Atomistic Wulff Constructions for Gold Nanoparticles

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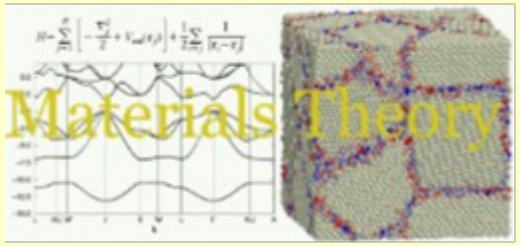
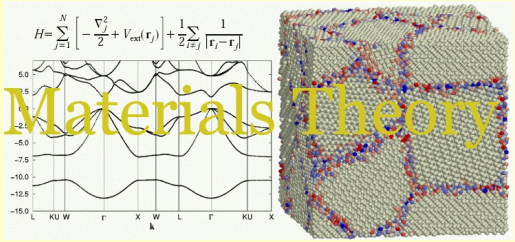


Software Frameworks for Challenging Computational Problems, ACMAC, Heraklion, Crete, 17/1/2013

Outline

- DFT calculations and the GPAW package.
- Equilibrium shape: 20th century and the nano-era (1995-).
- Equilibrium shape from first principles (2005-).
- Au nanoparticles from first principles and the atomistic Wulff construction method.
- Nanoparticles in reactive environment.



First-principles atomistic calculations

Input: Coordinates of the nuclei plus numerical parameters.

Output: equilibrium structure for given external fields, and/or response functions (usually).

Advantage: Understanding and design of materials at their ultimate level: elecrtrons and nuclei (or ions).

Density-functional Theory (DFT): $H\psi=E\psi$; $H=K+V_{e\text{-}ion}+V_{e\text{-}e}+V_{x\text{-}c}$:

$V_{e\text{-}ion}$:pseudopotential; $V_{e\text{-}e}$: mean-field electron-electron;

V_{xc}: many body plus self-interaction correction.

Here: DACAPO, GPAW and ASE (GPL'd open source software)

http://www.camd.dtu.dk/Software

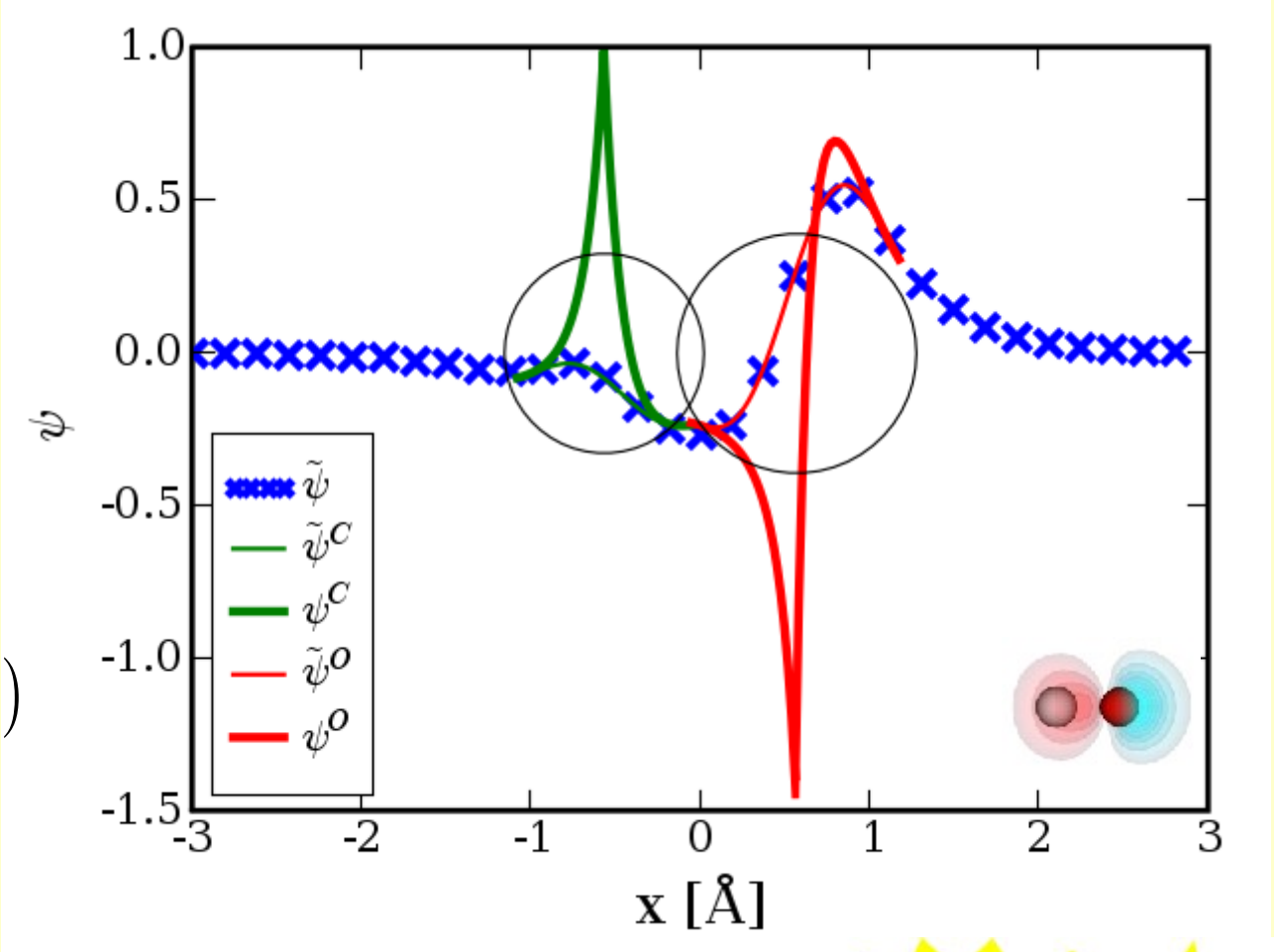
Center for Atomic-scale Materials Design

