Size & shape dependence of the activity of metallic nanoparticles

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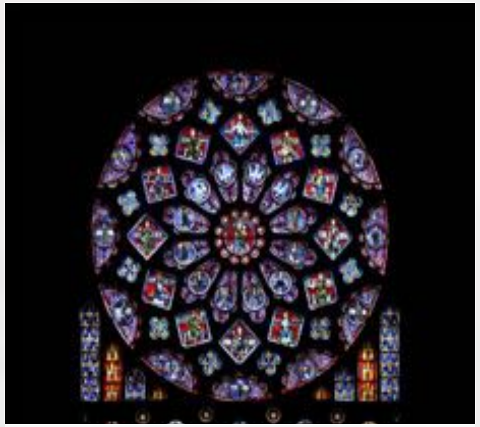
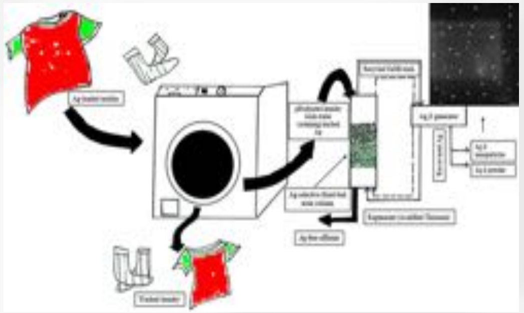
CSC/WCPM Seminar at Warwick, 24 June 2019

Nano is amazing

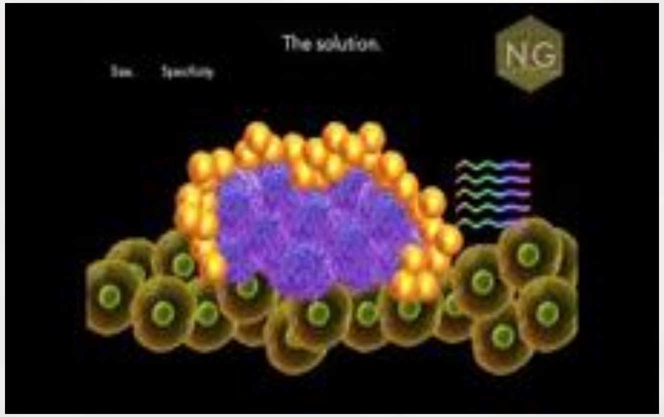
"Nanoparticles are everywhere"
L.D. Marks, L. Peng JPCM (2016)

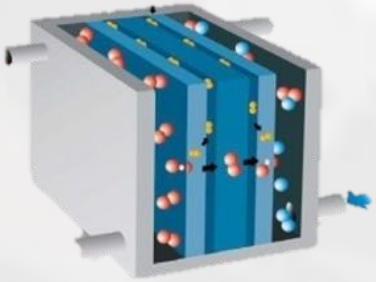
The ugly, the good, the beautiful and the useful!





Nawaz, ACS Sust. Chem. Eng.(2018)





Different **isomers** and **homotops** with peculiar (non-scalable) properties different from their bulk/atomic counterparts. A state of matter and building blocks for nanostructures materials.

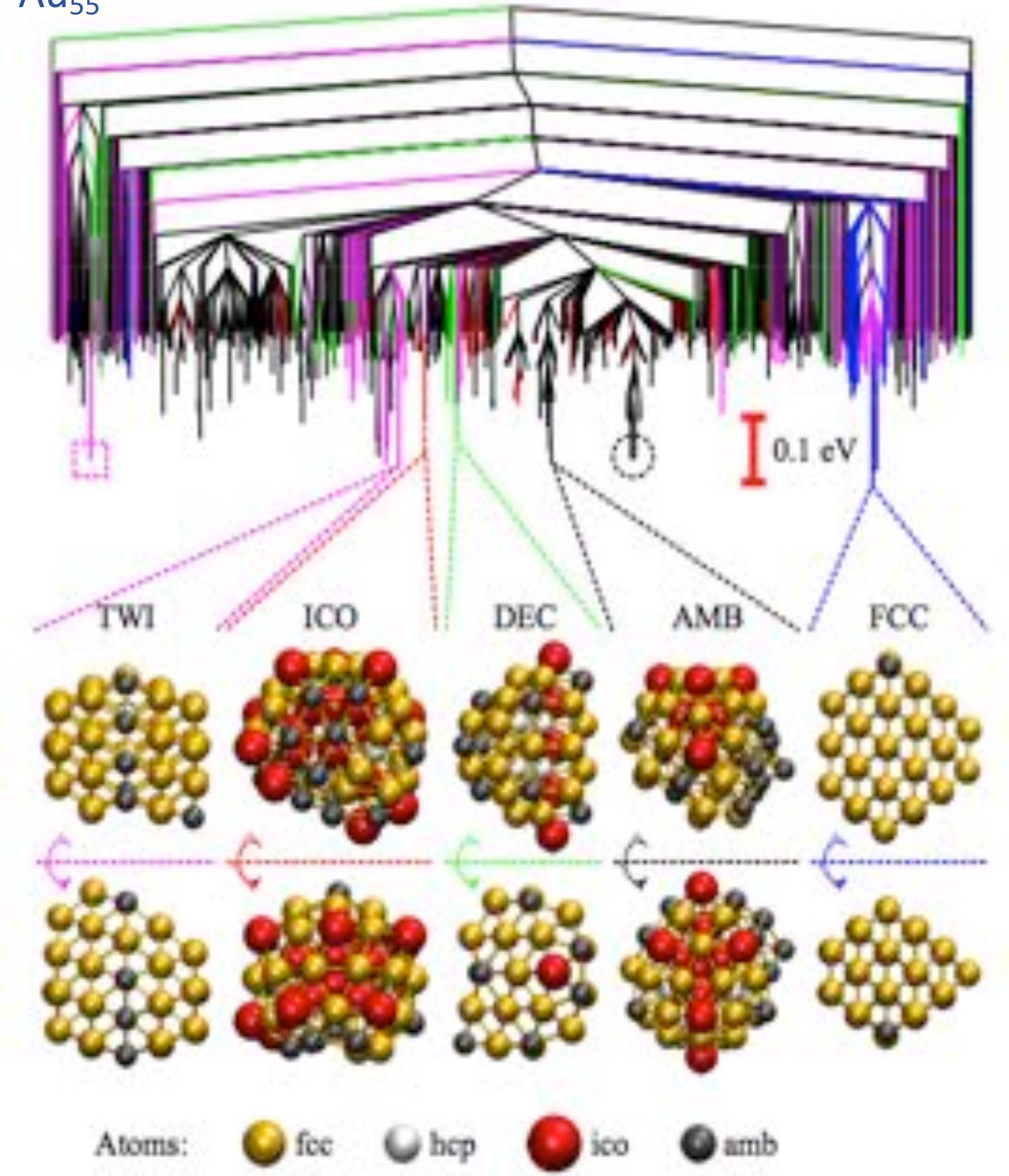
Amazingly different

Different shape; chemical orderings

"There is plenty of room at the bottom" by R. Feymann

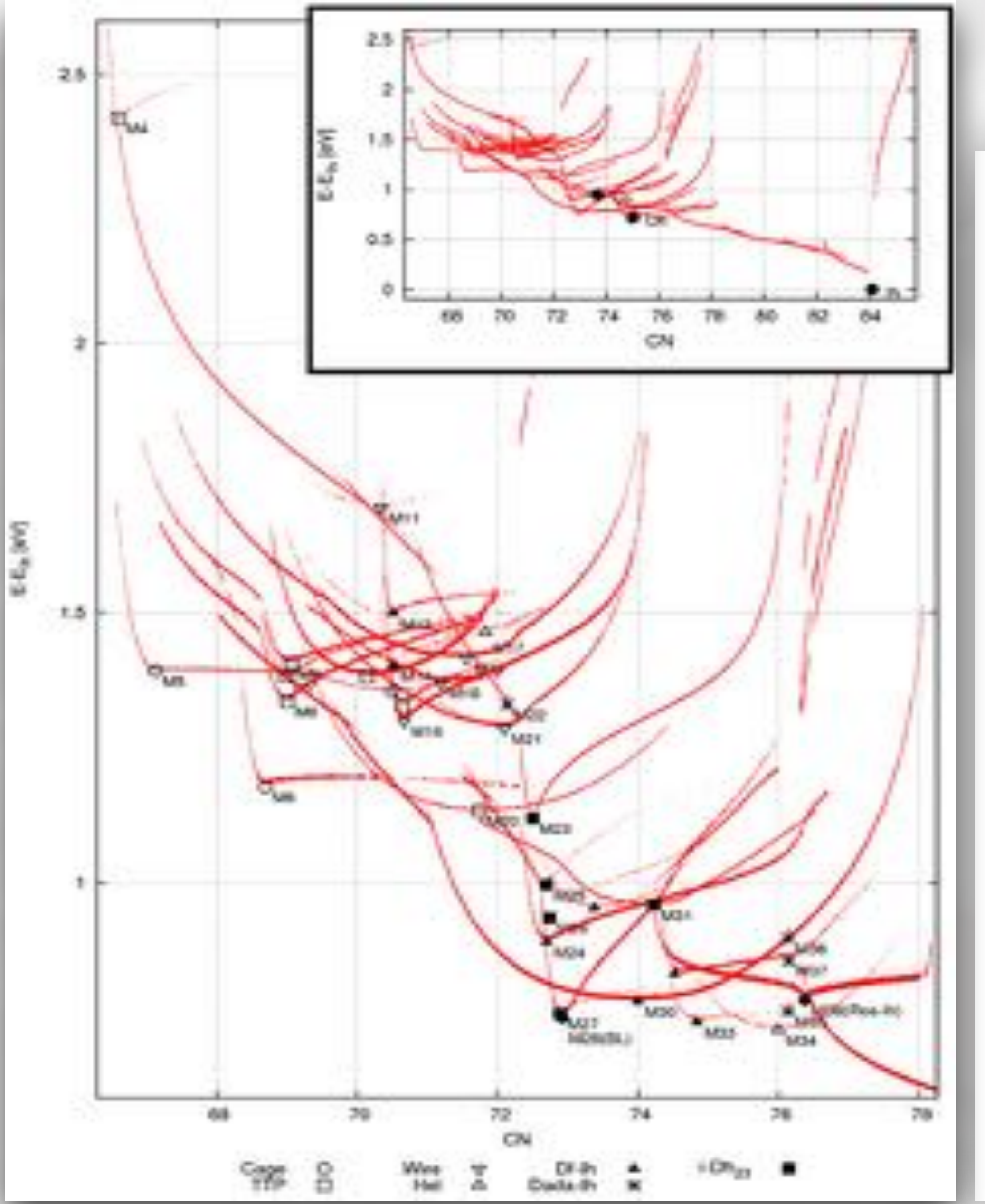
$Ag_{85}Cu_{62}$

K. Rossi et al. PCCP(2017) –Hot paper



Schebarchov, FB, Wales Nanoscale(2018)

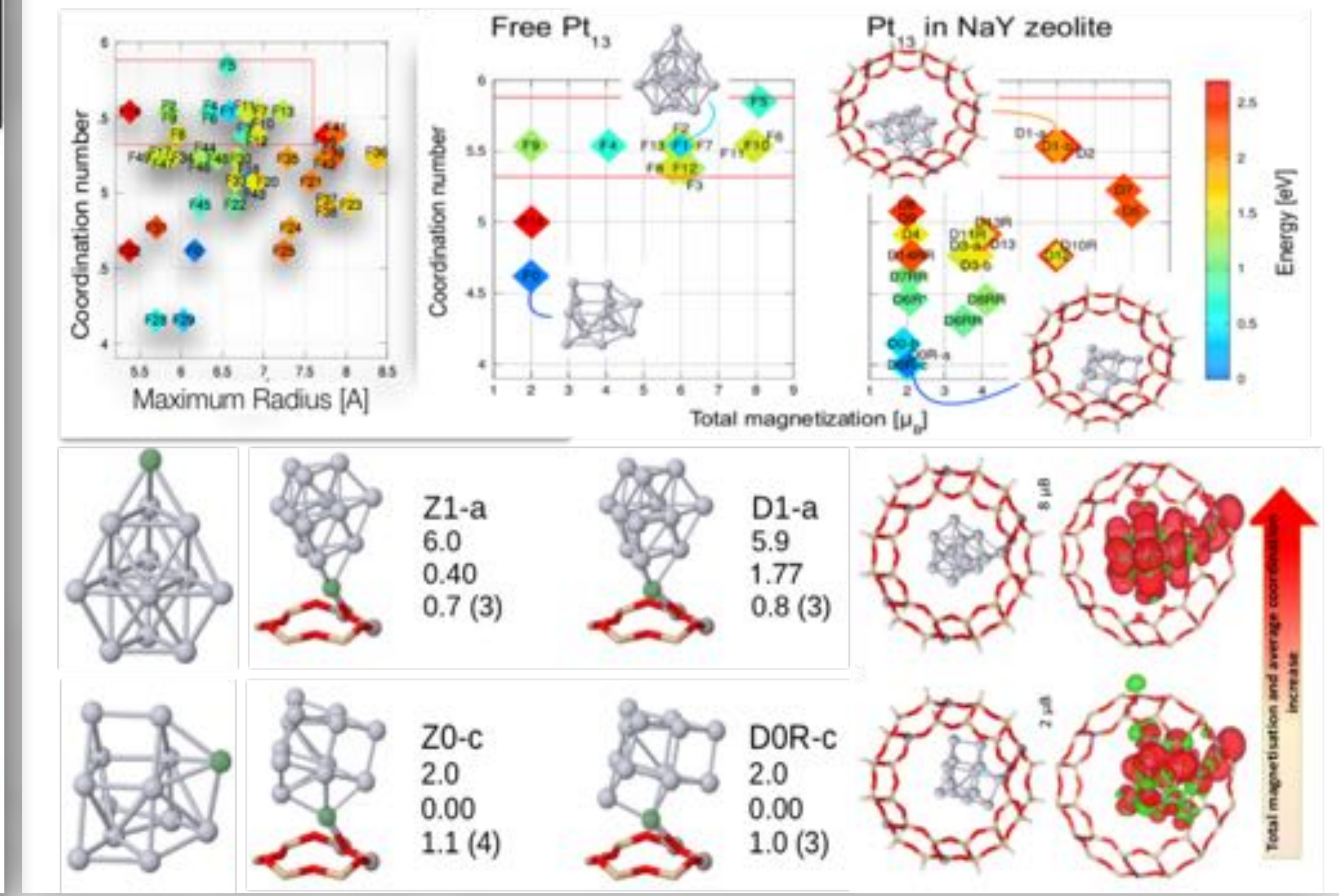
48 available isomers for Pt_{13} in the vacuum



Pavan, et al. EPJD(2013)

Environment effect

15 isomers can be inserted into a zeolite pore



DiPaola, et al. Nanoscale(2017)

Different time-scales

Different shape; chemical orderings; environment effect

Different time scale
(from 0D to 4D materials; out-of-equilibrium)

Long-lived excited state; vibrational properties; isomerization…

from fs to ns to … years (for applications)

Amazingly different

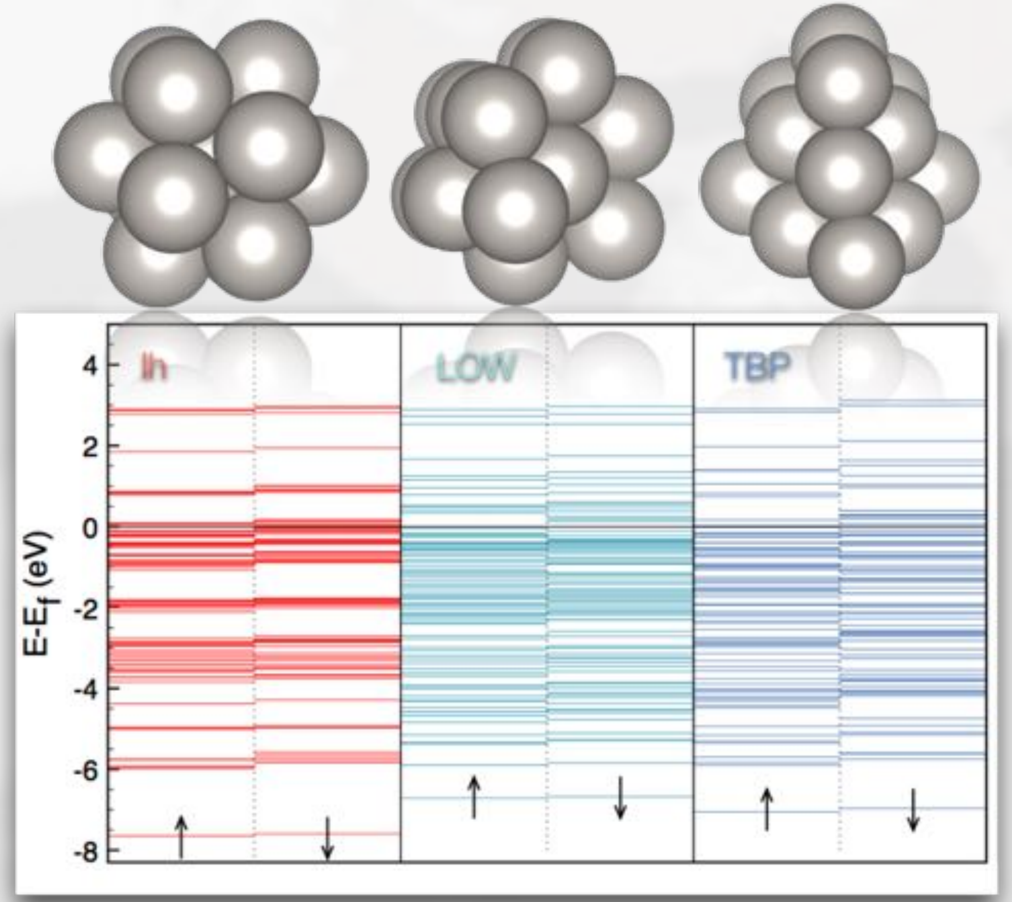
Different shape; chemical orderings; environment effect

Different time scale
(from 0D to 4D materials; out-of-equilibrium)

Shape&size-dependent electronic structure

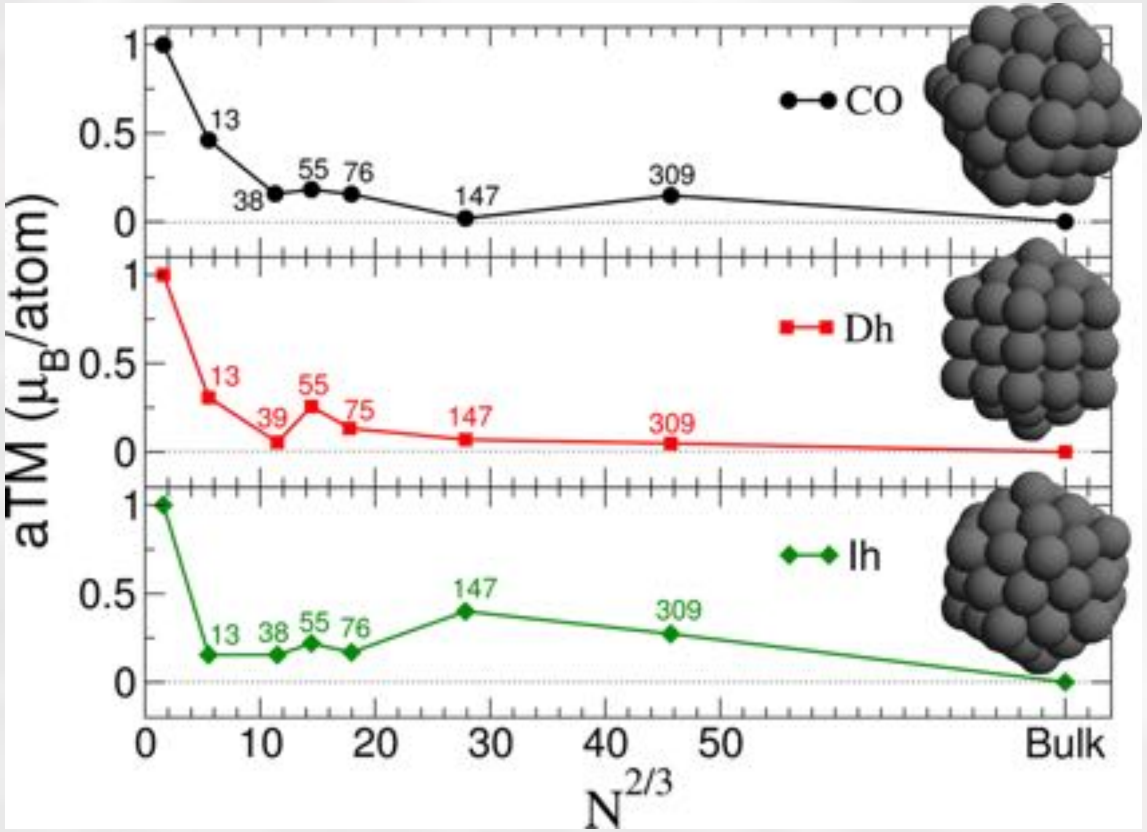
A 3D periodic table?

