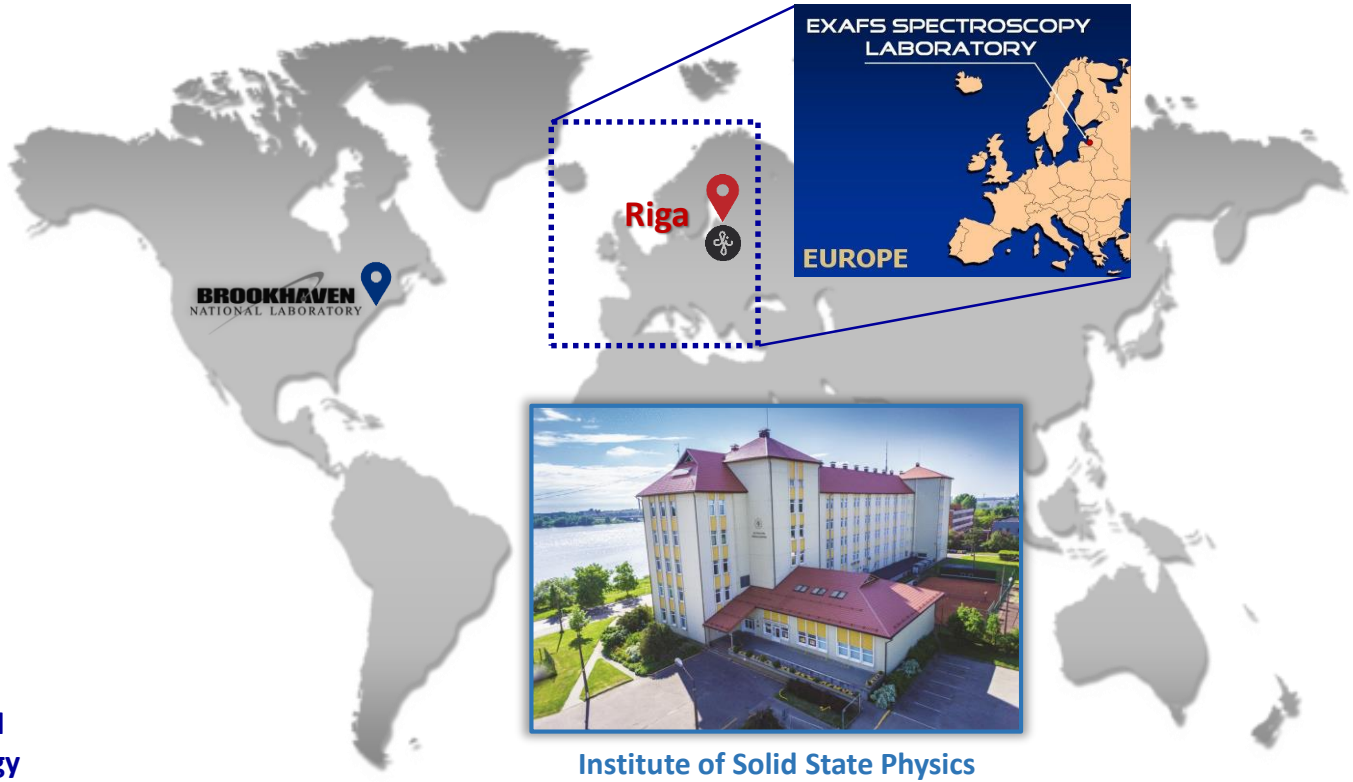
The use of Molecular Dynamics simulations for the interpretation of EXAFS spectra

Alexei Kuzmin
Dr.phys., Head of the Lab

Institute of Solid State Physics, University of Latvia
Kengaraga street 8, LV-1063 Riga, Latvia

E-mail: a.kuzmin@cfi.lu.lv
Internet: www.cfi.lu.lv Internet: www.dragon.lv/exafs

EXAFS Spectroscopy Laboratory



CAMART²

Centre of Excellence in Advanced Material Research and Technology

Institute of Solid State Physics
University of Latvia

Outline

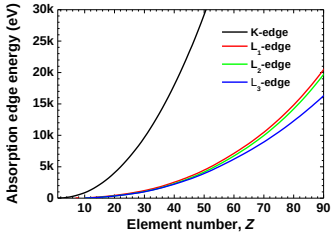
- **Introduction**
  - Motivation & problems
- **MD-EXAFS approach**
  - Concept
  - State of the Art
  - Basics of Molecular Dynamics (MD)
  - EXAFS simulations
  - Interpretation of results
- **Examples of MD-EXAFS simulations**
  - ReO_3, ScF_3, BCC & FCC metals
- **Conclusions**

Introduction

- Characteristic times in X-ray absorption process vs thermal vibrations
- How local is X-ray absorption spectroscopy?
- EXAFS formalism beyond the first coordination shell: multiple-scattering effects
- Problems and possible solutions

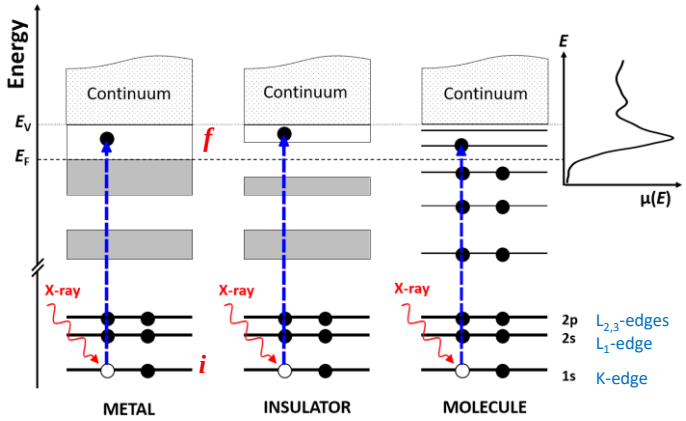
Basics of X-ray absorption spectroscopy (XAS)

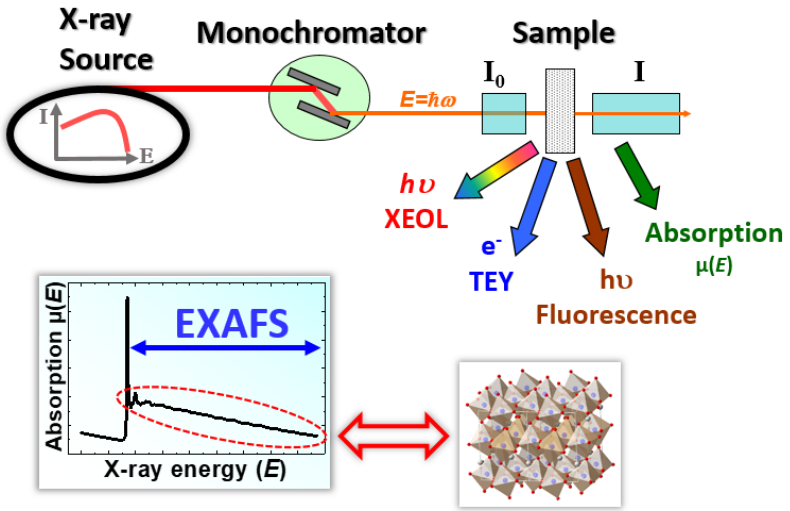
X-rays:
soft (<5 keV)
hard (>5 keV)



Fermi's Golden Rule:

$$\mu(E) \propto \sum_f \left|\langle f|\hat{\mathbf{H}}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$





$$\mu(E) = \frac{1}{x}\ln\left(\frac{I_0(E)}{I(E)}\right)$$

$$\mu(E) \propto \frac{I_{\text{fluo}}(E)}{I_0(E)}$$

$$\mu(E) \propto \frac{I_{\text{TEY}}(E)}{I_0(E)}$$

$$\mu(E) \propto \frac{I_{\text{XEOL}}(E)}{I_0(E)}$$

Characteristic time of X-ray absorption process:

$t_{ab} \sim 10^{-15}$-10^{-16} s

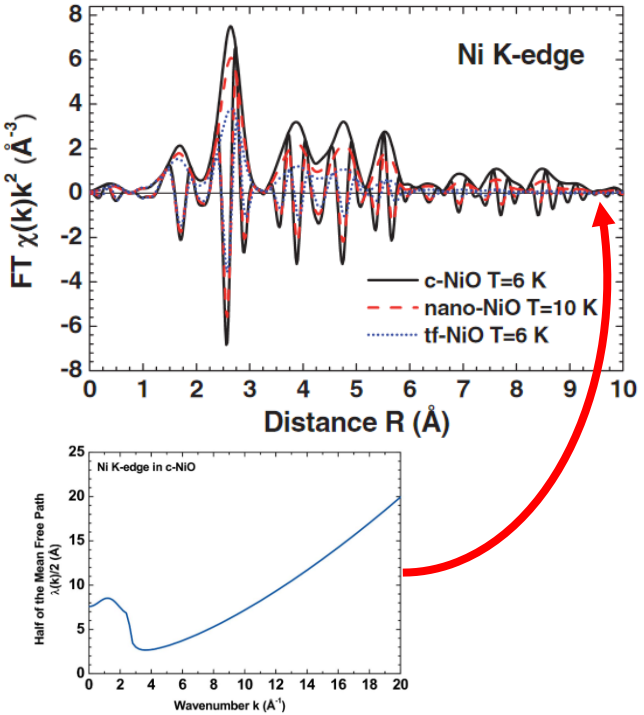
Characteristic time of thermal vibrations:

$t_{th} \sim 10^{-13}$-10^{-14} s

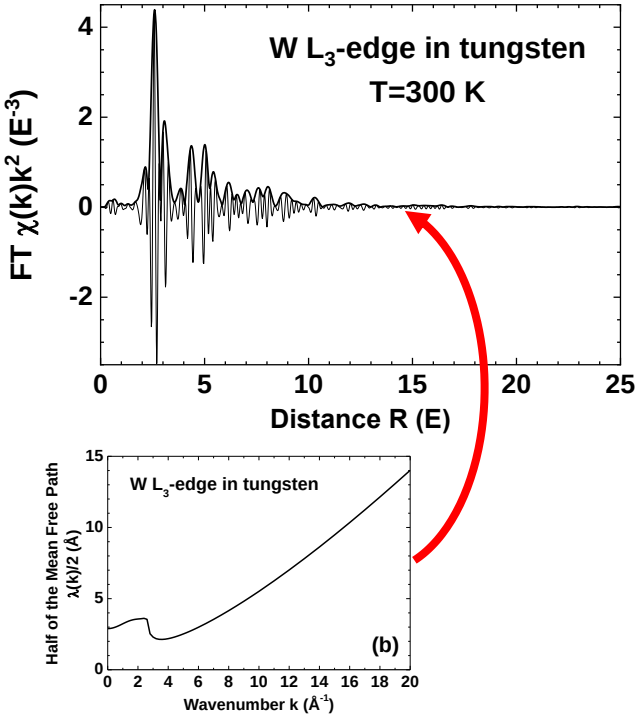
- **Atoms are frozen during X-ray absorption**
- **Static & thermal disorder contribute similarly**

How local is X-ray absorption spectroscopy?

