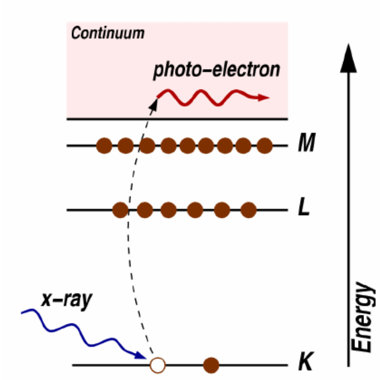
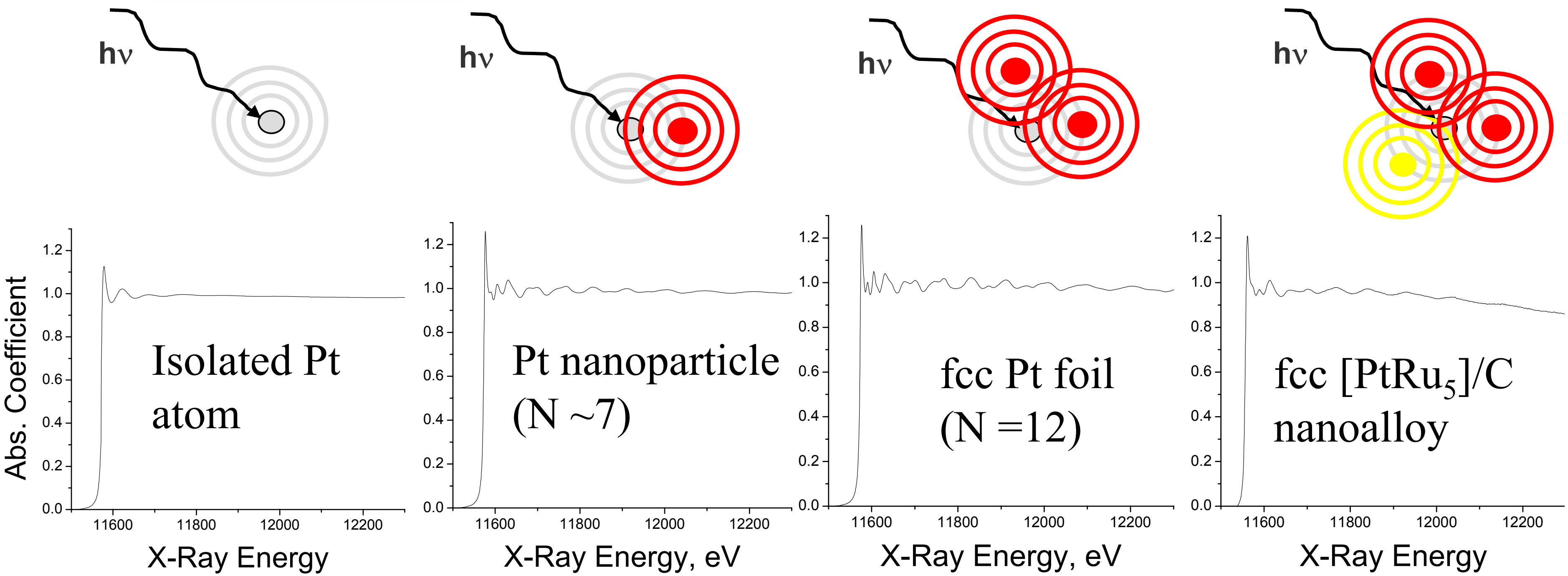
Advanced modeling of EXAFS data: concepts

Anatoly Frenkel

Physics Department, Yeshiva University, New York, NY 10016
frenkel@bnl.gov



X-Ray Absorption Fine Structure (XAFS)



$$\chi(k) \sim N\, e^{-2k^2\sigma^2} f(k) \sin(2kr + \delta)$$

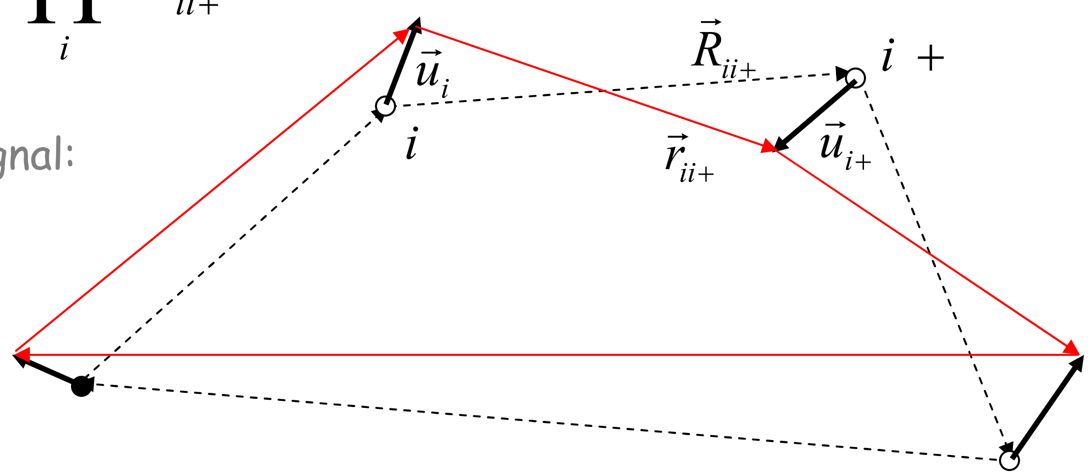
Theoretical EXAFS Equation:

Single scattering path:

$$\chi_\Gamma(k) = \frac{NS_0^2}{kR^2}\left|f^{\text{eff}}(k)\right| \mathrm{e}^{-2\sigma^2k^2}\, e^{\frac{-2R}{\lambda}} \sin\left[2kR - \tfrac{4}{3}C_3k^3 + \delta(k)\right]$$

Multiple-scattering path:

$$\chi_\Gamma(k) = \mathrm{Im}\, \mathrm{N}S_0^2 \frac{e^{i\left(k\sum_i R_{ii+} + 2\delta(k)\right)}}{\prod_i kR_{ii+}} \mathrm{e}^{-2\sigma^2k^2}\, e^{\frac{-2R}{\lambda}}\, \mathrm{Tr}\, MF^N \cdots F^2F^1$$



Theoretical EXAFS signal:

$$\chi(k) = \sum_\Gamma \chi_\Gamma(k)$$

Definition of Parameter Space:

In IFEFFIT, parametrization is the same for SS and MS paths:

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)}$$

$$E_0 = E_0^{\mathrm{bkg}} + \Delta E_0$$

$$R = R_{\mathrm{model}} + \Delta R$$

Amplitude

$$\chi_\Gamma(k) = \frac{NS_0^2}{kR^2}\left|f^{\mathrm{eff}}(k)\right| \mathrm{e}^{-2\sigma^2 k^2}\, e^{\frac{-2R}{\lambda}} \sin\left[2kR - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

