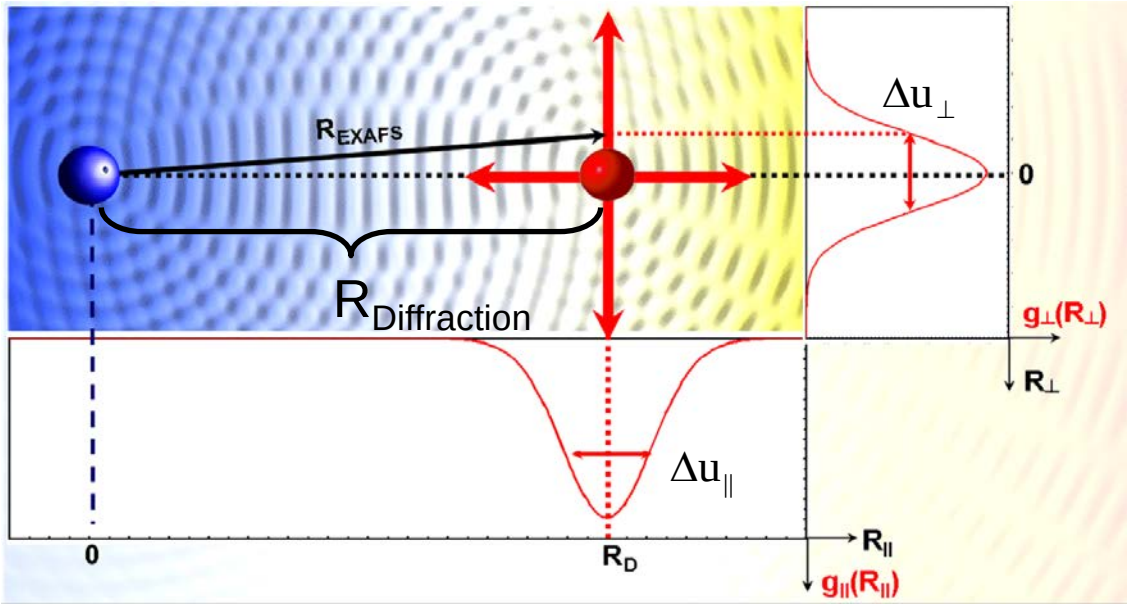
Measuring bond length disorder by EXAFS



Janis Timoshenko

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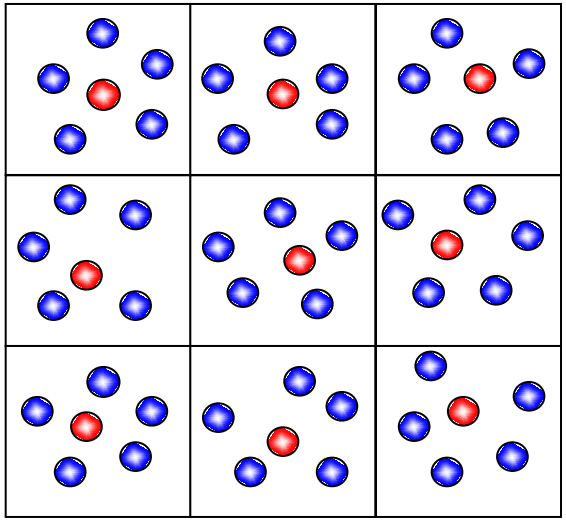
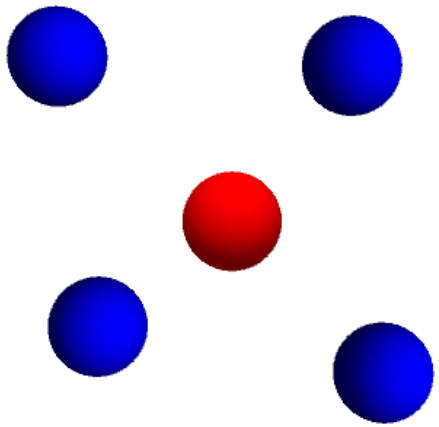
Static disorder and thermal disorder

Two kinds of disorder have similar effect on EXAFS:

Static disorder:



Thermal (vibrational) disorder:



- Life-time of core-hole is one of the factors that limits the time-scale of EXAFS formation process to a few femtoseconds (10^{-15} s).
- Characteristic atomic vibrational frequencies ~ 10^{13} Hz $\longrightarrow$ 10^{-13} s.

Each X-ray absorption event probes some "frozen", "stroboscopic image" of the material.

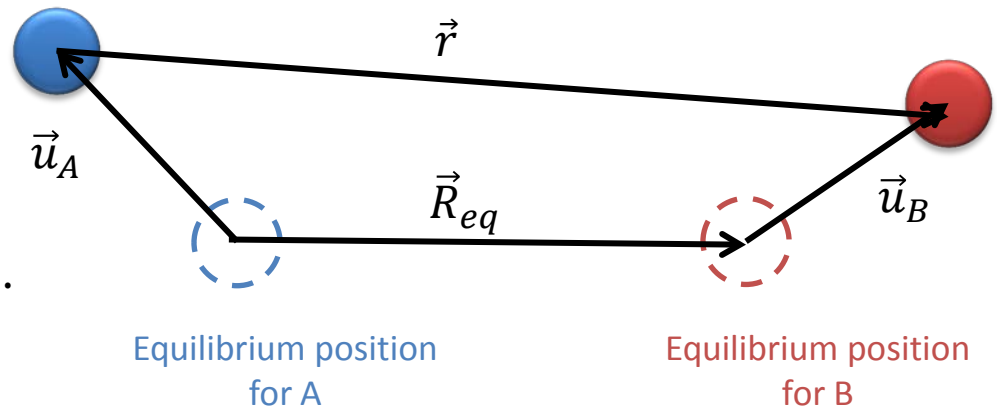
Disorder is one of the most important pieces of information that can be extracted from EXAFS (especially for crystalline materials), since interatomic distances can be probed by, e.g., diffraction with much better accuracy than by EXAFS.

Disorder and bond lengths

P. Fornasini, J. Phys.: Condens. Matter 13 (2001) 7859-7872.

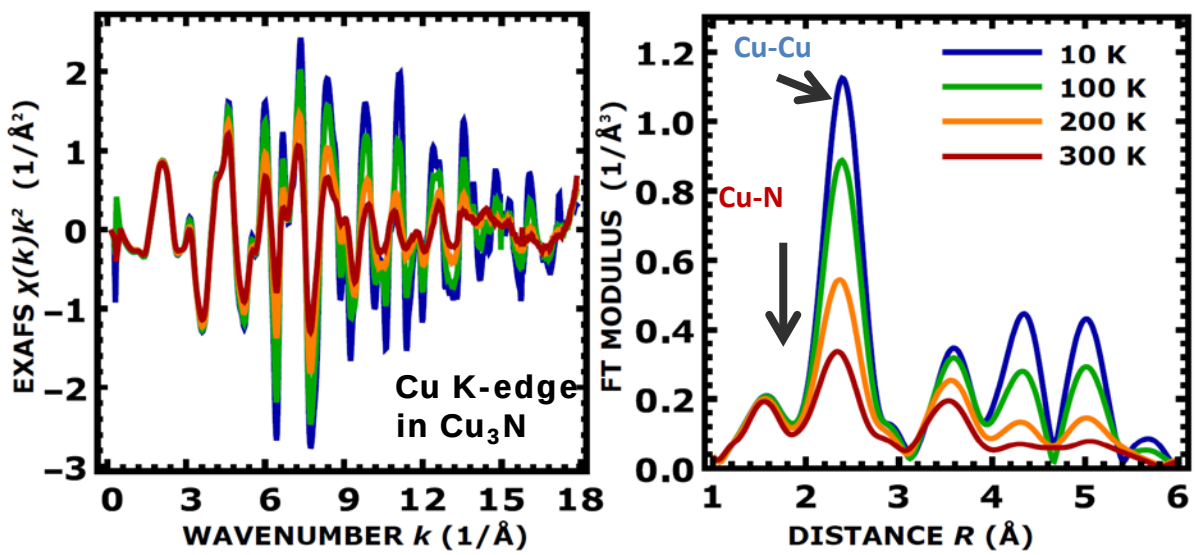
Actual A-B distance:

$$R = |\vec{r}| = |\vec{R}_{eq} + (\vec{u}_B - \vec{u}_A)| =$$
$$= |\vec{R}_{eq} + \Delta\vec{u}| =$$
$$= R_{eq} + \Delta u_{\parallel} + \frac{(\Delta u_{\perp})^2}{2R_{eq}} + \cdots$$



Total configuration- and time-averaged EXAFS will contain contributions of many slightly different *R* values: *sin* functions with slightly different frequencies cancel each other at high values of wavenumber *k:*

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



Disorder results in reduced EXAFS amplitudes at high values of *k*.