Projected Augmented Wave method

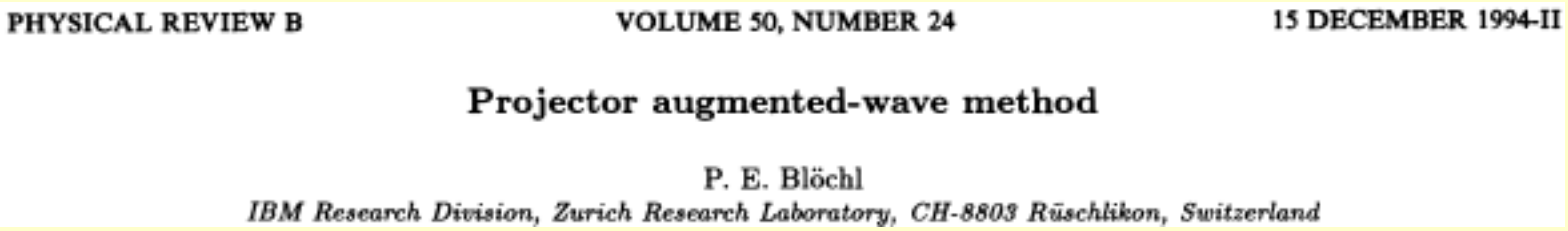
$$|\psi\rangle = \left(1 + \sum_a T_a\right)|\tilde{\psi}\rangle$$