FEFF

Fitting of EXAFS Theory to the Data:

$$f(R_i) = \tilde{\chi}(R_i) - \tilde{\chi}_{\mathrm{M}}(R_i)$$

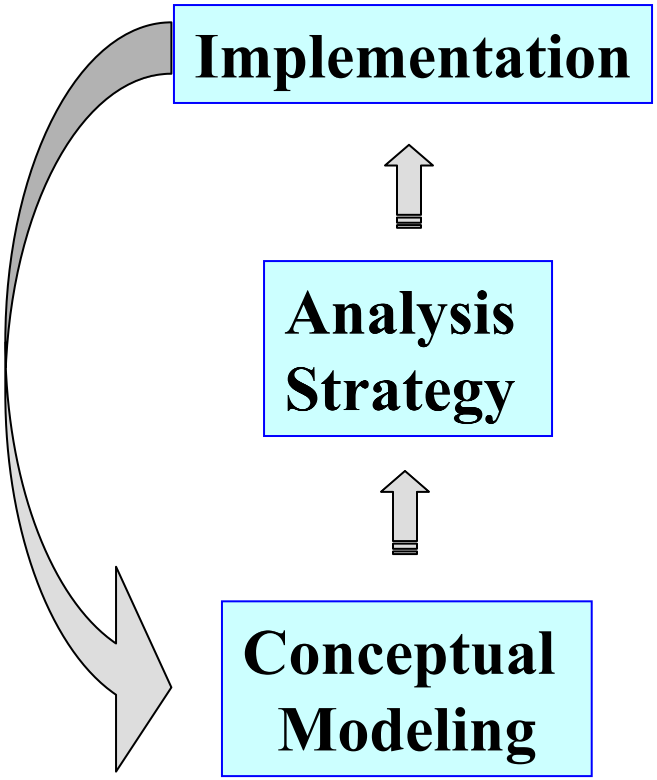
$$\chi_\nu^2 = \frac{1}{\nu}\sum_{i=1}^{N_{\mathrm{idp}}}\left(\frac{f_i}{\varepsilon_i}\right)^2 = \frac{N_{\mathrm{idp}}}{N\nu}\sum_{i=1}^{N}\left(\frac{f_i}{\varepsilon_i}\right)^2$$

$$\nu = N_{\mathrm{idp}} - P$$ (Number of degrees of freedom)

$$N_{\mathrm{idp}} = \frac{2\Delta k \Delta R}{\pi}$$ (Number of relevant independent data points)

E. A. Stern
Phys. Rev. B **48**, 9825-9827 (1993)

$$\chi_\nu^2 = \frac{1}{\nu}\sum_{i=1}^{N_{\mathrm{idp}}}\left(\frac{f_i}{\varepsilon_i}\right)^2 = \frac{N_{\mathrm{idp}}}{N\nu\varepsilon^2}\sum_{i=1}^{N}\left[\mathrm{Re}(f_i)^2 + \mathrm{Im}(f_i)^2\right]$$



Find the best analysis software that can implement your strategy.
IFEFFIT has convenient interface and allows for a large variety of strategies

-Plan on doing reality checks;
-Reference compounds should be measured and analyzed first;
-Try to maximize the number of degrees of freedom in the fits
(use constraints, experimental/theoretical info etc.)

-Start with the crude picture first, then refine it;
-Homogeneous or heterogeneous environment?
(bulk or nano, eq. or ineq. unit cell positions, solution or separate phases etc.)

FEFF Fitting and Error Analysis

AUTOBK algorithm: M. Newville, P. Livins, Y. Yacoby, E. A. Stern, and J. J. Rehr, Phys. Rev. **B**47, 14126-14131 (1993).

Remove background: $\mu(E) \rightarrow \chi(\mathrm{k})$.

