First Shell EXAFS Analysis

"It is very difficult to find a black cat in a dark room, especially if it is not there…"

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1) Pre-requisites, or what to do first, before jumping at your data

2) Why to use reference compounds and how to use them.

3) Be conservative with the number of parameters
   (If you added the fifth cumulant and it solved your problem, start over and pick a better model!)

“Bottom-up” approach – the preferred strategy of the First Shell Analysis:

(You will avoid going in the wrong direction too early…)

Implementation

Find the best analysis software that can implement your strategy.
Not all packages are universally good.

Analysis Strategy

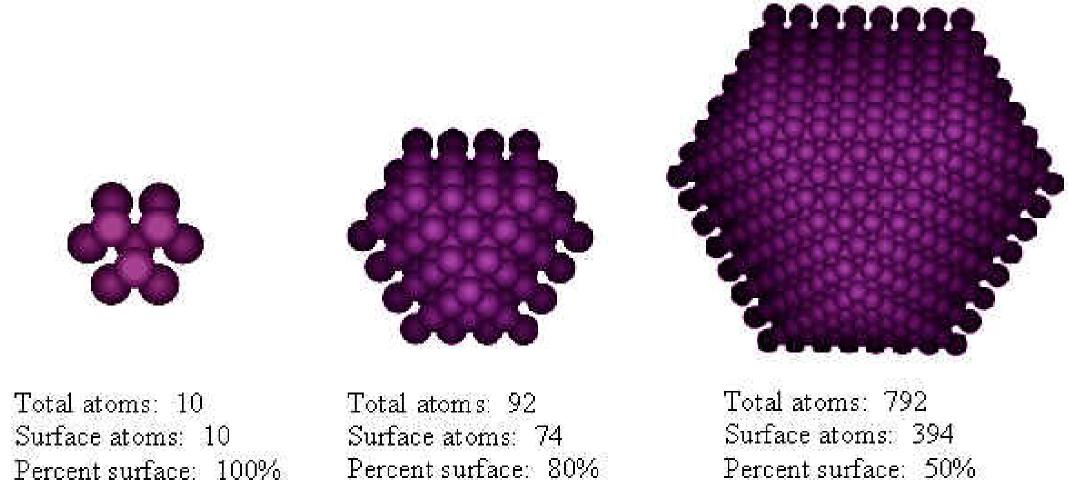
-Plan on doing reality checks;
-Reference compounds should be measured and analyzed first;
-Try to maximize the number of degrees of freedom in the fits
(use constraints, experimental/theoretical info etc.)

Linear fit is better than nonlinear fit!

Conceptual Modeling

-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.)

Test case: supported Pt nanoparticles

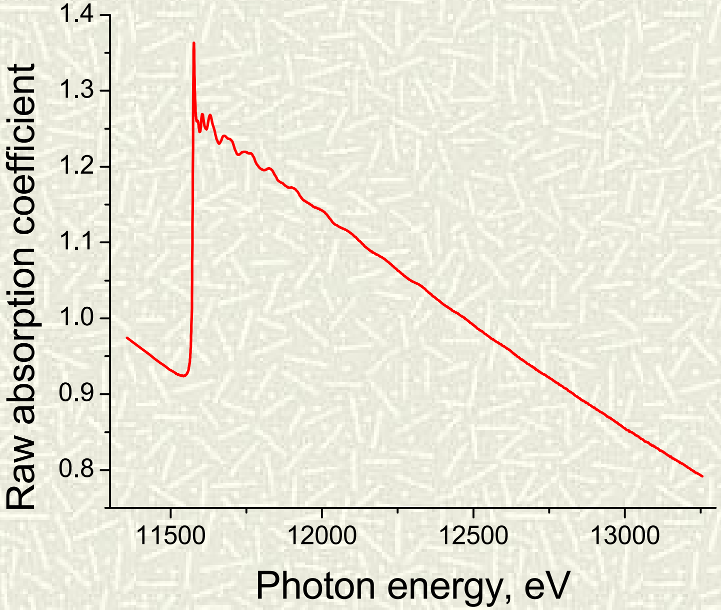


Scheme 1.

What are we after?

-Size,
-Structure,
-Thermal properties.

