Multiscale Modelling of Gold Clusters and Nanoparticles

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Outline

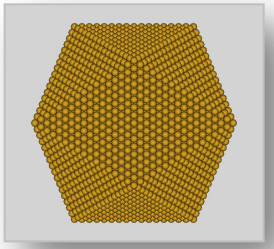
1. Introduction & motivation
2. Simulation method
3. Thiol adsorption simulations
4. Nanocrystals in superlattices
5. DFT calculations of gold nanoclusters
6. Conclusions
7. The future

Introduction

Our object of interest

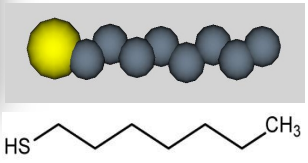
From the bottom to the top

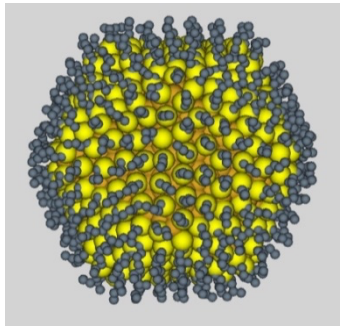
NANOCRYSTAL OF GOLD



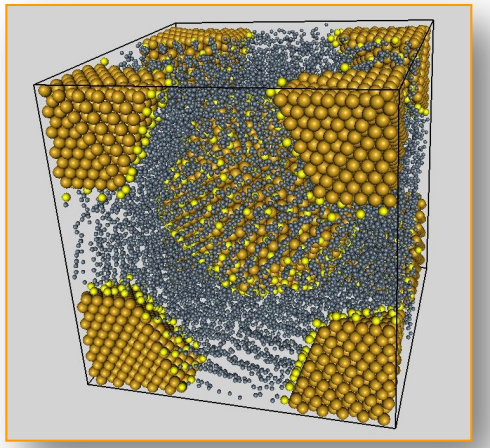
Icosahedron

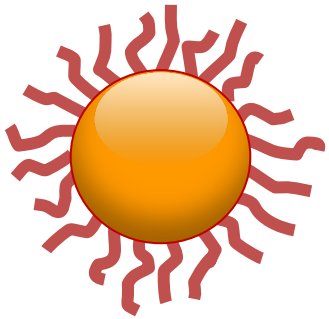
Adsorption of thiols

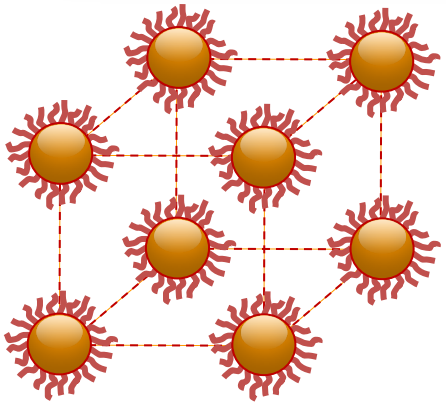




Formation of superlattices





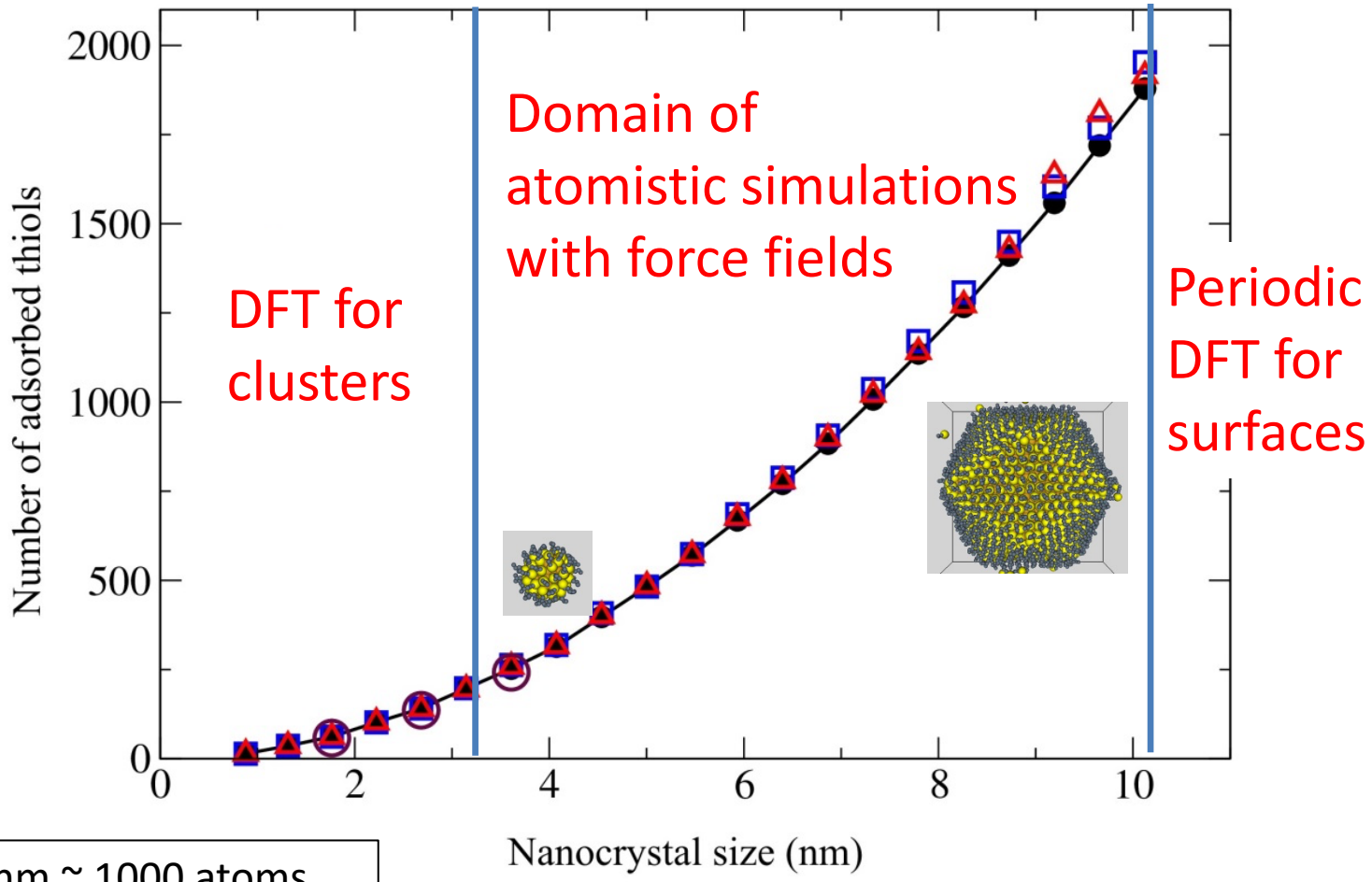


Unsolved problems in nanoparticles science:

1. What does **control the growth** of nanoparticles?
2. How do **ligands adsorb** on nanoparticles?
3. How do **nanoparticles interact**?
4. How can we **control the assembly** of nanoparticles?
5. How do some nanoparticles **catalyze reactions**?
6. How nanoparticles can be **used in applications**?

2. Simulation method

Why do we use classical methods?



2 nm ~ 1000 atoms
5 nm ~ 10000 atoms
10 nm ~ 50000 atoms

Nanocrystals between 3 and 10 nm cannot be studied by quantum chemical methods.

2. Simulation method

Natomos-Gromacs: acceleration of simulations

- Simulations limited to nanocrystal diameter of 5 nm in literature.
- Nanocrystals between 4 and 10 nm in many experiments.
- Our simulations: nanocrystals until 10 nm never reached before.

Simulation methods

Natomos

Home-made Monte Carlo & Molecular Dynamics code

Gromacs

Public Molecular Dynamics code
massive parallel computing

NATOMOS

- Definition of configuration
- Parameterization of force field

GROMACS

MD simulations

Up to 400x faster simulations

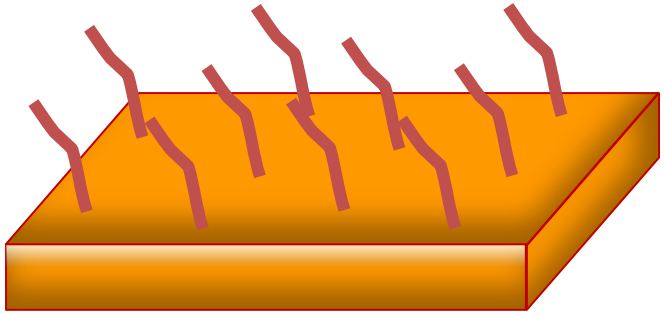
NATOMOS

Analysis of results

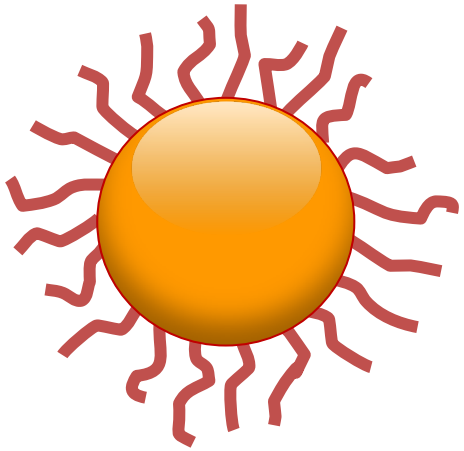
3. Thiols adsorption simulations

How do **ligands adsorb** on nanoparticles?

Why can we put more ligands on a nanocrystal surface ?



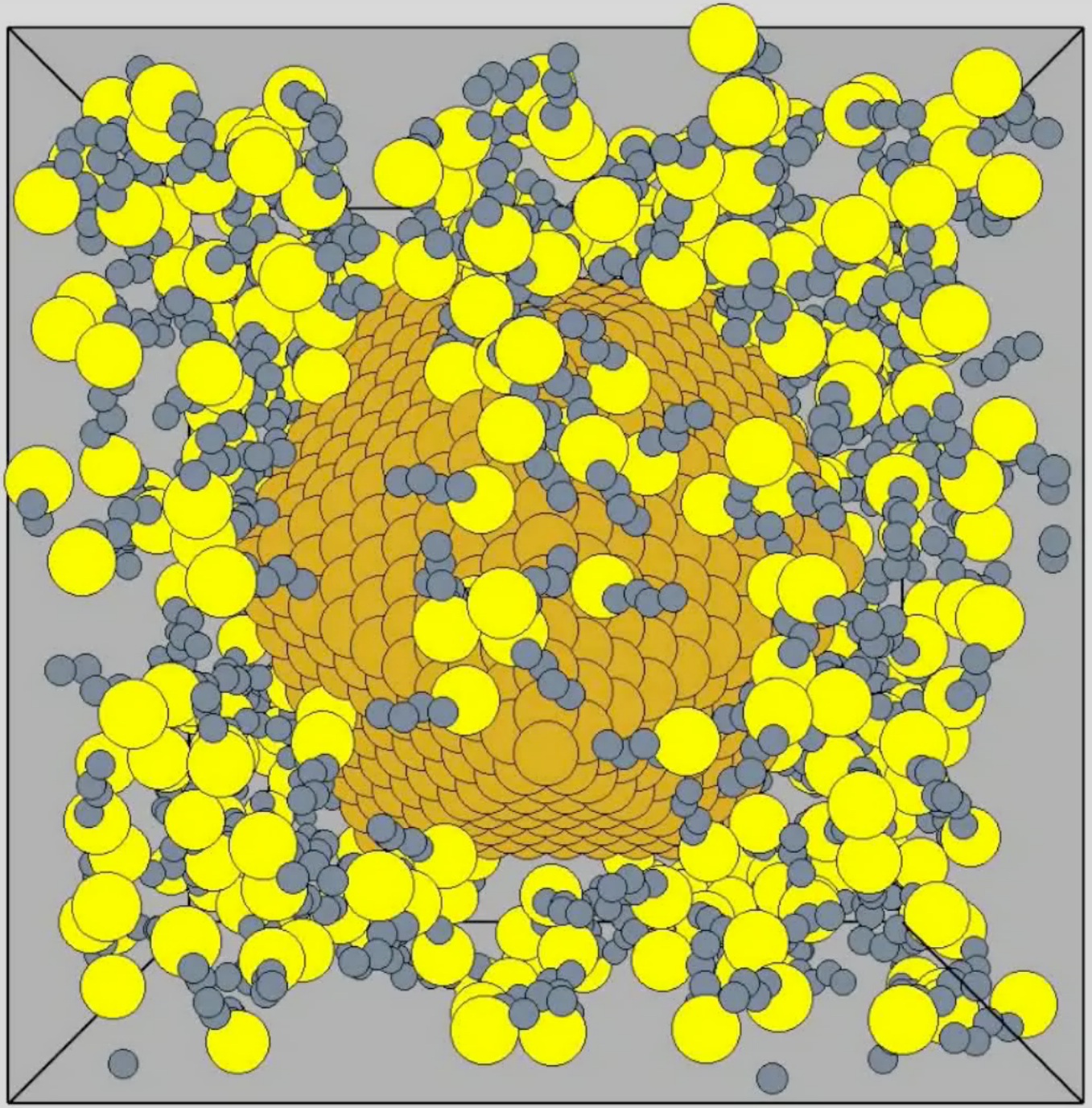
Au(111) planar surface[1]
21.4 Å^2/thiol



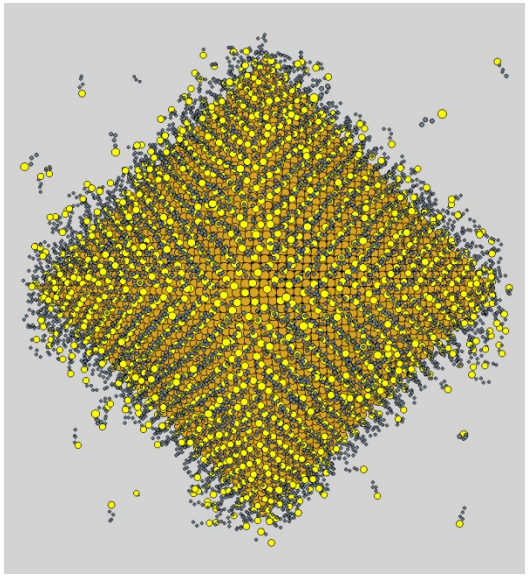
Au nanocrystal[2]
15.2 - 17.2 Å^2/thiol

From which size does a nanocrystal behaves like the bulk material?

