Simulations for Gold Nanoparticles: Electronic Structure, Multi-scale and Data-driven Approaches

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Simulations for Gold Nanoparticles: Outline

- Atomistic quantum-mechanical simulations.
- Self-assembled monolayers on gold.
- Shape of gold nanoparticles
  - Theory
  - Catalysis
  - Polymer-gold nanocomposite.

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Quantum-mechanical atomistic simulations: an example

```
>>> # Example: structure optimization of hydrogen
>>> from ase import Atoms
>>> from ase.optimize import BFGS
>>> from ase.calculators.nwchem import NWChem
>>> from ase.io import write
>>> h2 = Atoms('H2',
...            positions=[[0, 0, 0],
...                       [0, 0, 0.7]])
>>> h2.calc = NWChem(xc='PBE')
>>> opt = BFGS(h2)
>>> opt.run(fmax=0.02)
BFGS:    0  19:10:49    -31.435229     2.2691
BFGS:    1  19:10:50    -31.490773     0.3740
BFGS:    2  19:10:50    -31.492791     0.0630
BFGS:    3  19:10:51    -31.492848     0.0023
>>> write('H2.xyz', h2)
>>> h2.get_potential_energy()
-31.492847800329216
```

Structure

Calculator

Task

Output

https://wiki.fysik.dtu.dk/ase/

Calculators

- Set of functions like $E(R_1, R_2)$, $F_{1x}(R_1, R_2)$.
- Empirical functions (fast, problem-specific,~ 1ns)
- Quantum-mechanical: system of coupled non-linear PDEs (slow, transferable, ~1h).

Tasks of atomistic simulations

- 1. Optimization (*e.g structural chemistry*).
- 2. Response (*e.g Young's modulus*).
- 3. Dynamics (*e.g viscosity*).
- 4. Rates of rare events (*e.g turnover of a reaction*).

- 2 and 4 demand for quantum-mechanical calculators.

From Hamilton to Schrödinger

- Hamilton (1827): every physical system is described by two functions, $\mathcal{H}, \mathcal{S}$, that depend on positions, x, and momenta, p:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(x_1, x_2, \ldots, x_N). \tag{1}$$

- For stationary states/equilibrium, $\mathcal{H} = E$, where $E =$ constant (energy).
- Schrödinger (1926): $\mathcal{H}$ is an **operator** that is constructed by replacing $p \to -i\hbar\frac{\partial}{\partial x}$ into the Hamiltonian function.
- the energies of stationary states satisfy the equation

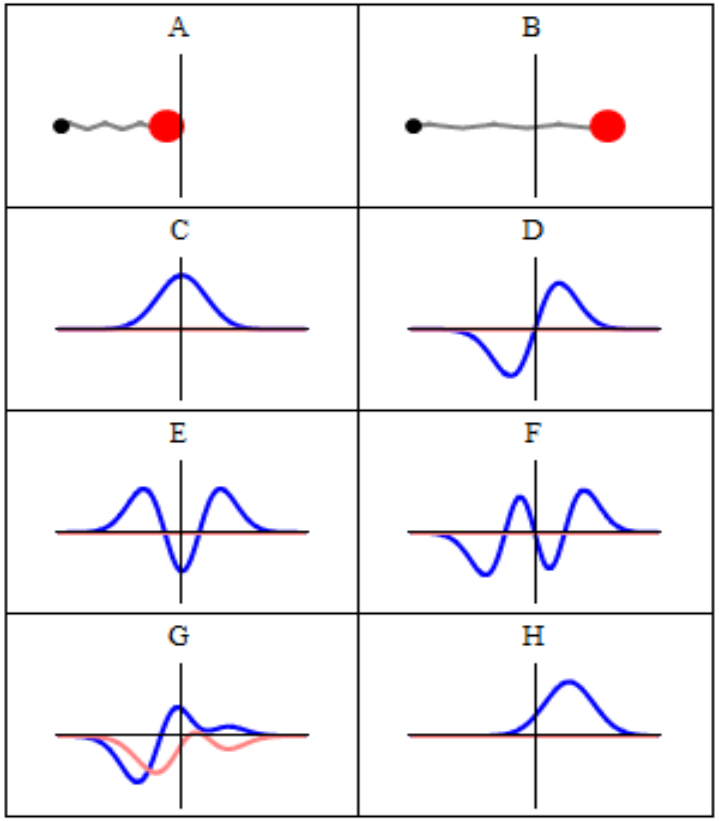
$$\mathcal{H}\psi = E\psi. \tag{2}$$

http://en.wikipedia.org/wiki/William_Rowan_Hamilton http://en.wikipedia.org/wiki/Erwin_Schr%C3%B6dinger

What is ψ;

Statistical interpretation

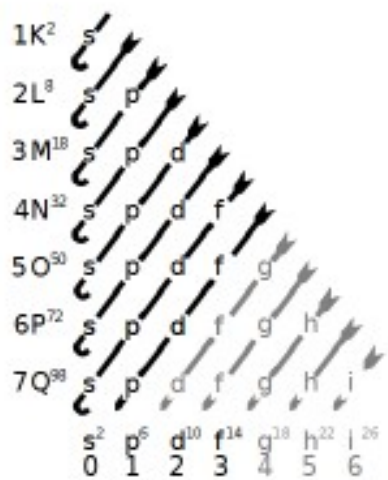
- $\psi =$ **Wavefunction**.
- Copenhagen interpretation: $|\psi(x, y, z)|^2 \Delta V$ is the probability to find an electron in a region of volume ΔV centered at point (x, y, z) of space.

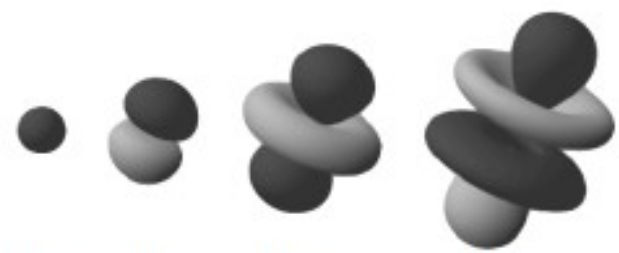


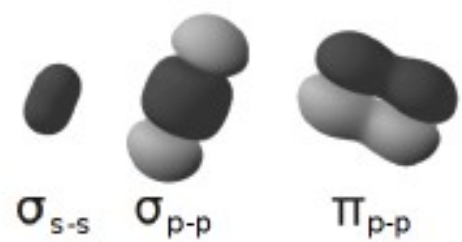
http://en.wikipedia.org/wiki/Wave_function

From one particle to many electrons

- **Exchange**:
  $\psi(x_1, x_2) = -\psi(x_2, x_1) \Rightarrow$ Pauli principle
- **Correlation**:
  $V = \frac{e^2}{4\pi\varepsilon_0 r} \Rightarrow$ Coupled probabilities plus infinite repulsion.
- **Entaglement**:
  Measuring one electron affects the wavefunctions of others.
- But...







$1s^2_2\,2s^2_4\,2p^6_{10}\,3s^2_{12}\,3p^6_{18}\,4s^2_{20}\,3d^{10}_{30}\,4p^6_{36}\,5s^2_{38}\,4d^{10}_{48}\,5p^6_{54}\,6s^2_{56}\,4f^{14}_{70}\,5d^{10}_{80}\,6p^6_{86}\,7s^2_{88}\,5f^{14}_{102}\,6d^{10}_{112}\,7p^6_{118}$

Density-functional theory (DFT)

- For each electron, all other electrons can be replaced by an effective potential $V(\mathbf{r})$ in Schödinger equation.
- DFT: $V(\mathbf{r})$ exists and is unique functional of the number density, $n(\mathbf{r})$.
- $V(\mathbf{r}) = V_H + V_{xc}$, where
  - V_H (*Hartree*) is the electrostatic potential energy generated by charge density $-en(\mathbf{r})$.
  - V_{xc} (exchange and correlation) potential includes:
    - Self-interaction correction.
    - Virtual repulsion due to Pauli principle (exchange).
    - Infinite Coulomb repulsion due to $V_C \sim 1/r$ (correlation).

https://en.wikipedia.org/wiki/Walter_Kohn

Electronic structure with DFT: A flowchart

1. Density $n(\mathbf{r}) \longrightarrow$
2. Effective potential $V(\mathbf{r}) \longrightarrow$
3. Wavefunctions, energies $\{\psi, \epsilon\}$ through Kohn-Sham equation $\longrightarrow$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

4. Density $n(\mathbf{r})$

$$n(\mathbf{r}) = \sum_i f(\epsilon_i)|\psi_i(\mathbf{r})|^2$$

- Occupations, usually Fermi-Dirac: $f(\epsilon) = \dfrac{1}{1 + e^{-(\epsilon-\mu)/k_B T}}$

Density-Functional Theory (DFT) Milestones

- 1964: Publication of Hohenberg-Kohn theorem.
- 1970: Energy levels in crystals (band structure).
- 1980: Bond lengths, mechanical properties.
- 1990: Surfaces, electric properties.
- 2000: Chemical reactions, optical properties.
- 2010: Nanostructures, dynamical properties.
- 2020: Photonics, light-matter interaction.

Multi-scale simulations

- DFT can treat few hundreds of atoms at most.
- Other length- and time-scales are accessed through empirical/semiempirical model.
  - At the handshake scale, we make sure DFT and model give identical results.
- Examples:
  - Fit of V(x,y,z), use it for atomistic simulation.
  - Wulff construction → nanoparticle shape.
  - Use DFT geometry for classical dynamics.