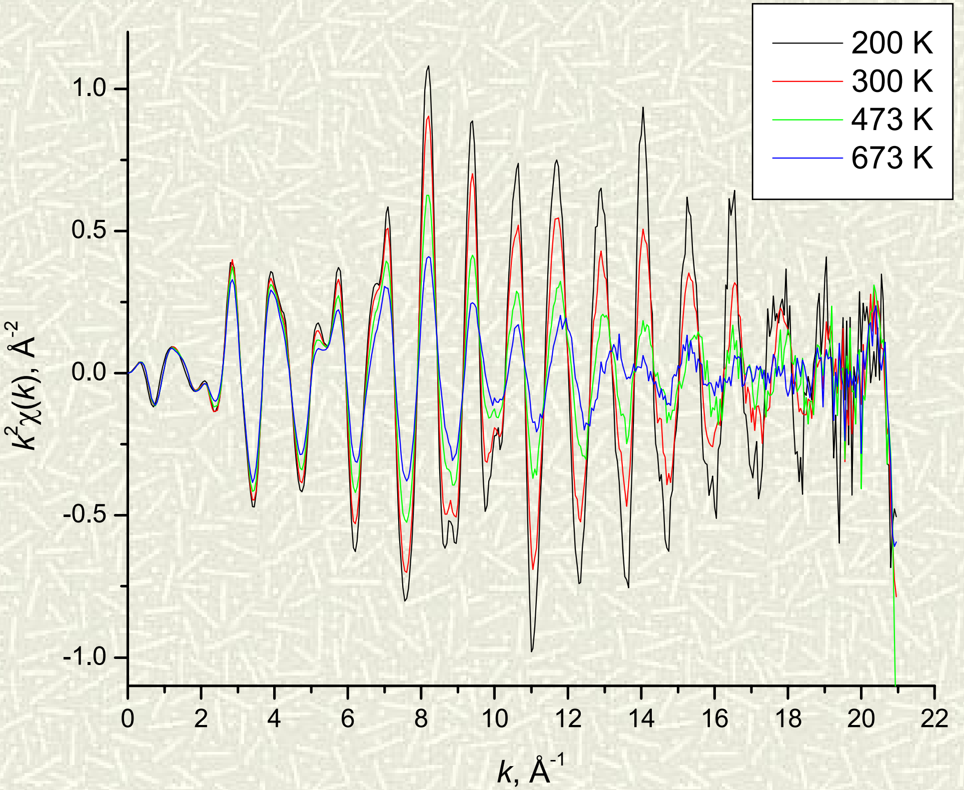
(Beamline: X16C, NSLS)



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:



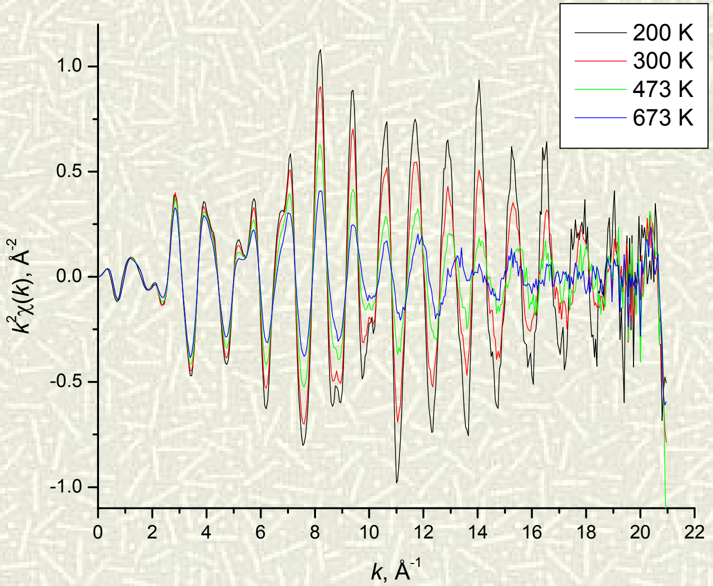
Can we tell what is the particle's structure?

Whether particles agglomerate at high T?

