Size and Geometry of Nanoparticles

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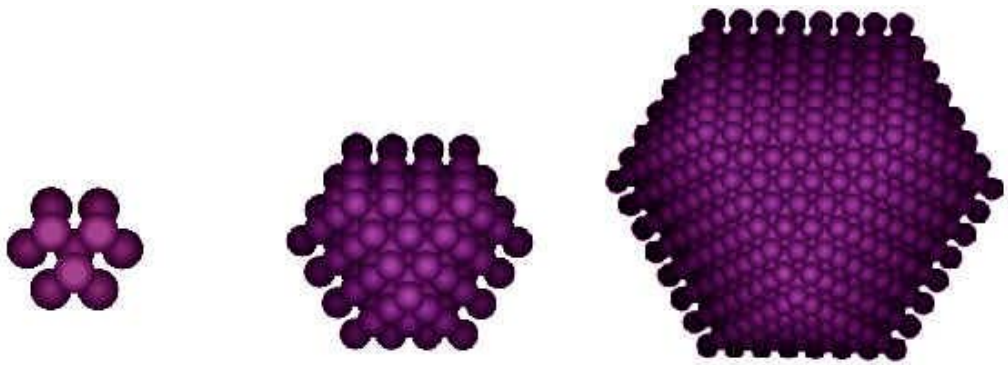
- First shell analysis: temperature dependence

- Multiple-scattering analysis

- Interpretation of EXAFS results

Test case: supported Pt nanoparticles



Total atoms: 10
Surface atoms: 10
Percent surface: 100%

Total atoms: 92
Surface atoms: 74
Percent surface: 80%

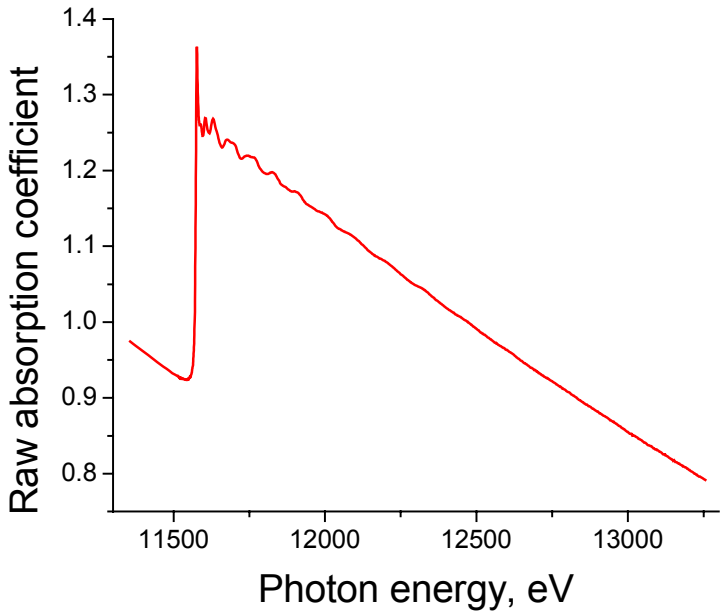
Total atoms: 792
Surface atoms: 394
Percent surface: 50%

Scheme 1.

What are we after?

-Size,
-Structure,
-Thermal properties.

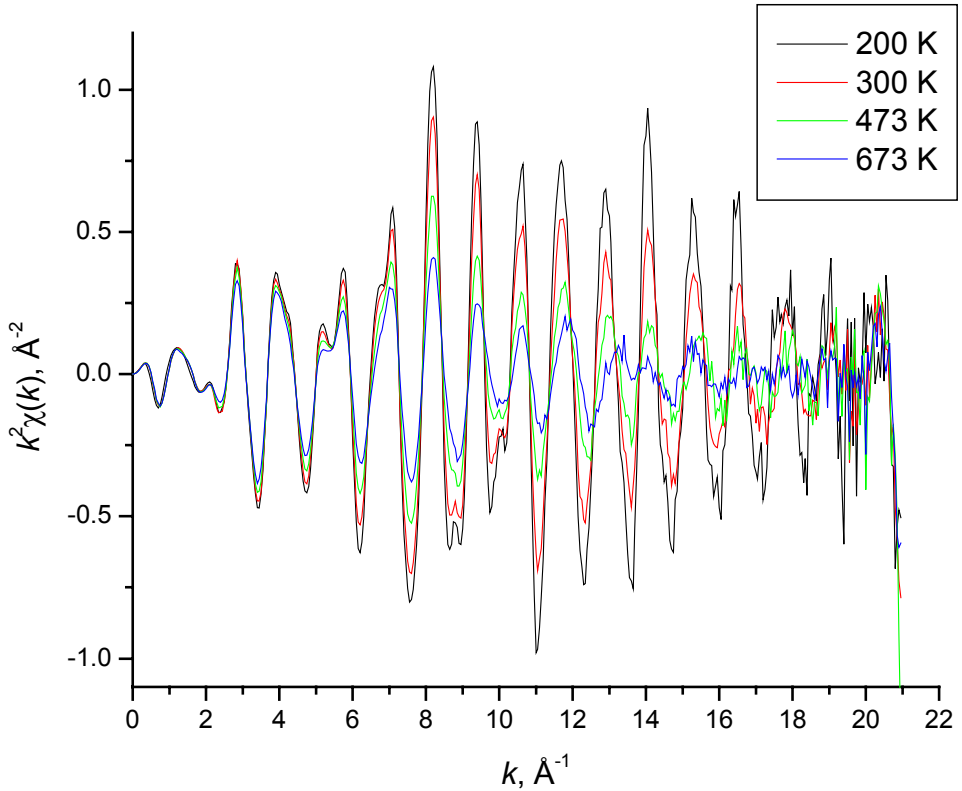
(Beamline: X16C, NSLS)



What relevant info can be found from EXAFS?

-Model of atomic packing,
-Average CN,
-Average distances,
-Average disorder

EXAFS data measured of particles of ~20 Å in size:

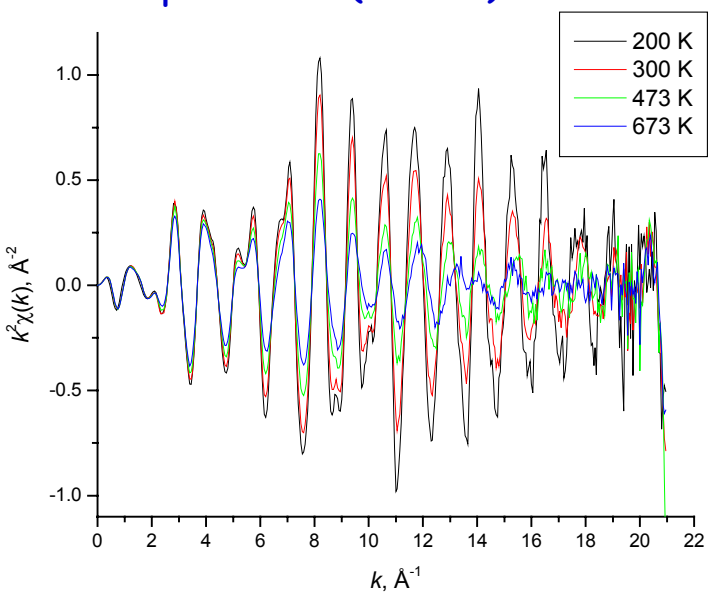


Can we tell what is the particle's structure?

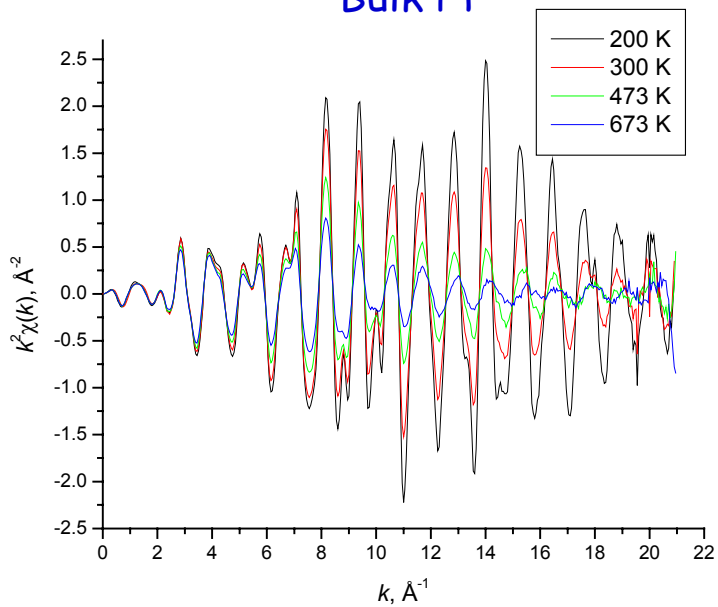
Whether the changes are dominated by atomic rearrangements or by thermal disorder?

Can we answer the same questions if a reference compound is measured as well?