Outline

- Atomistic quantum-mechanical simulations.
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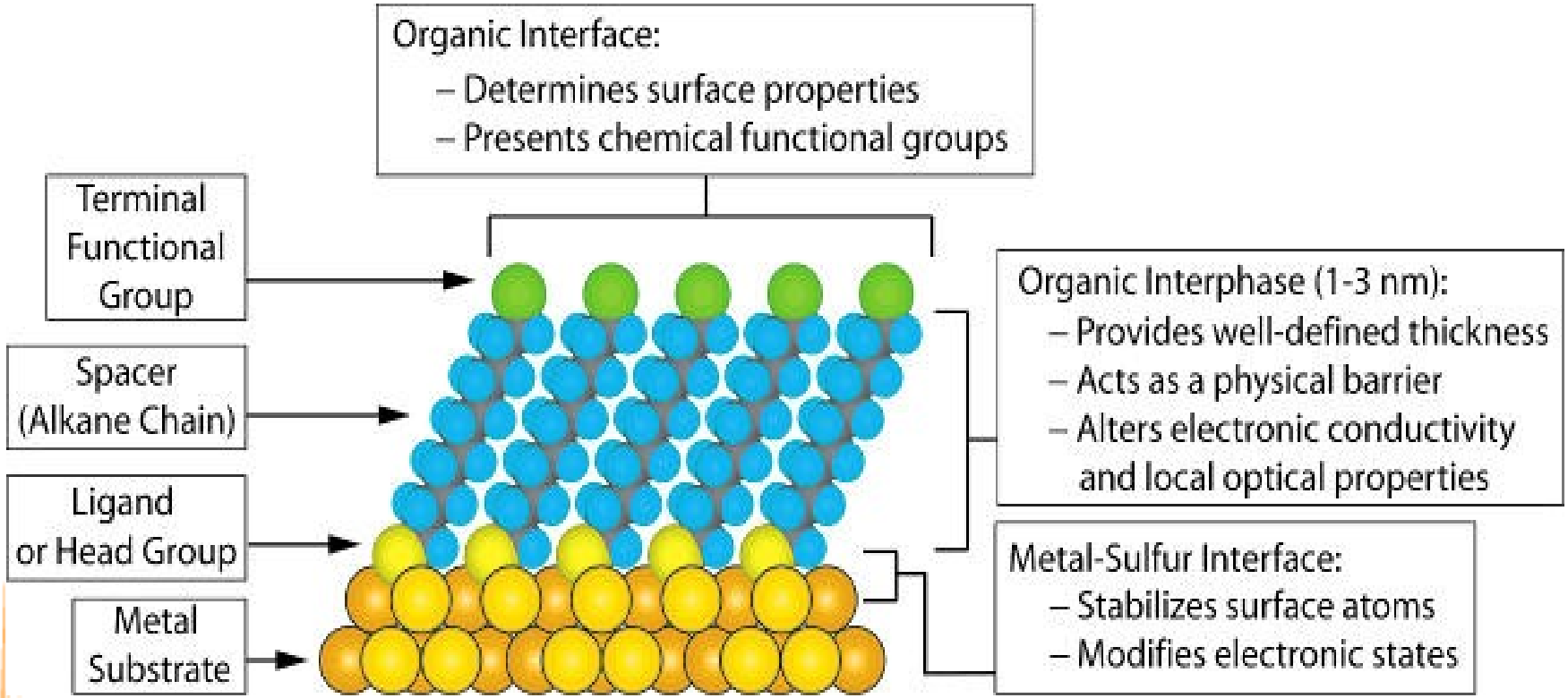
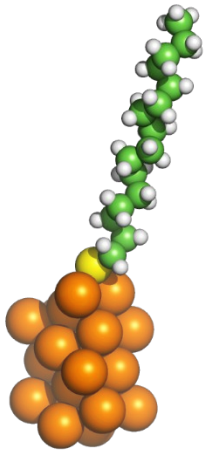
DFT coupled to Molecular Dynamics: Self-assembled monolayers

- PhD work (and slides) of Dimitris Stefanakis
- In collaboration with G. Kopidakis and V. Harmandaris.



Self Assembled Monolayers (SAMs) in brief



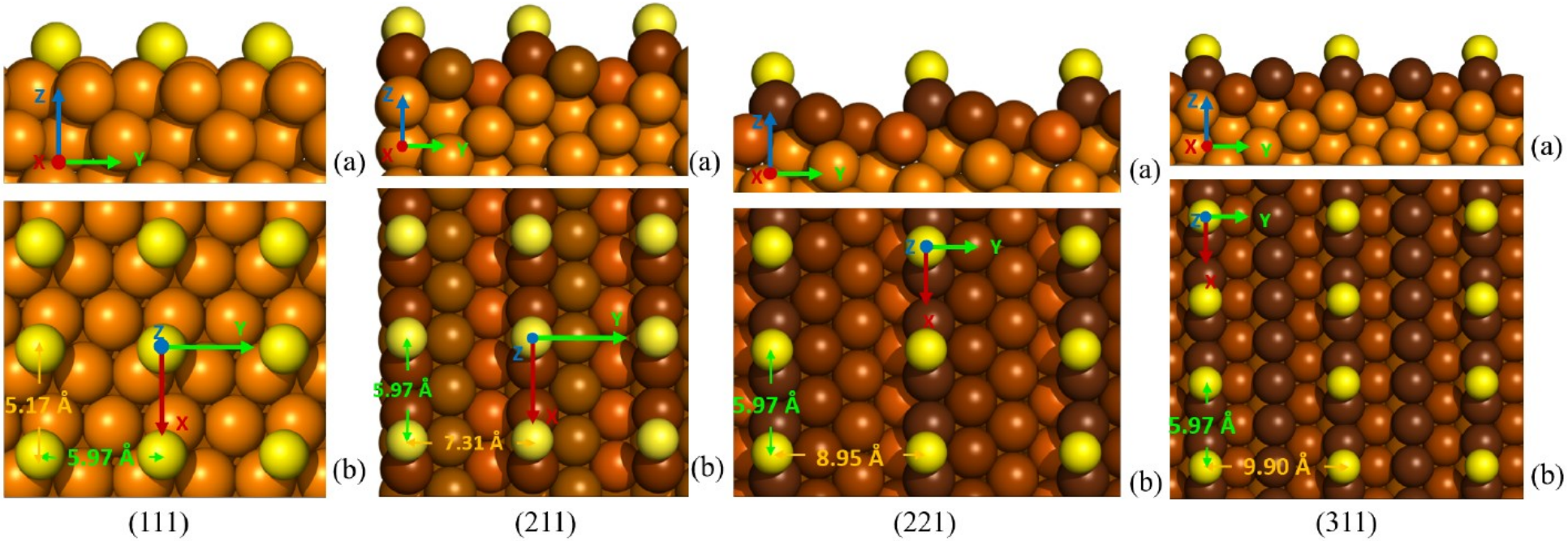


J. Christopher Love et al. Chem. Rev., 2005, 105 (4), pp 1103–1170

Functional Group Examples:

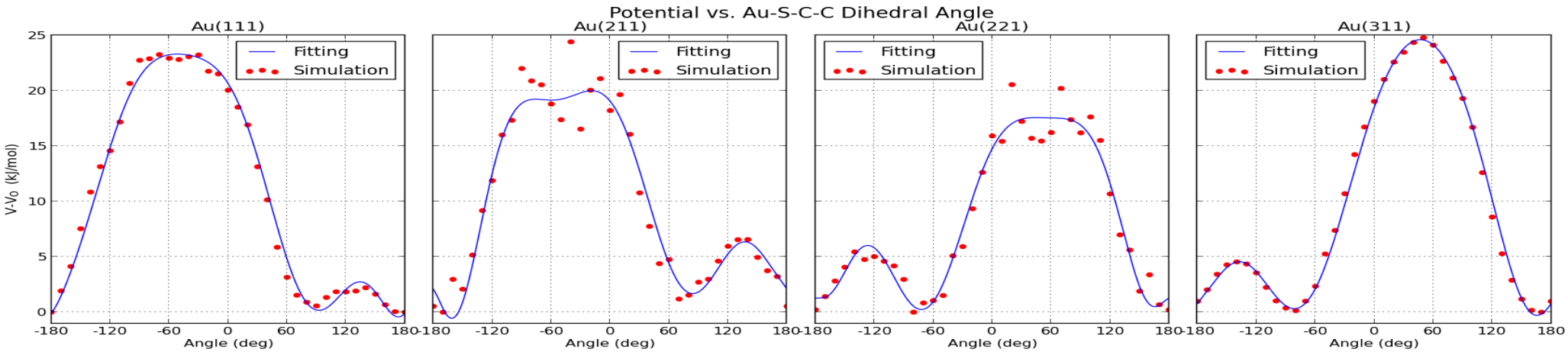
- $-CH_3$, $-CF_3$ (hydrophobic, metalophobic and highly anti-adherent)
- -COOH, $-NH_2$, -OH (hydrophilic, good metal ion and protein binding properties)
- -SH (efficiently bind metallic ions and nanoparticles to the SAMs)