$$|\varphi_a\rangle = \left(1 + T_a\right)|\tilde{\varphi}_a\rangle$$

$$\tilde{\psi}(x, y, z) = \tilde{\psi}(ih, jh, kh)$$



http://www.camd.dtu.dk/Software

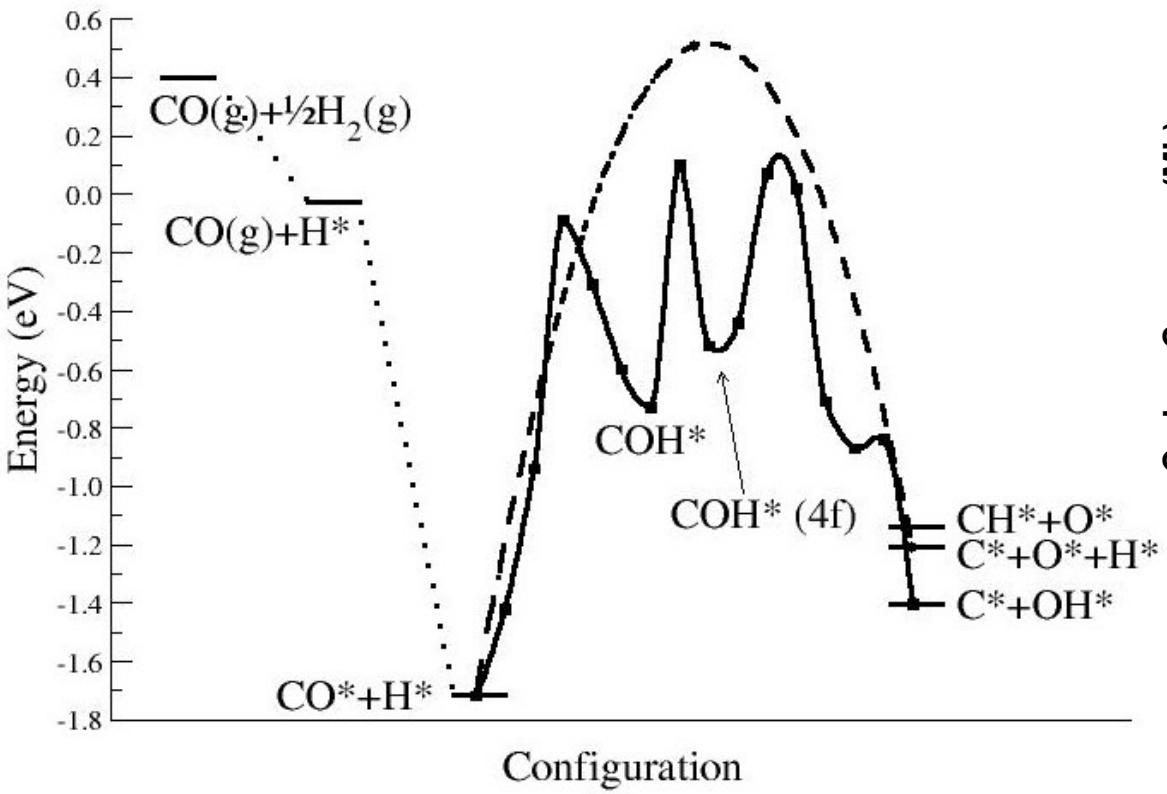

PHYSICAL REVIEW B VOLUME 50, NUMBER 24 15 DECEMBER 1994-II

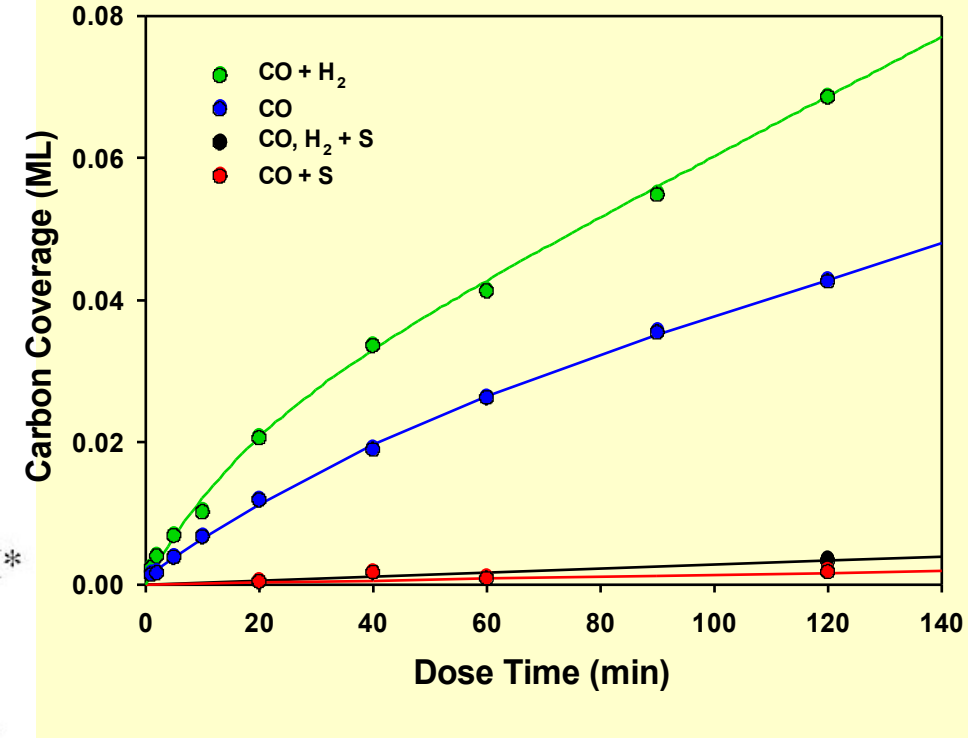
Projector augmented-wave method

P. E. Blöchl

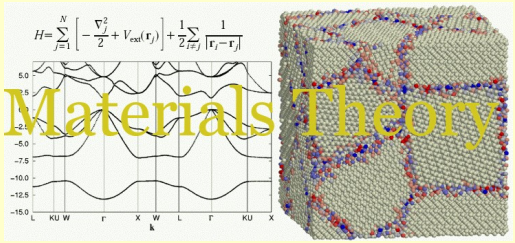