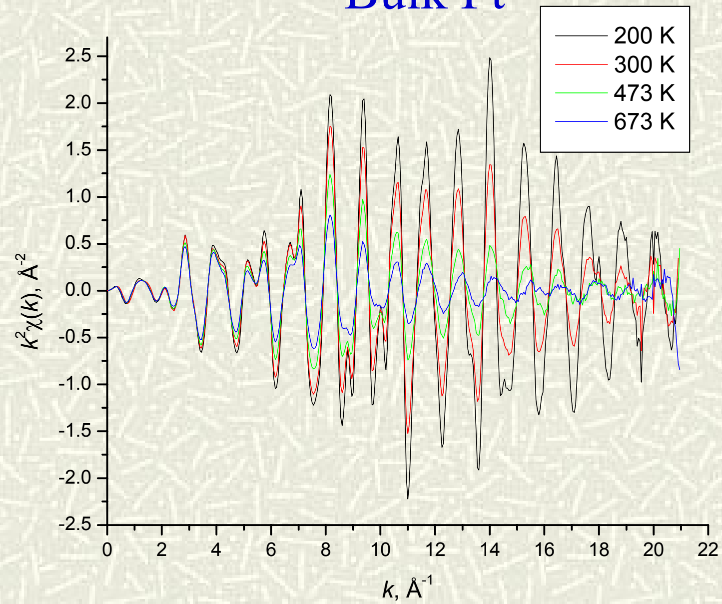
Whether the changes are dominated by atomic rearrangements or by thermal disorder?

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

Pt particles (~20 Å)



Bulk Pt



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

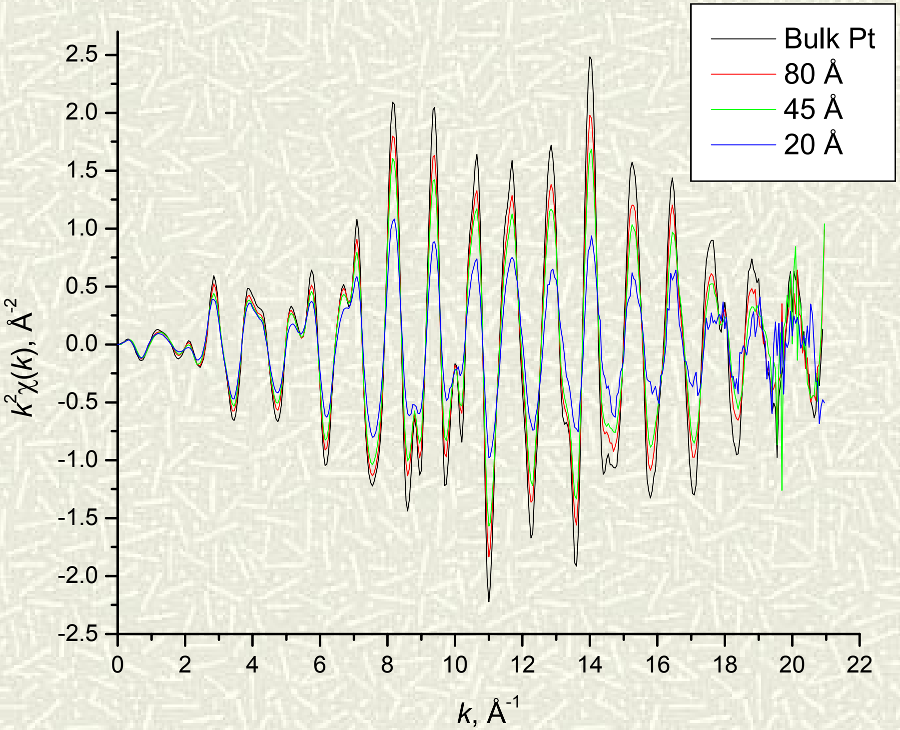
Can we tell what is the particle's structure? -Yes, consistent with *fcc*

Whether particles agglomerate at high T? - Most likely no, the size effect is not evident

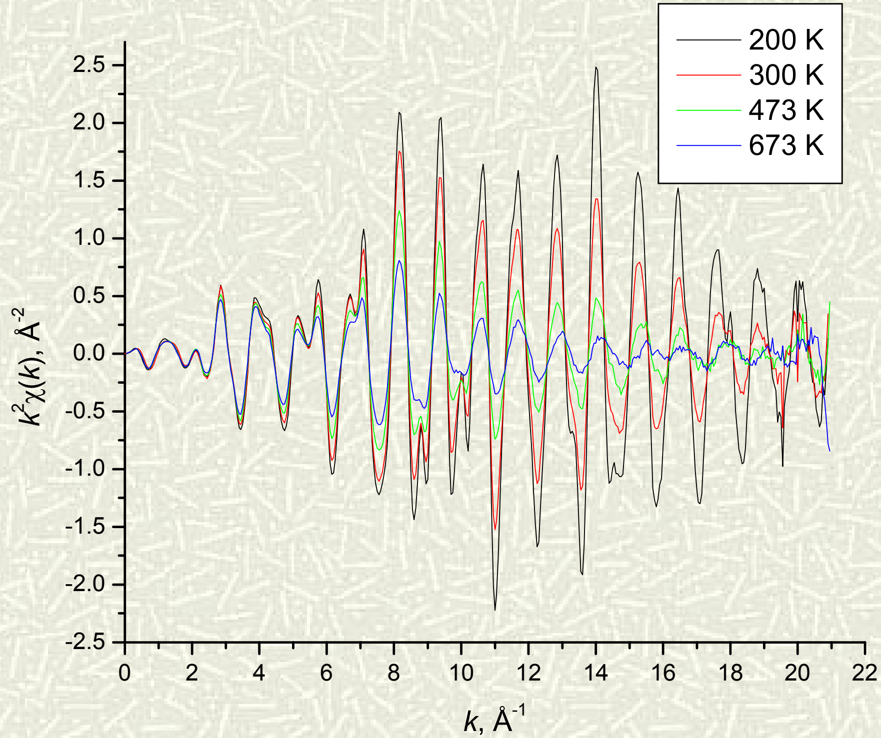
Whether the changes are dominated by atomic rearrangements or by thermal disorder?