Average interatomic distance

$$R = R_{eq} + \Delta u_{\parallel} + \frac{(\Delta u_{\perp})^2}{2R_{eq}} + \cdots$$

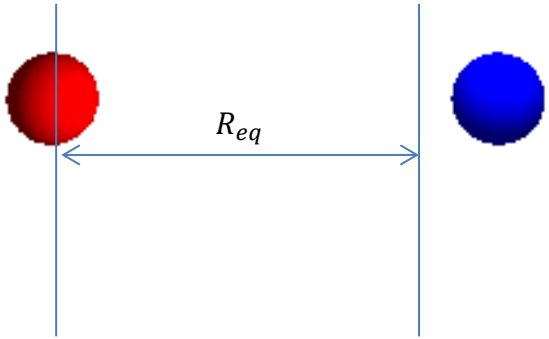
$$\chi_p(k) = S_0^2 \int_{-\infty}^{+\infty} \boldsymbol{g_p(R)} \frac{f_p(k,R)}{kR^2} \sin\left(2kR + \phi_p(k)\right) dR$$

Using EXAFS, we try to determine parameters RDF function $g(R)$: i.e., average R value

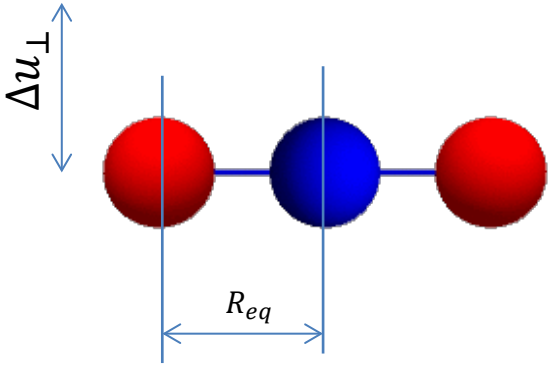
$$R_{EXAFS} = \langle R \rangle = \frac{1}{N} \int_{-\infty}^{+\infty} \boldsymbol{g_p(R)} R \; dR,$$

variance of the g(R) distribution σ^2, …

In **harmonic approximation** $\Delta\vec{u}$ component that is parallel to $\vec{R}_{eq}$ cannot affect the average interatomic distance, as probed by EXAFS:



Perpendicular atomic motion, in turn, affects the average interatomic distances directly:



In harmonic approximation

$$R_{EXAFS} \approx R_{eq} + \frac{\langle \Delta u^2{}_{\perp} \rangle}{2R_{eq}}$$

Interatomic distances, as measured by EXAFS, should be normally larger than the ones, measured by diffraction!

Average interatomic distance

$$R = R_{eq} + \Delta u_{\parallel} + \frac{(\Delta u_{\perp})^2}{2R_{eq}} + \cdots$$

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

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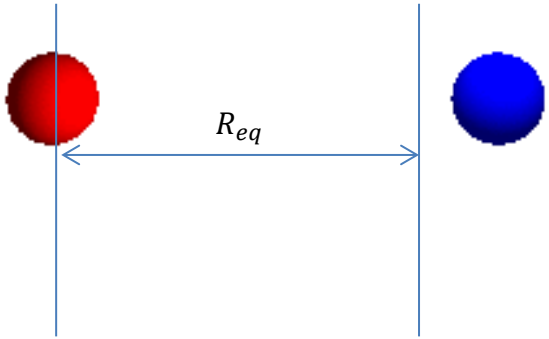

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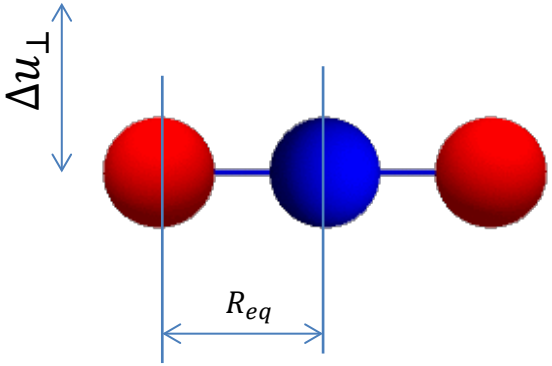


In harmonic approximation

$$R_{EXAFS} \approx R_{eq} + \frac{\langle \Delta u^2{}_{\perp} \rangle}{2R_{eq}}$$

Perpendicular Relative Displacement

Variance of interatomic distances

$$R = R_{eq} + \Delta u_{\parallel} + \frac{(\Delta u_{\perp})^2}{2R_{eq}} + \cdots$$

Motion of atoms in the direction parallel to $\vec{R}_{eq}$, however, directly affects the variance of bond length distribution. In harmonic approximation

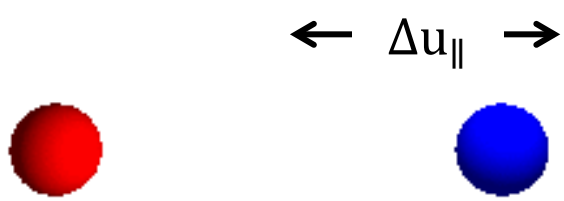
$$\sigma^2 = \frac{1}{N}\int_{-\infty}^{+\infty} g_p(R)(R - R_{EXAFS})^2\, dR \approx \left\langle \Delta\vec{u}_{\parallel}{}^2 \right\rangle$$

Parallel Relative Displacement

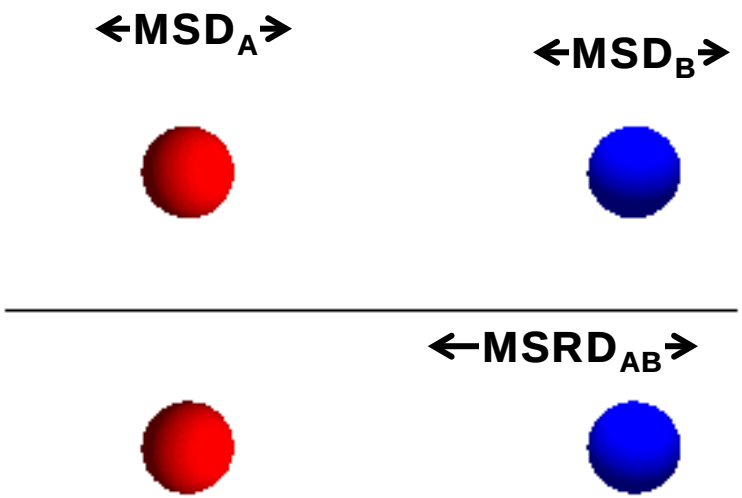
Mean Square Relative Displacement (MSRD) factor

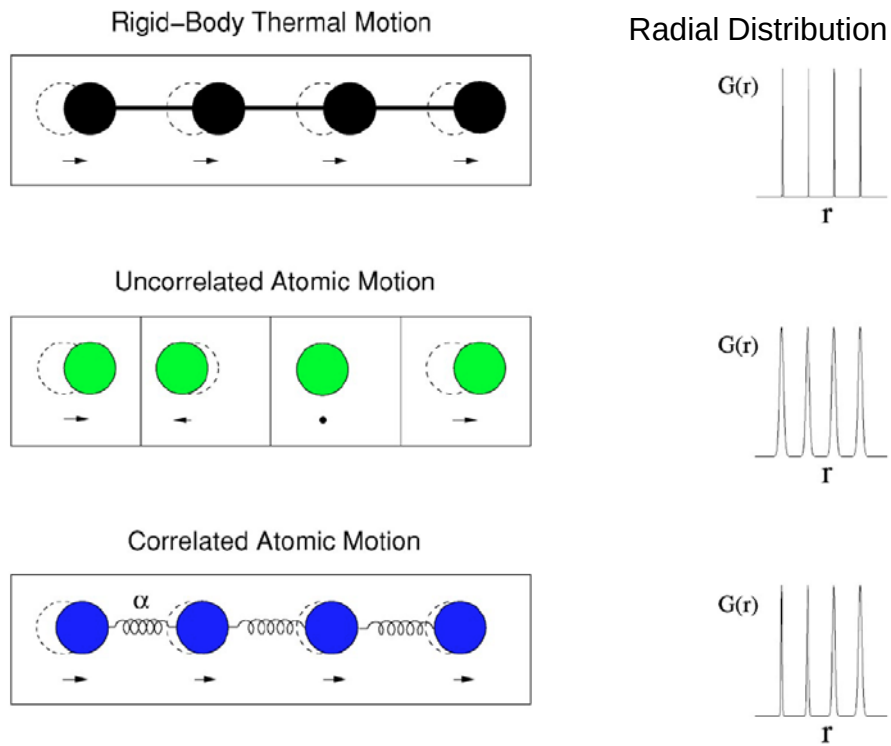
and results in Gaussian damping of EXAFS oscillations:

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



Correlations





MSRD factors, probed by EXAFS, are not the same as **Mean Square Displacement** (MSD) factors, probed, e.g., by diffraction methods!

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

Correlation effects contribute significantly to MSRD values!