Pt particles (~20 Å)



Bulk Pt



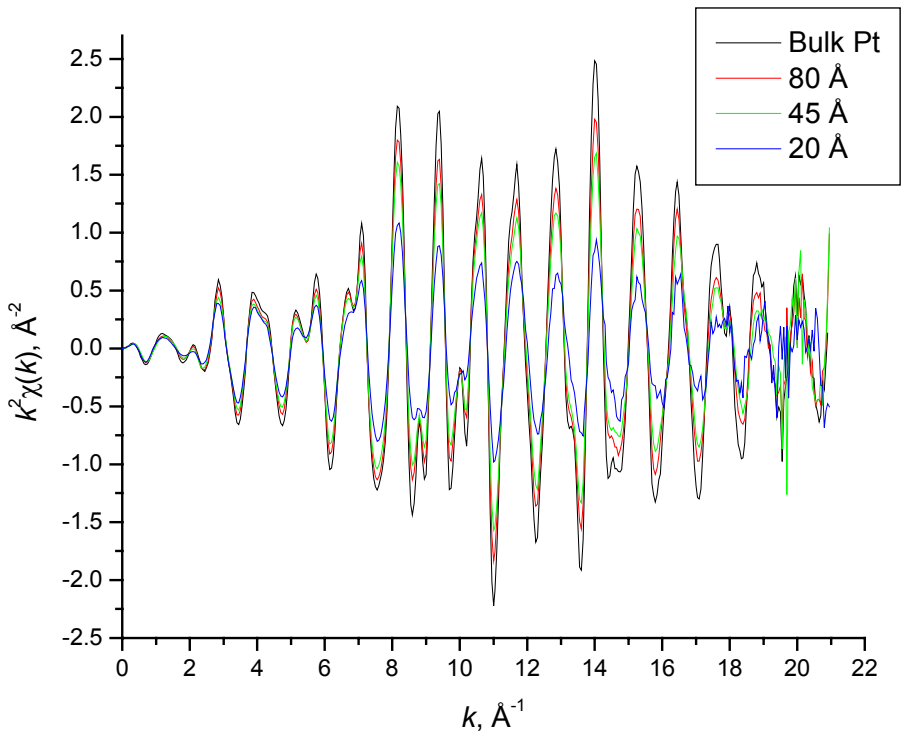
$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\mathrm{eff}}(k)\right| \mathrm{e}^{-2\sigma^2k^2}\, e^{2r/\lambda} \sin\left[2kr - \tfrac{4}{3}C_3k^3 + \delta(k)\right]$$

Can we tell what is the particle's structure? -Yes, consistent with *fcc*

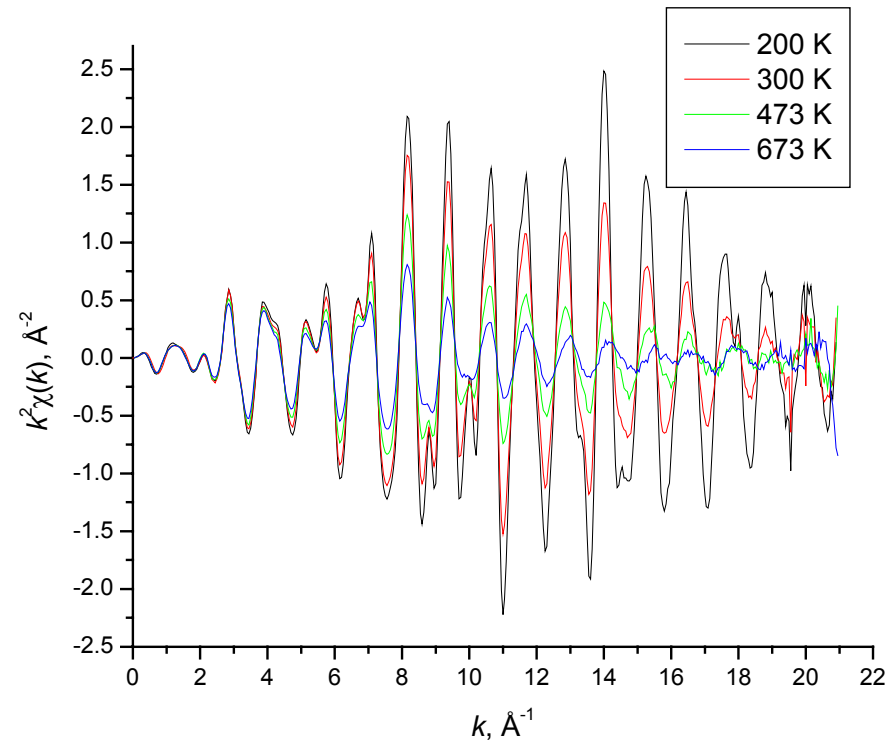
Whether the changes are dominated by atomic rearrangements or by <u>thermal disorder?</u>

How to tell size dependence from temperature dependence?

T=200 K; Size is varied



Bulk Pt; Temperature is varied



$$\chi(k) \sim N\,\mathrm{e}^{-2\sigma^2 k^2}$$

As a function of size, EXAFS amplitude is scaled ***uniformly*** throughout the *k*-range

As a function of temperature, EXAFS amplitude is scaled ***nonuniformly***

How to model metal (Pt) foil data:

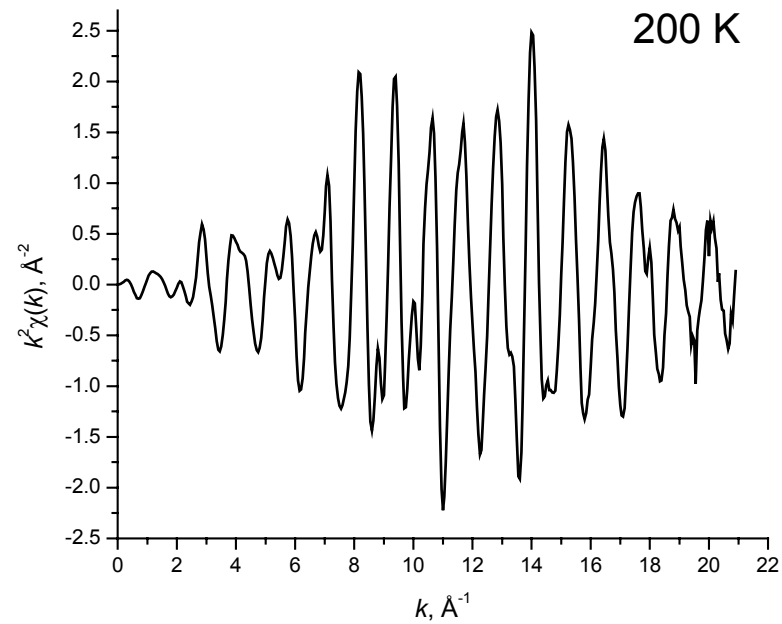
$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\text{eff}}(k)\right| e^{-2\sigma^2 k^2}\, e^{-2r/\lambda}$$
$$\times \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

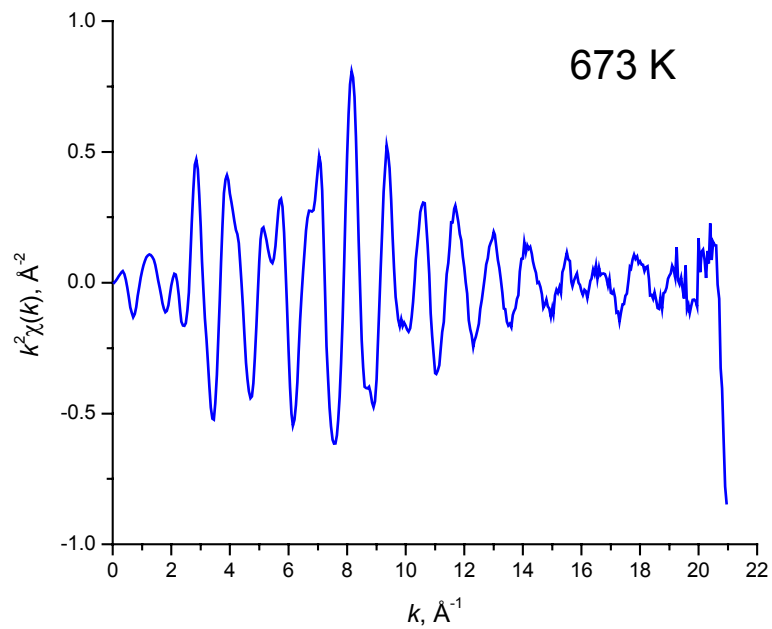
guess S02 = 0.9
guess ss1 = 0
guess dr1 = 0
guess th1 = 0
guess e0 = 0