How to tell size dependence from temperature dependence?

T=200 K; Size is varied



Bulk Pt; Temperature is varied



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

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:

Pt foil, T=200 K

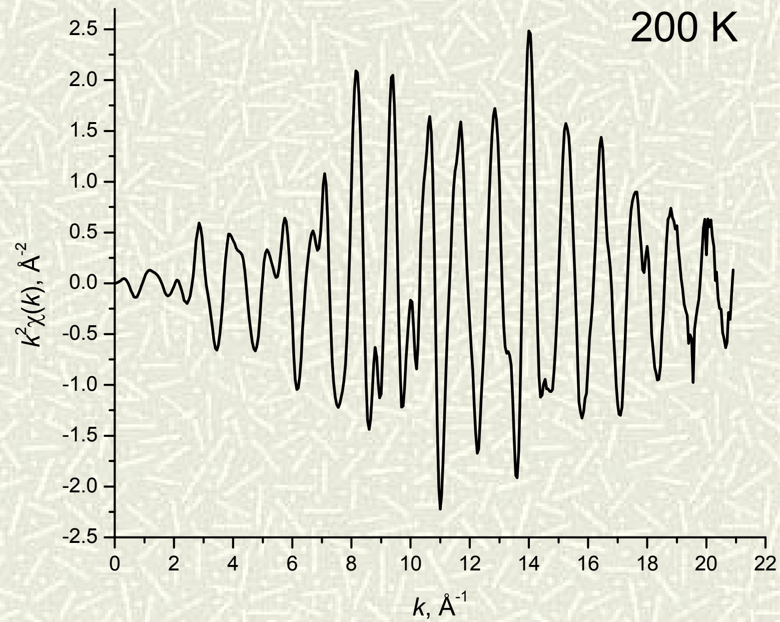
guess S02 = 0.9
guess ss1 = 0
guess dr1 = 0
guess th1 = 0
guess e0 = 0

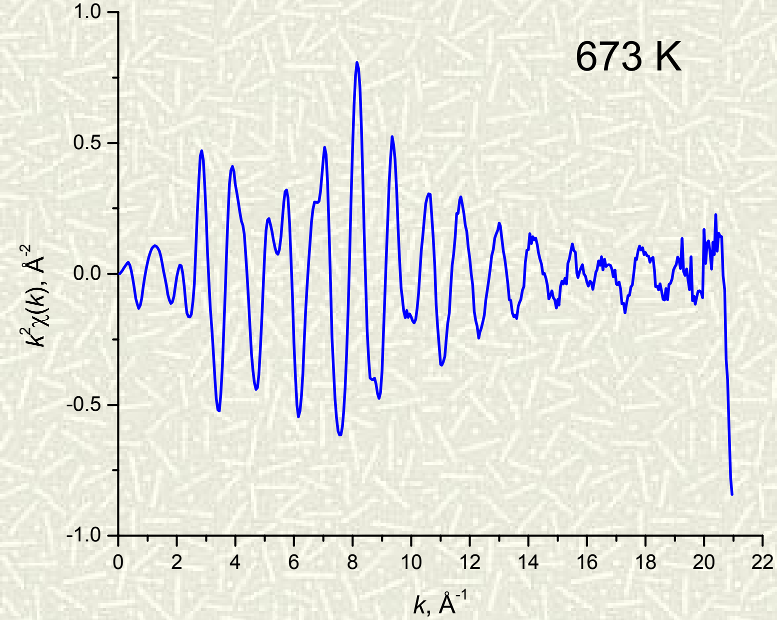
$$\chi(k) = \frac{NS_0^2}{kr^2}\left|f^{\mathrm{eff}}(k)\right| e^{-2\sigma^2 k^2} \times \sin\left[2kr - \tfrac{4}{3}C_3 k^3 + \delta(k)\right]$$