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Example: Catalysis from first principles





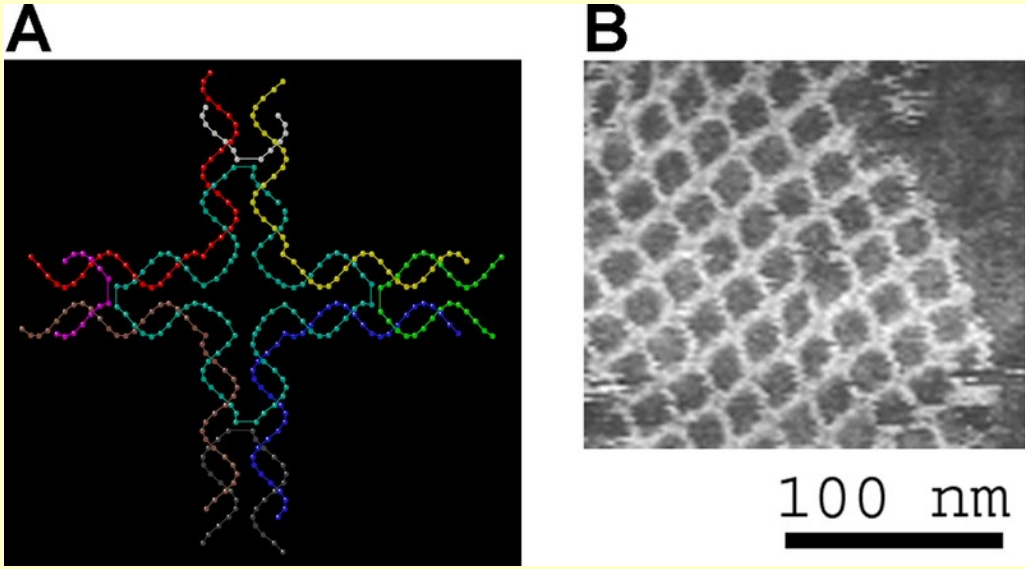
- $$\upsilon = (\upsilon^* \theta_{\text{active sites}}) \sqrt{P_{H_2}} \theta_{CO} \exp\left(\frac{-E_{a,COH}}{k_B T}\right),$$
- $\upsilon \sim \sqrt{P}$; E_a and υ agree with experiment.
- The CO bond weakens (e.g. by H) beore it breaks.

