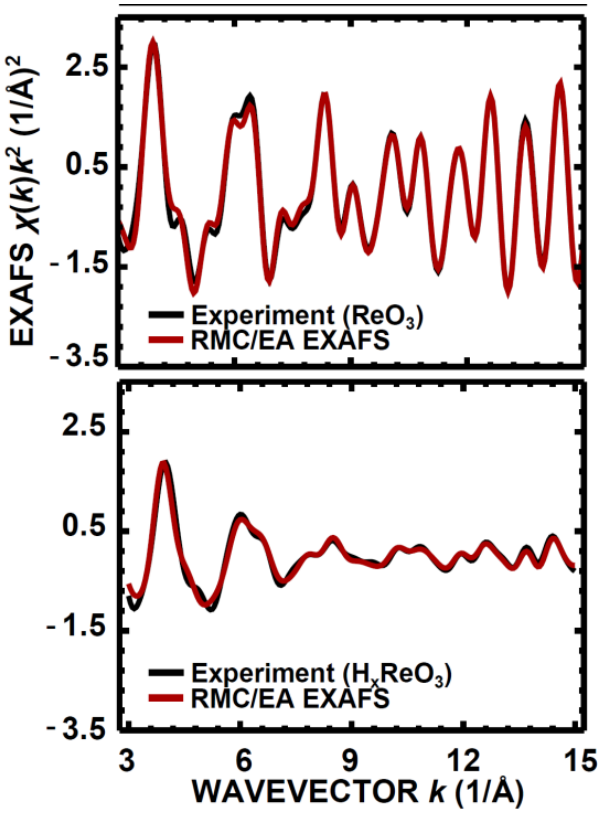


$$ReO_3 + x\,H_2 \underset{air}{\overset{Pt}{\rightleftharpoons}} H_{2x}ReO_3$$

XRD suggests only minor rotation of ReO_6 units upon hydrogen intercalation, no significant distortions



Changes in EXAFS, however, are dramatic



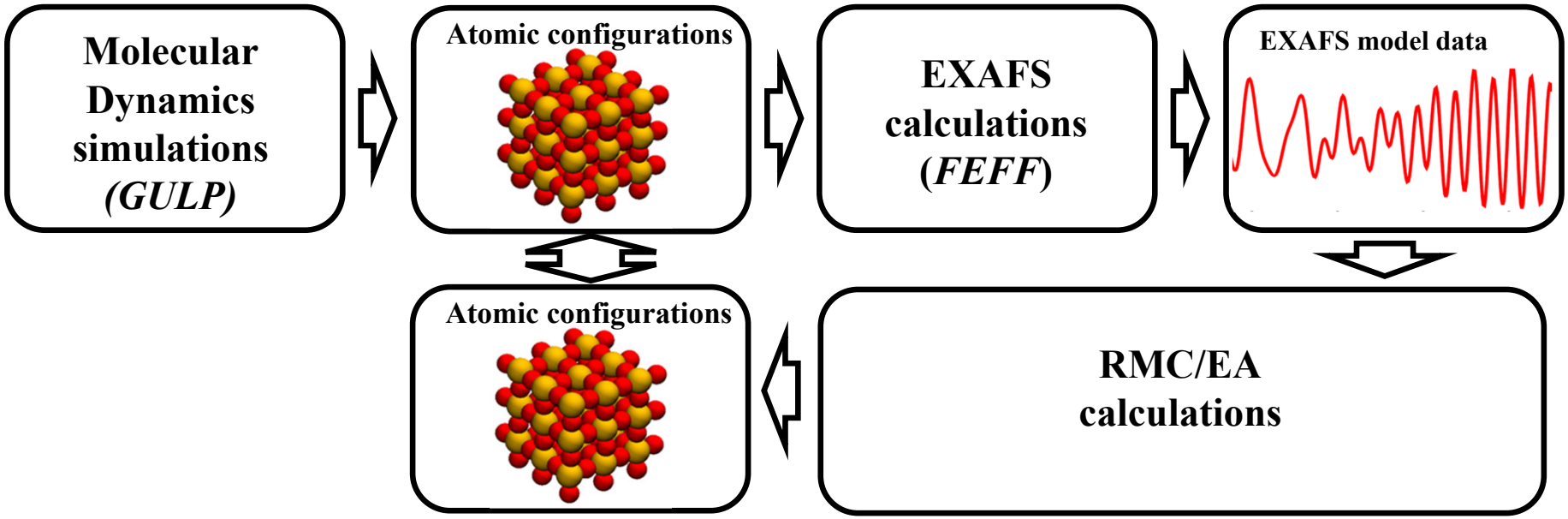
We use RMC/EA method to solve this controversy

Dickens P G and Weller M T, *J. Solid State Chem.* (1983)

J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.
J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

How accurate RMC-EXAFS can be?

Validation of RMC method with model data



A. Kalinko, R. A. Evarestov, A. Kuzmin, J. Purans, J. Phys.: Conf. Series 2009
J. D. Gale and A. L. Rohl.). Mol.Simul. 29 (2003) 291.

J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.
J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

How accurate RMC-EXAFS can be?

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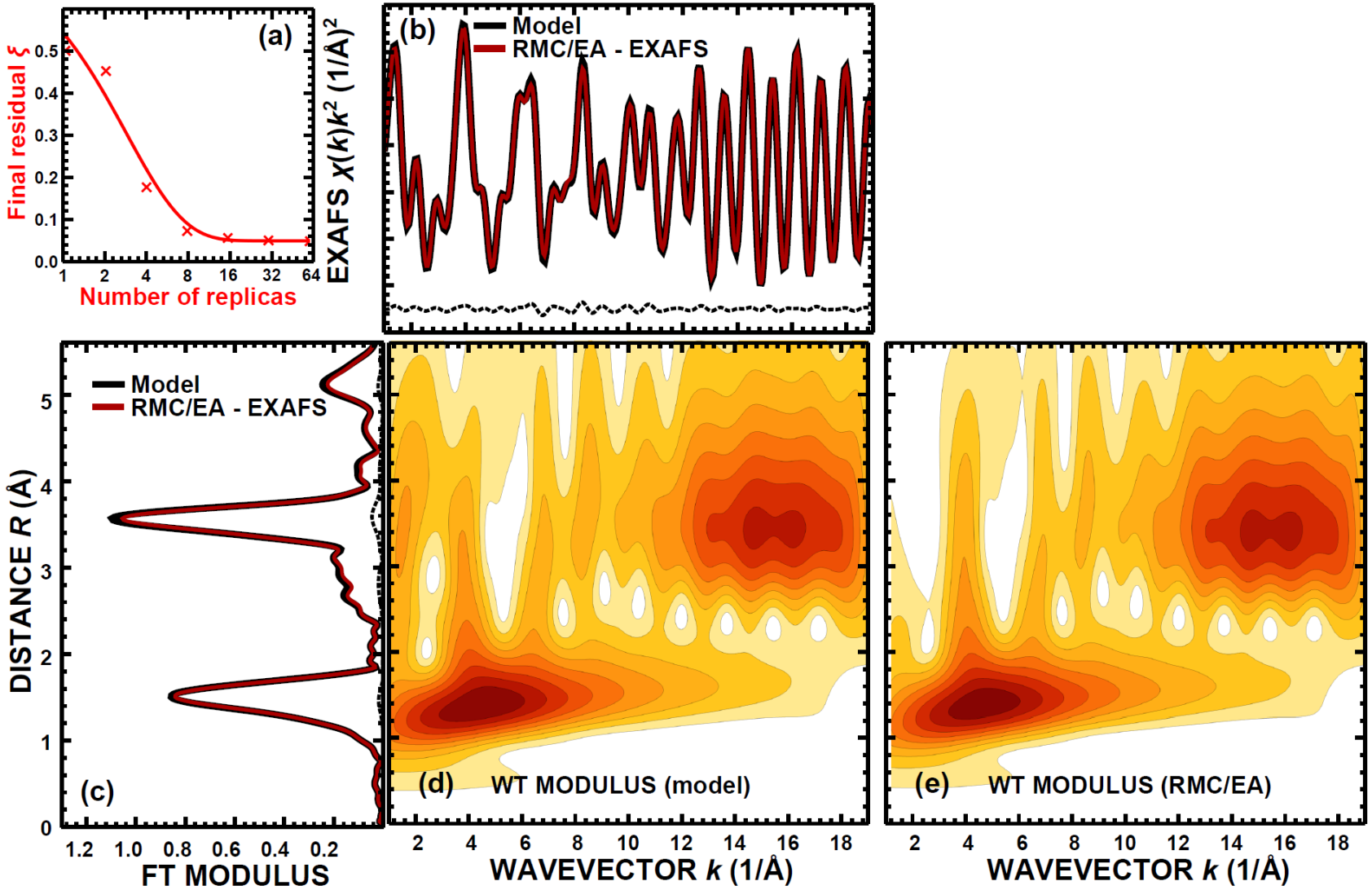
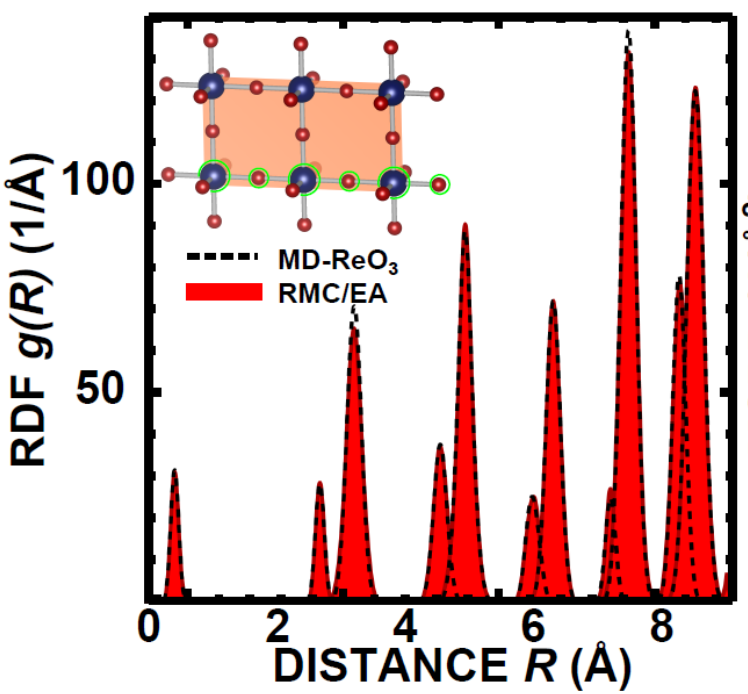
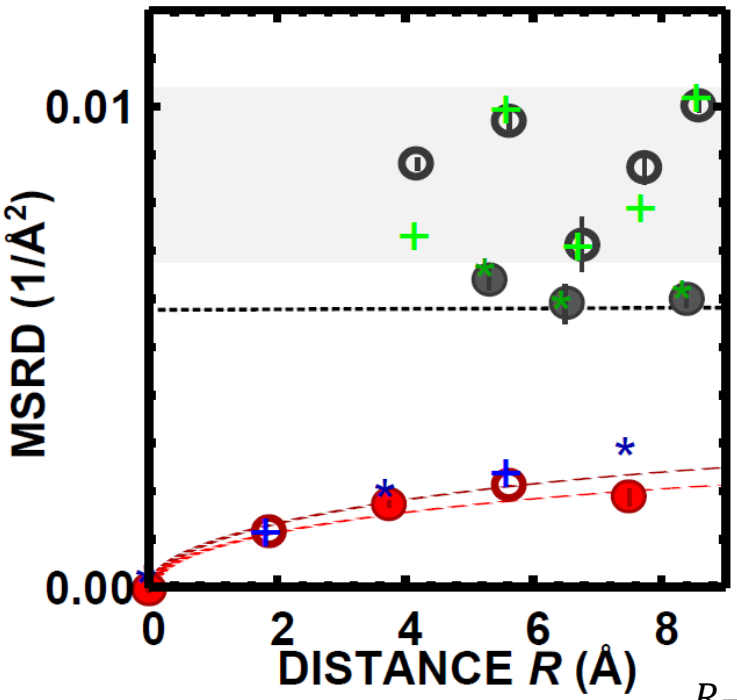
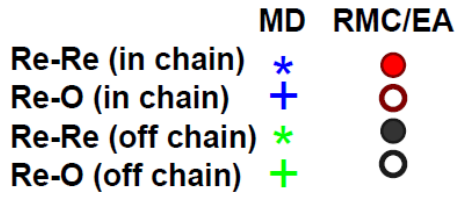


