XAFS Analysis of Nanostructured Materials

Anatoly Frenkel

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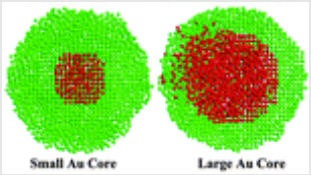
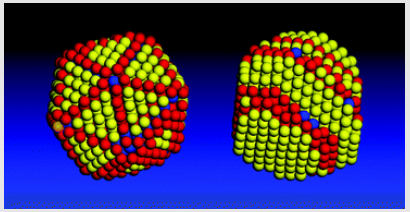
Synchrotron Catalysis Consortium, Brookhaven National Laboratory





“Core-shell motif” is in the eyes of the beholder:

EXAFS and nanomaterials

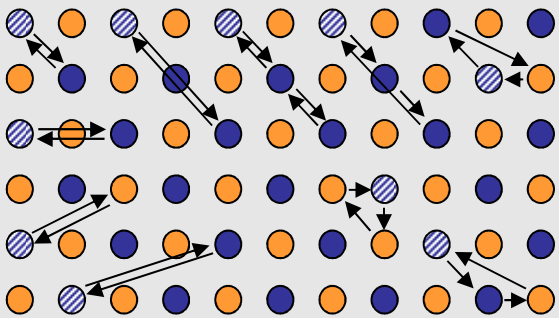
- structure, disorder in a nanoscale object,

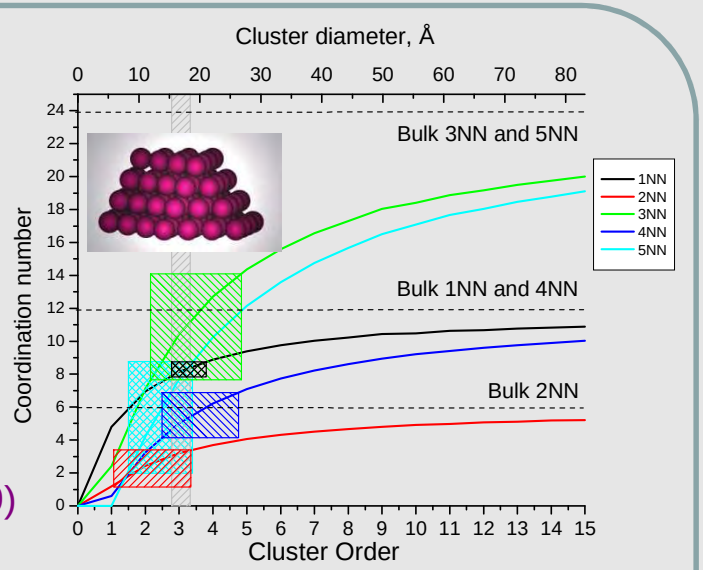
-dynamics and kinetics during in situ transformations

-investigation of mechanisms of work

- methods of *in-operando* studies

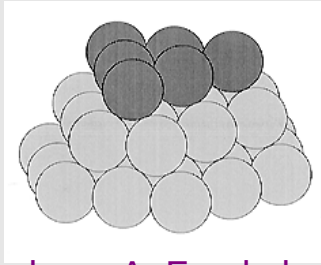
Getting size, shape, morphology from EXAFS



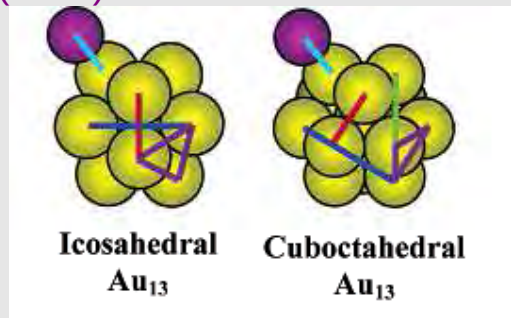


A. I. Frenkel,
J. Synchrotron Rad., **6**, 293 (1999)

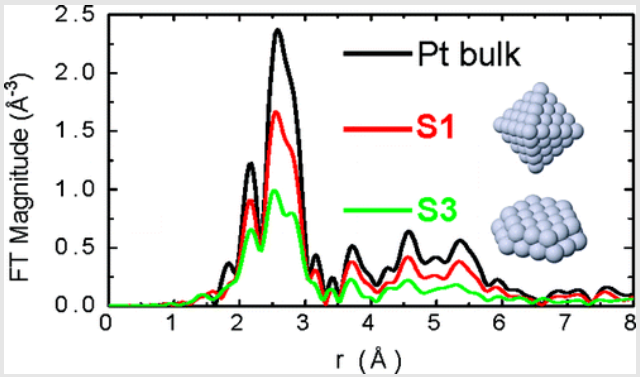
A. I. Frenkel, C. W. Hills, and R. G. Nuzzo,
J. Phys. Chem. B **105**, 12689 (2001).



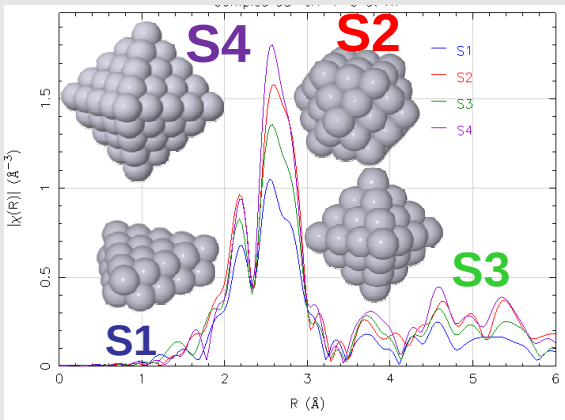
M. Nashner, A. Frenkel, et al,
J. Am. Chem. Soc. **119**, 7760 (1997)



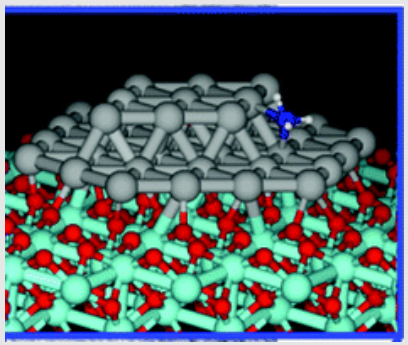
L. Menard et al,
J. Phys. Chem. B. **110**, 14564(2006)



B. R. Cuenya et al,
J. Am. Chem. Soc. **132**, 8747 (2010)

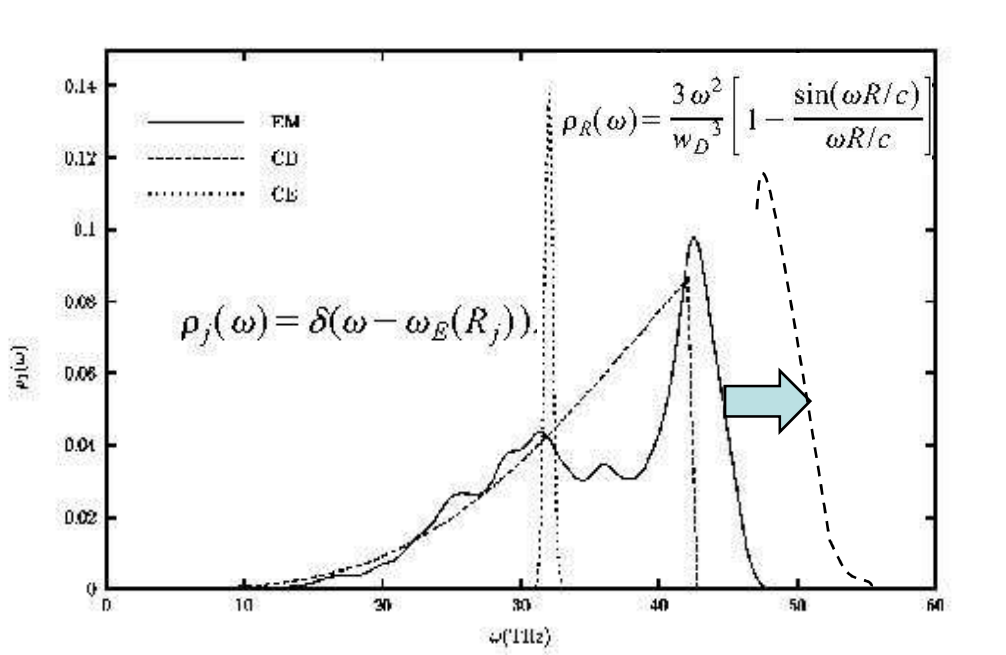


B. Roldan Cuenya, A. I. Frenkel, et al,
Phys. Rev. B. **82**, 155450 (2010)



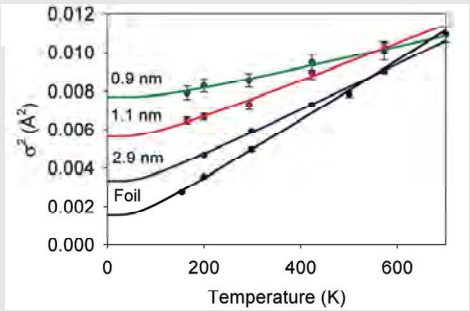
A. Karim, et al,
J. Am. Chem. Soc. **131**, 12230 (2009)

Projected vibrational density of states
vs Einstein and Debye models

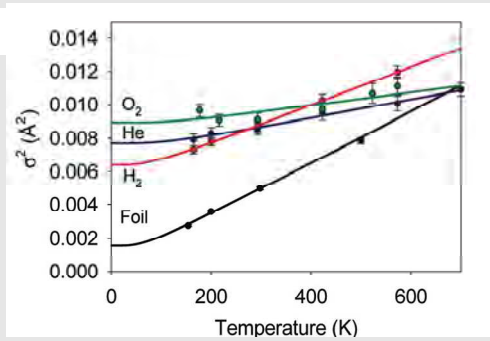


High frequency modes➔ force constant stiffening

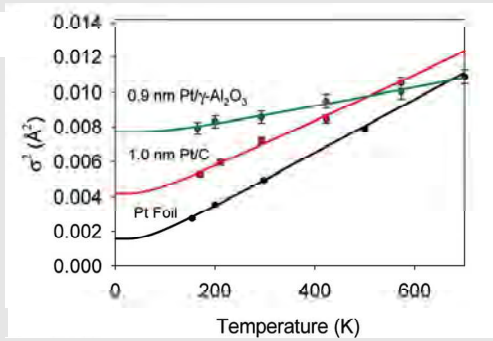
Nanoparticle dynamics



Cluster size effect



Ambient gas effect



Support effect

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

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

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

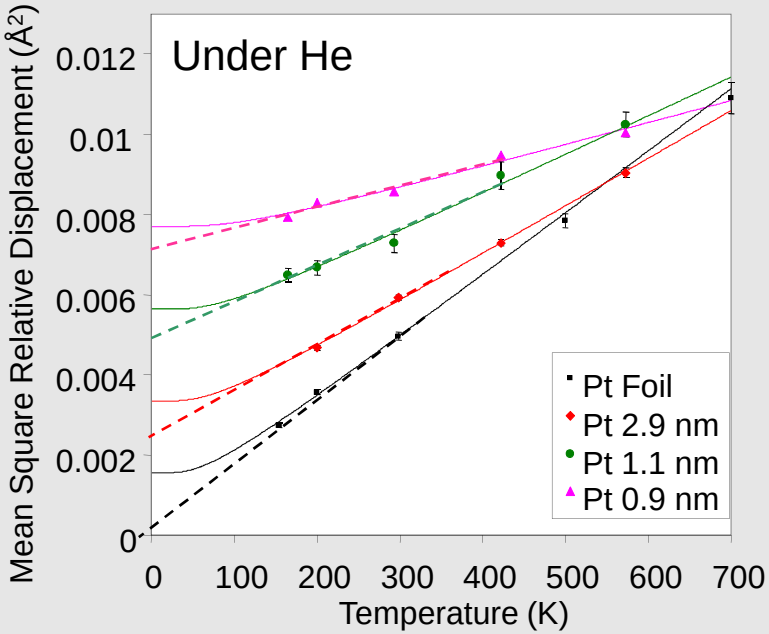
$$\sigma_j^2(T) = \frac{\hbar}{2\mu_j}\int_0^{\omega_{max}} \frac{d\omega}{\omega}\rho_j(\omega)\coth\frac{\beta\hbar\omega}{2}.$$

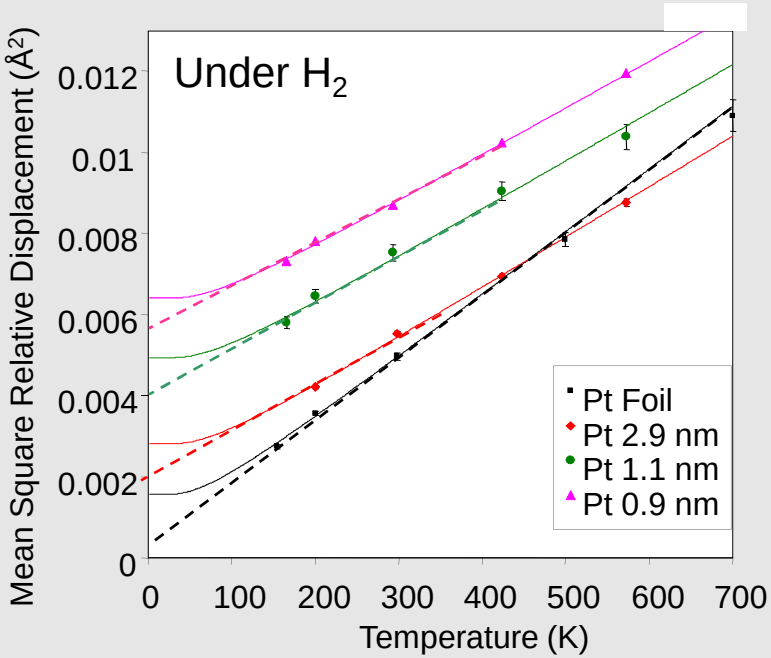
A. Poiarkova, J. Rehr, *Phys. Rev. B* **59**, 948 (1999)