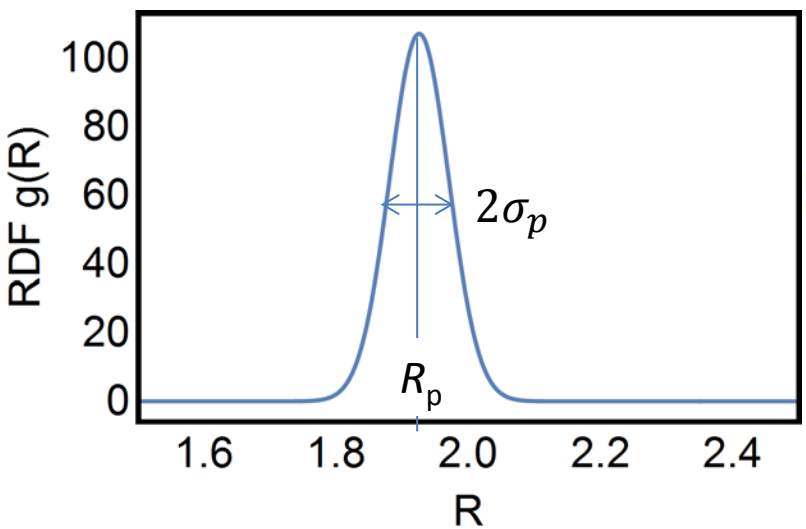
I.-K. Jeong et al, Phys. Rev. B 67 (2003) 104301:1-9.

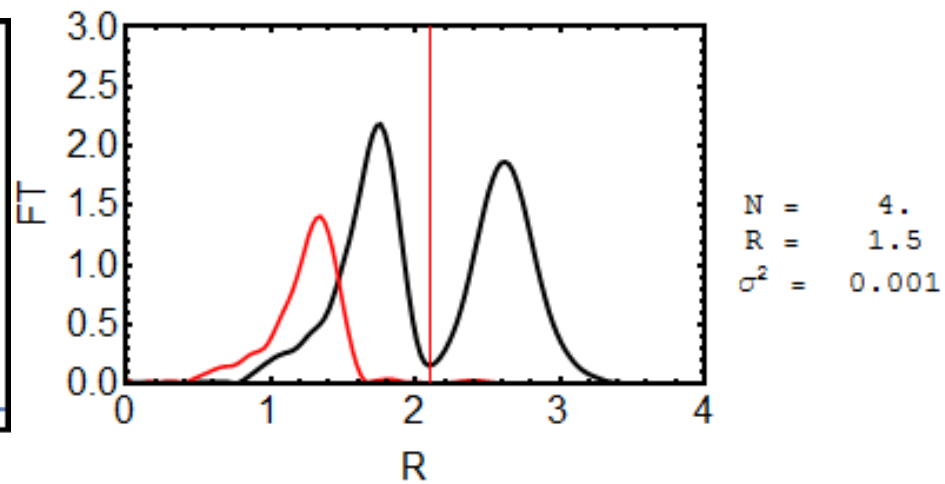
J. J. Rehr and R. C. Albers, Rev. Mod. Phys., 72 (2000).

Gaussian disorder

For systems with small disorder (e.g., crystalline materials), harmonic approximation is usually adequate and average interatomic distances and MSRD factors can be extracted by conventional EXAFS fitting (e.g., using IFEFFIT and phases and amplitudes, calculated by FEFF)

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





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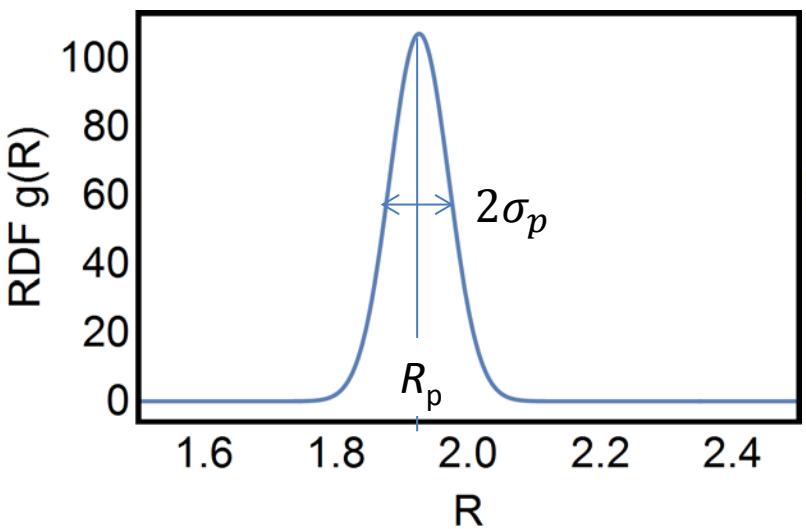
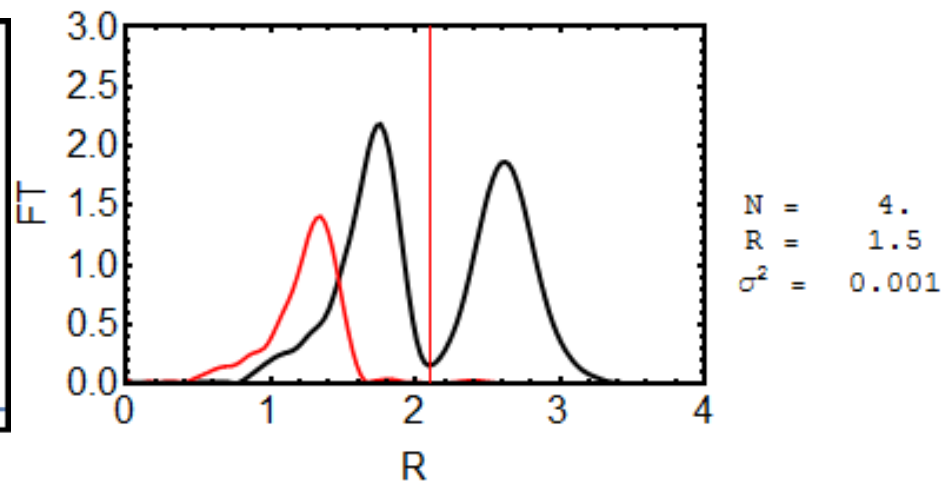


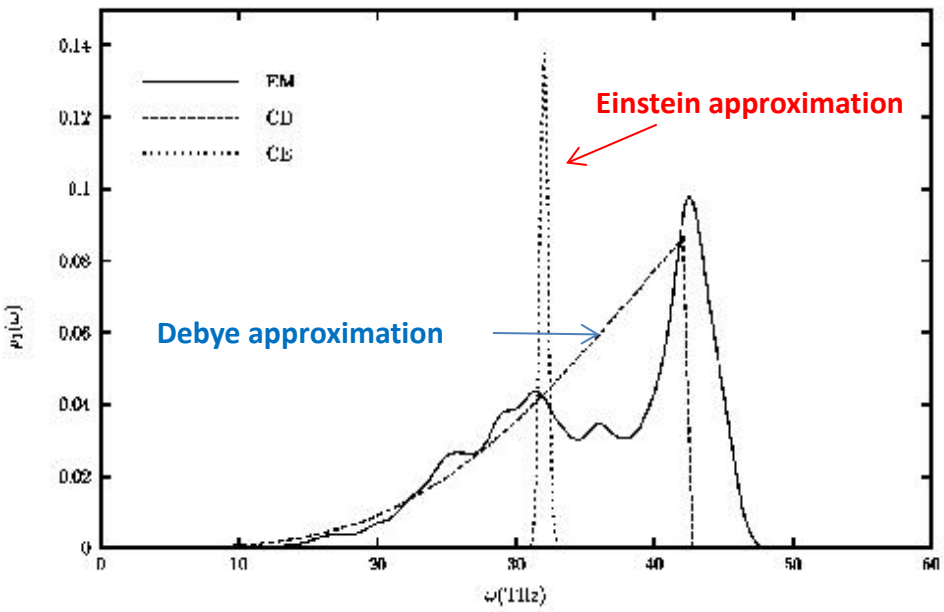


Thermal disorder. MSRD and vibrations.