rmin = 2.1 rmax = 3.3
kmin = 2 kmax= 20 w = 2 dk=2

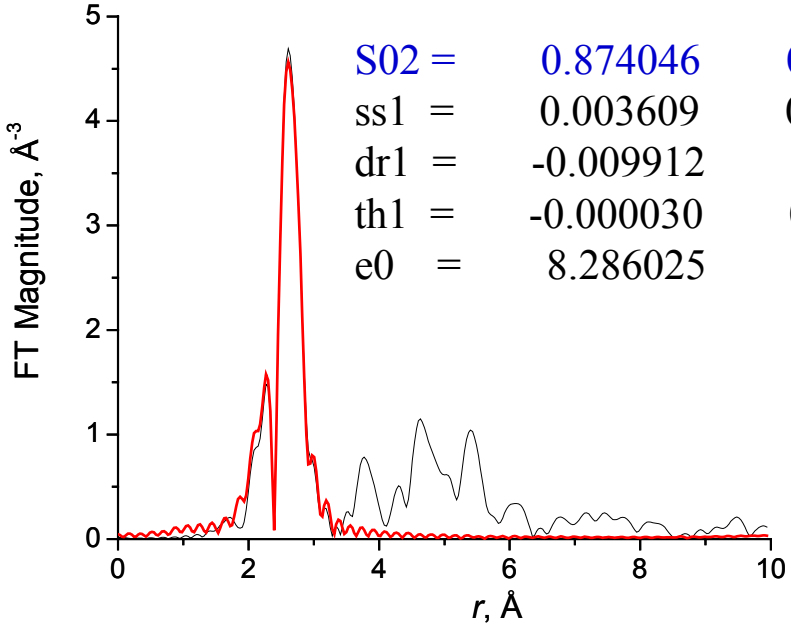
#1st path:

e0shift	1	e0
amp	1	S02
path	1	p1.dat
id	1	SS Pt-Pt(1), r=2.7719
delr	1	dr1
sigma2	1	abs(ss1)
third	1	th1



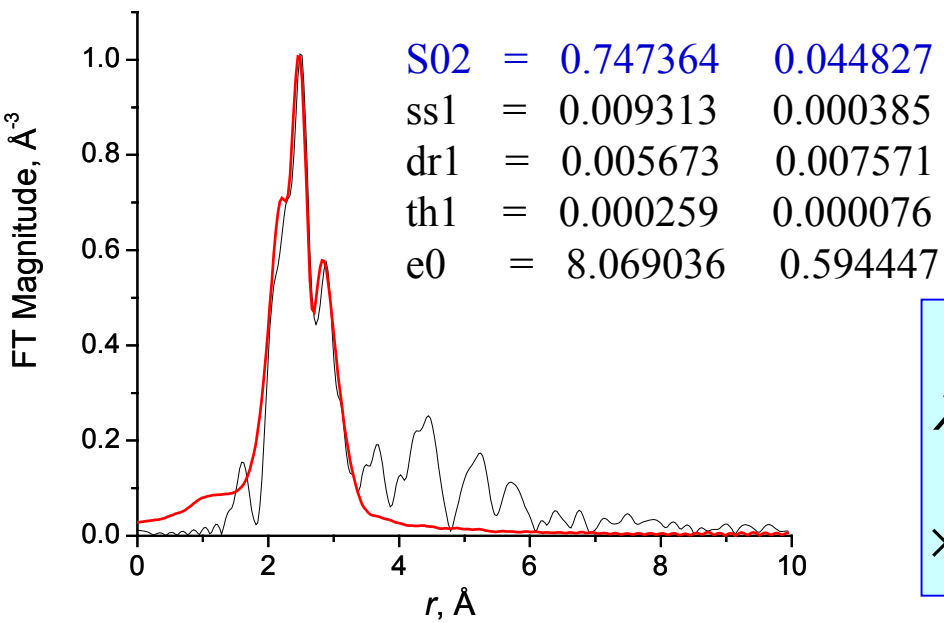


Fit Results



This is not physically reasonable….

What caused S02 to be different at 200 K and 673 K?

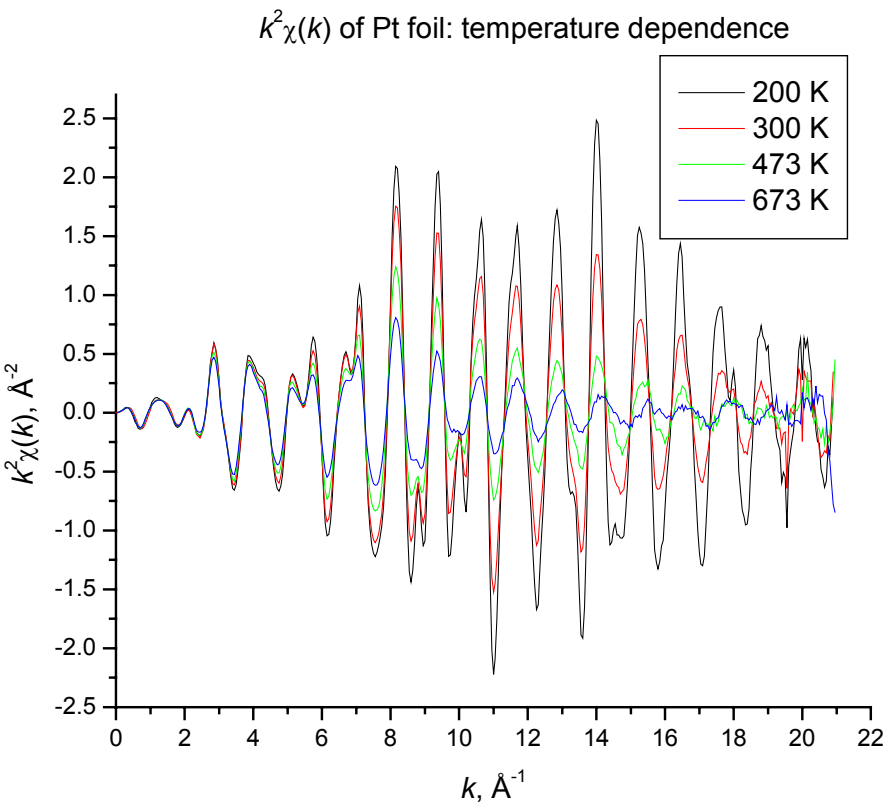


- correlation with other fit variables:

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

How to break the correlation?

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



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

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

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

A. I. Frenkel and J. J. Rehr, Phys. Rev. B **48**, 585 (1993).

Multiple-Data-Set Fit

```
title = Pt L3-edge, foil, 200 K

rmin  = 2.1   rmax = 3.3
kmin  = 2   kmax= 20    w = 2  dk =2

path        1  p1.dat
id          1  SS Pt-Pt1
e0shift     1  e0
amp         1  S02
delr        1  dr11
sigma2      1  abs(ss11)
third       1  th11

next data set

title = Pt L3-edge, foil, 300 K
rmin  = 2.1   rmax = 3.3
kmin  = 2   kmax= 20    w = 2  dk =2

path        1  p1.dat
id          1  SS Pt-Pt1
e0shift     1  e0
amp         1  S02
delr        1  dr12
sigma2      1  abs(ss12)
third       1  th12
```

```
next data set
…….. 473 K …….
next data set
…….. 673 K …….

set ss11     = abs(ss011) + eins(200, theins1)
set ss12     = abs(ss011) + eins(300, theins1)
set ss13     = abs(ss011) + eins(473, theins1)
set ss14     = abs(ss011) + eins(673, theins1)

guess e0      =   0.
guess s02     = 0.9
guess ss011 = 0
guess theins1 = 200
```

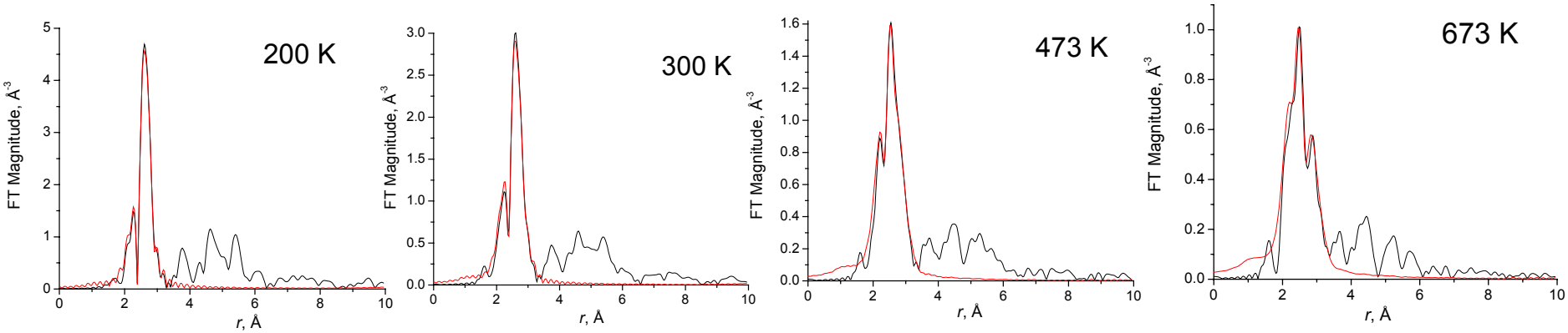
$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

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

```
guess dr11     =   0
guess dr12     =   0
guess dr13     =   0
guess dr14     =   0

guess th11     =   0
guess th12     =   0
guess th13     =   0
guess th14     =   0
```

MDS fit results



ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

Physical (chemical, engineering, mat.science, life science etc.)

reality checks:

1) Debye temperature: 240 K for Pt as obtained (through Θ_E): 253(3) K

2) Static disorder σ_s^2: ~0

3) Corrections to model distances: ~0

4) Thermal expansion: evident

5) S02: reasonable (between 0.7 and 1.0)

How to tell right from wrong?