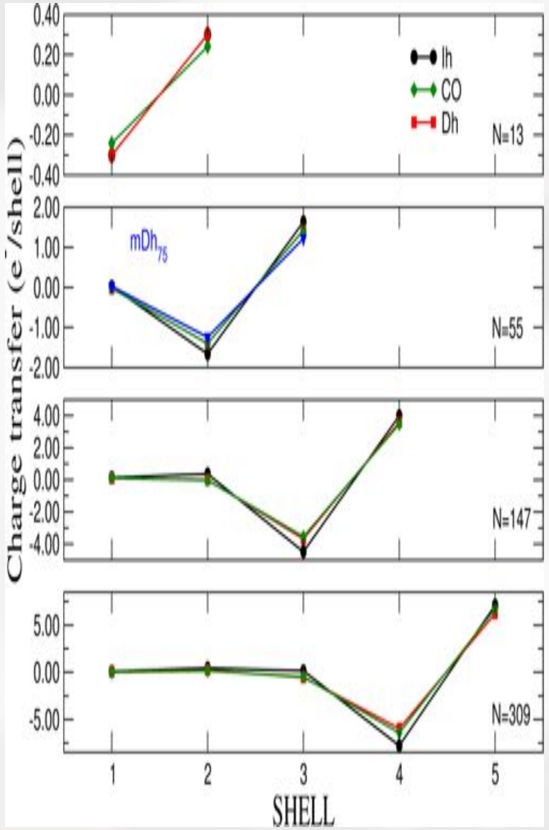
Electronic structure@DFT level Pt_{13}

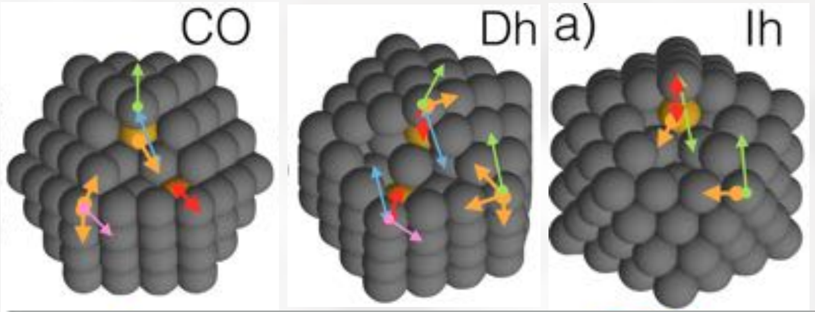


DiPaola, et al. Nanoscale(2017)

Amazingly different







		Ih_{147}	Ih_{309}	CO_{147}	CO_{309}	Dh_{147}	Dh_{309}
1[st] NN	V-SV	8%	7.9%	4.7%	5.9%	(6.5:8.7)%	(1.8:7.4)%
	SV-core	8%	5.6%	6%	6.7%	(6.4:7.4)%	(3.6:5.2)%
	V intra-shell	1.7%	2.7%	3.1%	2.8%	(2.4:5.2)%	(1.1:5)%
	SV intra-shell	1.9%	2.8%	4%	3.6%	(1.7:7.6)%	(1.3:3)%
2[nd] NN	V-SS	-15%	-16%	-16%	-16%	-(11:15)%	-(15:19)%
	V-(111)	-19%	-19%	-17%	-18%	-(15:18)%	-(18:19)%
	V-(100)	NA	NA	5%	4.9%	6.4%	5%

DiPaola, D'Agosta, FB Nano Lett. (2016)

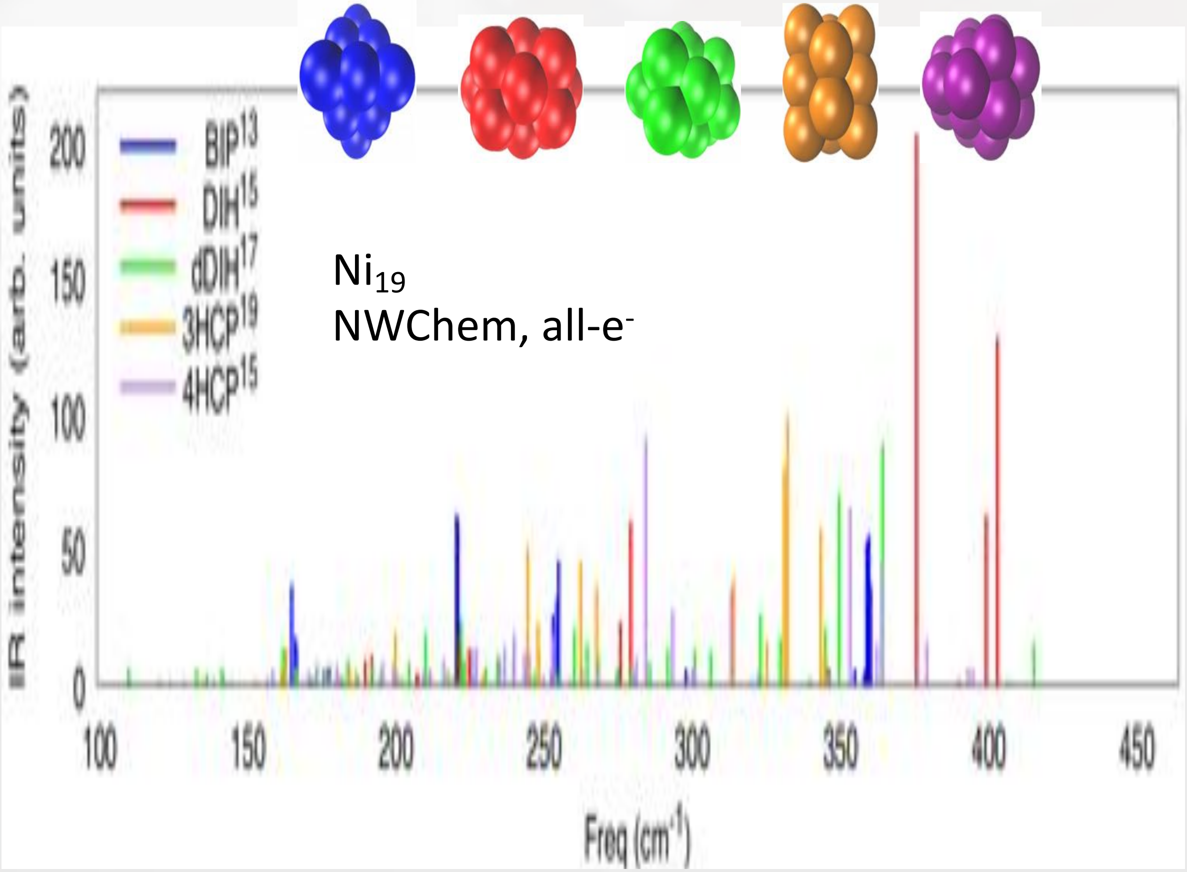
Amazingly different

Different shape; chemical orderings; environment effect

Different time scale
(from 0D to 4D materials/out-of-the-equilibrium)

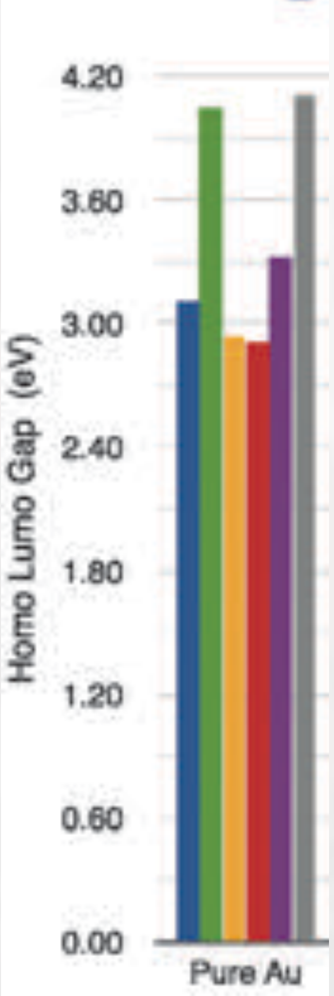
Shape&size-dependent electronic structure

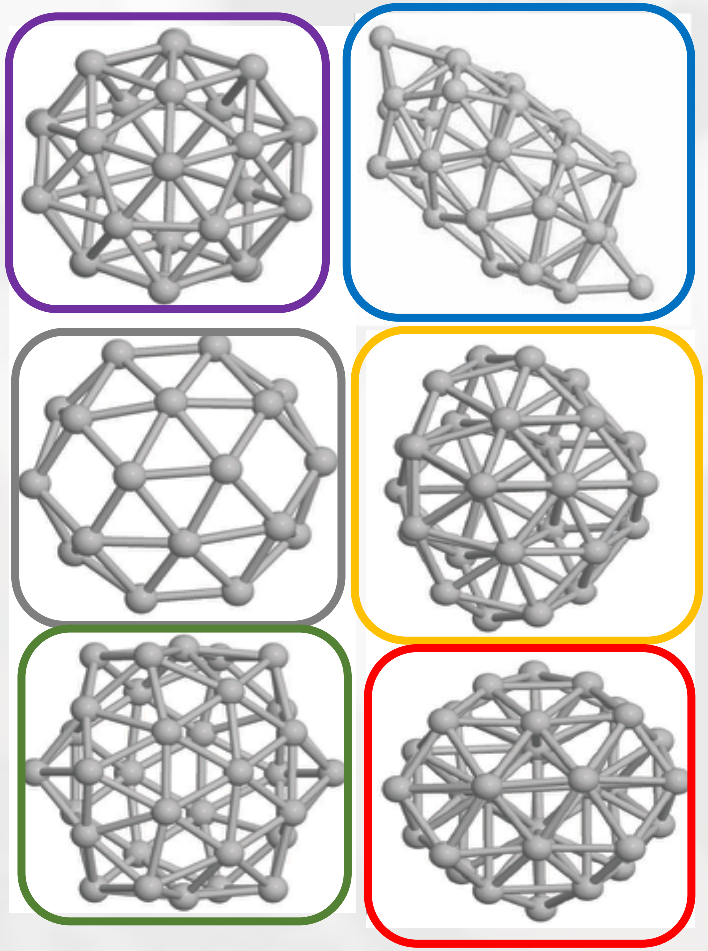
Shape-dependent vibrational spectrum

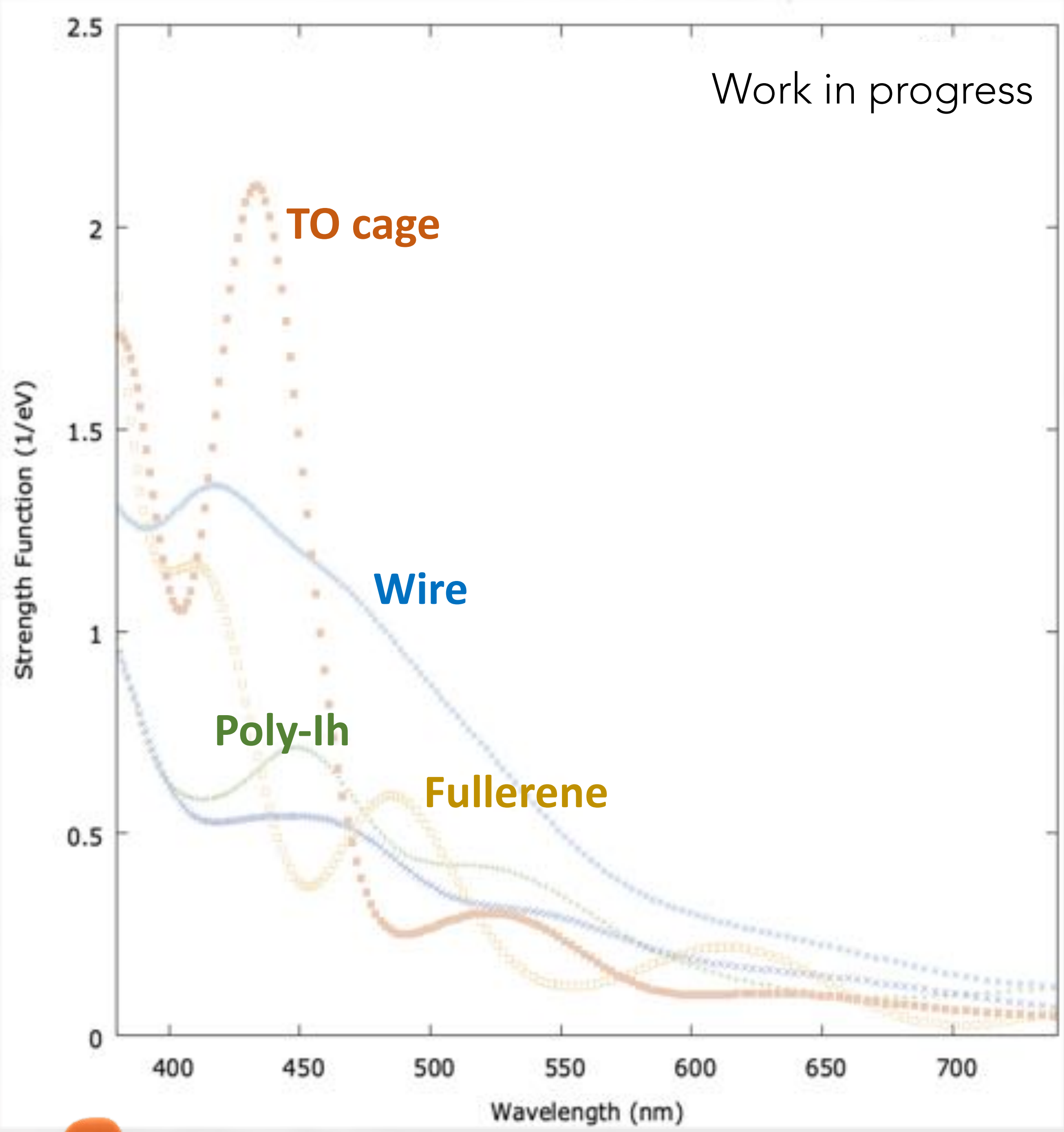


Laia Delgado, preliminary results

Amazingly different







DFT-PBE, ΔSCF

FB and Ferrando, PCCP (2015)

TD-DFT, PBE, "kick", 25000 steps

Amazingly fluxional

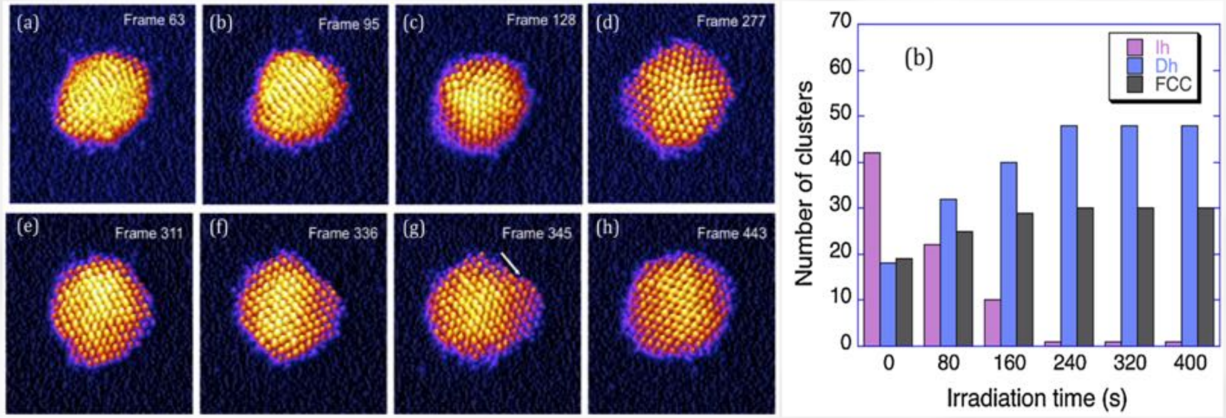
Different shape; chemical orderings; environment effect

Different time scale
(from 0D to 4D materials/out-of-equilibrium)