Both static and thermal disorder contribute similarly to the value of MSRD factor:

$$\sigma^2 = \sigma_{static}^2 + \sigma_{thermal}^2$$

The latter is related to **vibrational properties** of the material and **depends on temperature**



$$\sigma_{thermal}^2(T) = \frac{\hbar}{2\mu}\int_0^{\omega_{max}} \frac{d\omega}{\omega}\rho(\omega)\coth\frac{\hbar\omega}{2k_BT}$$

Two approximations of $\rho(\omega)$ function are often used:

Einstein model approximates the phonon spectrum with a single Einstein frequency ω_E

$$\rho(\omega) = \delta(\omega - \omega_E)$$

Debye model linearly approximates the (acoustic) phonon spectrum

$$\rho(\omega) = \frac{2\omega^2}{\omega_D^3}\left(1 - \frac{\sin(\omega R/c)}{\omega R/c}\right)$$

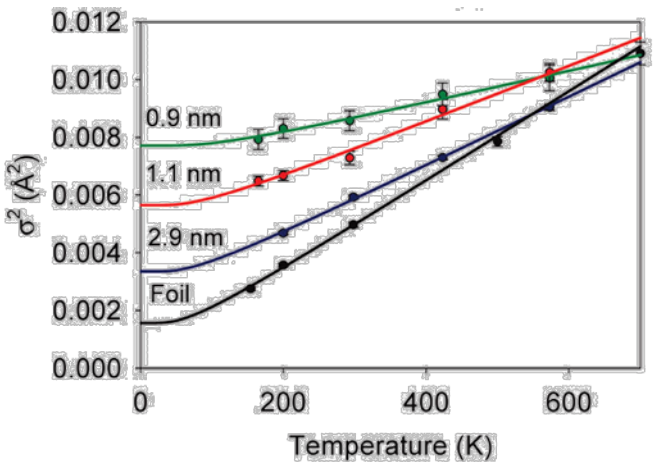
Einstein model

Within **Einstein model** $\sigma^2(T) = \sigma^2_{static} + \frac{\hbar}{2\mu\omega_E}\coth\frac{\hbar\omega_E}{2k_BT}$

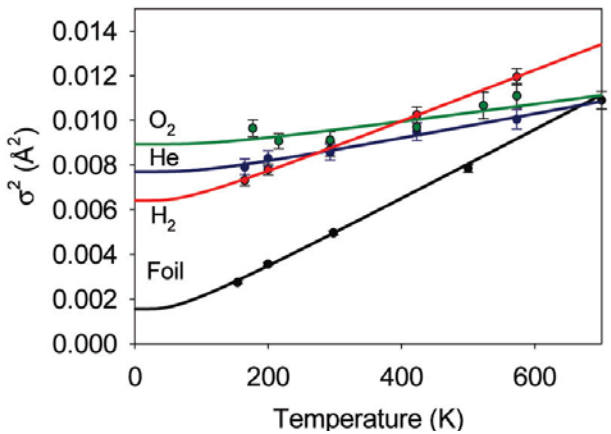
At low temperature ($k_BT \ll \hbar\omega_E$): $\sigma^2(T) = \sigma^2_{static} + \frac{\hbar}{2\mu\omega_E}$

At **high temperature** ($k_BT \gg \hbar\omega_E$): $\sigma^2(T) = \frac{k_BT}{\kappa}$, where

$\kappa = \mu\omega_E^2$ is **effective bond strength constant**



MSRD(T) for Pt nanoparticles of different sizes



MSRD(T) for Pt nanoparticles in different atmospheres

Using temperature-dependent EXAFS data one can separate contributions of static and thermal disorder

S. I. Sanchez et al., J. Am. Chem. Soc. **131** 7040 (2009)

Stress and strain energy

Knowing contribution of static disorder σ^2_{static} and effective bond strength constants κ, one can estimate the **residual strain energy** of the material:

$$U = V(T) + W$$

$$U = \frac{1}{2} N\kappa\, \sigma^2 \;\; , \;\; W = \frac{1}{2} N\kappa \sigma^2_{static}$$

Strain energies in $RbBr_xCl_{1-x}$

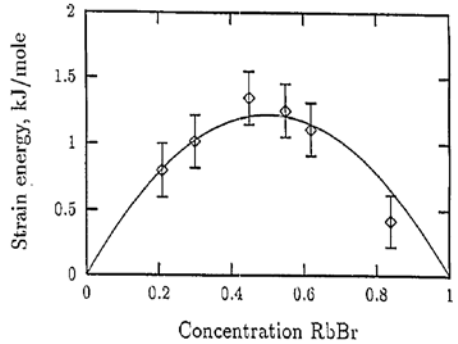


Fig. 4. Strain energy in crystalline $RbBr_xCl_{1-x}$. Shown by the solid curve is the best fit of the parabola $W = W_0 x(1-x)$ to the points.

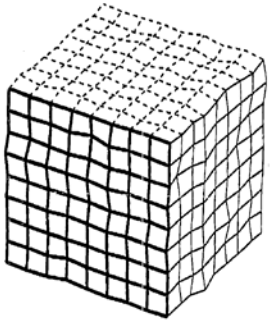
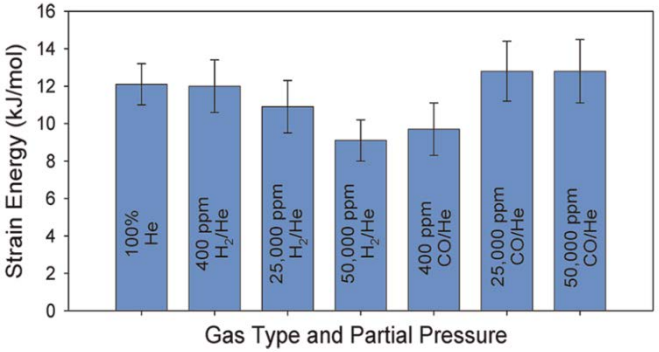


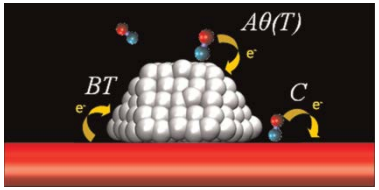
Fig. 5. Equilibrium atomic configurations in $RbBr_{0.55}Cl_{0.45}$.

$$\Delta T_m = \frac{T_m W(T_m)}{q}, \quad (3)$$

A. I. Frenkel, et al, *Solid State Commun*. 99, 67 (1996).

Strain energies in Pt NPs in different atmospheres



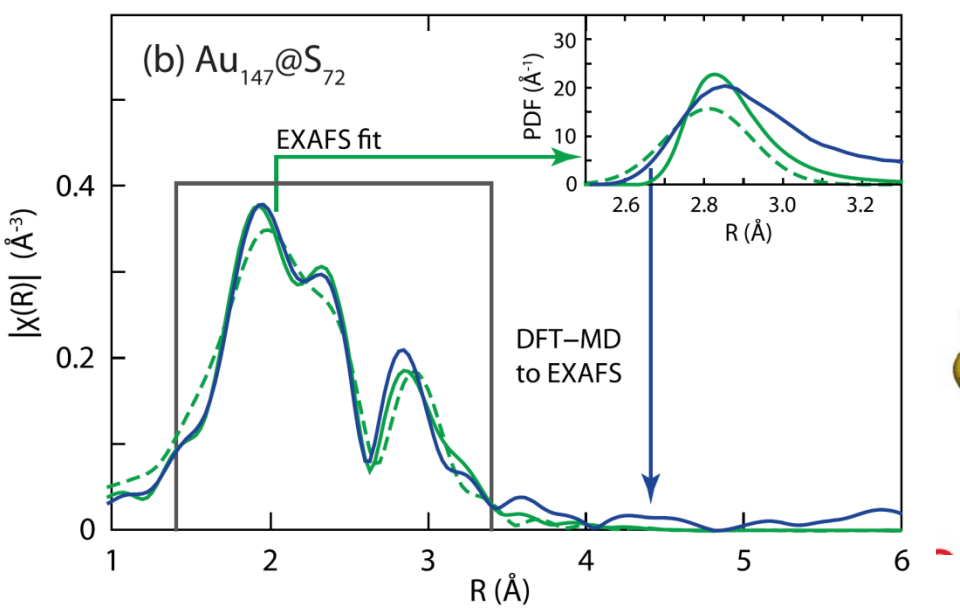


M. Small, et al *ACS Nano* 6, 5583 (2012)

Asymmetric disorder. Cumulant expansion.

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

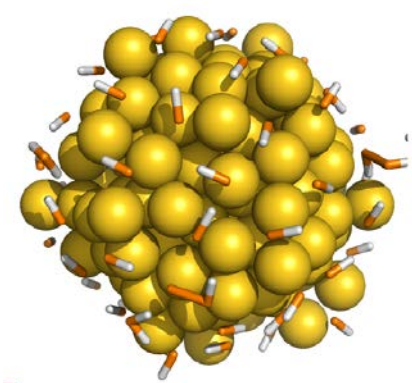
$$\chi_p(k) = S_0^2 \frac{1}{k} F(k) \exp\left(C_0 - 2C_2k^2 + \frac{2}{3}C_4k^4 - \frac{4}{45}C_6k^6\right) \times \sin\left(2kC_1 - \frac{4}{3}C_3k^3 + \frac{4}{15}C_5k^5 + \phi(k)\right)$$



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!