HT limit: $\sigma_d^2 = \frac{k_B T}{k}$

Force constant: $k = \mu\omega^2$

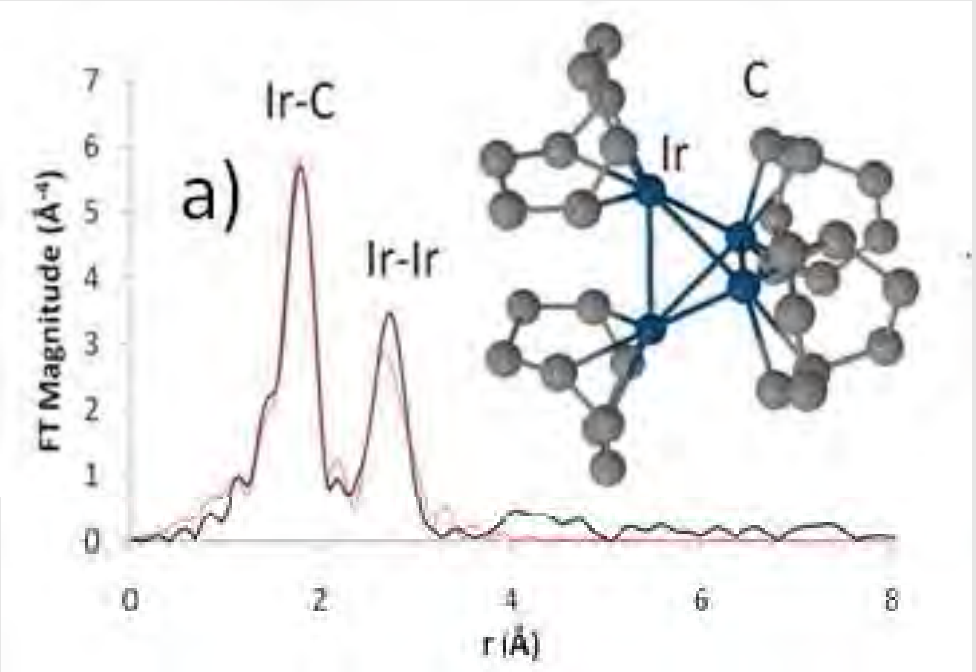
Einstein temperature: $\hbar\omega = k_B\Theta_E$

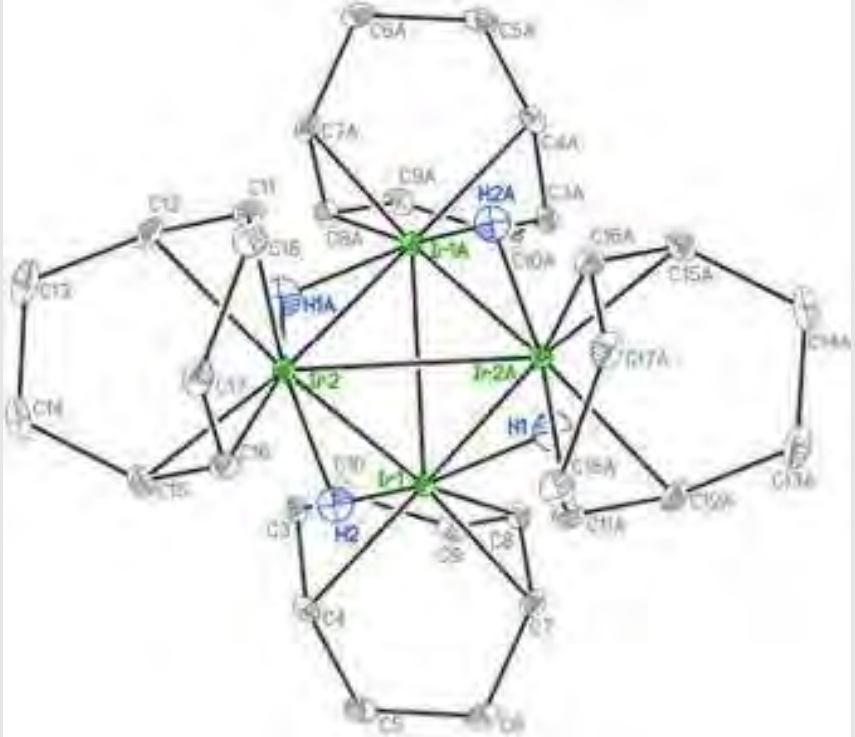




S. I. Sanchez, et al, *JACS*, **131** , 7040, 2009.

How do we know that the EXAFS results are correct at the finite size scale?





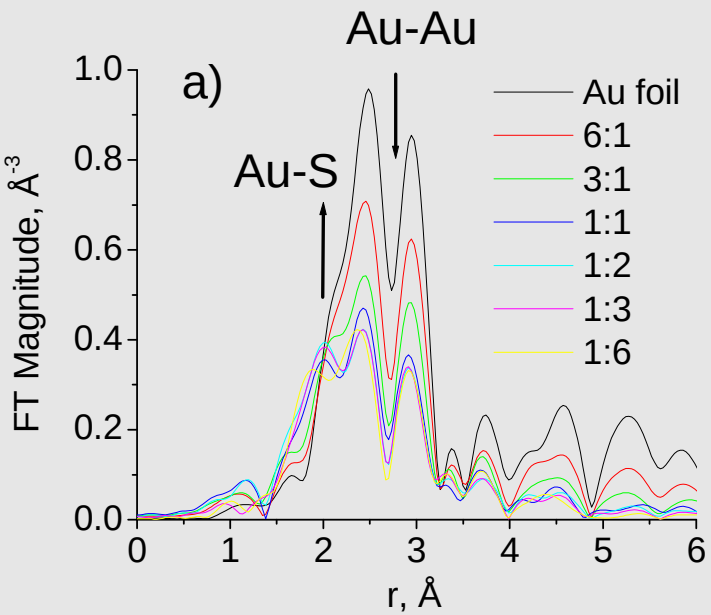
XRD-derived structure: CN(Ir-Ir) = **3**, CN(Ir-C) = **4**
EXAFS results: **2.9 ±1.2** and **4.5 ± 0.7**

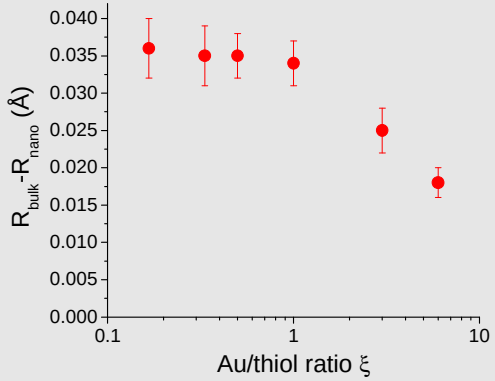
Average distance (over all Ir atoms in the structure):

Ir-Ir: XRD: **2.83 Å**; EXAFS: **2.81 ±0.01 Å**
Ir-C: XRD: **2.16 Å**; EXAFS: **2.15 ±0.01 Å**

K.-H. Yih, I. K. Hamdemir, et al, *Inorg. Chem.* 51, 3186 (2012)

Finite size effect on bond length: input for electronic structure theories ⇒ adsorption energy calculations



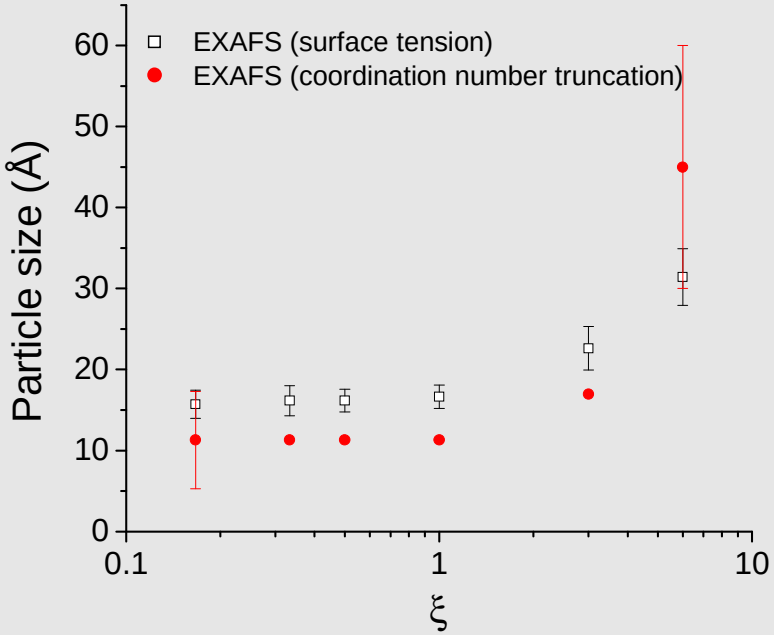


$$d = \frac{4}{3}\frac{\gamma\kappa}{\alpha}$$

Particle diameter:
measured by EXAFS/TEM

$$\alpha = \frac{\Delta R}{R} = \frac{\Delta a}{a}$$

Lattice contraction:
Measured by EXAFS



Mays, Vermaak, Kuhlmann-Wilsdorf, *Surf. Sci*. 12, 134 (1968).

A. I. Frenkel, S. Nemzer, I. Pister, et al *J. Chem. Phys*. 123, 184701 (2005).

Lattice dynamics measurements: input for surface free energy calculations

$$\Delta F^{vib} = -k_B T \ln Z^{vib}$$

$$\Delta F^{vib} = \frac{1}{N_{Pt}}\left(k_B T \sum_j \ln\left[2\sinh\left(\frac{h\nu_j}{2k_B T}\right)\right]\right)$$

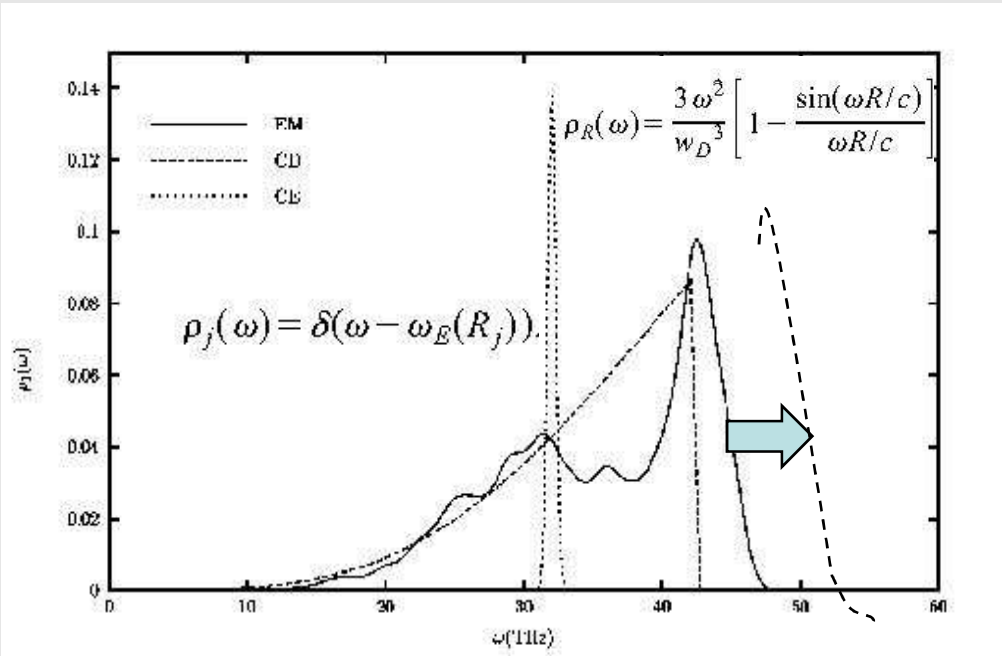
$$S = -\frac{\partial F}{\partial T}$$

$$E = F + TS$$

$$C = -\frac{\partial E}{\partial (k_B T)}$$

V. Grigoryan and M. Sprinberg *Phys. Rev. B* 83, 155413 (2011).

Lattice dynamics of NPs: Debye model + Debye temp→ V-DOS



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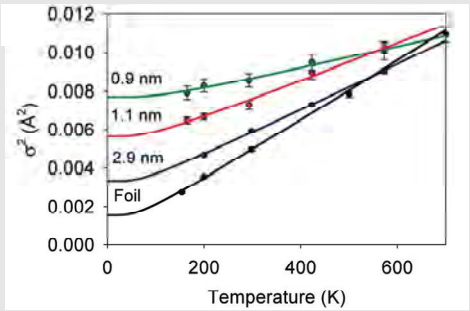

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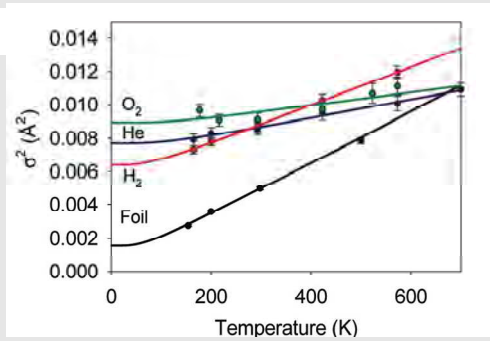

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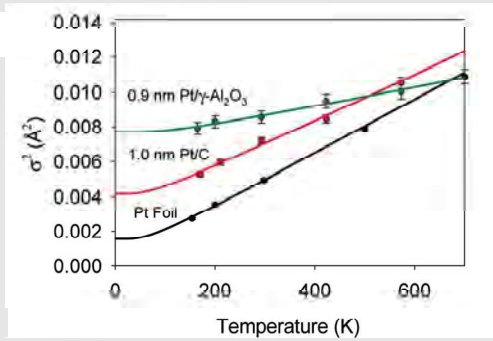

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A. Poiarkova, J. Rehr, *Phys. Rev. B* 59, 948 (1999)