$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\mathrm{eff}}(k)\right| \mathrm{e}^{-2\sigma^2k^2} \sin\left[2kr - \tfrac{4}{3}C_3k^3 + \delta(k)\right]$$

Pretend, there are no "third cumulants".

With C_3

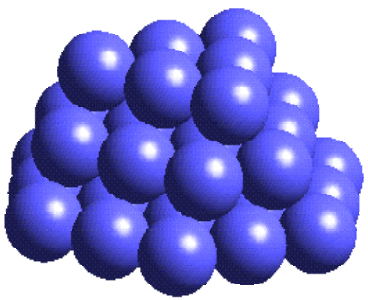
ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

Without C_3

ss011	=	0.000472	0.000127
theins1	=	187.676941	3.088949
s02	=	0.840180	0.024436
dr11	=	-0.007120	0.001032
dr12	=	-0.008353	0.001577
dr13	=	-0.010902	0.002108
dr14	=	-0.011235	0.002930
e0	=	7.728140	0.271577

How to model XAFS data in nanoparticles?

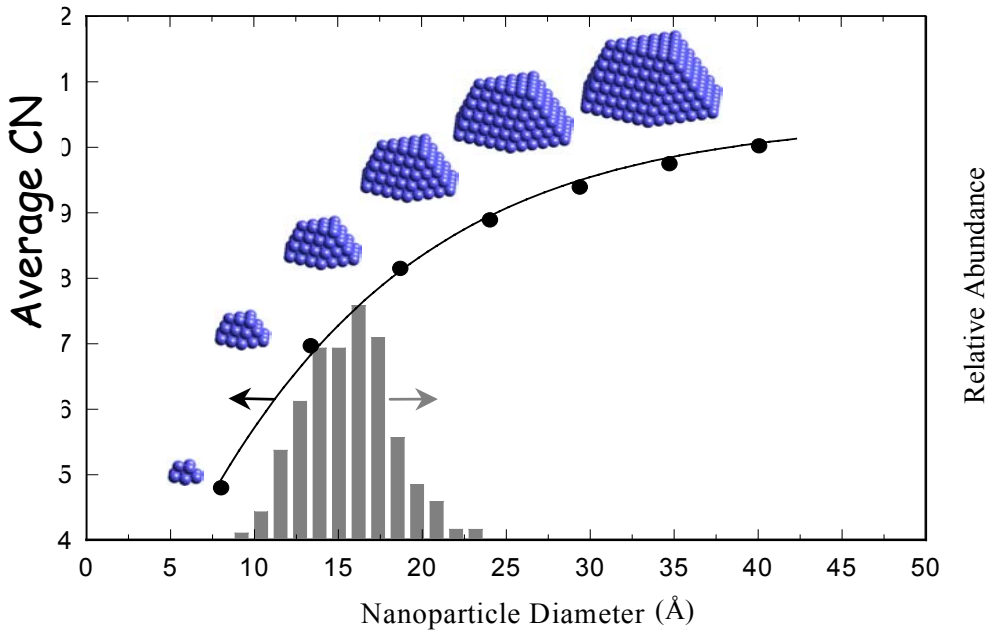
A priori knowledge or a working hypothesis must exist
(the "zero" approximation)
otherwise: the transferability of amplitude/phase will not work!)



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

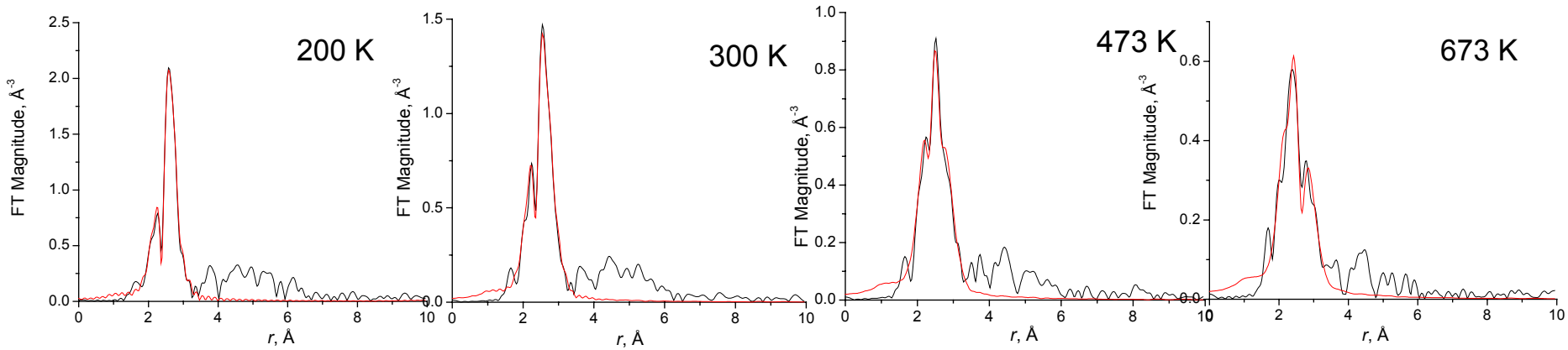
What information can be obtained from 1st shell EXAFS analysis?

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



MDS fit (1shell) to the nanoparticles EXAFS

- Coordination number is now guessed (a variable)
- S_0^2 is fixed to be equal to that in Pt foil EXAFS
- E0 is fixed to be equal to that in Pt foil EXAFS



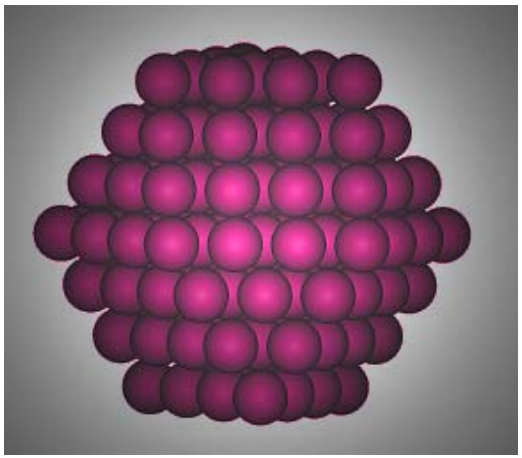
ss011	=	0.001676	0.000177
theins1	=	191.842209	3.893480
n1	=	7.879327	0.197850

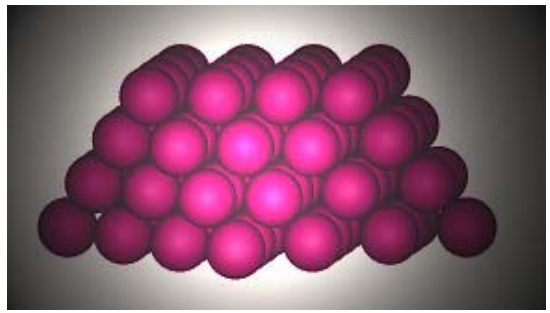
dr11	=	-0.015809	0.003938
dr12	=	-0.011870	0.002064
dr13	=	-0.008558	0.003883
dr14	=	-0.000845	0.004875
th11	=	-0.000017	0.000030
th12	=	0.000055	0.000019
th13	=	0.000159	0.000047
th14	=	0.000421	0.000079

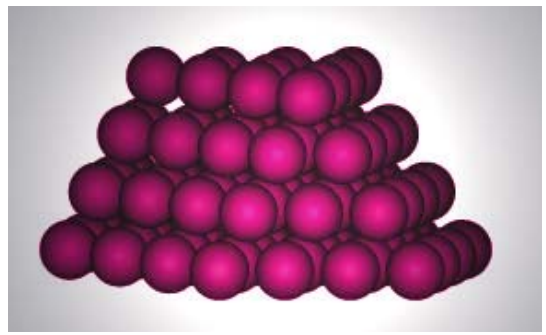
To get the most out of the data,
the Multiple-Scattering Analysis is often needed.

What are the limitations of the 1st Shell Analysis in the case of nanoparticles?