Skewness of the RDF

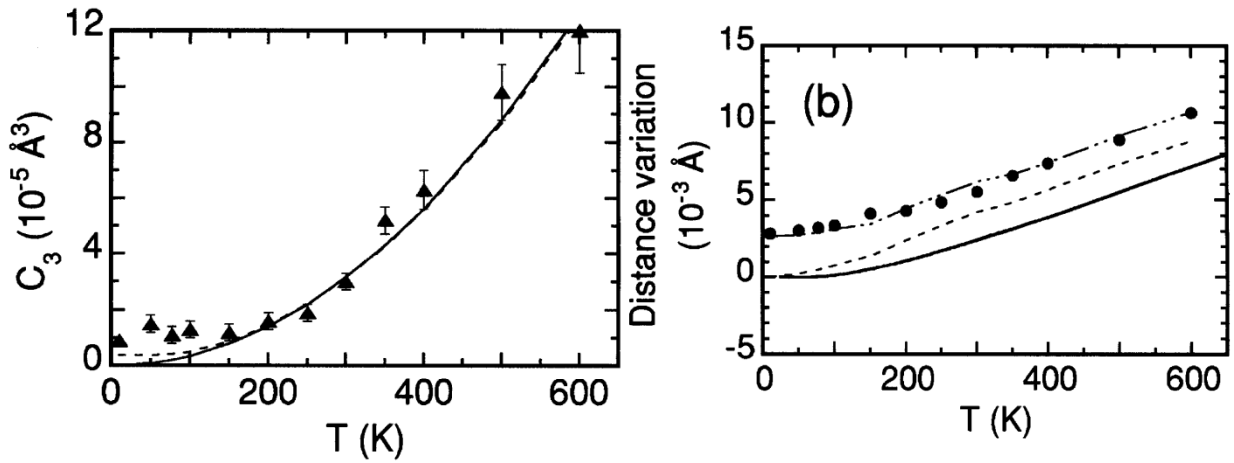
Most often just additional C_3 term is used that describes skewness of the distribution. It partially accounts for **anharmonicity** of atomic vibrations and, hence, is related to **thermal expansion coefficient**.

$$\chi(k) = S_0^2 \sum_{p=1}^{M} \frac{N_p f_p(k, R_p)}{k R_p^2} e^{-2k^2\sigma_p^2} \sin\left(2kR_p - \frac{4}{3} C_{3p} k^3 + \phi_p(k, R_p)\right)$$

where at high temperatures

$$\frac{\alpha R_{eq} T \sigma^2}{C_3} = \frac{1}{2}$$

$$\alpha = \frac{1}{R_{eq}} \frac{dR_{eq}}{dT}$$



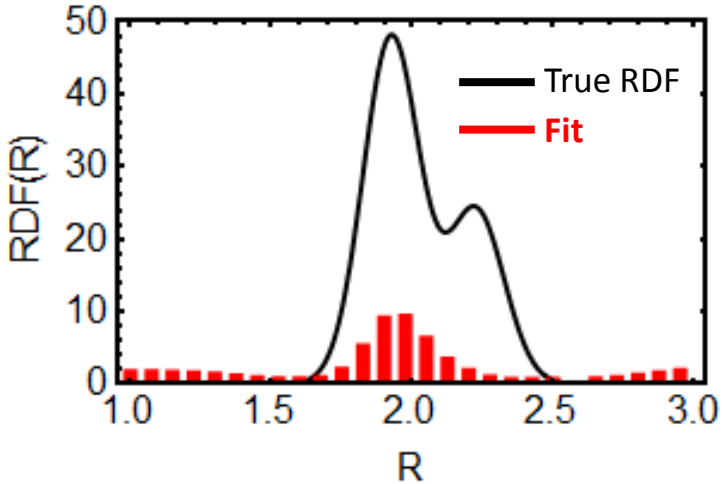
C_3 term and thermal expansion in crystalline germanium

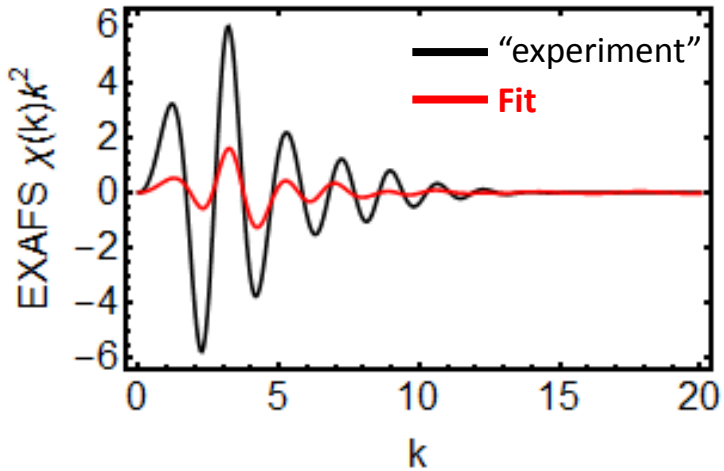
Frenkel & Rehr, Phys. Rev. B 48, 585, 1993
Dalbe et al, Phys. Rev. Lett 82, 4240, 1990

Parameter-free modeling of disorder

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

One can try to fit g(R) function directly (parametrized as histogram). Fit variables - heights of histogram bars



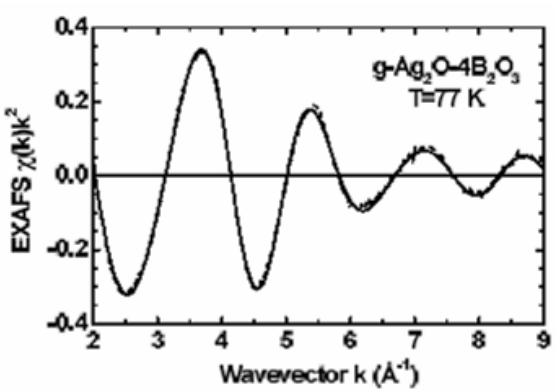


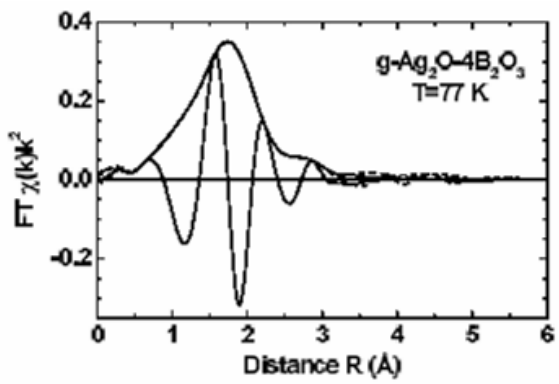
A. Kuzmin et al, Phys. Rev. B 73 (2006) 174110:1-12

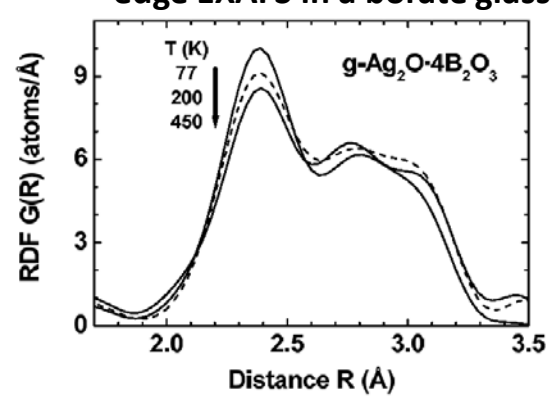
B. Ravel, et al, Phys. Rev. B, 60 (1999) 14632

- Numerically unstable problem. Additional constraints may be necessary (smoothness, non-negativity of RDF), good initial approximation may be important.
- Usually limited to the first coordination shell only.

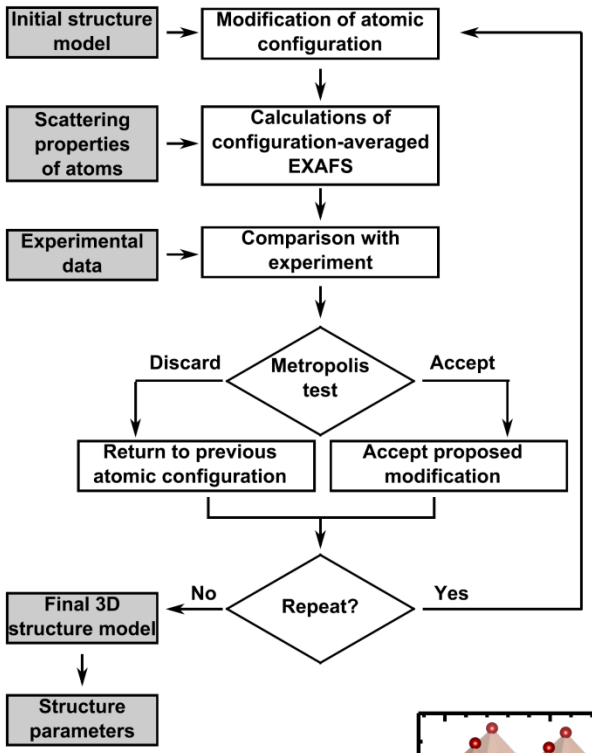
RDF, reconstructred from Ag K-edge EXAFS in a borate glass