Fourier transform data: $\chi(k) \rightarrow \tilde{\chi}(r)$

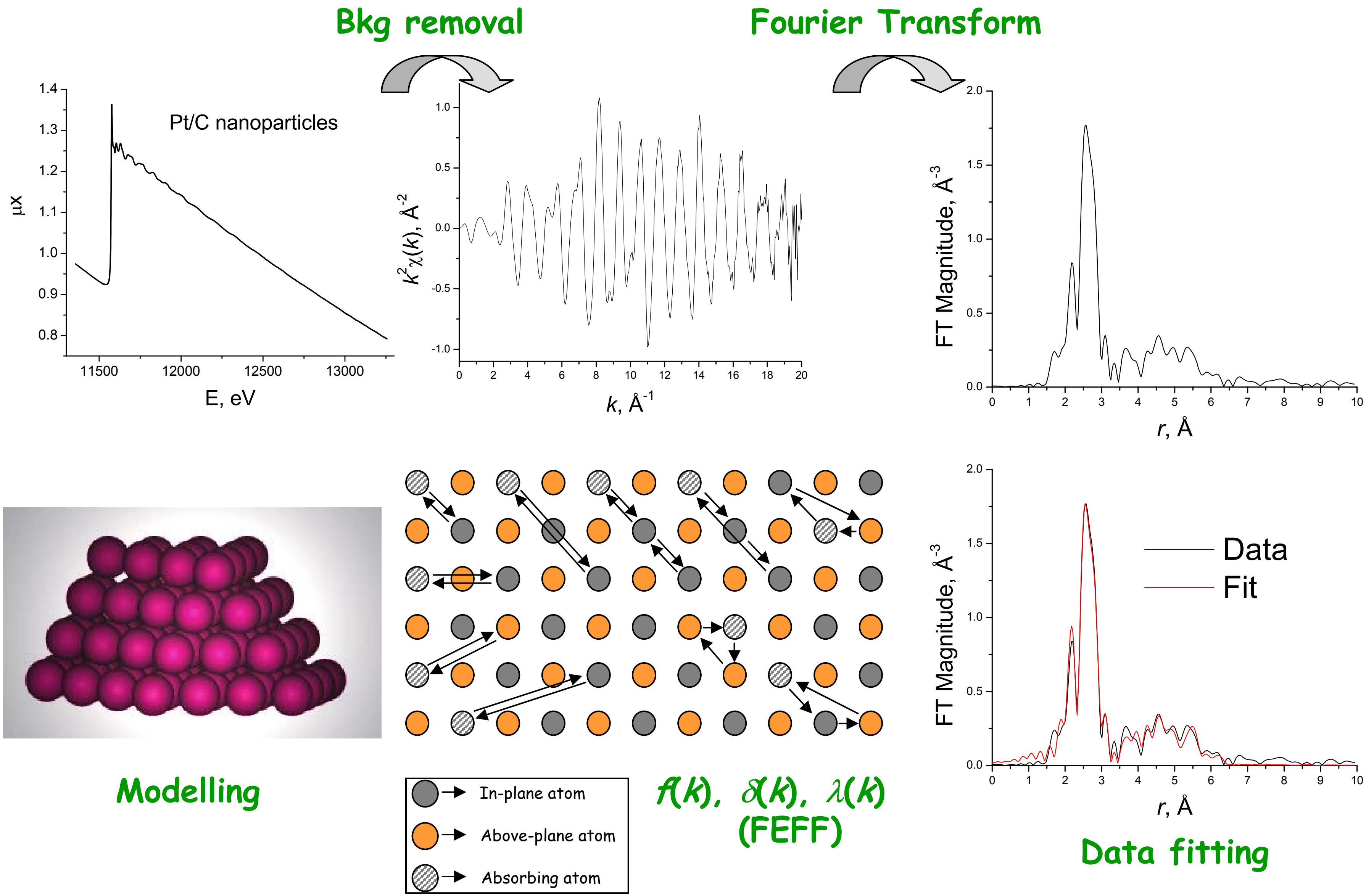
Pick a model

Calculate $f(k)$, $\delta(k)$ and $\lambda(k)$: FEFF

FEFF review: J.J. Rehr & R.C. Albers, *Rev. Mod. Phys.* (2000) 72, 621-654

Fit theory to data

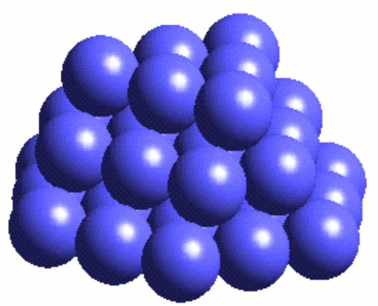
Error analysis $\{x_i \pm \delta x_i\}$



Bkg removal
Fourier Transform
Pt/C nanoparticles
μx
E, eV
$k^2\chi(k)$, Å^{-2}
k, Å^{-1}
FT Magnitude, Å^{-3}
r, Å
Data
Fit
Modelling
In-plane atom
Above-plane atom
Absorbing atom
$f(k)$, $\delta(k)$, $\lambda(k)$
(FEFF)
Data fitting

How to model XAFS data in nanoparticles?

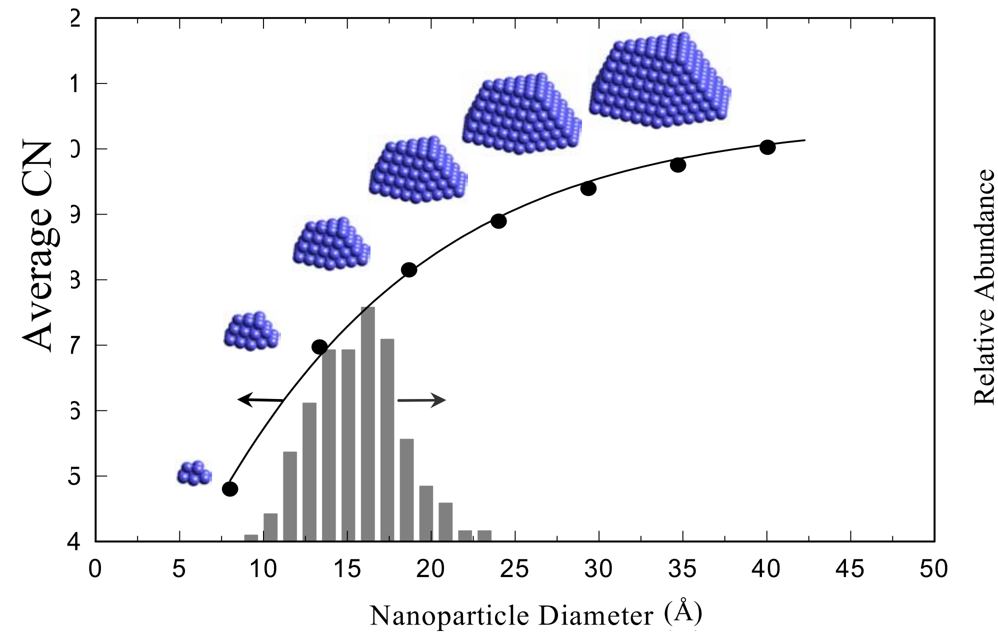
A priori knowledge or a working hypothesis must exist
(the “zero” approximation)
otherwise: the transferability of amplitude/phase will not work!)



1) Hemispherical
2) Crystal order
3) Size: about 20 Å

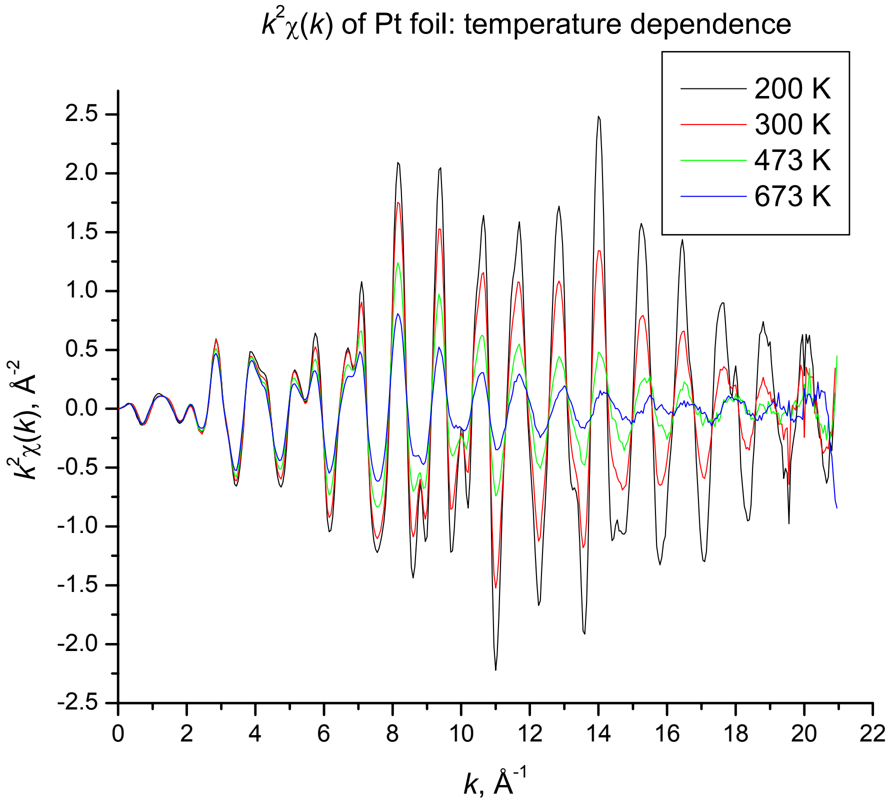
What information can be obtained from 1st shell EXAFS analysis?

1) Size of the particle (via N)
2) Distances, thermal vibration, expansion
3) Static disorder (icosahedral? surface tension?)



How to break the correlation?

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| \mathrm{e}^{-2\sigma^2 k^2} \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$



One possible solution:
a multiple-data-set (*mds*) fit.