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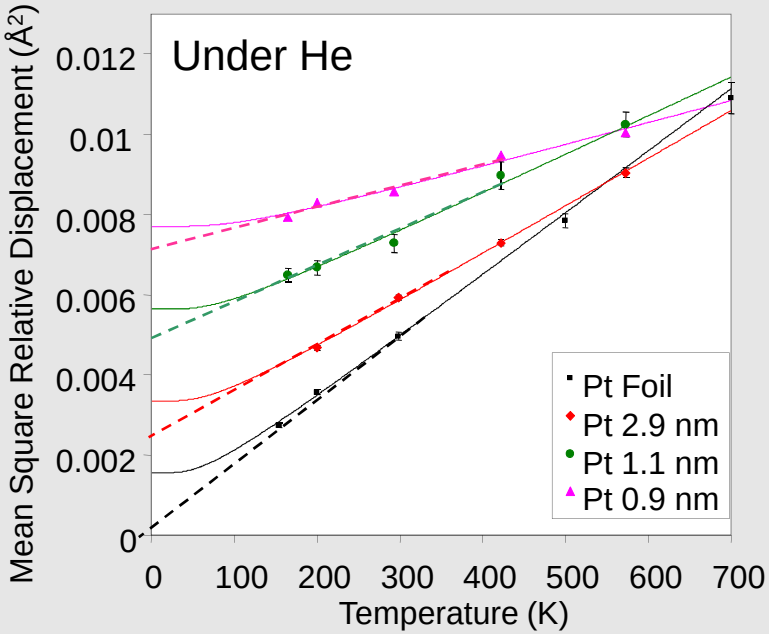
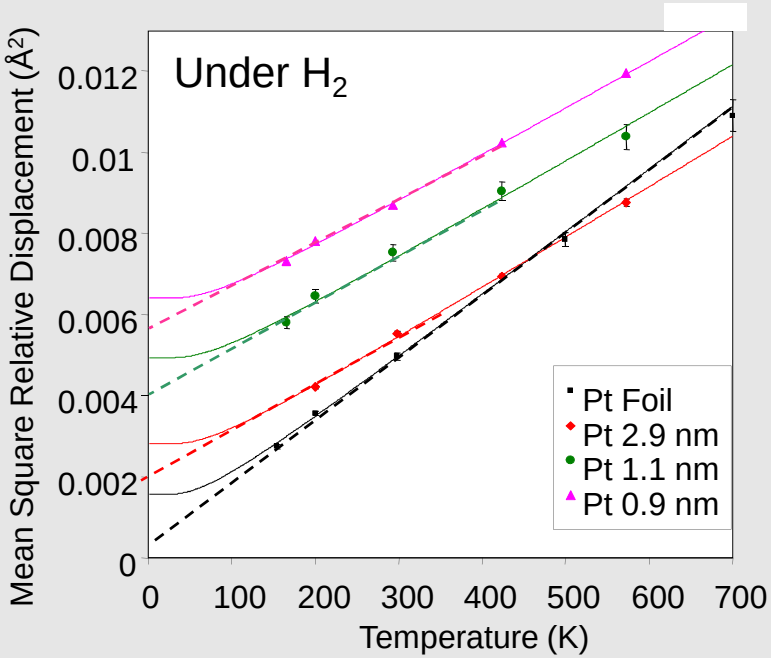
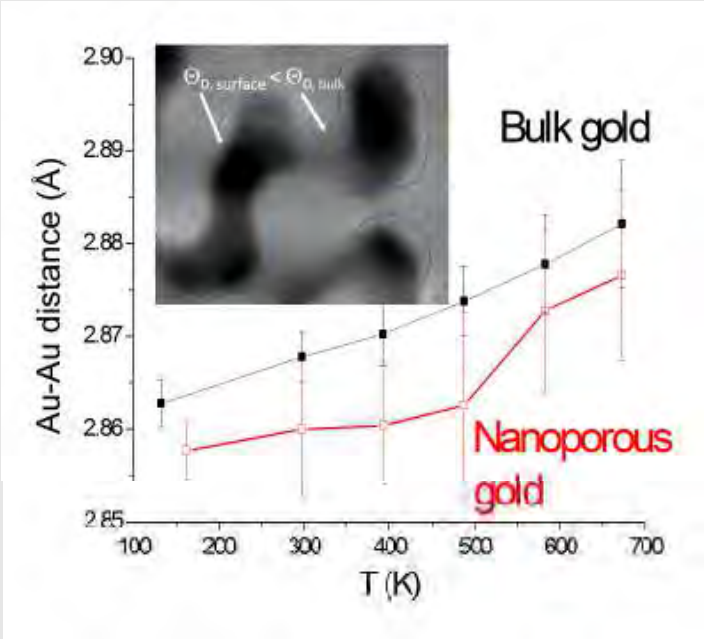
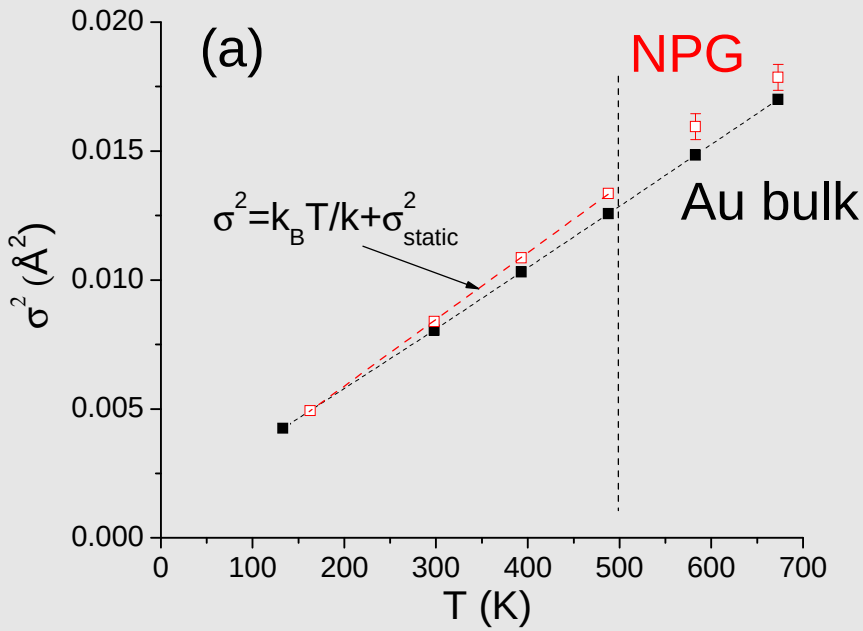




S. I. Sanchez, et al, *JACS*, 131 , 7040, 2009.

Finite size effects in nanoporous gold: structure and dynamics





Model: Bimodal bond distribution
(unimodal distribution contradicts the data)

$$\tilde{\Theta}_D = \frac{N_B}{N}\Theta_{D,\,bulk} + \frac{N_S}{N}\Theta_{D,surface}$$

High Debye T. in the bulk
Low Debye T. in the surface (*m* layers)

$$\xi = \frac{n_S}{n_B} = \frac{V_0/V}{1-V_0/V} = \frac{md\eta}{1-md\eta}$$

$m = 3.7 \pm 0.4$

A. Frenkel, R. Vasic, B. Dukesz, D. Li, M. Chen, L. Zhang, T. Fujita, *Phys. Rev. B*, 85, 195419, (2012).

Bond length disorder and strain energy

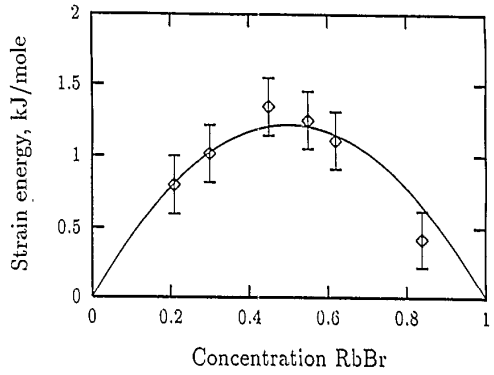


Fig. 4. Strain energy in crystalline $RbBr_xCl_{1-x}$. Shown by the solid curve is the best fit of the parabola $W = W_0 x(1-x)$ to the points.

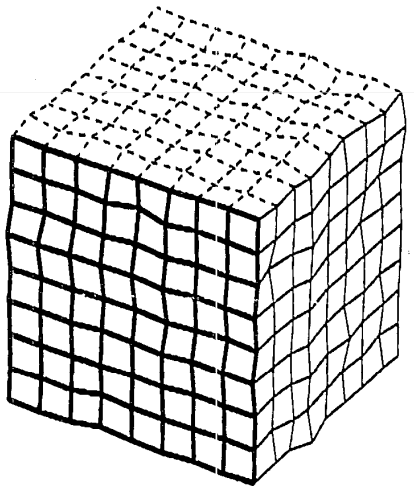
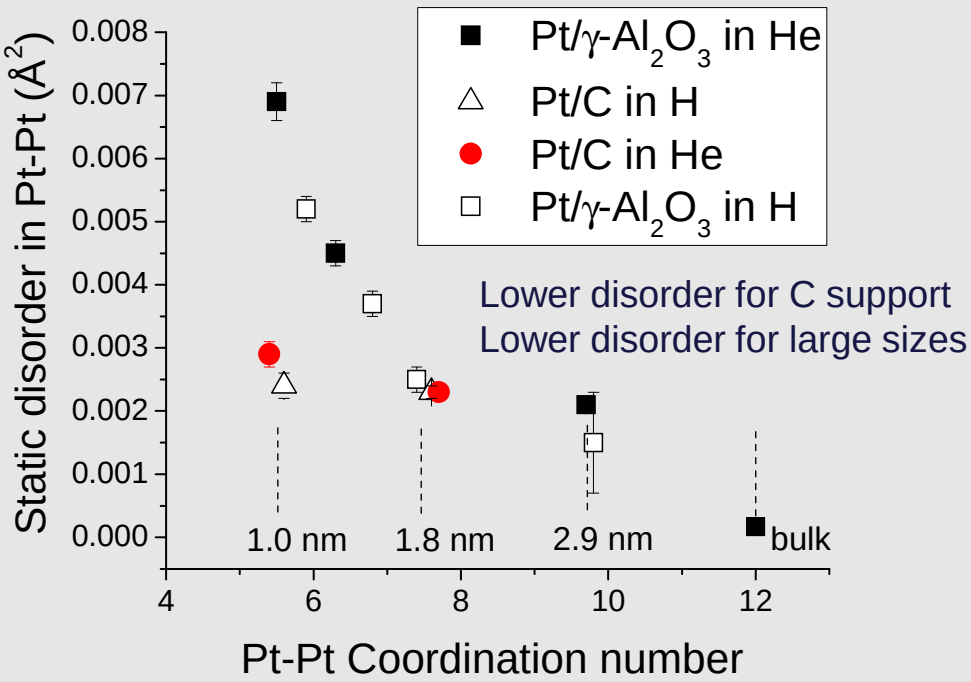


Fig. 5. Equilibrium atomic configurations in $RbBr_{0.55}Cl_{0.45}$.

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

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



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

$$U = \frac{1}{2} Nk\sigma^2$$

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

$$W = \frac{1}{2} Nk\sigma_s^2$$

Residual, static disorder can be used to calculate strain energy:

M. Small, S. Sanchez, N. Marinkovic, A.I. Frenkel, R. G. Nuzzo, *ACS Nano* 6, 5583 (2012)

Challenges: non-Gaussian disorder is typical in NPs.

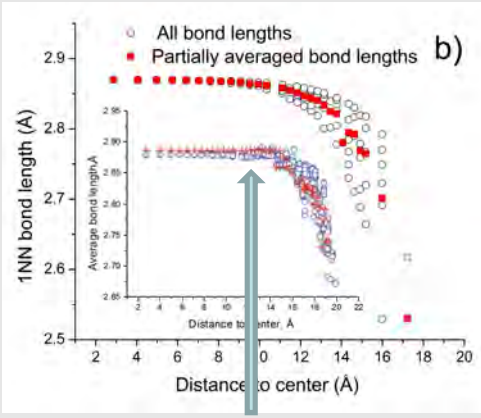
❖Estimating effect of surface tension on EXAFS results obtained by cumulant expansion methods

❖Histogram approach: generate RDF using MD/DFT simulations or XRD refinement data

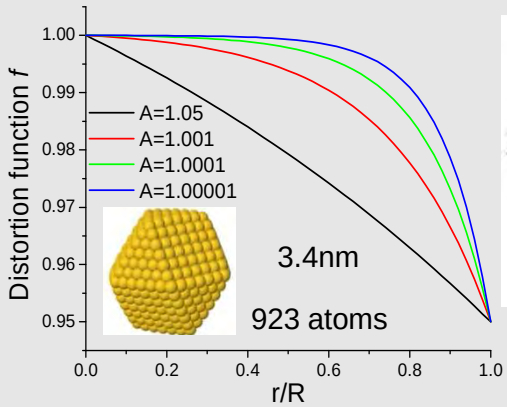
❖Generate model EXAFS data using FEFF

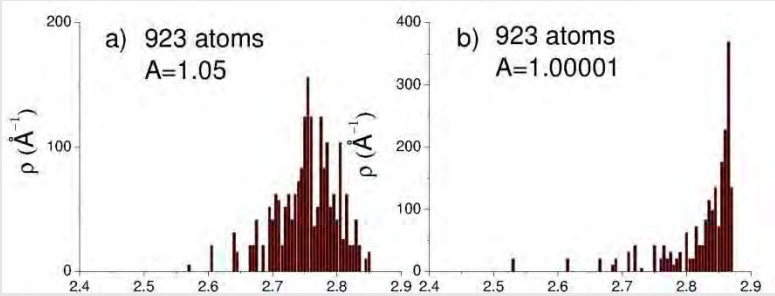
❖Evaluate artifacts by comparing with "known" structure