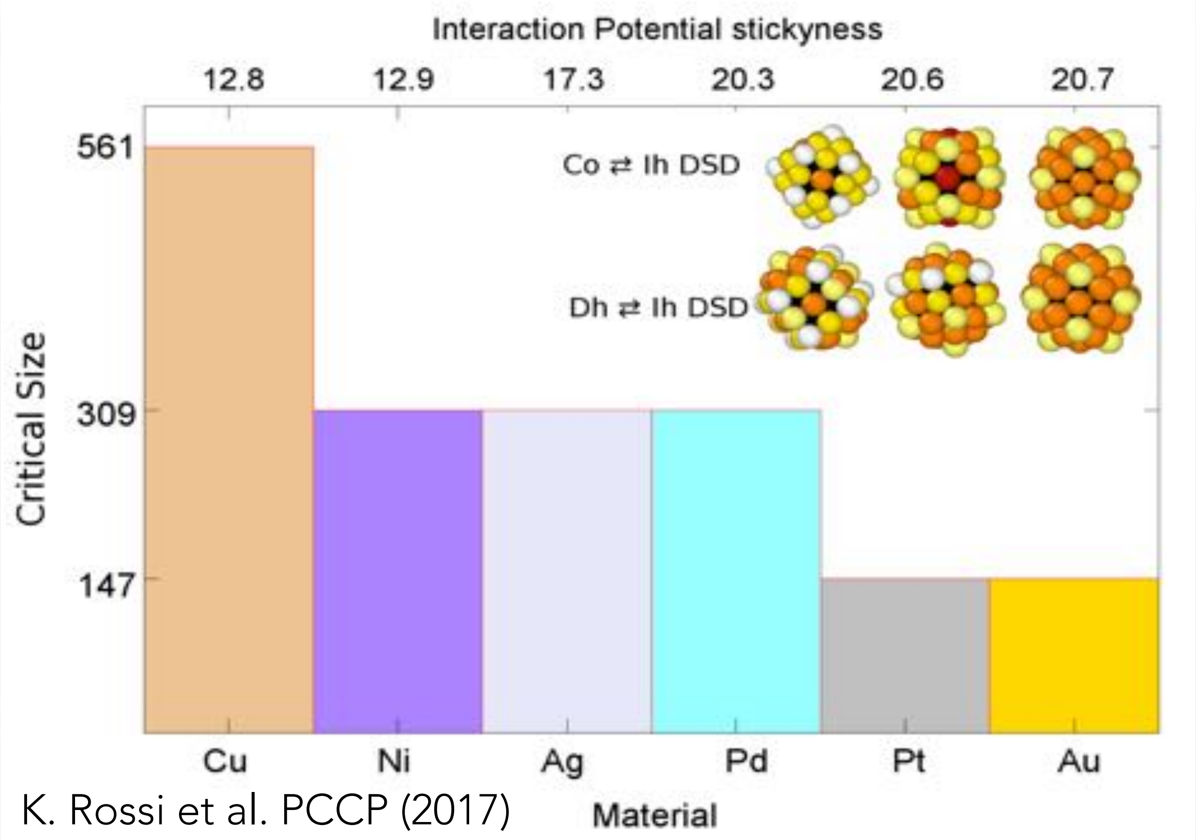
Different electronic structure

Different vibrational spectrum
Different optical properties

Isomerization

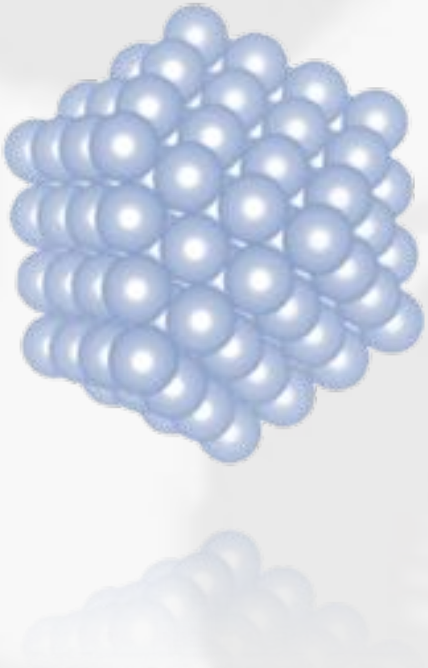


R.E. Palmer's group

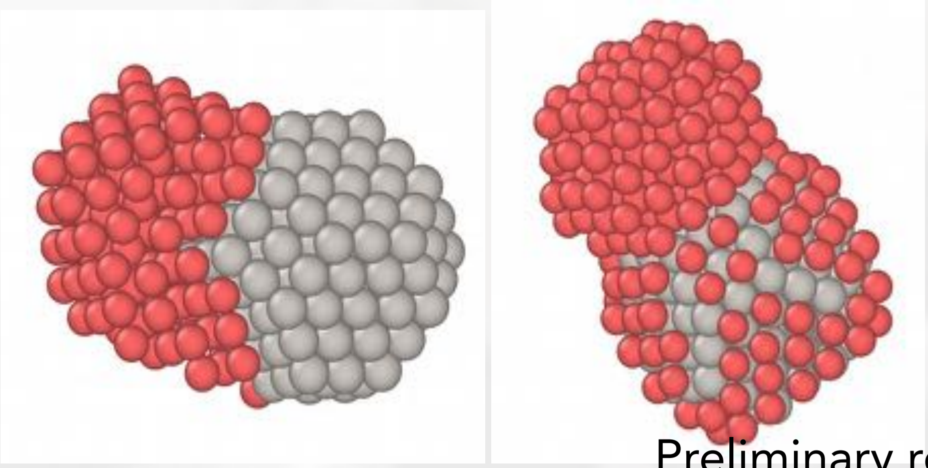


K. Rossi et al. PCCP (2017)

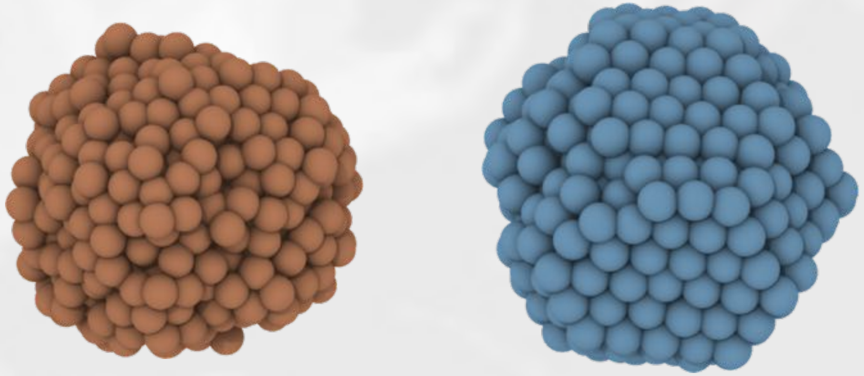
Nanoparticles-by-design



Coalescence Ag_{147} Pt_{201} and $Ag_{201}Pt_{201}$



Preliminary results

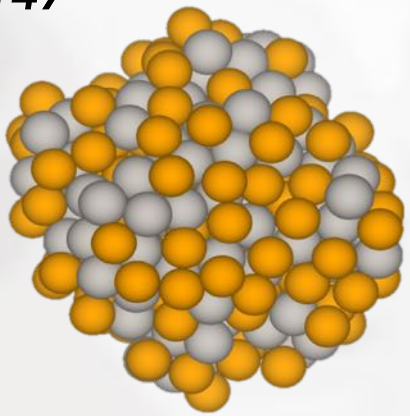


Baletto, JPCM (2019)

Size
Materials (composition/ordering)
Structure-property relationship
Stability & **Formation process**

Kinetic effect on T_m/T_f

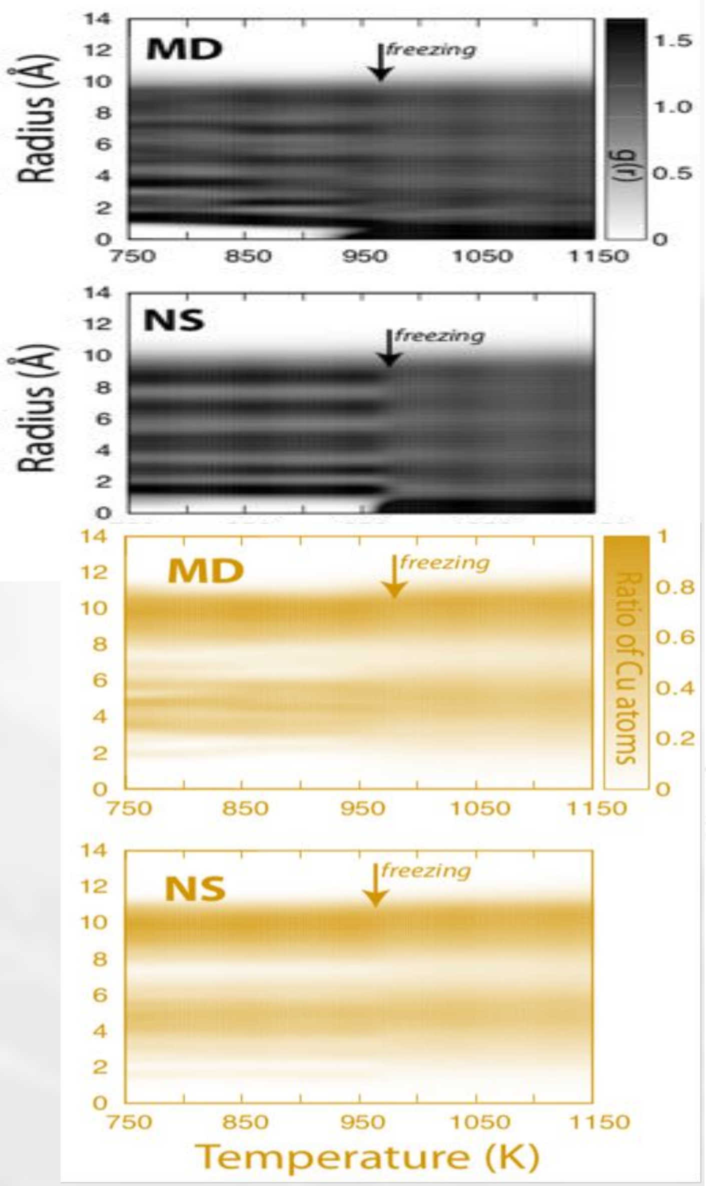
Cu162Pt147

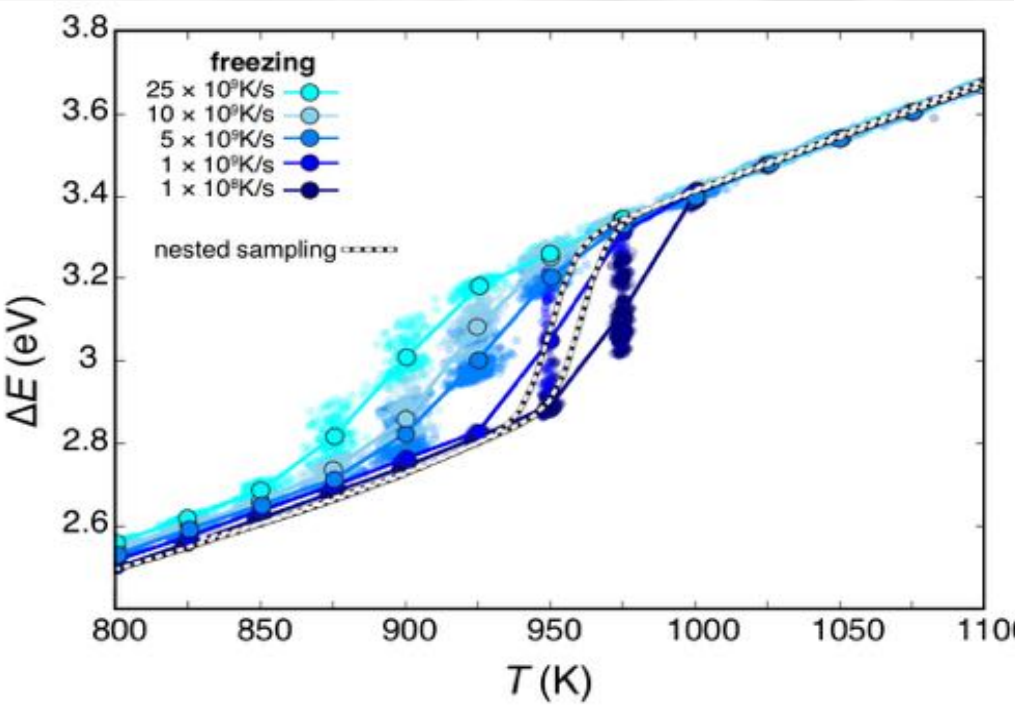


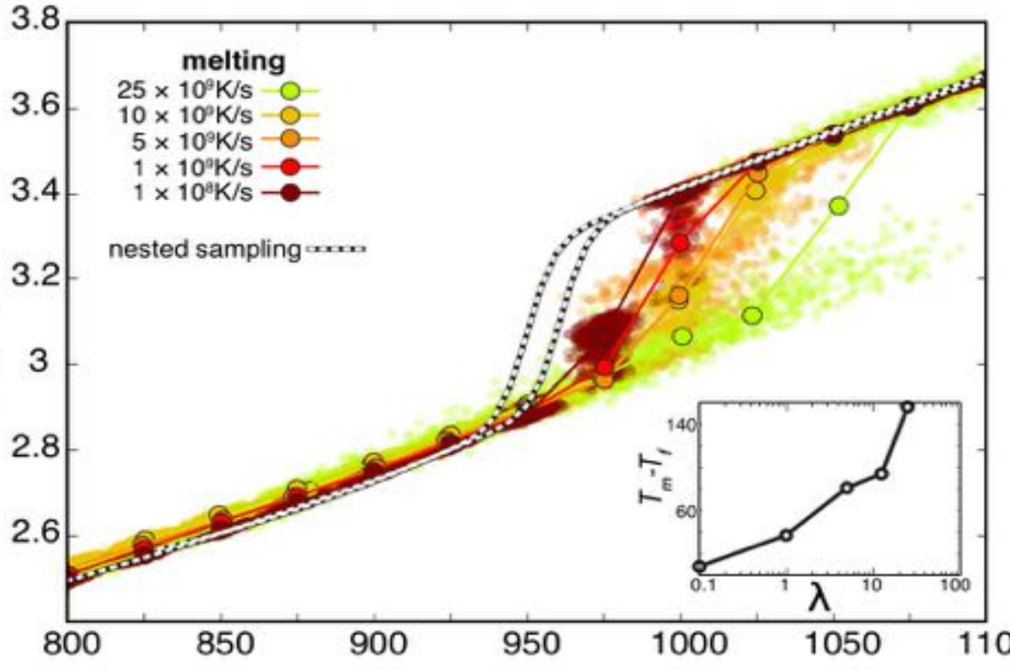
λ (10^9 K/s)	Ih	Dh	Cp
10	75	7	18
1	73	10	17
5	69	12	19
10	75	14	11
25	72	8	20
NS (850-900K)	58	18	24
NS (850-900K)	54	22	24

itMD vs nested Sampling

LoDiS

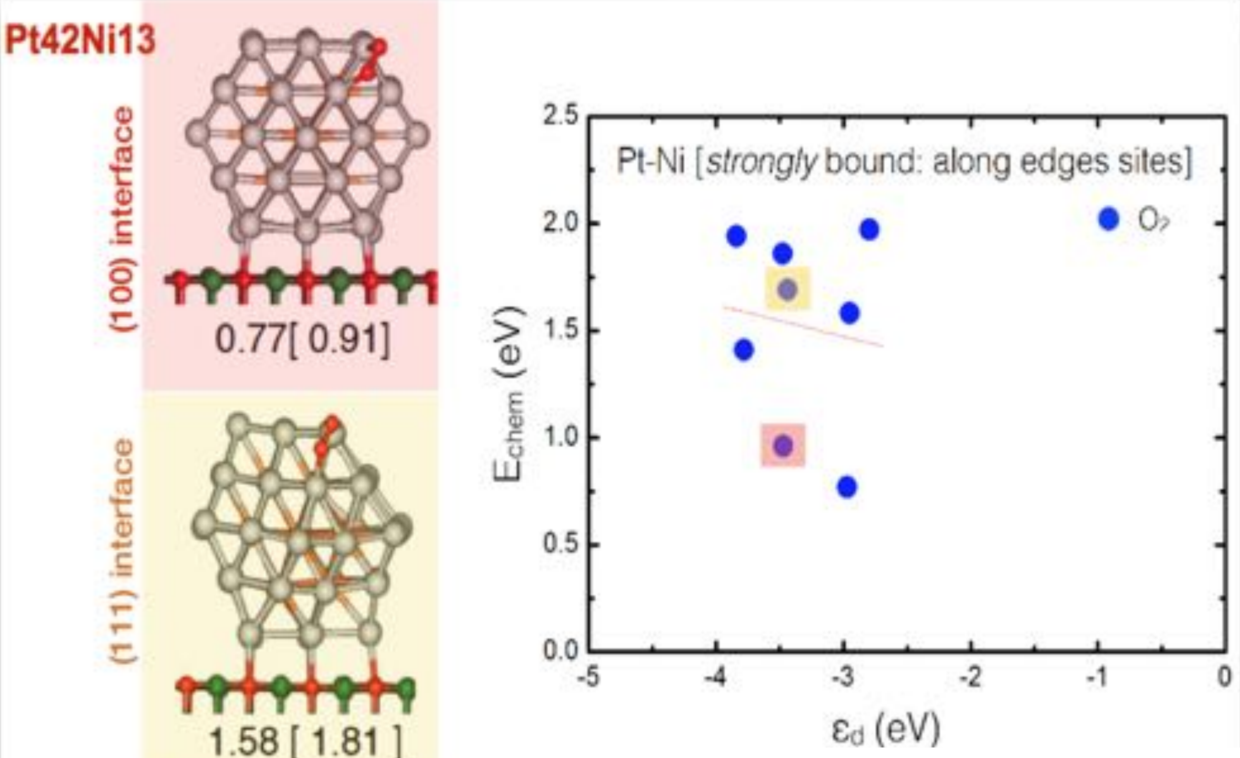






Rossi et al., SR (2018)

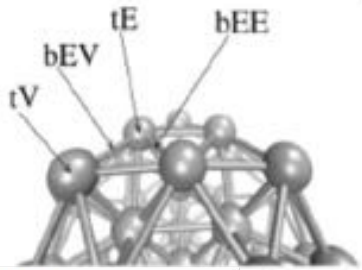
An unique example of diversity

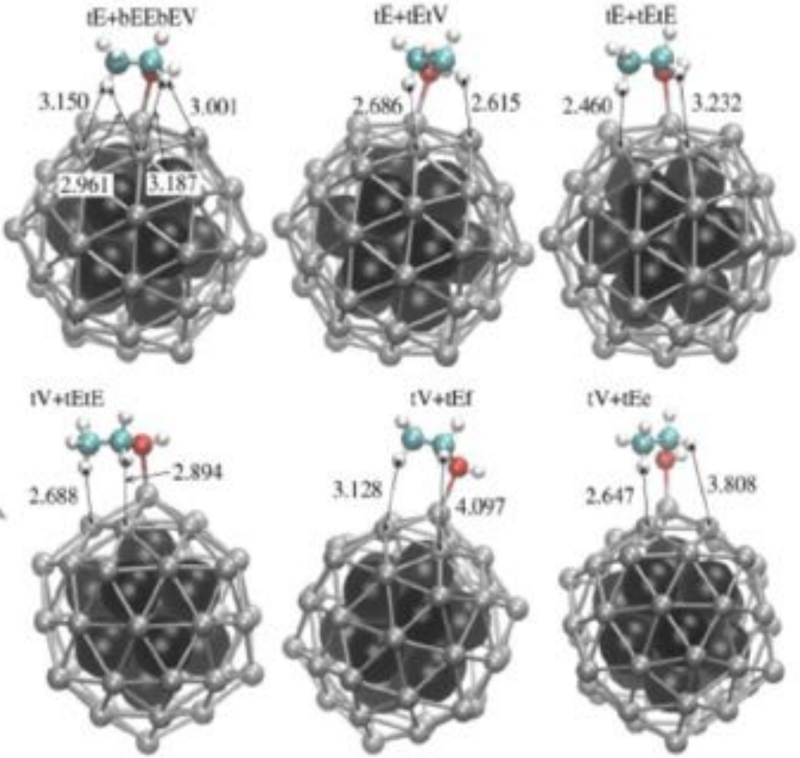


Paz-Borbon et al. Inorganics (2017)