J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.
J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

Validation of method:
RDF, MSRD, MSD

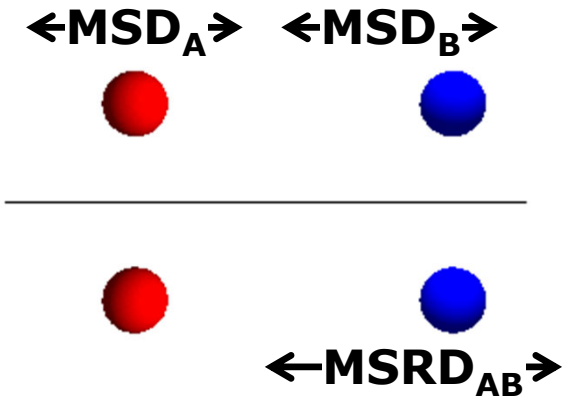






$$R_{EXAFS} = \langle R \rangle = \frac{1}{N}\int_{-\infty}^{+\infty} g_p(R) R \, dR$$

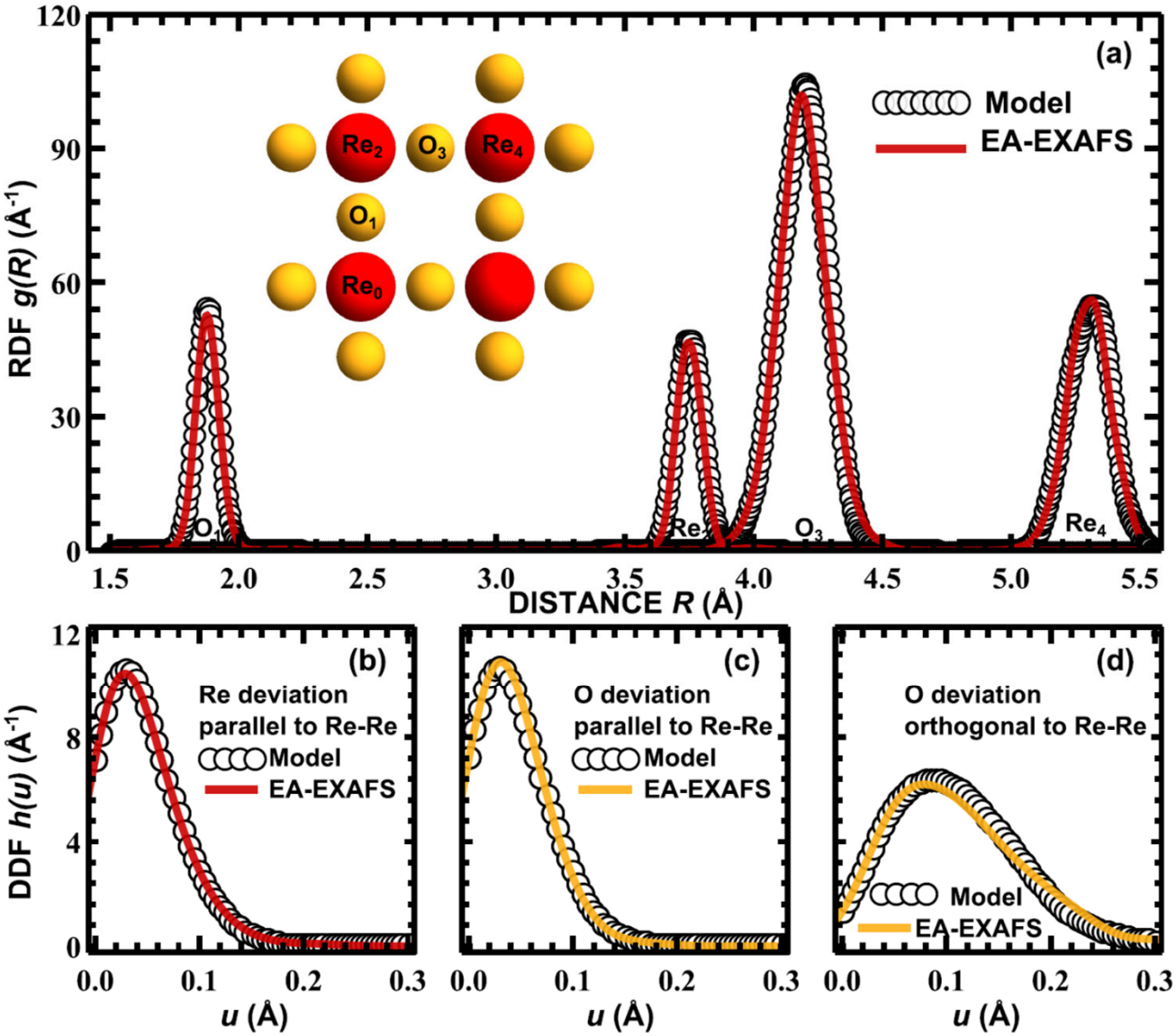
$$\sigma^2 = \frac{1}{N}\int_{-\infty}^{+\infty} g_p(R)(R - R_{EXAFS})^2 \, dR$$



$$\underbrace{\sigma^2_{AB}}_{\text{MSRD}} = \underbrace{\langle \vec{u}_A^2 \rangle}_{\text{MSD}} + \underbrace{\langle \vec{u}_B^2 \rangle}_{\text{MSD}} - \underbrace{2\langle \vec{u}_A \vec{u}_B \rangle}_{\text{Correlation}}$$

J. J. Rehr and R. C. Albers, Rev. Mod. Phys., 72 (2000).
J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.
J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

RMC/EA study of ReO_3: Validation of method: RDF

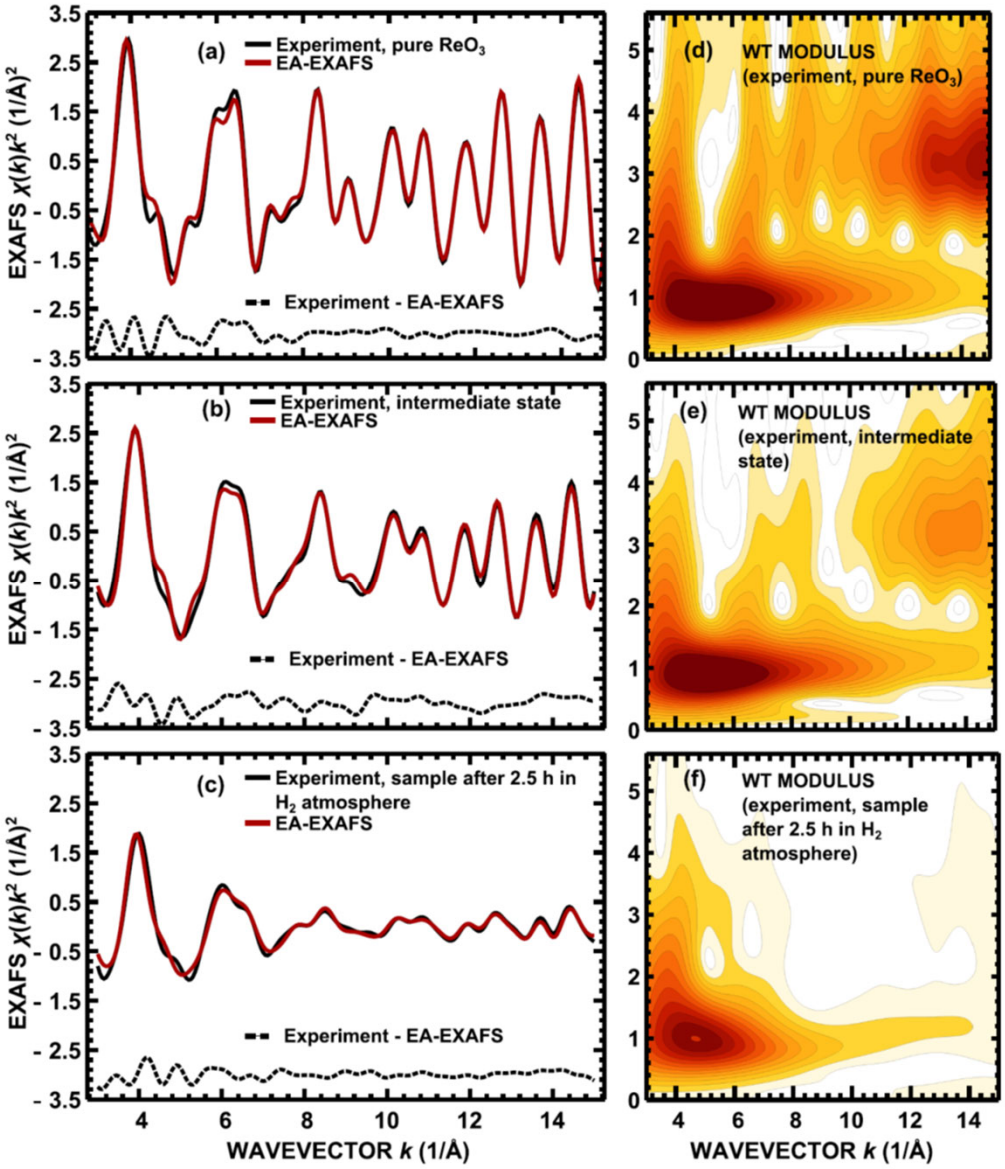


Not only relative, but also absolute atomic displacements can be accessed by RMC-EXAFS method!