The case of NiO.



The case of W foil.



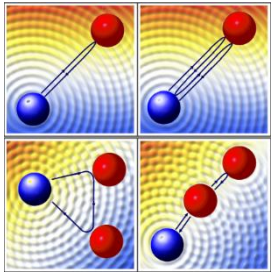
Contributions from outer shells are often available and contain useful structural information.

EXAFS simulations beyond the first coordination shell

1. Multiple-scattering (MS) expansion (FEFF code):

$$\chi^l(k) = \sum_{n=2}^{\infty} \chi_n^l(k) \qquad \chi_n^l(k) = \sum_i A_n^l(k, R_i) \sin(2kR_i + \Phi_n^l(k, R_i) + 2\delta_c^l(k))$$

A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565-7576.



2. N-body expansion (GNXAS code):

$$\begin{aligned}
\chi(k) \;=\; & \int 4\pi R^2 \rho_0 g_2(R) (\chi_2^{oio}(k) + \chi_4^{oioio}(k) + \ldots) \mathrm{d}R \\
& + \iiint 8\pi^2 R_1^2 R_2^2 \sin(\theta) \rho_0^2 g_3(R_1, R_2, \theta) \\
& \times (2\chi_3^{oijo}(k) + 2\chi_4^{oiojo}(k) + \chi_4^{oijio}(k) + \chi_4^{ojijo}(k) + \ldots) \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\theta \\
& + \iiiint\!\!\int 8\pi^2 R_1^2 R_2^2 R_3^2 \sin(\theta) \rho_0^3 g_4(R_1, R_2, \theta, R_3, \Omega) \\
& \times (2\chi_4^{oijko}(k) + 2\chi_4^{oikjo}(k) + 2\chi_4^{ojiko}(k) + \ldots) \mathrm{d}R_1 \mathrm{d}R_2 \mathrm{d}\theta \mathrm{d}R_3 \mathrm{d}\Omega \\
& + \ldots
\end{aligned}$$

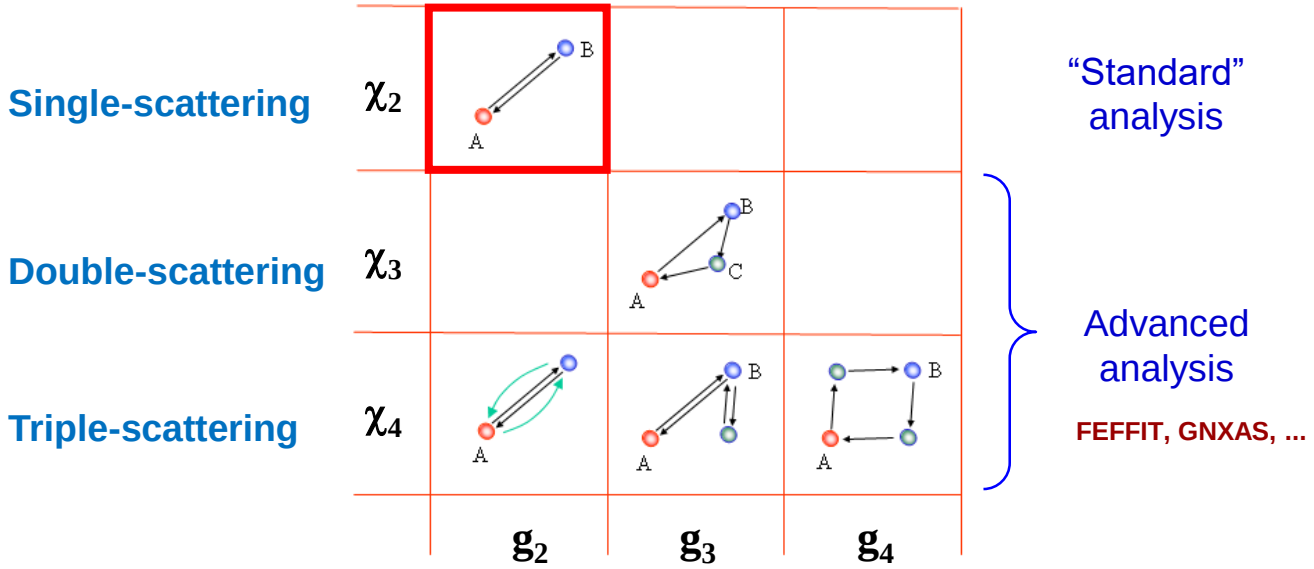
A. Filipponi, A. Di Cicco, C. R. Natoli, Phys. Rev. B 52 (1995) 15122-15134.

EXAFS depends on atomic distribution functions!

Multiple-scattering terms and many body correlation functions

$$\mu(k) = \mu_0(k)[1 + \chi_2(k) + \chi_3(k) + \chi_4(k) + \cdots]$$

$$\mu(k) = \mu_0(k)[1 + g_2(k) + g_3(k) + g_4(k) + \cdots]$$



The rows group the different possible paths which give the same order contributions to the absorption coefficient, χ_2, χ_3 or χ_4.
The columns group the paths corresponding to two, three, four body correlation functions g_i.

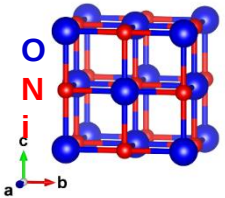
EXAFS problems (1)

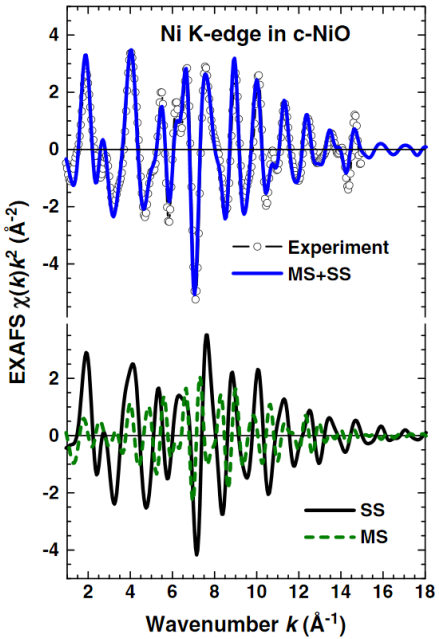
1) One needs to account for many-body correlations through the so-called multiple-scattering (MS) effects.

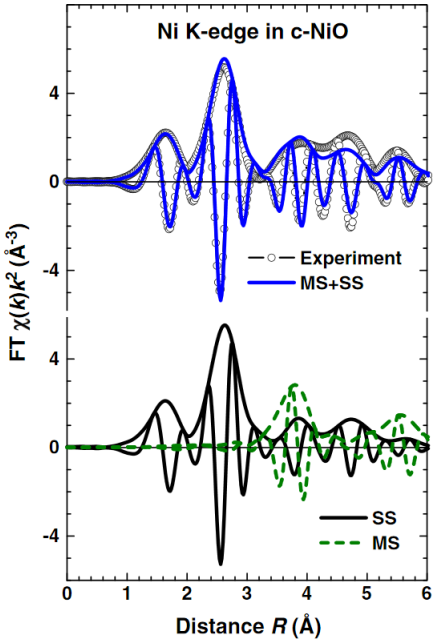
NiO

Space group Fm-3m

a_0= 4.1773 Å







A. Anspoks and A. Kuzmin,
J. Non-Cryst. Solids 357 (2011) 2604.

EXAFS problems (2)

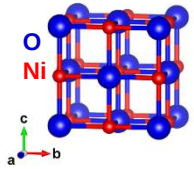
2) A number of fitting parameters grows rapidly upon an increase of analyzed region size around the absorbing atom. This problem is especially relevant for disordered and nanocrystalline materials.

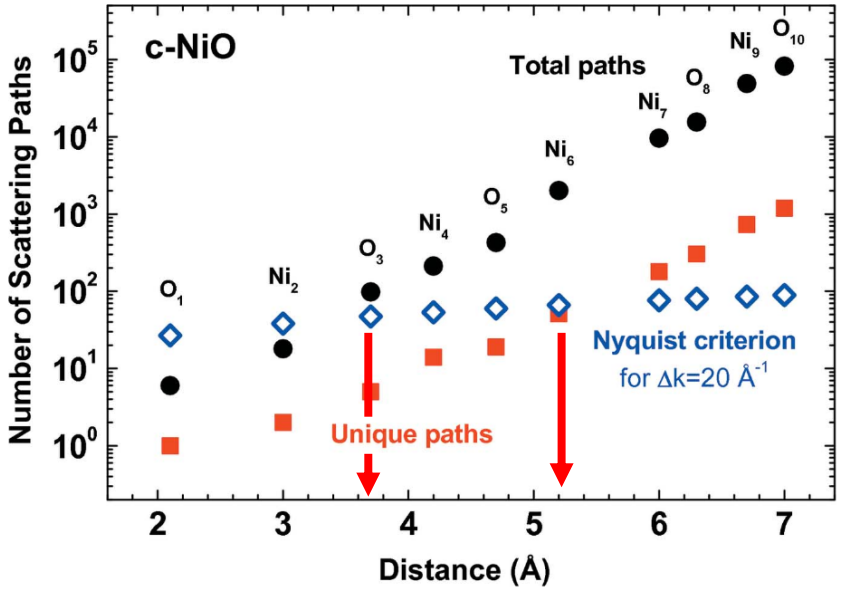
Number of scattering paths vs independent parameters N_{par}:

$$N_{\mathrm{par}} = \frac{2\Delta k \Delta R}{\pi}$$

NiO

Space group Fm-3m
a_0= 4.1773 Å





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

Possible solutions

The problem of disorder in EXAFS can be addressed using

- **Molecular Dynamics (MD),**
- **Monte Carlo (MC),**
- **Reverse Monte Carlo (RMC)**

simulations.