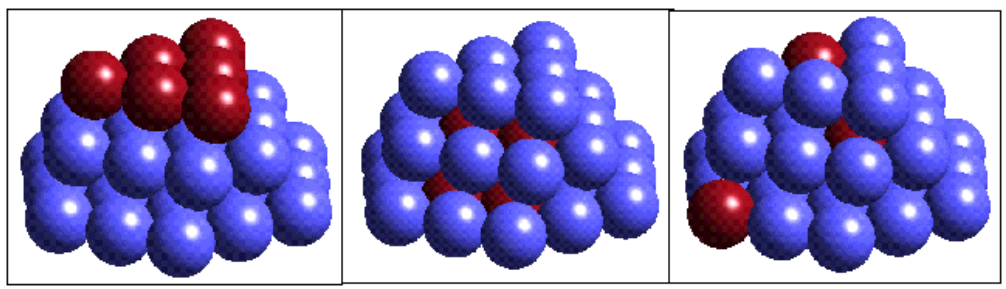
-Shape, Size, Surface orientation – are not revealed through the 1NN CN



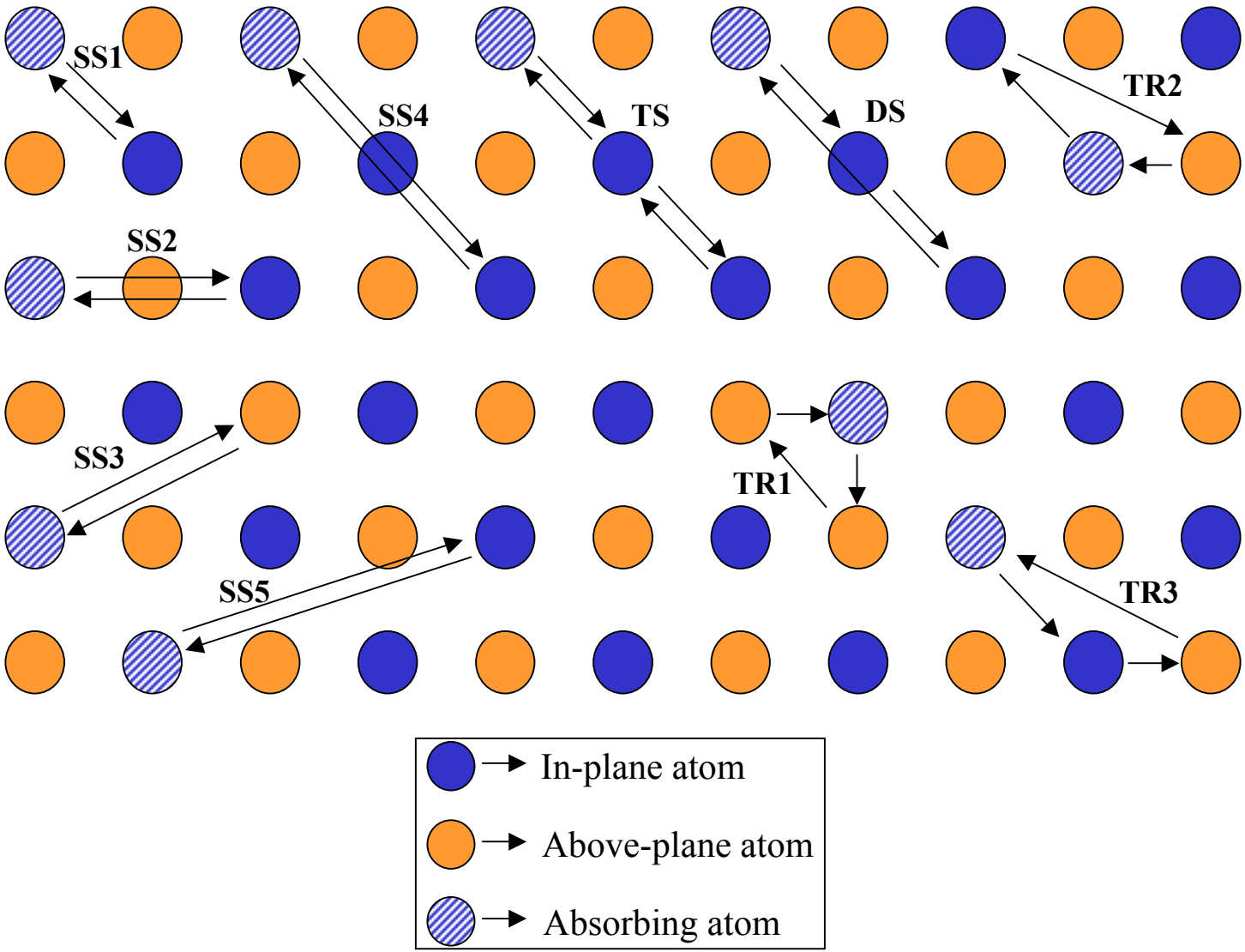




-Short Range Order
in nanoparticle alloys:



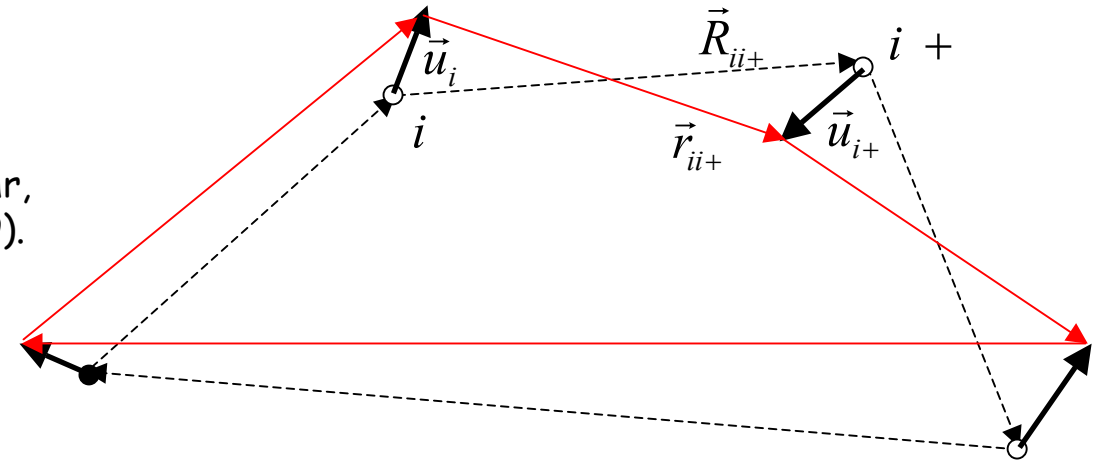
Multiple Scattering Paths



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).



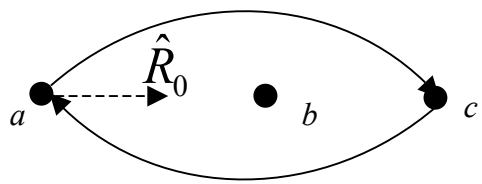
$$r_{ii+}^2 = \left(\vec{R}_{ii+} + \left(\vec{u}_{i+} - \vec{u}_i\right)\right)^2 \approx R_{ii+}^2 - 2R_{ii+}\hat{R}_{ii+}\left(\vec{u}_i - \vec{u}_{i+}\right)$$

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

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

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

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

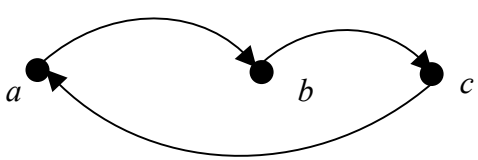


$$\sigma_{\mathrm{SS}}^2 = \frac{1}{4} \left\langle \left[\left(\vec{u}_a - \vec{u}_c\right) \hat{R}_0 + \left(\vec{u}_c - \vec{u}_a\right) \left(-\hat{R}_0\right) \right]^2 \right\rangle = \frac{1}{4} \left\langle \left[2 \left(\vec{u}_a - \vec{u}_c\right) \hat{R}_0 \right]^2 \right\rangle$$

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

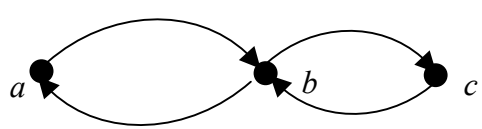
$$= \left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2 \left\langle u_{ax} u_{cx} \right\rangle,$$

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

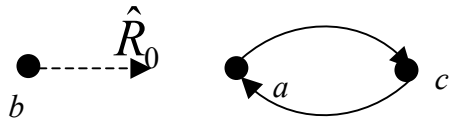


$$\sigma_{\mathrm{DS}}^2 = \frac{1}{4} \left\langle \left[\left(\vec{u}_a - \vec{u}_b\right) \hat{R}_0 + \left(\vec{u}_b - \vec{u}_c\right) \hat{R}_0 + \left(\vec{u}_c - \vec{u}_a\right) \left(-\hat{R}_0\right) \right]^2 \right\rangle$$

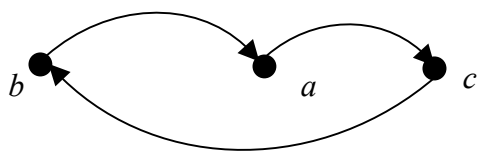
$$= \frac{1}{4} \left\langle \left[2 \left(\vec{u}_a - \vec{u}_c\right) \hat{R}_0 \right]^2 \right\rangle = \left\langle \left[\left(\vec{u}_a - \vec{u}_c\right) \hat{R}_0 \right]^2 \right\rangle = \sigma_{\mathrm{DS}}^2$$