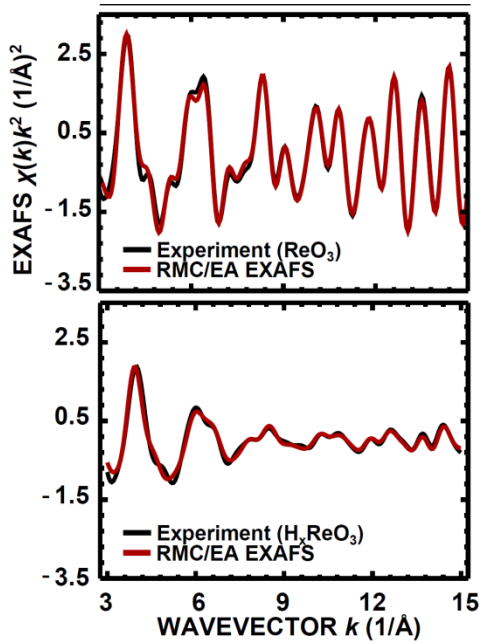


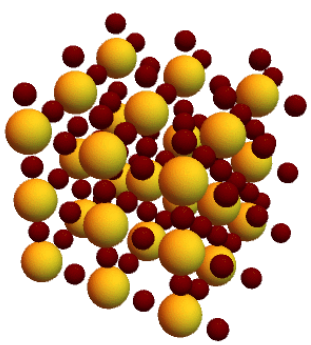


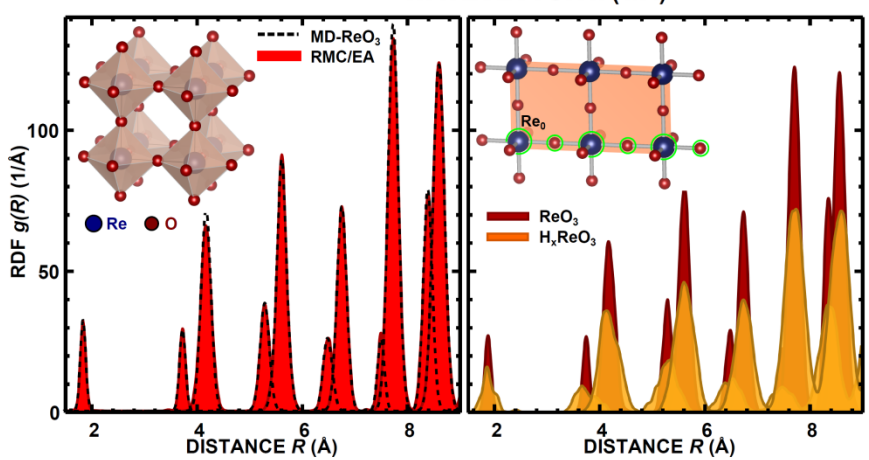
Reverse Monte Carlo method



RMC study or Re L_3-edge EXAFS in ReO_3 and H_xReO_3







Reconstruction of disorder in more complex cases can be done using RMC approach:

- RMC procedure fits the experimental EXAFS spectra, but the variables are now the atomic coordinates in 3D structure model of the material
- RMC allows analysis of distant coordination shell and MS effects
- No assumptions of the shape of bond length dsitribution is required
- Requires significant computational resources

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

J. Timoshenko et al, J. Phys.: Conf. Ser. 712 (2016) 012003:1-4.

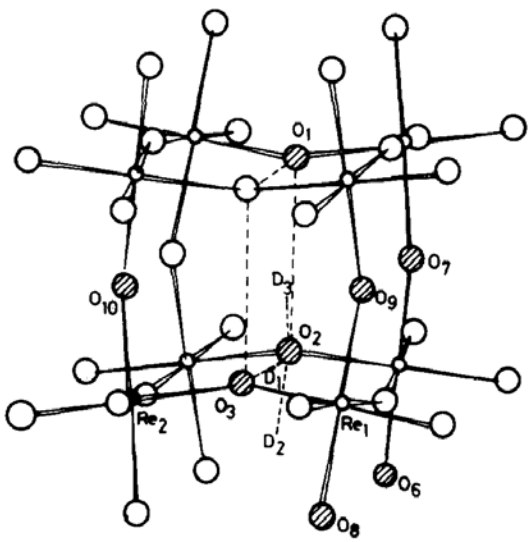
Timoshenko & Kuzmin, *International Tables for Crystallography I*, 2016 (in press)

RMC example: disappearance of correlations

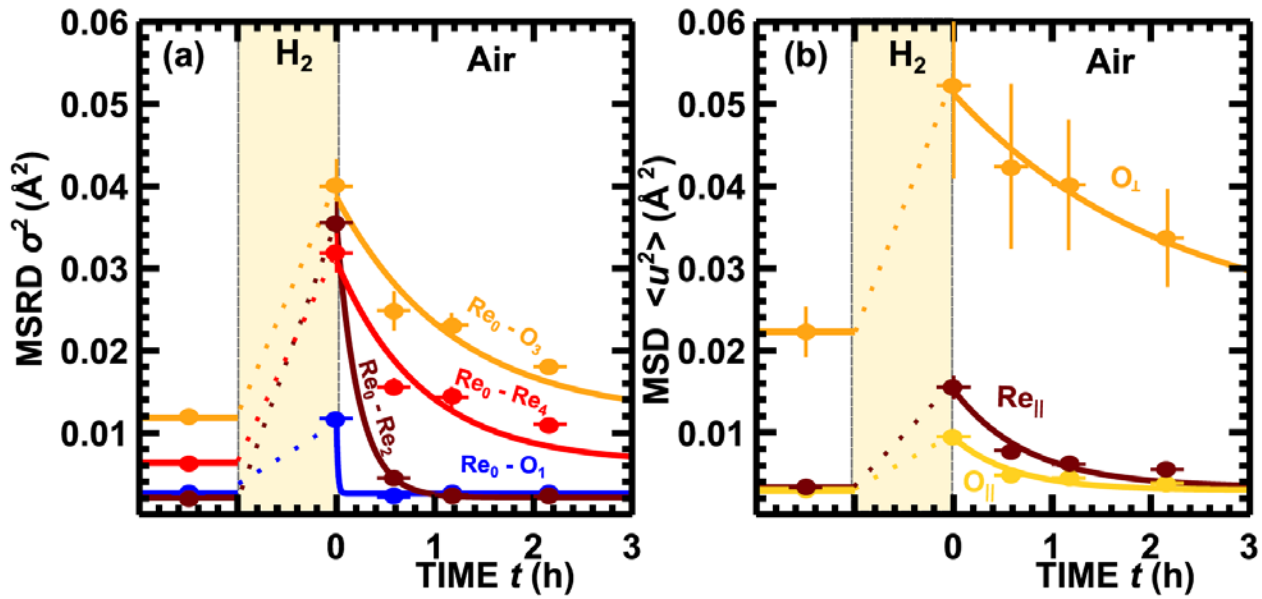
In some cases, RMC allows to estimate not only **MSRD**, but also **MSD** factors from the same EXAFS data, hence allowing advanced analysis of **correlation effects.**

In the example below RMC allowed to show very strong correlations in the motion of neighboring atoms in ReO_3, which disappear upon intercalation of ReO_3 lattice with H ions.

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



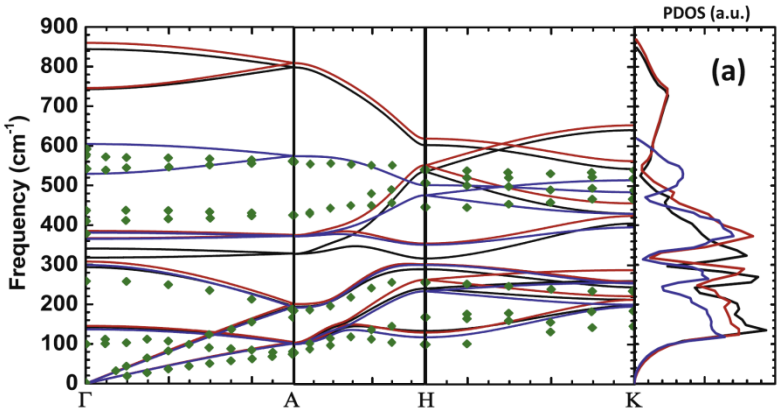
Dickens P G and Weller M T, *J. Solid State Chem.* (1983)