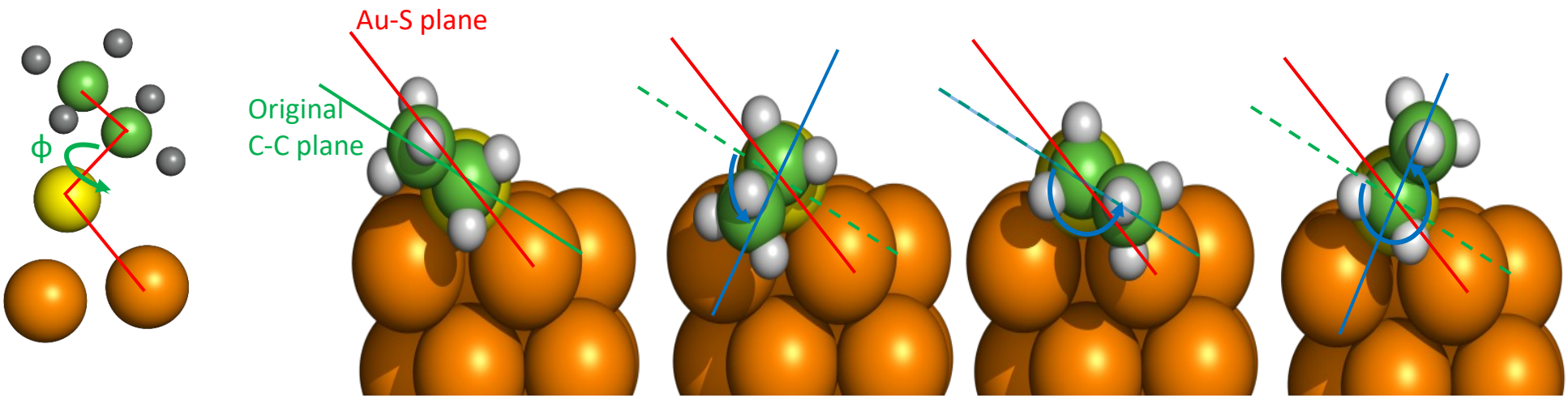
SAMs on Stepped Au surfaces



	Surfaces			
	Au(111)	Au(211)	Au(221)	Au(311)
Surface dimensions of a single cell (nm^2)	0.597 × 0.517	0.597 × 0.731	0.597 × 0.895	0.597 × 0.990
Surface area of a single cell (nm^2)	0.309	0.436	0.534	0.591
Grafting density (nm^{-2})	3.24	2.29	1.87	1.69
Total surface dimensions (nm)	17.9×15.5	17.9×21.9	17.9×26.9	17.9×29.7
Total slab surface (nm^2)	280.80	394.20	486.00	534.60
Number of Au atoms	25200	19800	30600	43200
Microfacet notation	...	3(111)×(100)	4(111)×(111)	2(111)×(100)

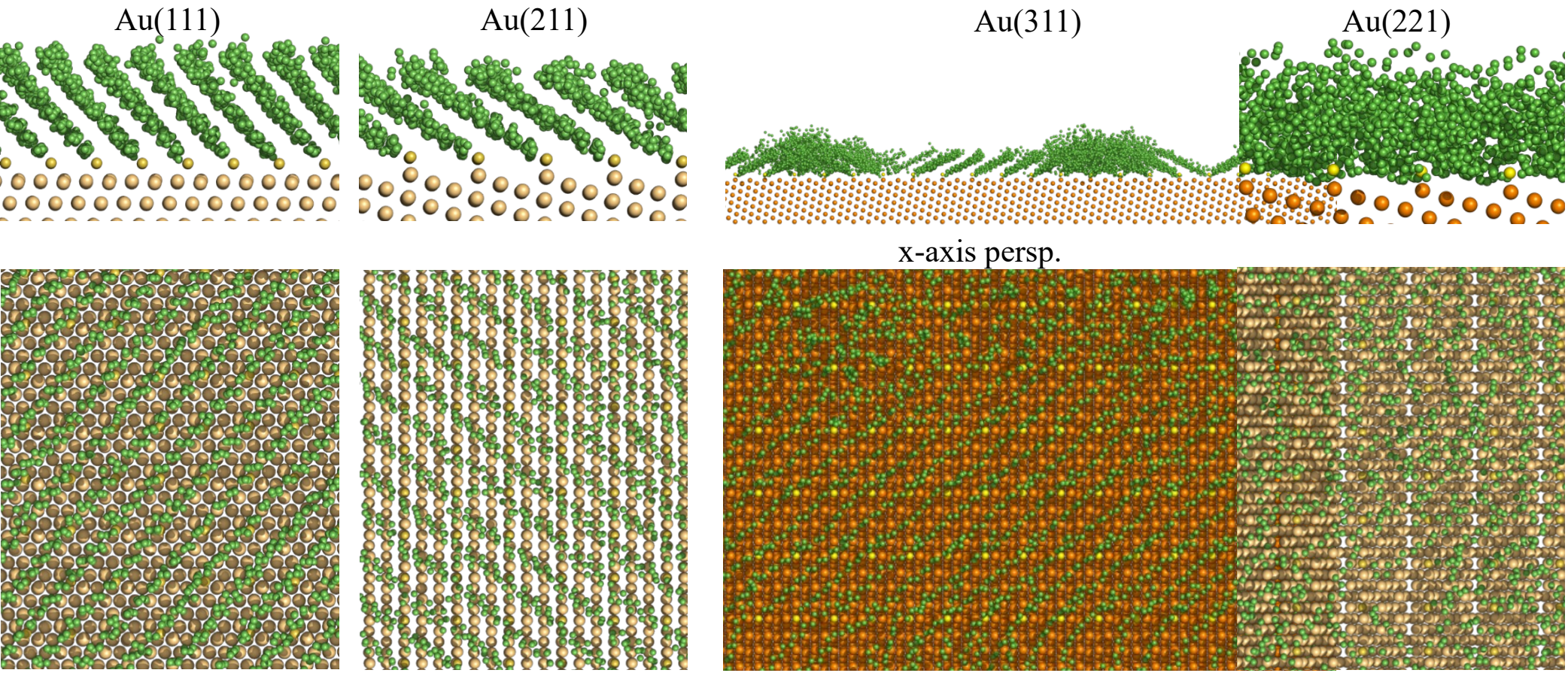
Calculation of the potential for the dihedral Au-S-C-C





(a) (b) (c) (d)

Atomistic simulations: Final formations of SAMs on Au su



Ordered systems

Semi-ordered system

Disordered system

From Order to Disorder of Alkanethiol Self-Assembled Monolayers on Complex Au (211), (221), and (311) Surfaces: Impact of the Substrate

Dimitrios Stefanakis, Vangelis Harmandaris, Georgios Kopidakis, and Ioannis Remediakis

The Journal of Physical Chemistry C 2021 125 (6), 3495-3508

Outline

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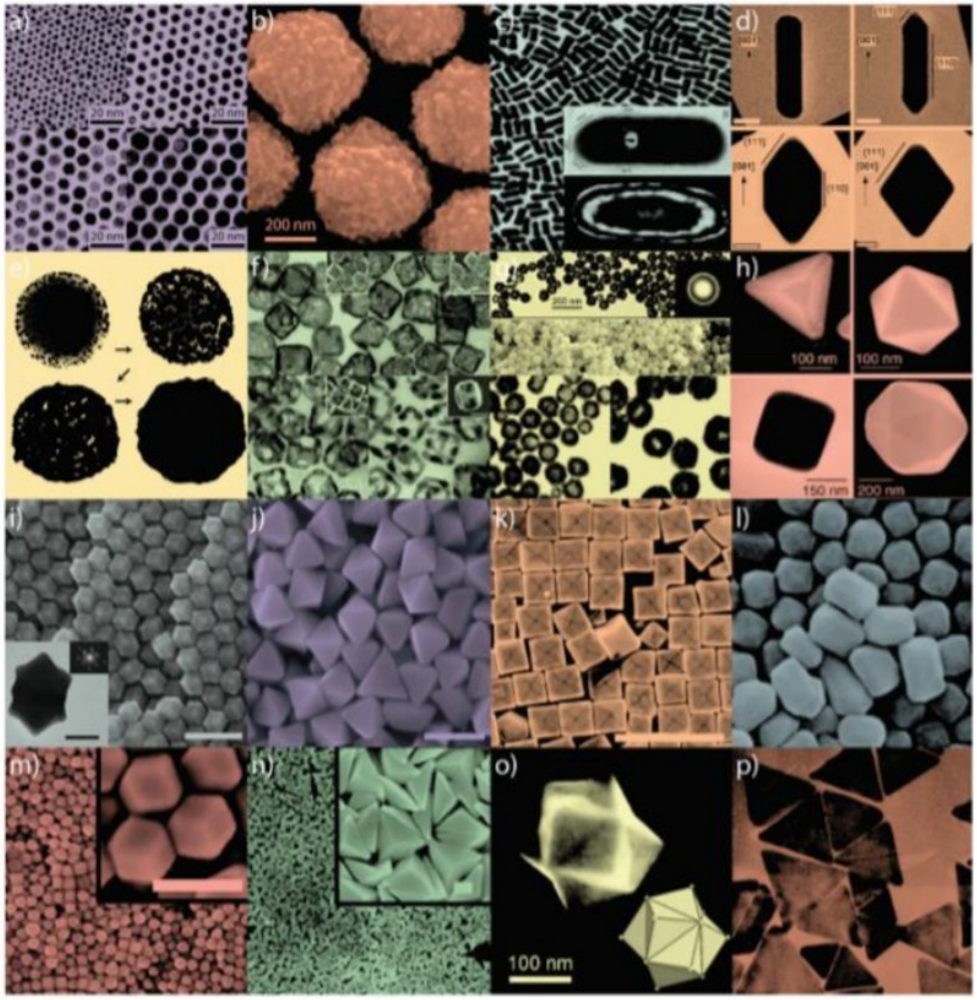
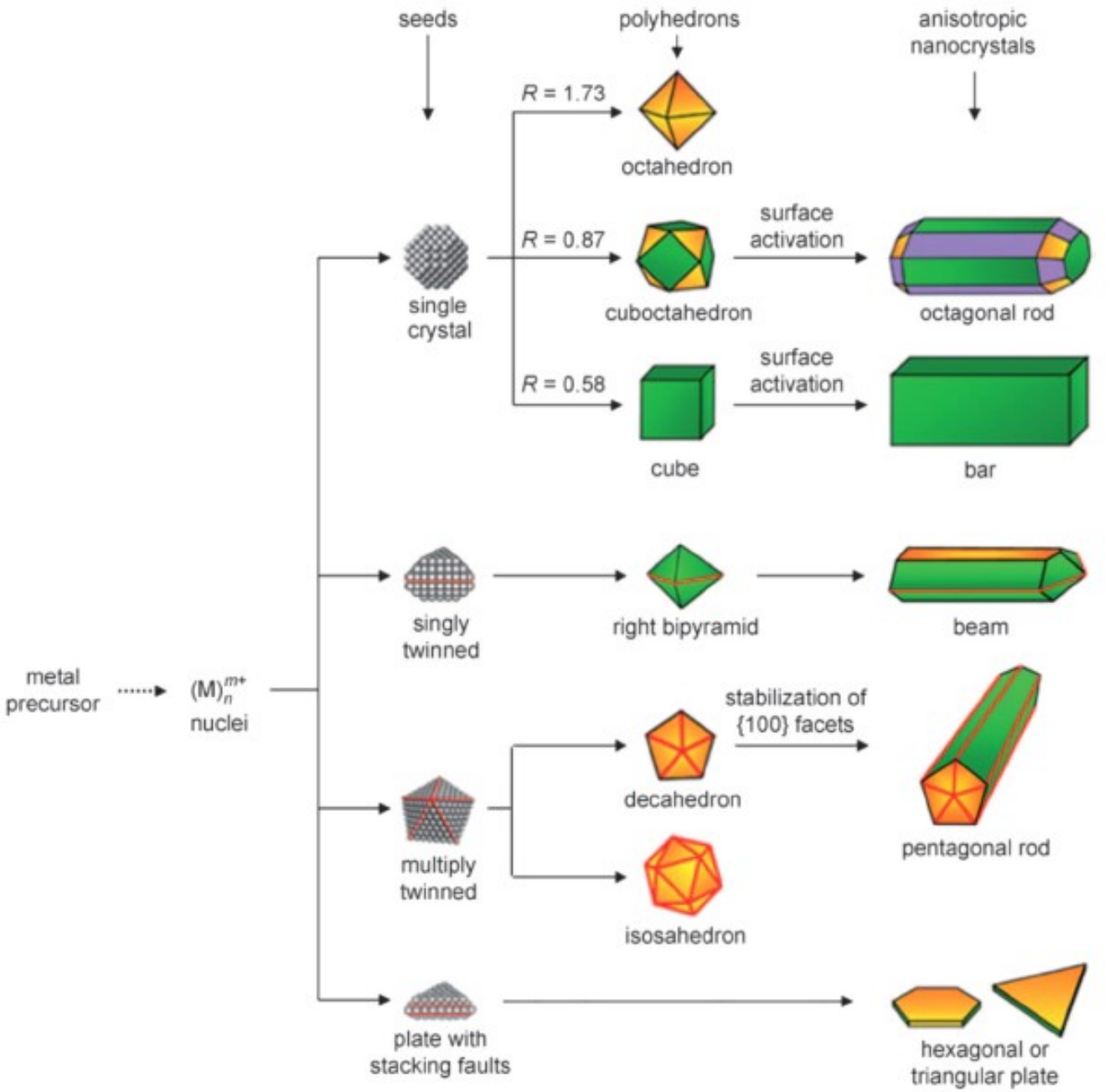
Shape of nanoparticles