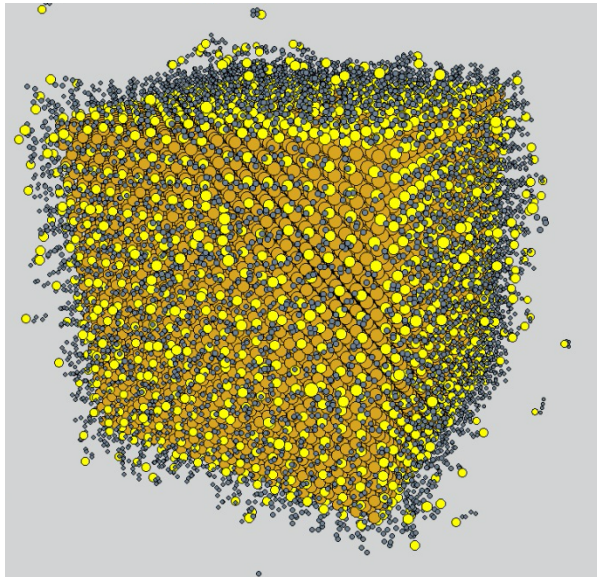
1: Ulman. Chemical Reviews 1996. 96. 1533–1554.
2: Lennox *et al*. Chemistry – A European Journal 1996. 2. 359–363.



Octahedron vs Cube



versus

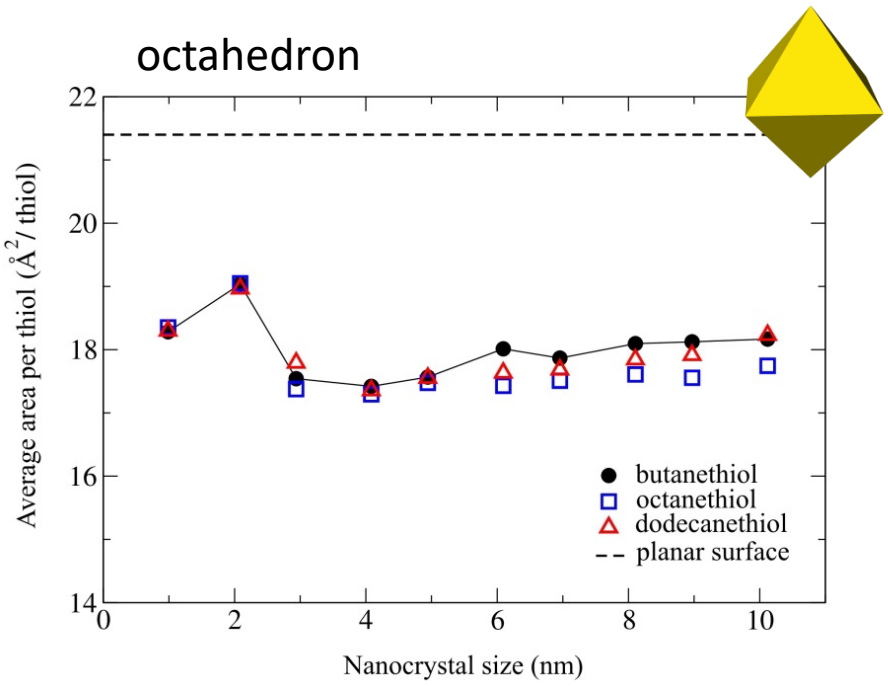


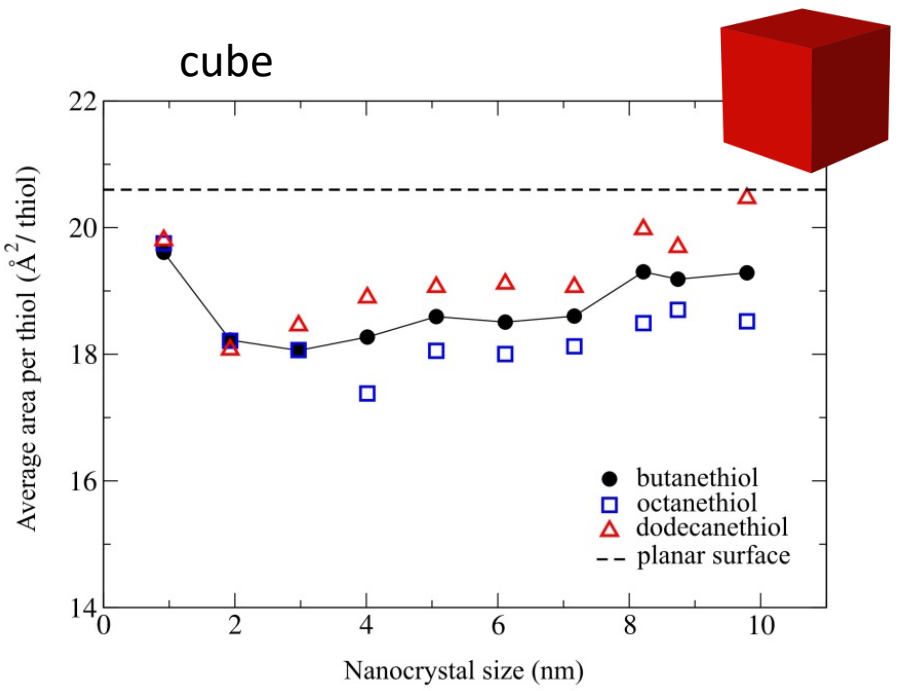
octahedron

cube

1. T. Djebaili, J. Richardi*, A. Abel et M. Marchi, J. Phys. Chem. C 117, 17791 (2013)
2. T. Djebaili, J. Richardi*, A. Abel et M. Marchi, J. Phys. Chem. C 119, 21146 (2015)

Average area per thiol





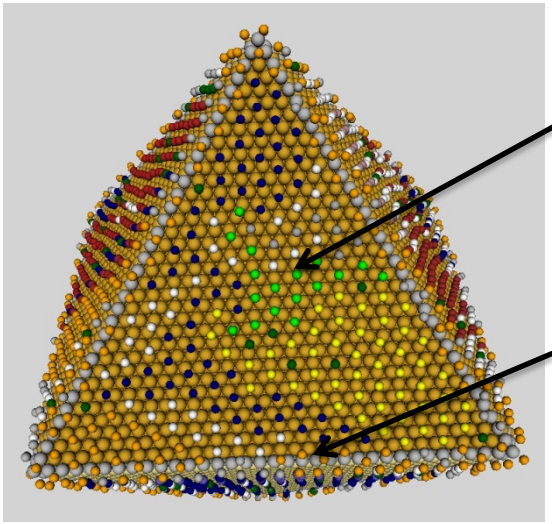
- Good agreement with experimental data by mass spectroscopy[1], thermogravimetry[2] and TEM,
- Small difference between cube and octahedron,
- The surface coverage slightly depends on the thiol chain length.

1. Läemmerhofer *et al*. ACS Nano 2013. 7. 1129–1136
2. Hostetler *et al*. Langmuir 1998, 14, 17–30.

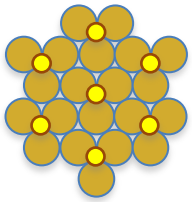
Thiol headgroup organization

What is the origin of the lower area per thiol? – It's the edges, stupid!

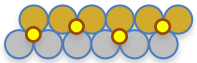
Octahedron (111) facets



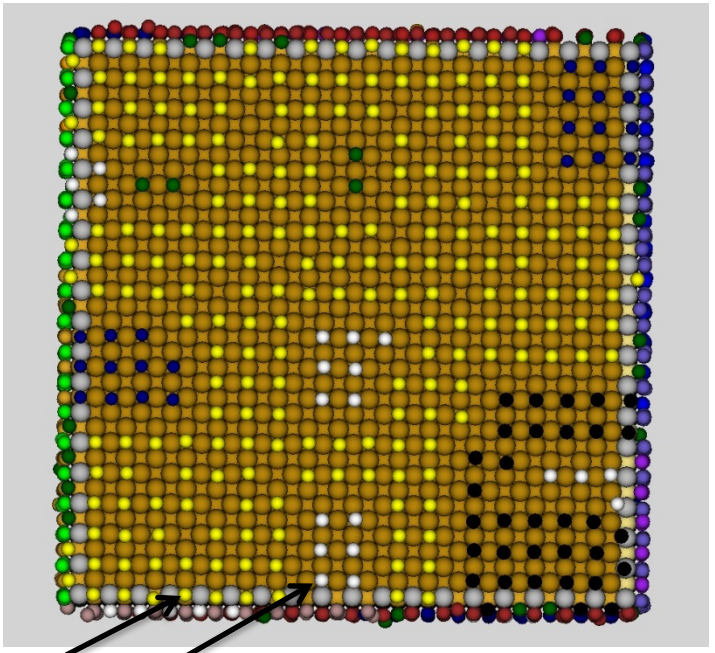
Hexagonal SAM



Zigzag SAM

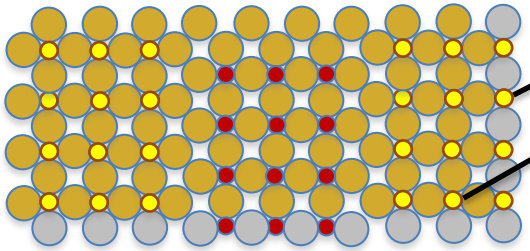


Cube (100) facets

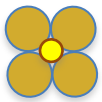


- Two different molecular organizations on the facet center & edges.

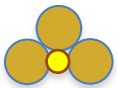
Square SAM



- occupation of new sites on the edges



4f- hollow



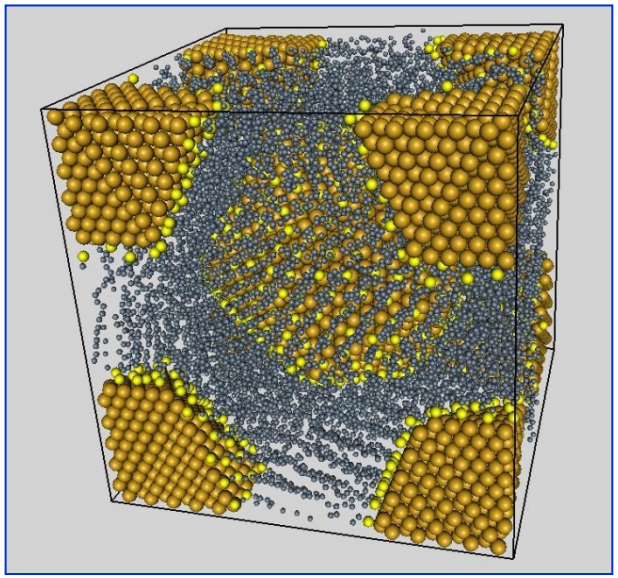
edge sites

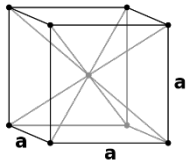
How do **nanoparticles interact**?