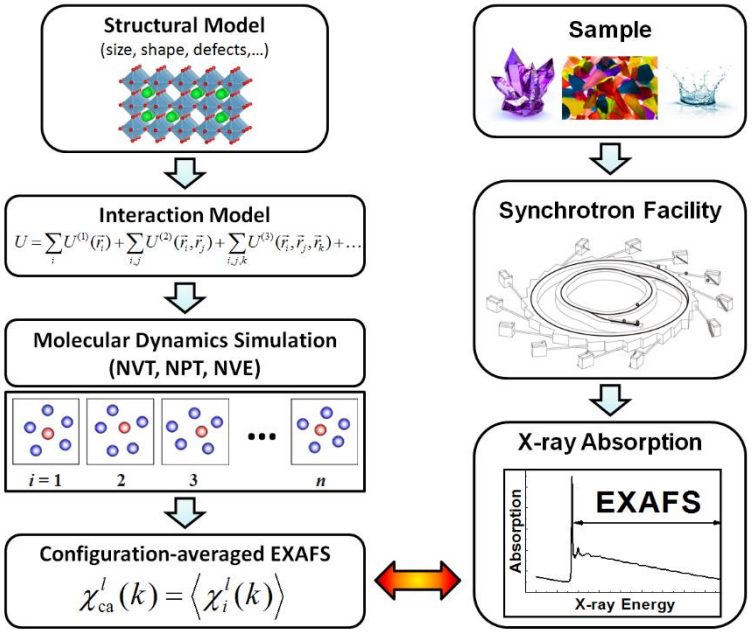
Configuration-averaged EXAFS

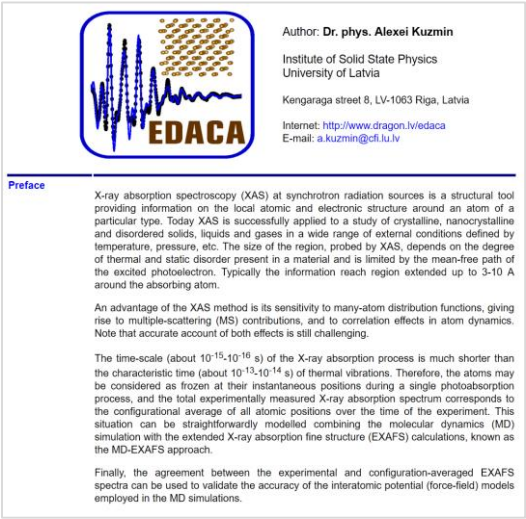
$$\chi^{l}_{\mathrm{ca}}(k) = \langle \chi^{l}(k) \rangle$$

Advantages of MD-EXAFS approach:

- ✓ **has no structural fitting parameters**
- ✓ **allows interpretation of EXAFS spectra far beyond the first coordination shell**
- ✓ **allows a validation of the interatomic potential models**

MD-EXAFS approach: Concept





EDACA

Author: **Dr. phys. Alexei Kuzmin**

Institute of Solid State Physics
University of Latvia

Kengaraga street 8, LV-1063 Riga, Latvia

Internet: http://www.dragon.lv/edaca
E-mail: a.kuzmin@cfi.lu.lv

Preface

X-ray absorption spectroscopy (XAS) at synchrotron radiation sources is a structural tool providing information on the local atomic and electronic structure around an atom of a particular type. Today XAS is successfully applied to a study of crystalline, nanocrystalline and disordered solids, liquids and gases in a wide range of external conditions defined by temperature, pressure, etc. The size of the region, probed by XAS, depends on the degree of thermal and static disorder present in a material and is limited by the mean-free path of the excited photoelectron. Typically the information reach region extended up to 3-10 A around the absorbing atom.

An advantage of the XAS method is its sensitivity to many-atom distribution functions, giving rise to multiple-scattering (MS) contributions, and to correlation effects in atom dynamics. Note that accurate account of both effects is still challenging.

The time-scale (about 10^{-15}-10^{-16} s) of the X-ray absorption process is much shorter than the characteristic time (about 10^{-13}-10^{-14} s) of thermal vibrations. Therefore, the atoms may be considered as frozen at their instantaneous positions during a single photoabsorption process, and the total experimentally measured X-ray absorption spectrum corresponds to the configurational average of all atomic positions over the time of the experiment. This situation can be straightforwardly modelled combining the molecular dynamics (MD) simulation with the extended X-ray absorption fine structure (EXAFS) calculations, known as the MD-EXAFS approach.

Finally, the agreement between the experimental and configuration-averaged EXAFS spectra can be used to validate the accuracy of the interatomic potential (force-field) models employed in the MD simulations.

http://www.dragon.lv/edaca/

EDACA code:

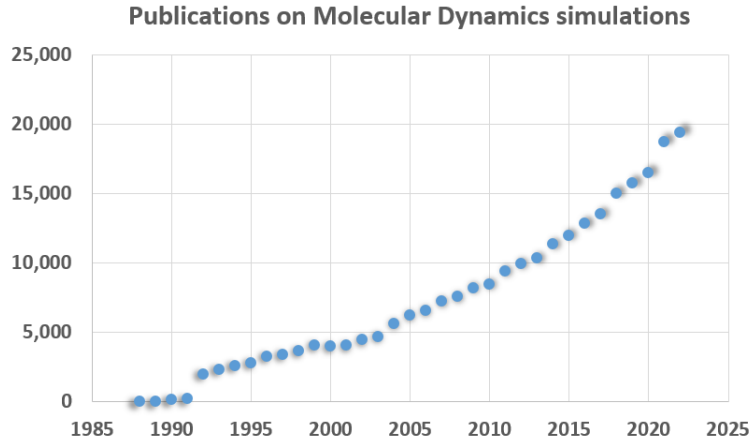
A. Kuzmin and R.A. Evarestov, J. Phys.: Condens. Matter 21 (2009) 055401.
A. Kuzmin and J. Chaboy, IUCrJ 1 (2014) 571-589.
A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko, Z. Phys. Chem. 230 (2016) 537-549.

First Molecular Dynamics Simulation

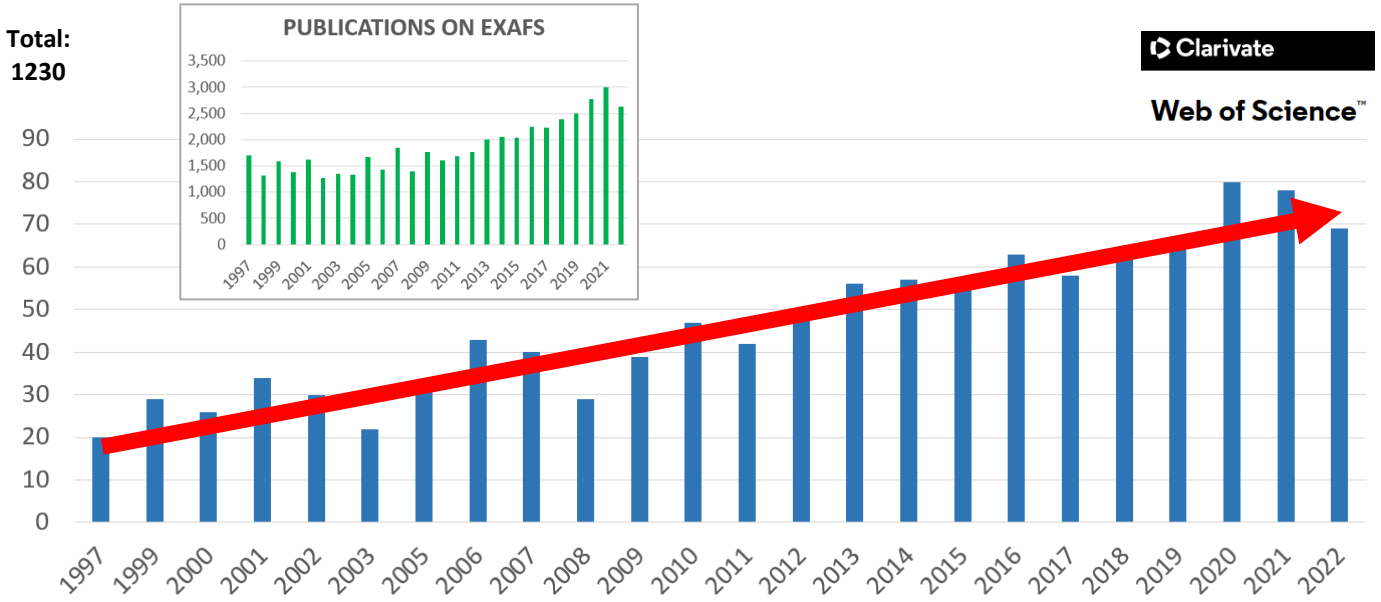
Phase Transition for a Hard Sphere System