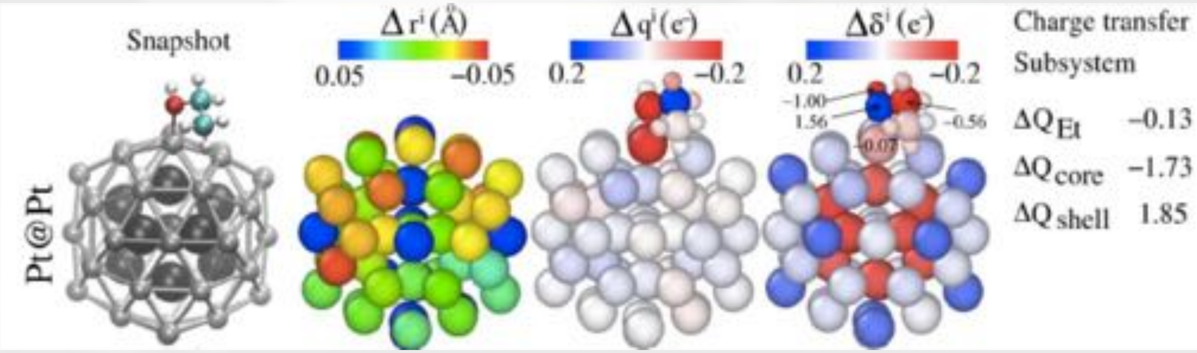
DFT-PBE [Grimme correction]

Ethanol on Pt_{55}



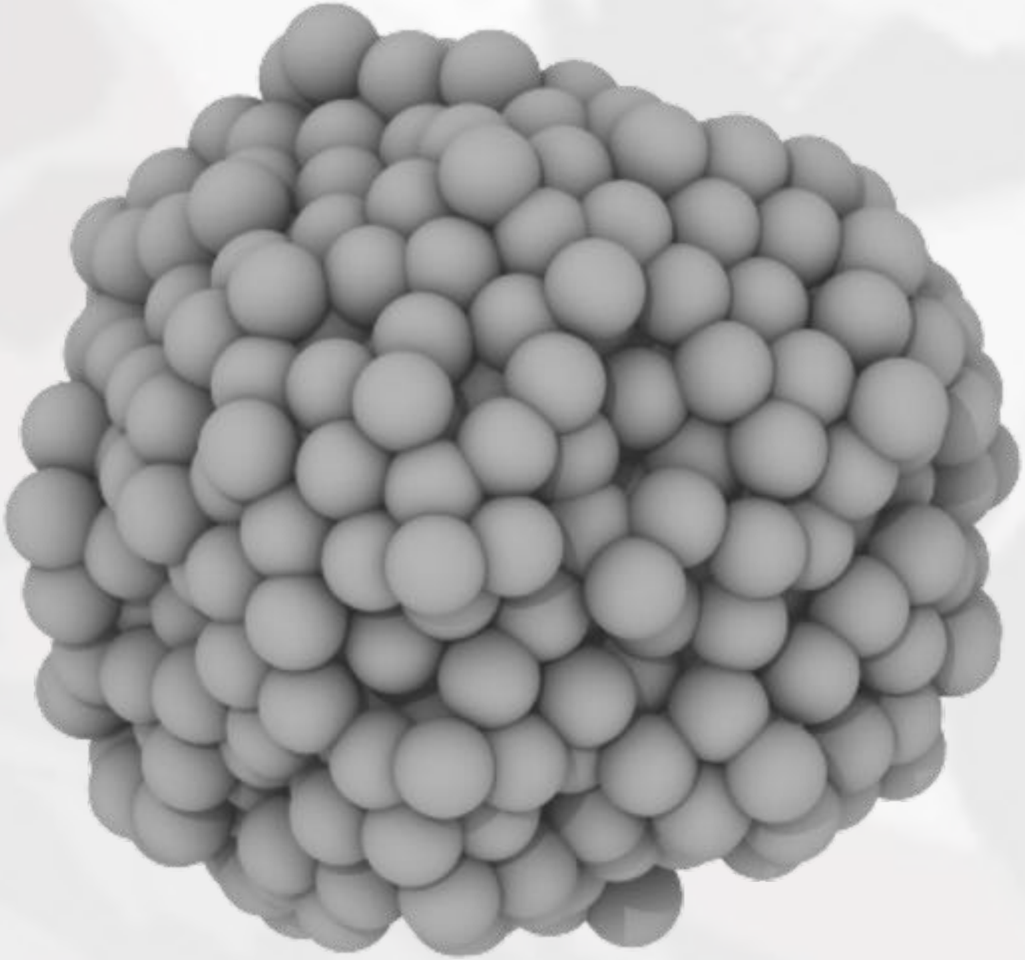


DFT-PBE

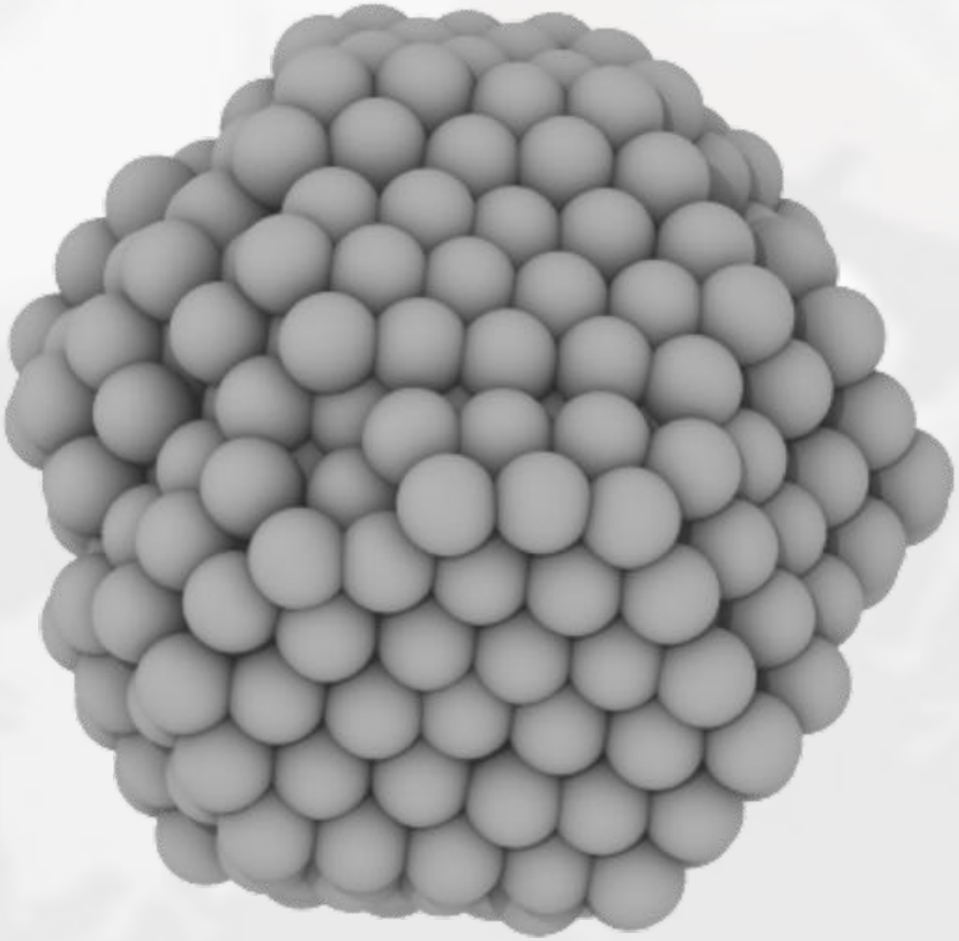


Rigo et al. EPJB (2019)

Characterisation, classification

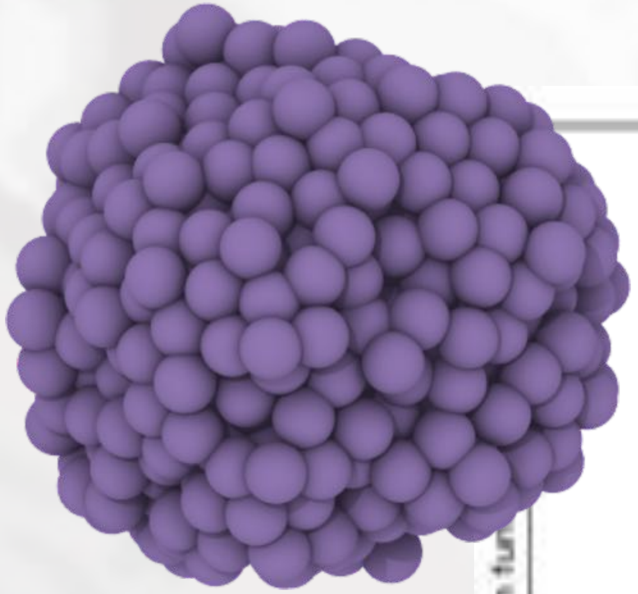


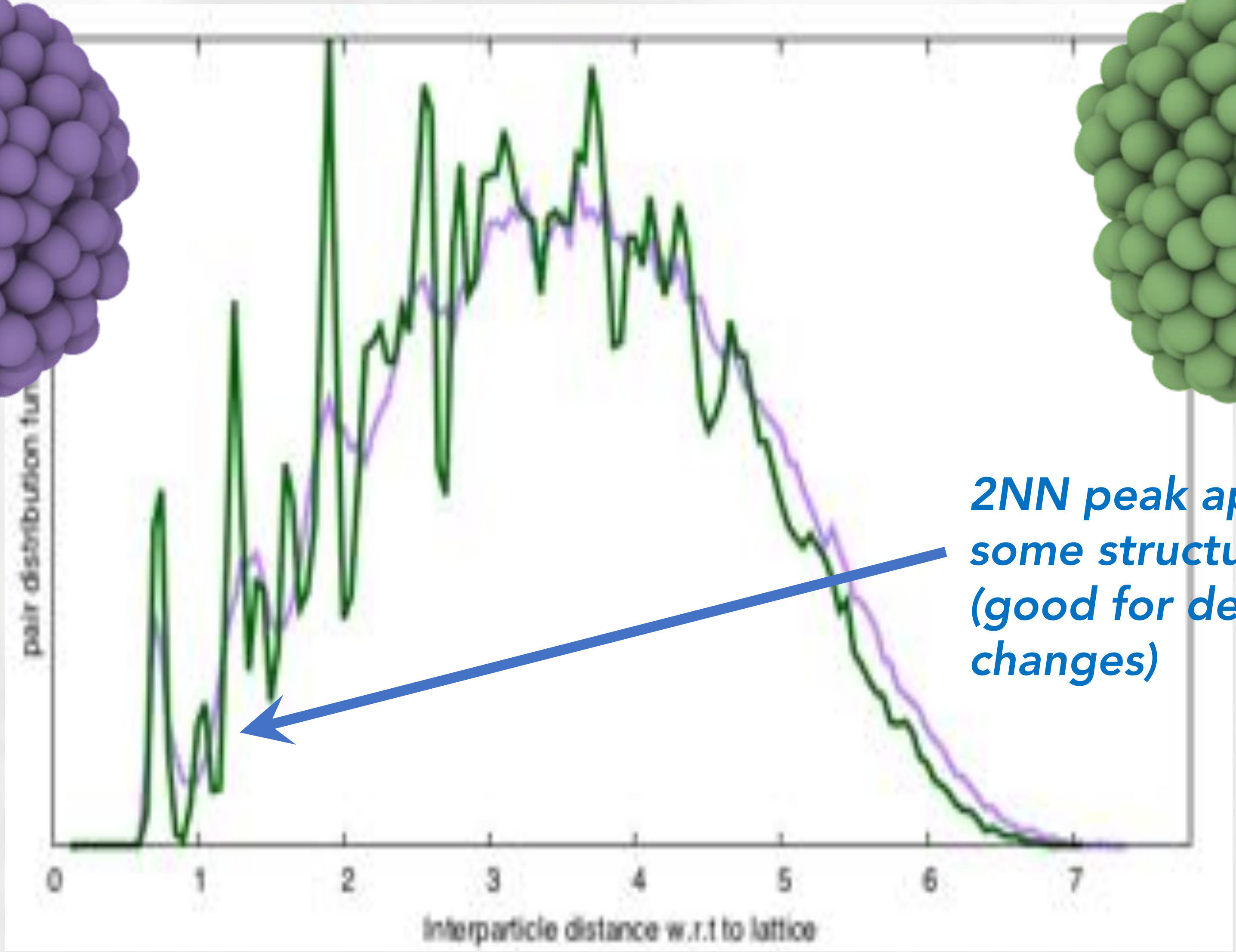
Number of atoms/Mass = 561
Radius of gyration = 2.612 nm
Deformation parameter = 1.34/1.2/1.25

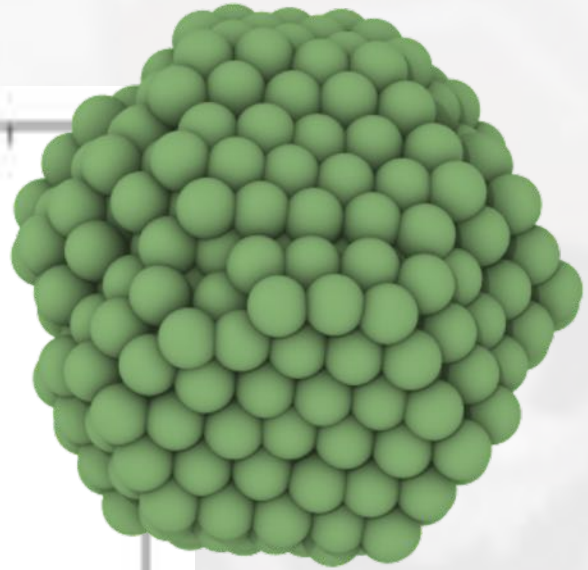


561
2.526 nm
1.13/1.24/1.30

Characterisation, classification







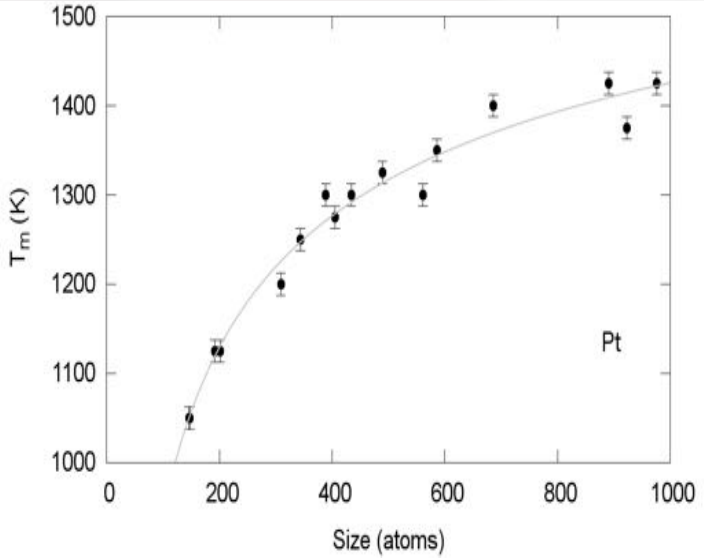
1NN peak in good approximation at the same position

2NN peak appears when some structural order does (good for detecting phase changes)

Characterisation, classification

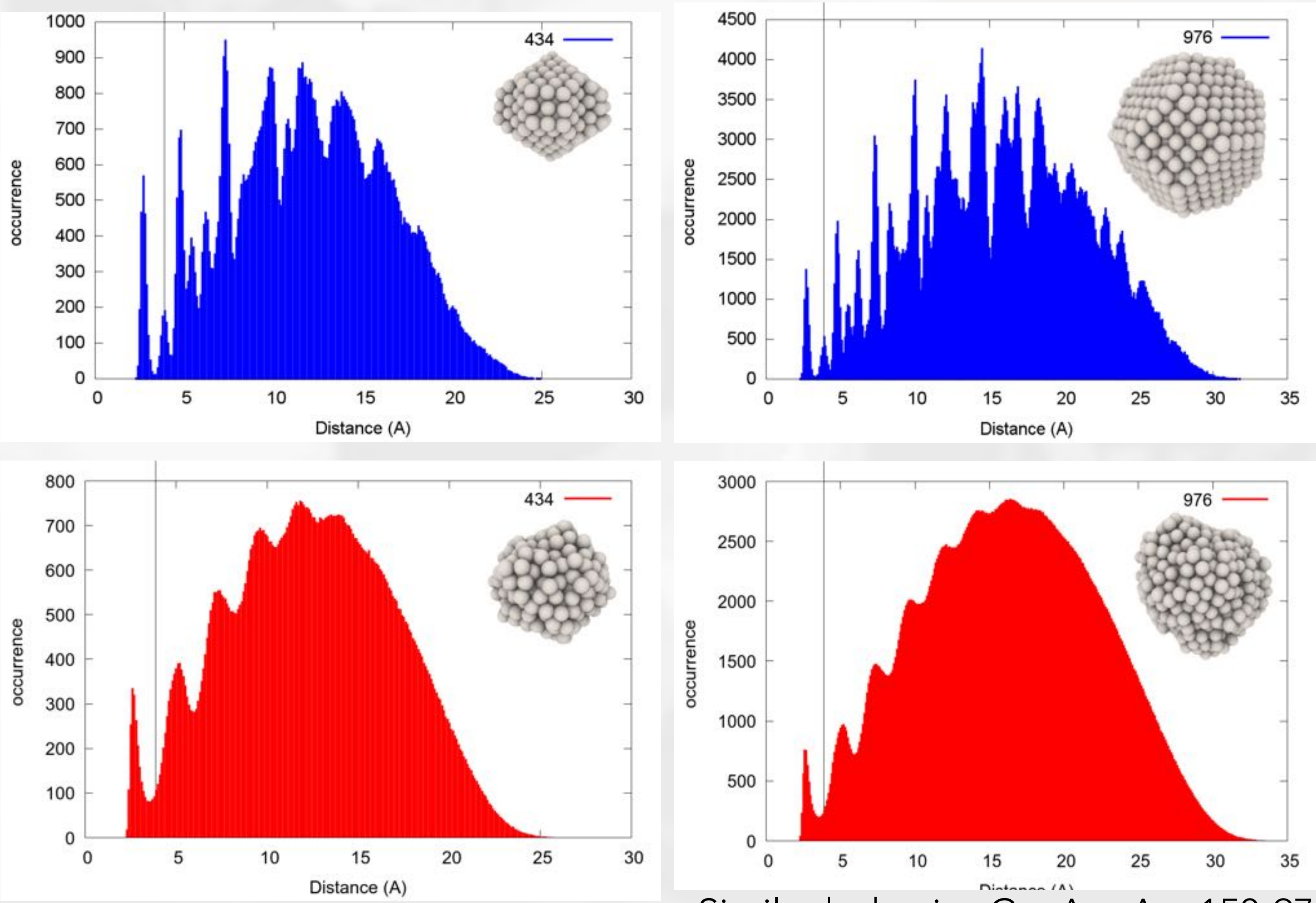
1NN peak in good approximation at the same position