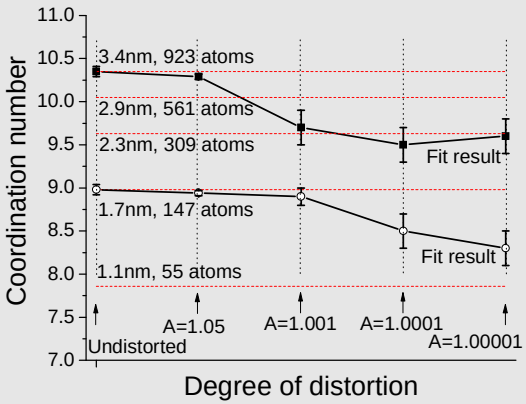
Surface tension effect

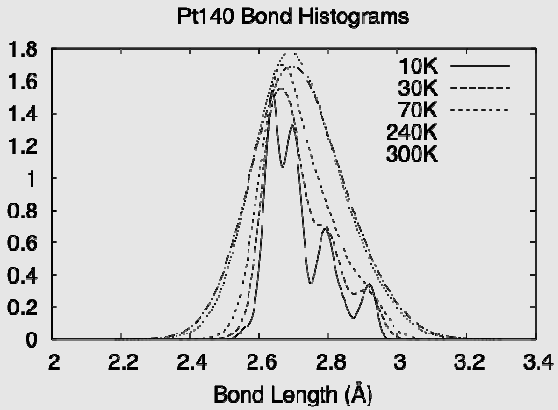


W. Huang, et al, *Nature Materials* **7**, 308 (2008)







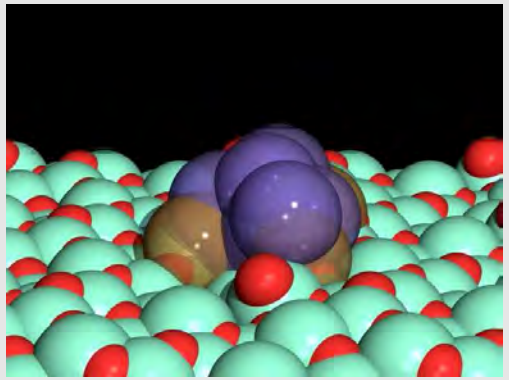


S. Chill, G. Henkelman, A. Yevick, A. I. Frenkel, unpublished

A. Yevick, A. I. Frenkel, *Phys. Rev. B* **81**, 115451 (2010)

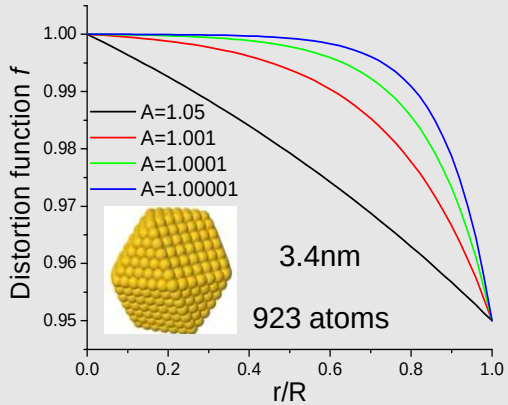
How to account for non-bulklike structural dynamics?

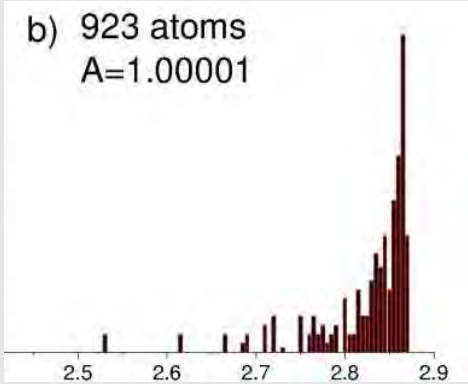
MD/DFT/FEFF



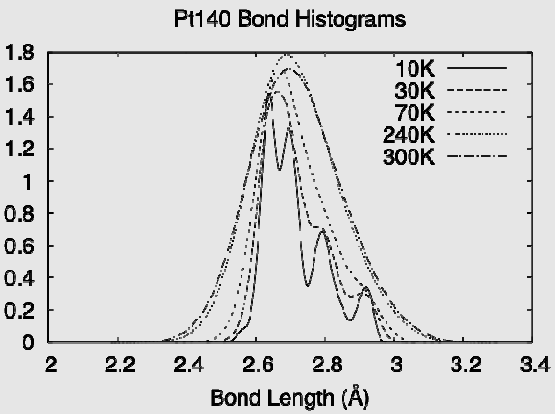
F. Vila, J. Rehr, J. Kas, R. Nuzzo, A. Frenkel
Phys. Rev. B 78, 121404 (2008)

Histogram approaches

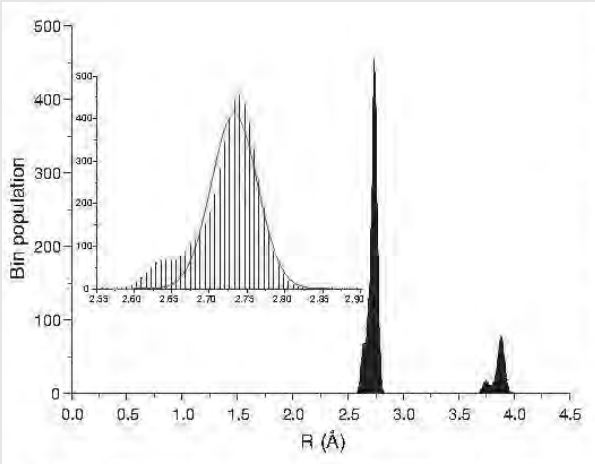




A. Yevick, A. I. Frenkel,
Phys. Rev. B 81, 115451 (2010)

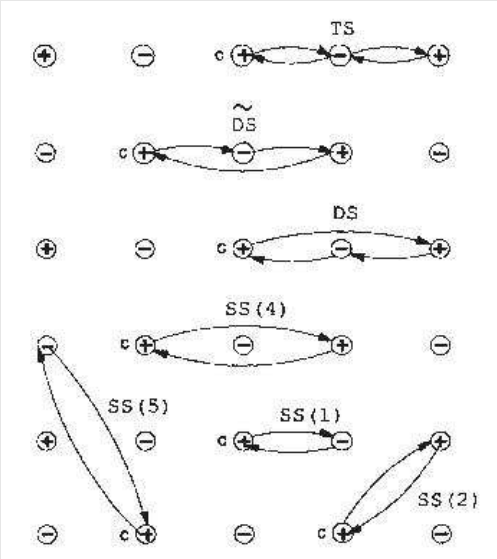


S. Chill, G. Henkelman, A. Yevick, A. I. Frenkel, unpublished



S. Price, N. Zonias, C. Skylaris, T. Hyde, B. Ravel, A. Russell
Phys. Rev. B 85, 075439 (2012)

Challenges: Effects of bond buckling on multiple scattering EXAFS analysis results



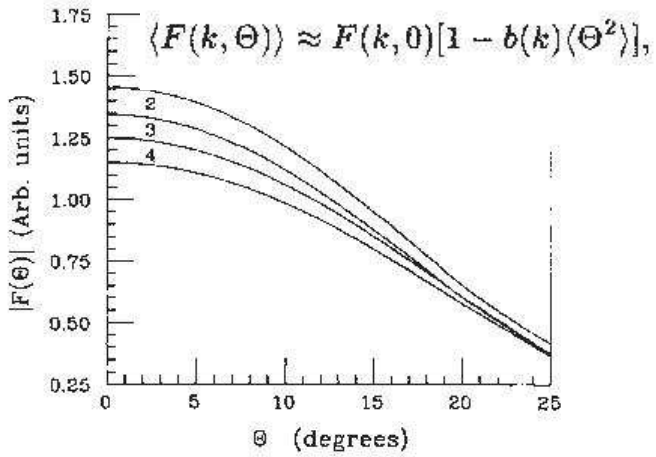
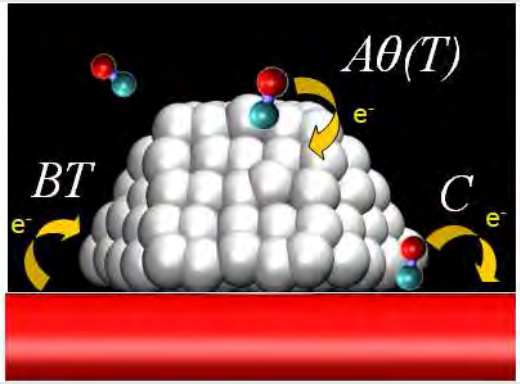
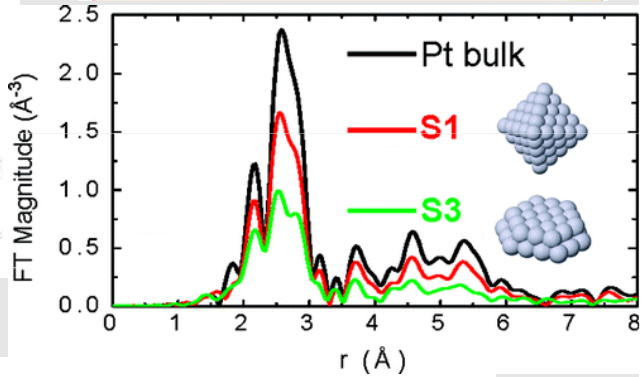


FIG. 4. $F(k,\Theta)$ ($k = 8\,\text{Å}^{-1}$) of nearly collinear DS paths: (1) Br-Rb^1-Br^4-Br; (2) Rb-Br^1-Rb^4-Rb; (3) Br-K^1-Br^4-Br; (4) Rb-Cl^1-Rb^4-Rb. Superscripts indicate the coordination shell.





VOLUME 71, NUMBER 21 PHYSICAL REVIEW LETTERS 22 NOVEMBER 1993

Buckled Crystalline Structure of Mixed Ionic Salts

A. Frenkel,[1] E. A. Stern,[2] A. Voronel,[1] M. Qian,[2] and M. Newville[2]
[1] *School of Physics and Astronomy, Tel Aviv University, Ramat Aviv 69978, Israel*
[2] *Department of Physics, FM-15, University of Washington, Seattle, Washington 98195*

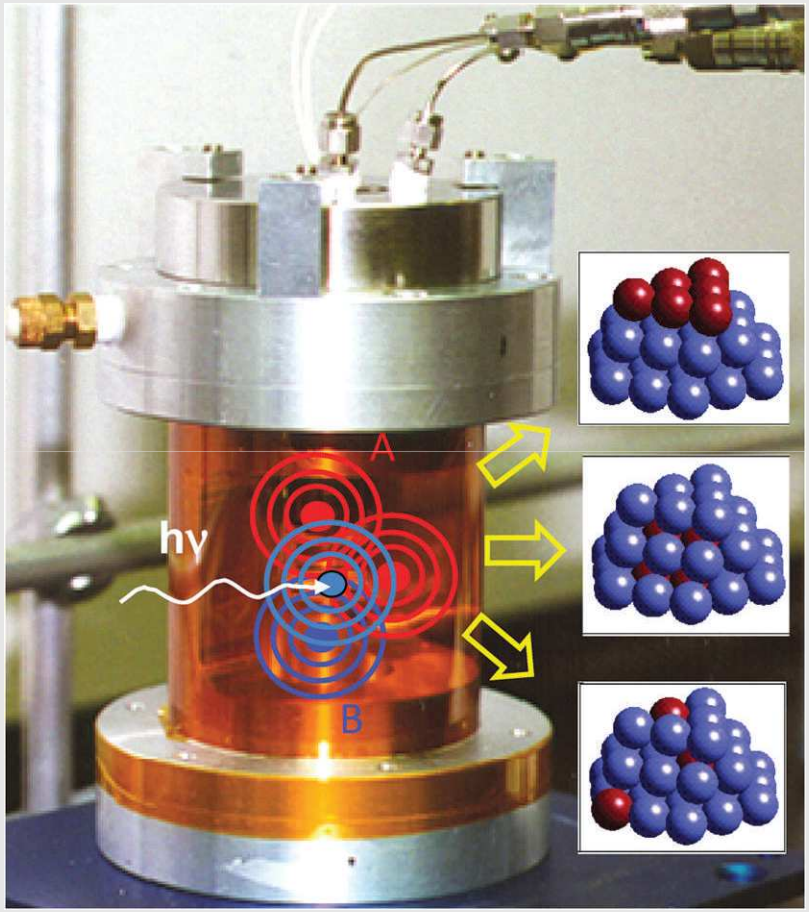
PHYSICAL REVIEW B VOLUME 49, NUMBER 17 1 MAY 1994-I

Solving the structure of disordered mixed salts

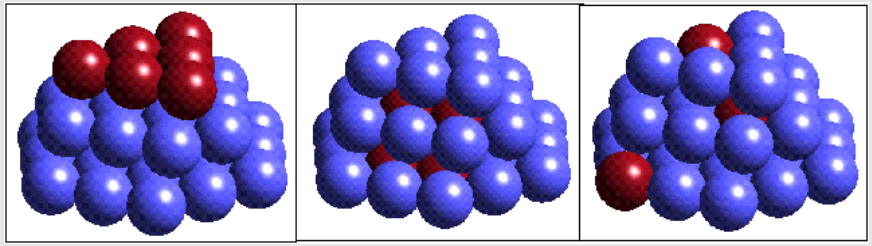
Alloys at the Nanoscale

❖Coordination numbers and S.R.O

❖Artifacts due to ensemble averaging



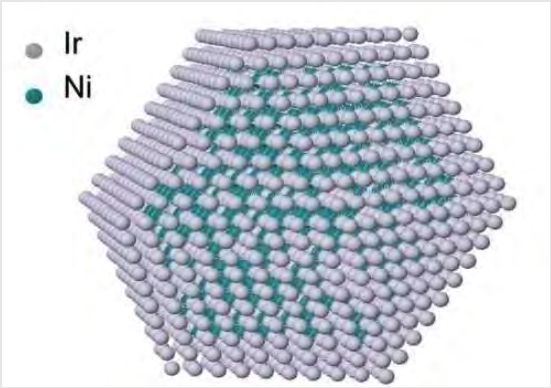
Homogeneity and short range order in nanoparticle alloys:



Homogeneity: n_{AM}, n_{BM}, n_{MM}

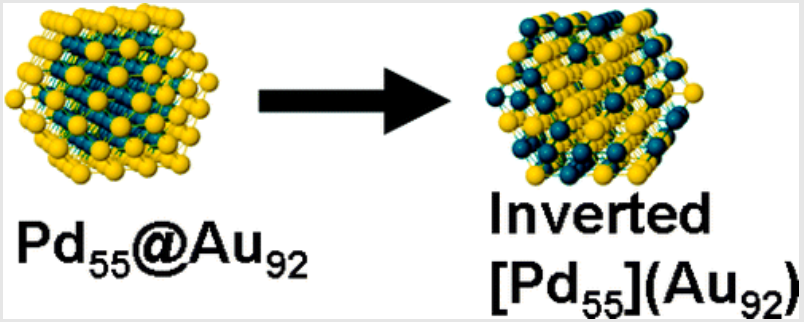
Short range order: $\alpha = 1 - \frac{n_{AB}/n_{AM}}{x_B}$

A. Frenkel
Z. Kristallogr., **222**, 605 (2007)

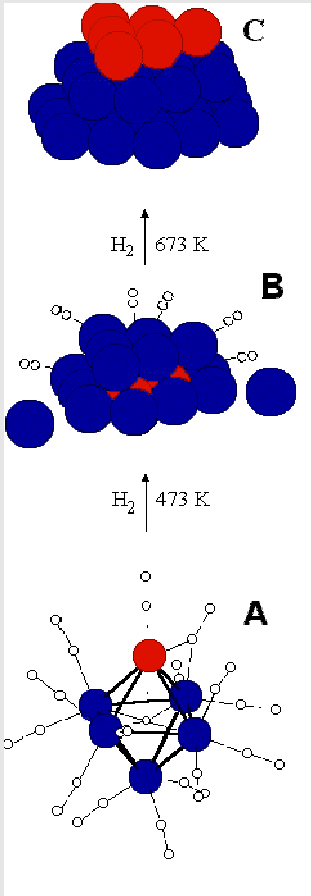


K. Sasaki, et al
J. Phys. Chem. C **115**, 9894 (2011)

S. Alayoglu, et al
ACS Nano **3**, 3127 (2009)



M. Weir, M. Knecht, A. Frenkel,
R. Crooks, *Langmuir* **26**, 1137 (2010)



M. Nashner, A. Frenkel, et al,
J. Am. Chem. Soc. **120**, 8093 (1998)

PHYSICAL REVIEW VOLUME 77, NUMBER 5 MARCH 1, 1950

An Approximate Theory of Order in Alloys*,**

J. M. COWLEY***
Department of Physics, Massachusetts Institute of Technology, Cambridge,
(Received October 26, 1949)

PHYSICAL REVIEW VOLUME 120, NUMBER 5 0

Short- and Long-Range Order Parameters in Disordere

J. M. COWLEY
Division of Chemical Physics, Commonwealth Scientific and Industrial Research Organiz
(Received June 23, 1960)

PHYSICAL REVIEW VOLUME 138, NUMBER 5A

Short-Range Order and Long-Range Order Parameters

J. M. COWLEY
Department of Physics, University of Melbourne, Victoria, Australia
(Received 28 August 1964)

The equations for the short-range order parameters relating to ordering in binary solid solutions, as previously derived by the author, have been rederived in a more satisfactory manner. Applying the equations to situations with long-range order, a more complete analysis of predictions regarding multiple long-range order parameters has been made. It is shown that long-range order parameters may be redefined in such a way that they provide a reasonable description of the state of order in situations involving finite crystal size, finite out-of-phase domain size, and fluctuations in composition.

DEFINITION OF SHORT-RANGE ORDER PARAMETERS

For an alloy consisting of A and B atoms, present in the proportions m_A and m_B, we define the short-range order parameter for the atomic site with coordinates l, m, n with respect to a given B atom as $\alpha_{lmn} = 1 - p_{lmn}/m_A$ where p_{lmn} is the probability that the atomic site is occupied by an A atom. Then

$$p_{lmn} = m_A(1 - \alpha_{lmn}).$$

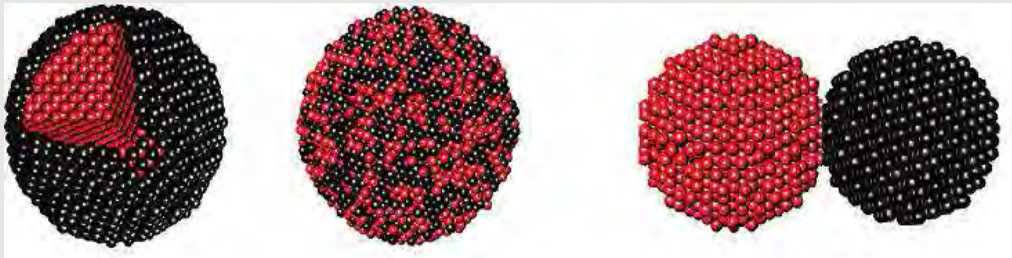
Alternatively, if the atom with coordinates l, m, n is considered to belong to the ith shell of neighbors surrounding a B atom, we may write $\alpha_i = 1 - n_i/m_A c_i$, where n_i is the number of A atoms among the c_i atoms of the ith shell.

J. Cowley,
Phys. Rev. 77, 669, 1950

Coordination numbers in clusters:

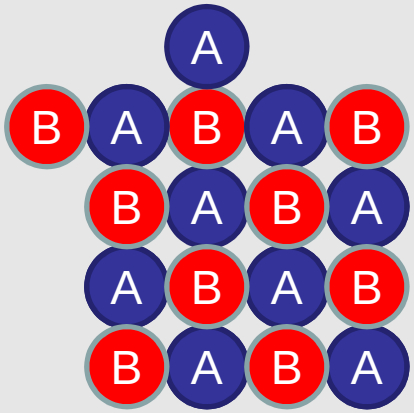
$$n_{AA} = \frac{2N_{AA}}{N_A} \qquad n_{AB} = \frac{N_{AB}}{N_A} \qquad n_{AM} = n_{AA} + n_{AB}$$

$$n_{MM} = x_A n_{AM} + x_B n_{BM}$$ -used for cluster size determination

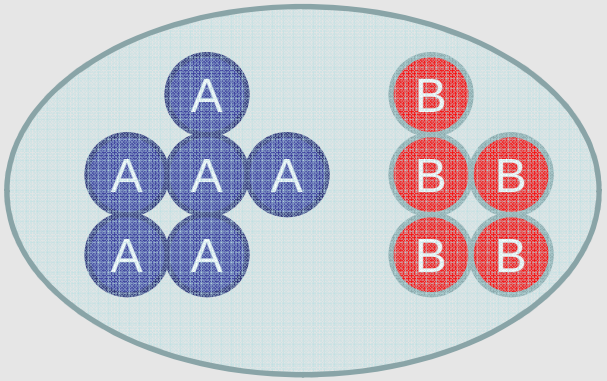


Short Range Order Parameter:

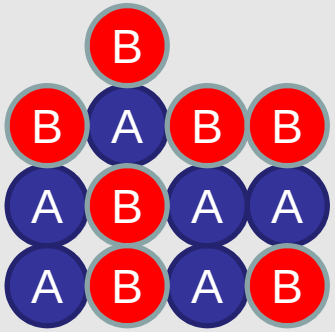
$$\alpha_{AB} = 1 - \frac{n_{AB} / n_{AM}}{x_B}$$



$$\alpha_{AB} = -1$$
$$\alpha_{BA} = -1$$



$$\alpha_{AB} = +1$$
$$\alpha_{BA} = +1$$



$$\alpha_{AB} = 0$$
$$\alpha_{BA} = 0$$

A. Frenkel, *Z. Kristallogr.*, 222, 605 (2007)

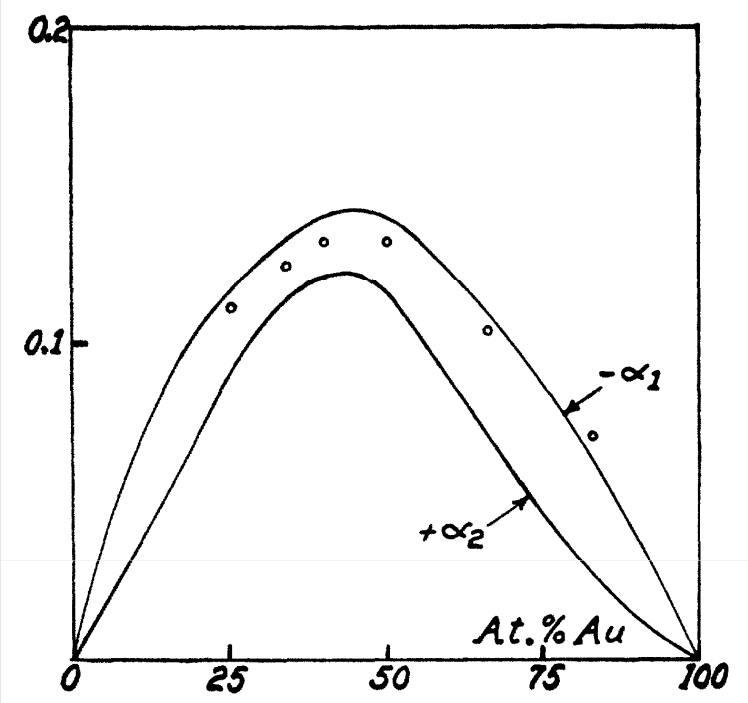
Short Range Order and Homogeneity

$$\alpha_{AB} = -1$$

$$+L.R.O.$$

$$\alpha_{AB} = 0$$

$$+L.R.O.$$



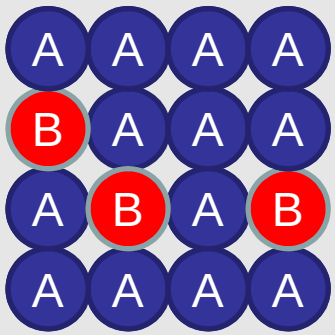
J. Cowley,
Phys. Rev. 77, 669, 1950

Homogeneity: $-1 \le \alpha_{AB} \le 0$

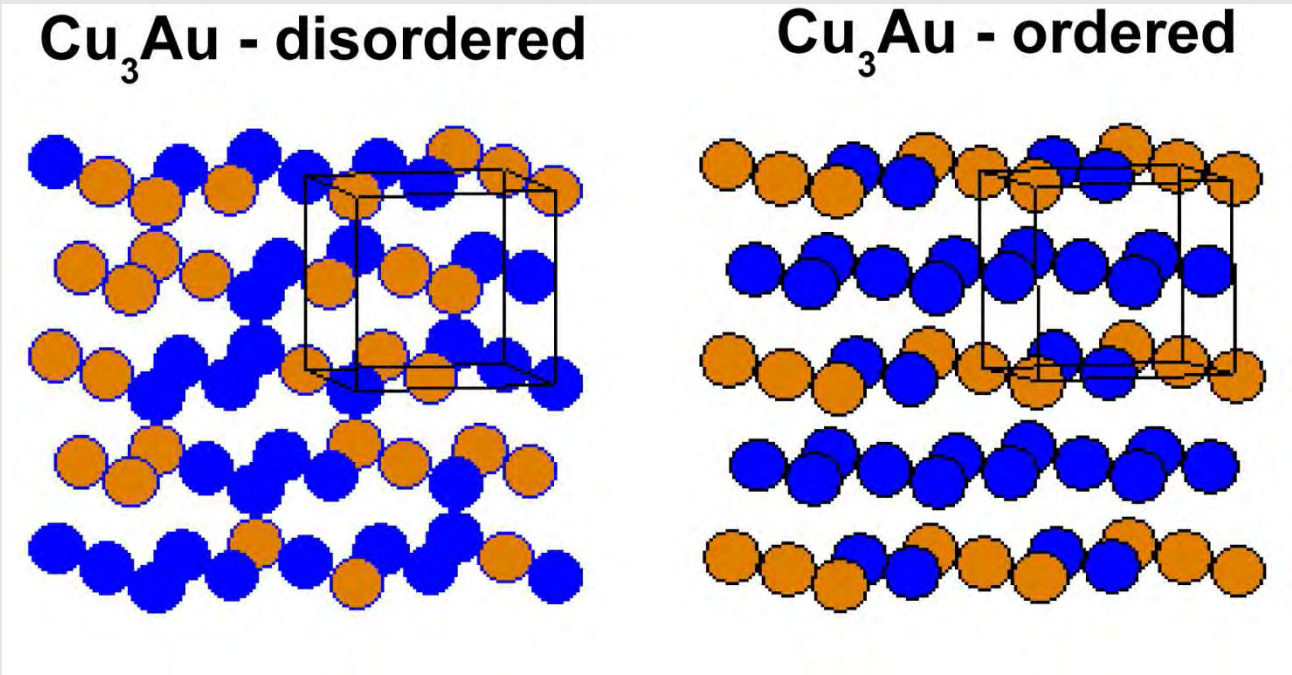
$2 \le N_{AB} \le 4$

Segregation tendency. (core/shell etc.) $\alpha_{AB} > 0$

$0 \le N_{AB} \le 2$

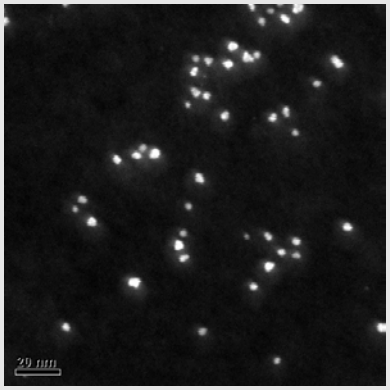


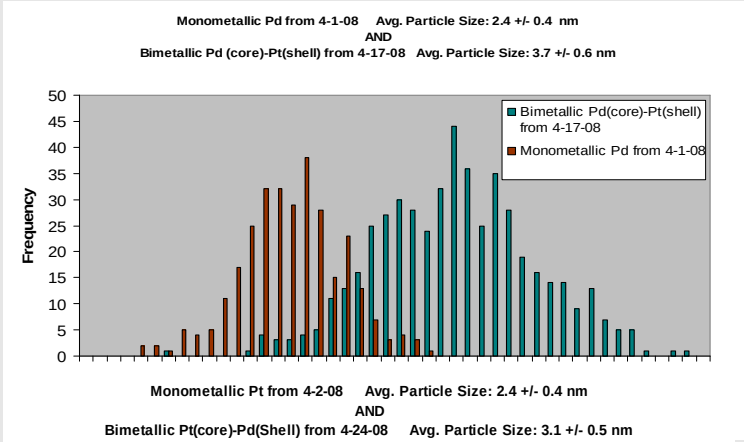
Binary alloys: Homogeneity and SRO in 3D



Homogeneity: $$-\frac{1}{3} \leq \alpha_{AB} \leq 0$$

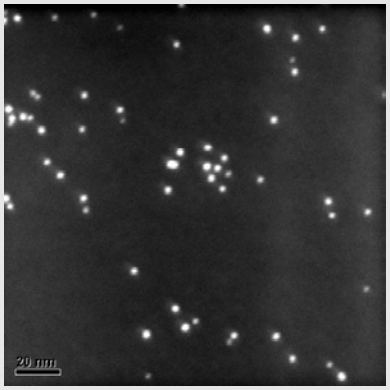
How accurate can such analysis be? A test is needed.