$$\underbrace{\sigma^2_{AB}}_{\text{MSRD}} = \underbrace{\langle \vec{u}_A^2 \rangle}_{\text{MSD}} + \underbrace{\langle \vec{u}_B^2 \rangle}_{\text{MSD}} - 2\underbrace{\langle \vec{u}_A \vec{u}_B \rangle}_{\text{Correlation}}$$

J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.
J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

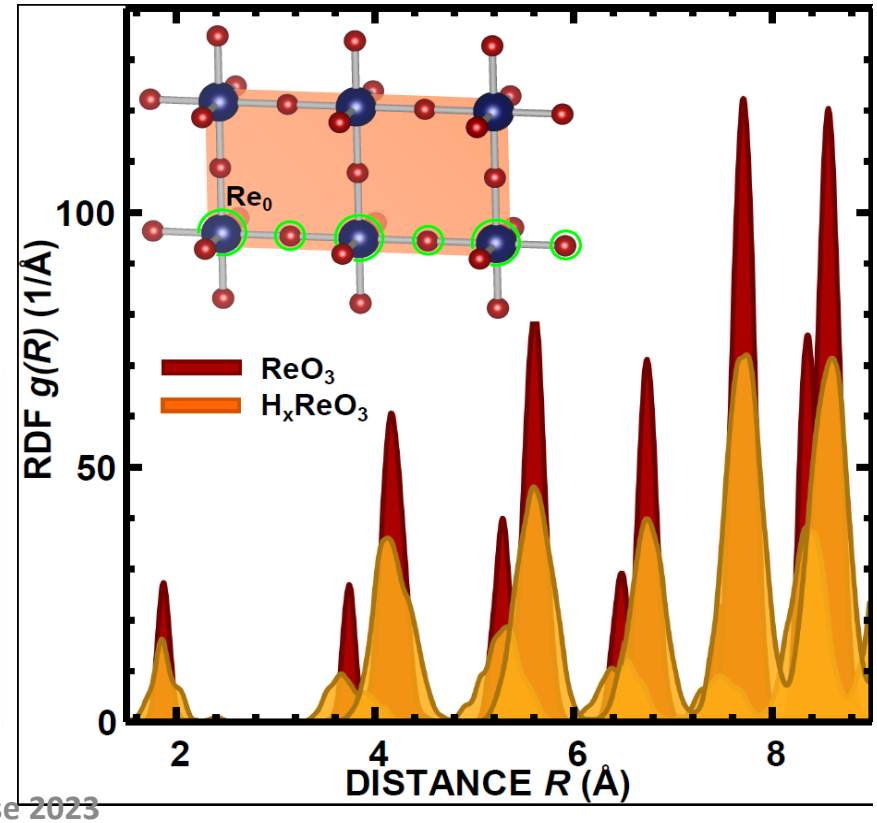
RMC/EA study of H_xReO_3:
Hydrogen intercalation into ReO_3 lattice

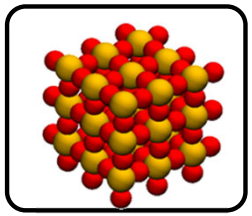


J. Gaidelene, A. Kuzmin, J. Purans, and C. Guery, Phys. Status Sol. C, 2005.
J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.

LURE DCI storage ring, EXAFS-3 beamline

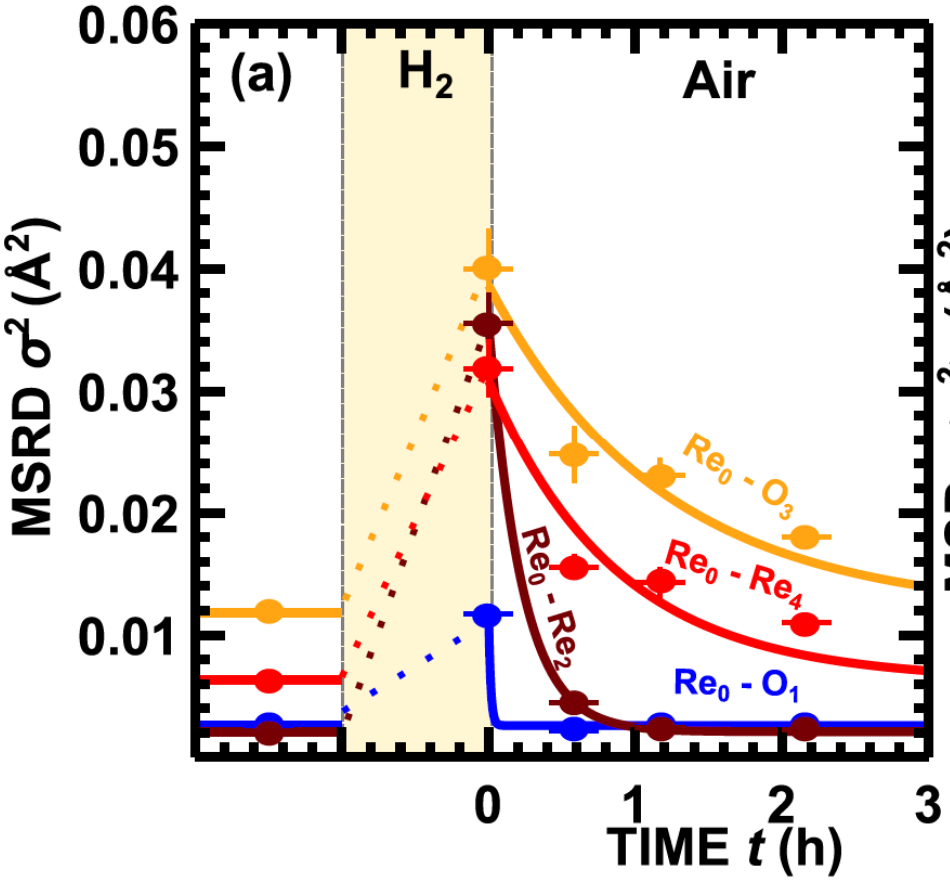
$$ReO_3 + x\,H_2 \underset{air}{\overset{Pt}{\rightleftharpoons}} H_{2x}ReO_3$$

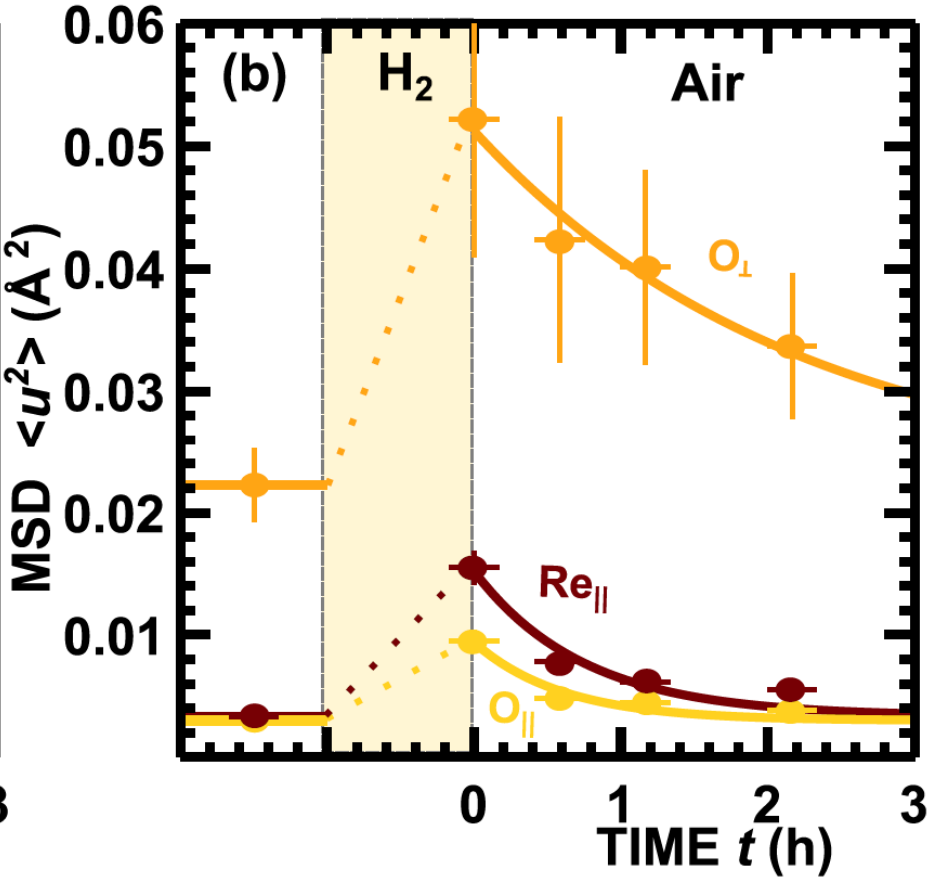




RMC/EA study of H_xReO_3:
MSRD &MSD

J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.