B. J. Alder and T. E. Wainwright
University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

J. Chem. Phys. 27, 1208 (1957); doi: http://dx.doi.org/10.1063/1.1743957
J. Chem. Phys. 31, 459 (1959); doi: http://dx.doi.org/10.1063/1.1730376

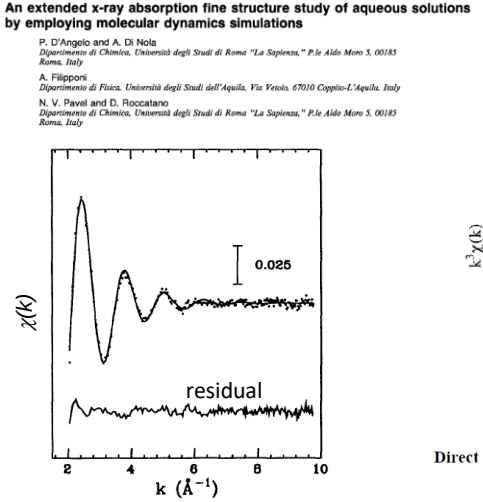


MD-EXAFS approach: State of the Art



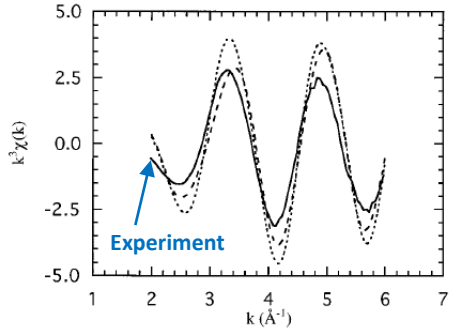
- Comparison of MD and EXAFS results
- **Using MD results for EXAFS calculation**

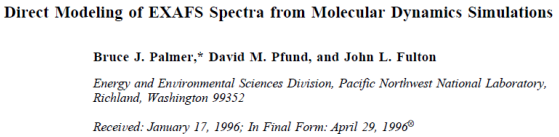
MD-EXAFS approach: History

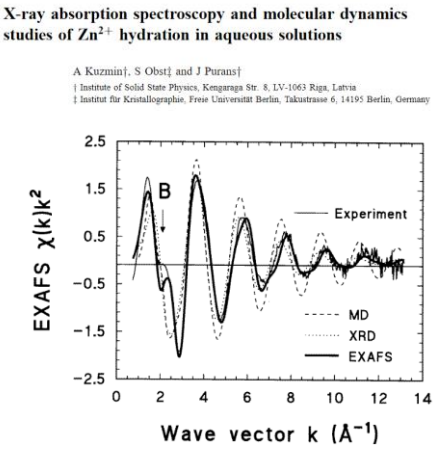


Br K-edge in 0.15M RbBr aqueous solution

Sr K-edge in strontium nitrate aqueous solution







Zn K-edge in the 0.125M aqueous solution of $ZnSO_4$

[1] P. D'Angelo, A.D. Nola, A. Filipponi, N.V. Pavel, D. Roccatano, J. Chem. Phys. 100 (1994) 985-994.
[2] P. D'Angelo, A.D. Nola, M. Mangoni, N.V. Pavel, J. Chem. Phys. 104 (1996) 1779-1790.
[3] B.J. Palmer, D.M. Pfund, J.L. Fulton, J. Phys. Chem. 100 (1996) 13393.
[4] A. Kuzmin, S. Obst, J. Purans, J. Phys.: Condensed Matter 9 (1997) 10069-10078.
[5] M. I. McCarthy, G. K. Schenter, M. R. Chacon-Taylor, J. J. Rehr, G. E. Brown, Jr., Phys. Rev. B 56 (1997) 9925-9936.

aqueous solutions

$Na^+(H_2O)_n$-MgO (100) interface

Basics of classical Molecular Dynamics (I)

Molecular dynamics (MD) simulation is a technique to simulate the motion of atoms under predefined conditions, such as **temperature (T)**, **pressure (P)**, etc.

The **NVT** ensemble is also called the *canonical* ensemble. In the **NVT** ensemble, the number (N) of particles (atoms) and the supercell size (V) are fixed, whereas the temperature (T) is controlled using a surrounding virtual heat bath (**thermostat**).

The **NPT** ensemble is also called *isothermal-isobaric* ensemble. In the **NPT** ensemble, the number (N) of particles (atoms) is fixed, whereas the temperature (T) and pressure (P) are controlled using a **thermostat** and a **barostat**.

- **J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, J. R. Haak, Molecular-Dynamics with Coupling to an External Bath, J. Chem. Phys. 81 (1982) 3684.**
- **G. J. Martyna, M. L. Klein, M. Tuckerman, Nosé-Hoover chains: The canonical ensemble via continuous dynamics, J. Chem. Phys. 97 (1992) 2635.**
- **G. J. Martyna, D. J. Tobias, M. L. Klein, Constant pressure molecular dynamics algorithms, J. Chem. Phys. 101 (1994) 4177.**

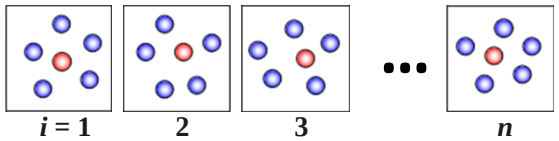
Basics of classical Molecular Dynamics (II)

During classical MD simulation the **Newton's equations** of motion are numerically integrated for a set of atoms starting from a given **initial configuration**. This is performed via numerical integration by discretizing time into small intervals called the **time step (Δt)**. The time step must be smaller than the fastest vibrational frequency in the system, typically in the order of 1 femtosecond ($\approx 10^{-15}$ s).

The interactions between the atoms, i.e. the interatomic forces, can be calculated based on **empirical potentials** or **first-principles theory (*ab initio*)**.

Machine Learning (ML) potentials become popular nowadays.

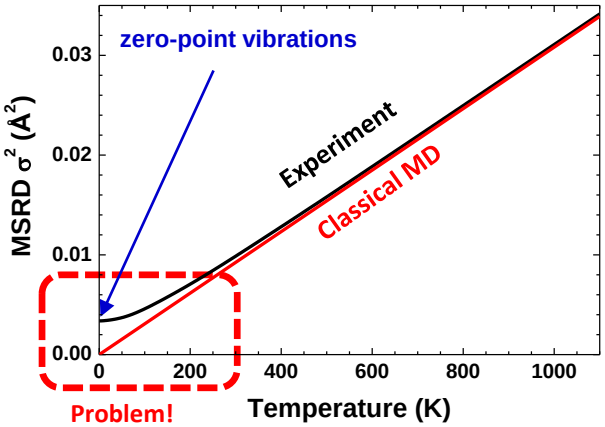
These interatomic forces determine the acceleration of the atoms, allowing the positions and velocities propagate towards the next time step. Repeating this procedure many times yields **a series of snapshots**, describing the trajectory of the system in phase space, which can be analyzed to extract the desired properties, including EXAFS/XANES.



Temperature in the classical MD simulation

$$\langle E_k \rangle = \left\langle \frac{1}{2}\sum_{i=1}^{N}(m_i\vec{v}_i)^2 \right\rangle = \frac{3}{2}Nk_BT$$

$$T \to 0\text{K}, \quad v_i \to 0$$



The Debye temperature (θ_D) and characteristic temperature (T_0) of zero-point vibration. The unit for temperature is K.

Element	θ_D	T_0
Be	1440	481.06
Al	428	142.98
Ti	420	140.31
Ta	240	80.18
Pb	105	35.08

Y. Yang and Y. Kawazoe, EPL 98 (2012) 66007

N.B. The magnitude of zero-point vibrations at T_0 equals that of the excited vibrations.

Measurements are often performed using cryostats!

Quantum effects

Quantum effects are expected to become significant when the thermal de Broglie wavelength

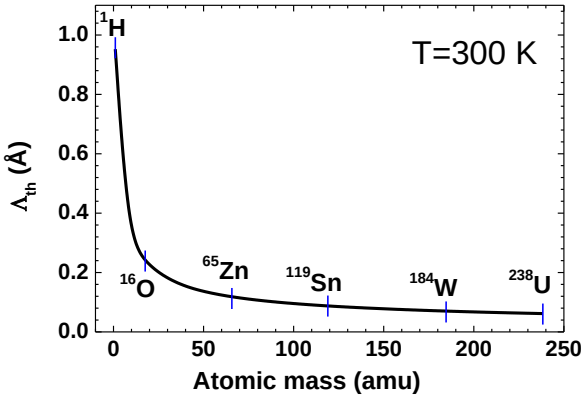
$$\Lambda_{\mathrm{th}} = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$

is much larger than the interatomic distance *d*.

Typical interatomic distance in solids is about $d \approx$ 1-3 Å.

For example, at T = 300 K:

Λ_{th} = 1 Å for a H atom (m_H = 1 amu)
Λ_{th} = 0.24 Å for a O atom (m_O = 16 amu)
Λ_{th} = 0.12 Å for a Zn atom (m_{Zn} = 65 amu)
Λ_{th} = 0.09 Å for a Sn atom (m_{Sn} = 119 amu)
Λ_{th} = 0.06 Å for a U atom (m_U = 238 amu)



All atoms, except for the lightest ones such as H, He, can be considered as "point" particles at **sufficiently high temperature** (or $d >> \Lambda_{th}$), and classical mechanics can be used to describe their motion.

Interatomic potentials

Empirical potentials

- Depend on a set of parameters which must be determined in advance by fitting to some physical properties (structure, phonons, elastic constants, etc).
- Must be validated using experiment or more accurate simulation.
- MD simulations are fast and can be done using desktop computer or a server.

Machine Learning potentials

- Must be trained using ab initio (DFT) simulations.
- Must be validated using experiment.
- MD simulations are slower than with empirical potentials but much faster than doing ab initio simulations. Server or cluster are required.

Ab initio (DFT) potentials

- Calculated from first principles.
- Must be validated using experiment.
- MD simulations are slow. Supercomputer is required.