- Shape affects functionality:
  - Determines number of active sites for catalysis.
  - Determines plasmon energies for optoelectronics.
- Shape is determined by the relative surface energies of different facets.
- Shape can be tuned by functional groups.



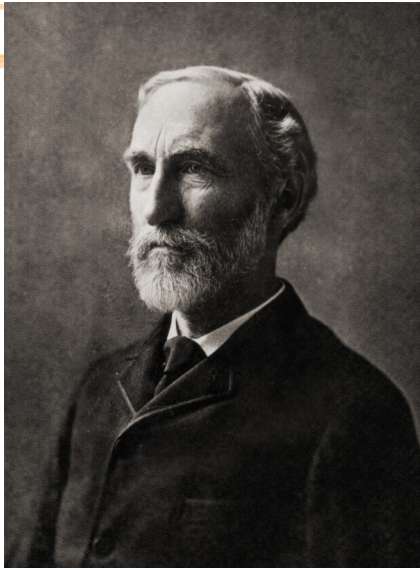
Eric C. Dreaden et al, Ch. Soc. Rev., 2012

Shapes of catalytic nanoparticles



Heinz et al., Surf. Sci. Rep. 72, 1 (2017)

What determines shape?



ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES.
BY J. WILLARD GIBBS.

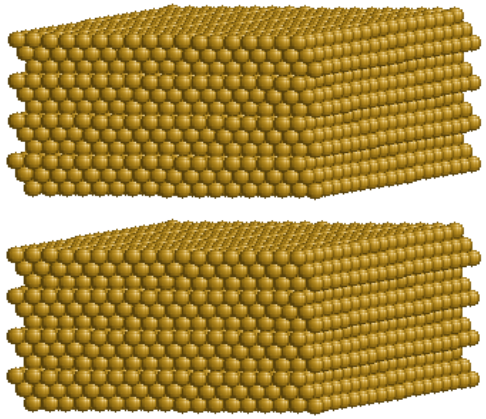
"Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu."
CLAUSIUS.*

al... hed from the surfaces. Equation (664) may then be written

$$-\delta W_{\mathrm{v}} + \Sigma(\sigma\,\delta s) = 0. \qquad (667)$$

Gibbs (1875):

$$G = G_{bulk} + \Sigma\, \gamma_{hkl} A_{hkl}$$



Surface tension γ = (Surface energy) / (area)

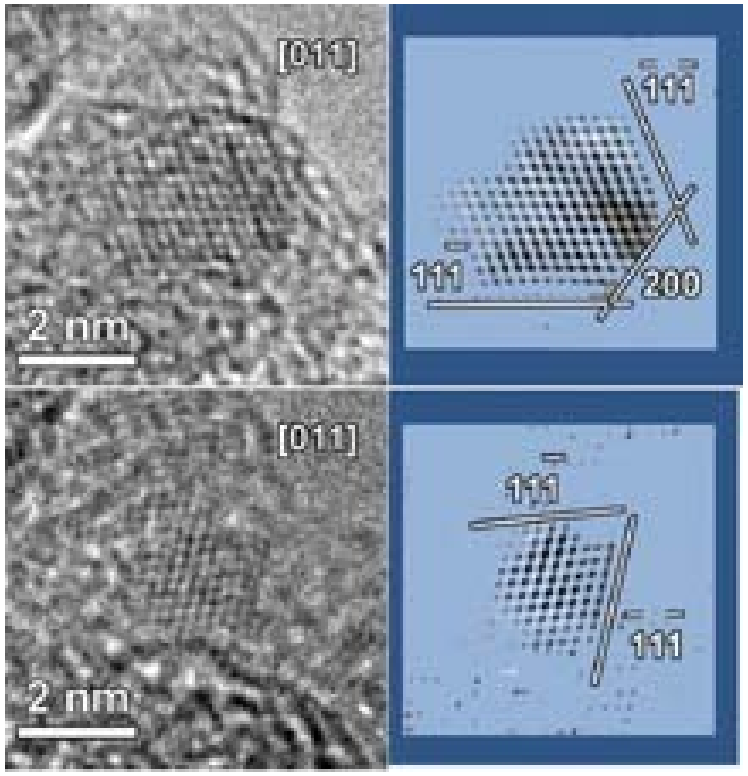
(Surface energy) = (Energy)- (Energy of bulk)

Equilibrium shapes

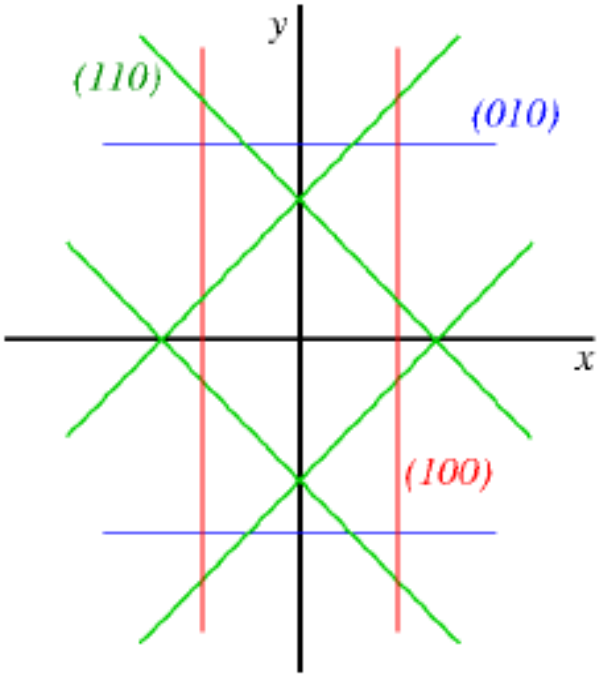
Minerals (billions of years to equilibrate) or
nanoparticles (small size).