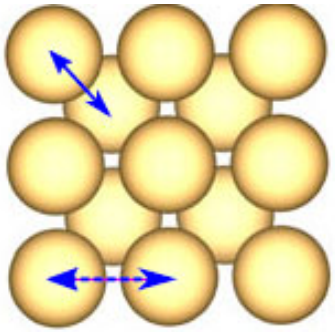
$$\underbrace{\sigma^2_{AB}}_{\text{MSRD}} = \underbrace{\langle \vec{u}^2_A \rangle}_{\text{MSD}} + \underbrace{\langle \vec{u}^2_B \rangle}_{\text{MSD}} - 2\underbrace{\langle \vec{u}_A \vec{u}_B \rangle}_{\text{Correlation}}$$

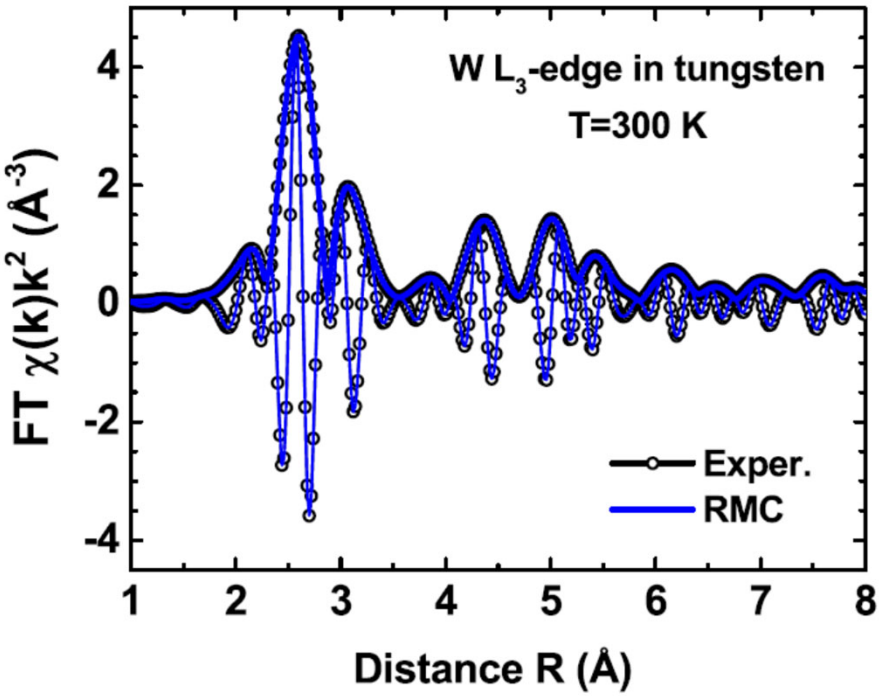
Intercalation of hydrogen ions results in two separate effects with different characteristic relaxation times:

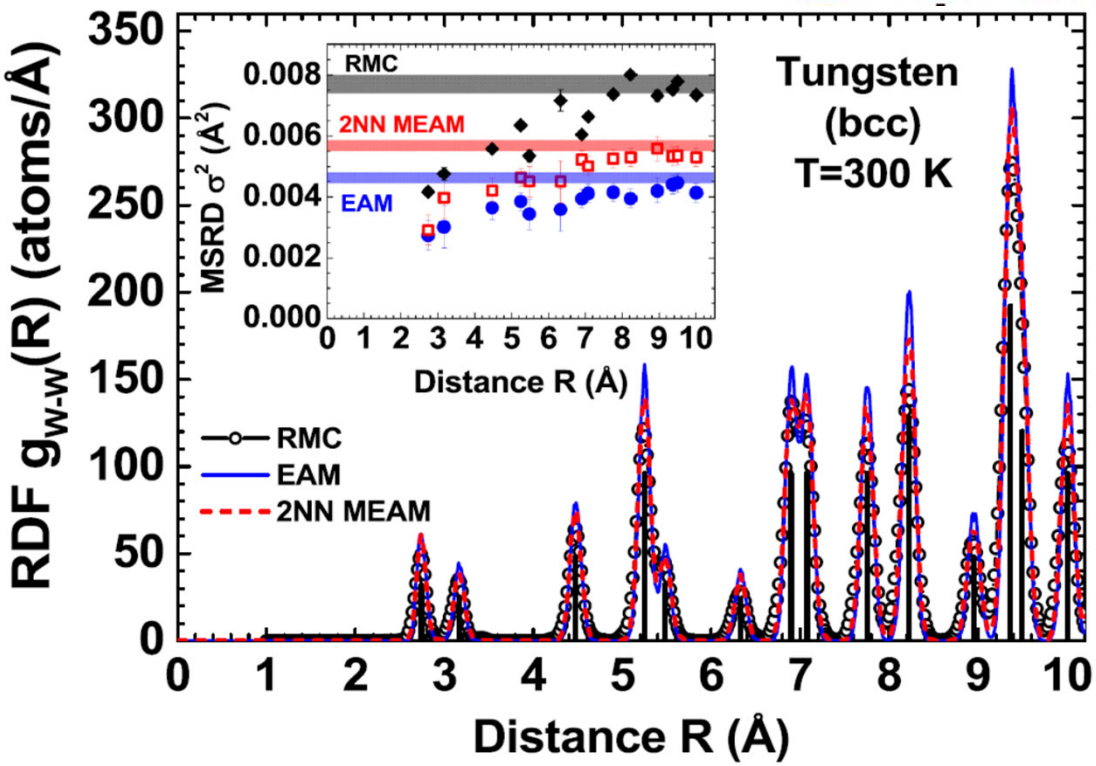
(i) the disappearance of correlation in the atomic motion (fast process with electronic origin)
(ii) the tilting of ReO_6 octahedra (much slower process).

How far we can go with RMC?

EXAFS analysis for metallic tungsten





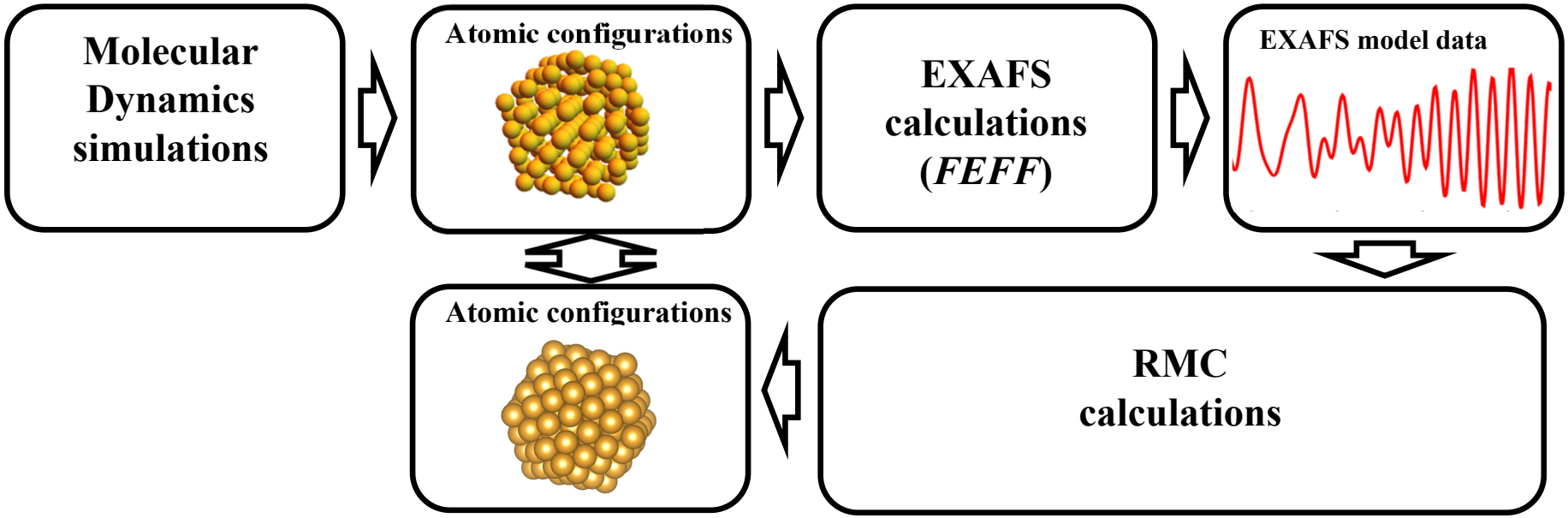


Jonane et al, Modelling Simul. Mater. Sci. Eng. 26 (2018) 025004

In crystalline materials, analysis up to R = 10 Å is possible using RMC approach!

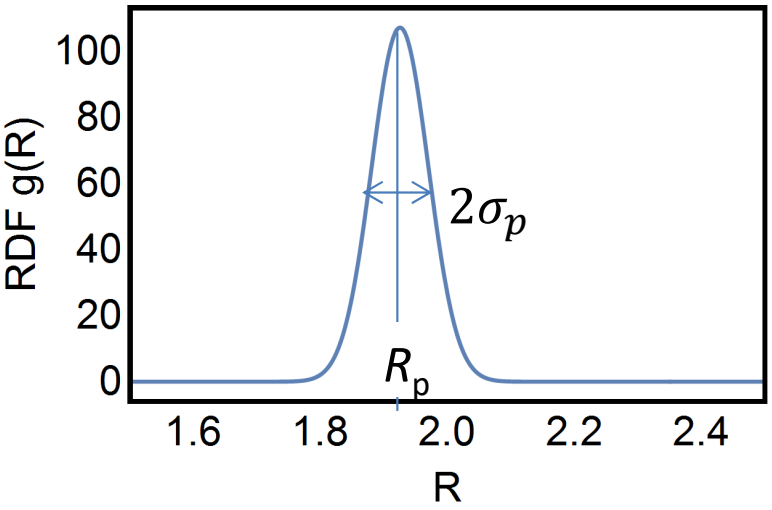
Can non-Gaussian effects be reliably probed by RMC?