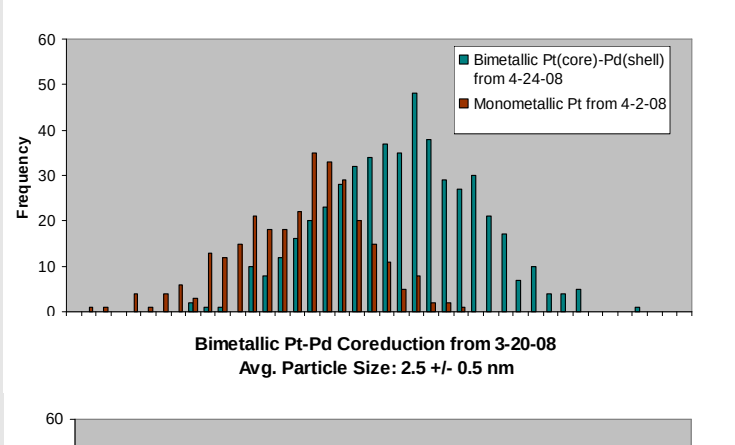




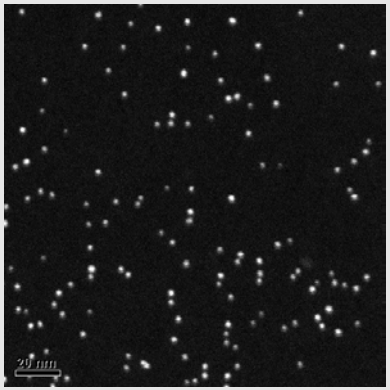
-A well controlled Pt-Pd bimetallic system (PVP-capped)

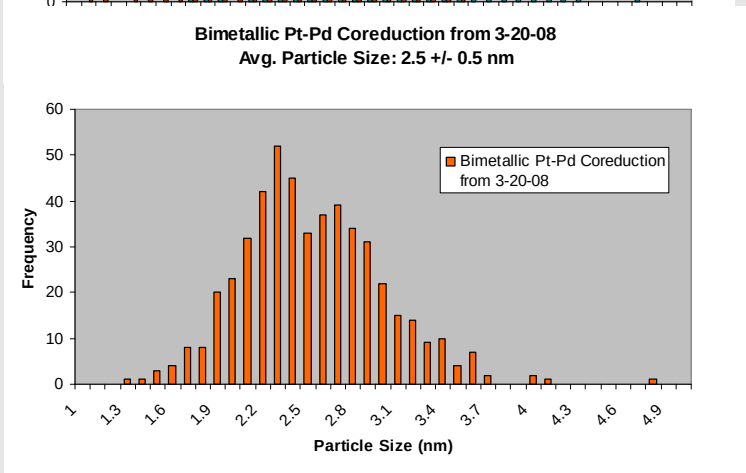
Pd(core) Pt(shell)





Pt(core) Pd(shell)

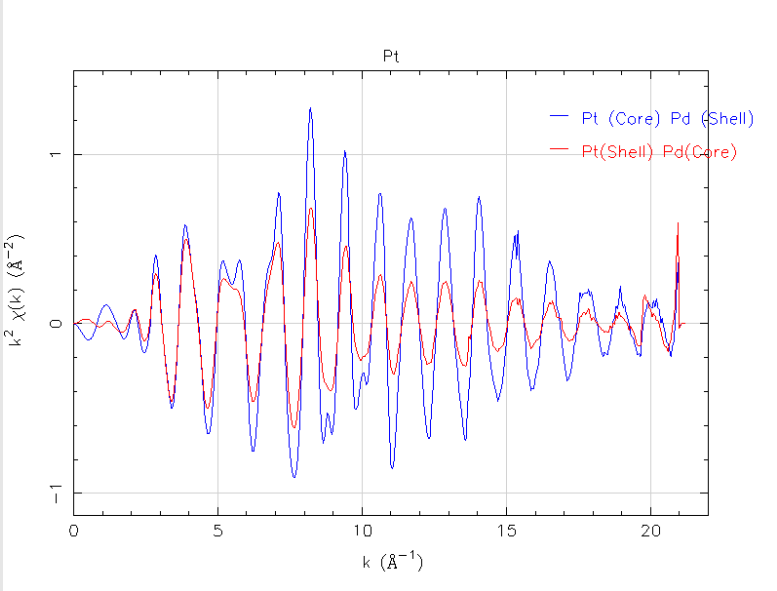


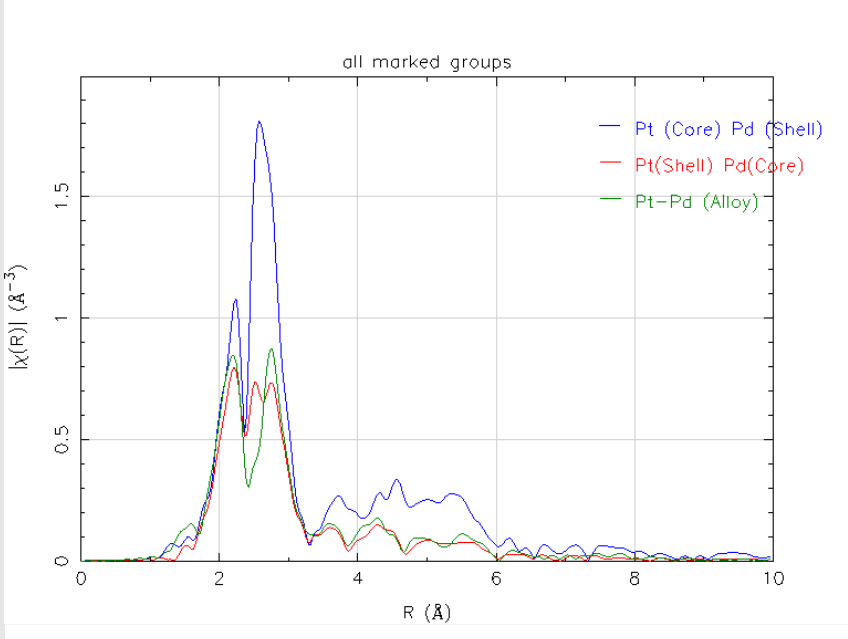


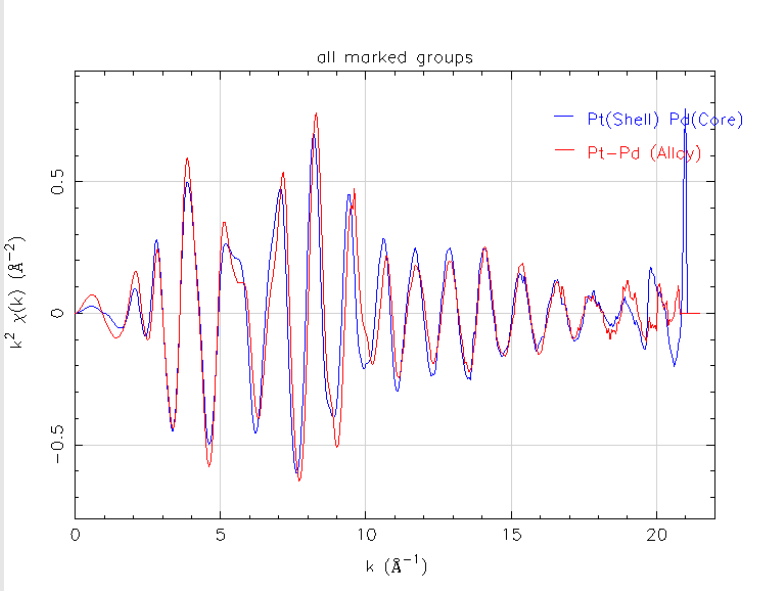
Pt-Pd alloy

S. Sanchez, M. Small, J. Zuo, R. Nuzzo
***J. Am. Chem. Soc*. 131, 8683 (2009)**

Representative EXAFS data







Q. Wang, S. Sanchez, M. Small, R. Nuzzo, A. Frenkel (submitted)

Data analysis:

Multiple data set fits;
Artemis+FEFF6;

Constraints in the fits:

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

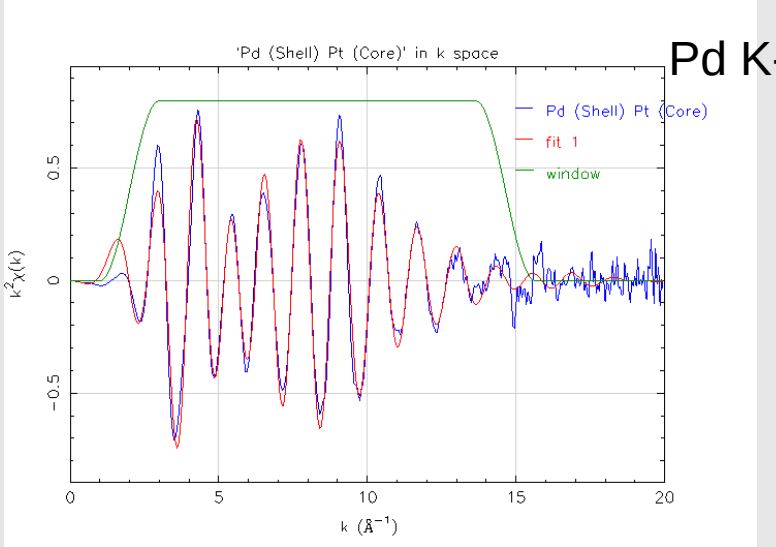
$$R_{AB} = R_{BA}$$

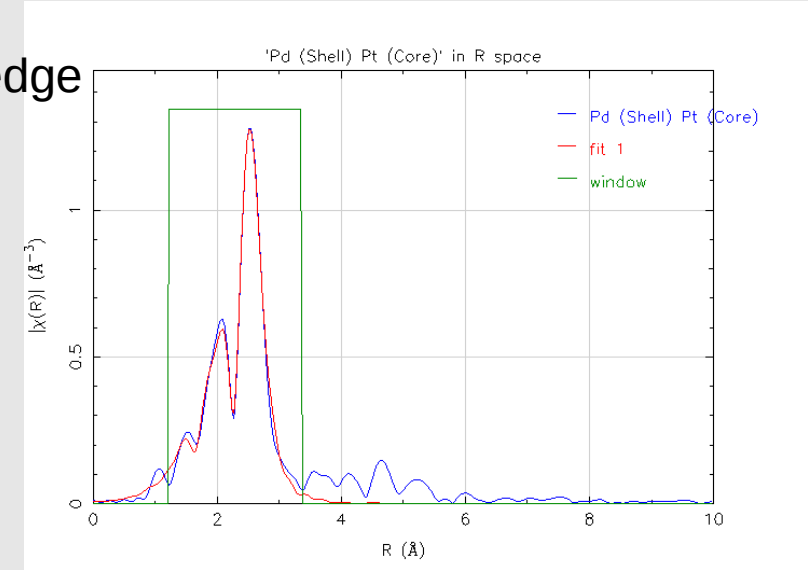
$$\sigma^2_{AB} = \sigma^2_{BA}$$

G. H. Via, et al,
***Catalysis Letters*, 1990, 5, 25-33.**

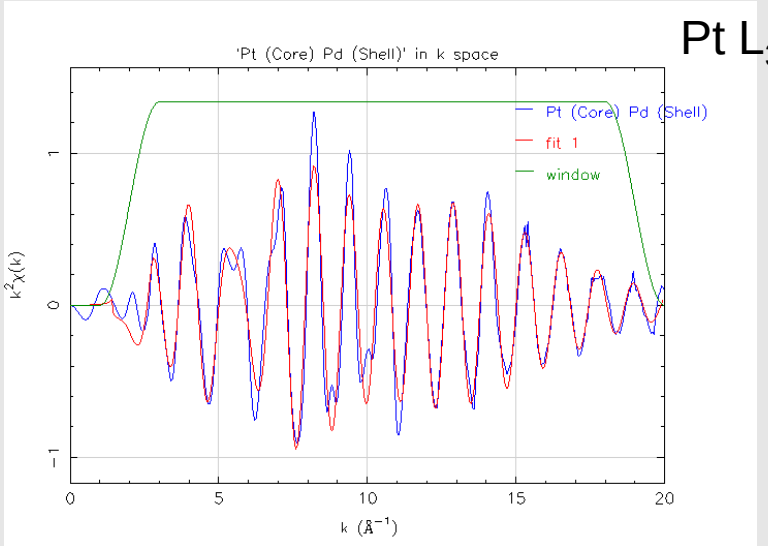
Representative fits

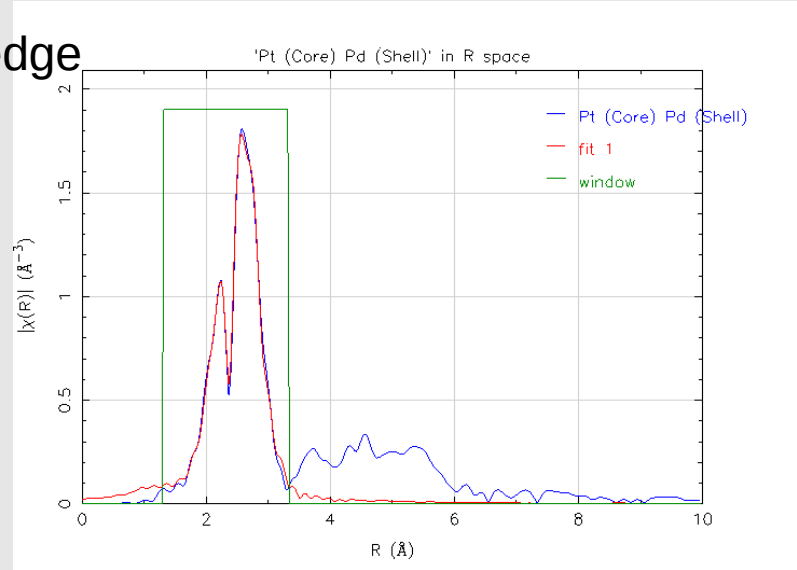
Pd K-edge





Pt L_3-edge





Q. Wang, S. Sanchez, M. Small, R. Nuzzo, A. Frenkel (submitted)

Results

	N(Pt-Pt)	N(Pt-Pd)	N(Pd-Pt)	N(Pd-Pd)
Pt(C)Pd(S)	9.8(4)	1.0(2)	2.1(4)	6.6(4)
Pt(S)Pd(C)	7.9(6)	1.3(3)	2.7(7)	7.9(6)
Pt-Pd(Alloy)	6.3(4)	2.6(3)	3.7(5)	3.2(5)

How to use them?