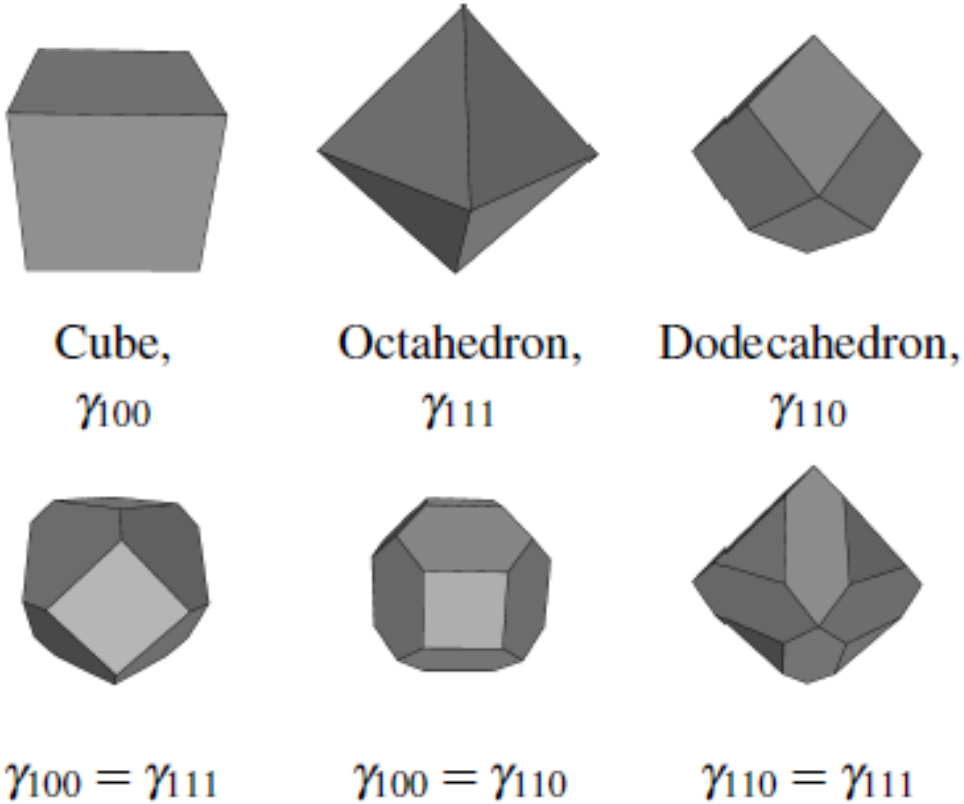
www.mindat.org

Turner et al., Adv. Func. Mater. 2009



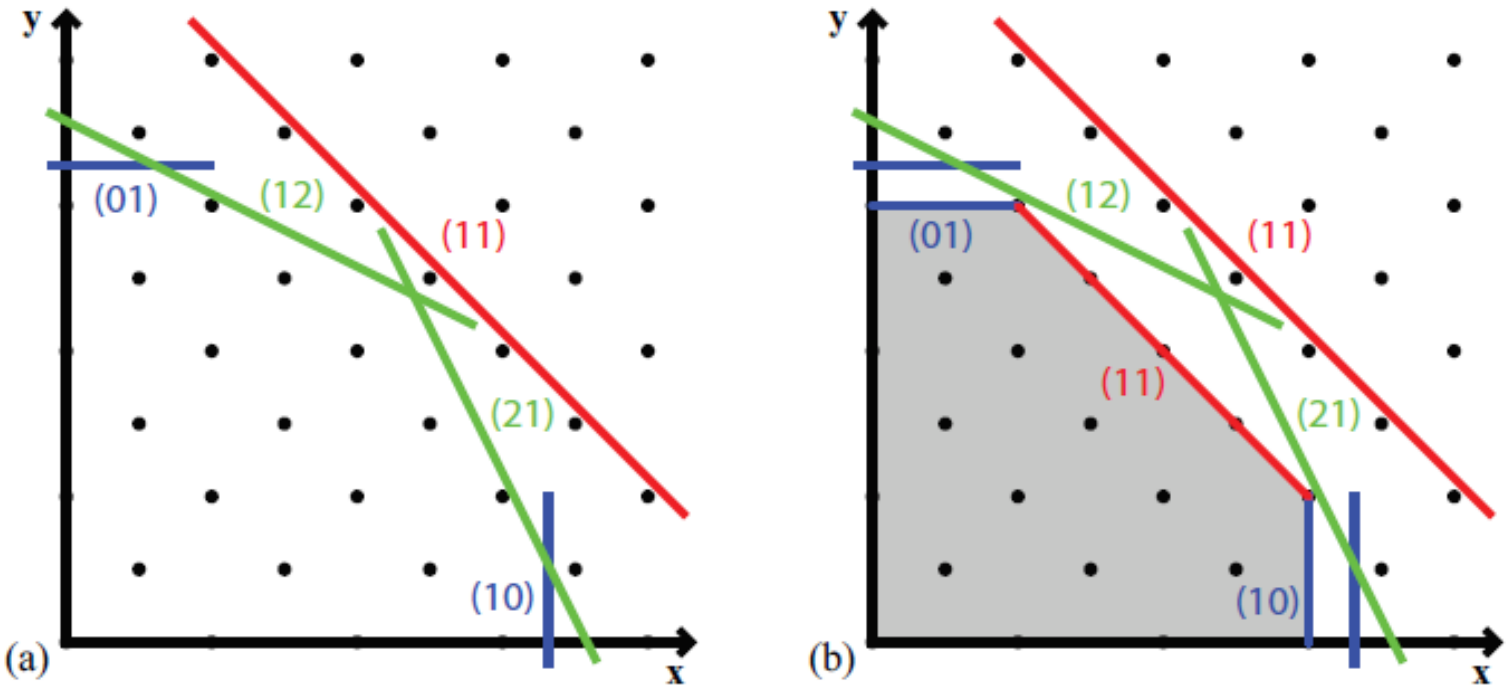
Wulff construction: $d_{hkl} / \gamma_{hkl} = c$





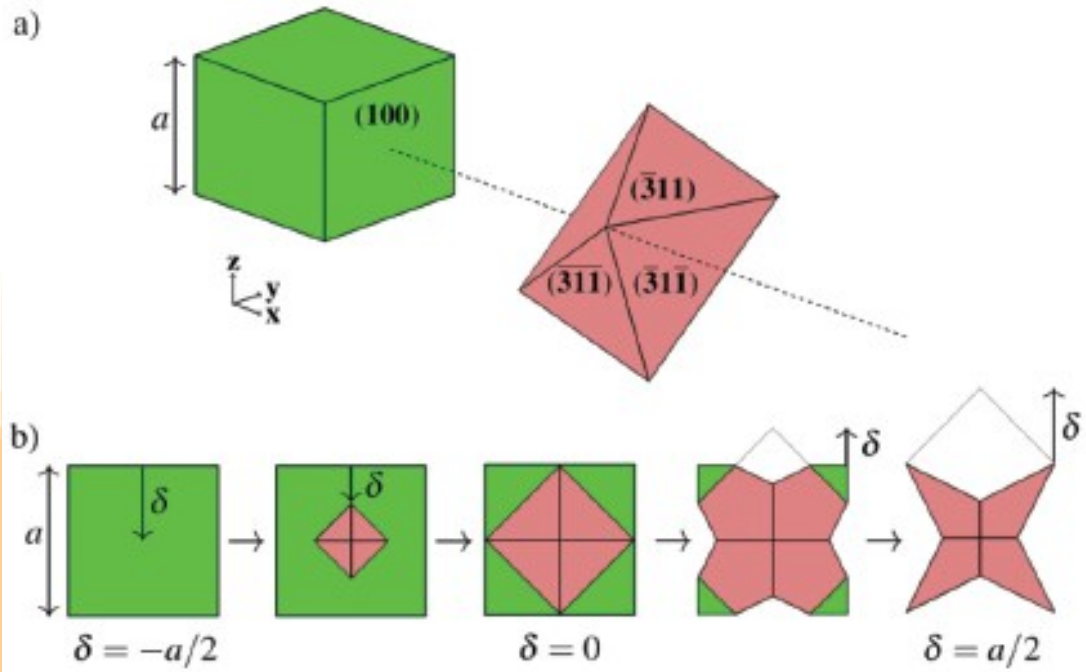
Barmparis, Lodziana, Lopez, Remediakis, Beilstein J. Nanotechn. 6, 361 (2015)

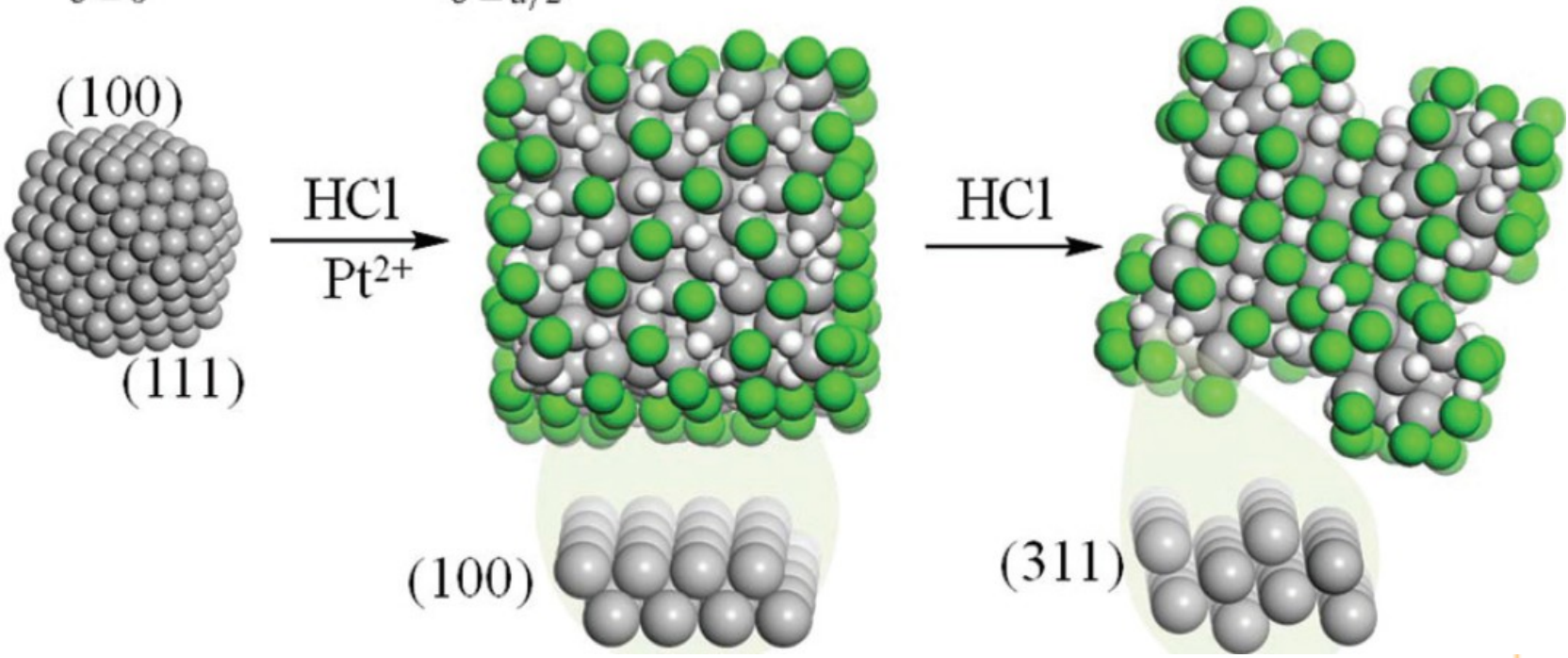
From continuum to atomistic



- Wulff construction is correct for large nanoparticles.
- For small ones, different shapes appear for different values of c in $d_{hkl} / \gamma_{hkl} = c$.
- <u>Atomistic Wulff</u> (*Barmparis and Remediakis, PRB 2012*).