Validation of RMC method with model data: Au_{147}



J. Timoshenko et al, J. Phys.: Condens. Matter 26 (2014) 055401.

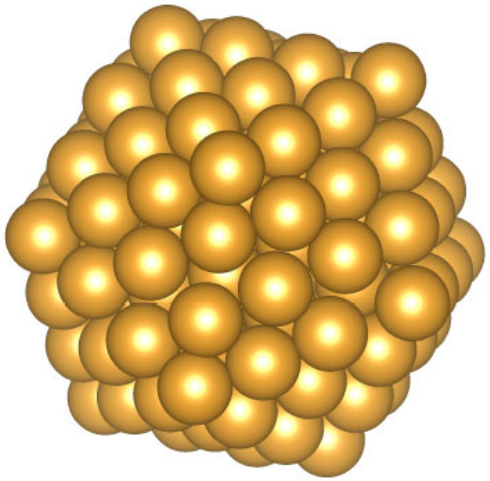
EXAFS for disordered materials

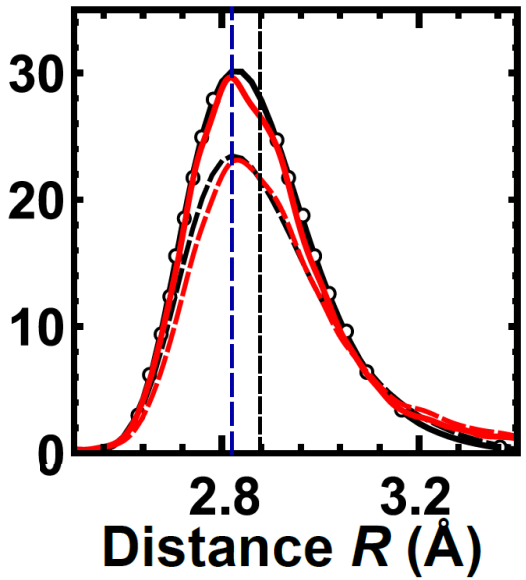


For systems with small **disorder** (e.g., crystalline materials), **harmonic approximation** is usually adequate

$$\chi_p(k) = S_0^2 N_p \frac{f_p(k)}{kR_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p + \phi_p(k)\right)$$

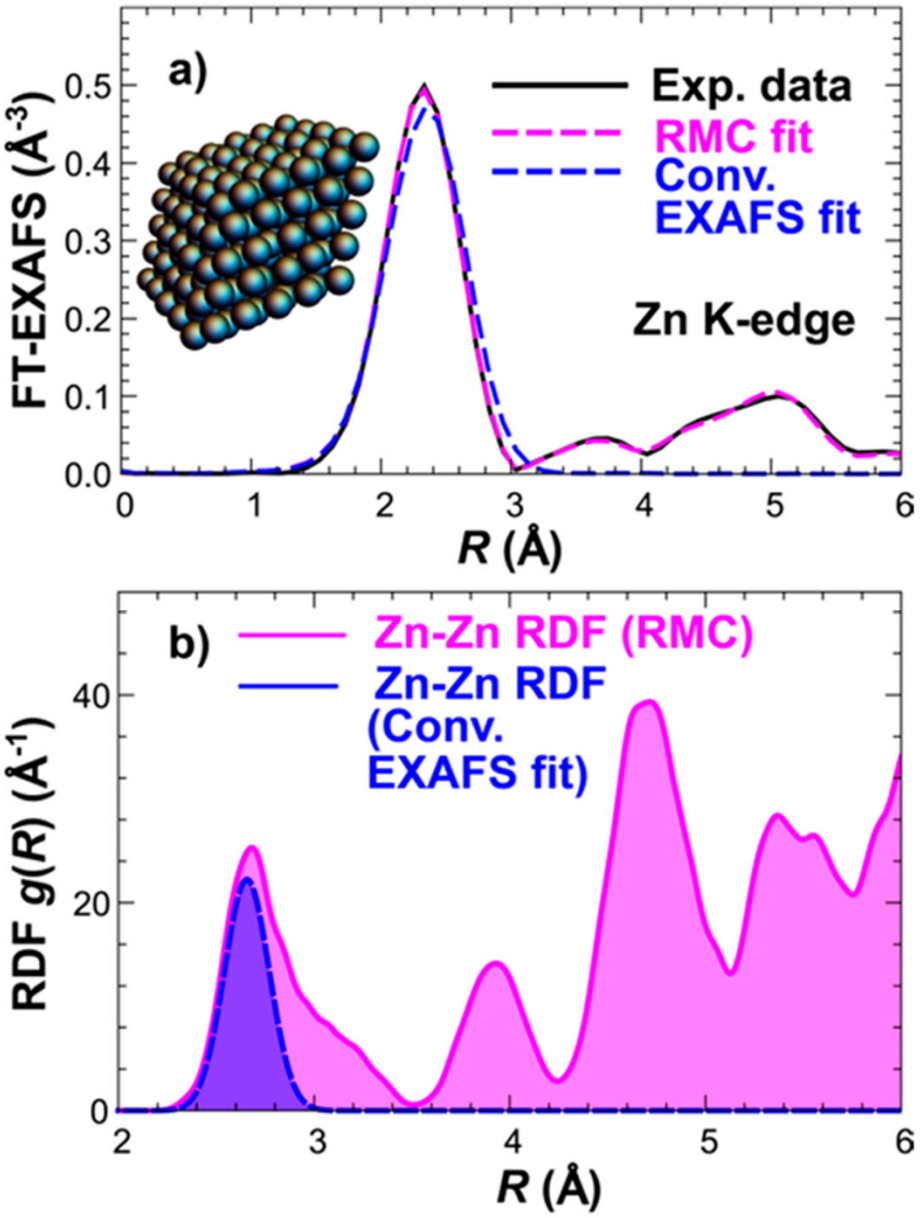
For disordered materials (e.g., small nanoparticles) distribution of bond lengths is often **non-Gaussian**. Conventional approach will be inacurate!





EXAFS for disordered materials. How bad can it be?

RMC simulations for metallic Zn

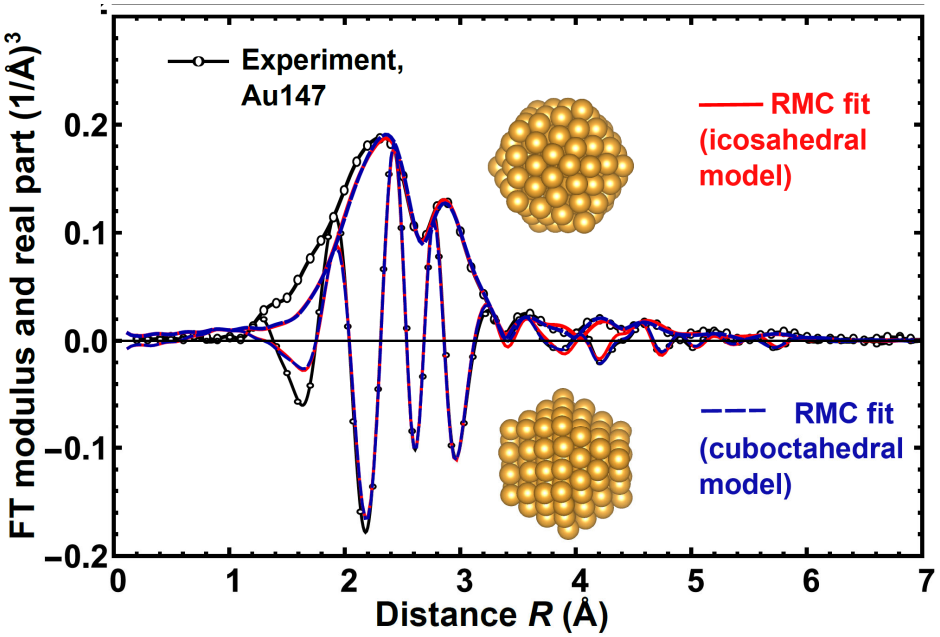


Conventional fitting can underestimate number of nearest neighbors by 50%!

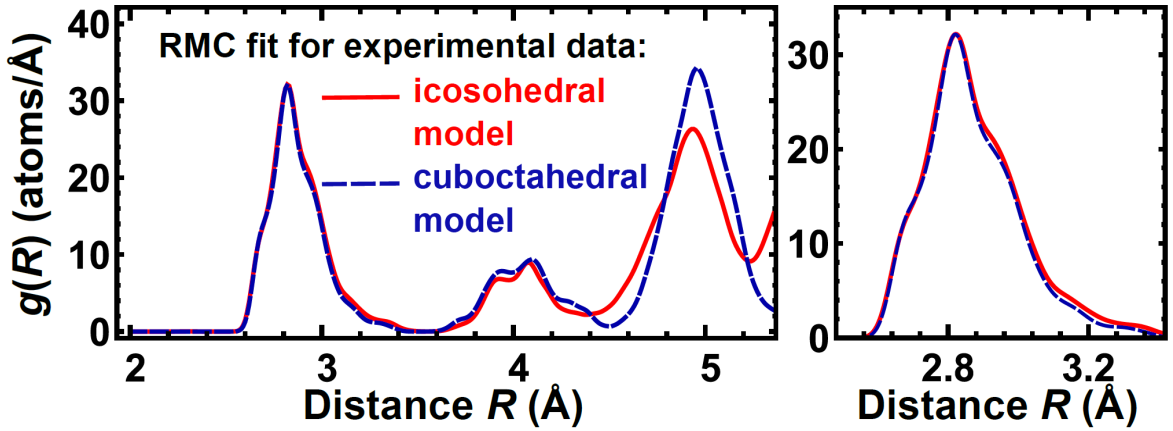
Interatomic distances and disorder factors are also strongly underestimated