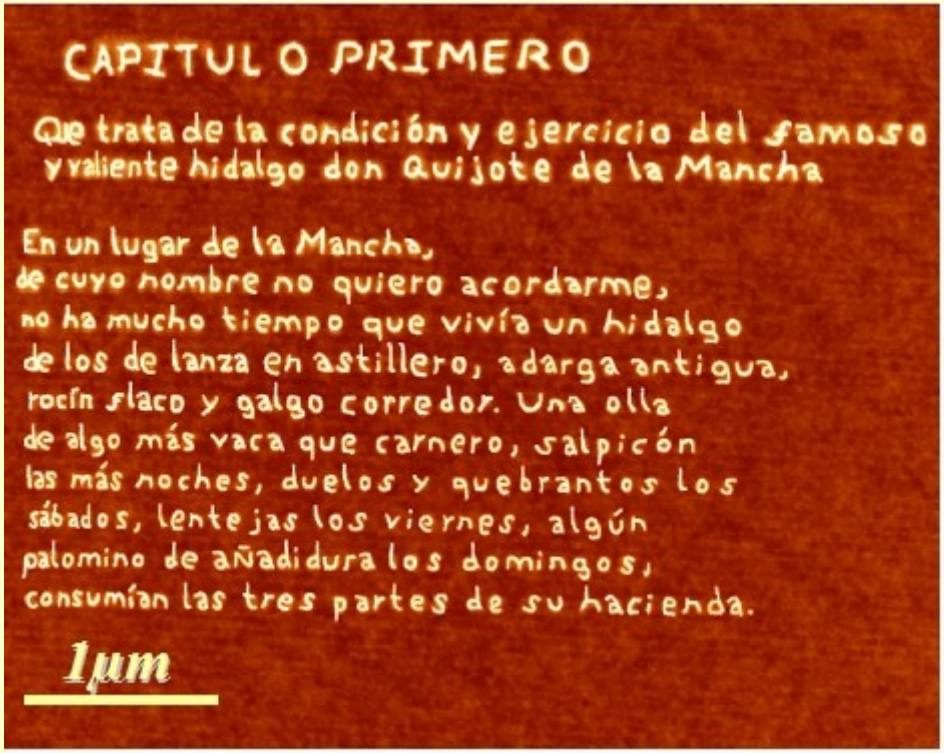


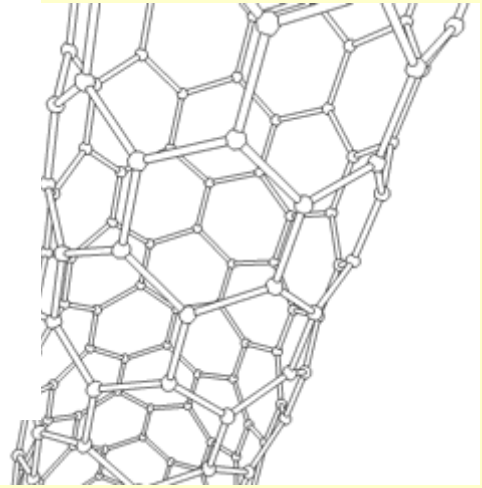
Andersson et al., J. Catal. ***255****, 6 (2008).*

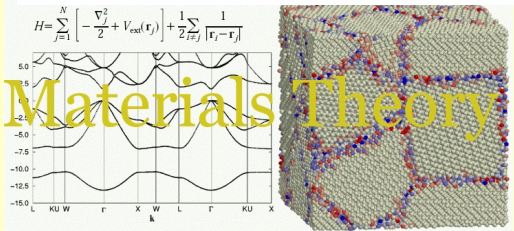
Nanomaterials

Building blocks of the order of few nm (10^{-9} m)