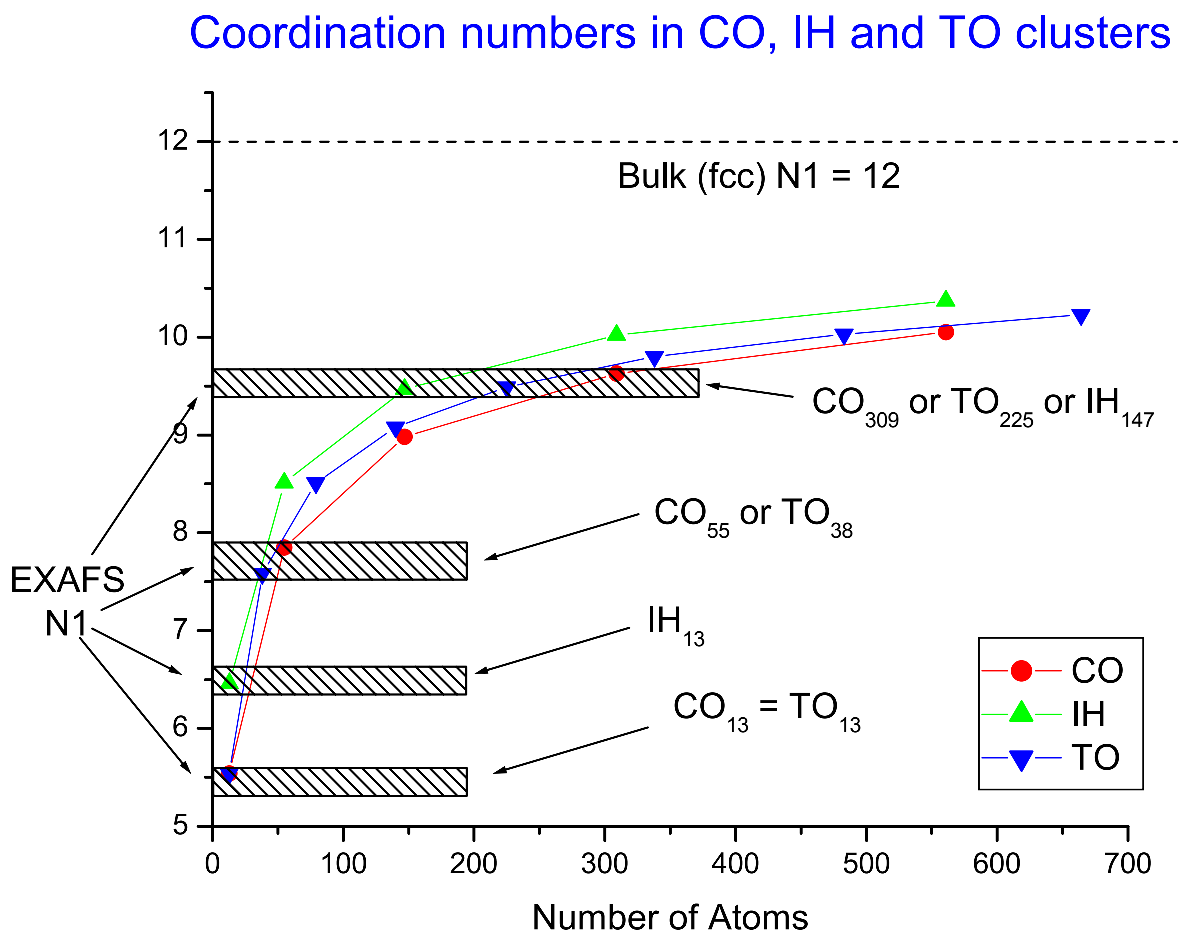
What variables are not expected to change at different temperatures?

ΔE_0, N $\qquad \sigma_s^2$, Θ_E

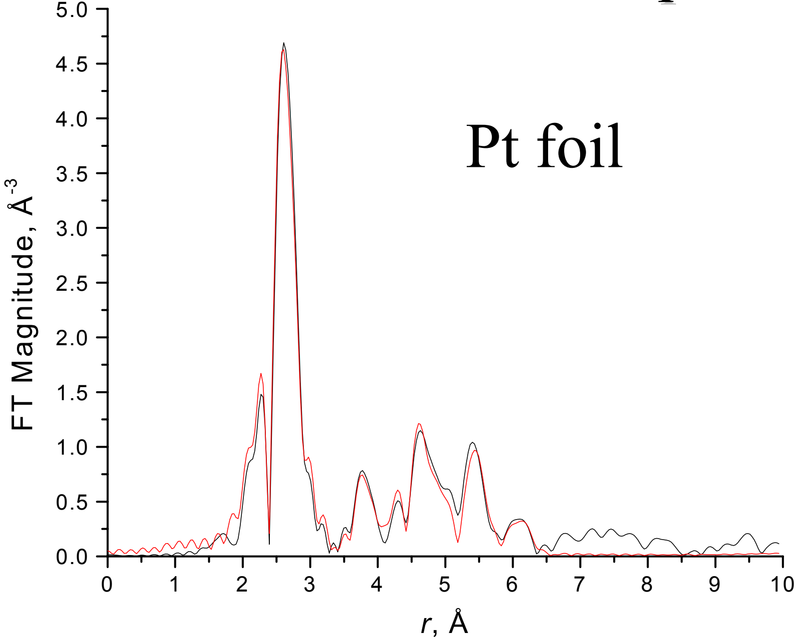
$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

$$\sigma_d^2 = \frac{\hbar}{2\omega\mu}\frac{1+\exp(-\Theta_E/T)}{1-\exp(-\Theta_E/T)}$$

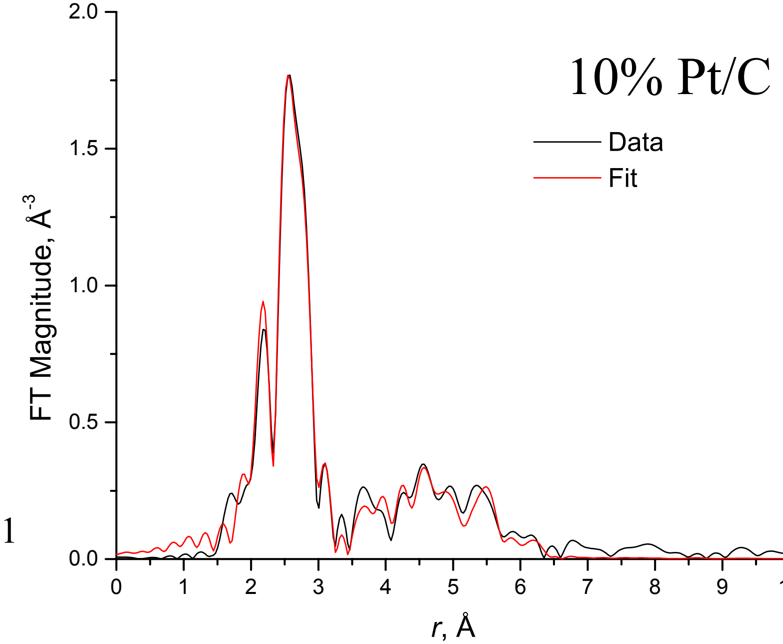
First shell analysis is not adequate for full structural studies of small clusters