Simulation of BCC and FCC superlattices

BCC

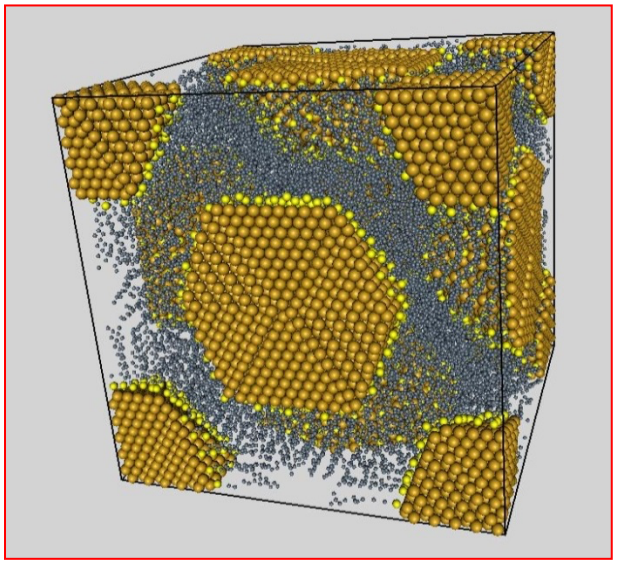
Body Centered Cubic

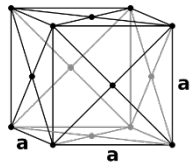




FCC

Face Centered Cubic

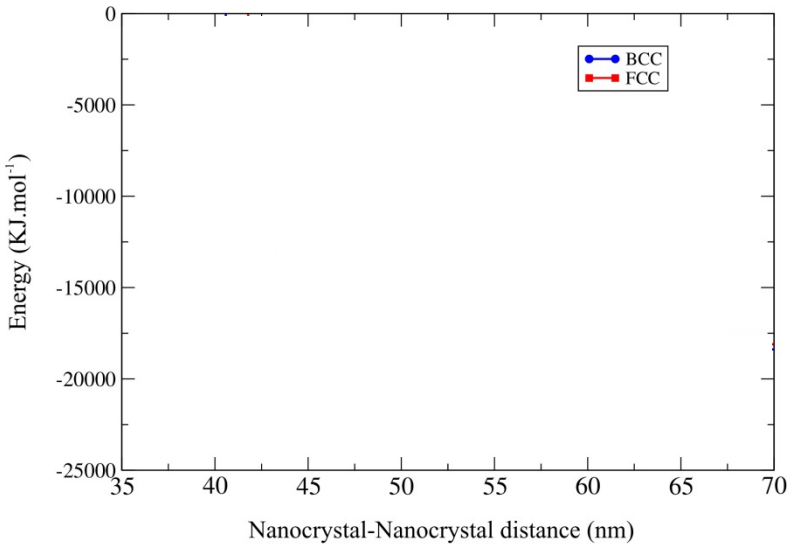


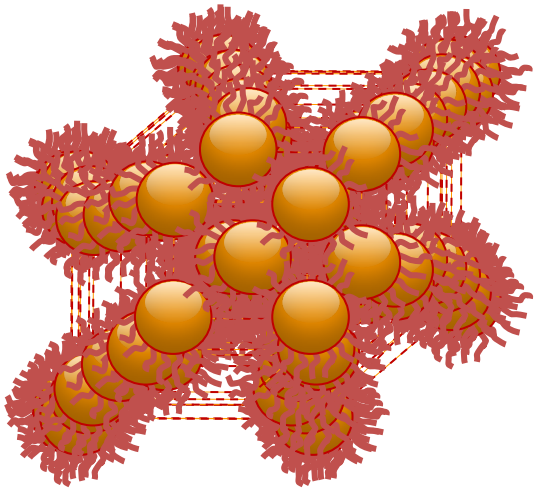


Method : evolution of potential energy with Nanocrystal-Nanocrystal distance

Simulation results :
- Lattice type: structure with the lowest energy.
- Optimal Nanocrystal-Nanocrystal distance.

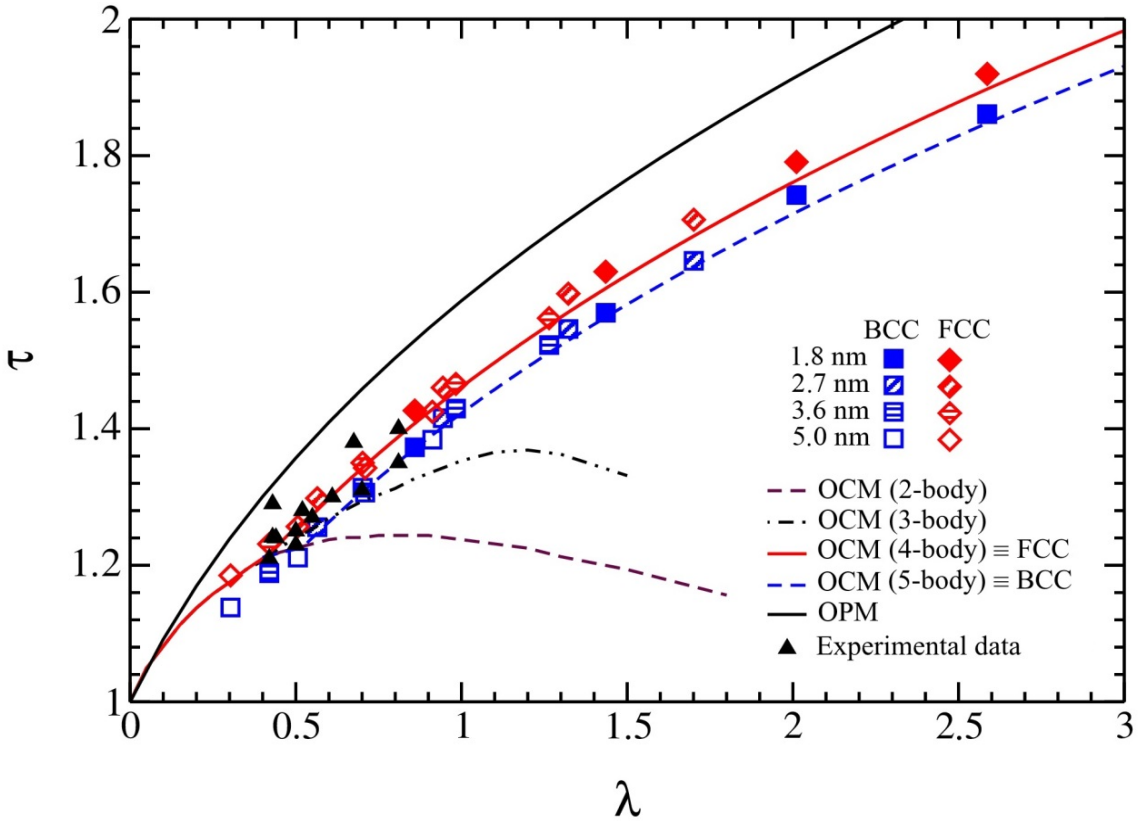
2.7 nm / hexadecanethiol





Smaller nanocrystal distance in BCC

Evolution of the nanocrystal distance with ligand length



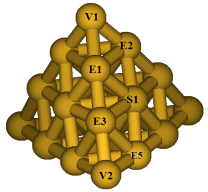
NC-NC distance measurement error : ± 0.2%

- Excellent agreement with OCM theory. OPM theory by Landman is wrong.
- This shows the importance of many-body interactions.
- The smaller Nanocrystal-Nanocrystal distance in BCC can be confirmed.

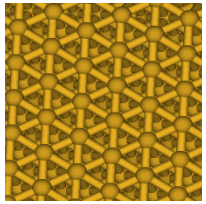
Methods for gold clusters and periodic surfaces

Ab initio calculations

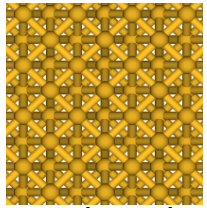
Software: Quantum espresso
DFT: *PBE* (GGA functional)
Pseudopotentials: *Ultrasoft*



Au20 Pyramid


Au(111)

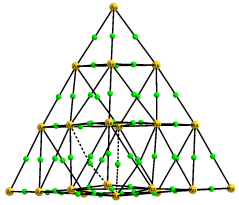
Optimized geometries
Relative energies


Au(100)

Quantum theory of an atom in molecule (QTAIM)

Generation of density file:
Gaussian09,
PBE/mod-LANL2DZ[1]

Topological Analysis
AIMStudio

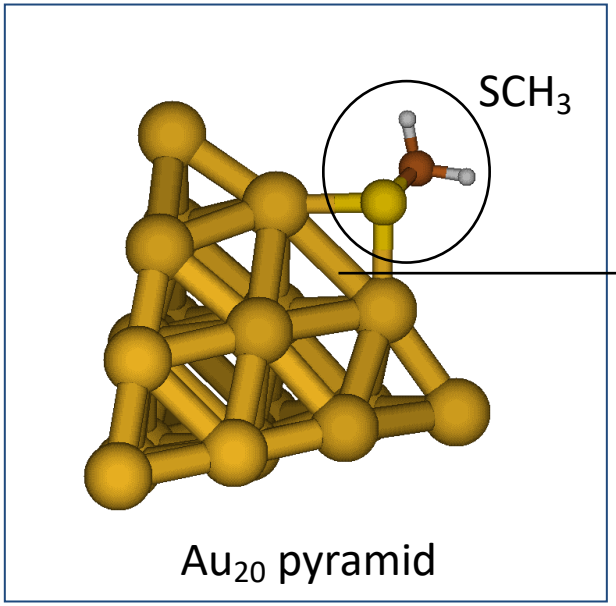


Critical points analysis
(Bond, ring, cage)
Partial charges per atom

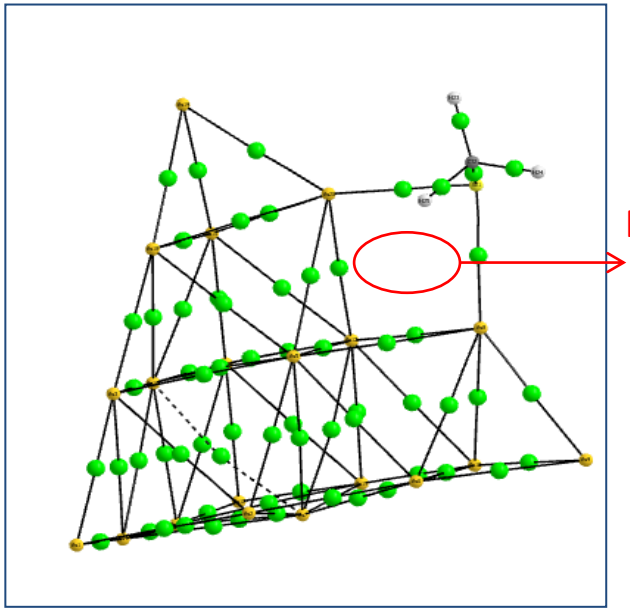
Energy, geometry and physical criteria for bond breaking

1 . Muniz-Miranda, F., Menziani, M. C., & Pedone, A. (2014). Assessment of exchange-correlation functionals in reproducing the structure and optical gap of organic-protected gold nanoclusters. *The Journal of Physical Chemistry C*, *118*(14), 7532-7544.

Example: Au_{20}-Methyl thiolate



Bond deformation
2.67 → 3.25 Å



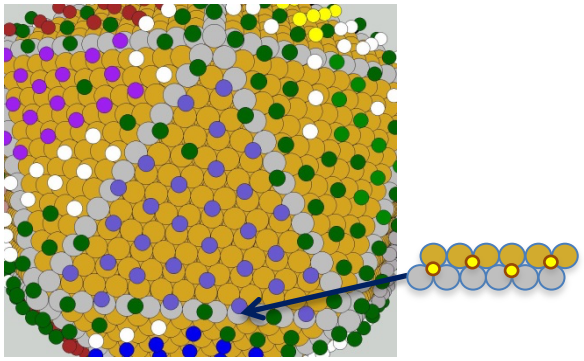
Most stable isomer

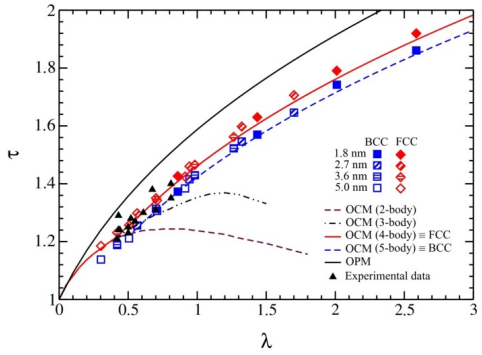
Green: bond critical points

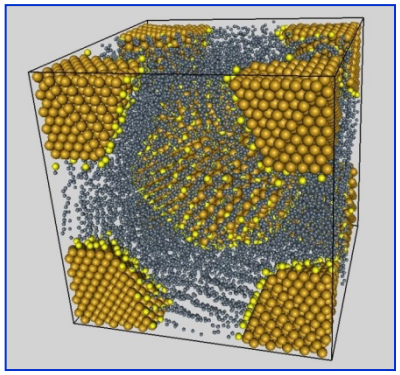
For larger Nanocrystals:
Use these informations to improve Reax force fields
for diffusion of gold atoms and Au-Au / Au-S bond breaking

5. Conclusions

- How do **ligands adsorb** on nanoparticles?
- We **reproduce experimental surface coverage**.
- **Edges are the origin** of different surface coverage for nanocrystals..
- A **new molecular organization** on the edges.
- **Bond breaking** due to thiolate adsorption
- How do **nanoparticles interact**?
- We **reproduce experimental distances**.
- Distances are related to **many body interactions**.