2NN peak appears when some structural order does (good for detecting phase changes)



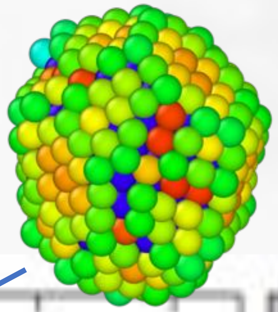
K. Rossi in preparation

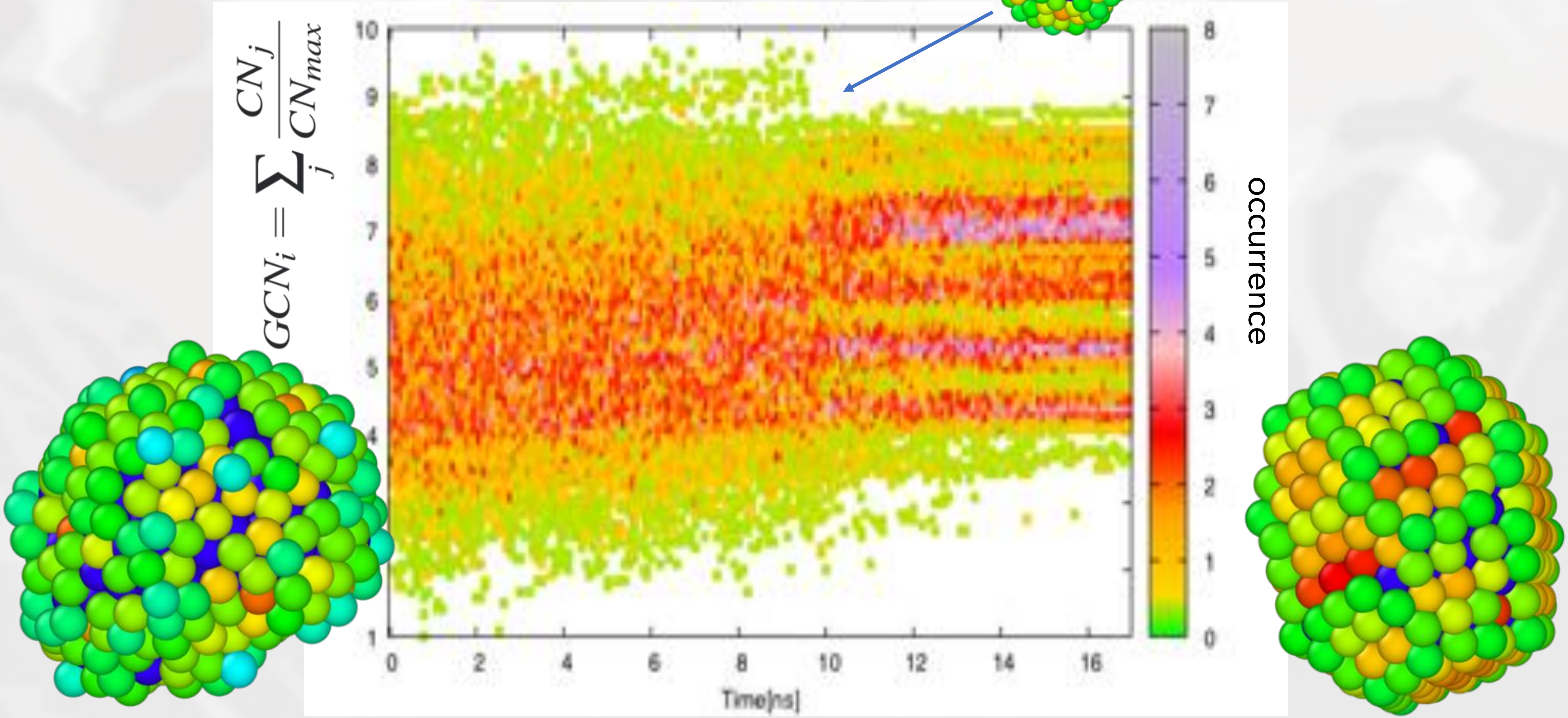
Pt



Similar behavior Cu, Ag, Au, 150-976

Surface characterisation

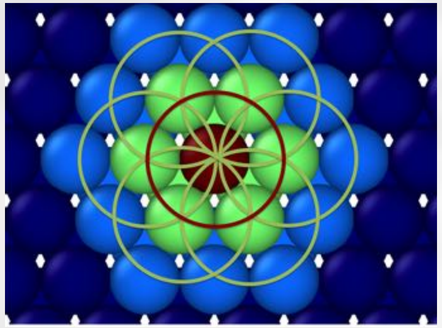


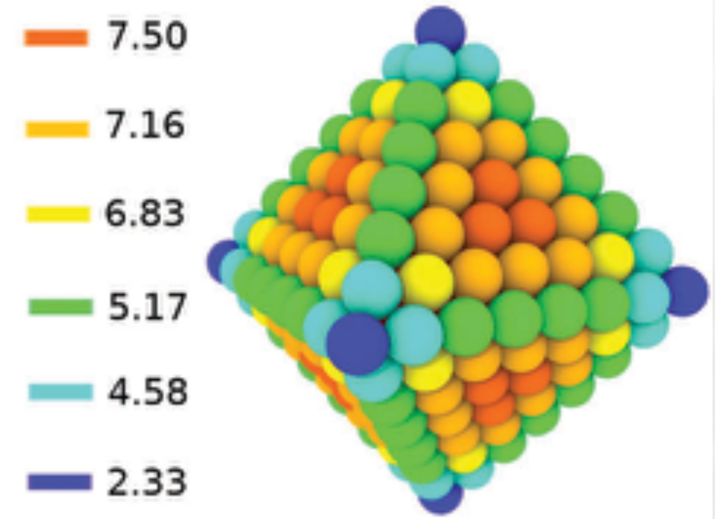


Nanogenomics

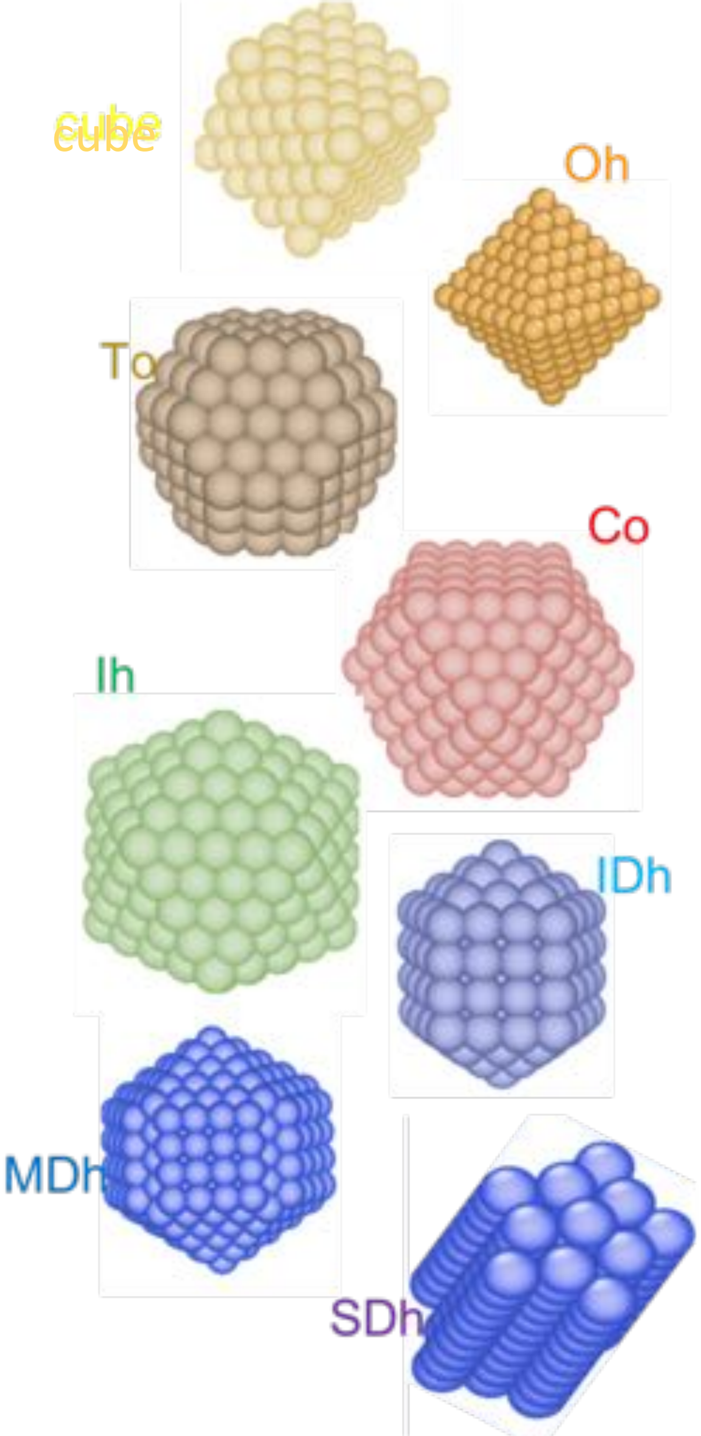
$$GCN_i = \sum_j \frac{CN_j}{CN_{max}}$$

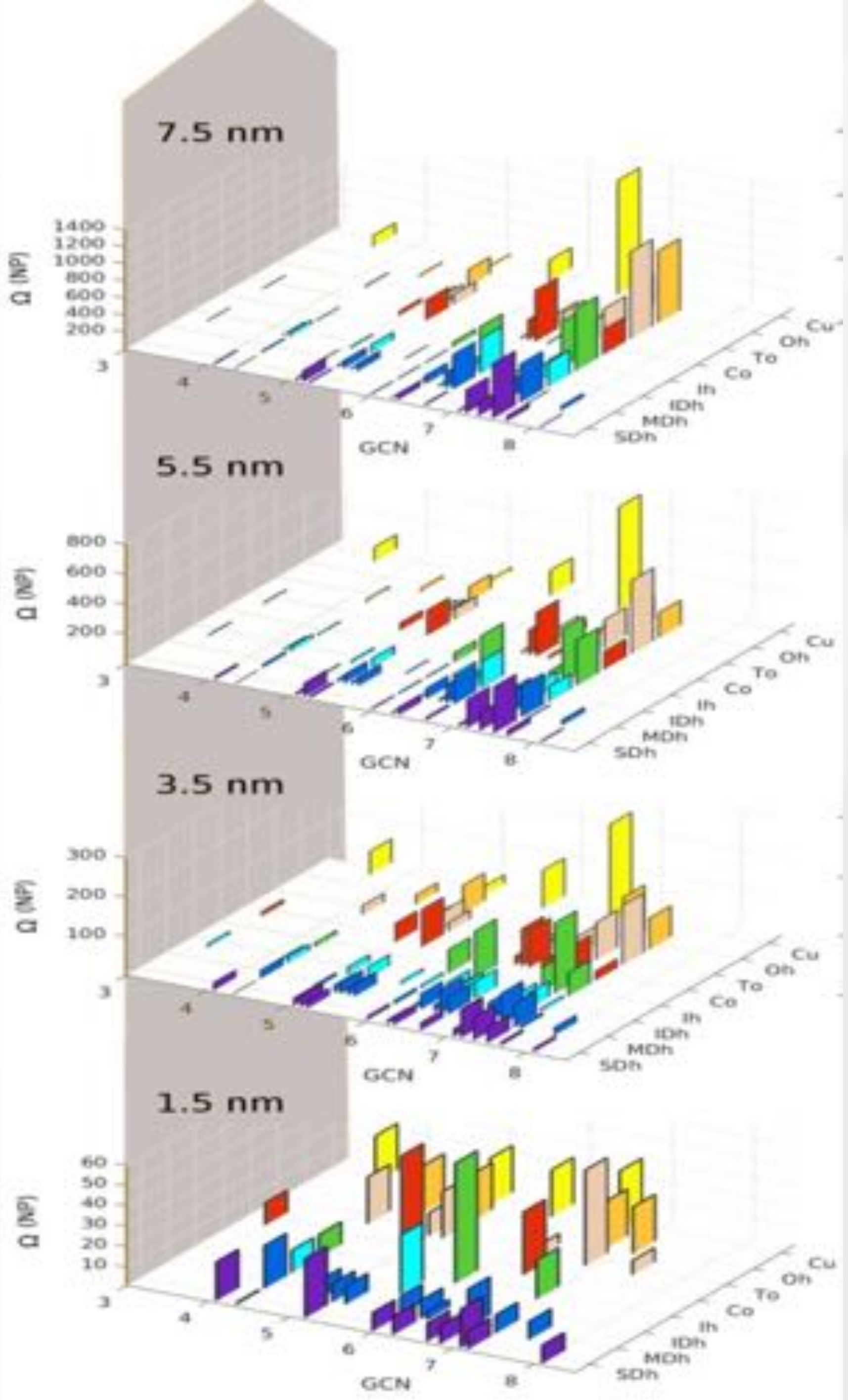
Sautet&Calle-Vallejo Angew. Chem(2014)



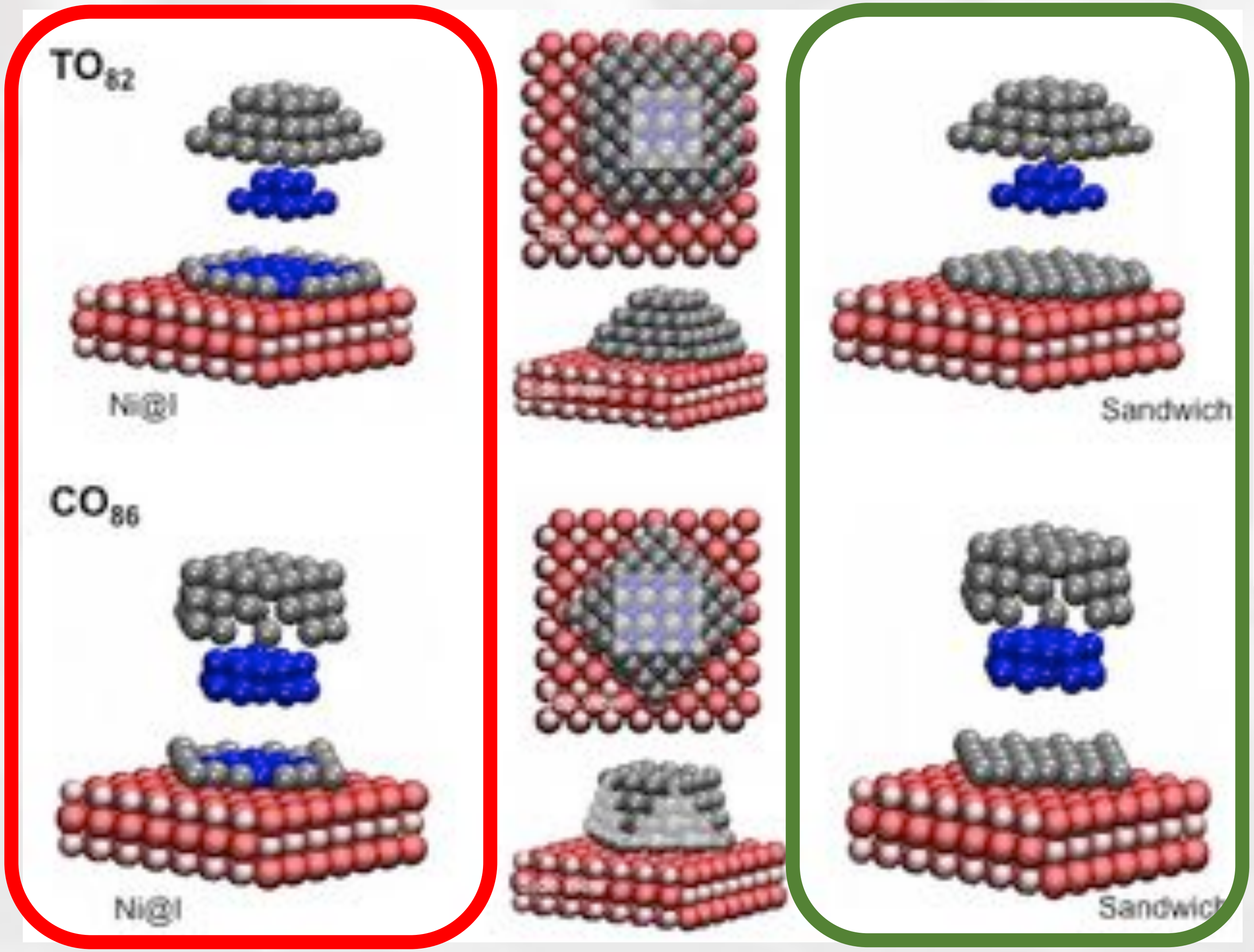


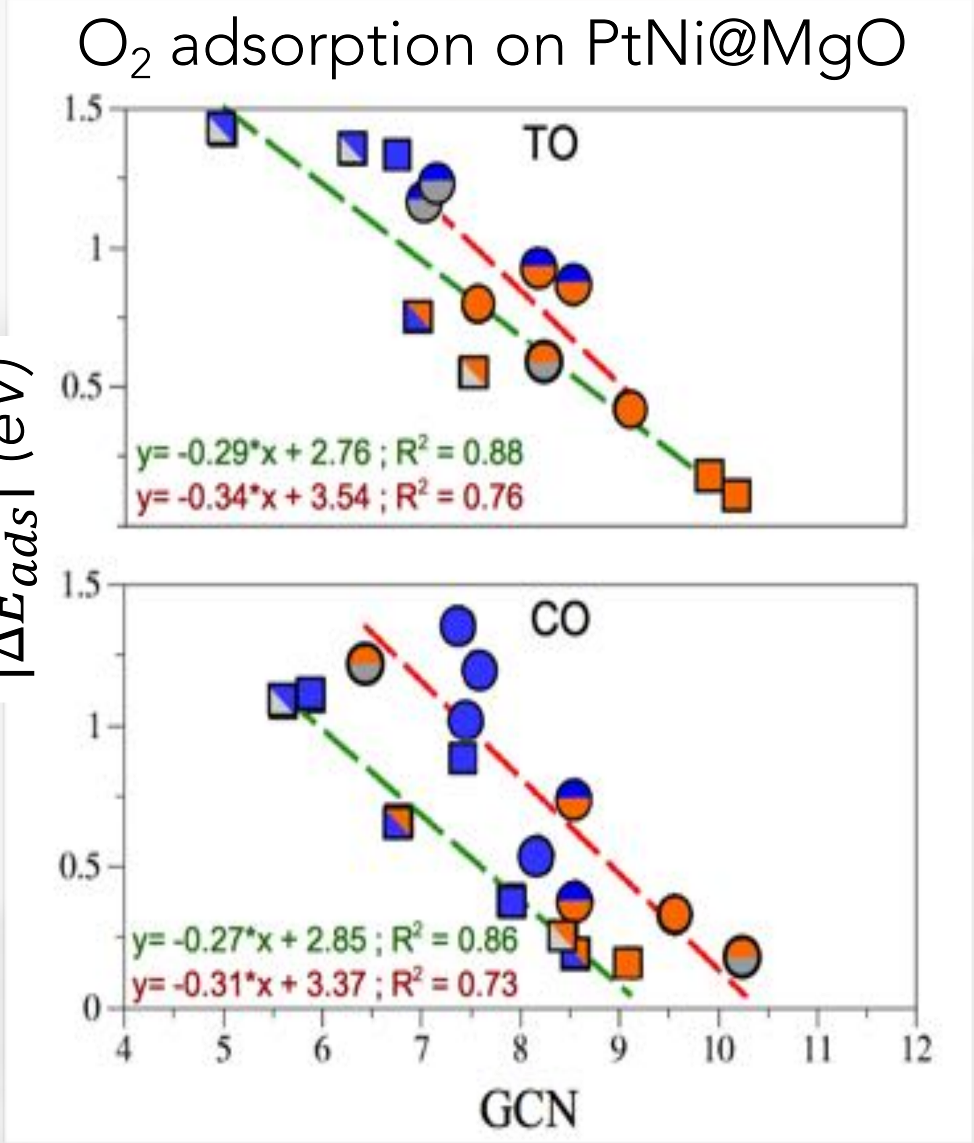
K. Rossi, et al. PCCP (2019)