Pt in HCl: from convex to concave shape

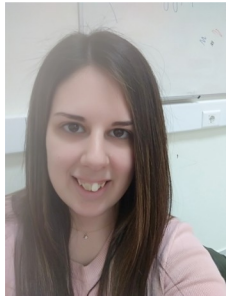




Q. Li, M. Rellán-Piñeiro, N. Almora-Barrios, M. Garcia-Ratés, I. N. Remediakis, N. López, Nanoscale 9, 13089 (2017).

DFT coupled to Data Science: Machine-learning prediction of energies

- PhD work (and slides) of Emmanuel Pervolarakis/
- In collaboration with A. Mpoumpaki, G. Tritsaris and P. Rosakis.

Machine learning for Au energies

- Data: Energy of nanoparticles, nanowires, slabs.
  - DFT/PBE calculations with VASP.
  - All known interatomic potentials (OPENKIM/LAMMPS).
- Linear regression model
  - python pandas and scikit-learn
  - Features: N, N_b, N_s, N_e, N_v.
  - Property: total energy.
  - Excellent fit (score = 0.99999991)
  - Accurate predictions (avg. Error = 0.4%).
- No need for expensive calculations for large nanoparticles!

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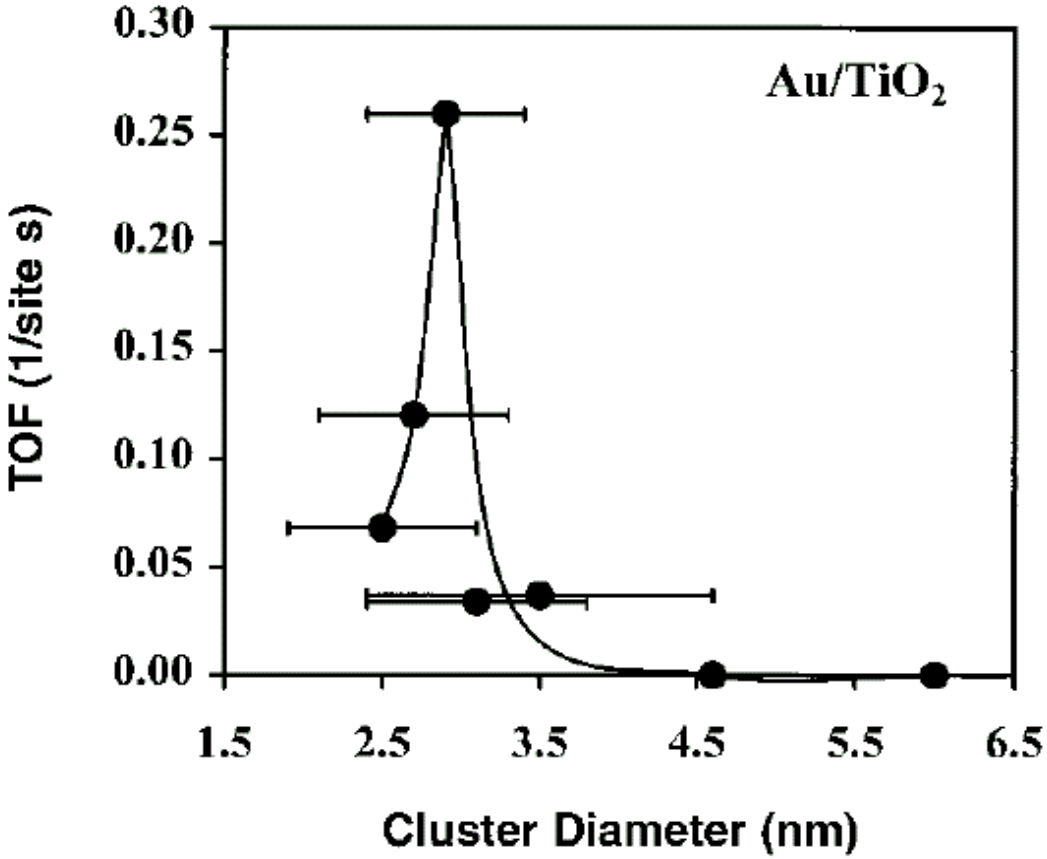
Nano is different

Gold is noble

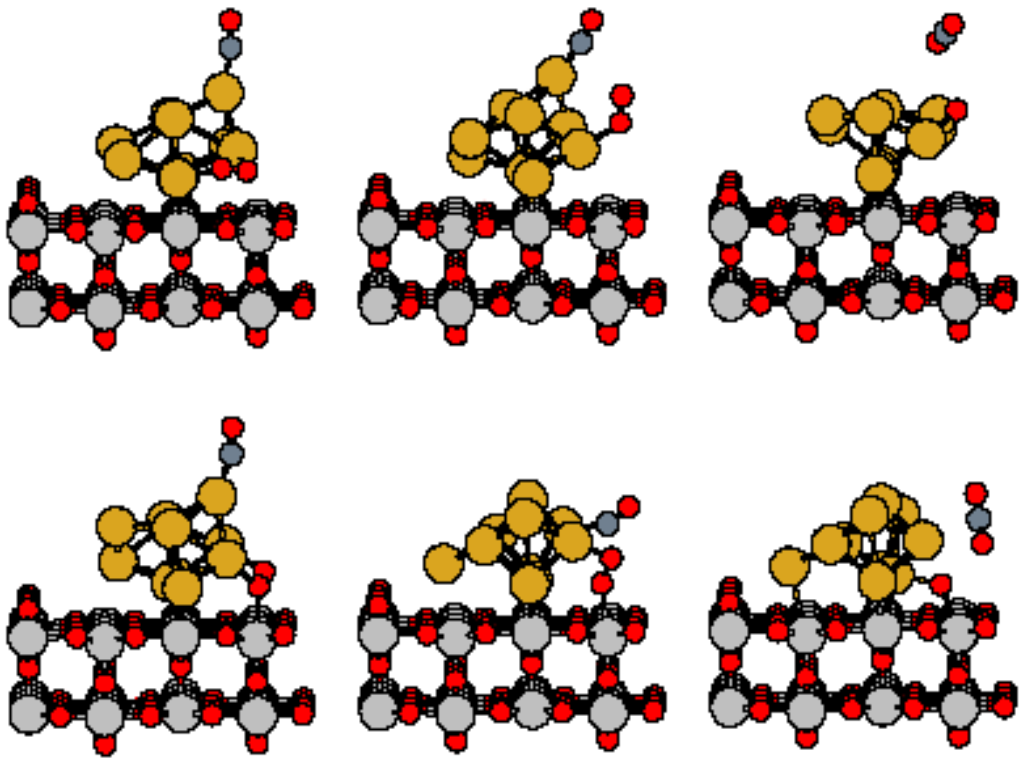


...but nano-gold is a superb catalyst.

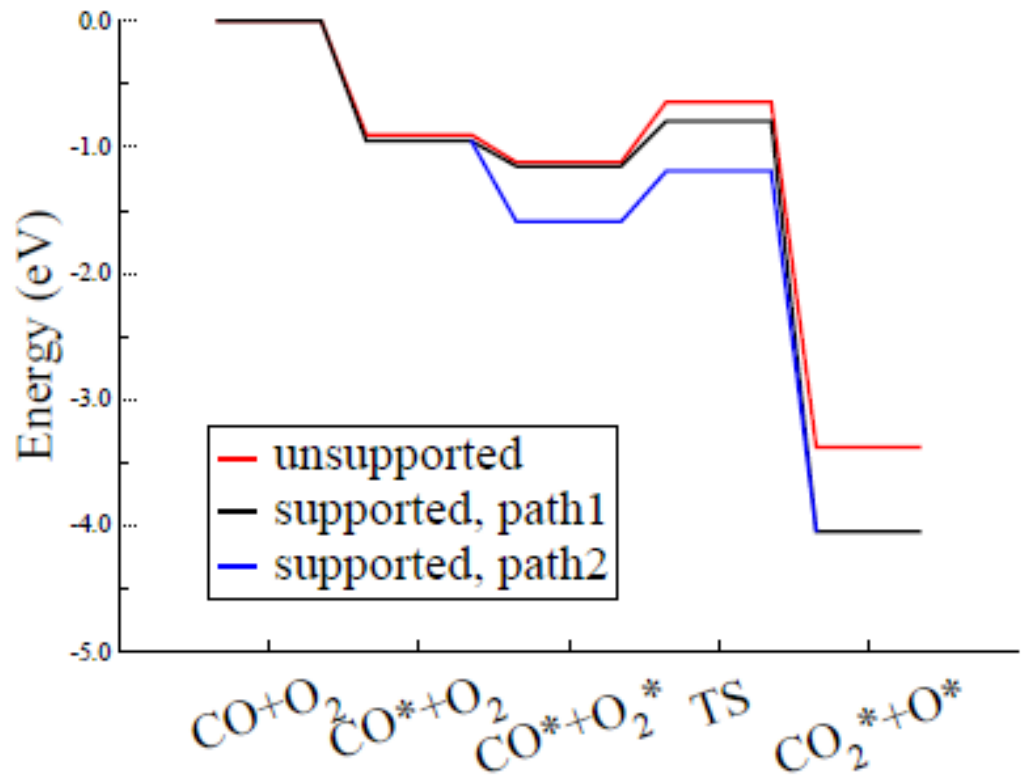
Left: Jewel from Malia, Crete (ca. 1800 BC)