Interatomic potentials or force-fields

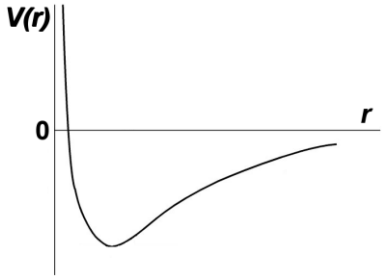
as a consequence of the Born-Oppenheimer separation of electrons and nuclei motion

$$V_{TOT} = \sum_{i}^{N} V_1(\vec{r_i}) + \sum_{i,j}^{N} V_2(\vec{r_i}, \vec{r_j}) + \sum_{i,j,k}^{N} V_3(\vec{r_i}, \vec{r_j}, \vec{r_k}) + \ldots$$

External field **Two-body** **Three-body**

Example:

The *Born-Mayer* potential $V(r) = Ae^{-\alpha r} - \frac{C}{r^6}$



Databases of interatomic potentials:

https://gulp.curtin.edu.au/gulp/models.cfm
https://www.ucl.ac.uk/klmc/Potentials/
https://www.ctcms.nist.gov/potentials/
https://openkim.org/

When more accurate description is needed, electronic behavior can be obtained from first-principles calculations using ab initio Molecular Dynamics (AIMD).

Molecular Dynamics Programs

https://en.wikipedia.org/wiki/Comparison_of_software_for_molecular_mechanics_modeling

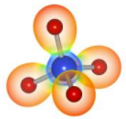
LAMMPS	- a Large-scale Atomic/Molecular Massively Parallel Simulator. https://www.lammps.org/
GULP	- the General Utility Lattice Program. https://gulp.curtin.edu.au/gulp/
DL_POLY	- a general purpose serial and parallel molecular dynamics simulation package. https://www.scd.stfc.ac.uk/Pages/DL_POLY.aspx
CP2K	- a program to perform atomistic and molecular simulations of solid state, liquid, molecular, and biological systems. (also ab initio) https://www.cp2k.org/

Important: MD trajectory must be saved as *.XYZ file with a specific structure.

Interpretation of results

VESTA a 3D visualization program for structural models, volumetric data such as electron/nuclear densities, and crystal morphologies.

http://jp-minerals.org/vesta/en/



OVITO a scientific visualization and data analysis solution for atomistic and other particle-based models.

https://www.ovito.org/

MD-EXAFS simulation related parameters

- Equilibration time
- Proper averaging (number of configurations & time step)
- The simulation box size must be large enough to avoid boundary condition artifacts such as, for example, artificial correlations (simulation box size > $2R_{max}$)
- Multiple-scattering series truncation problem in FEFF8.5L:

  NLEG = 8 default 8 order * (bond length 2-3 Å) / 2 = 8-12 Å

  CRITERIA 4.0 2.5 * default critcw=4.0% critpw=2.5%
  CRITERIA 0 0 * use all paths, if possible (cw and pw criteria turned off)

- A “configuration” average over the spectra of multiple absorbing atoms (for nanoparticles)

  CFAVERAGE iphabs nabs rclabs

  iphabs potential index for the type of absorbing atoms over which to make the configuration average
  nabs the configuration average is made over the first nabs absorbers in the `feff.inp' file of type iphabs.
  rclabs radius to make a small atom list from a bigger one allowed in `feff.inp'.

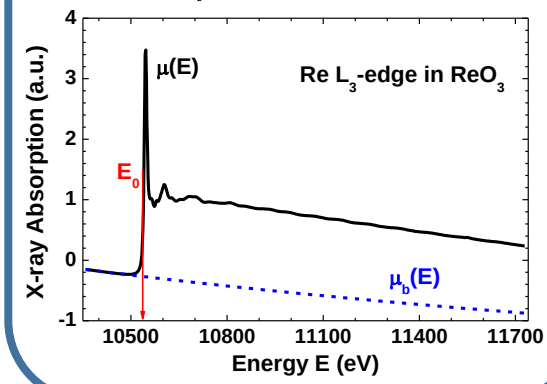
Non-structural parameters in MD-EXAFS simulation

The configuration-averaged EXAFS spectrum $\chi_{ca}(k)$ is calculated **uniquely** from the results of the MD simulation.

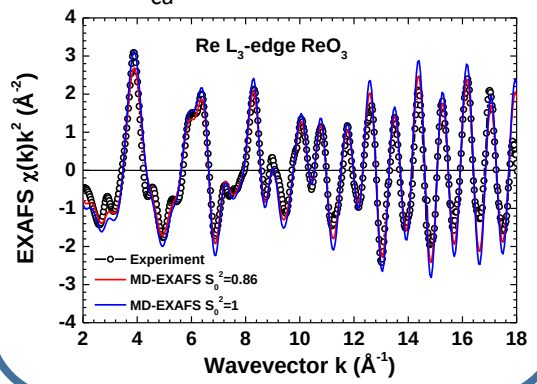
Comparison with the experiment requires two more parameters:

E_0 and **S_0^2**

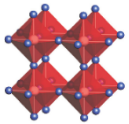
$$k = \sqrt{(2m_e/\hbar^2)(E - E_0)}$$



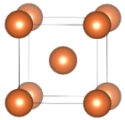
$$\chi^l_{ca}(k) = S_0^2 \langle \chi^l(k) \rangle$$



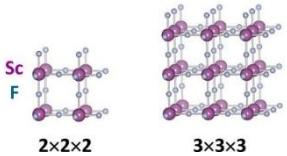
Examples of MD-EXAFS simulations



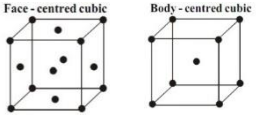
Cubic perovskite-type ReO_3 - force-field development



Bcc tungsten - validation of interatomic potentials

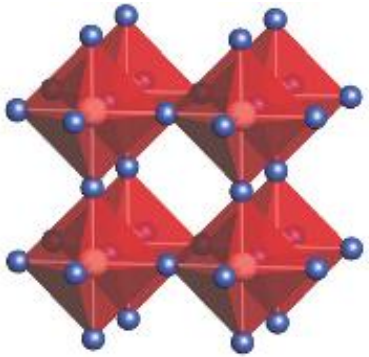


Cubic perovskite-type ScF_3 - the effect of the supercell size



FCC and BCC metals - validation of Machine Learning potentials

Cubic perovskite-type ReO_3



A. Kalinko, R.A. Evarestov, A. Kuzmin, J. Purans, J. Phys.: Conf. Ser. 190 (2009) 012080.

Force-field model for ReO_3 used in the MD simulations

	Exper.*	Calc.	
Lattice constant (Å)	3.75	3.75	
Bulk Modulus (GPa)	211	198	
Elastic constants (Gpa)			
C_{11}	572	503	
C_{12}	7	46	for central pairwise forces
C_{44}	68	46	

* T. Chatterji, P. F. Henry, R. Mittal, S. L. Chaplot, Phys. Rev. B 78 (2008) 134105;
N. Tsuda, Y. Sumino, I. Ohno, T. Akahane, J. Phys. Soc. Jpn. 41 (1976) 1153–1158.

Buckingham Potential

$$U_{ij} = Ae^{\frac{-r_{ij}}{\rho}} + \frac{C}{r_{ij}^6}$$

Covalent Exponential Potential

$$U_{ij} = -De^{\frac{-n(r_{ij}-r_0)^2}{2r_{ij}}}$$

The parameters of the force-field model for cubic ReO_3

Coulomb potential

Atom	Z, e
Re	3.36
O	-1.12

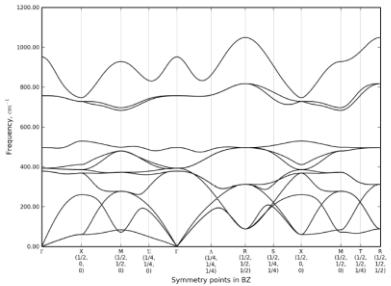
← from Quantum Chemistry

Buckingham potential, cutoff 20 Å

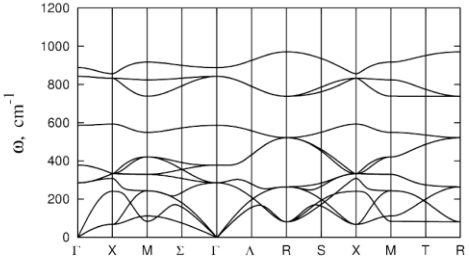
Pair of atoms	A, eV	ρ, Å	C, eVÅ^2
Re–O	1194.24	0.3426	98.10
O–O	3224.54	0.2652	47.40

Covalent exponential potential, cutoff 2 Å

Pair of atoms	D	n	r_0, Å
Re–O	4.8283	6.2107	1.875



Phonon dispersion curves calculated using frozen phonon (LCAO, CRYSTAL06) method.



Phonon dispersion curves calculated by the force-field (GULP 3.1) method.

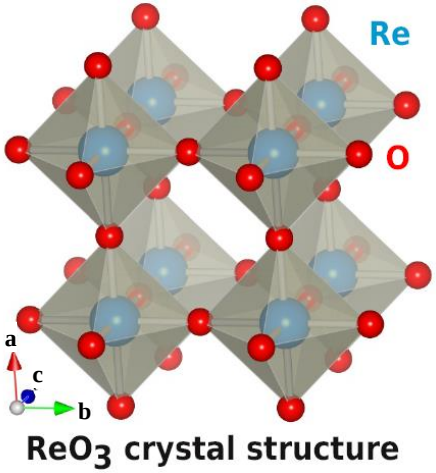
Force-field parameters were optimized to reproduce:

- structural parameters,
- elastic constants,
- ab initio phonon frequencies.