Timoshenko & Roldan Cuenya
Chem. Rev. 2021

RMC for Au_{147}



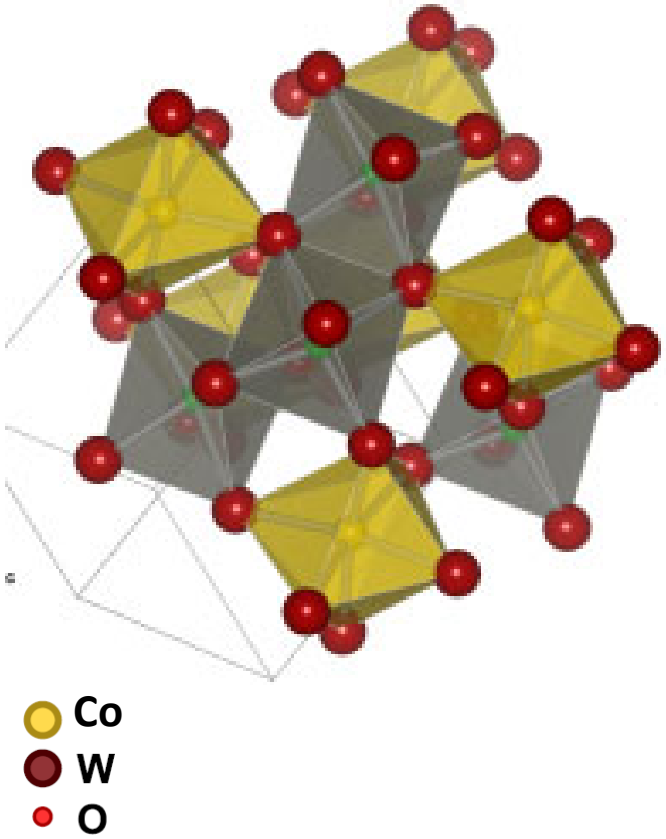
- RMC/EA method provides excellent fit of experimental data, and allows to reconstruct reliably the asymmetric RDF
- Due to limited information, contained in EXAFS data, RMC/EA cannot distinguish between two different structure models
- Additional information can be used here (in this case we know from MD that ioosohedral model is better)
- Results or RMC/EA analysis can be directly compared with DFT modelling results



Parameter	FEFFIT$_H$	RMC/EA	ab initio MD
N_1	9(1)	9.47	9.47
R_1 (Å)	2.816(5)	2.881(4)	2.871
σ_1^2 (Å^2)	0.012(1)	0.017(1)	0.00173
N_2	–	3.27	–
R_2^2 (Å)	–	4.05(1)	–
σ_2^2 (Å^2)	–	0.025(1)	–

Timoshenko & Frenkel, Catalysis Today, 2016

Nanosized tungstates



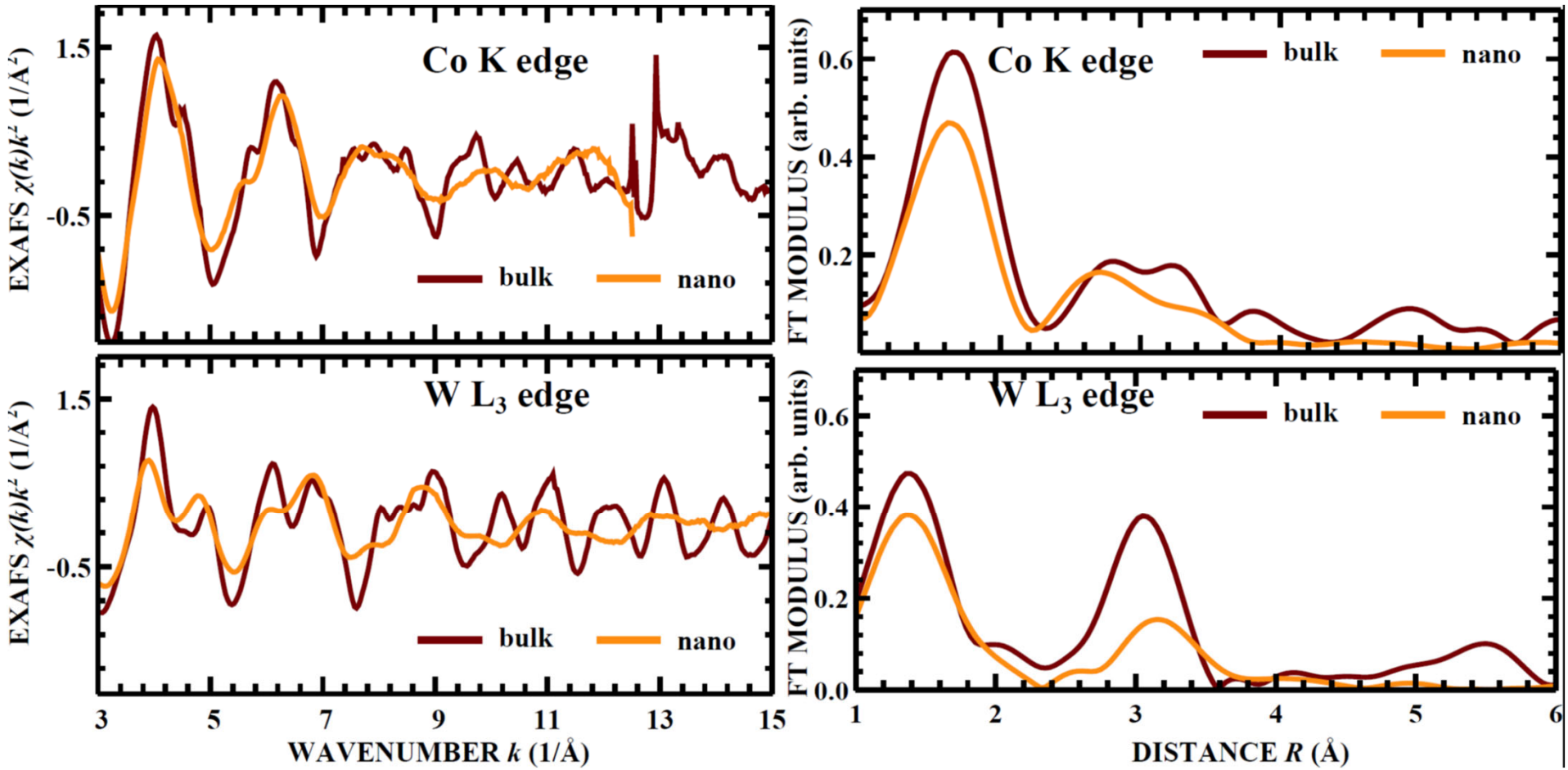
Bulk $CoWO_4$ is wolframite-type compounds with monoclinic symmetry ($P_{2/c}$ space group)

$CoWO_4$ – antiferromagnetic material
(T_N = 55 K)

Nanosized $CoWO_4$ has very small sizes of nanocrystallites (smaller than 2 nm) and has pronounced catalytic properties.

Sj.J. Naik and A.V.Salker, Solid State Sciences 2010'
H. Weitzel, Solid State Commun. 1970;
Y.S. Song *et al,* Phys. Rev. B 2009;
P. Schmitt *et al* Adv. Funct. Mater. 2011.

Co K-edge and W-L_3 edge EXAFS for bulk and nano $CoWO_4$

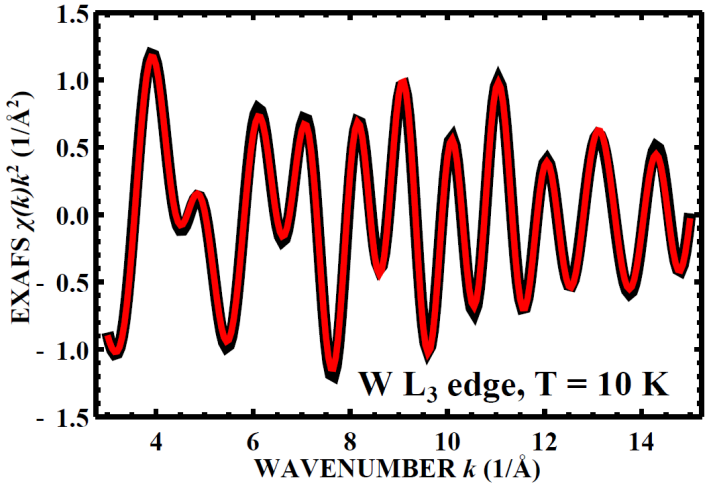


EXAFS measurements for crystalline and nanocrystalline $CuWO_4$ and $CoWO_4$ powders have been performed in transmission mode at HASYLAB/DESY C beamline (Hamburg). The intensity of X-rays was measured with ionization chambers, filled with argon an krypton mixture. Energy scan of incident radiation ensured by rotation of Si(111) double-crystal monochromator. Crystalline and nanocrystalline tungstates powders were deposited on Millipore filter and fixed by Scotch tape. For temperature control liquid helium cryostat has been employed.