Multiple Shell Fitting Analysis



S1

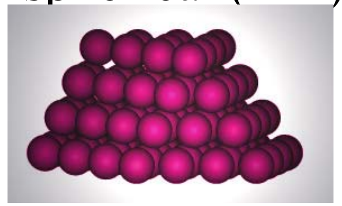


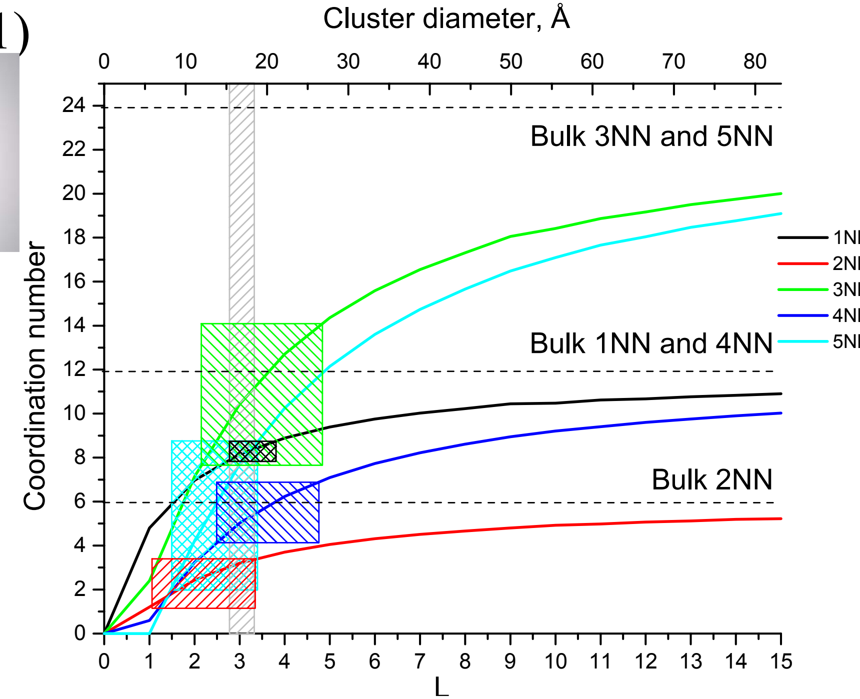
Coordination numbers for the first 5 shells:

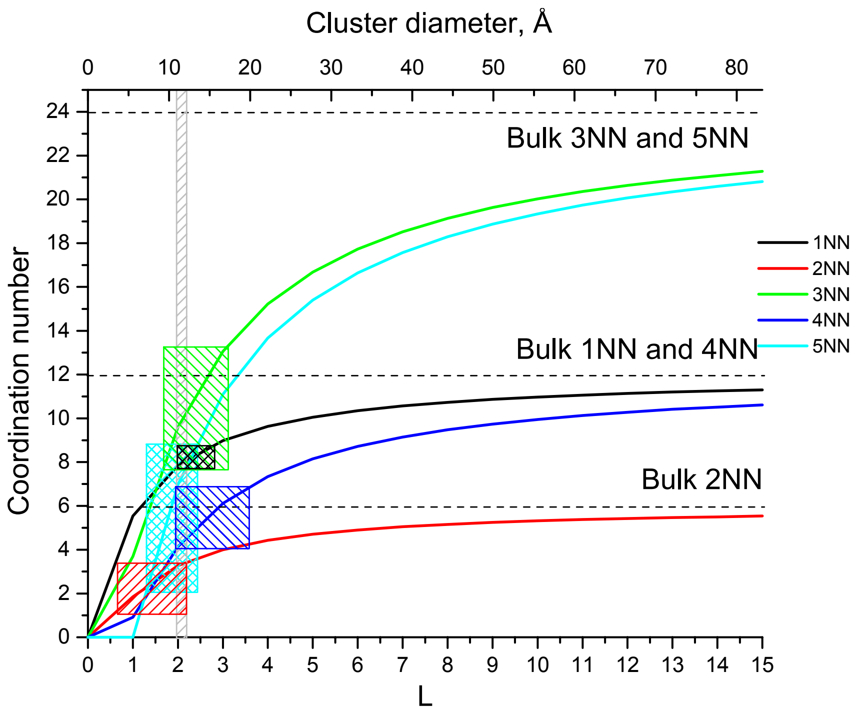
i	10% Pt/C	40% Pt/C	60% Pt/C	Pt foil	Bulk fcc
1	8.3(5)	10.5(5)	11.4(6)	12.6(7)	12
2	2.3(1.1)	4.0(1.3)	4.7(1.7)	5.9(2.0)	6
3	10.9(3.2)	16.8(3.5)	19(4)	23(5)	24
4	5.5(1.4)	7.6(1.4)	8.5(1.6)	11(2)	12
5	5.4(3.4)	10(4)	11(4)	14(5)	24

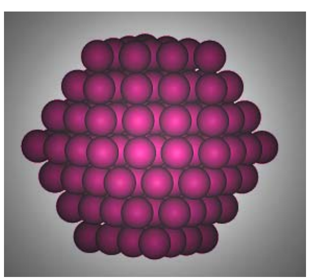
Size, Shape, Morphology…

Hemispherical (111)