ORR on supported PtNi

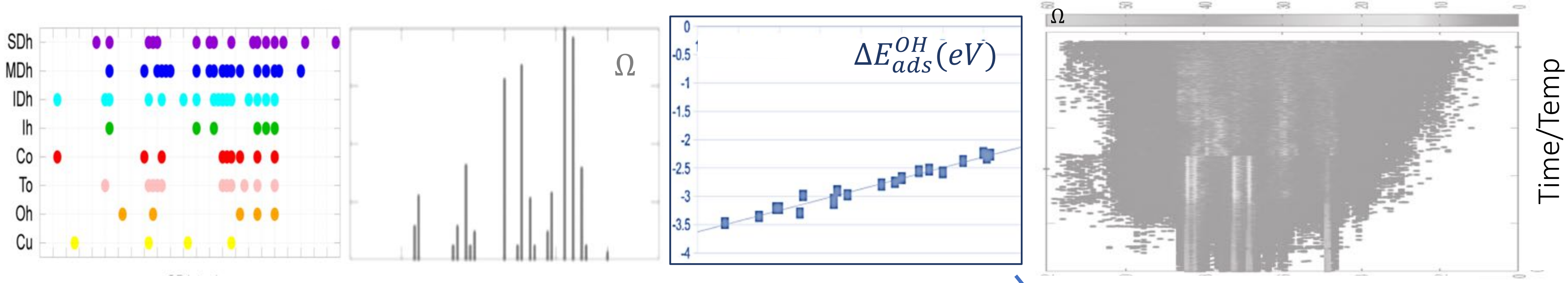




Interface effect?

Asara et al. ACS Cat. (2016)

From geometry to properties

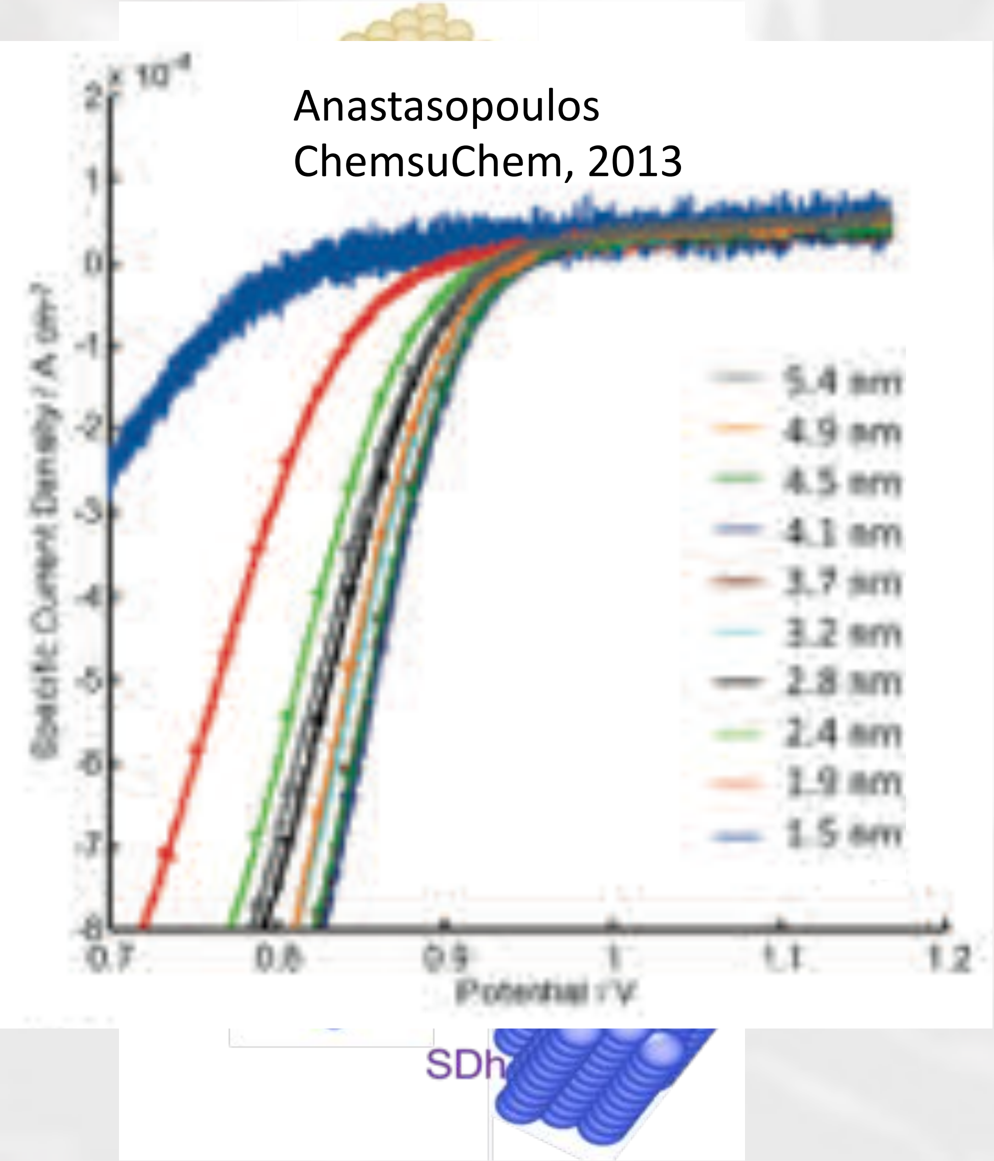


atop Generalized Coordination Number (GCN)

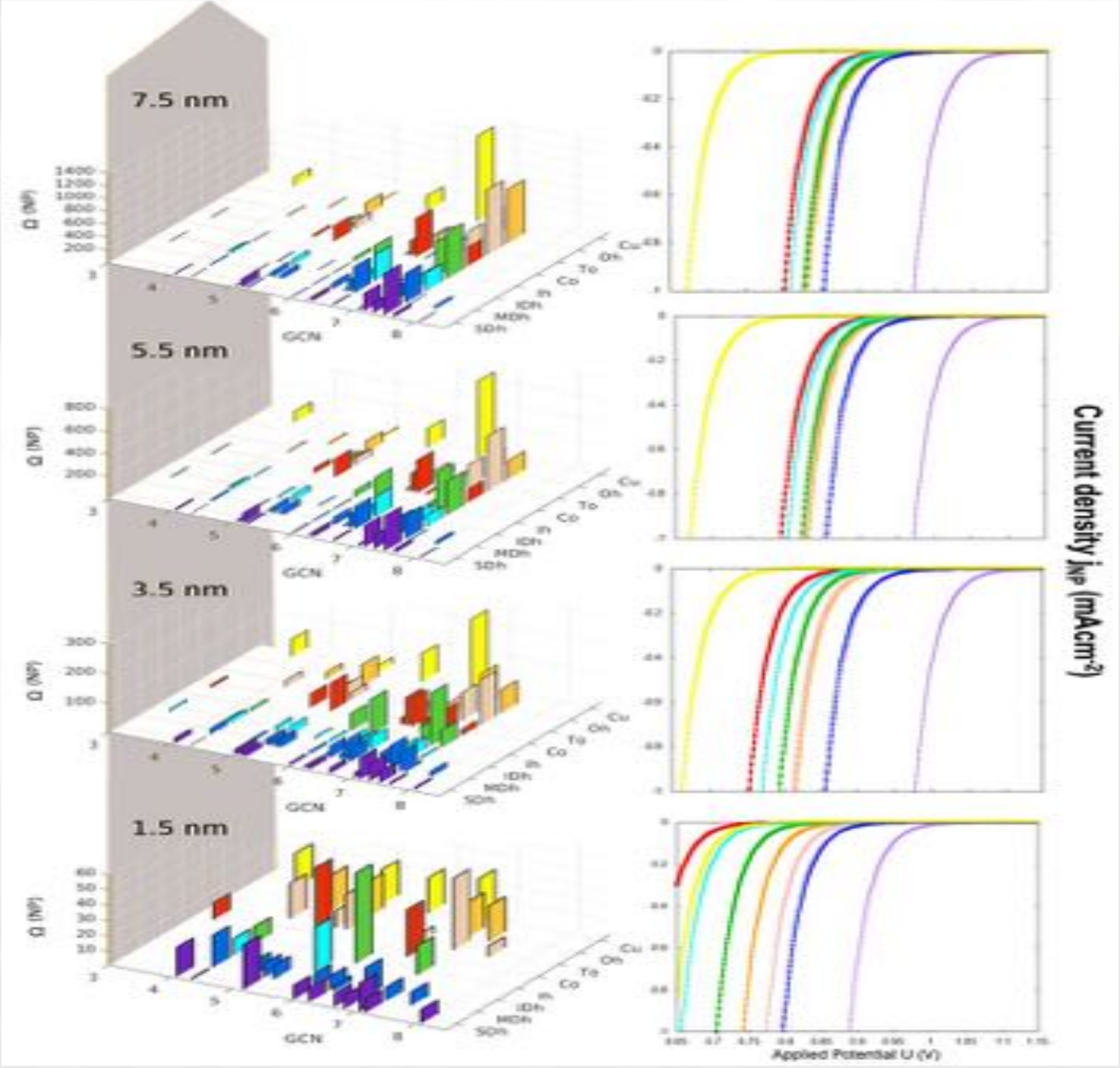
$$j_{NP}(t,T,U) = \sum_{\alpha \in GCN} \mathcal{L} \frac{\Omega(\alpha)\alpha}{N_{NP}} e^{\beta(\Delta G(\alpha) - eU)}$$

Kulkarni et al., Chem Rev 2018
Ruck et al. JPCL (2018)
Pt-NPs in $HClO_4$

ORR on Pt-NPs



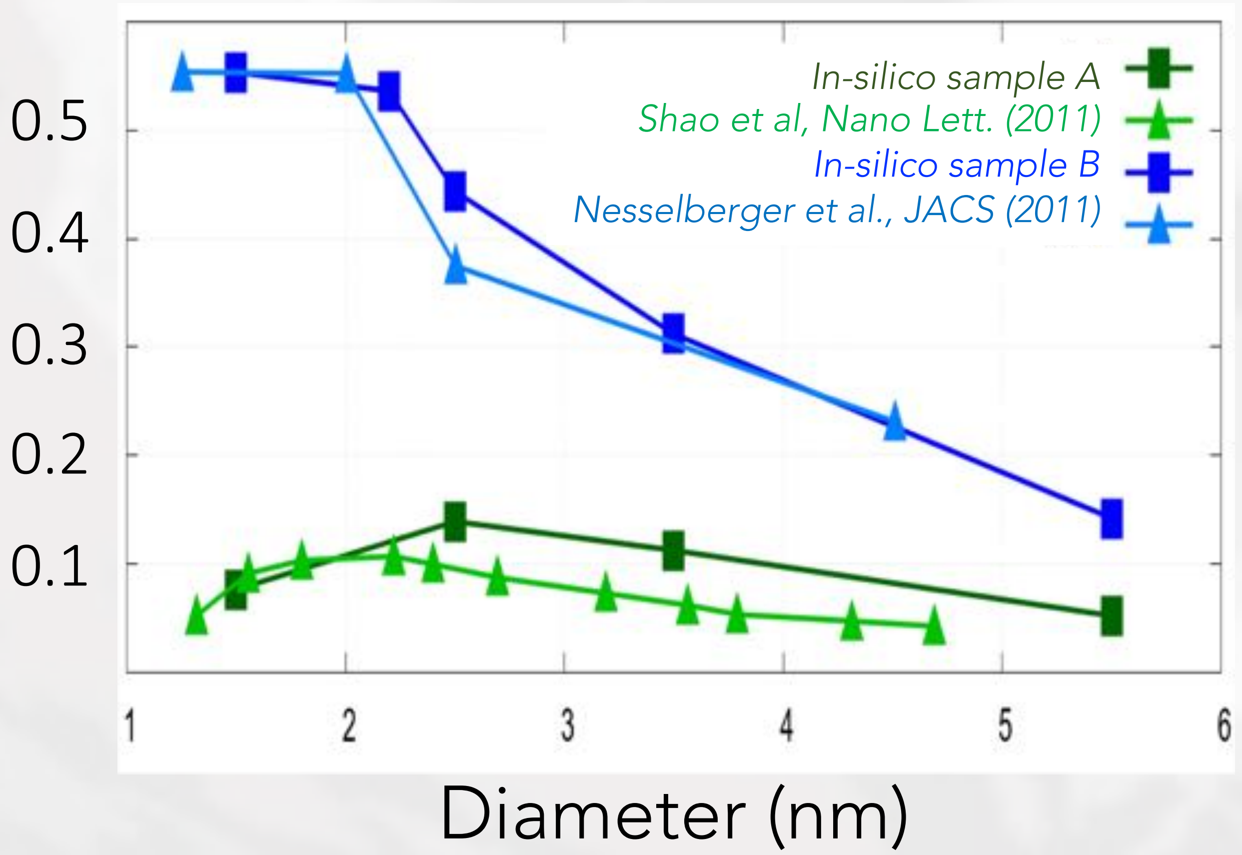
Anastasopoulos
ChemsuChem, 2013

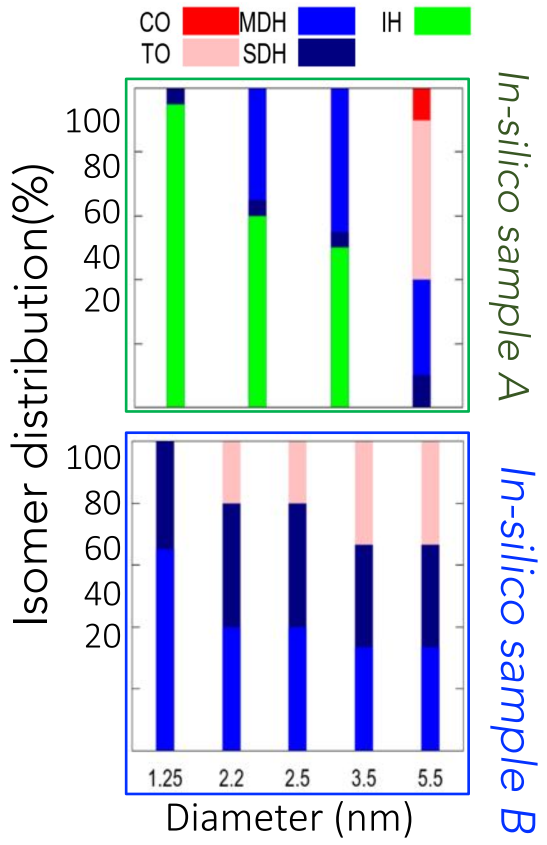


K. Rossi, submitted

ORR-activity of Pt samples

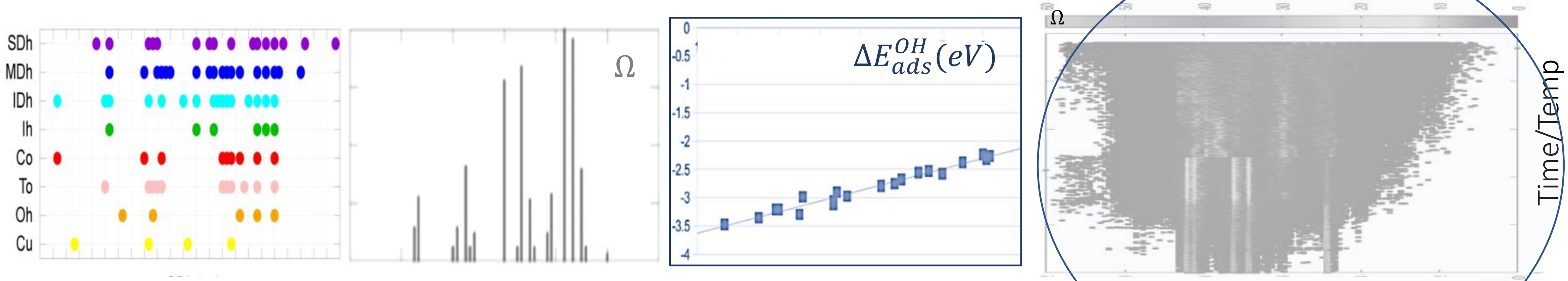
Mass Activity (A/mg) $= \sum_{NP \in ID} \frac{j_{NP} A_{NP}}{M_{NP}}$