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

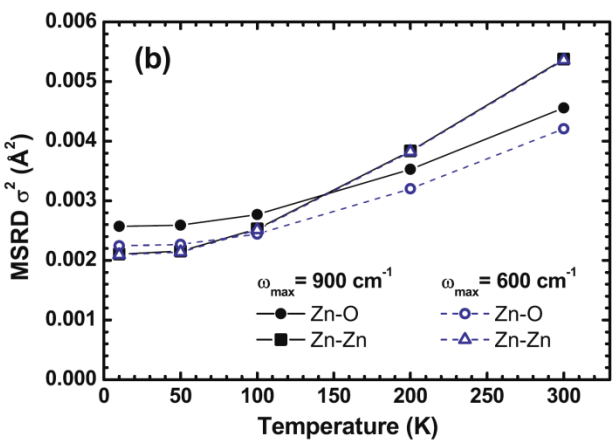
Direct modelling: lattice dynamics methods

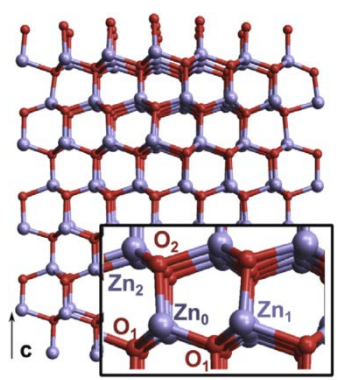
1 Ab-initio or empirical potential calculations of phonon spectra (**harmonic approximation**)



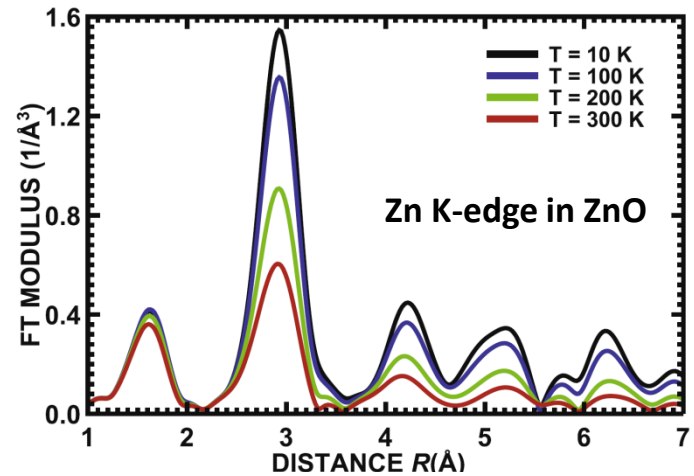
2 Integration of phonon spectra:

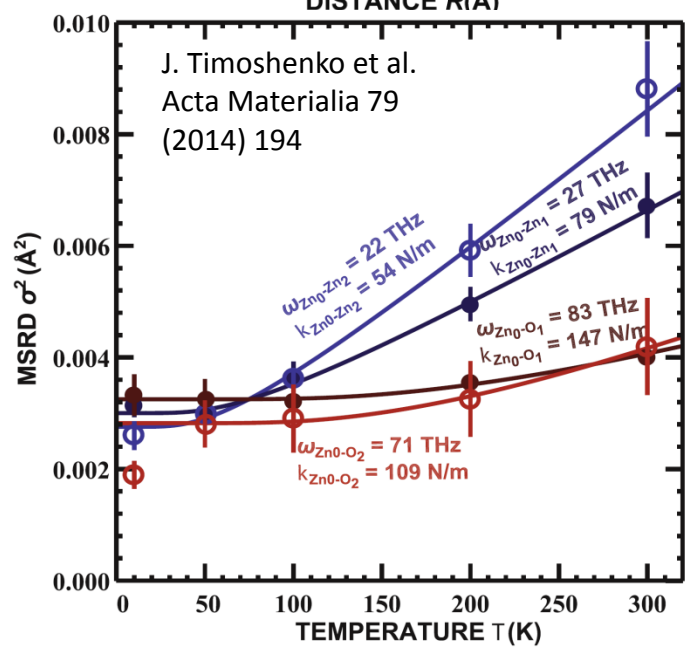
$$\sigma^2_{thermal}(T) = \frac{\hbar}{2\mu}\int_0^{\omega_{max}} \frac{d\omega}{\omega}\rho(\omega)\coth\frac{\hbar\omega}{2k_BT}$$





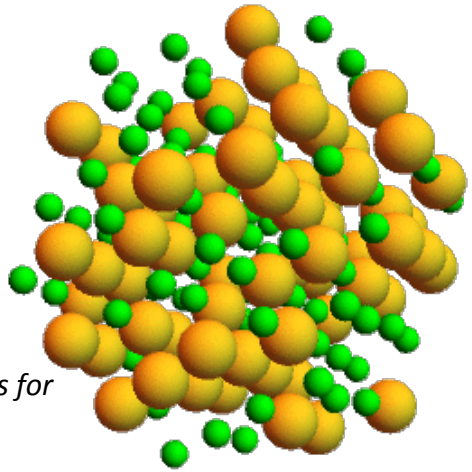
3 Comparison with experiment



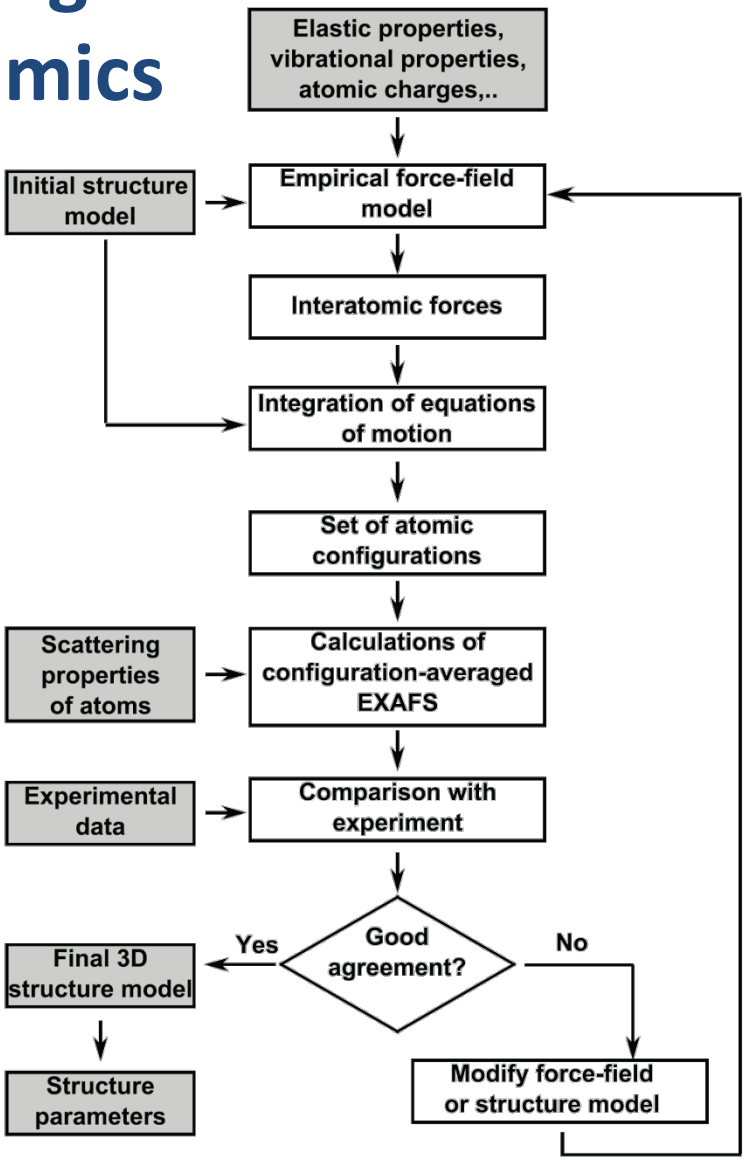


Direct modelling: Molecular dynamics

- MD approach yield a **time-dependent** 3D model of the investigated structure.
- Initial structure model is evolving in time accordingly to classical **Newtonian laws of motion**, which allow one to account for the atomic thermal disorder in the system.
- Cannot be used to model the motion of atoms at low temperatures
- At high temperatures MD can be employed to model **anharmonic** motion of atoms, leading to asymmetric distributions of bond lengths.