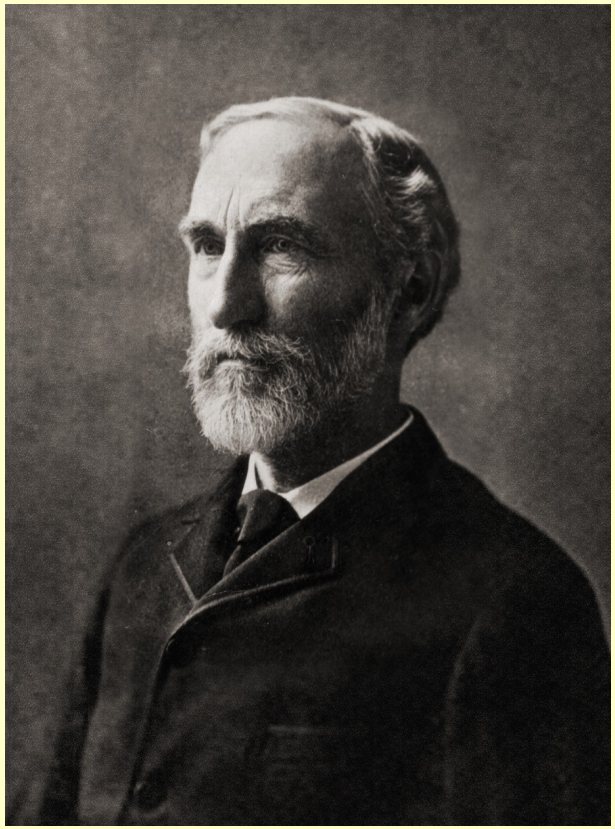






Nanoparticle sizes at equilibrium

$$G = U + PV - TS$$



J. W. Gibbs (1839-1903)

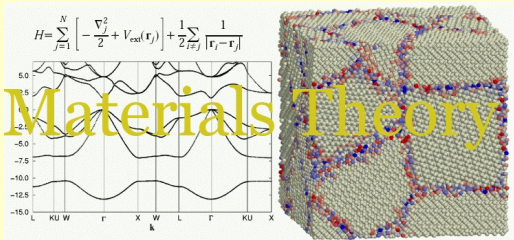
"Bottom up" synthesis (self-assembly):

T→0 favors few big particles (**low U**).

T→∞ favors many small particles (**high S**).

T-dependent size.

Similarly, size depends on other synthesis parameters, such as PH, concentrations, etc.



Equilibrium shape (1878)

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.*

crystal but regarded as without surfaces. We may denote the work required to form the crystal by

$$W_s - W_v,$$

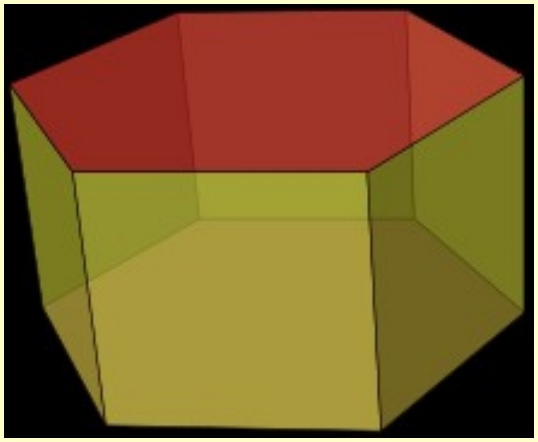
W_s denoting the work required to form the surfaces [*i. e.*, $\Sigma(\sigma s)$], and W_v the work gained in forming the mass as distinguished from the surfaces. Equation (664) may then be written

$$-\delta W_v + \Sigma(\sigma \delta s) = 0. \qquad (667)$$

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

Surface tension γ = (Surface energy) / (area)
(Surface energy) = (Energy)- (Energy of bulk)

Wulff's theorem



(Wulff 1901) Minimum energy polyhedron:

$d_{hkl} / \gamma_{hkl} = \text{constant}$

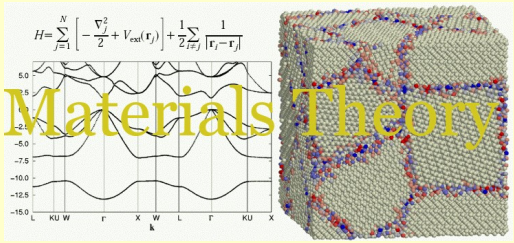
Low-energy -> large area -> closer to center.

First Proof: M. Von Laue (1943).