Isomer distribution as a new parameter to design nanocatalysts

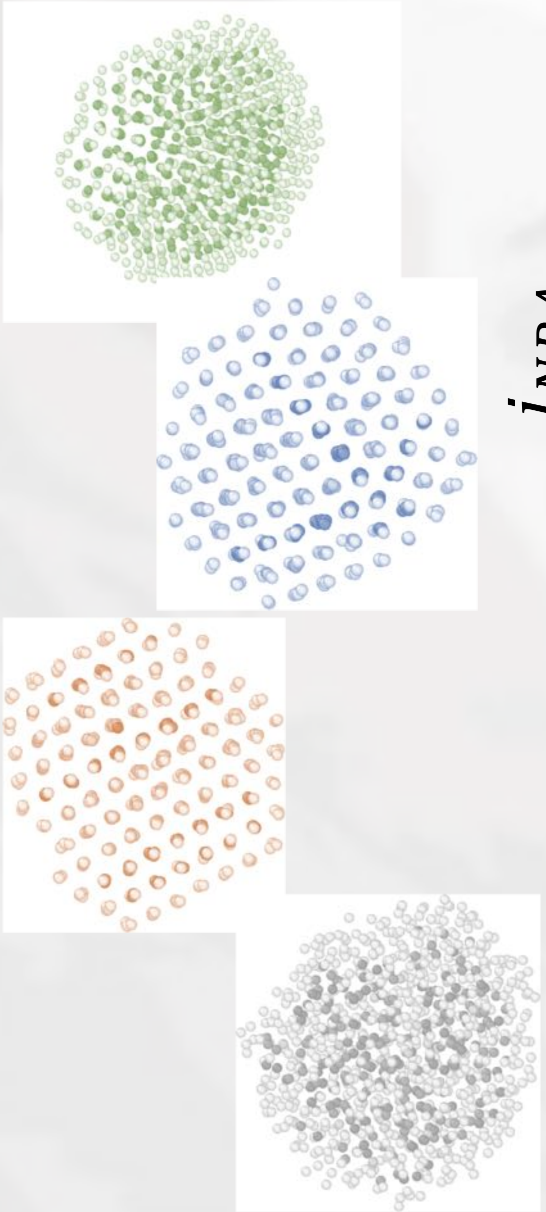
From geometry to properties

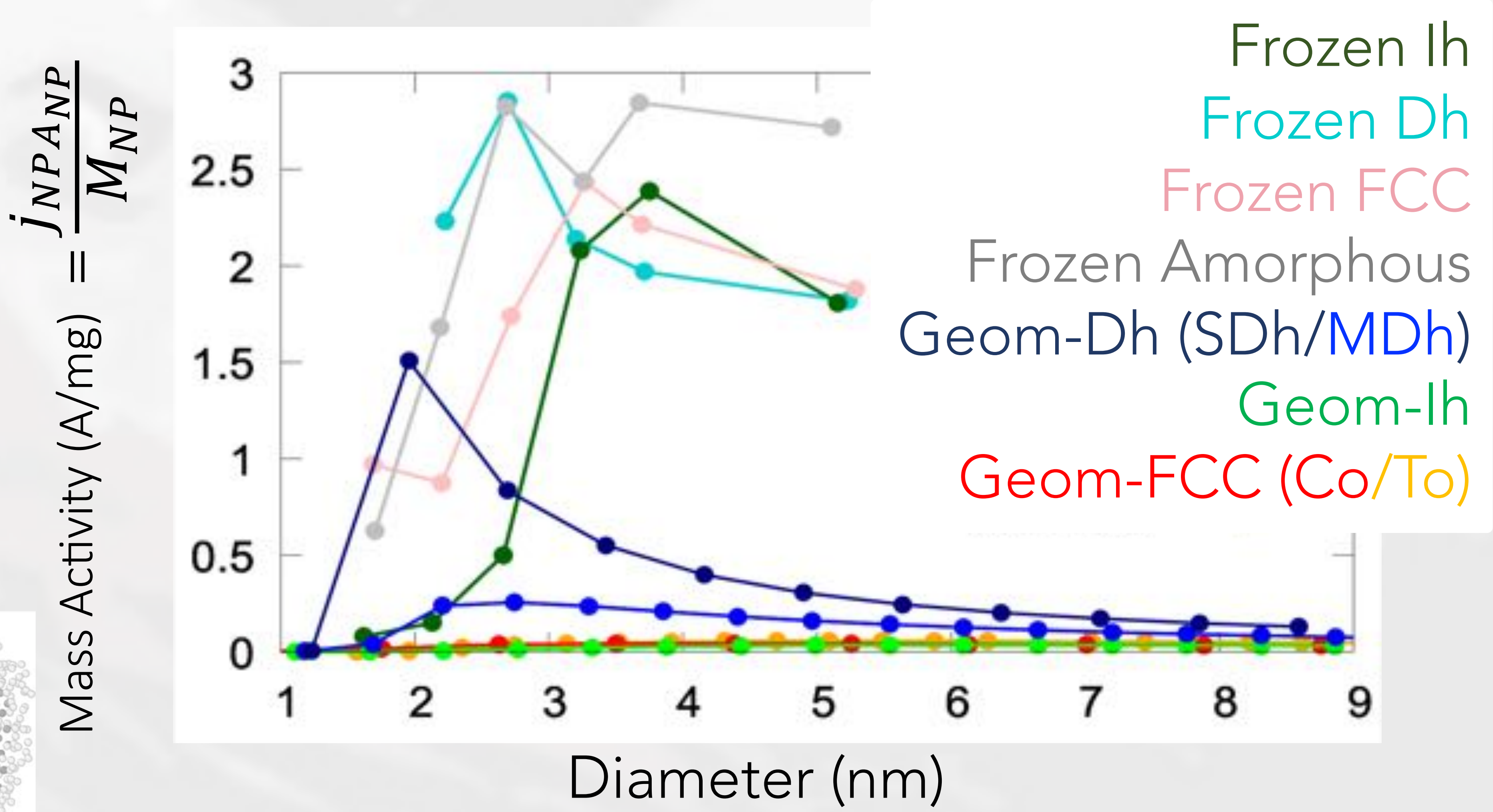


atop Generalised Coordination Number (GCN)

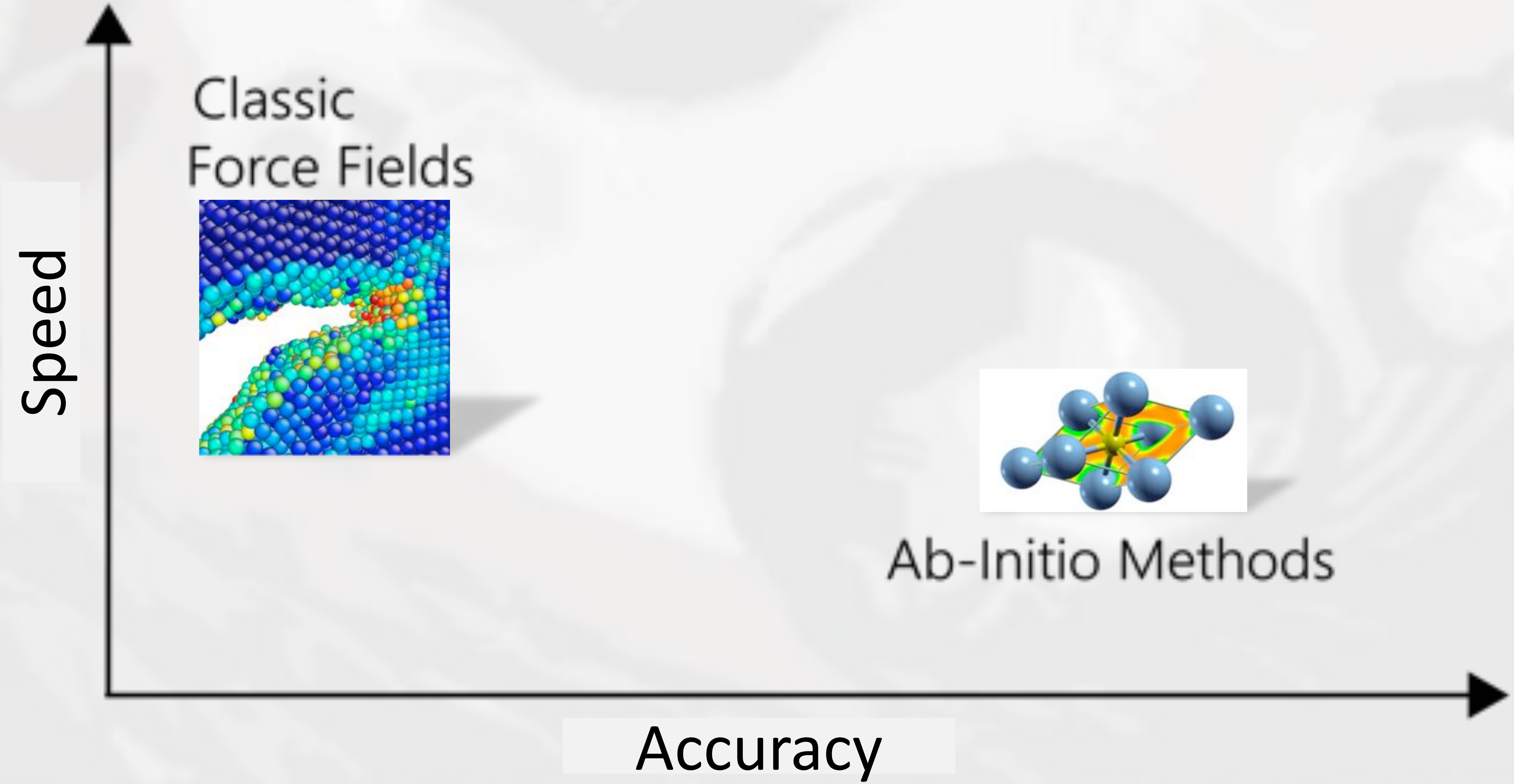
$$j_{NP}(t,T,U) = \sum_{\alpha \in GCN} \mathcal{L} \frac{\Omega(\alpha)\alpha}{N_{NP}} e^{\beta(\Delta G(\alpha) - eU)}$$

ORR on mobile Pt nanoparticles

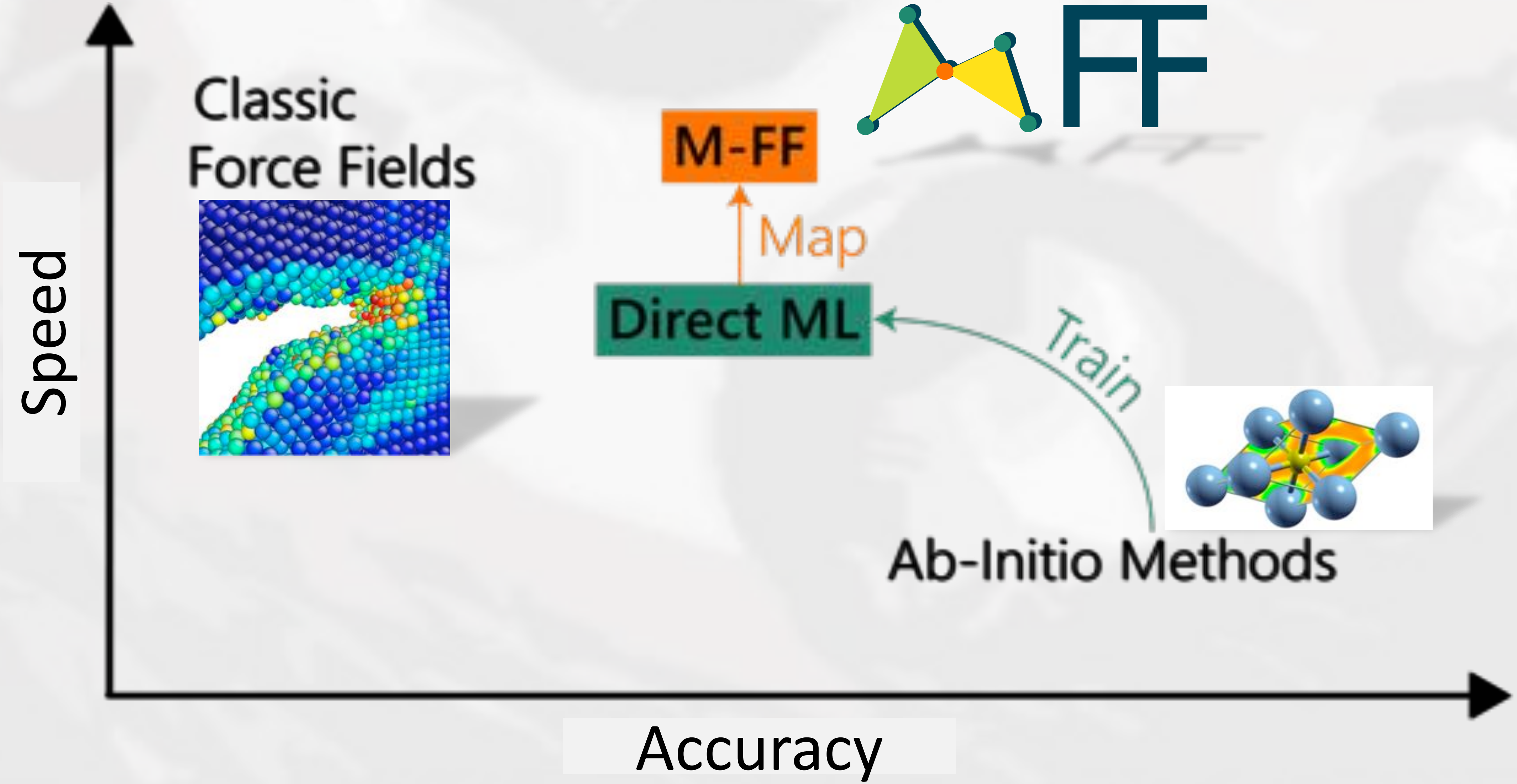




Fast & accurate MD



Fast & accurate MD: with ML

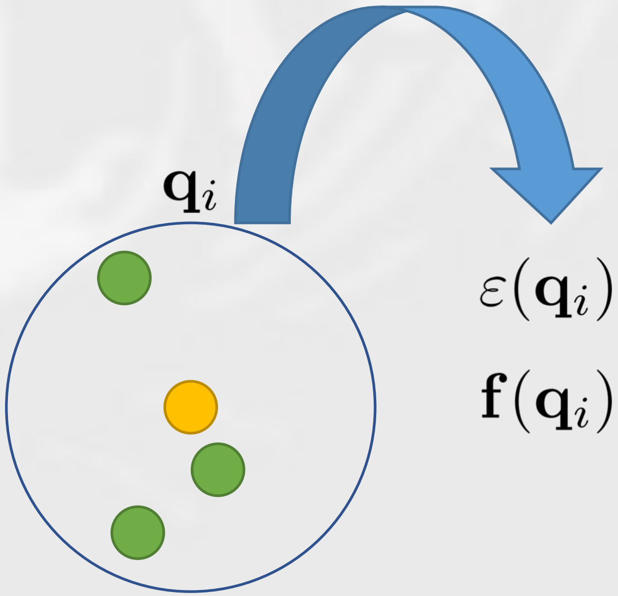


Learning set-up

- Infer a function that maps atomic coordinates and species to global energy
- Make a locality assumption for the energy:
- Learn the local energy function $\varepsilon_i(\mathbf{q}_i)$ and/or the force function $\mathbf{f}_i(\mathbf{q}_i)$
- Database $\mathcal{D}$ containing N-pairs $\{\mathbf{q}_i, \varepsilon(\mathbf{q}_i)\}$
- Input: 3M-6 dimensions, Output: 1 dimension (or 3 for forces)

$$E(\mathbf{R}_n)$$

$$E(\mathbf{R_n}) = \sum_{i \in \mathbf{R}_n} \varepsilon(\mathbf{q}_i)$$



Courtesy by Claudio Zeni

Gaussian regression progress

- ✓ Easy to encode prior information
- ✓ Work with small datasets
- ✓ Simple to interpret
- X Require user knowledge
- X Computational scaling

Kernels and descriptors must encode physical properties:

$$\hat{\varepsilon}(\mathbf{q}) = \sum_{n}^{N_{tr}} k(\mathbf{q}, \mathbf{q}_n)\alpha_n$$

Permutational invariance k(A, B) = k(A, P B)

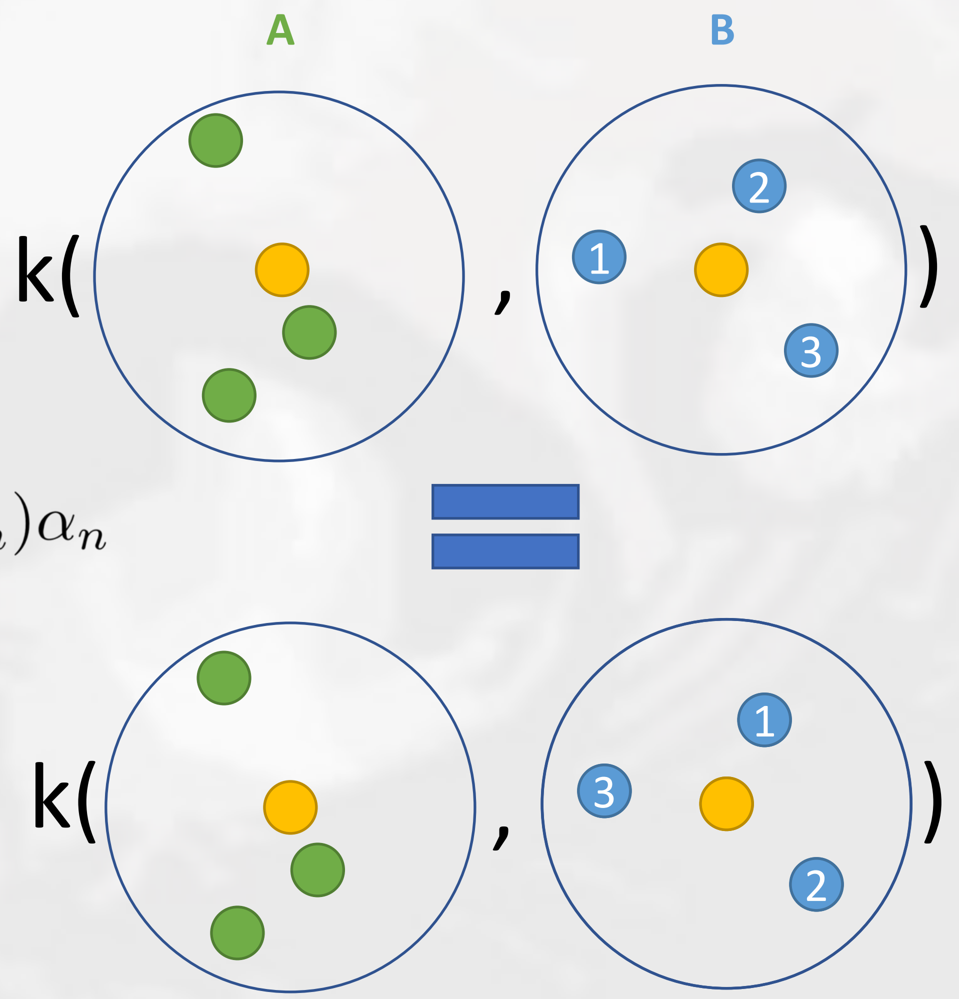
Translational Invariance k(A, B) = k(A, T B)

Rotational Invariance k(A, B) = k(A, R B)

Must be also differentiable and smooth,

so that forces can be calculated:

$$\mathbf{f}(\mathbf{q}_i) = -\frac{\partial E(\mathbf{R}_n)}{\partial \mathbf{r}_i}$$

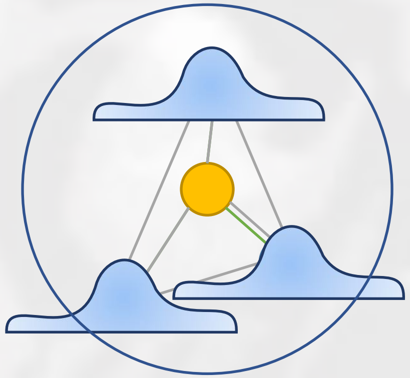


Courtesy by Claudio Zeni

Local Atomic Environment descriptors

Array $\mathbf{q}_i$ that encodes all the relevant features of the local atomic environment ρ_i, e.g.:

List of distances from central atom $\mathbf{q}_i = \{r_{ij}\}_{j \in \rho_i}$



List of triplets of distances $\mathbf{q}_i = \{(r_{ij}, r_{ik}, r_{jk})\}_{j,k \in \rho_i}$

Spherical harmonics power spectrum of the smoothed atomic positions $\rho_i(\mathbf{r}) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{nlm}^{i}\, g_n(r) Y_{lm}(\hat{\mathbf{r}})$

A descriptor should be: fast to compute, invariant to physical symmetries, differentiable, informative.