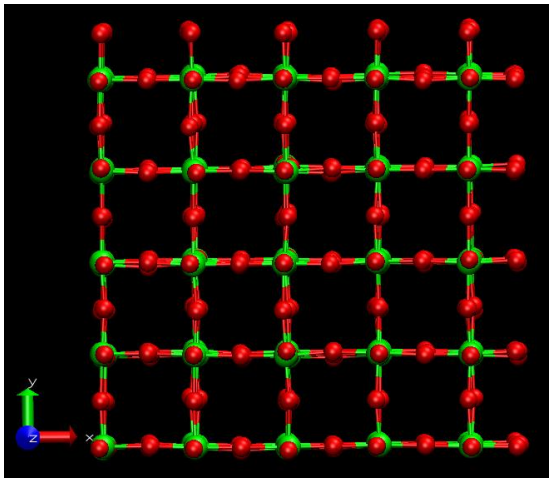
R. A. Evarestov, A. Kalinko, A. Kuzmin, M. Losev, J. Purans, Integr. Ferroelectrics 108 (2009) 1-10.

Molecular Dynamics simulations of ReO_3

using the rigid-ion model as implemented in the GULP3.1 code*



ReO_3 crystal structure

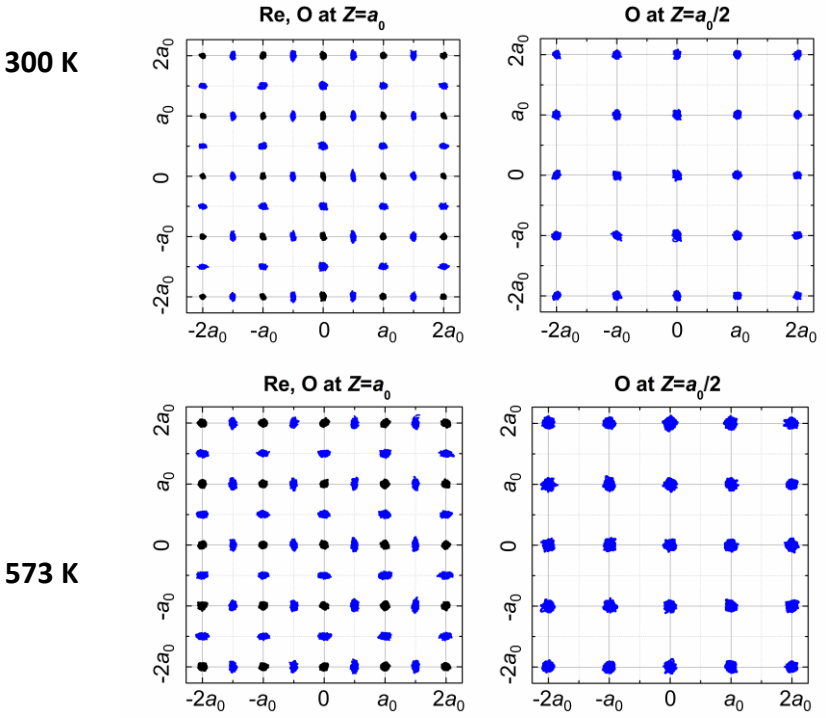


Cubic perovskite ReO_3
Space group No. 221, *Pm*-3*m*
Lattice parameter a_0 = 3.7477 Å

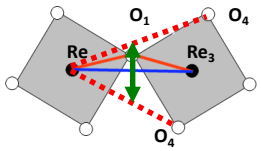
NVT/NPT ensembles
Leap-frog Verlet integration
Supercell **5x5x5** (500 atoms)
T = 300 K, 423 K, 573 K
Simulation time: 20 ps equilibration + 20 ps production
Time step: 0.5 fs
4000 atomic configurations

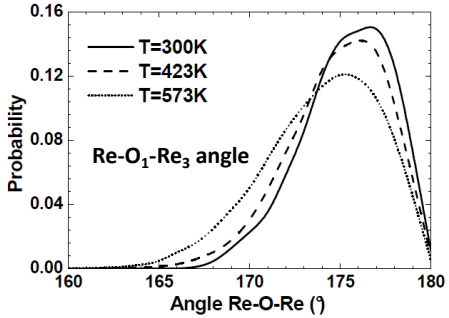
*** J.D. Gale and A.L. Rohl, Mol. Simul. 9 (2003) 291.**

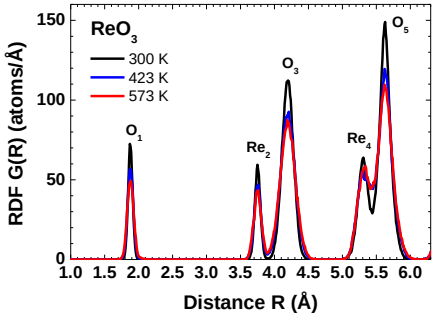
Thermal disorder from MD simulations in ReO_3



Representation of MD trajectories for Re (black) and O (blue) atoms located in a plane $Z = a_0$. (a_0 is the lattice parameter.)

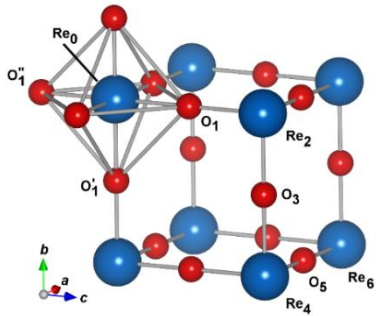




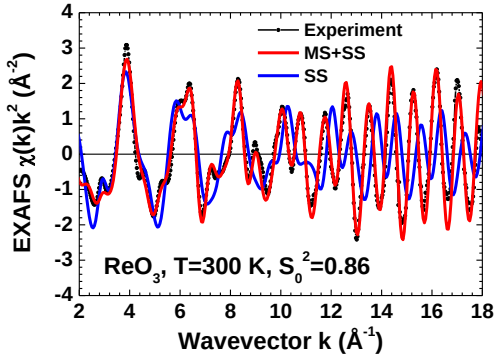


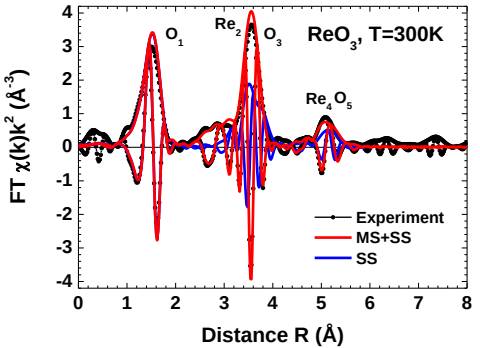
A. Kalinko, R.A. Evarestov, A. Kuzmin, J. Purans, J. Phys.: Conf. Ser. 190 (2009) 012080.

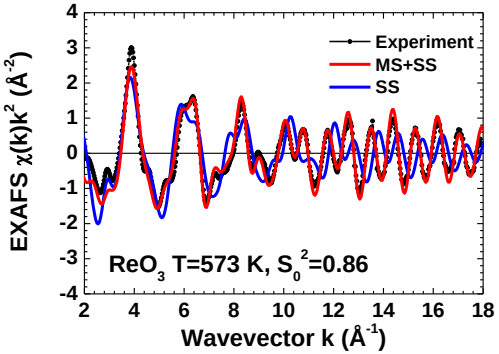
Comparison between experimental and configuration-averaged Re L_3-edge EXAFS signals and their Fourier transforms in ReO_3

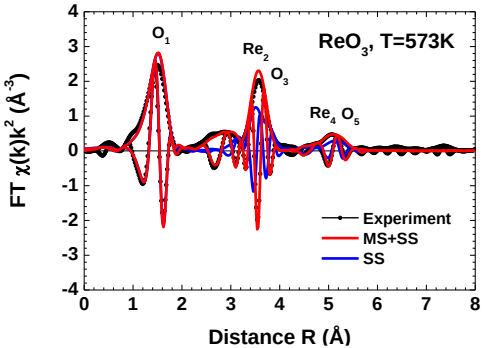


Index	Path	Path type	Path degener.	Half-path length (Å)
1	Re_0-O_1-Re_0	SS	6	1.875
2	Re_0-O_1-O_1'-Re_0	DS	24	3.201
3	Re_0-Re_2-Re_0	SS	6	3.750
4	Re_0-O_1-O_1''-Re_0	DS	6	3.750
5	Re_0-O_1-Re_2-Re_0	DS	12	3.750
6	Re_0-O_1-Re_0-O_1''-Re_0	TS	6	3.750
7	Re_0-O_1-Re_0-O_1-Re_0	TS	6	3.750
8	Re_0-O_1-Re_2-O_1-Re_0	TS	6	3.750
9	Re_0-O_1-Re_0-O_1'-Re_0	TS	24	3.750
10	Re_0-O_3-Re_0	SS	24	4.193
11	Re_0-O_1-O_3-Re_0	DS	48	4.360
12	Re_0-O_1-O_1'-O_1-Re_0	TS	24	4.527
13	Re_0-O_1-O_3-O_1-Re_0	TS	24	4.527
14	Re_0-Re_4-Re_0	SS	12	5.303
15	Re_0-O_5-Re_0	SS	30	5.625





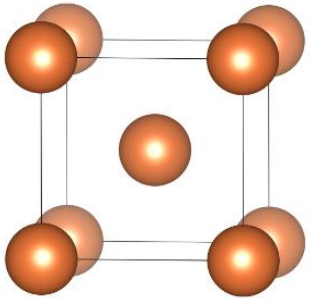




A. Kalinko, R.A. Evarestov, A. Kuzmin, J. Purans, J. Phys.: Conf. Ser. 190 (2009) 012080.

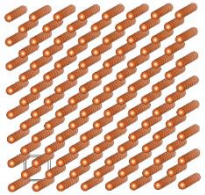
Validation of interatomic potentials for bcc tungsten using the W L_3-edge EXAFS

$$\sigma_{\mathrm{th}}^2 = \langle u_{\mathrm{A}}^2 \rangle + \langle u_{\mathrm{B}}^2 \rangle - 2\langle u_{\mathrm{A}} u_{\mathrm{B}} \rangle$$



I. Jonane, A. Anspoks, A. Kuzmin, Modelling Simul. Mater. Sci. Eng. 26 (2018) 025004.

Validation of Molecular Dynamics simulations: How accurate are force-fields? EAM vs 2NN-MEAM