data = ptfoil-200avk.chi
out = ptfoil-200avk

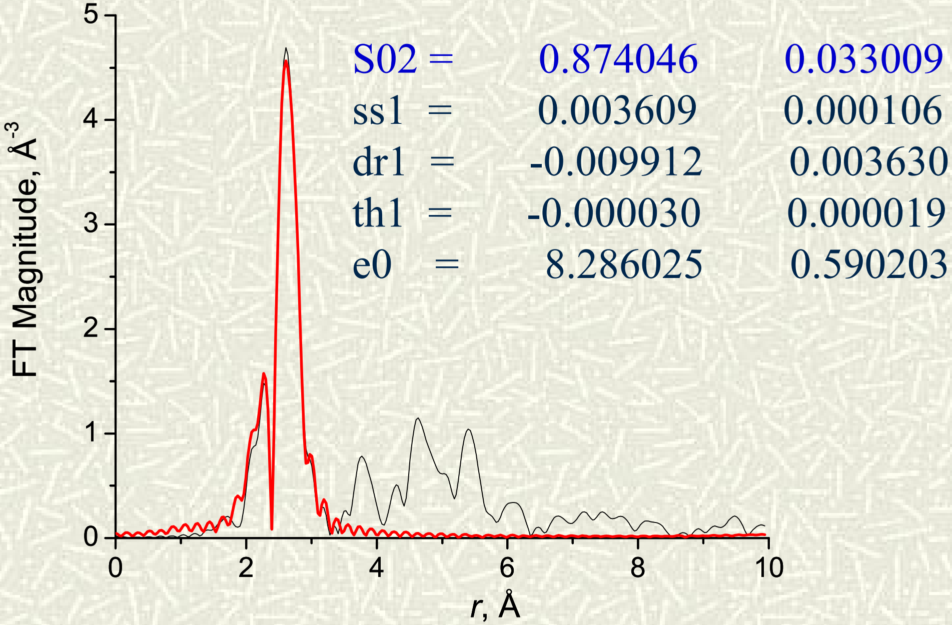
rmin = 2.1 rmax = 3.3
kmin = 2 kmax= 20 w = 2 dk=2

```
!% 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
```



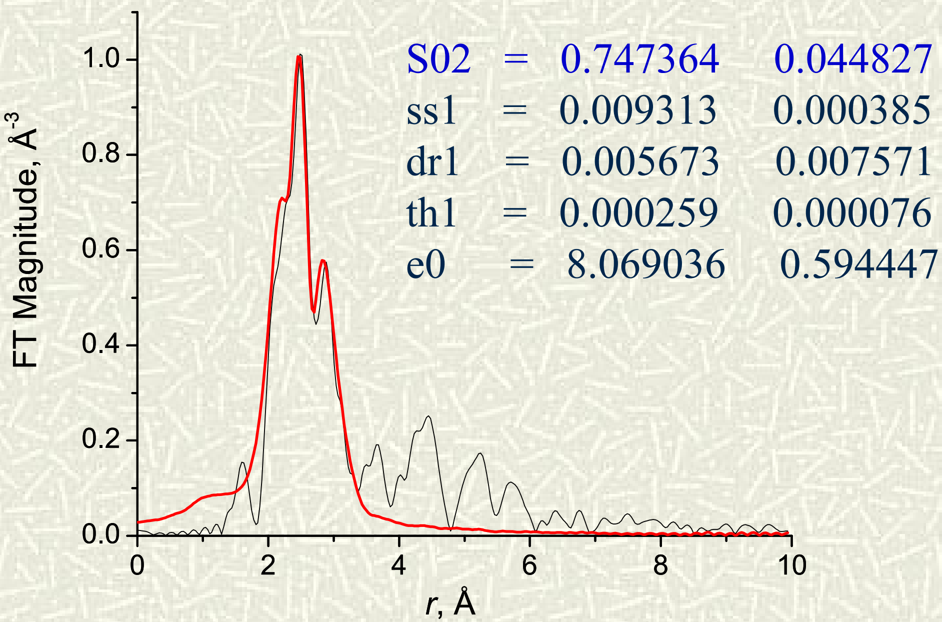


Fit Results



This is not physically reasonable….