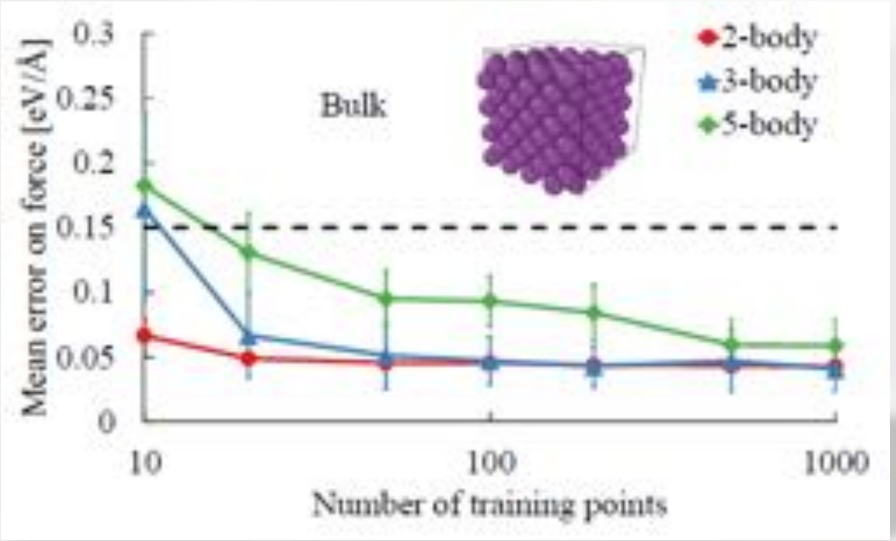
C. Zeni et al. submitted

Interaction Order

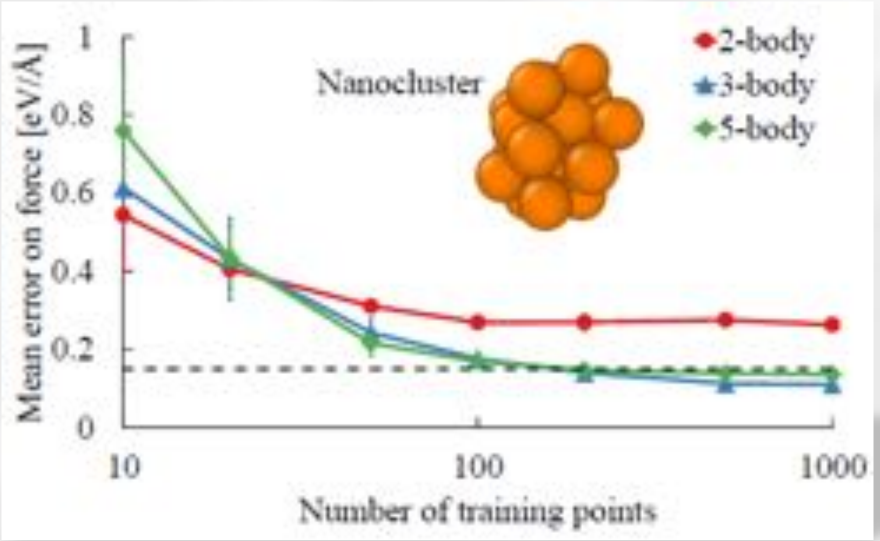
Number of simultaneously interacting particles the potential can describe.
Examples:

Lennard-Jones potential	2-body
Tersoff potential	3-body
EAM/RGL potential	many-body

Bulk Nickel: 2-body



Nickel Nanoparticle: 3-body

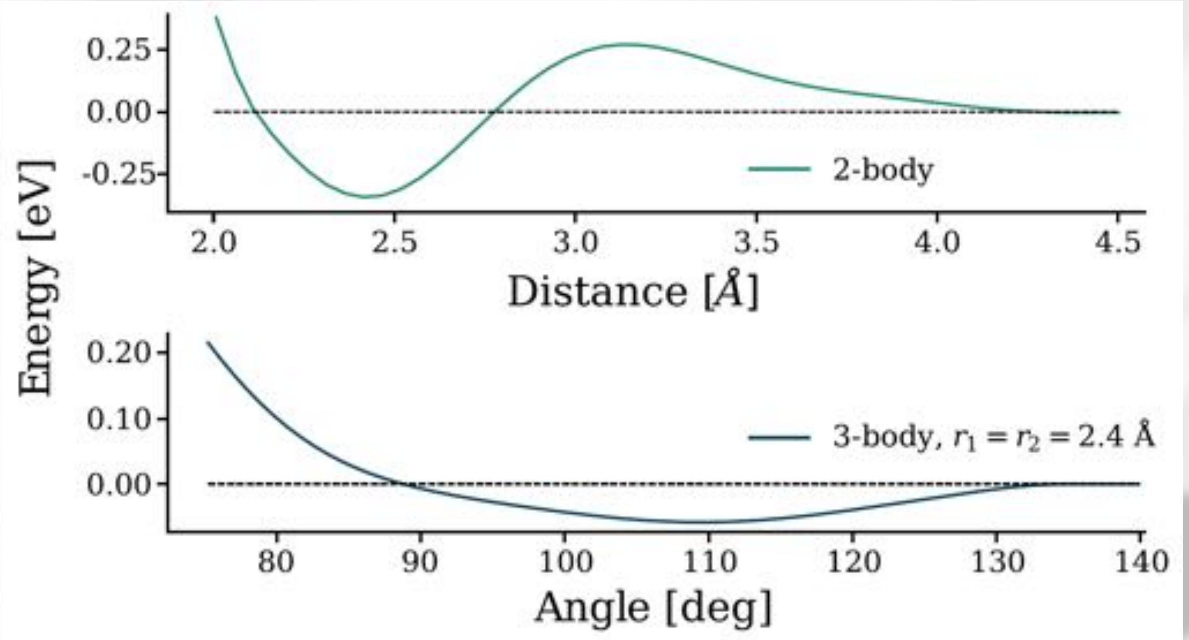


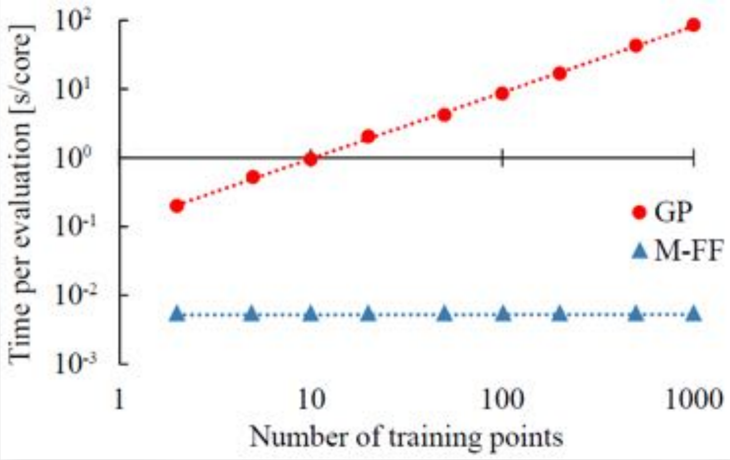
A. Glielmo et al. PRB (2019)

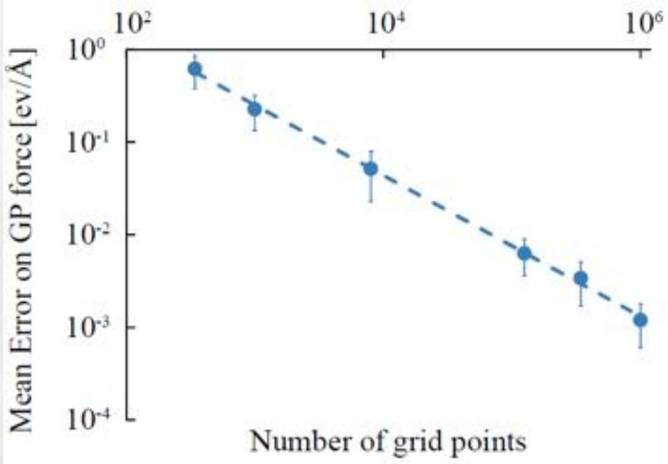
Courtesy by Claudio Zeni

Mapping-FF

Idea: take non-parametric GP force fields and tabulate them, similarly to classic potentials







Computational speedup of 10^4 -10^5

No accuracy loss

Can only be done for finite-body kernels (and practically for 2-, 3-, 4-body kernels)

Courtesy by Claudio Zeni

MFF: a Python package

https://github.com/kcl-tscm/mff

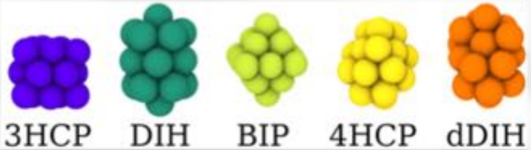
DFT

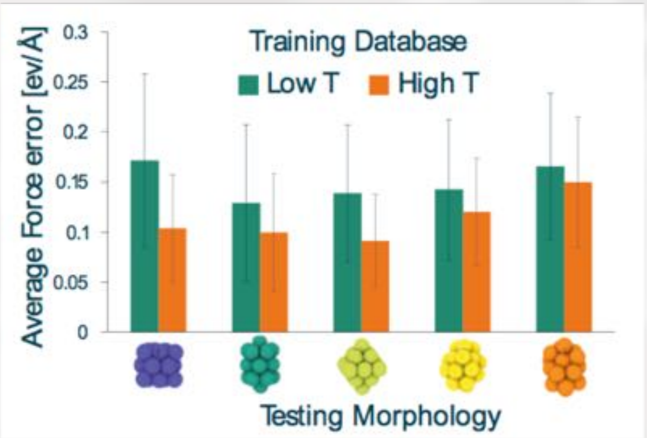
- Run short MD ab-initio simulations to produce a database

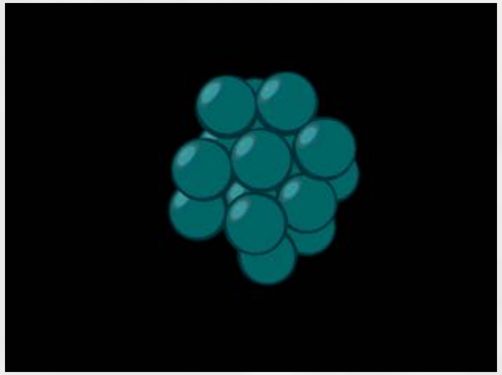
Courtesy by Claudio Zeni

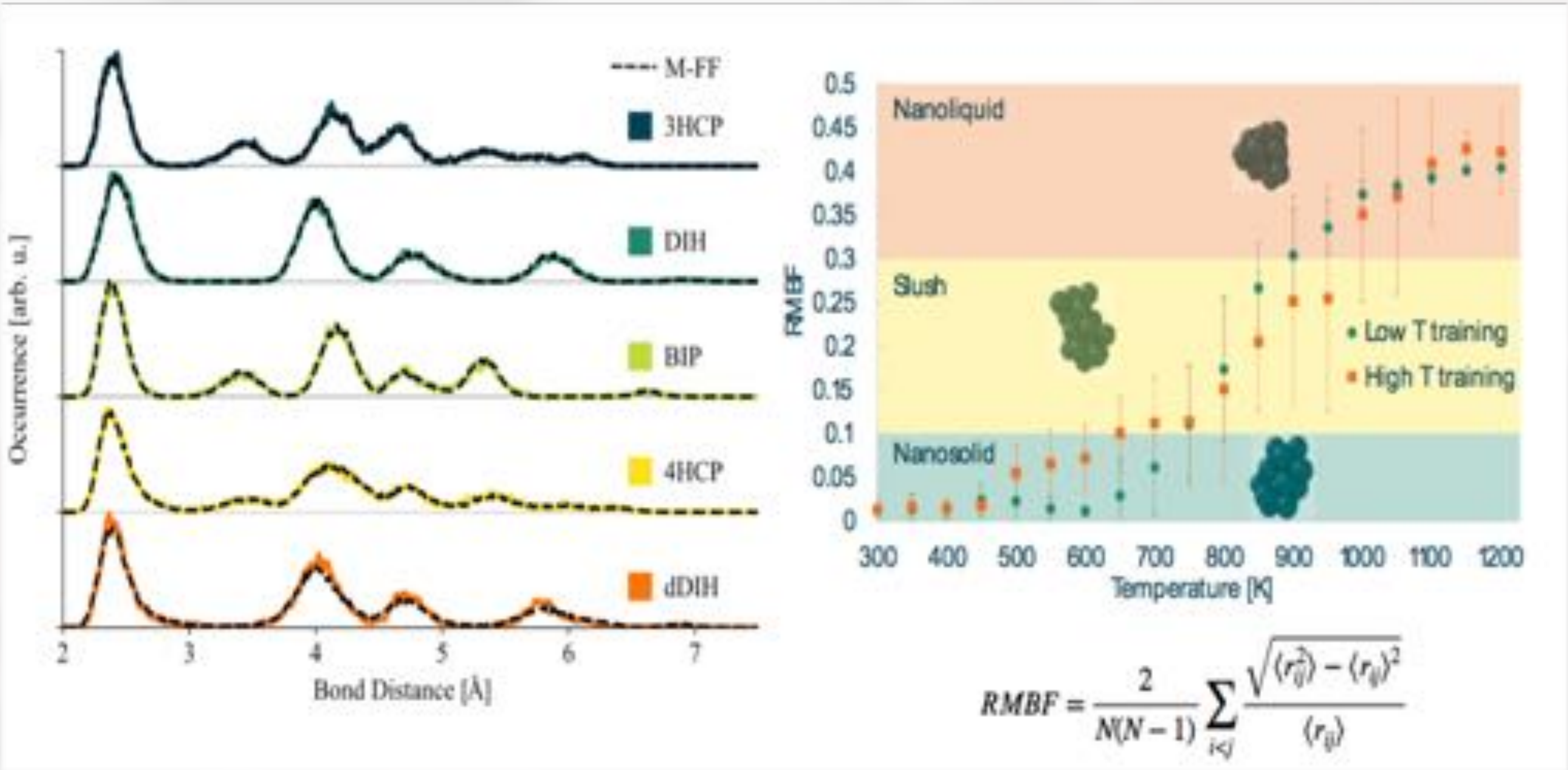
Fast & accurate MD

Ni_{19}









C. Zeni et al. JCP (2018); CZ et al. submitted

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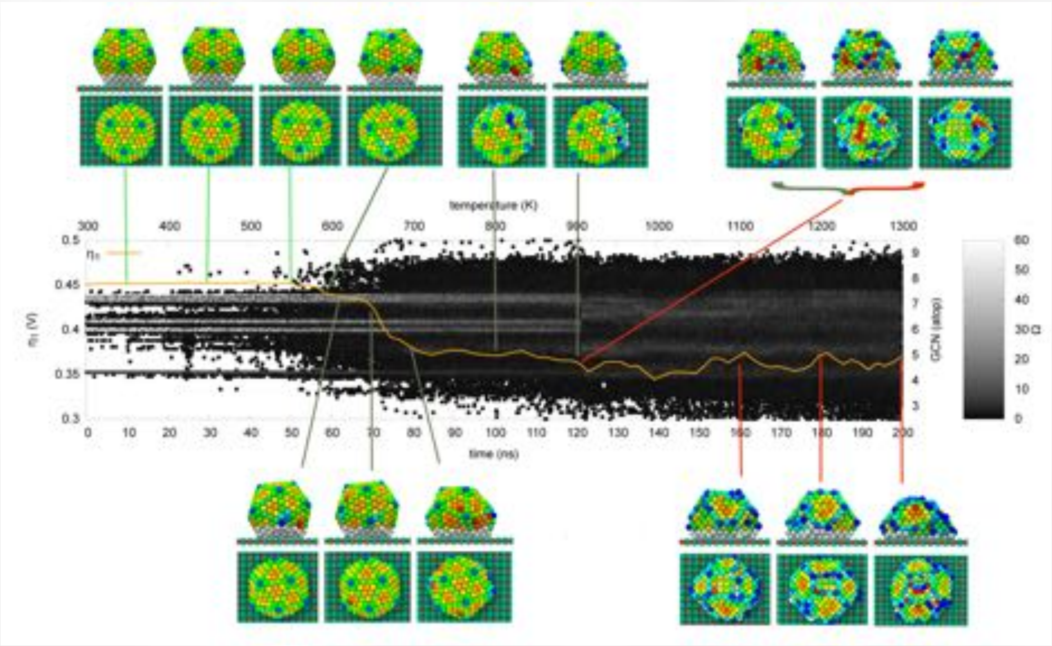
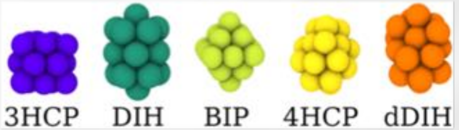
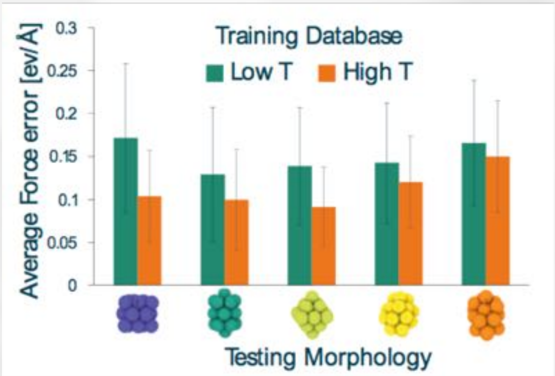
Nanoparticles-by-design: a today challenge



- Size
- Materials (composition/ordering)
- Stability & formation process
- Structure-property relationship





Thank you for your attention!!!