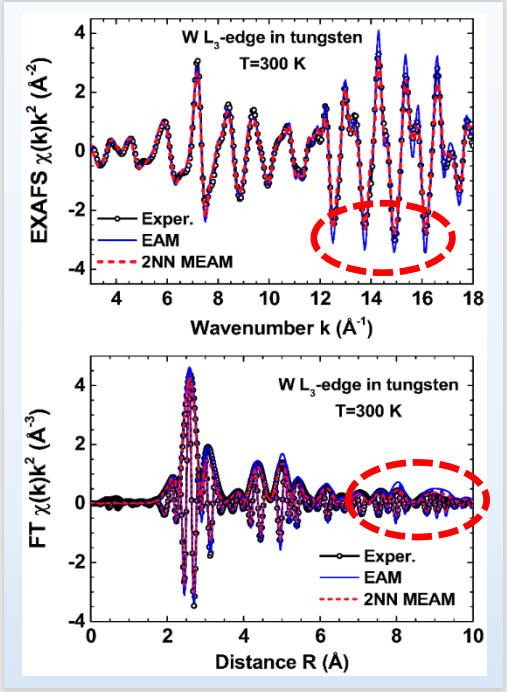


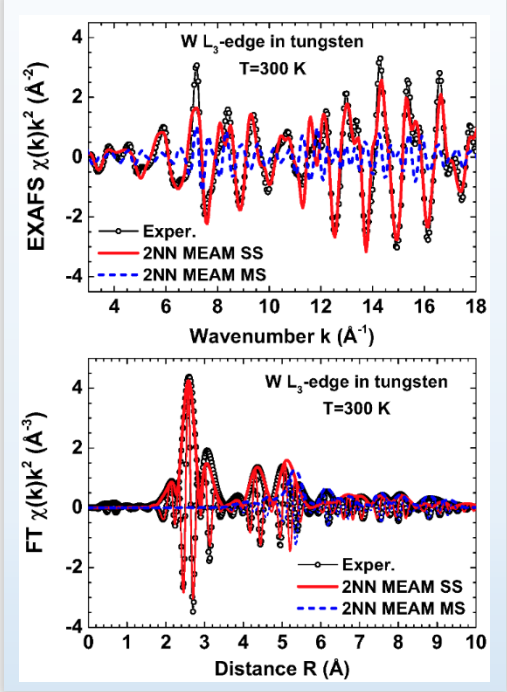
bcc W a = 3.165 Å

Supercell:
7*a* × 7*a* × 7*a*
686 atoms

MD GULP code
NVT
T=300 K
Δt=0.5 fs
20 ps + 20 ps

EDACA + FEFF8.50L





Embedded Atom Model (EAM): *M.W. Finnis and J.E. Sinclair, Phil. Mag. A 50 (1984) 45-55.*
2nd Nearest-Neighbor Modified EAM (2NN-MEAM): *B.J. Lee, M. Baskes, H. Kim, Y. Koo Cho, Phys. Rev. B 64 (2001) 184102.*

I. Jonane, A. Anspoks, A. Kuzmin, Modelling Simul. Mater. Sci. Eng. 26 (2018) 025004.

Simultaneous MSRD and MSD determination from EXAFS

$$\mathrm{MSRD}_{AB} = \mathrm{MSD}_A + \mathrm{MSD}_B - 2\varphi\sqrt{\mathrm{MSD}_A}\sqrt{\mathrm{MSD}_B}$$

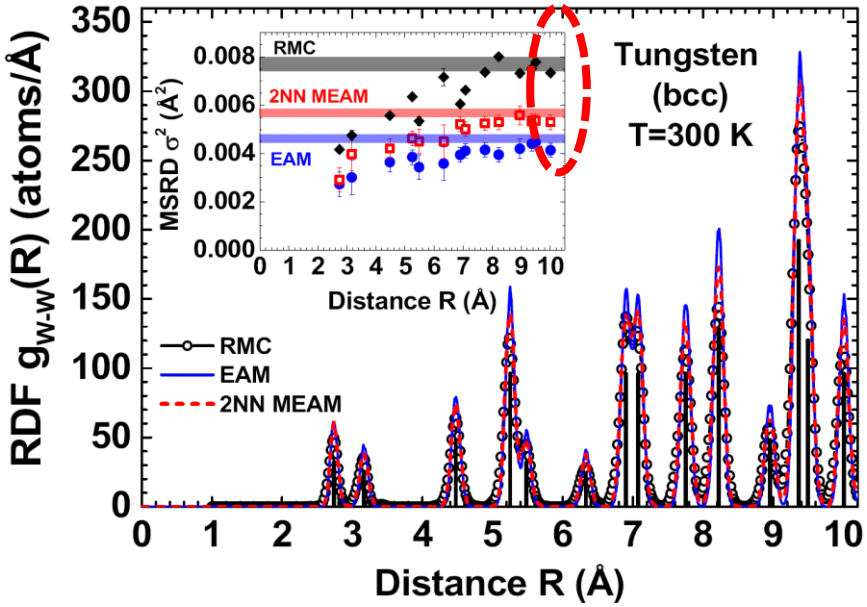
$$\mathbf{R \to \infty, \varphi \to 0\ \&\ MSRD_{AB} \to MSD_A + MSD_B}$$

MD:
MSD(EAM)=0.0023 Å²
MSD(MEAM)=0.0029 Å²

RMC:
MSD(RMC)=0.0039 Å²

X-ray diffraction:
MSD=0.0061 Å² [1]
MSD=0.0022 Å² [2]

Lattice dynamics calculations:
MSD=0.0023 Å² [3]
MSD=0.0018 Å² [4]

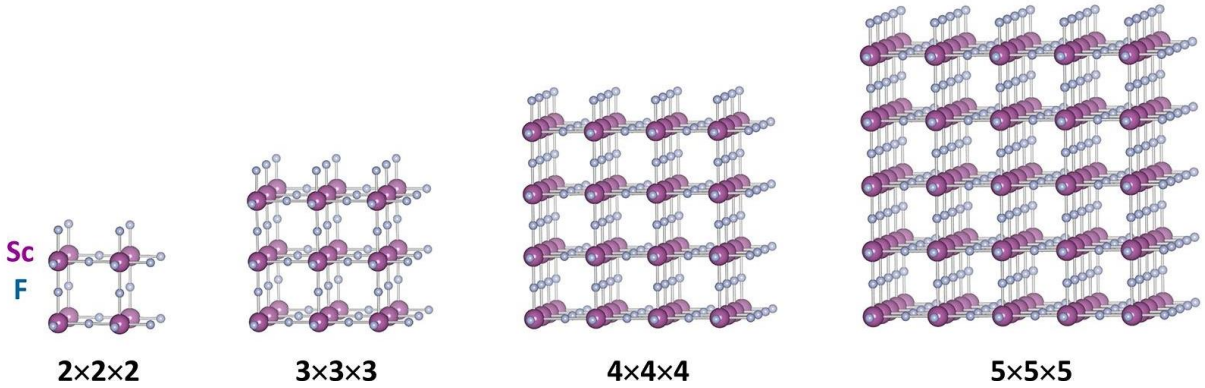


φ is a dimensionless correlation parameter

I. Jonane, A. Anspoks, A. Kuzmin, Modelling Simul. Mater. Sci. Eng. 26 (2018) 025004.

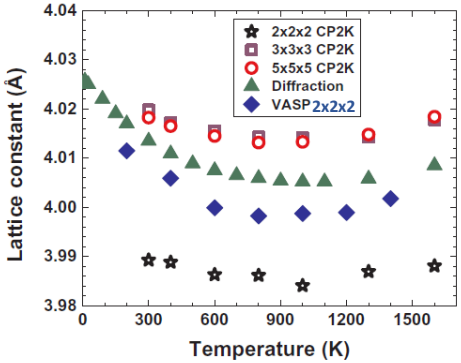
[1] C.R. Houska, J. Phys. Chem. Solids 25 (1964) 359.
[2] T. Paakkari, Acta Crystallogr. A 30 (1974) 83.
[3] P.C. Fine, Phys. Rev. 56 (1939) 355.
[4] L. Dobrzynski, P. Masri, J. Phys. Chem. Solids 33 (1972) 1603.

Cubic perovskite ScF_3 - the effect of the supercell size

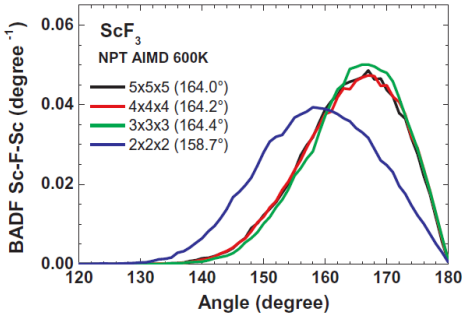


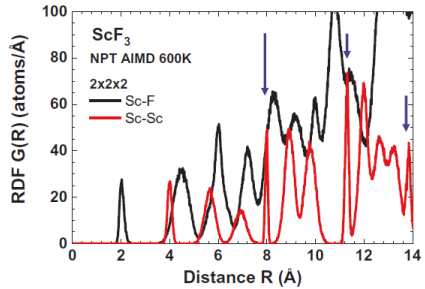
D. Bocharov, M. Krack, Yu. Rafalskij, A. Kuzmin, J. Purans, Comp. Mater. Sci. 171 (2020) 109198.