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



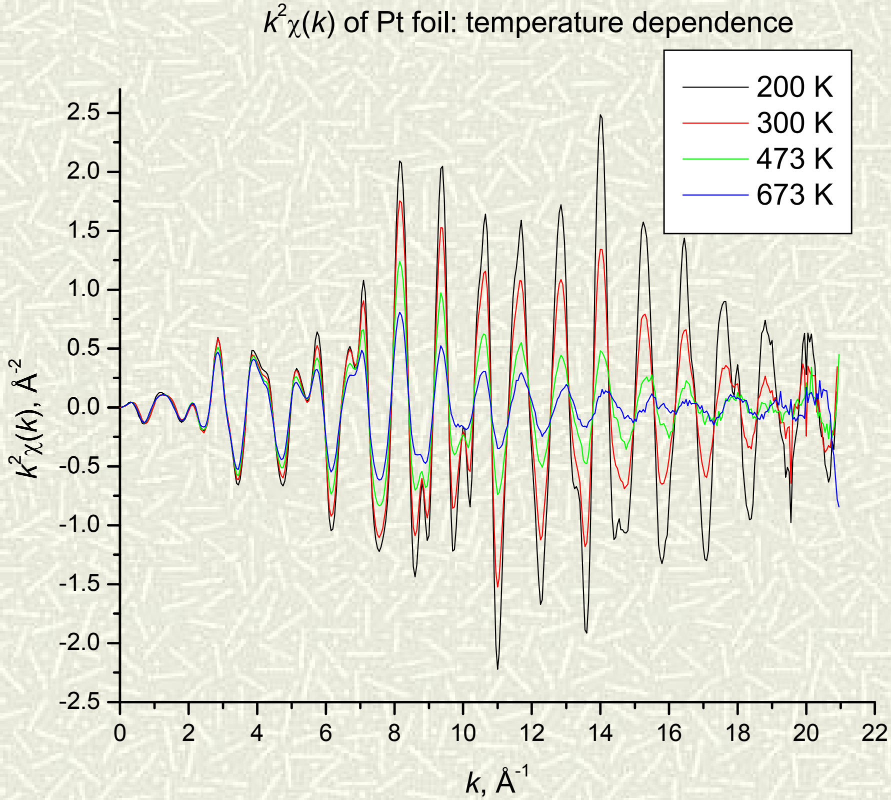
- correlation with other fit variables:

$$\chi(k)=\frac{NS_0^2}{kr^2}\left|f^{\mathrm{eff}}(k)\right|\mathrm{e}^{-2\sigma^2k^2}$$

$$\times\sin\left[2kr-\tfrac{4}{3}C_3k^3+\delta(k)\right]$$

How to break the correlation?

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



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

What variables are not expected to change at different temperatures?

ΔE_0, N $\qquad \sigma_s^2, \Theta_E$

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

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

Multiple-Data-Set Fit

```
title = Pt L3-edge, foil
data  = ptfoil-200avk.chi    out = ptfoil-200avk
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

data  = ptfoil-300avk.chi   out = ptfoil-300avk
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
........ ptfoil-473avk.chi .......
next data set
........ ptfoil-673avk.chi .......

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
```