1. The alloy (Pt_xPd_y) composition by multiple edge EXAFS analysis:

$$\frac{x}{y} = \frac{x}{1-x} = \frac{N_{Pd-Pt}}{N_{Pt-Pd}}$$

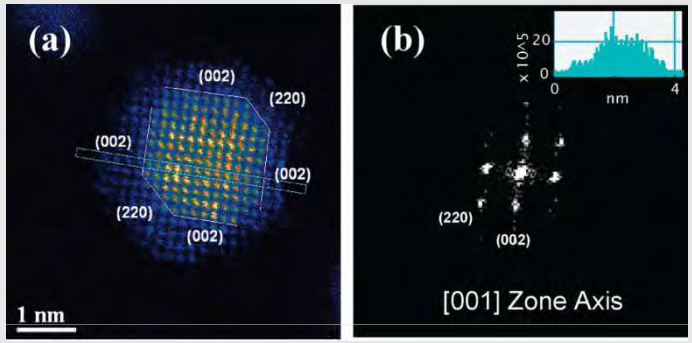
Accuracy in the alloy composition: ~25%

2. Homogeneity or heterogeneity (e.g., core/shell): N(Pt-M) *versus* N(Pd-M)

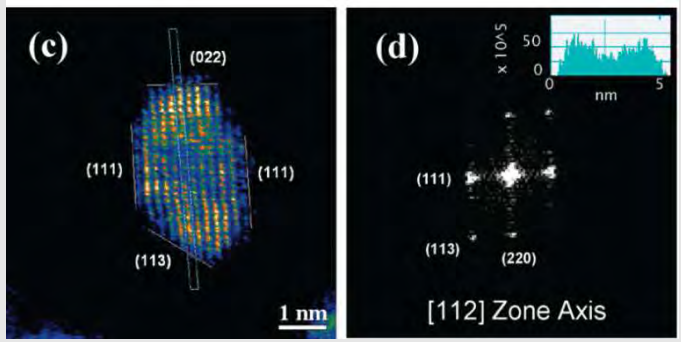
3. The particle size: N(M-M)

4. The short range order within the alloy: $\alpha_{Pd-Pt} = 1 - \frac{1}{x_{Pt}} \frac{N_{Pd-Pt}}{N_{Pd-M}}$

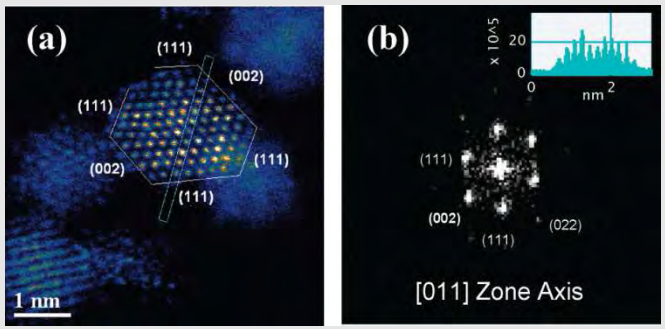
	$(Pt_xPd_y)_{EXAFS}$	$(Pt_xPd_y)_{EDS}$	N(Pt-M)	N(Pd-M)	α_{Pt-Pd}	α_{Pd-Pt}
Pt(C)Pd(S)	(0.7, 0.3)	(0.5, 0.5)	10.8(5) >	8.7(6)	+0.70	+0.66
Pt(S)Pd(C)	(0.7, 0.3)	(0.5, 0.5)	9.2(7) <	10.6(9)	+0.53	+0.64
Pt-Pd(Alloy)	(0.6, 0.4)	(0.5, 0.5)	8.9(5) >	6.9(7)	+0.27	+0.11



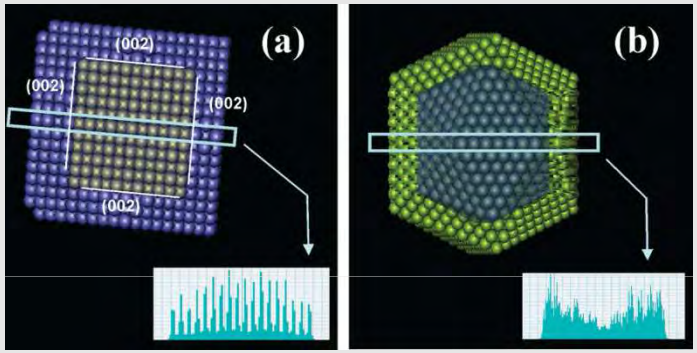
Pt(core)-Pd(shell)



Pt(shell)-Pd(core)



Pt-Pd (Alloy)



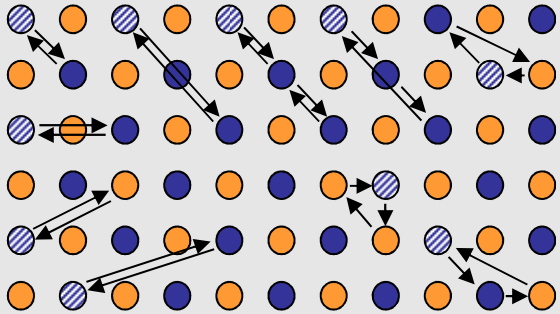
a) Simulated Pt(core)-Pd(shell)
b) Simulated Pd(core)-Pt (shell)
Icosahedral Pd core assumed

S. Sanchez, M. Small, J. Zuo, R. Nuzzo
***J. Am. Chem. Soc*. 131, 8683 (2009)**

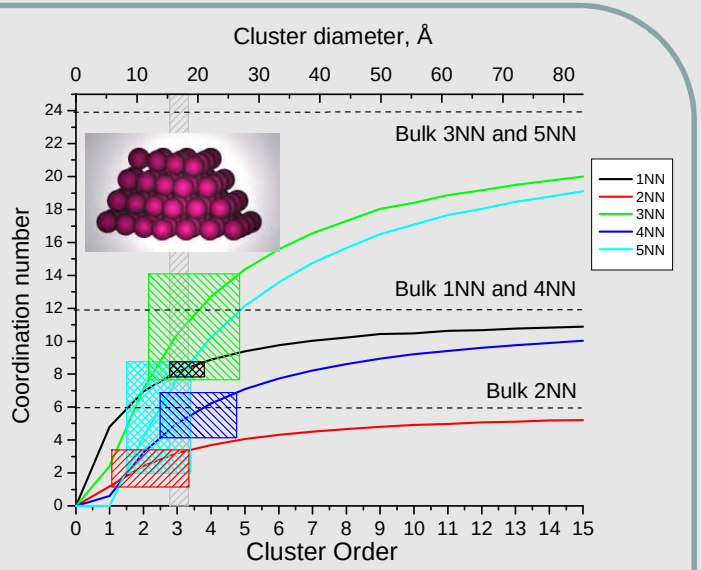
Conclusions:

- Good agreement with TEM regarding the core/shell vs. alloyed structure,
- Unique information about the SRO

What else coordination numbers are good for?



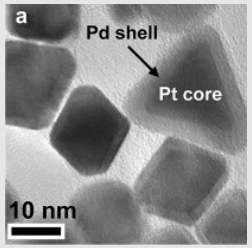
A. I. Frenkel,
J. Synchrotron Rad., 6, 293 (1999)



A. I. Frenkel, C. W. Hills, and R. G. Nuzzo,
J. Phys. Chem. B 105, 12689 (2001).

In monometallic NPs:

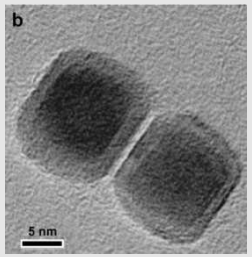
Shape, Size, Structure, Morphology



N. Long, et al, *Int. J. Hydrog. Energy 36*, 8478 (2011).

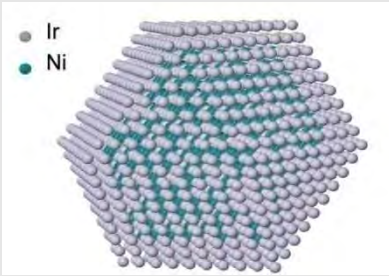
In bimetallic NPs:

Shape, Size, Structure, Morphology + SRO

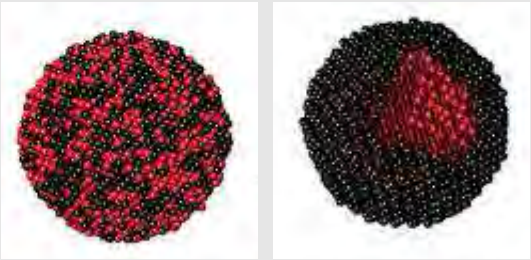


N. Long, et al, *Acta Mater. 59*, 2901 (2011).

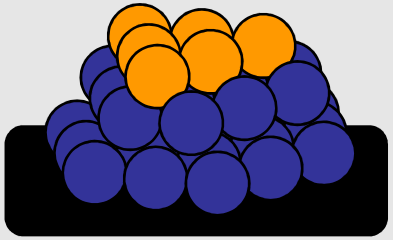
Examples:



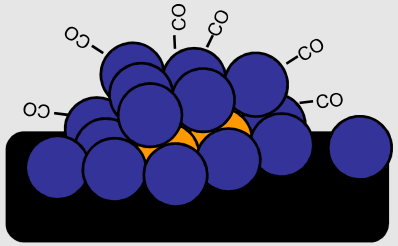
K. Sasaki, et al
J. Phys. Chem. C 115, 9894 (2011)



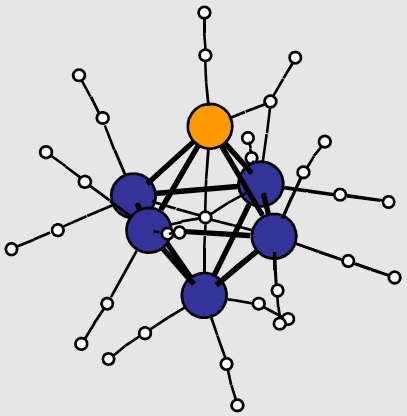
S. Alayoglu, et al
ACS Nano 3, 3127 (2009)

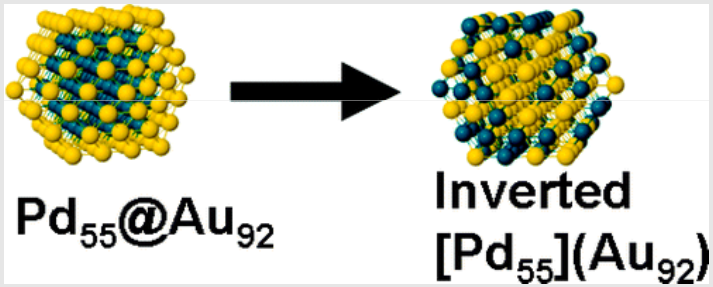


H_2 673 K



H_2 473 K





M. Weir, M. Knecht, A. Frenkel,
R. Crooks, *Langmuir* 26, 1137 (2010)

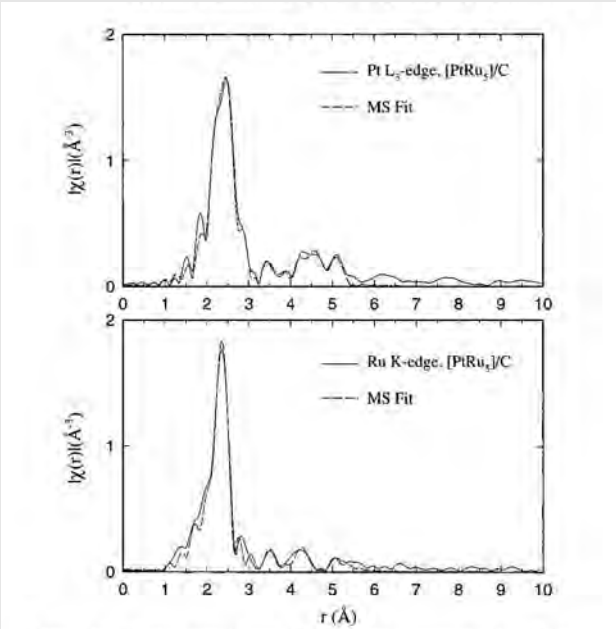


Figure 10. Fourier-transformed EXAFS data measured at 190 K from the carbon-supported $[PtRu_5]/C$ nanoparticles after activation at 673 K under H_2 (solid) and the multiple scattering fit results (dash): (a) Pt L_3 and (b) Ru K edges.