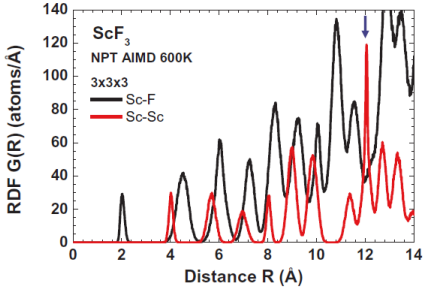
Ab initio molecular dynamics simulations of negative thermal expansion in ScF_3: the effect of the supercell size

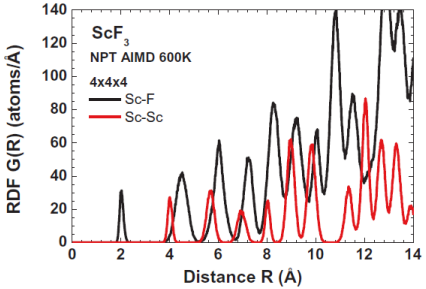


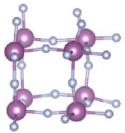
♦ P. Lazar, T. Bučko, J. Hafner, Phys. Rev. B 92 (2015) 224302.



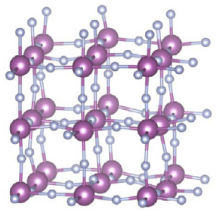




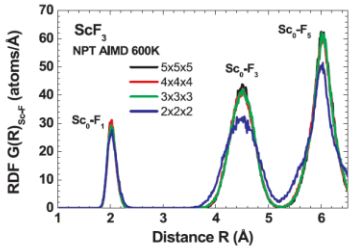


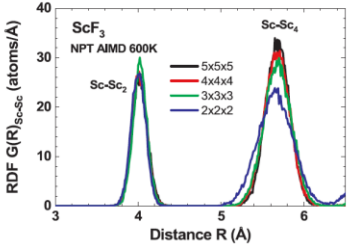


$2a_0 \times 2a_0 \times 2a_0$



$3a_0 \times 3a_0 \times 3a_0$



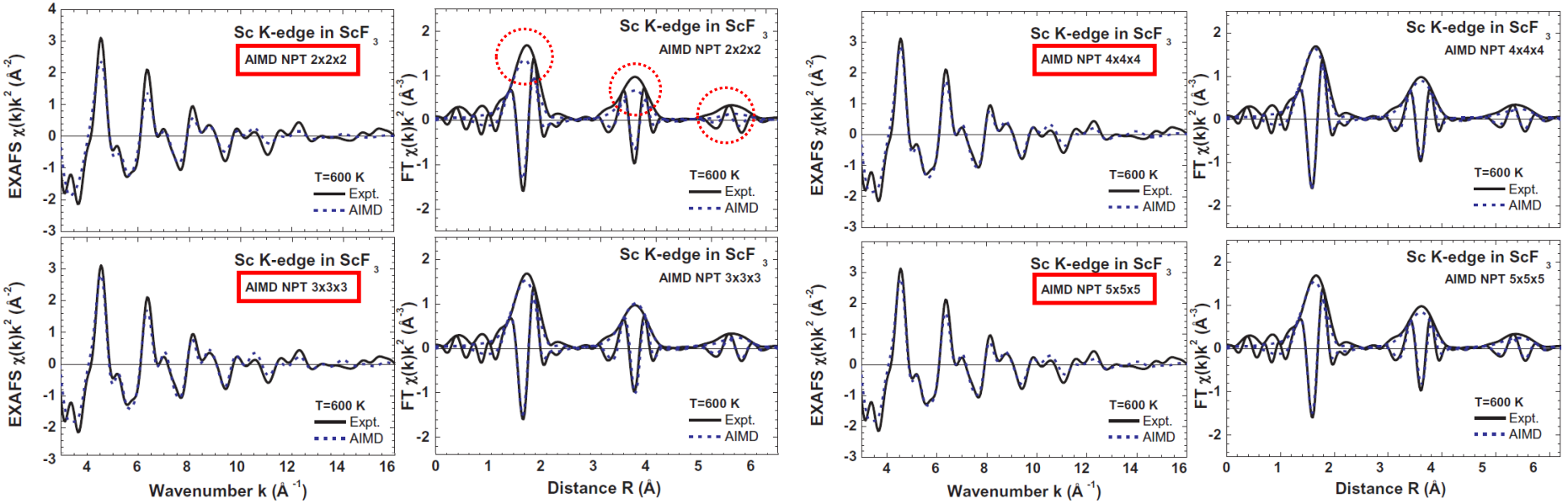


NpT AIMD simulations were performed using CP2K code.

D. Bocharov, M. Krack, Yu. Rafalskij, A. Kuzmin, J. Purans, Comp. Mater. Sci. 171 (2020) 109198.

https://www.cp2k.org/

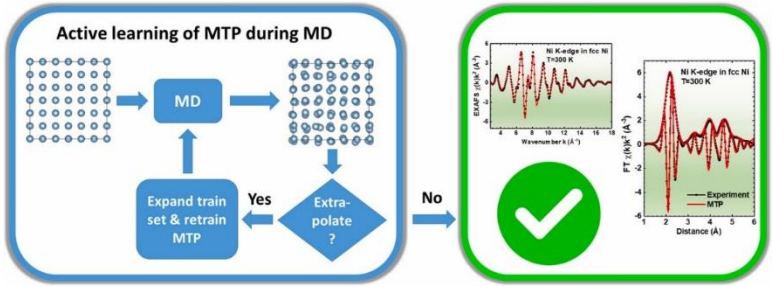
Ab initio molecular dynamics simulations of negative thermal expansion in ScF_3: the effect of the supercell size



Small supercell size introduces artefacts into RDFs and results in inaccurate RDFs and BADFs.

D. Bocharov, M. Krack, Yu. Rafalskij, A. Kuzmin, J. Purans, Comp. Mater. Sci. 171 (2020) 109198.

Validation of Machine Learning potentials

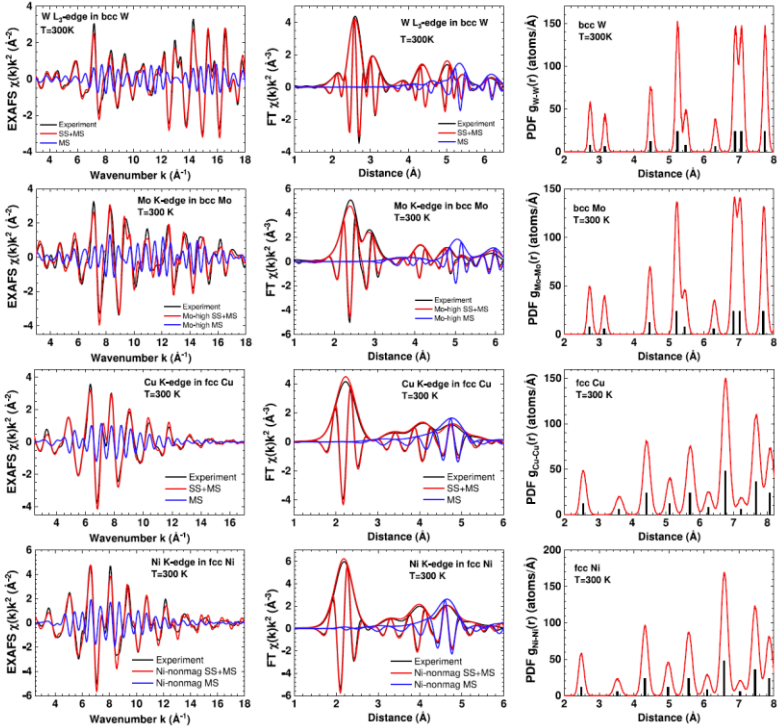


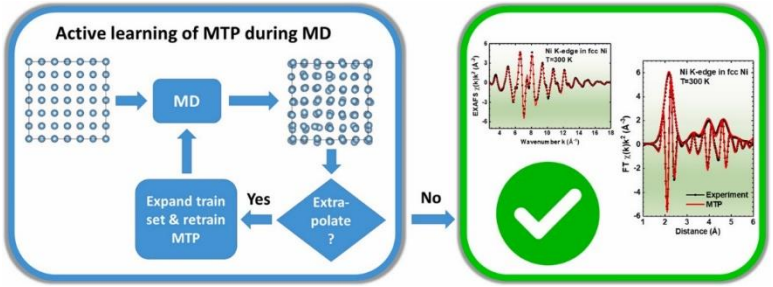
A. V. Shapeev, D. Bocharov, A. Kuzmin, Comput. Mater. Sci. 210 (2022) 111028.

Validation of moment tensor potentials for fcc and bcc metals using EXAFS spectra

Body - centred cubic

Face - centred cubic





NVT MD simulations were performed by LAMMPS using Moment Tensor Potentials (MTPs) [1,2] as implemented in the MLIP-2 software package [3].

MTP potentials were trained on-the-fly using the results of AIMD by VASP.

[1] A.V. Shapeev, Multisc. Model. Simul. 14 (2016) 1153–1173.
[2] K. Gubaev, E.V. Podryabinkin, G.L. Hart, A.V. Shapeev, Comput. Mater. Sci. 156 (2019) 148–156.

[3] I.S. Novikov, K. Gubaev, E.V. Podryabinkin, A.V. Shapeev, Mach. Learn.: Sci. Technol. 2 (2020) 025002.

https://github.com/materialsvirtuallab/mlearn

A. V. Shapeev, D. Bocharov, A. Kuzmin, Comput. Mater. Sci. 210 (2022) 111028.

Conclusions

- Molecular Dynamics is a natural way to include disorder (static and dynamic) into EXAFS simulations taking into account multiple-scattering effects.

- The MD-EXAFS approach allows one to interpret EXAFS spectra based on the multiple-scattering formalism far beyond the first coordination shell.

  Good for EXAFS!

- No structural fitting parameters is used in the MD-EXAFS approach. The structural model is uniquely defined from the results of the MD simulation. But your EXAFS results will be as good as the MD ones.

- EXAFS spectra can be used as an additional physical property for interatomic potential/theory validation.

  Good for Molecular Dynamics!

- Care should be taken regarding the temperature. At low temperature, special treatment is required, e.g. based on path-integral methodology*.

  *** D. Marx, M. Parrinello, J. Chem. Phys. 104 (1996) 4077-4082**

Thank you for your attention!