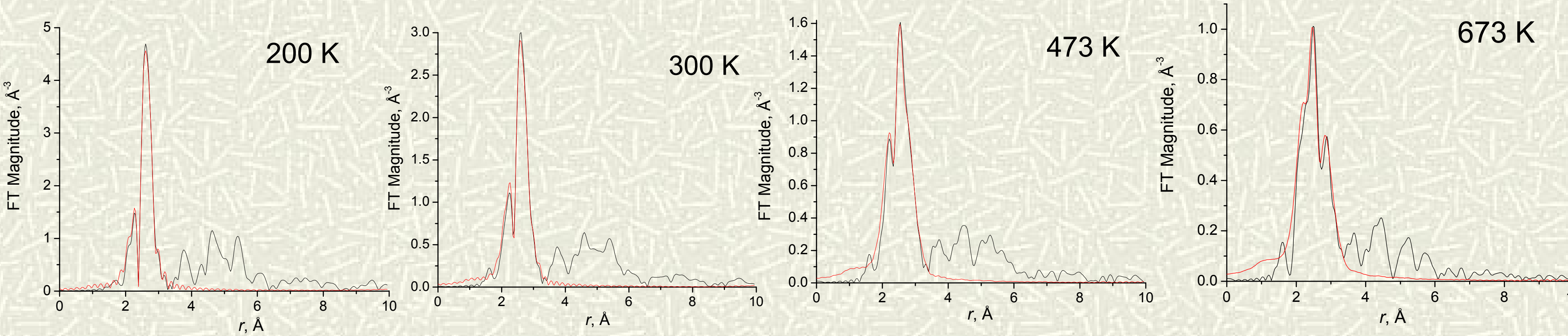
$$\sigma^2 = \sigma_s^2 + \sigma_d^2$$

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

```
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?

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

Pretend, we do not believe in "third cumulants".

With C_3

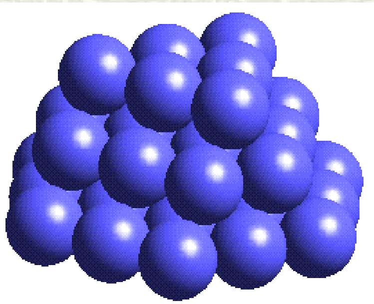
ss011	=	0.000533	0.000093
theins1	=	189.743073	2.311668
s02	=	0.836704	0.017830
dr11	=	-0.011222	0.002248
dr12	=	-0.009361	0.003034
dr13	=	-0.000354	0.003642
dr14	=	0.006588	0.004801
th11	=	-0.000035	0.000013
th12	=	-0.000017	0.000022
th13	=	0.000113	0.000033
th14	=	0.000267	0.000060
e0	=	8.064717	0.271896

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?

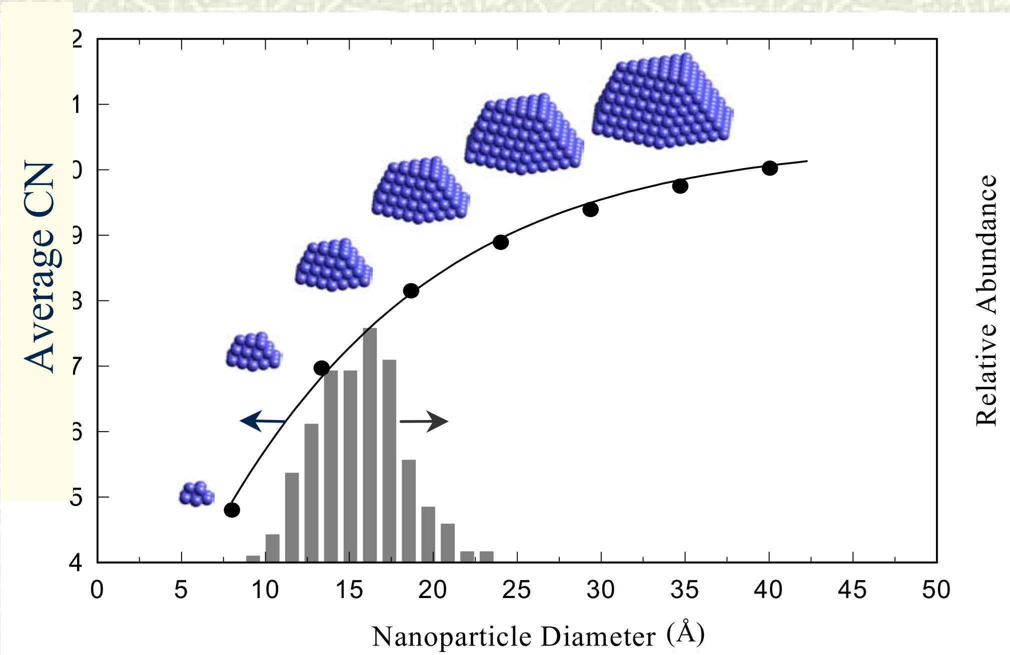
A priori knowledge or a working hypothesis must exist