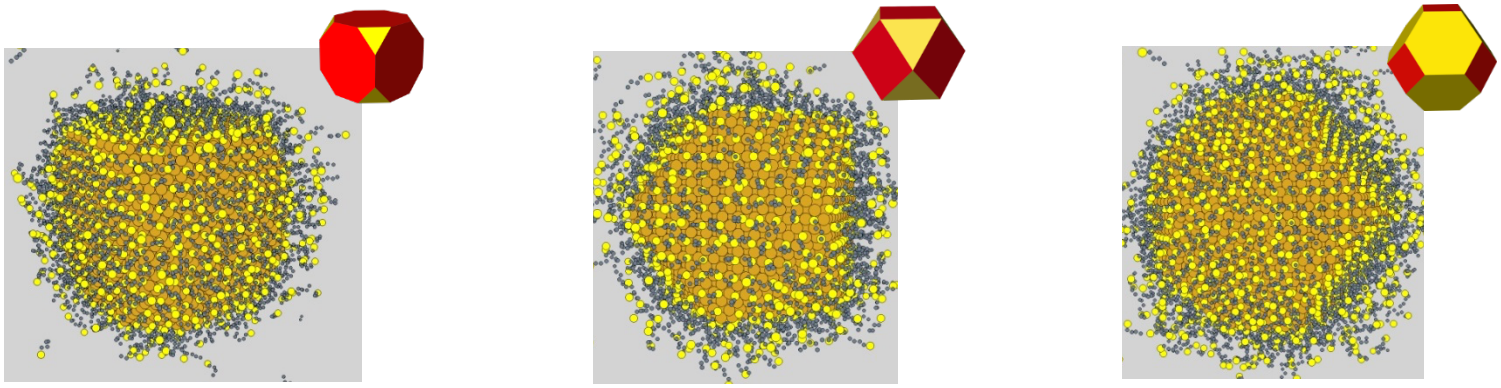






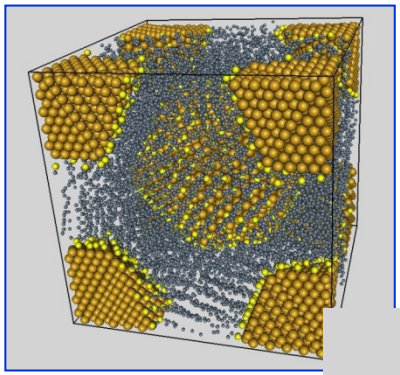
Perspectives

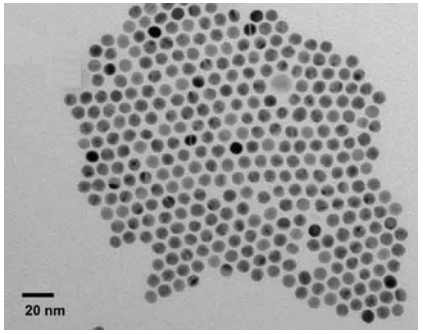
- Improve force fields.
- New materials (Ag, Pt, Co, Cu).
- Addition of solvent (e.g: hexane).
- Simulation of non ideal truncated NCs shapes.

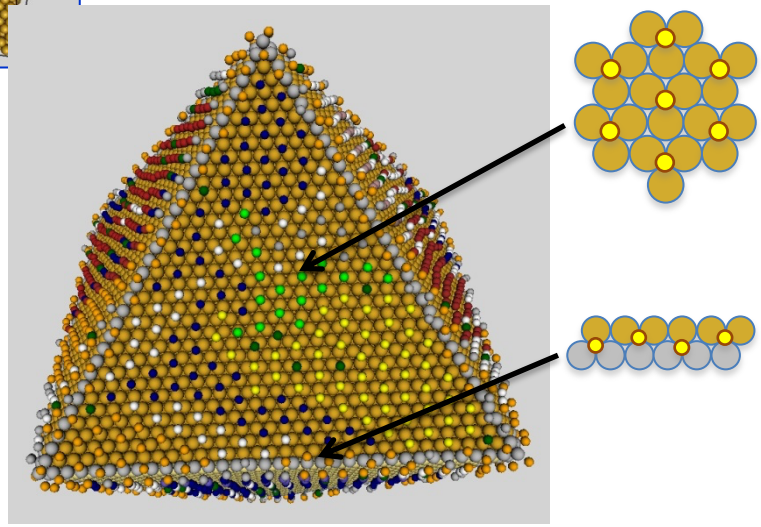


- Analysis of dynamic & structural properties of ligands :
  - ligand diffusion.
  - tilt angle.
  - frequency of trans conformations.

THANK YOU



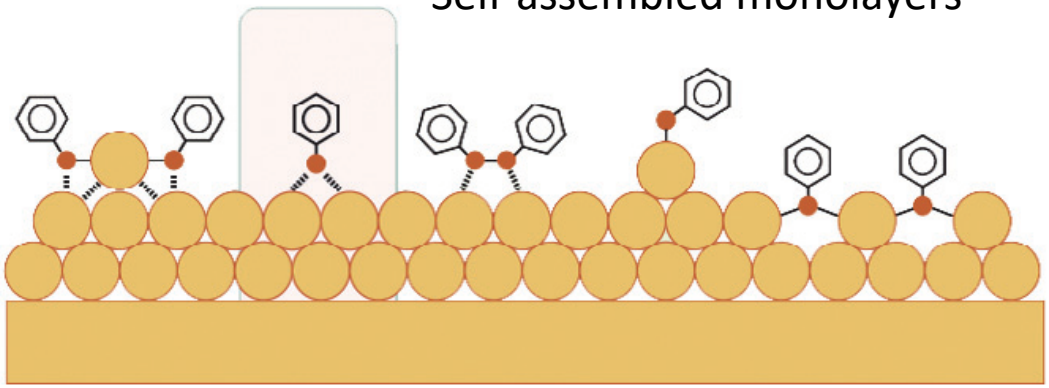


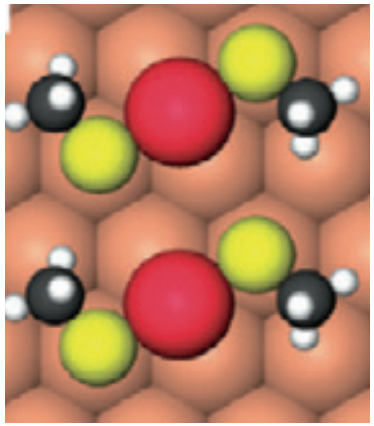


Perspectives

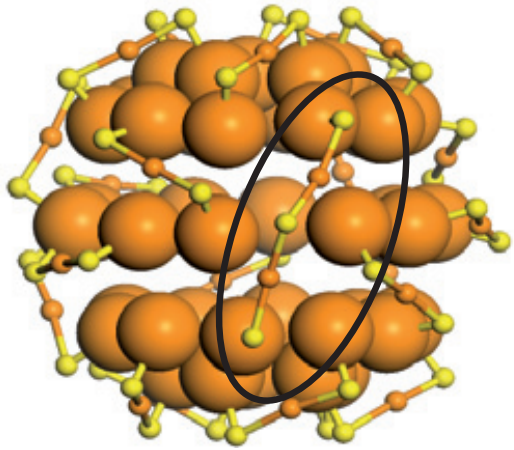
$A\ revolutionary\ finding: S-Au-S$ lines on gold.

Self-assembled monolayers





Cluster



1. Häkkinen, H. Nature Chemistry, 2012, 4, 443-455.
2. Jadzinsky et al. Science 2007 318, 430–433.
3. Cossaro, A. et al. Science 2008 321, 943–946.

Perspectives

Current interaction models do not give these S-AU-S lines.

We need better interaction models including polarizability:

- Polarization > 20 % of binding energies for molecules on gold.
- important charge transfer of -0.33 e between silver and thiolates

Li, A.; Piquemal, J. P.; Richardi, J.; Calatayud, M. Butanethiol adsorption and dissociation on Ag (111): A periodic DFT study. Surf. Sci., 2016, 646, 247-252

Interaction model

Intramolecular interaction parameters

$$U_{intra} = U_{bond} + U_{bend} + U_{torsion}$$

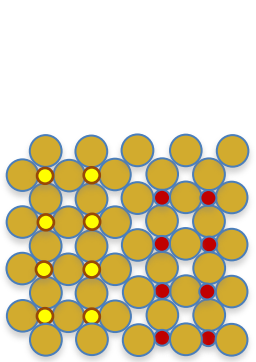
(Dubbeldam *et al.* JPC. B 2004)

Intermolecular interaction parameters

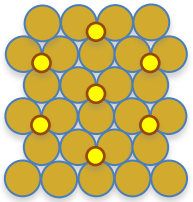
$$U_{inter} = U_{non-bonded} = U_{\mathrm{LJ}} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

	CH_3		CH_2		S	
	ε/k_B[K]	σ[Å]	ε/k_B[K]	σ[Å]	ε/k_B[K]	σ[Å]
Pool *et al.* JPC 2007	108	3.76	56	3.96	**126**	**4.45**
Hautman *et al.* JCP 1989	88.1	3.905	59.4	3.905	**200**	**4.25**
Siepmann *et al.* Langmuir 1993	88.1	3.905	59.4	3.905	**200**	**4.97**
Lal *et al.* JPC 2004	98	3.75	46	3.95	126	4.45
Lubna *et al.* JPC 2005	98	3.75	46	3.95	232	3.62

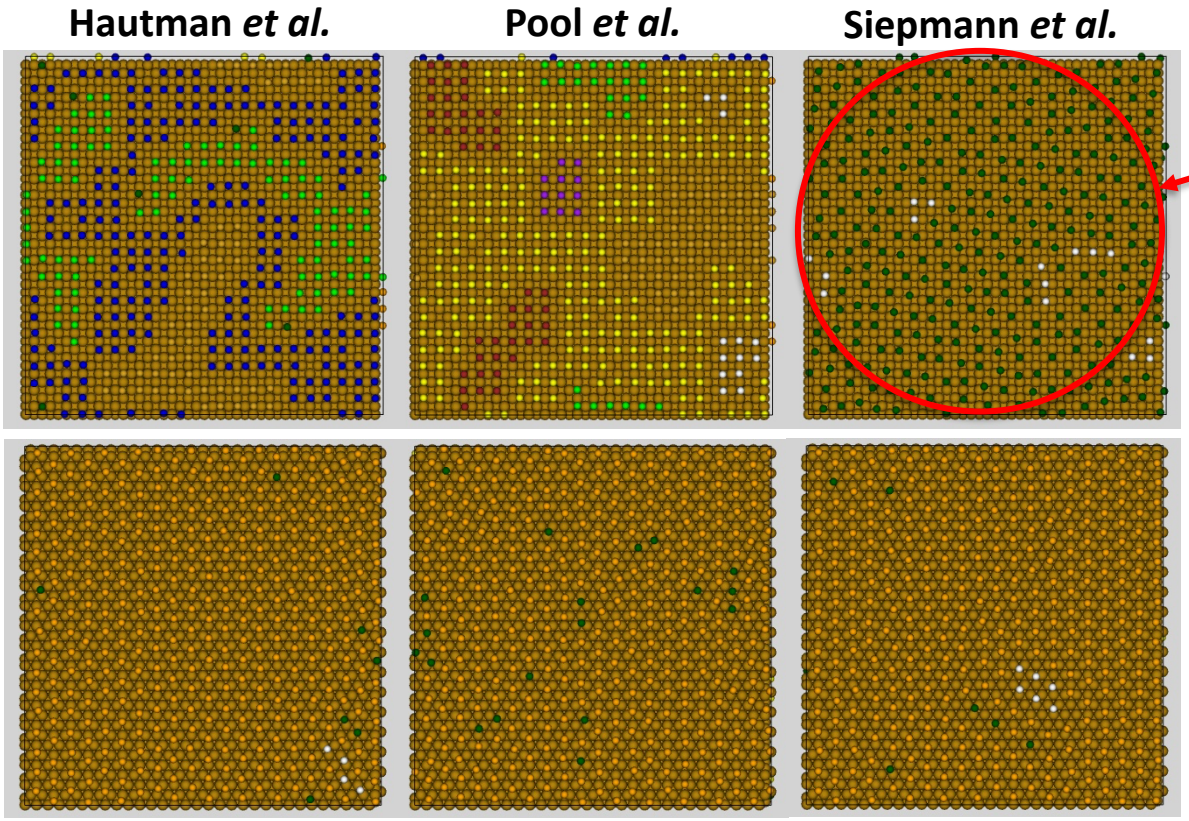
Simulation of planar Au(111) & Au(100) surfaces for three models



(100)



(111)