Right: CO oxidation at room T on rutile-supported Au, Valden, Lei, Goodman, Science (1998)

Two paths for CO oxidation



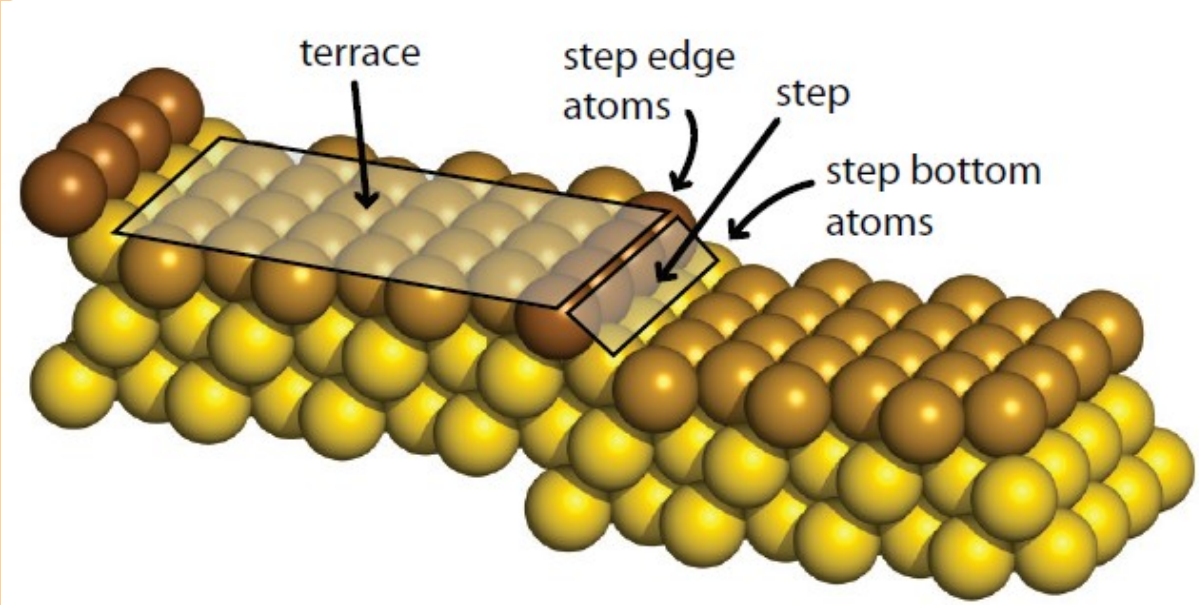
Initial *Transition* *Final State*

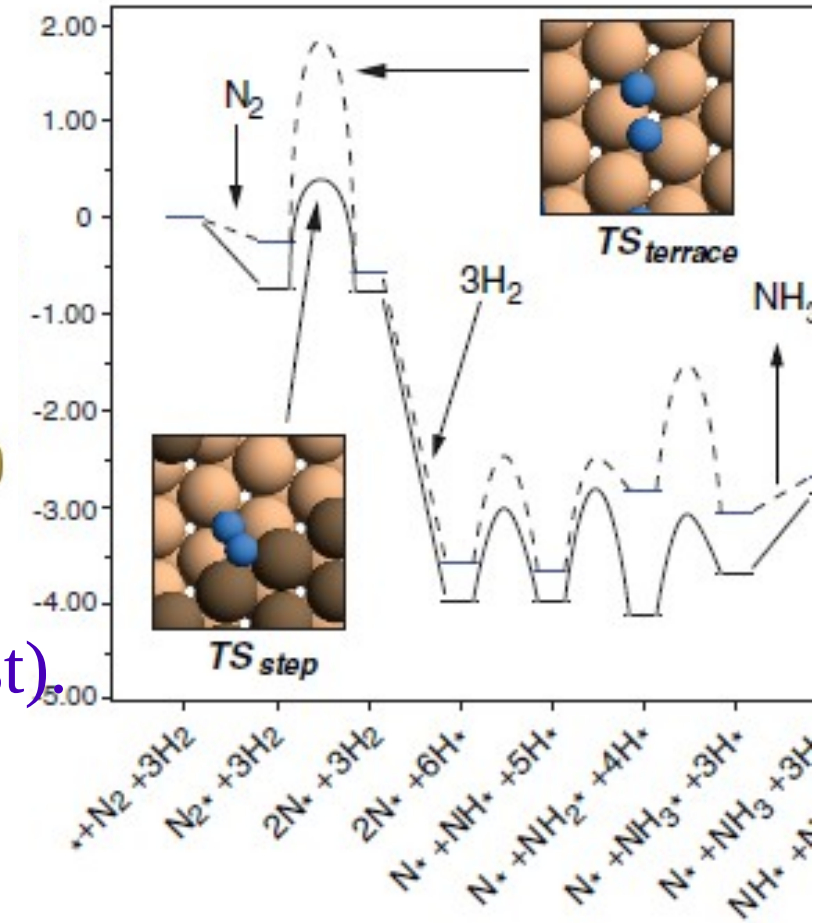


Gold-only (top) and Gold-oxide interface path (bottom).

I. N. Remediakis, N. Lopez and J. K. Nørskov, Angew. Chemie Int. Ed. ***44****, 1824 (2005)*

Chemical reactions take place only on specific types of sites



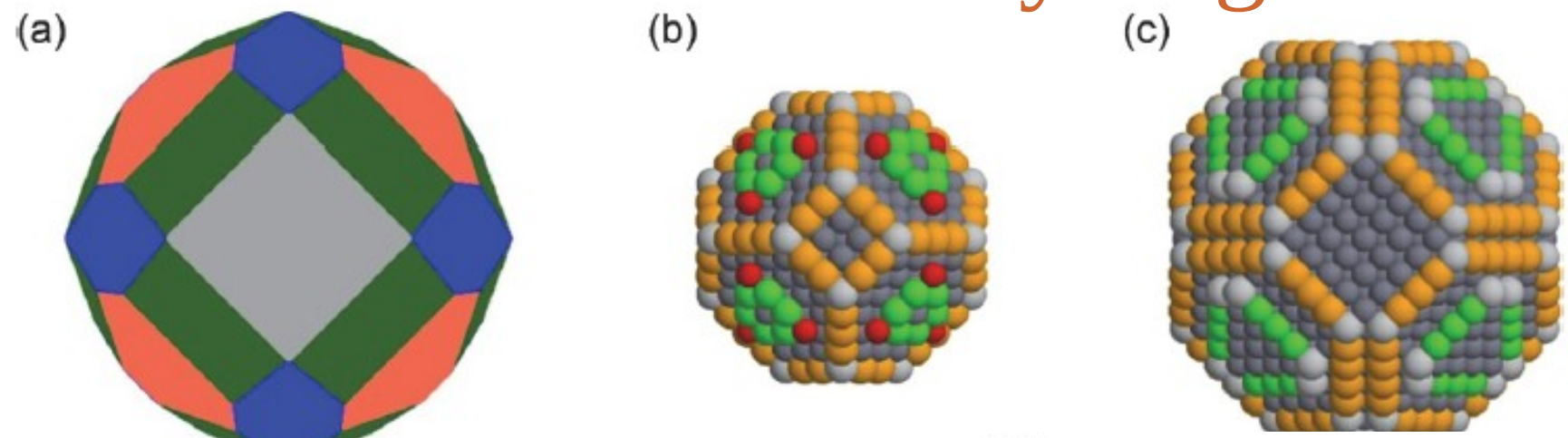


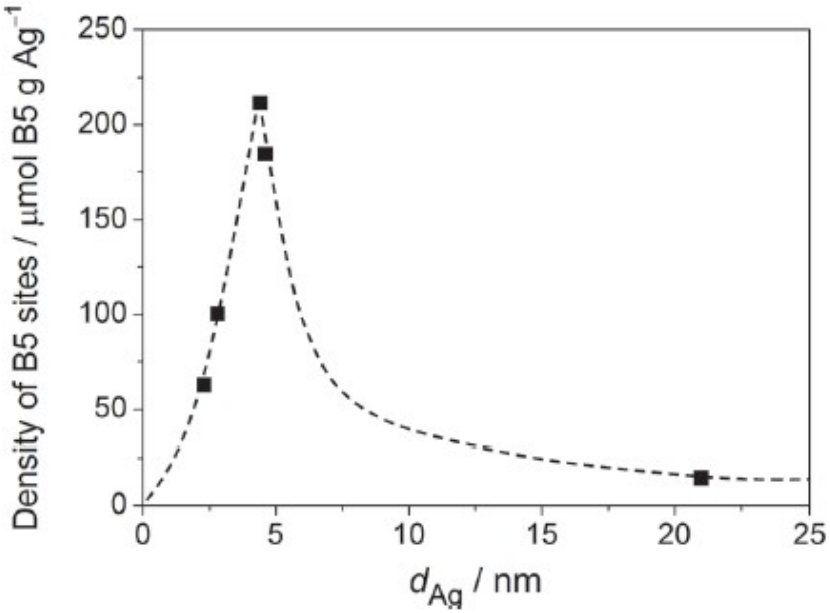
- Turnover = reactions/(mass of catalyst).
- Nano = huge fraction of edge atoms.