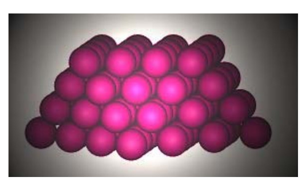




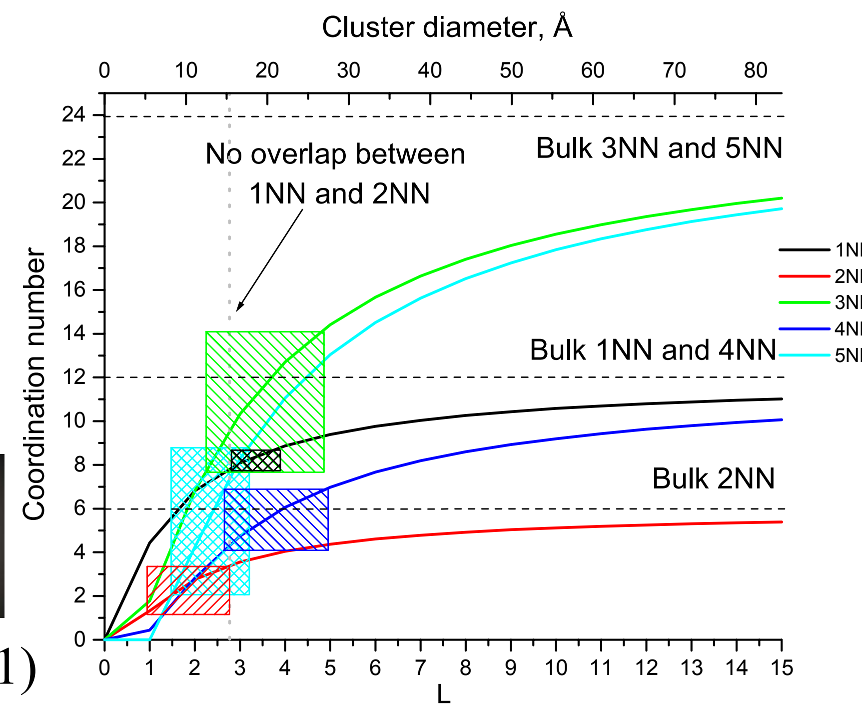




Spherical



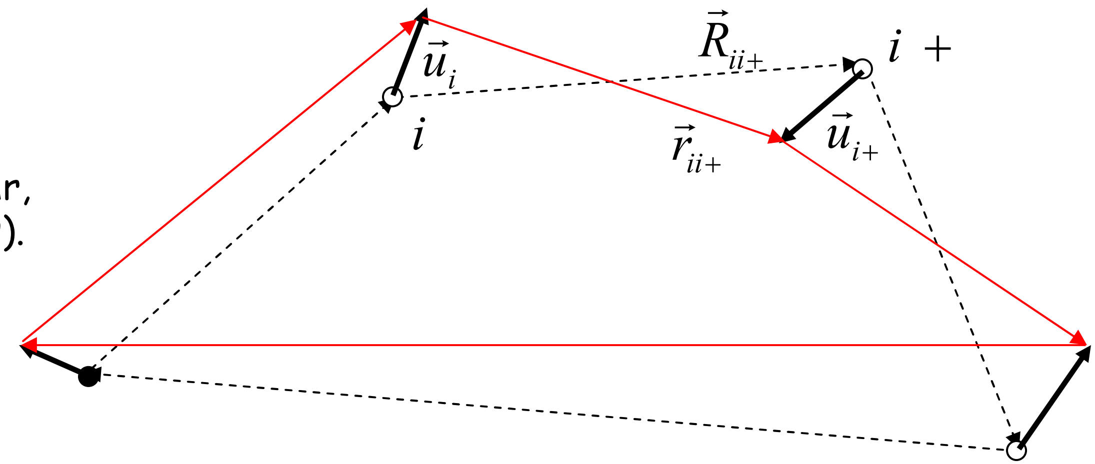
Hemispherical (001)



Debye Waller Factors of Collinear Multiple-Scattering Paths

$$\vec{r}_{ii+} = \vec{R}_{ii+} + \vec{u}_{i+} - \vec{u}_i$$

Notation:
A.V.Poiarkova and J.J. Rehr,
Phys. Rev. **B** 59, 948 (1999).



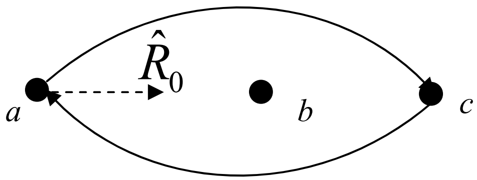
$$r_{ii+}^2 = \left(\vec{R}_{ii+} + \left(\vec{u}_{i+} - \vec{u}_i\right)\right)^2 \approx R_{ii+}^2 - 2R_{ii+}\hat{R}_{ii+}\left(\vec{u}_i - \vec{u}_{i+}\right)$$

$$r_{ii+} = R_{ii+}\sqrt{1 - 2\frac{\hat{R}_{ii+}}{R_{ii+}}\left(\vec{u}_i - \vec{u}_{i+}\right)} \approx R_{ii+}\left(1 + \frac{\hat{R}_{ii+}}{R_{ii+}}\left(\vec{u}_i - \vec{u}_{i+}\right)\right) = R_{ii+} + \left(\vec{u}_i - \vec{u}_{i+}\right)\hat{R}_{ii+}$$

$$r_j \equiv \frac{1}{2}\sum_{i=1}^{n_j} r_{ii+} = R_j + \frac{1}{2}\sum_{i=1}^{n_j}\left(\vec{u}_i - \vec{u}_{i+}\right)\hat{R}_{ii+}$$

$$R_j \equiv \frac{1}{2}\sum_{i=1}^{n_j} R_{ii+}$$

$$\sigma_j^2 \equiv \left\langle \left(r_j - R_j\right)^2 \right\rangle = \left\langle \left(\frac{1}{2} \sum_{i=1}^{n_j} \left(\vec{u}_i - \vec{u}_{i+}\right) \hat{R}_{ii+} \right)^2 \right\rangle = \frac{1}{4} \left\langle \left(\sum_{i=1}^{n_j} \left(\vec{u}_i - \vec{u}_{i+}\right) \hat{R}_{ii+} \right)^2 \right\rangle$$

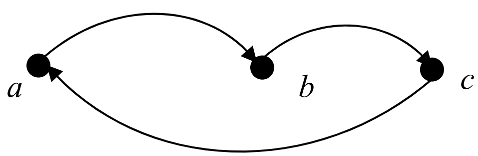


$$\sigma_{\mathrm{SS}}^2 = \frac{1}{4} \left\langle \left[\left(\vec{u}_a - \vec{u}_c\right)\hat{R}_0 + \left(\vec{u}_c - \vec{u}_a\right)\left(-\hat{R}_0\right) \right]^2 \right\rangle = \frac{1}{4} \left\langle \left[2\left(\vec{u}_a - \vec{u}_c\right)\hat{R}_0 \right]^2 \right\rangle$$

$$= \left\langle \left[\left(\vec{u}_a - \vec{u}_c\right)\hat{R}_0 \right]^2 \right\rangle = \left\langle \left(\vec{u}_a \hat{R}_0\right)^2 \right\rangle + \left\langle \left(\vec{u}_c \hat{R}_0\right)^2 \right\rangle - 2 \left\langle \left(\vec{u}_a \hat{R}_0\right)\left(\vec{u}_c \hat{R}_0\right) \right\rangle$$

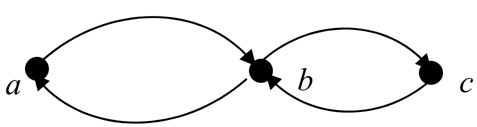
$$= \left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2 \left\langle u_{ax} u_{cx} \right\rangle,$$

$$\hat{R}_{ab} = \hat{R}_{bc} = -\hat{R}_{ca} \equiv \hat{R}_0$$

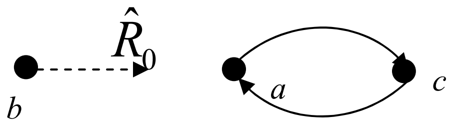


$$\sigma_{\mathrm{DS}}^2 = \frac{1}{4} \left\langle \left[\left(\vec{u}_a - \vec{u}_b\right)\hat{R}_0 + \left(\vec{u}_b - \vec{u}_c\right)\hat{R}_0 + \left(\vec{u}_c - \vec{u}_a\right)\left(-\hat{R}_0\right) \right]^2 \right\rangle$$

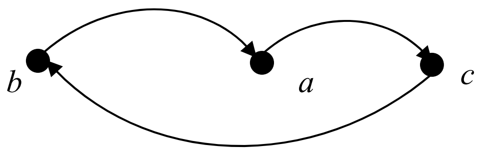
$$= \frac{1}{4} \left\langle \left[2\left(\vec{u}_a - \vec{u}_c\right)\hat{R}_0 \right]^2 \right\rangle = \left\langle \left[\left(\vec{u}_a - \vec{u}_c\right)\hat{R}_0 \right]^2 \right\rangle = \sigma_{\mathrm{DS}}^2$$



$$\boxed{\sigma_{\mathrm{TS}}^2 = \sigma_{\mathrm{DS}}^2 = \sigma_{\mathrm{SS}}^2}$$