M. Nashner, A. Frenkel, et al,
J. Am. Chem. Soc. 119, 7760
(1997)

M. Nashner, A. Frenkel, et
al, *J. Am. Chem. Soc.* 120,
8093 (1998)

Revisiting criteria for SRO and homogeneity

$$\alpha_{AB} = 1 - \frac{n_{AB}/n_{AM}}{x_B}$$

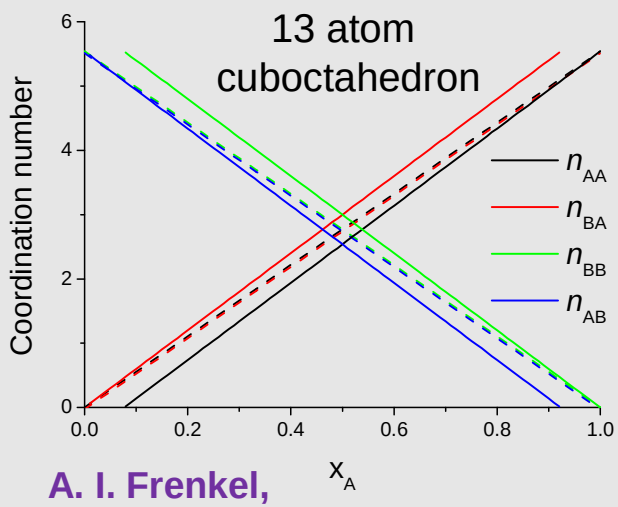
SRO: obtained by comparing $\frac{n_{AB}}{n_{AM}}$ and x_B

In random bulk alloys:

$$n_{AA} = n_{BA} = x_A n_{MM}$$

$$n_{AB} = n_{BB} = (1 - x_A) n_{MM}$$

$$n_{AA} + n_{BB} = n_{AA} + n_{AB}$$
$$= n_{AM} = n_{MM}$$



A. I. Frenkel,
Chem. Soc. Reviews, 2012
DOI: 10.1039/c2cs35174a

In random nanocluster alloys:

$$n_{AA} = \frac{N_A - 1}{N - 1} n_{MM} = \frac{N x_A - 1}{N - 1} n_{MM}$$

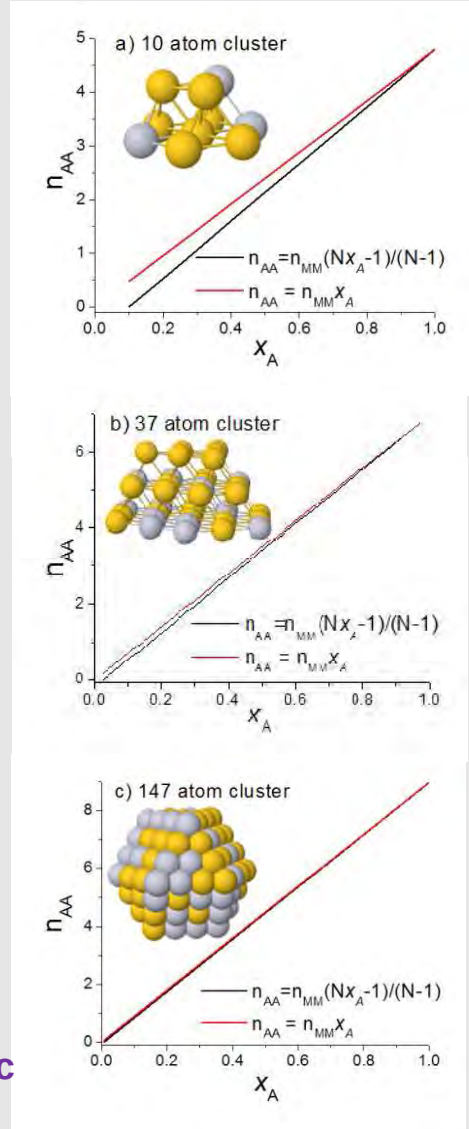
$$n_{AB} = \frac{N - N_A}{N - 1} n_{MM} = \frac{N}{N - 1}(1 - x_A) n_{MM}$$

$$n_{BA} = \frac{N_A}{N - 1} n_{MM} = \frac{N}{N - 1} x_A n_{MM}$$

$$n_{BB} = \frac{N_B - 1}{N - 1} n_{MM} = \left(1 - \frac{N x_A}{N - 1}\right) n_{MM}$$

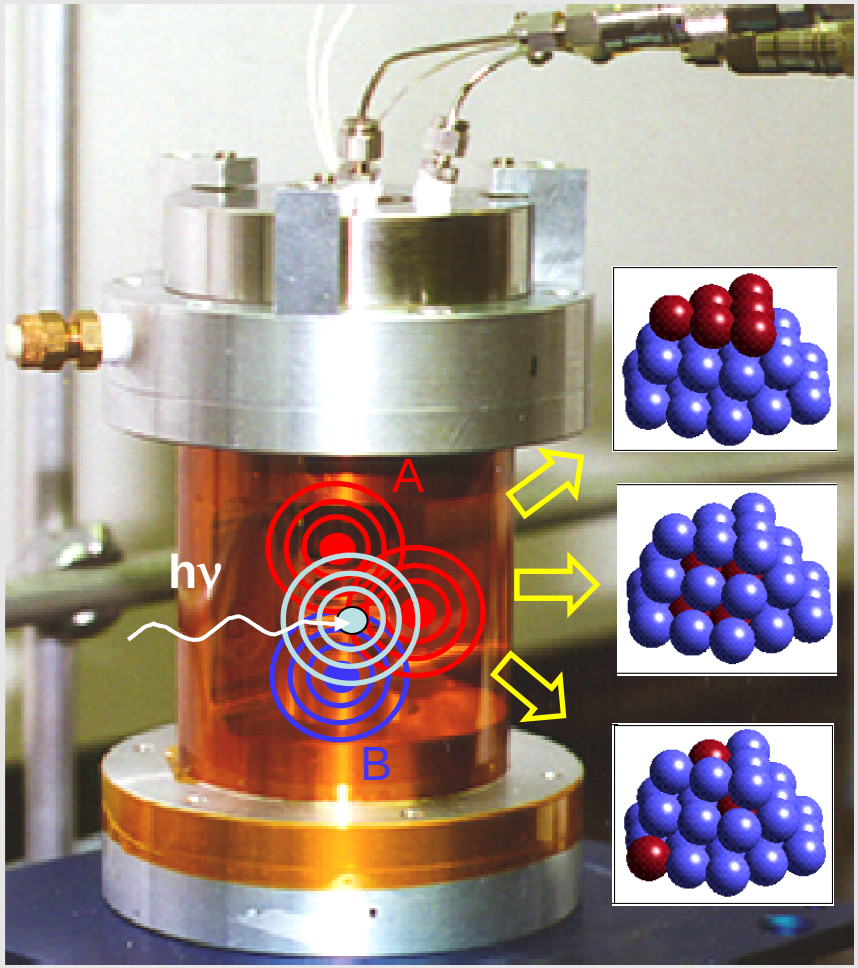
$$n_{AA} + n_{AB} = n_{AM} = n_{MM}$$

$$n_{AA} + n_{BB} = \frac{N - 2}{N - 1} n_{MM}$$



A. Frenkel, A. Yevick, C. Cooper, R. Vasic
Ann. Rev. Anal. Chem. 4, 23 (2011)

How forgiving is CN analysis to intra- and inter-cluster compositional disorder?



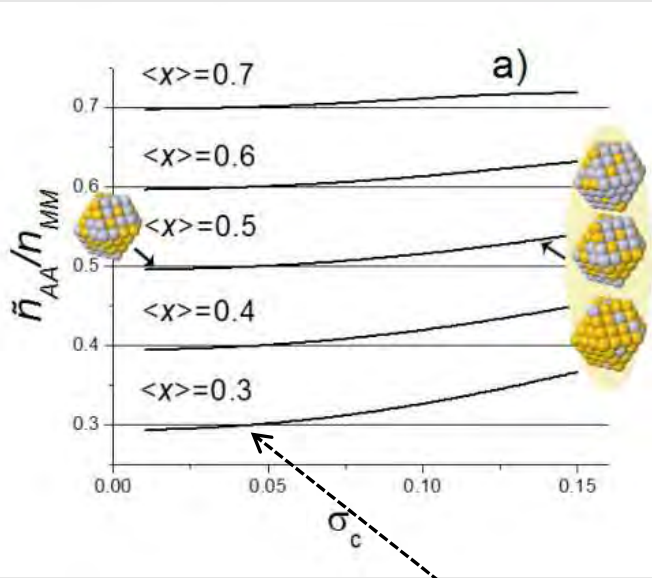
Assume that particles are random alloys (α=0), of the same size (n_{MM}), but have inter-particle compositional disorder:

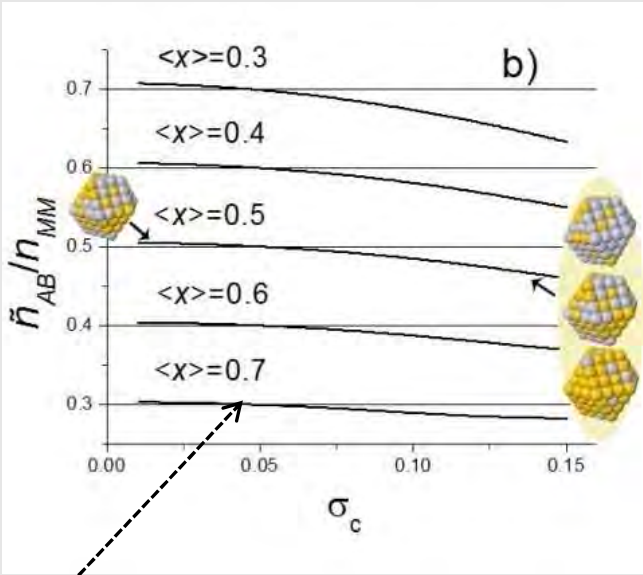
$$\rho(x) \propto \exp\left(-\frac{(x-\bar{x})^2}{2\sigma_c^2}\right)$$

What coordination numbers will be measured in EXAFS experiment, as a function of σ?

$$\tilde{n}_{AA} = \frac{\int_0^1 \rho(x)\, x\, n_{AA}(x)\, dx}{\int_0^1 \rho(x)\, x\, dx}$$

Theoretical coordination numbers for clusters of *N* = 100 atoms, calculated assuming Gaussian compositional distribution.





$$\sigma_c = \sqrt{x(1-x)/N}$$

At this value normal distribution coincides with binominal distribution

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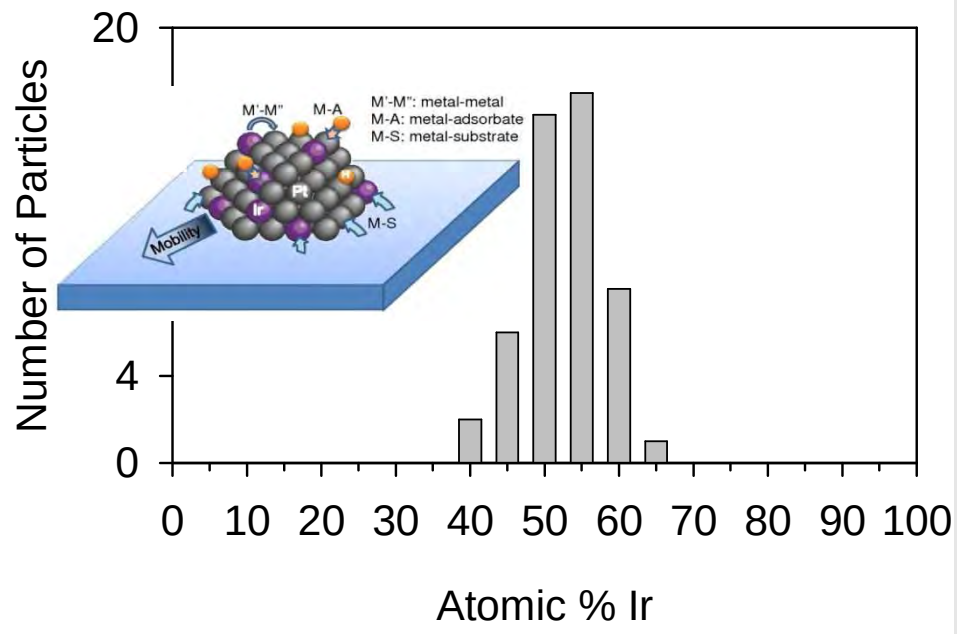
How narrow should the cluster composition be for SRO analysis to be reliable?

σ= 0.15 will cause 10-20% error in CN
Well defined clusters have much narrower distributions:



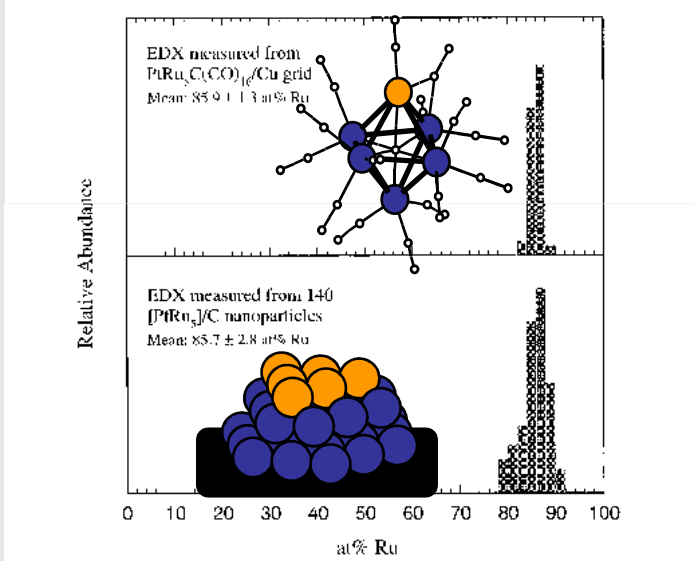


Figure 4. Comparison between the atomic fraction of Pt and Ru determined by quantitatively analyzing the EDX spectra measured from the reference $PtRu_5C(CO)_{16}$ cluster (top) and from 140 $[PtRu_5]/C$ nanoparticles (bottom).

M. W. Small, S. I. Sanchez, L. D. Menard, J. H. Kang, A. I. Frenkel, R. G. Nuzzo
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