(the "zero" approximation)
otherwise: the transferability of amplitude/phase will not work!)



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

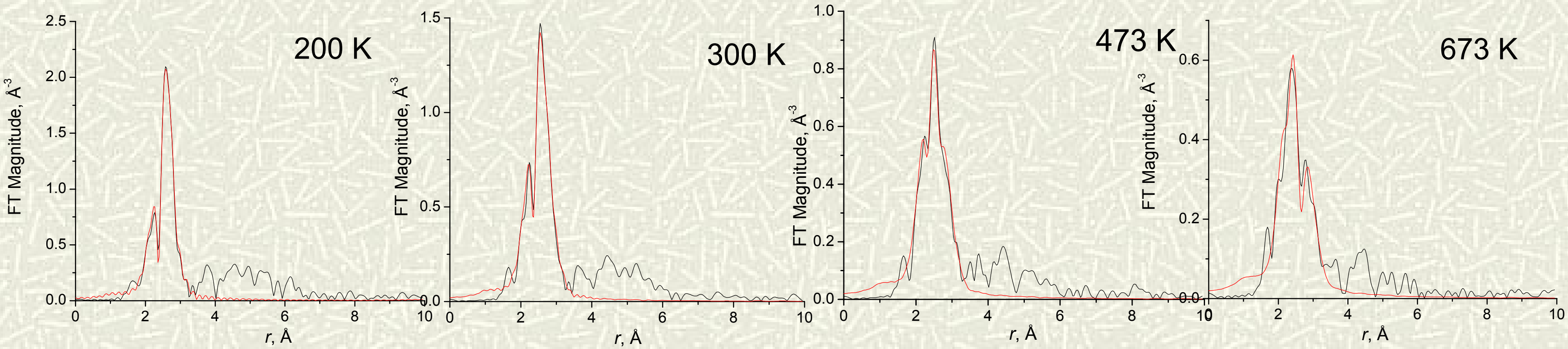
What information can be obtained from 1st shell EXAFS analysis?

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



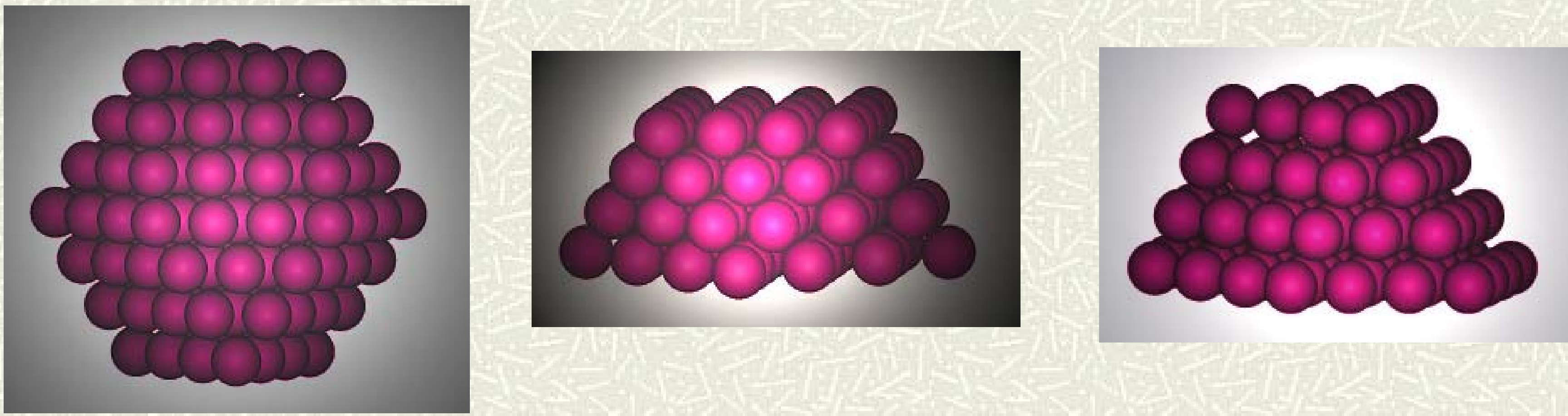
ss011	=	0.001676	0.000177
theins1	=	191.842209	3.893480
n1	=	7.879327	0.197850

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

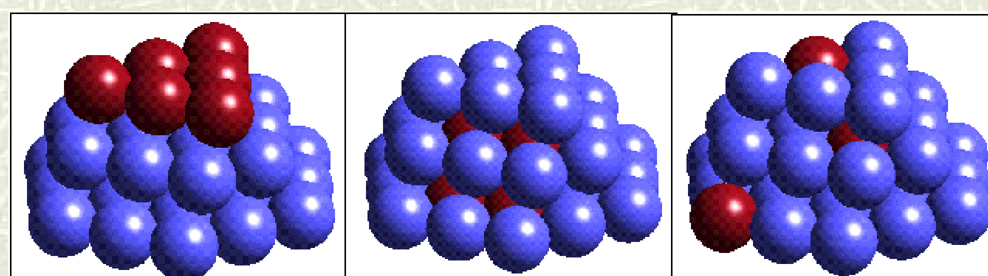
To get the most out of the data, the Multiple-Scattering Analysis is often needed.

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:



References

(send reprint requests to: frenkel@bnl.gov)

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