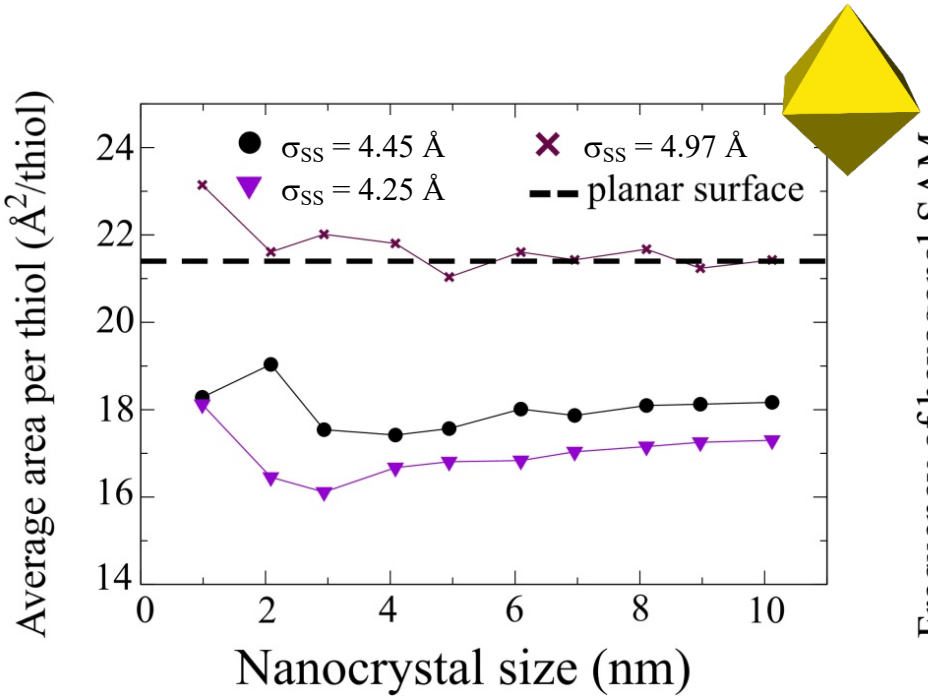
Planar surface	Hautman *et al.*	Pool *et al.*	Siepmann *et al.*	Experiment
Au(100)	19.9 ± 0.6	21.0 ± 0.6	25.1 ± 0.8	20.6[1]
Au(111)	20.7 ± 0.6	21.2 ± 0.6	22.3 ± 0.7	21.4[1]

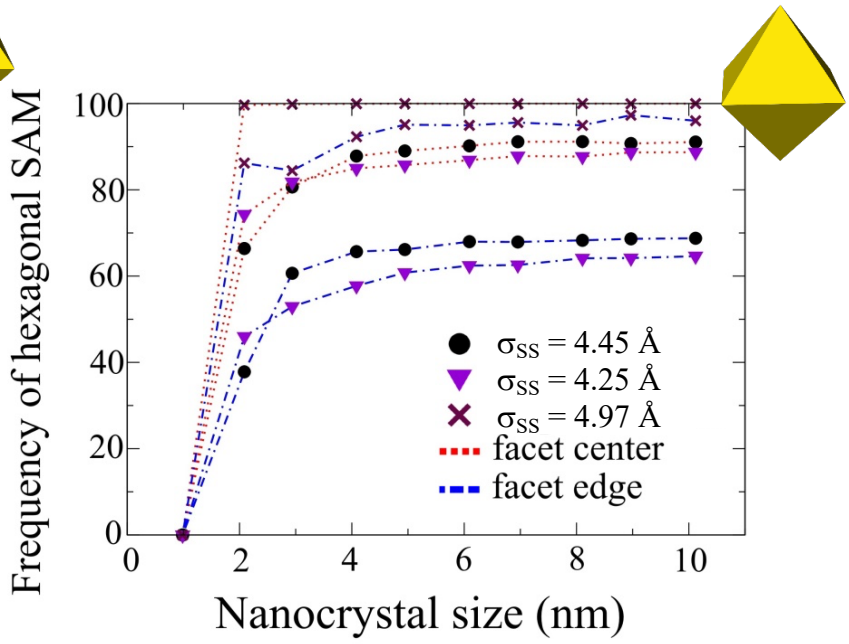
Pool *et al.* → closest to experimental results.

1: Strong *et al.* Langmuir 1988, 4, 546–558.

Simulation of Nanocrystals for three models

Siepmann model works for Au(111) surfaces,
Will it also work for nanocrystals with Au(111) facets? NO



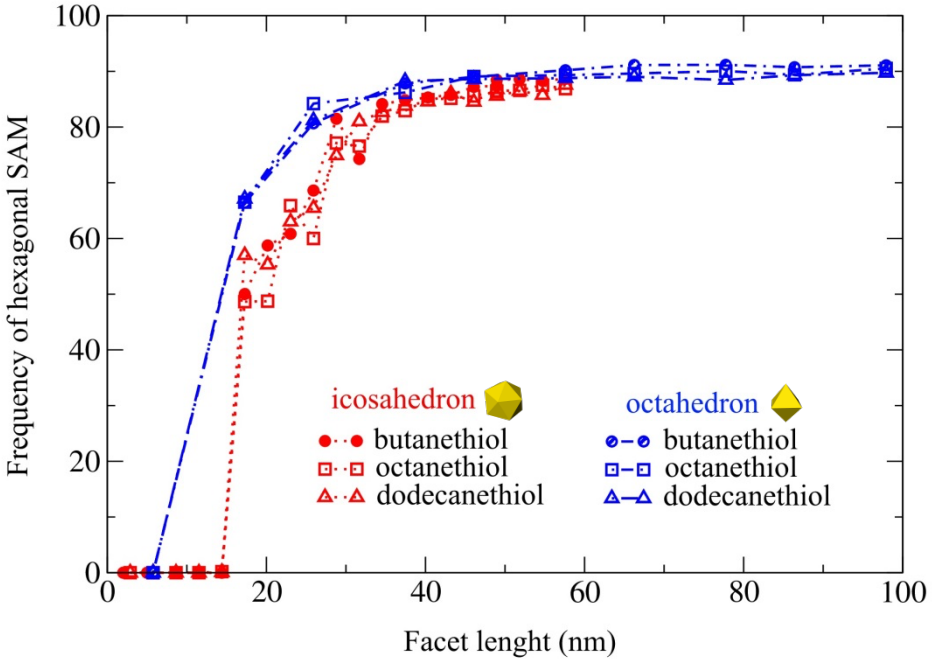


No change of surface coverage with Siepmann model
Second zig-zag organization disappears on edges.

Interaction models have to be carefully tested.

Frequency of hexagonal SAMs

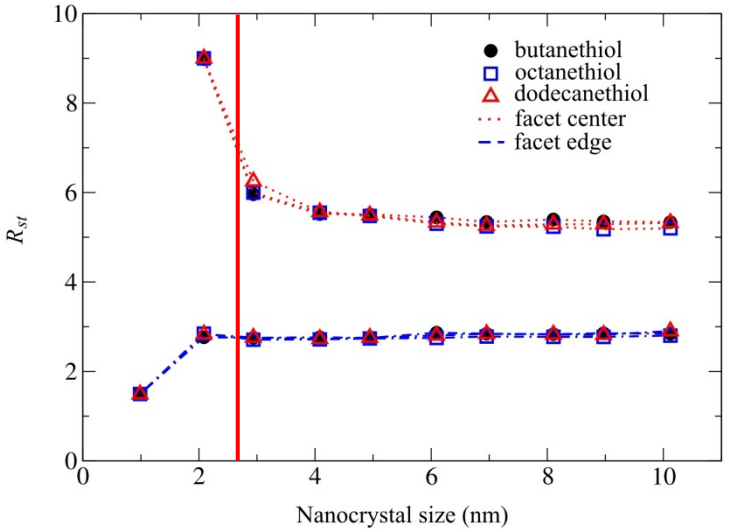
How can we explain the difference between octahedral & icosahedral for NCs < 5 nm ?



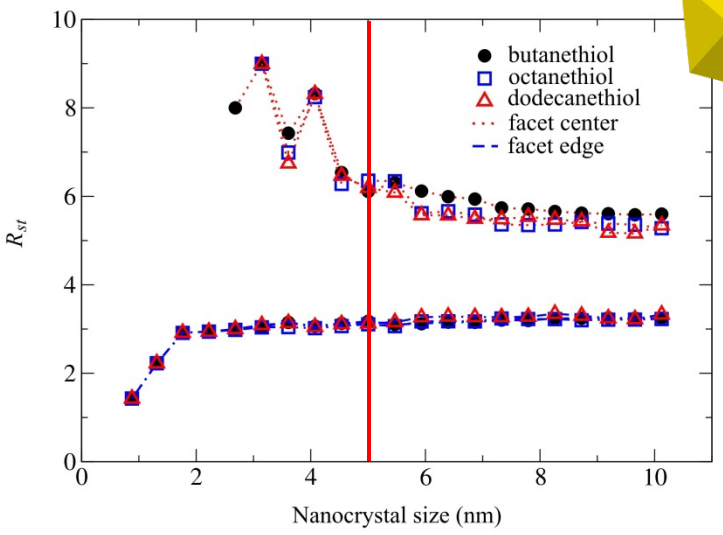
→ due to larger facets for octahedral NCs.

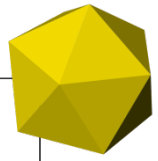
Ratio between adsorption sites and adsorbed thiols R_{st}

octahedron



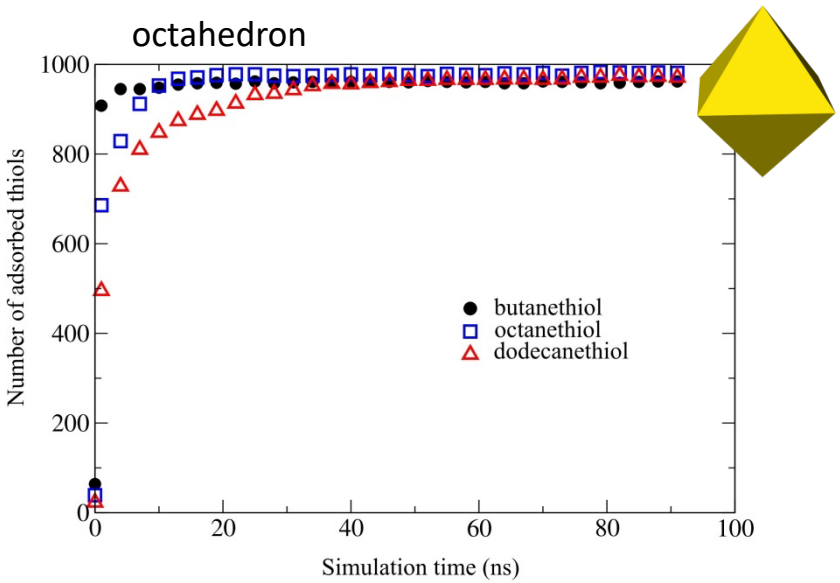
icosahedron

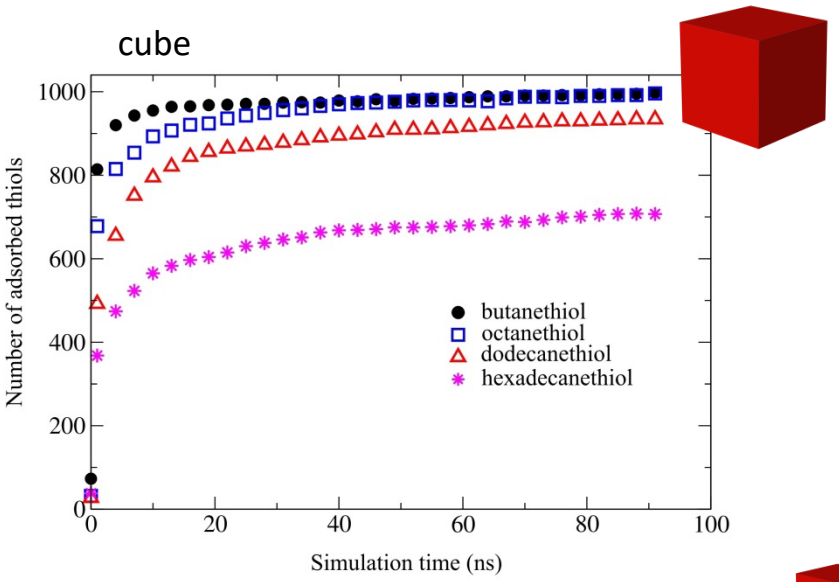




- Same constant R_{st} on the facets edges (facet angle effect).
- R_{st} in the facets centers stabilizes around 6 for octahedral NC > 2 nm, and for icosahedral NC > 5 nm.