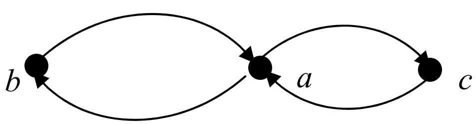


$$\sigma^2_{\mathrm{SS1}} = \left\langle u^2_{ax} \right\rangle + \left\langle u^2_{cx} \right\rangle - 2\left\langle u_{ax} u_{cx} \right\rangle,$$

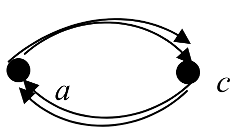


$$\sigma^2_{\mathrm{DS}} = \frac{1}{4}\left\langle \left[(\vec{u}_a - \vec{u}_c)\hat{R}_0 + (\vec{u}_c - \vec{u}_b)(-\hat{R}_0) + (\vec{u}_b - \vec{u}_a)\hat{R}_0 \right]^2 \right\rangle$$

$$= \frac{1}{4}\left\langle \left[2(\vec{u}_b - \vec{u}_c)\hat{R}_0 \right]^2 \right\rangle = \left\langle \left[(\vec{u}_b - \vec{u}_c)\hat{R}_0 \right]^2 \right\rangle = \left\langle u^2_{bx} \right\rangle + \left\langle u^2_{cx} \right\rangle - 2\left\langle u_{bx} u_{cx} \right\rangle$$

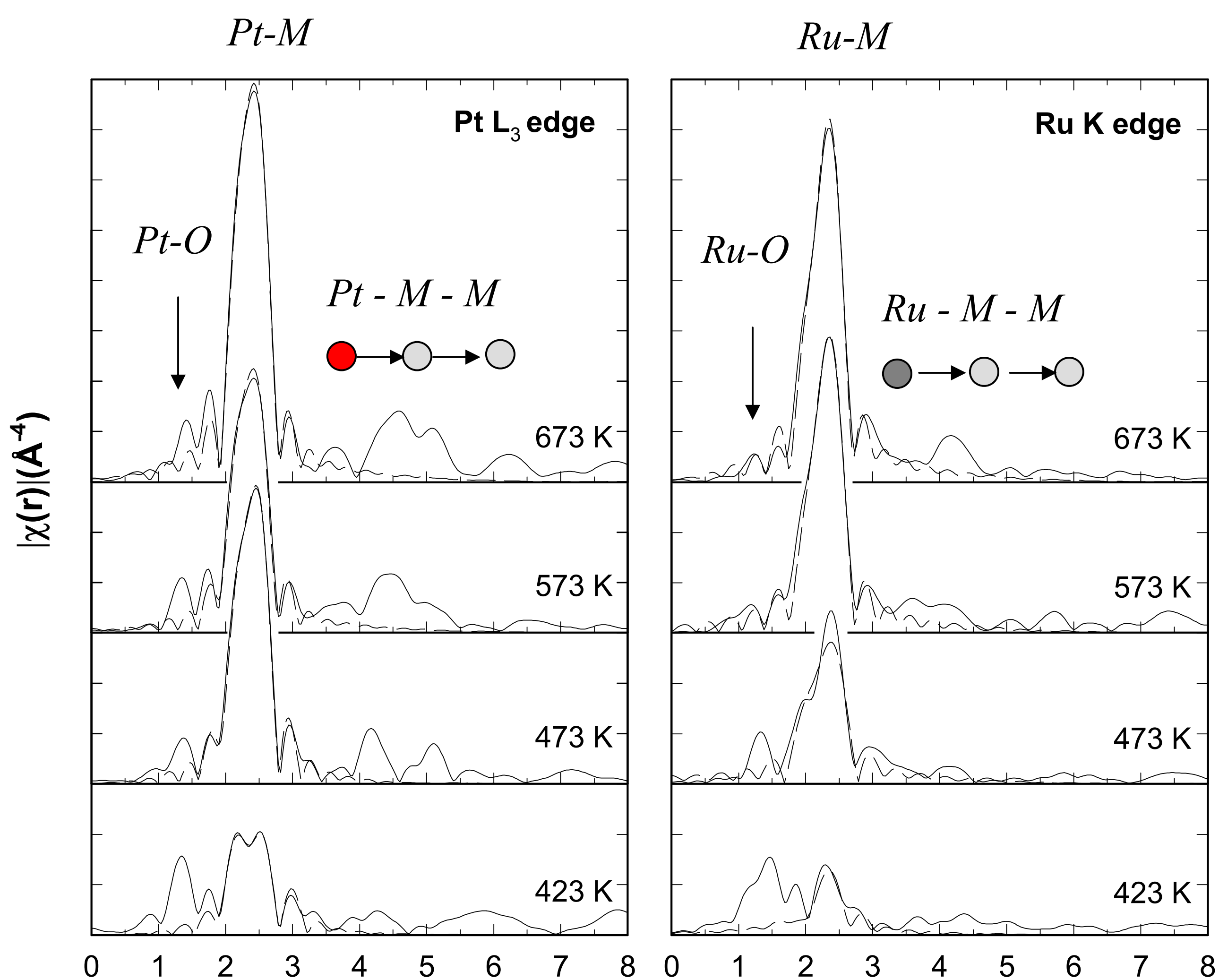


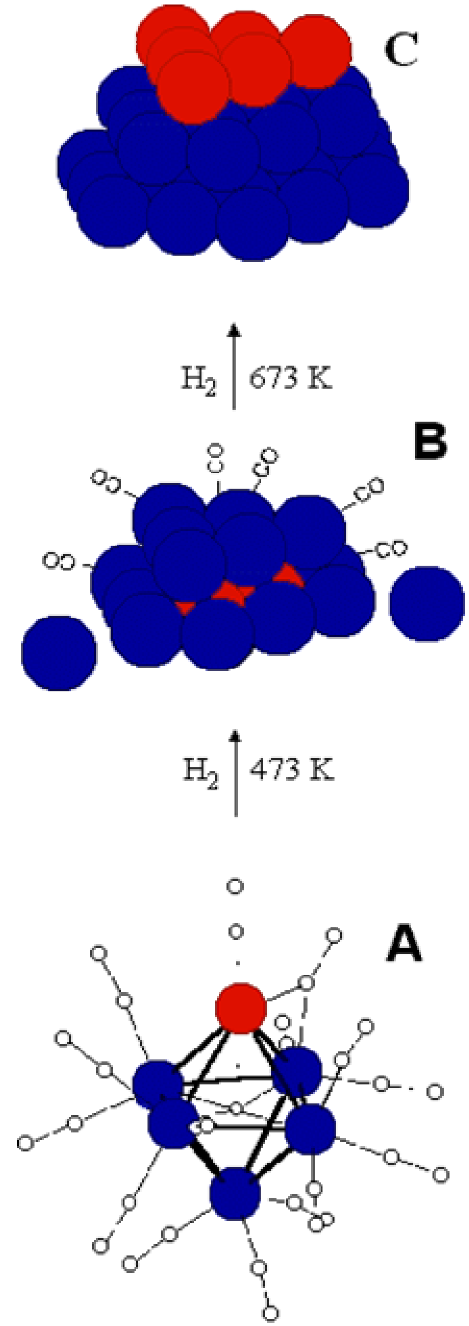
$$= 2\left\langle u^2_{bx} \right\rangle - 2\left\langle u_{bx} u_{cx} \right\rangle = \sigma^2_{\mathrm{TS}}$$



$$\sigma^2_{\mathrm{TS}} = \frac{1}{4}\left\langle 2\left[(\vec{u}_a - \vec{u}_c)\hat{R}_0 + 2(\vec{u}_c - \vec{u}_a)(-\hat{R}_0) \right]^2 \right\rangle$$

$$= \frac{1}{4}\left\langle \left[4(\vec{u}_a - \vec{u}_c)\hat{R}_0 \right]^2 \right\rangle = 4\left\langle \left[(\vec{u}_a - \vec{u}_c)\hat{R}_0 \right]^2 \right\rangle = 4\left[\left\langle u^2_{ax} \right\rangle + \left\langle u^2_{cx} \right\rangle - 2\left\langle u_{ax} u_{cx} \right\rangle \right] = 4\sigma^2_{\mathrm{SS1}}$$