Short proof by R. F. Strickland-Constable (1968):

$G=\Sigma\gamma_{hkl}A_{hkl}$ minimized for constant $V=\Sigma(1/3)d_{hkl}A_{hkl}$:

$\delta(G-\lambda V)=0 \Rightarrow \Sigma(\gamma_{hkl}-cd_{hkl})\delta A_{hkl}=0 \Rightarrow \gamma_{hkl}=cd_{hkl}$ (QED).



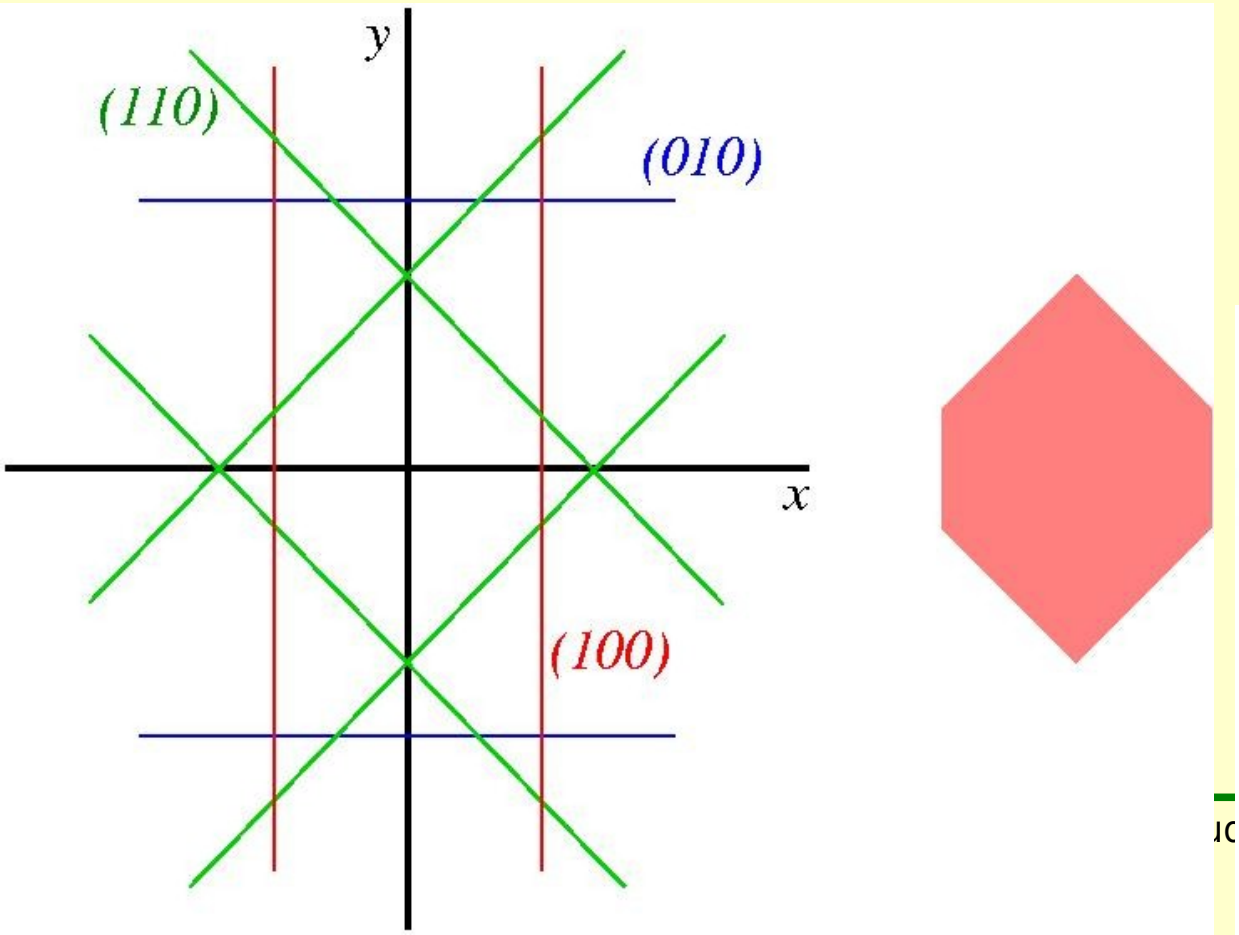
An example of Wulff construction

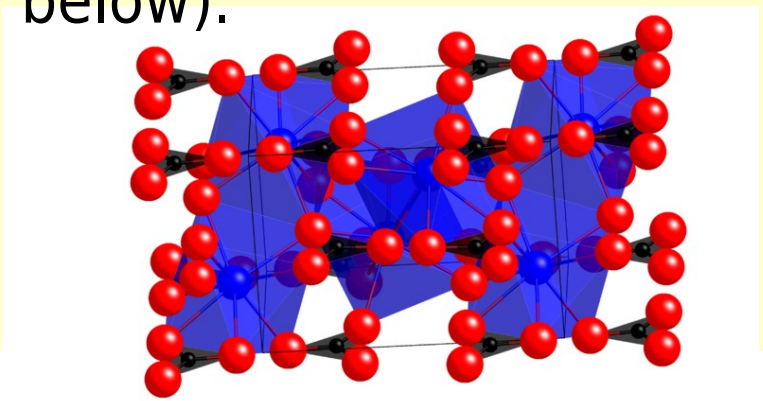
d_{hkl}/γ_{hkl} = constant (d=distance from center).

Orthorhombic material (e.g aragonite $CaCO_3$) with

$$\gamma_{100}=\gamma_{110}=\gamma=0.5\gamma_{010} << \gamma_{001} << \gamma_{hkl}.$$