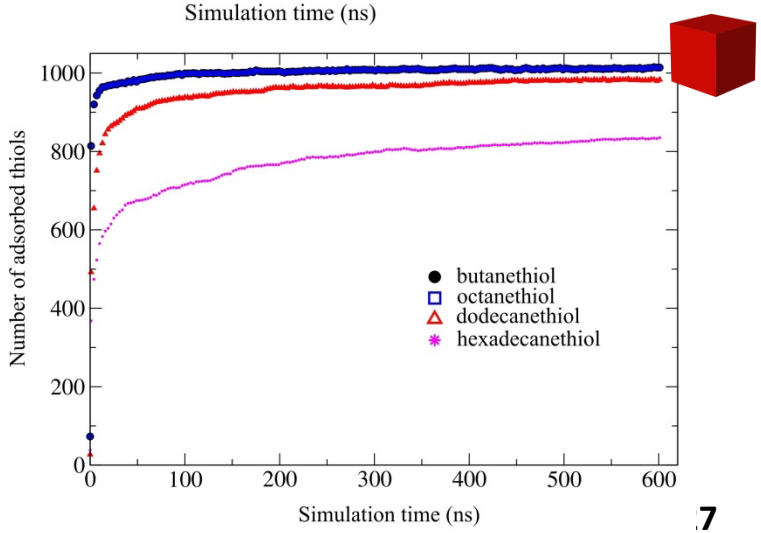
Time evolution of thiol adsorption on 7 nm NCs





For cube NCs:

- Slow convergence compared to octahedral & icosahedral NCS.
- Limited accuracy for dodecanethiol results, even after 600 ns.



BCC or FCC ?

In experiments[1] : transition FCC → BCC for λ = 0.8

$$\lambda = 2L/d_{NC}$$

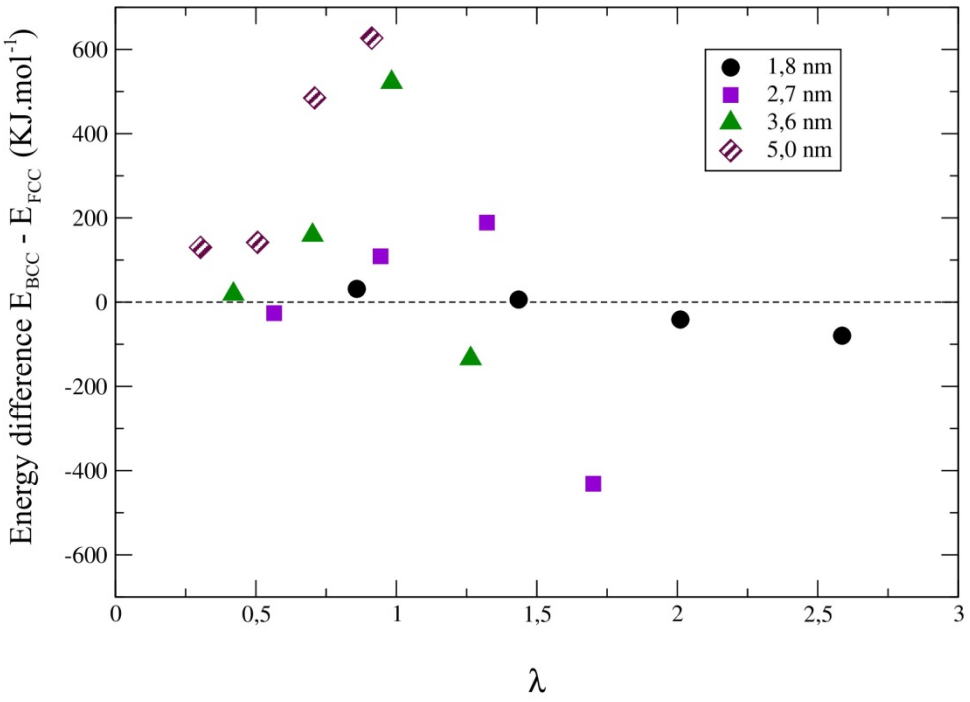
L: ligand chain length

d_{NC}: NC diameter

Approximation

↓

neglect of entropy

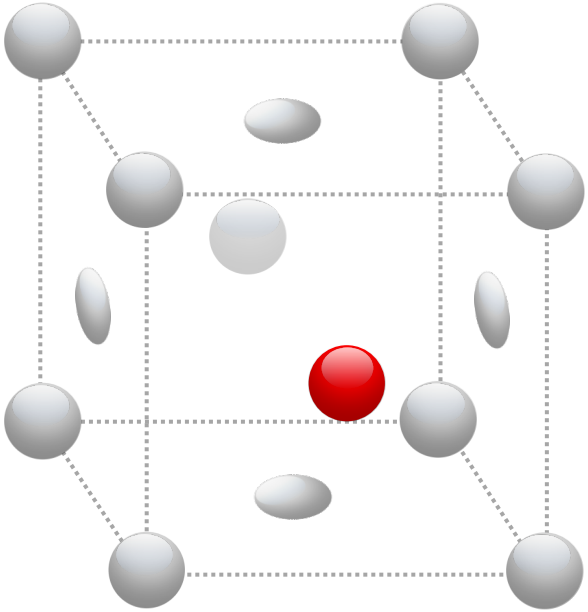


Transition FCC → BCC for λ > 1.0

BCC or FCC ?

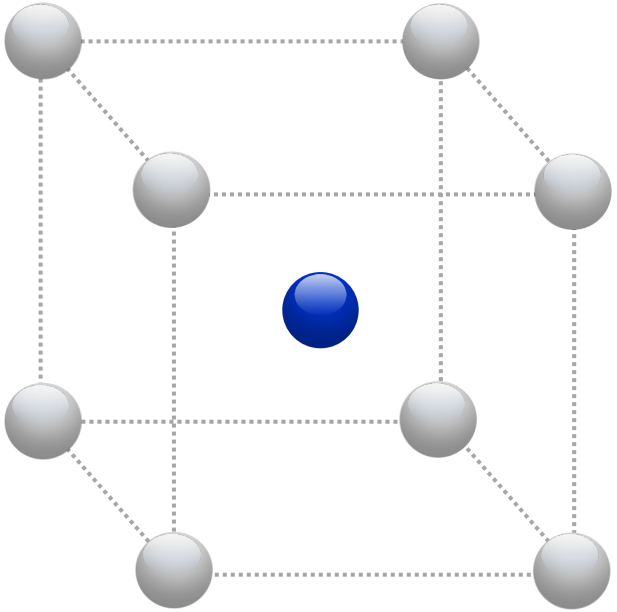
Where does the transition from FCC to BCC come from?

FCC



12 first neighbors

BCC



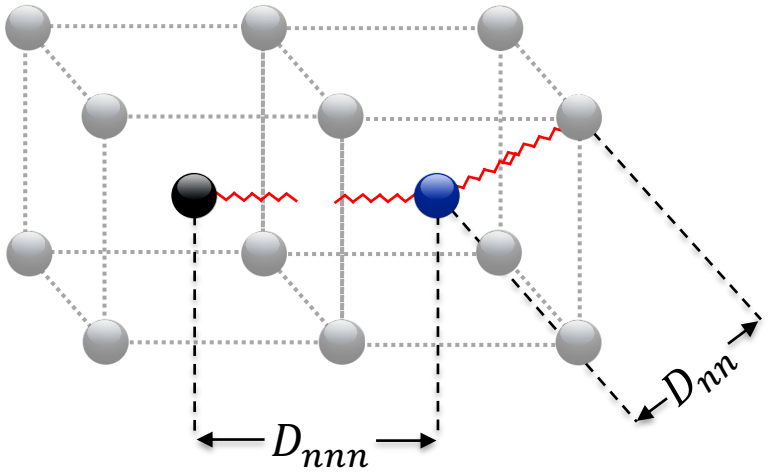
8 first neighbors
14 second neighbors

BCC or FCC ?

Where does the transition from FCC to BCC come from?

Idea in the literature[1] :

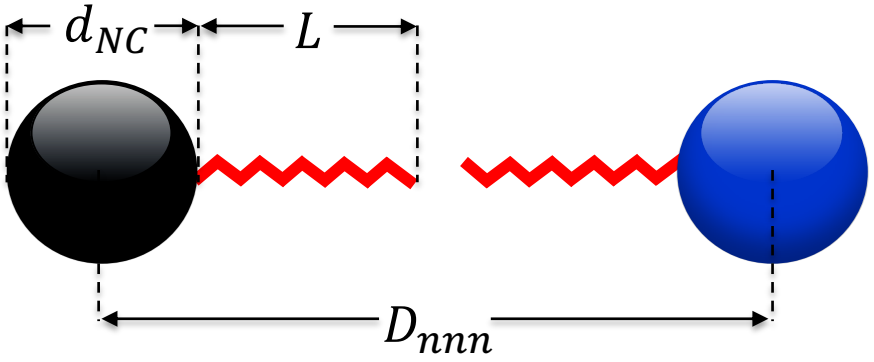
For BCC, the coating of the second neighbors can touch when $\lambda > 0.8$



$$D_{nnn} = \frac{\sqrt{2}}{3} D_{nn}$$

Second neighbor contact (BCC)

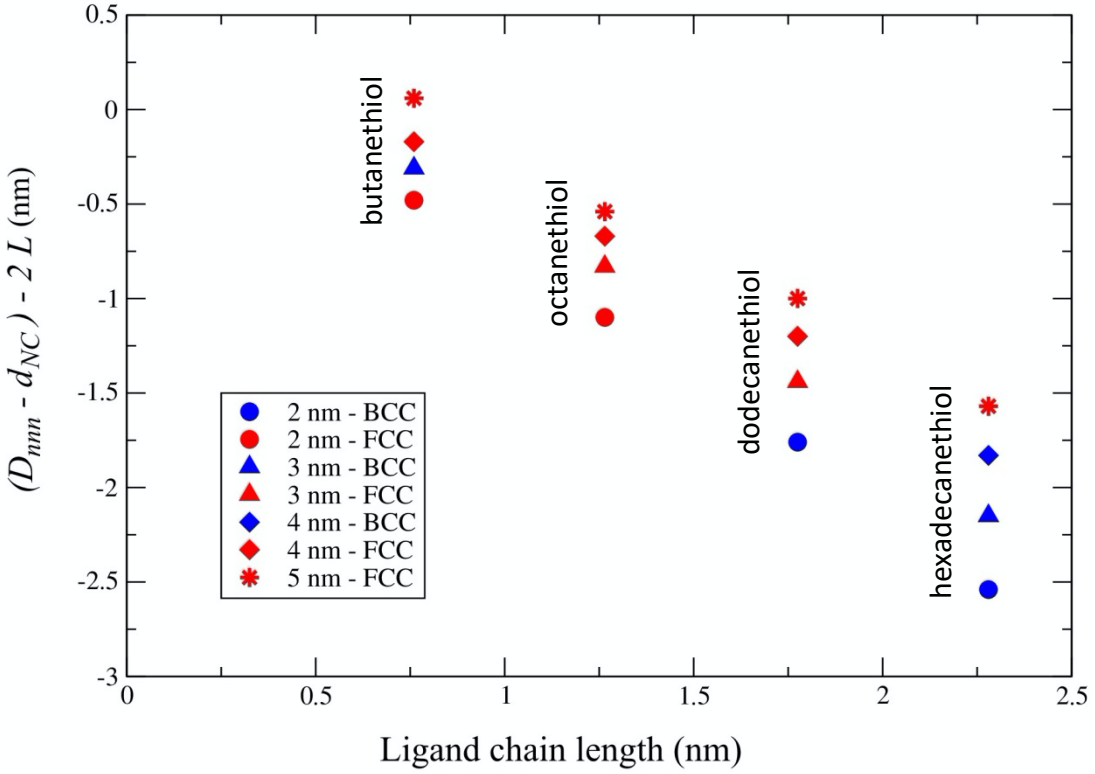
$$(\boldsymbol{D_{nnn} - d_{NC}}) - \boldsymbol{2L} \leq \boldsymbol{0}$$