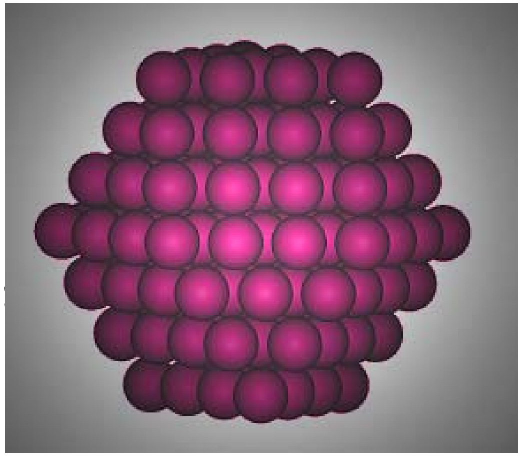
$$\text{Alloy} : A_{x_A} B_{x_B} \ (Au_{29} Pd_{118})$$

$$N_{AB} = \frac{x_B}{x_A} N_{BA}$$

M. S. Nashner, A. I. Frenkel, et al., JACS,1998.

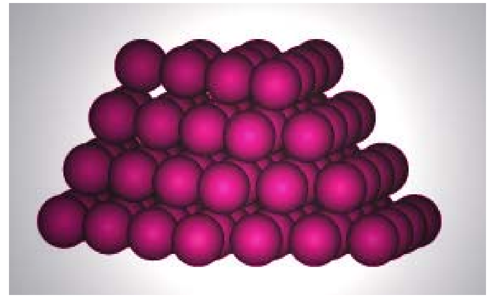
Capabilities of EXAFS

- Shape and texture:



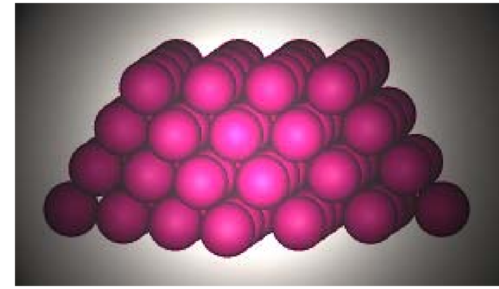
Cuboctahedron

or



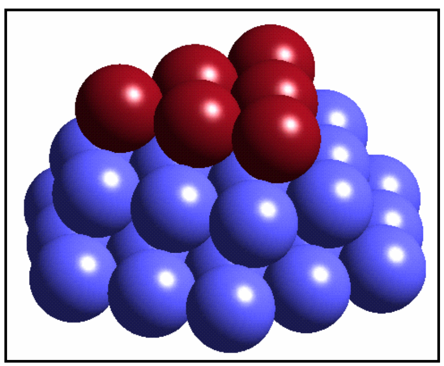
Hemispherical cuboctahedron (111)

or



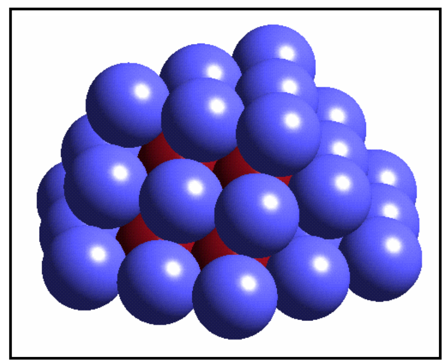
Hemispherical cuboctahedron (001)

- Short range order:



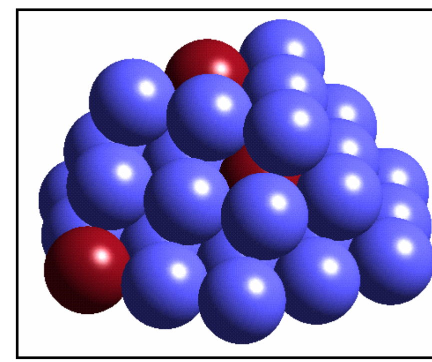
Surface segregation

or



Core segregation

or

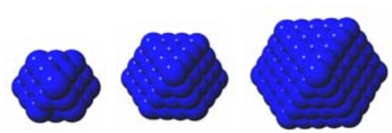


Random

Cluster Geometry Generator Program at YU

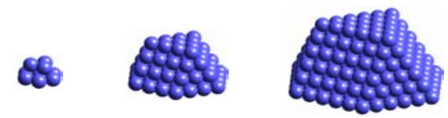
(Dana Glasner and A.F.)

Cuboctahedron



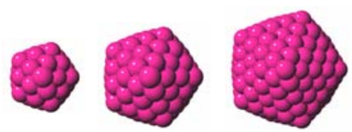
13, 55, 147, 309, 561…

Truncated (111) Cuboctahedron



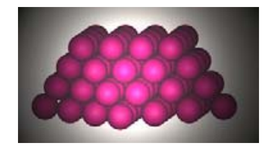
10, 37, 92, 185, 326, 525,…

Icosahedron



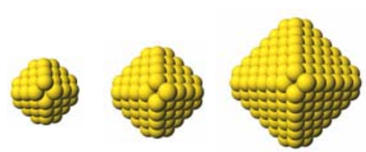
13, 55, 147, 309, 561…

Truncated (001) Cuboctahedron



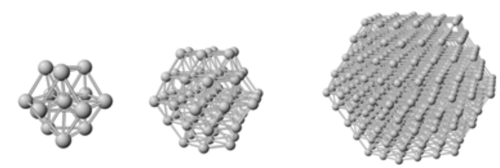
9, 34, 86, 175, 311, 504…

Truncated octahedron



13, 38, 79, 140, 225, 338, 483, 664…

HCP



13, 26, 57, 89, 153, 214, 323, 421, 587

Summary: EXAFS analysis of bimetallic nanoparticles

-Collect EXAFS data for the both edges

-Perform simultaneous multiple-data-set, multiple-edge refinement

-When possible, take into account multiple-scatterings

-Employ constraints for heterometallic bonds A-B
 Distances, DWFs are equal as measured from either edge
 Coordination numbers are constrained

-Compare different structural models
 Closed packed, non-closed packed
 Different shapes
 Different morphologies
 Different sizes

-Evaluate theoretically coordination numbers and compare with EXAFS results