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

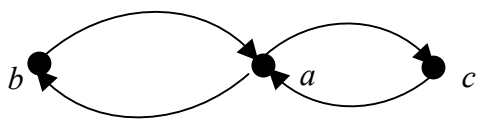


$$\sigma_{\mathrm{SS1}}^2 = \left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2\left\langle u_{ax} u_{cx} \right\rangle,$$

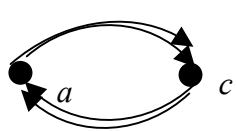


$$\sigma_{\mathrm{DS}}^2 = \frac{1}{4}\left\langle \left[(\vec{u}_a - \vec{u}_c)\hat{R}_0 + (\vec{u}_c - \vec{u}_b)(-\hat{R}_0) + (\vec{u}_b - \vec{u}_a)\hat{R}_0 \right]^2 \right\rangle$$

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



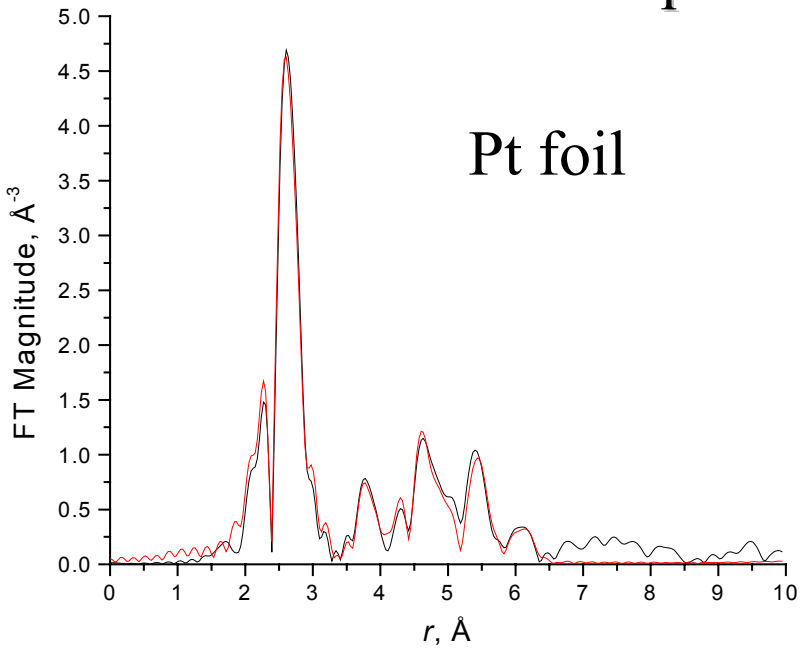
$$= 2\left\langle u_{bx}^2 \right\rangle - 2\left\langle u_{bx} u_{cx} \right\rangle = \sigma_{\mathrm{TS}}^2$$

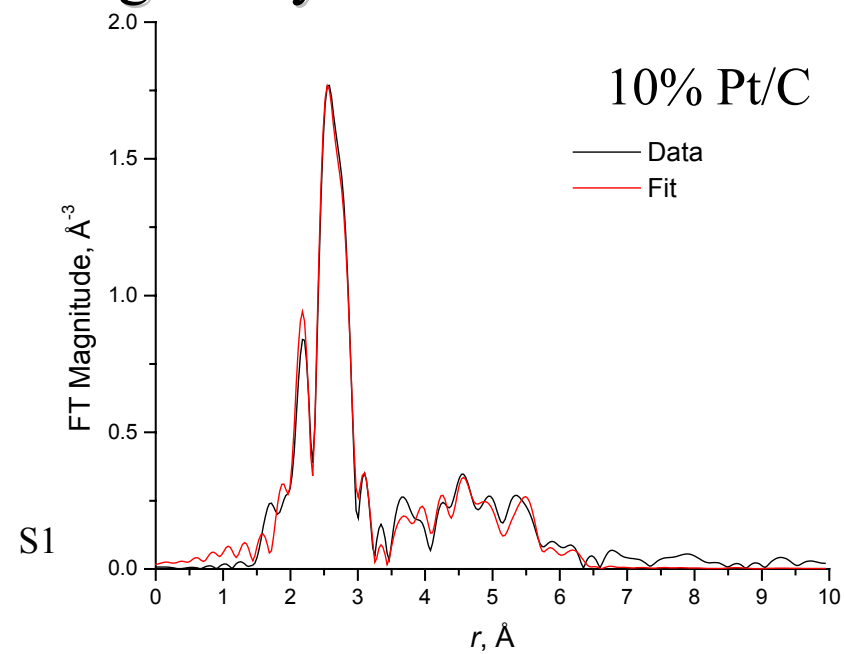


$$\sigma_{\mathrm{TS}}^2 = \frac{1}{4}\left\langle 2\left[(\vec{u}_a - \vec{u}_c)\hat{R}_0 + 2(\vec{u}_c - \vec{u}_a)(-\hat{R}_0) \right]^2 \right\rangle$$

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

Multiple Shell Fitting Analysis



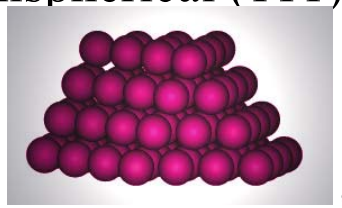


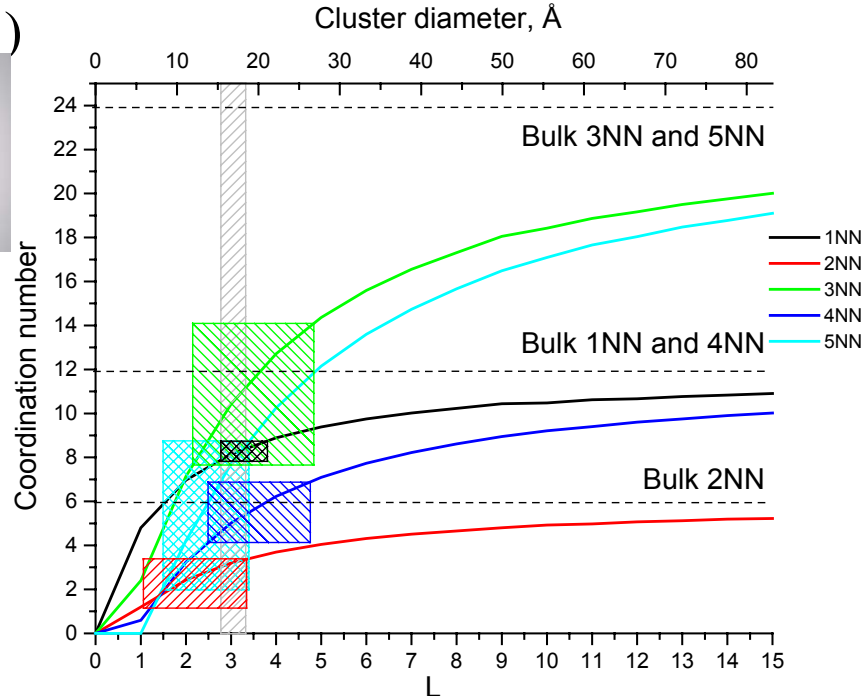
Coordination numbers for the first 5 shells:

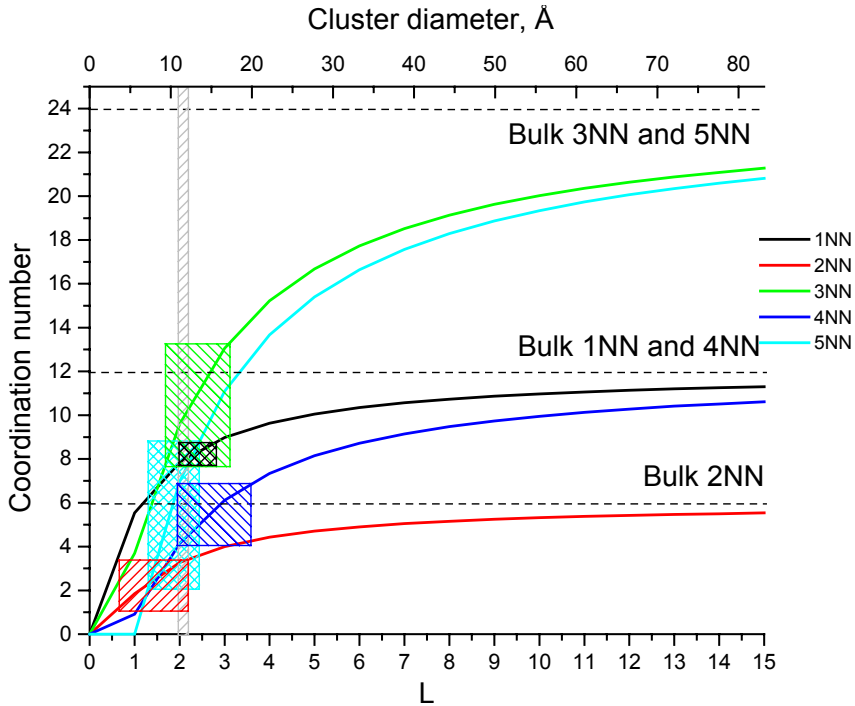
i	10% Pt/C	40% Pt/C	60% Pt/C	Pt foil	Bulk fcc
1	8.3(5)	10.5(5)	11.4(6)	12.6(7)	12
2	2.3(1.1)	4.0(1.3)	4.7(1.7)	5.9(2.0)	6
3	10.9(3.2)	16.8(3.5)	19(4)	23(5)	24
4	5.5(1.4)	7.6(1.4)	8.5(1.6)	11(2)	12
5	5.4(3.4)	10(4)	11(4)	14(5)	24