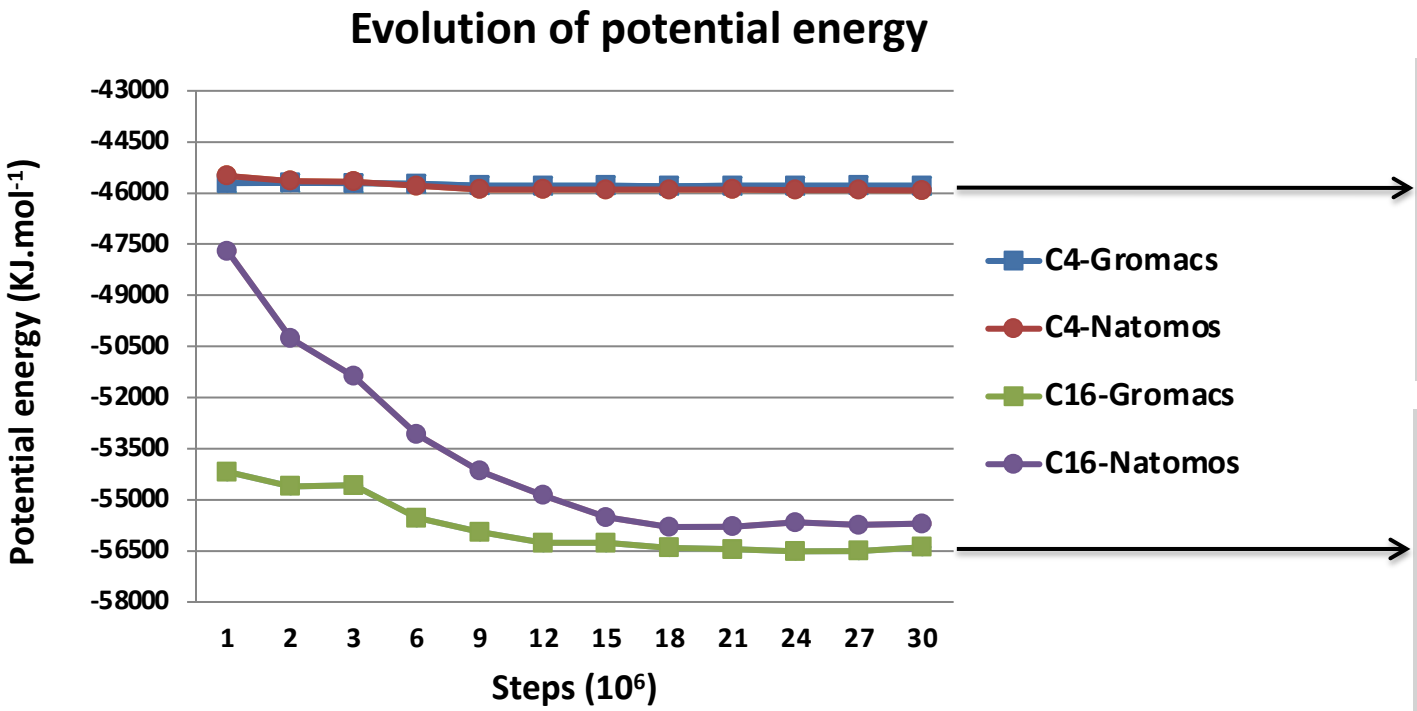
1: Landman *et al*. Faraday Discuss. 2004. 125. 1

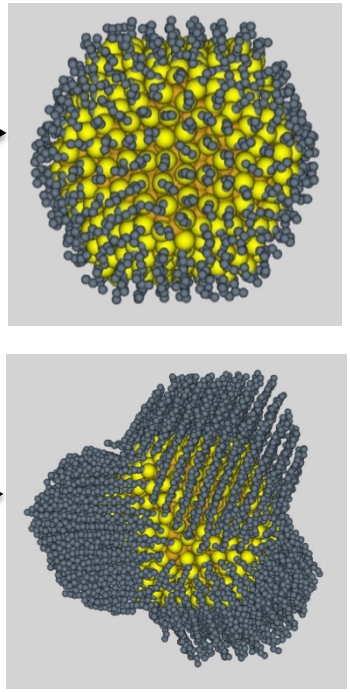
BCC or FCC ?

Second neighbor contact



Strong second neighbor contact → BCC.





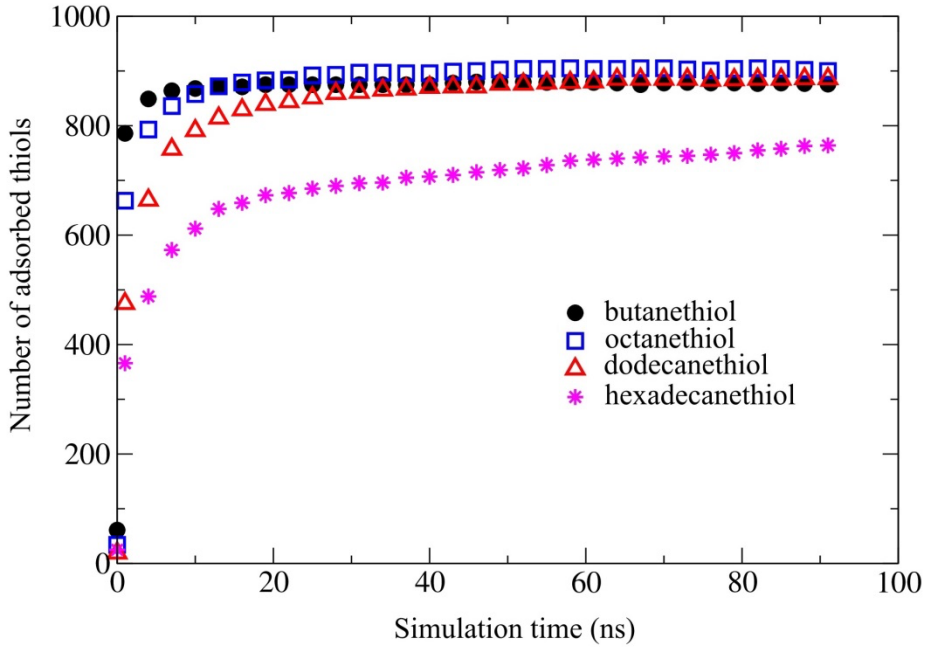
Gromacs simulations converge more rapidly than Natomos

NC size			Energy (KJ.mol^{-1})		Time for 3x10^6 steps		
			Natomos	Gromacs	Natomos 1 CPU	Gromacs 10 CPU	Ratio
2 nm		C_4	-5995.60	-5994.33	250 min	15 min	**15**
		C_{16}	-6646.44	-7012.62	1070 min	40 min	**25**
5 nm		C_4	-45921.97	-45783.20	60 h	2.1 h	**30**
		C_{16}	-55703,76	-56391.90	250 h	3.2 h	**80**

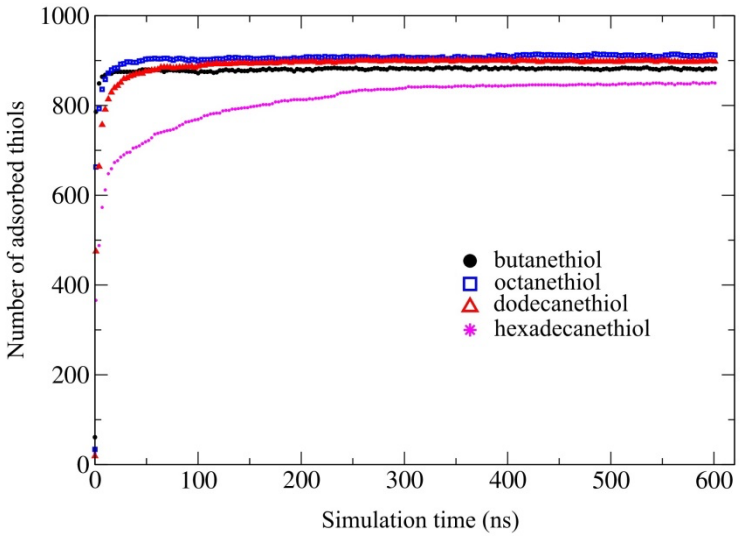
Acceleration of simulation time by a factor up to 400

Time evolution of thiol adsorption on 7 nm NCs

Is the simulation time sufficiently long ?

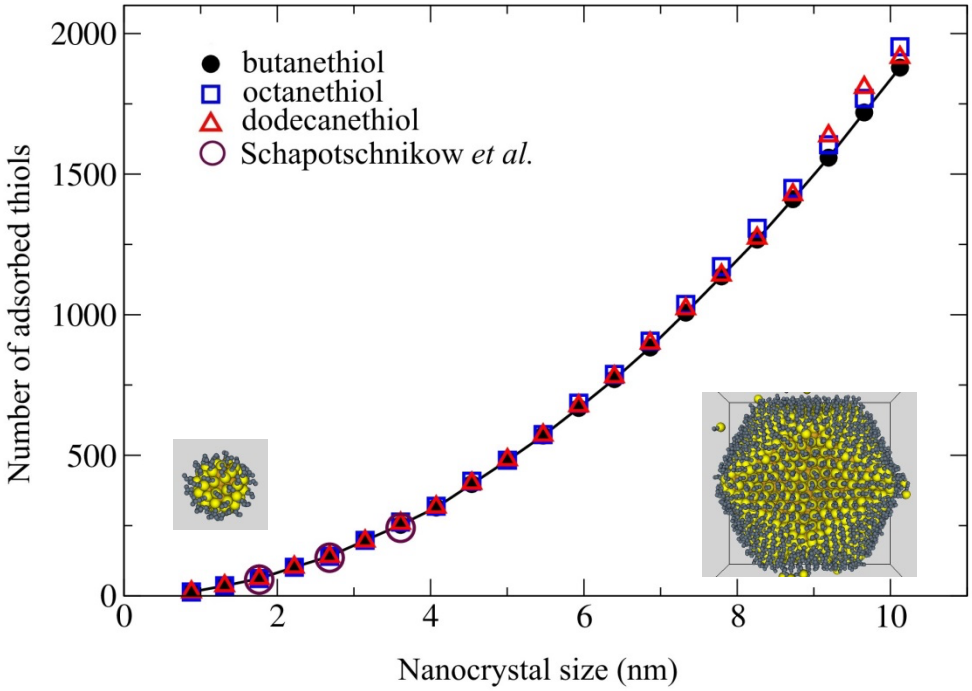


Thiol adorption simulation
error : ± 1%



- Time evolution of thiol adsorption depends on the thiol chain length.
- Adsorption convergence is very slow for hexadecanethiol even after 600 ns
  → no further simulations.

Number of adsorbed thiol molecules

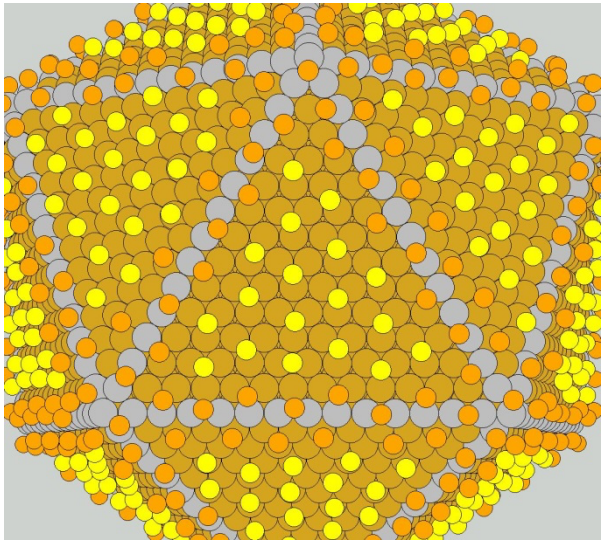


- the number of adsorbed thiols depends only slightly on the alkane chain length.
- In good agreement with simulation results in the literature[1] (same interaction model).

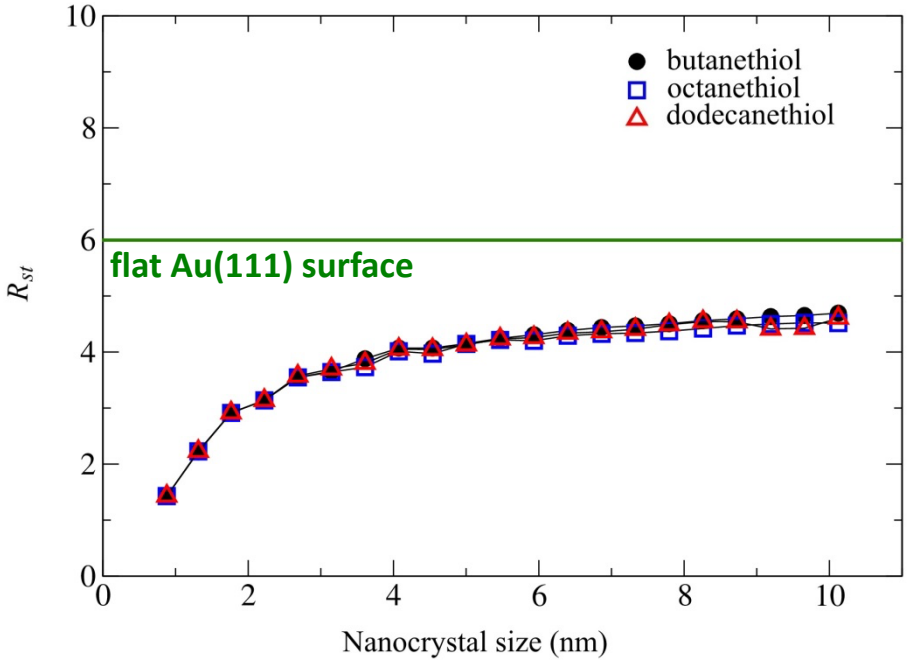
1: Schapotschnikow *et al*. J. Chem. Phys. 2009. 131.

Ratio between adsorption sites and adsorbed thiols

- R_{st} = number of adsorption sites / number of adsorbed thiols.
- R_{st} = 6 for planar Au(111) surface. Will we find R_{st}= 6?