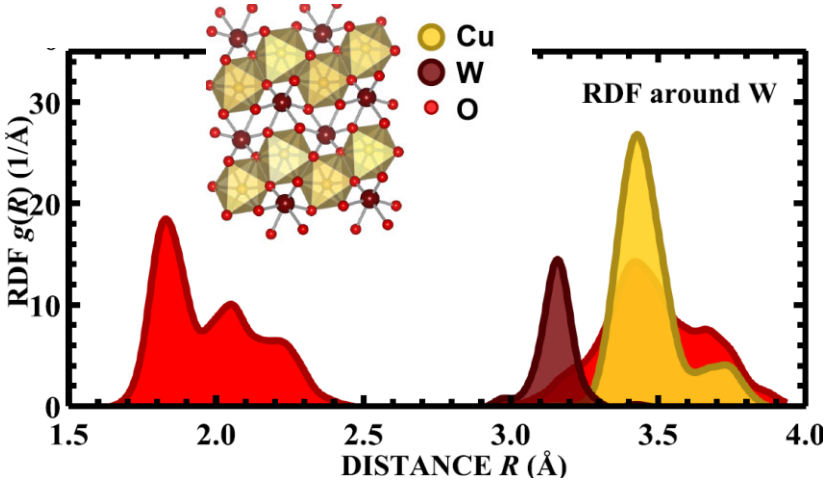
Polycrystalline $CuWO_4$

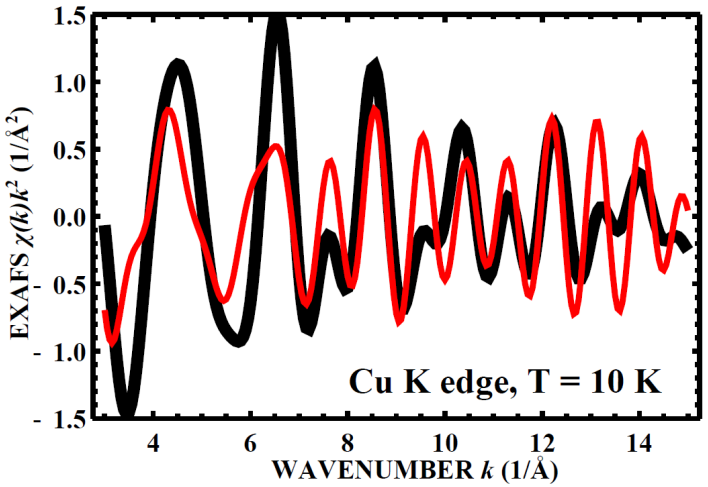
RMC-EXAFS analysis

1 RMC calculations using W L_3 edge EXAFS



2 Structure model



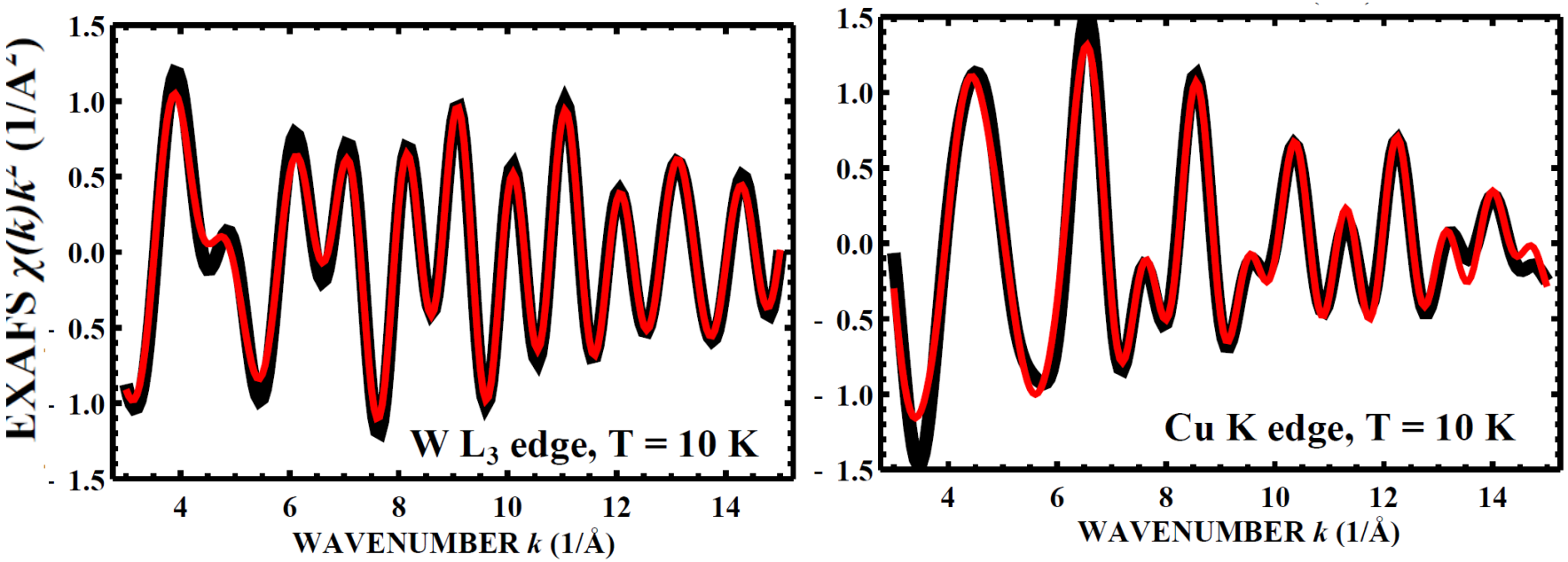


3 Calculations of Cu K-edge EXAFS

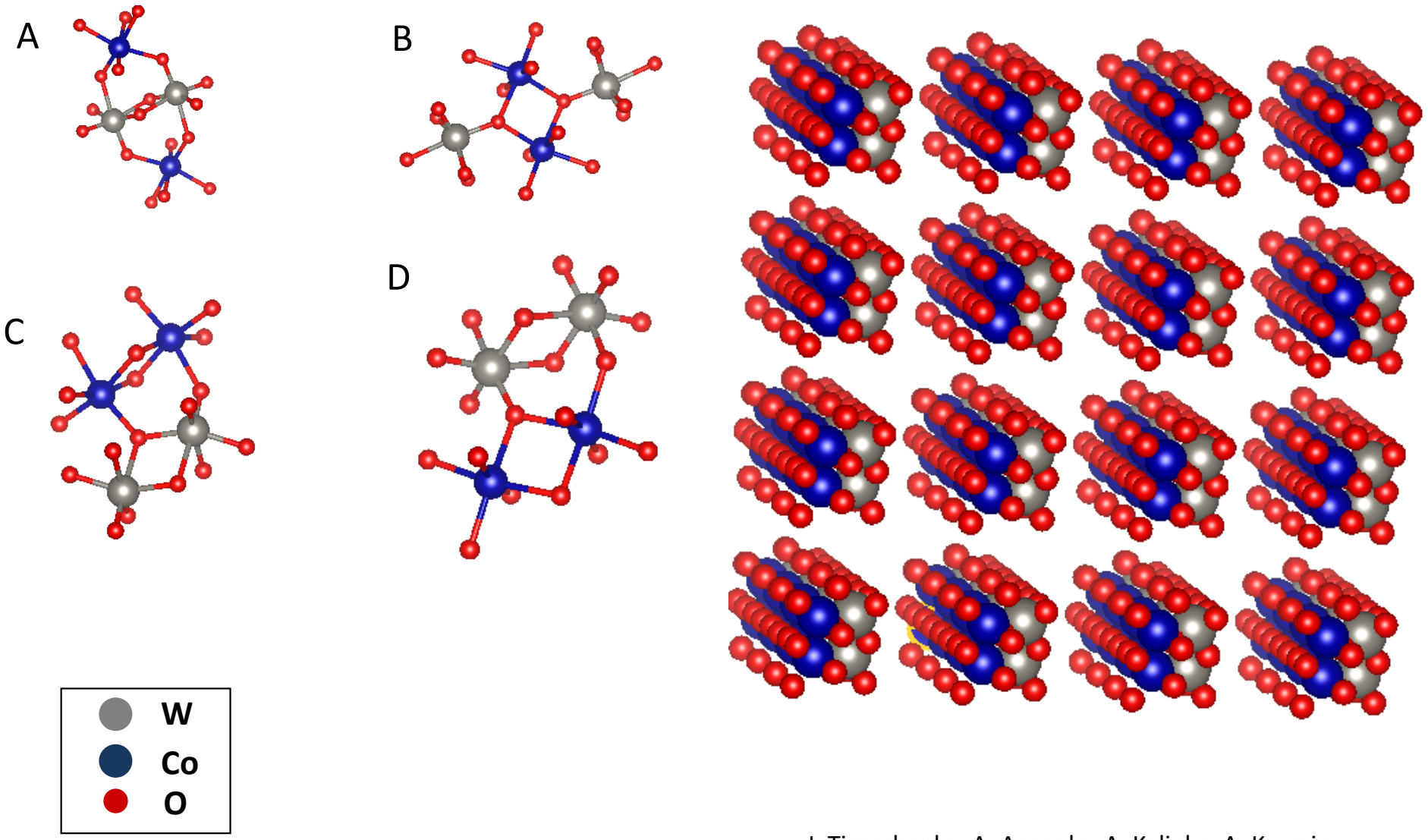
Polycrystalline $CuWO_4$

RMC-EXAFS analysis

④ RMC fit of single structure model using W L_3 edge and Cu K-edge EXAFS simultaneously:



Nanosized $CoWO_4$
RMC/EA modeling

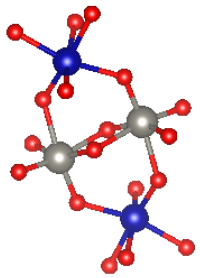


J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin, Phys. Status Solidi A 212 (2015) 265-273