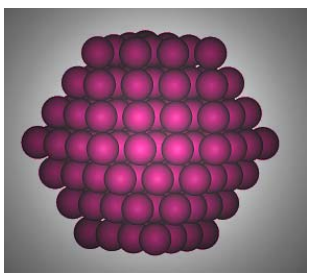
Size, Shape, Morphology…

Hemispherical (111)

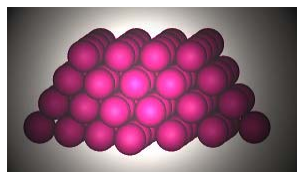




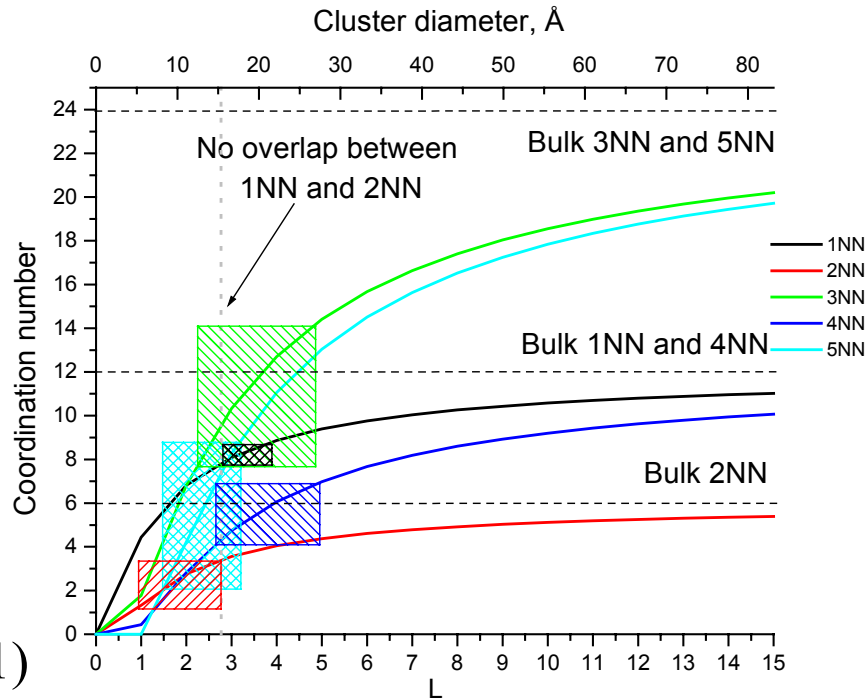




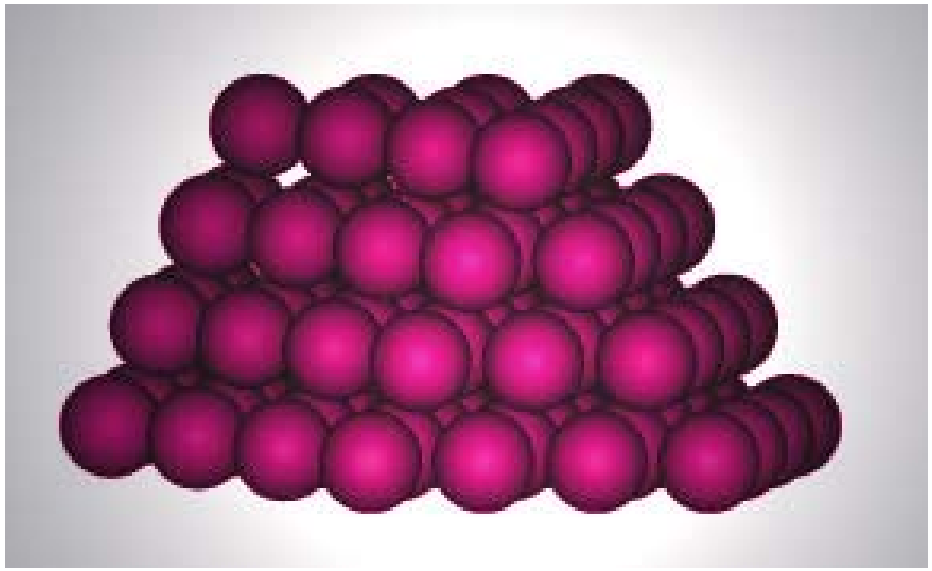
Spherical



Hemispherical (001)



Results for the monoatomic Pt/C nanoparticles:



Structure:

-Atomic packing: face center cubic.
-Cluster shape: hemispherical cuboctahedron.
-Texture: basal plane is (111)
-Surface disorder. Surface layers relaxed inward (surface tension)

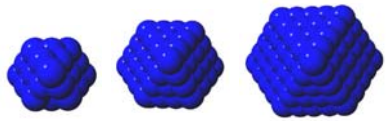
Electronic structure:

-Reduced particles are metallic.
-Bulk-like electronic DOS.

Cluster Geometry Generator Program at YU

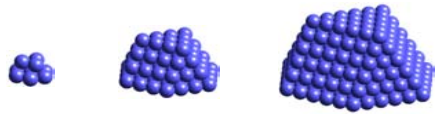
(Dana Glasner and A.F.)