Timoshenko & Kuzmin, *International Tables for Crystallography I*, 2016 (in press)

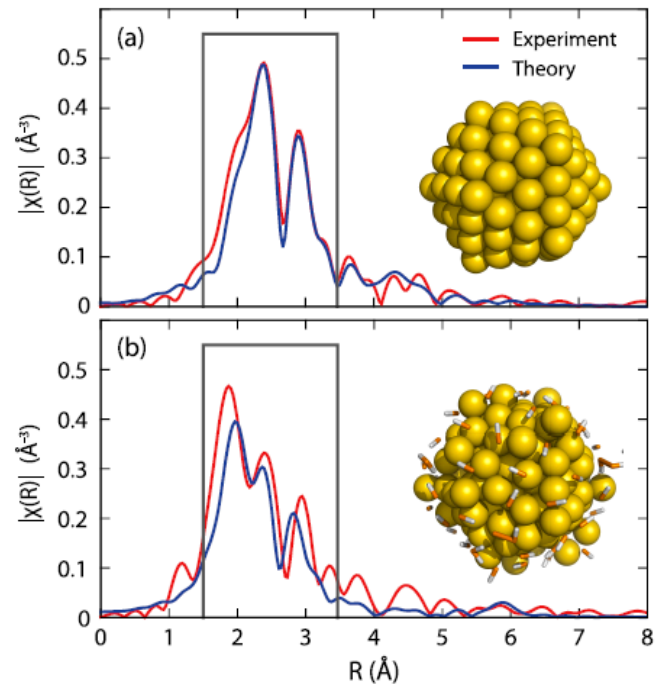


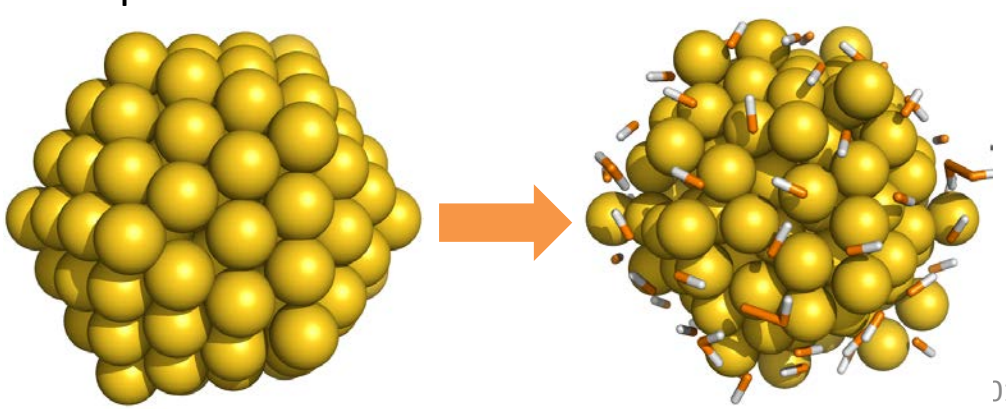
Direct modelling:
Ab-initio Molecular dynamics

In **ab-initio MD** commonly Born-Oppenheimer approximation is employed, i.e., it is assumed that the relatively slow motion of heavy atomic nuclei can be separated from the motion of electrons.

Shrödinger equation is solved for electrons in the electrostatic field produced by a frozen configuration of atomic nuclei for calculations of forces within **DFT**.

Obtained potential energy $V(\vec{r}_1, \vec{r}_2, \dots \vec{r}_n)$ of the system is known, one can calculate the force $\vec{F}_i$ acting on the *i*-th atom as $\vec{F}_i = -\nabla_{\vec{r}_i} V$ where vectors $\vec{r}_1, \vec{r}_2, \dots \vec{r}_n$ correspond to the positions of atomic nuclei





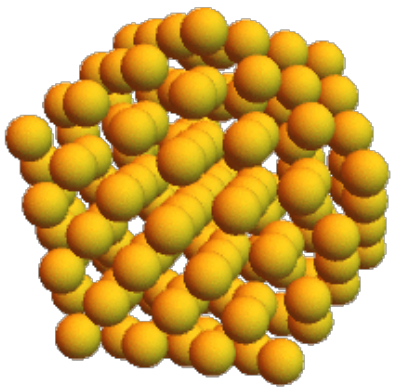
S. T. Chill et al, ACS Nano **9**, 4036-4042 (2015)
D. F. Yancey et al, *Chem. Science* **4**, 2912-2921 (2013)

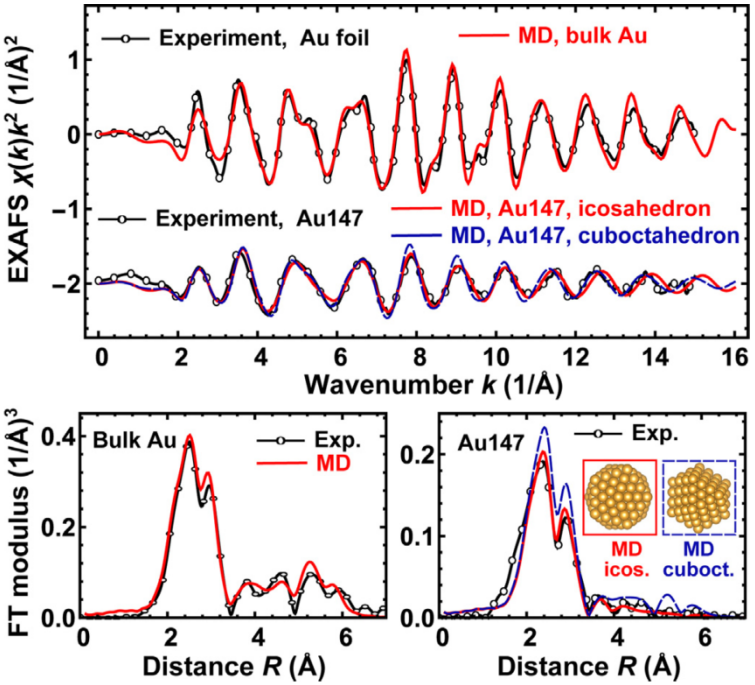
Direct modelling: Classical Molecular dynamics

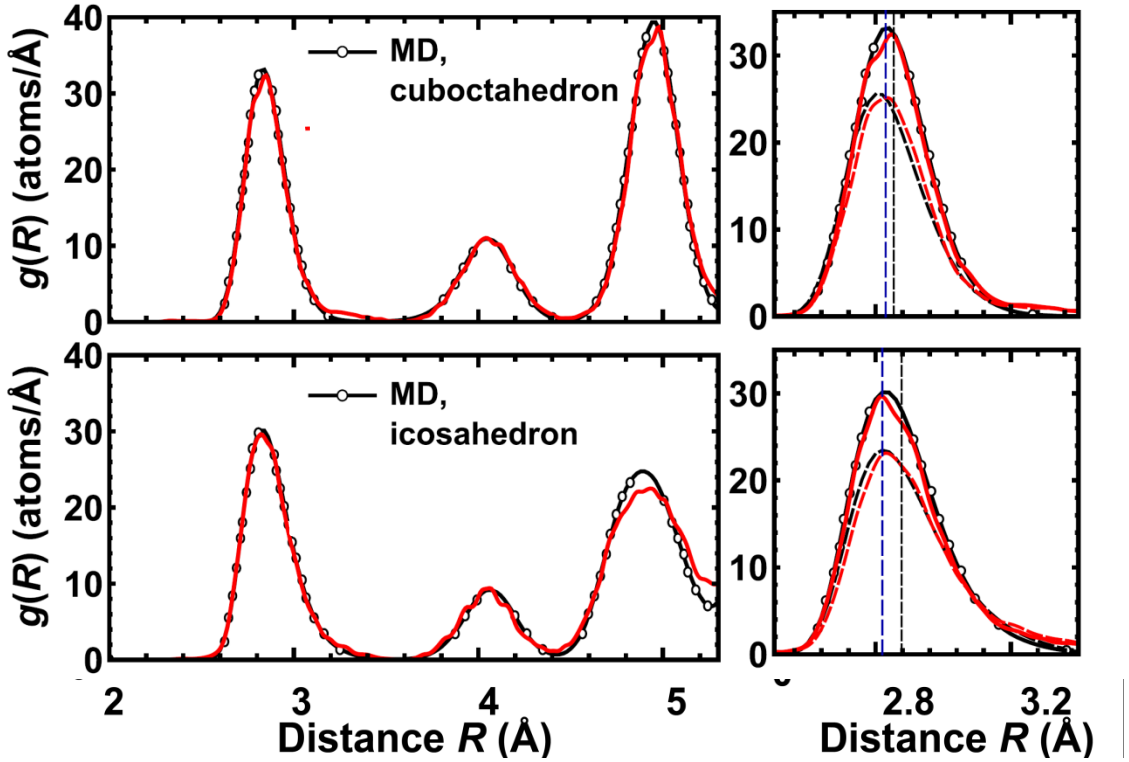
For some cases, **classical MD** based on **empirical potential** is also able to give accurate description of disorder in the material and a good agreement with experimental data.

$$U = \sum_i \left[\sum_{j \neq i} \frac{1}{2} \varepsilon \left(\frac{a_0}{r_{ij}} \right)^n - c\varepsilon(\rho_i)^{1/2} \right]$$

$$\rho_i = \sum_{j \neq i} \left(\frac{a_0}{r_{ij}} \right)^m$$







Timoshenko & Frenkel, Catalysis Toc

Summary and conclusions

- Information on disorder effects is important for deep understanding of material local structure, atomic dynamics and their relation to the properties of the material.

- EXAFS analysis is very poweful tool to probe disorder effects.

- Special attention is required for EXAFS studies of materials with pronounced, asymmetric bond length distributions. Combination of EXAFS analysis with theoretical simulations of material structure and dynamics may help to address this problem.

Thank you for your attention!