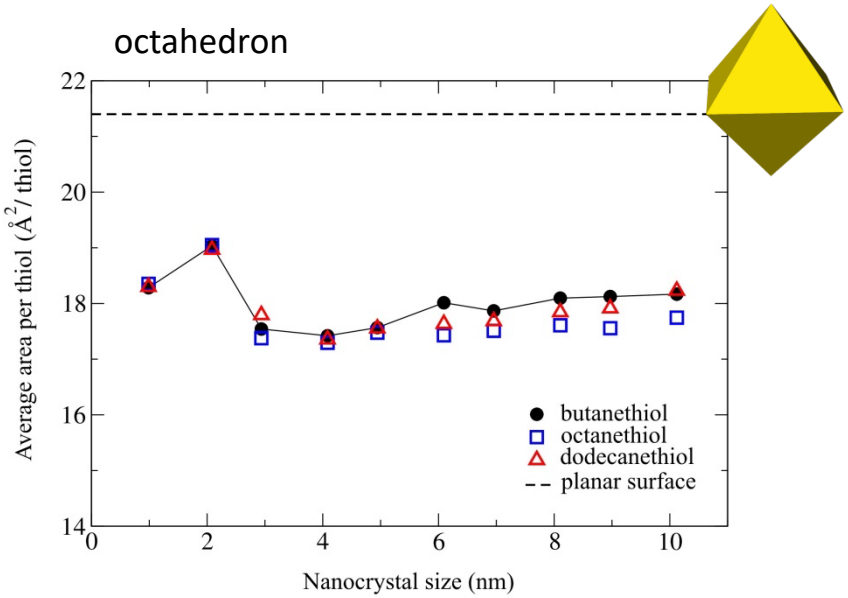


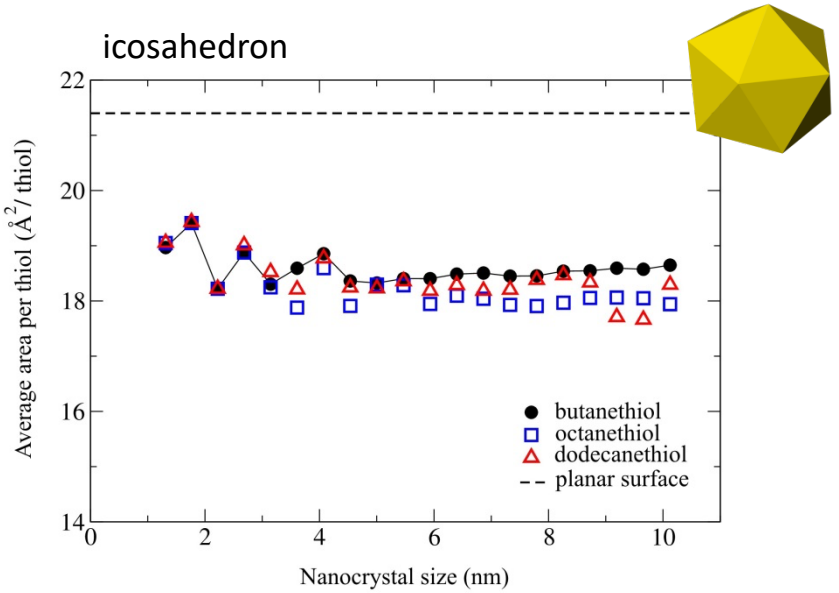
Positions of SH groups on a nanocrystal facet



- Total R_{st} < 6 (value for planar Au(111) surface).

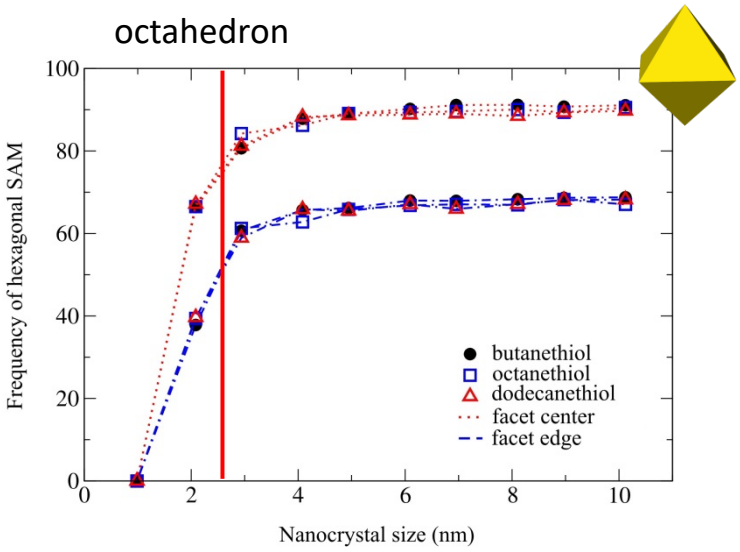
Average area per thiol

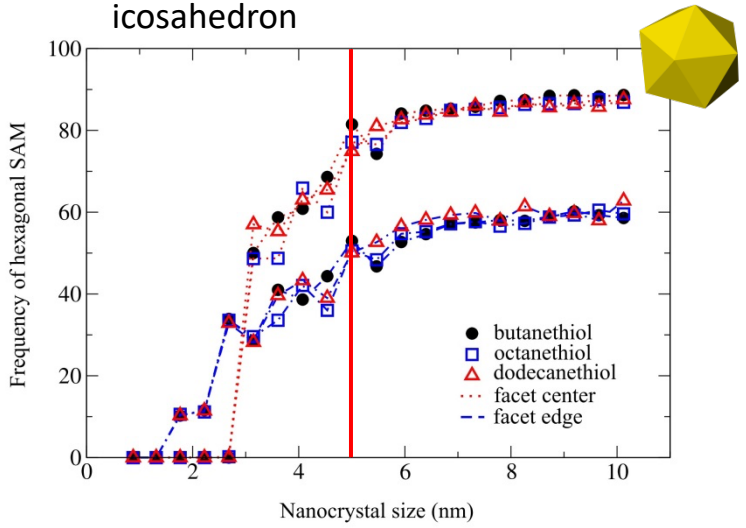




- Similar results for octahedral & icosahedral NCs.

Frequency of hexagonal SAMs

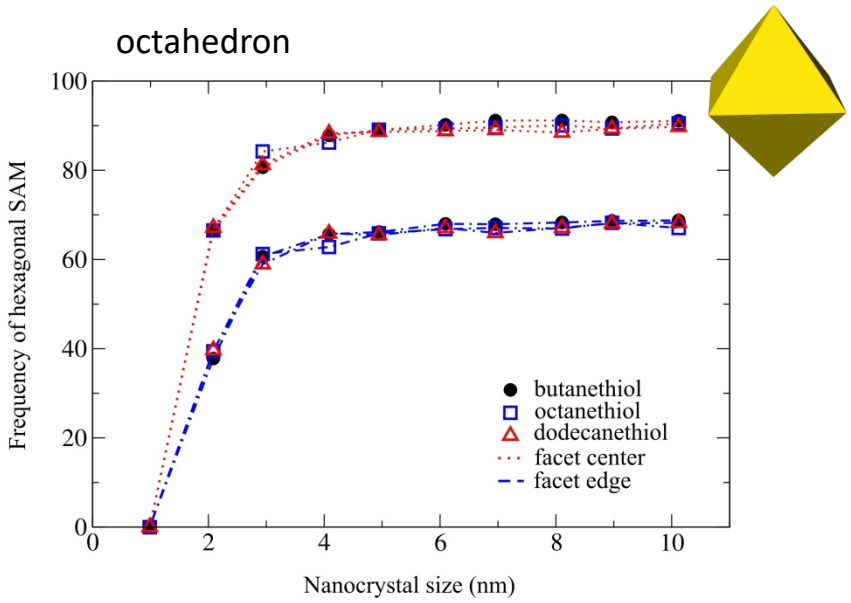


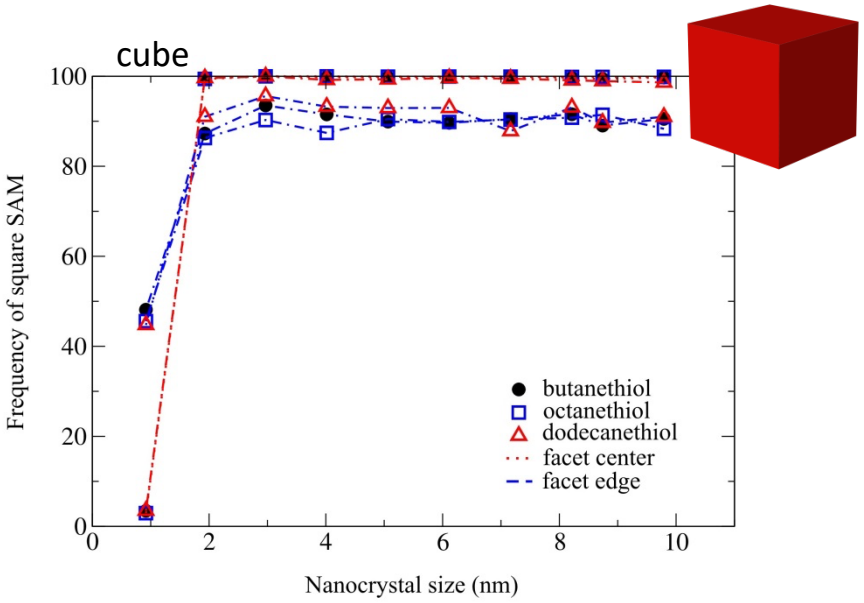


Octahedral NCs reach behaviour of Au(111) for smaller nanocrystals.

At a given nanocrystal size, the facets are larger.

Frequency of hexagonal & square SAM

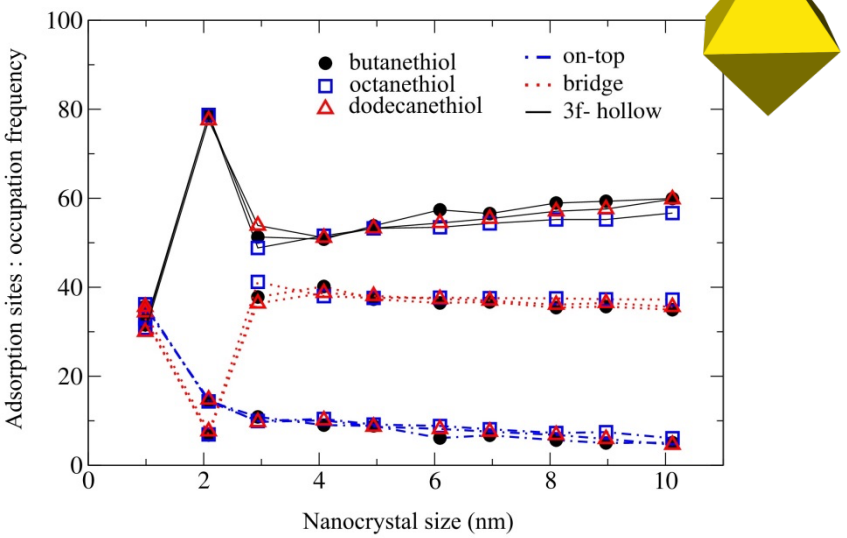




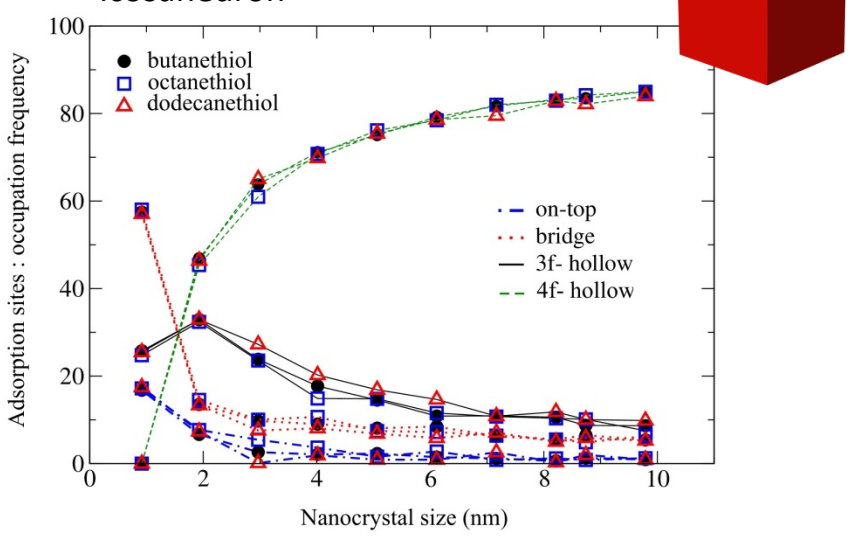
Square SAM frequencies confirm the same molecular organization on (100) facet center & edges.

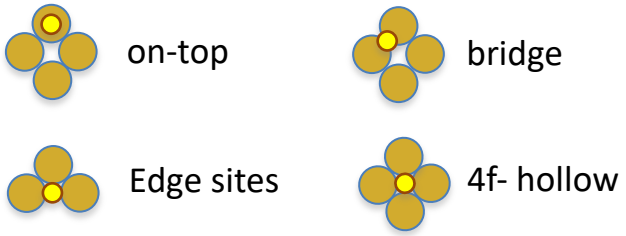
Adsorption sites : occupation frequencies

octahedron



icosahedron





- Octahedron : 3f- hollow & shifted bridge adsorption site.
- Cubes : mainly 4f- hollow adsorption site: Slow saturation due to edge sites.