Cuboctahedron



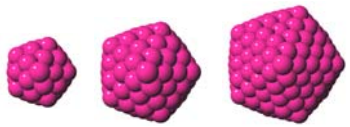
13, 55, 147, 309, 561…

Truncated (111) Cuboctahedron



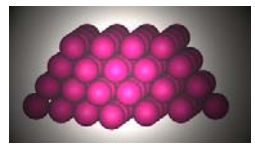
10, 37, 92, 185, 326, 525,…

Icosahedron



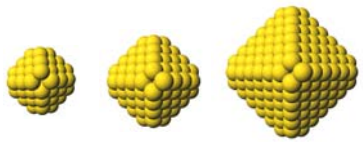
13, 55, 147, 309, 561…

Truncated (001) Cuboctahedron



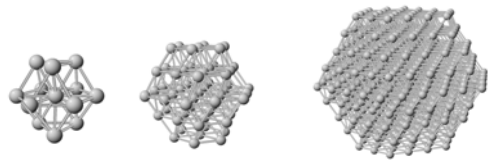
9, 34, 86, 175, 311, 504…

Truncated octahedron



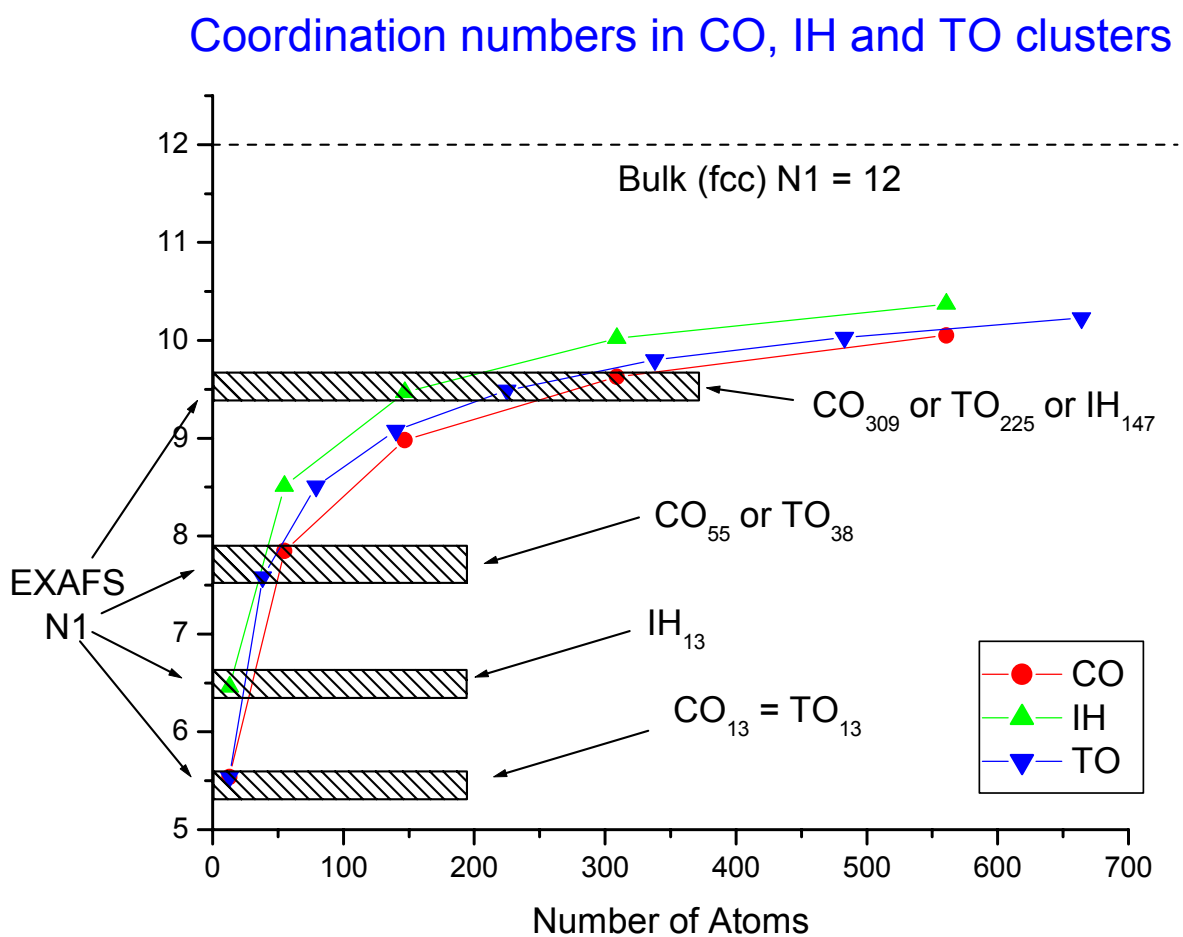
13, 38, 79, 140, 225, 338, 483, 664…

HCP

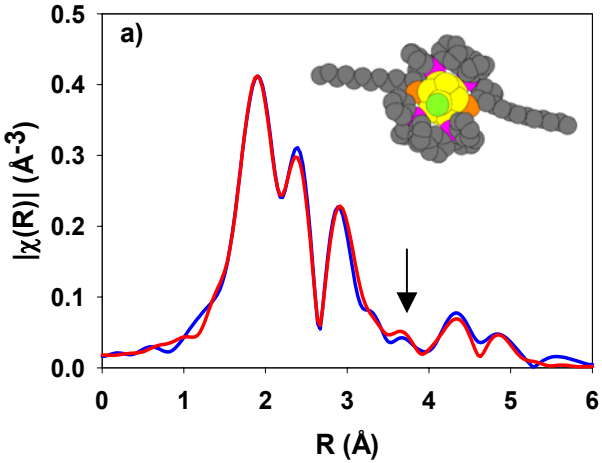


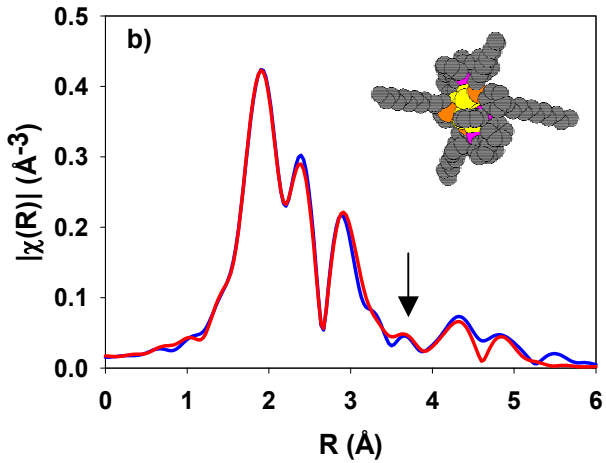
13, 26, 57, 89, 153, 214, 323, 421, 587

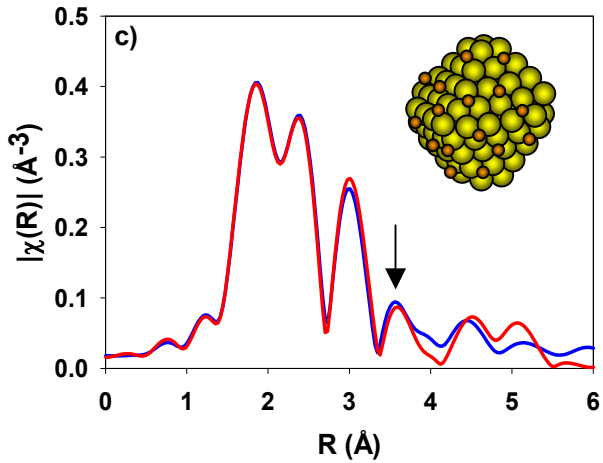
First shell analysis is not adequate for full structural studies of small clusters



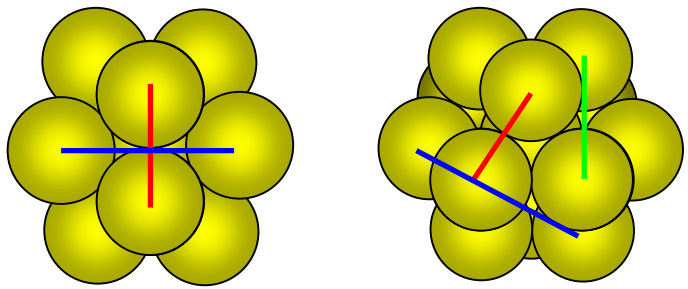
L. Menard (UIUC)

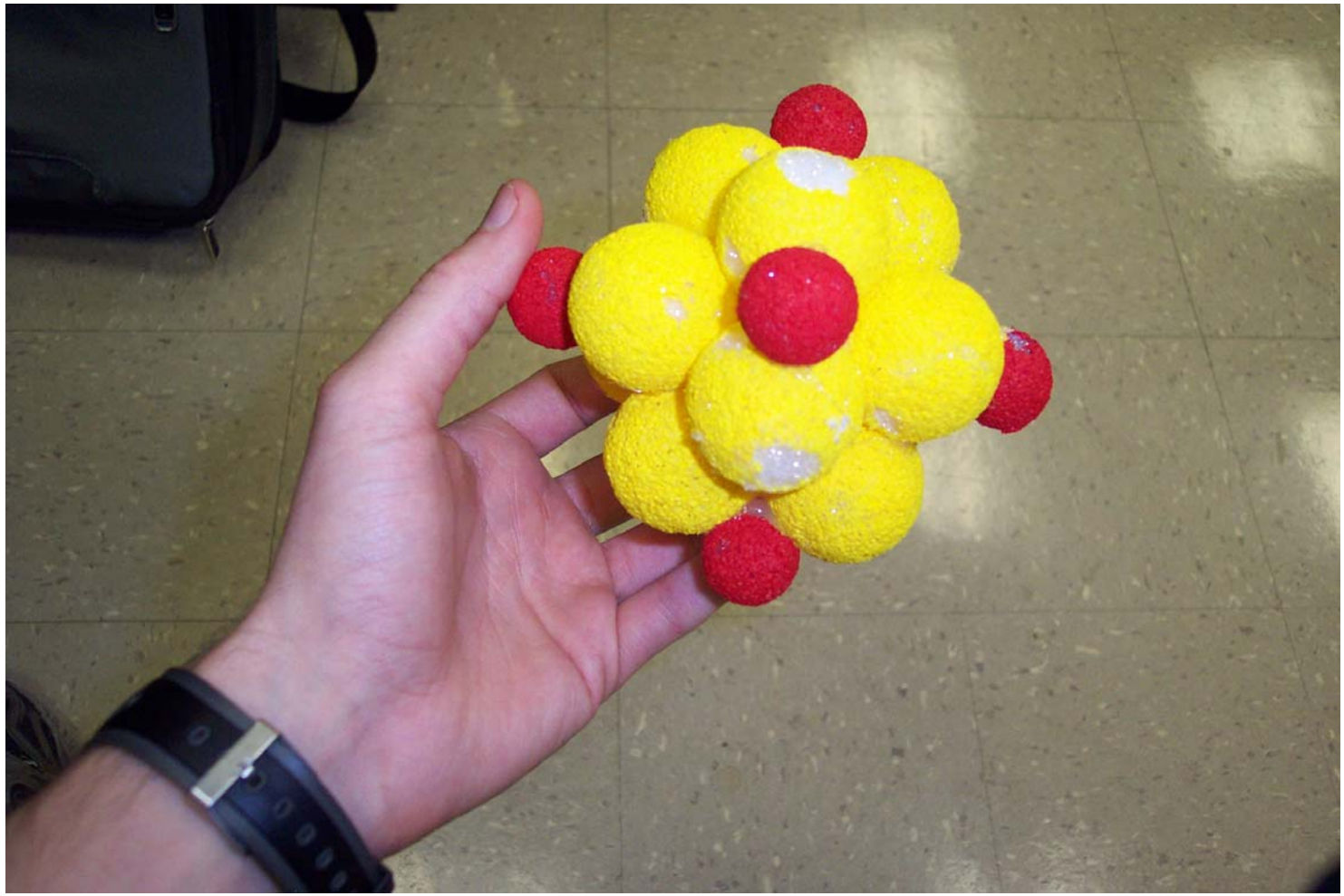






$Au_{13}(PPh_3)_4(SC12)_2Cl_2$ $Au_{13}(PPh_3)_4(SC12)_4$ fully-thiolated clusters



Icosahedral or cuboctahedral?

Poor man's nanocluster