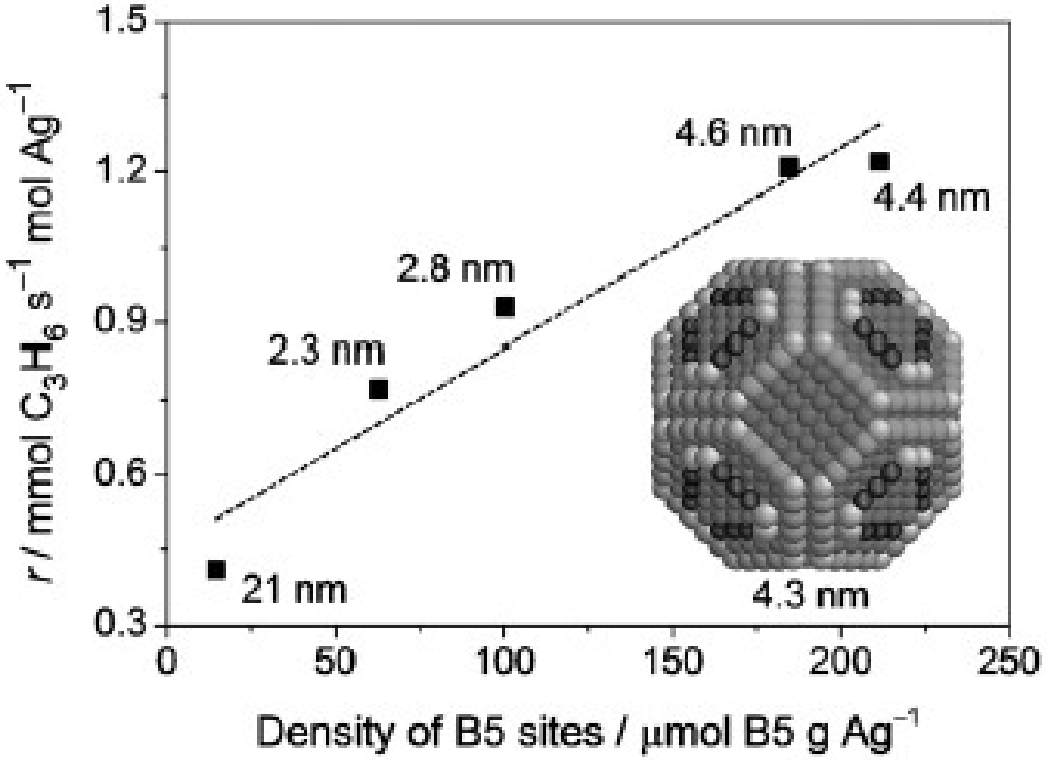
<u>Left:</u> G. D. Barmparis, PhD Thesis (2012).

<u>Right:</u> K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen, J. K. Nørskov, Science, 307 558 (2005)

Active sites for C≡C hydrogenation on Ag







Vilé, Baudouin, Remediakis, Copéret, López, Pérez-Ramírez, ChemCatChem 5, 3750 (2013);

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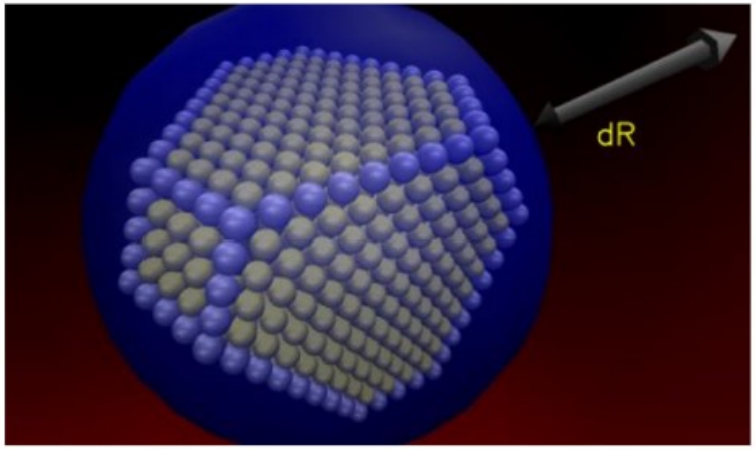
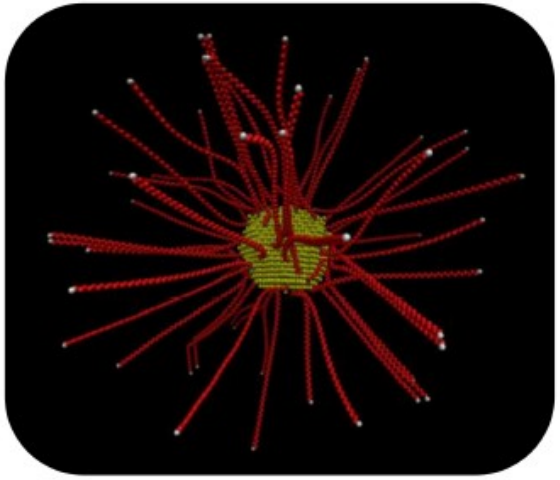
DFT coupled to MD: Polymer-gold nanocomposites

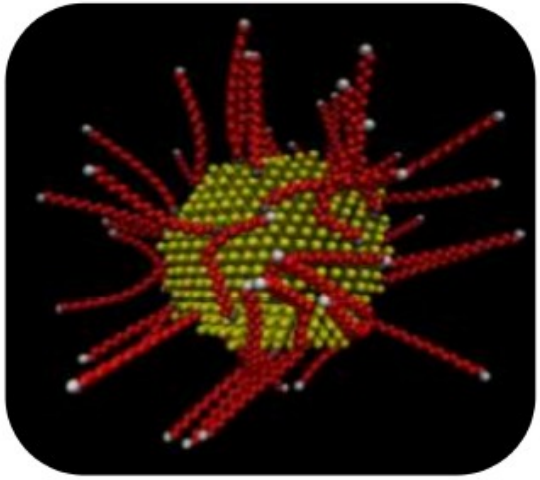
- PhD work of Albert John Power
- In collaboration with V. Harmandaris.

From Au to PS composite

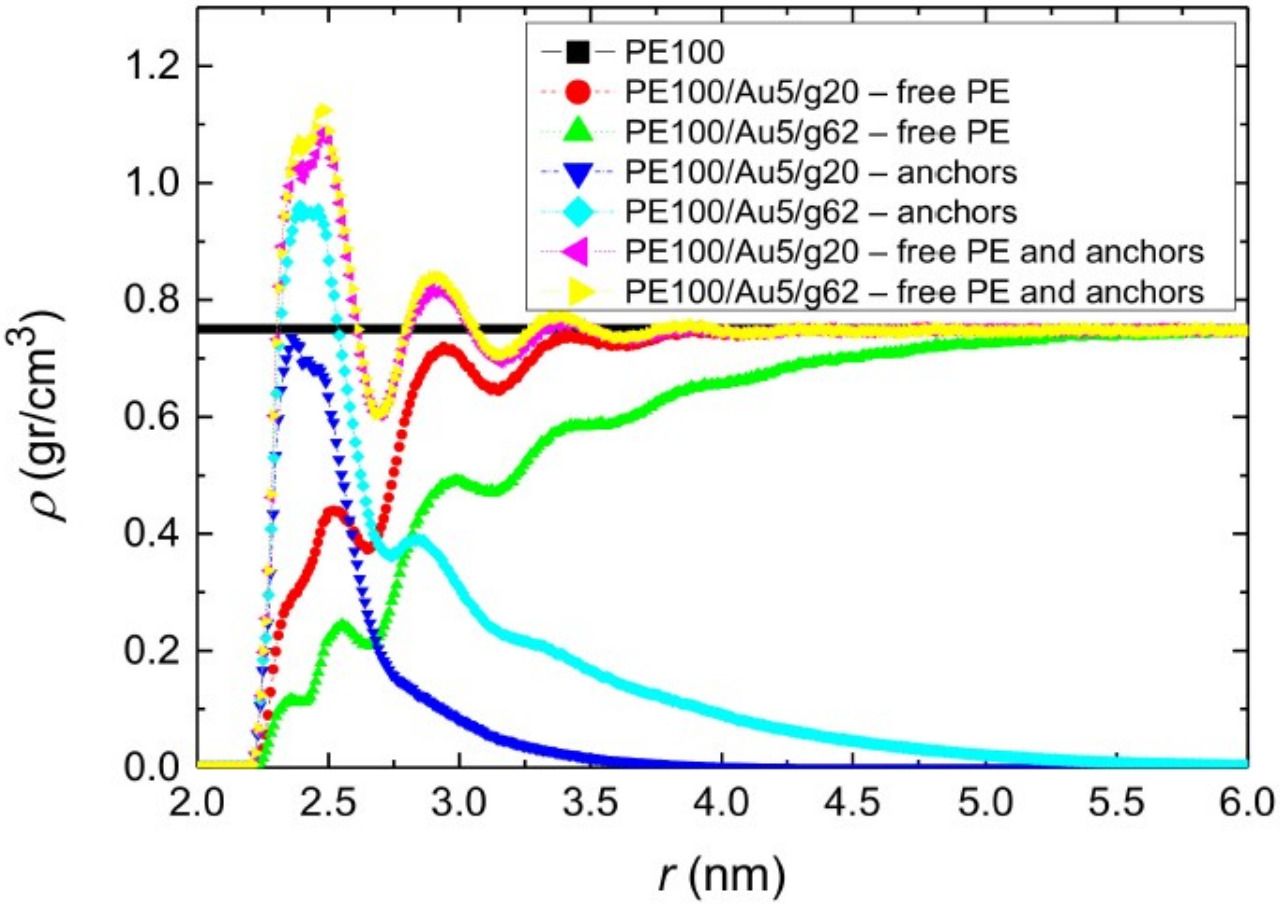
- Wulff shape of thiol-covered Au of different sizes.
- Covered by polyethelene of different lengths and concentrations.







Interface and Interphase



polymers

Article

Interface and Interphase in Polymer Nanocomposites with Bare and Core-Shell Gold Nanoparticles

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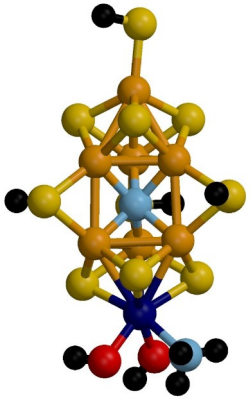
  - GROMACS, LAMMPS, OPENKIM (MD)
  - scikit-learn, pandas (machine learning, data)



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