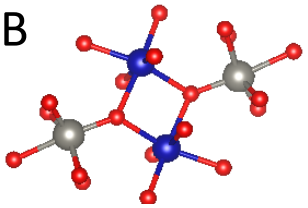
Nanosized $CoWO_4$

RMC/EA results

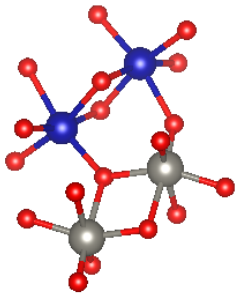
A



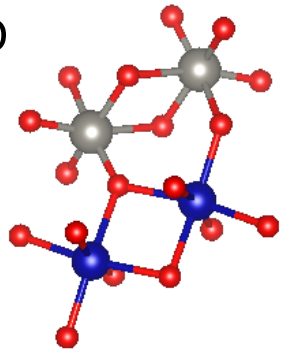
B

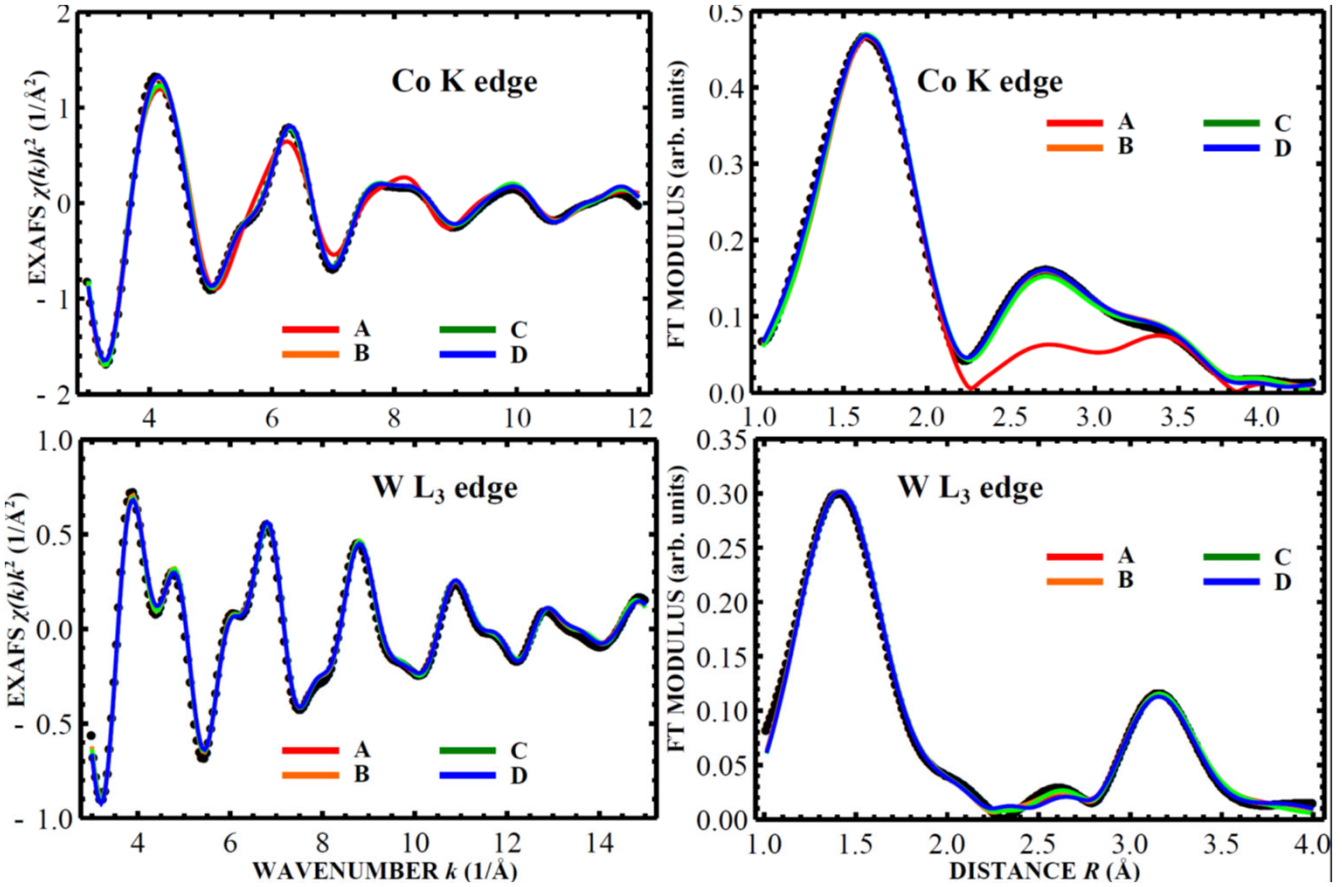


C



D

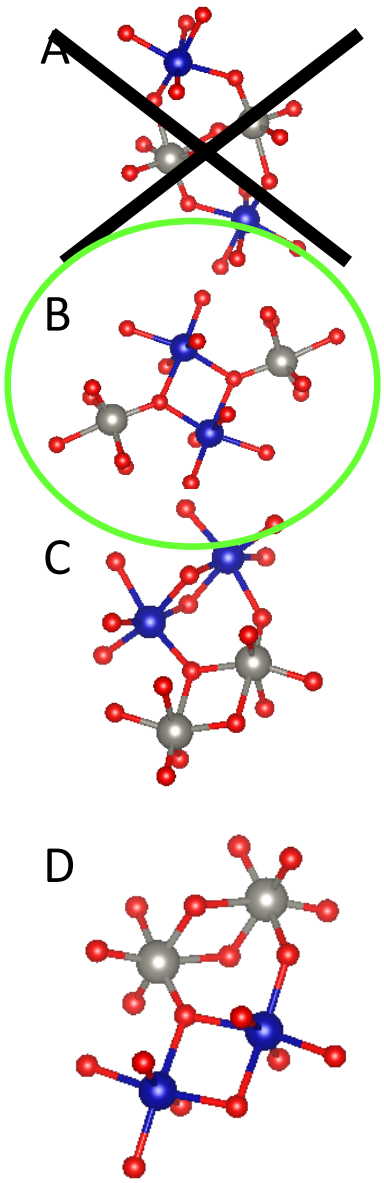


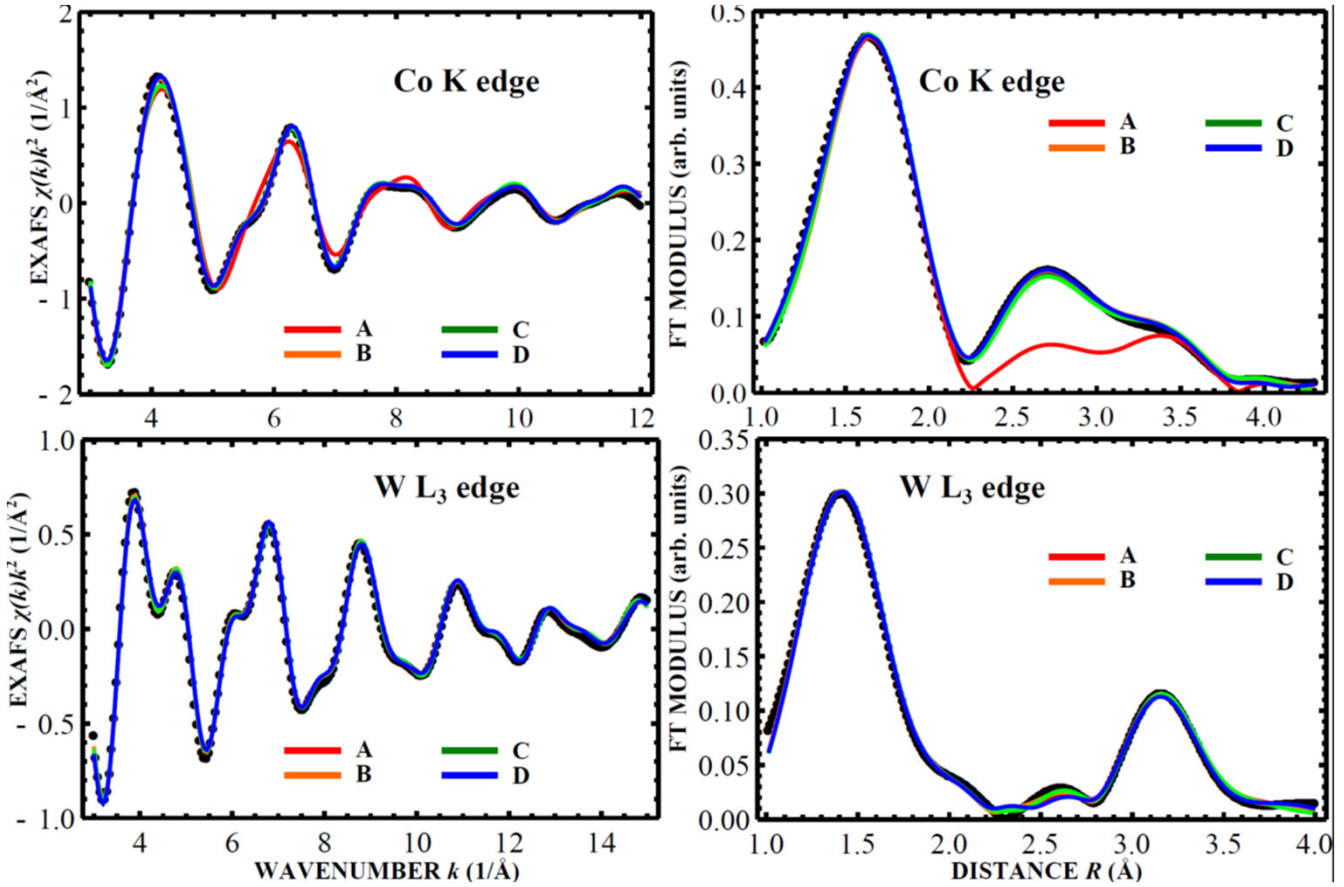


Model	Co K-edge residual	W L_3-edge residual	Average residual
A	0.183(8)	0.057(5)	0.120(2)
B	0.053(5)	0.053(2)	0.053(4)
C	0.093(8)	0.056(5)	0.075(2)
D	0.061(3)	0.070(9)	0.066(3)

Nanosized $CoWO_4$

RMC/EA results





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Summary and conclusions

START

Experimental EXAFS data

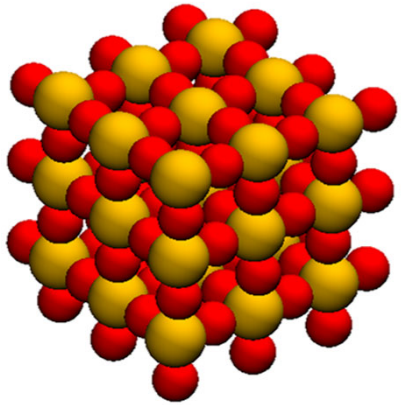
Ab-initio calculations of scattering properties of atoms

Initial structure model (XRD, etc.)

RMC/EA calculations

3D structure model of

- crystalline materials
- disorder crystals
- nanostructured materials



Accounts for

- multiple-scattering effects
- contributions of further coordination shells
- thermal and static disorder of the system
- anisotropy and anharmonicity of atom dynamics
- correlations of atomic motion

Summary and conclusions

Additonal advantages:

- 3D structure models, obtained in RMC-EXAFS, can be directly compared with the results of theoretical simulations (MD, DFT)
- "Easy" to incorporate information from other experiments (XRD, total scattering, NMR, etc.)
- Easy to incorporate constraints (ensure physically reasonable values for coordination numbers, bond-lengths, bonding angles)

The structure model, obtained in RMC simulations, is only as good as experimental data. If experimental data are not sensitive to some structure feature, it will not be possible to probe it in RMC analysis: it is always a good idea to **validate RMC accuracy** for particular task with some model data.

More details:

J. Timoshenko, A. Kuzmins, J. Purans, EXAFS STUDY OF HYDROGEN INTERCALATION INTO ReO_3 USING THE EVOLUTIONARY ALGORITHM; *J. Phys.: Condens. Mat.* (2014)

www.dragon.lv/evax

When to use RMC?

Whenever you have a good initial structure guess.

- Crystalline materials with structure known from XRD
- Nanocrystalline materials with well-defined particles
- Amorphous materials with known density (input from other experimental techniques besides EXAFS may be needed)

When NOT to use RMC?

- Mixtures
- Materials experiencing phase transitions

} Machine learning methods may be better suited

- Caution is needed, if EXAFS spectra are very short (< 10 $Å^{-1}$)

Thank you for your attention!