Crystal habit: elongated rods (Cross section below).



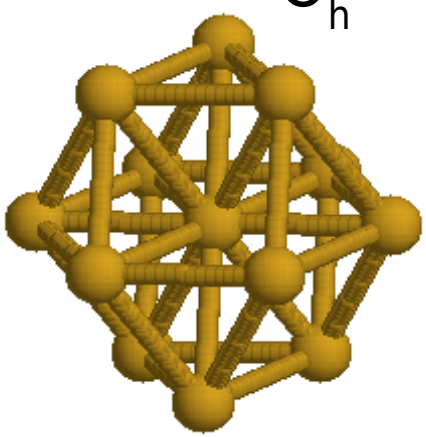


Symmetry-allowed shapes

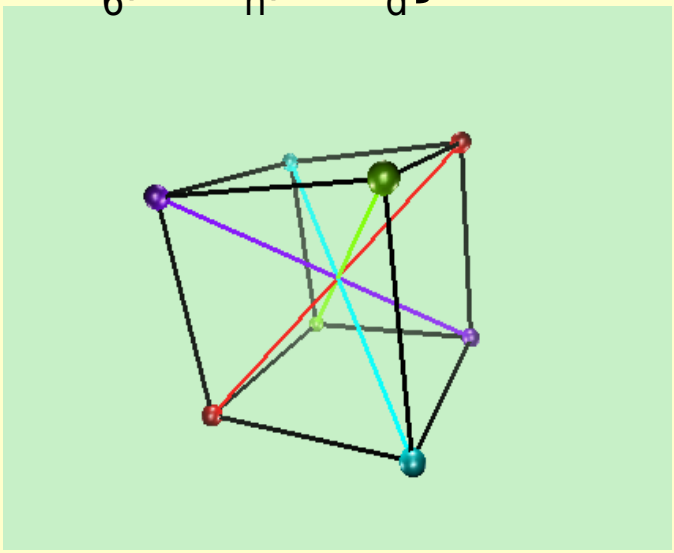
The Wulff polyhedron belongs to the same point group as its building blocks.

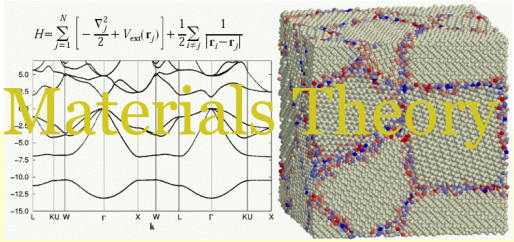
FCC: the most symmetric close-packed structure, found in most metals and several molecular crystals.

$O_h = \{E, 8C_3, 6C_2, 6C_4, 3C_4^2, I, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d\}$



(48 operations)

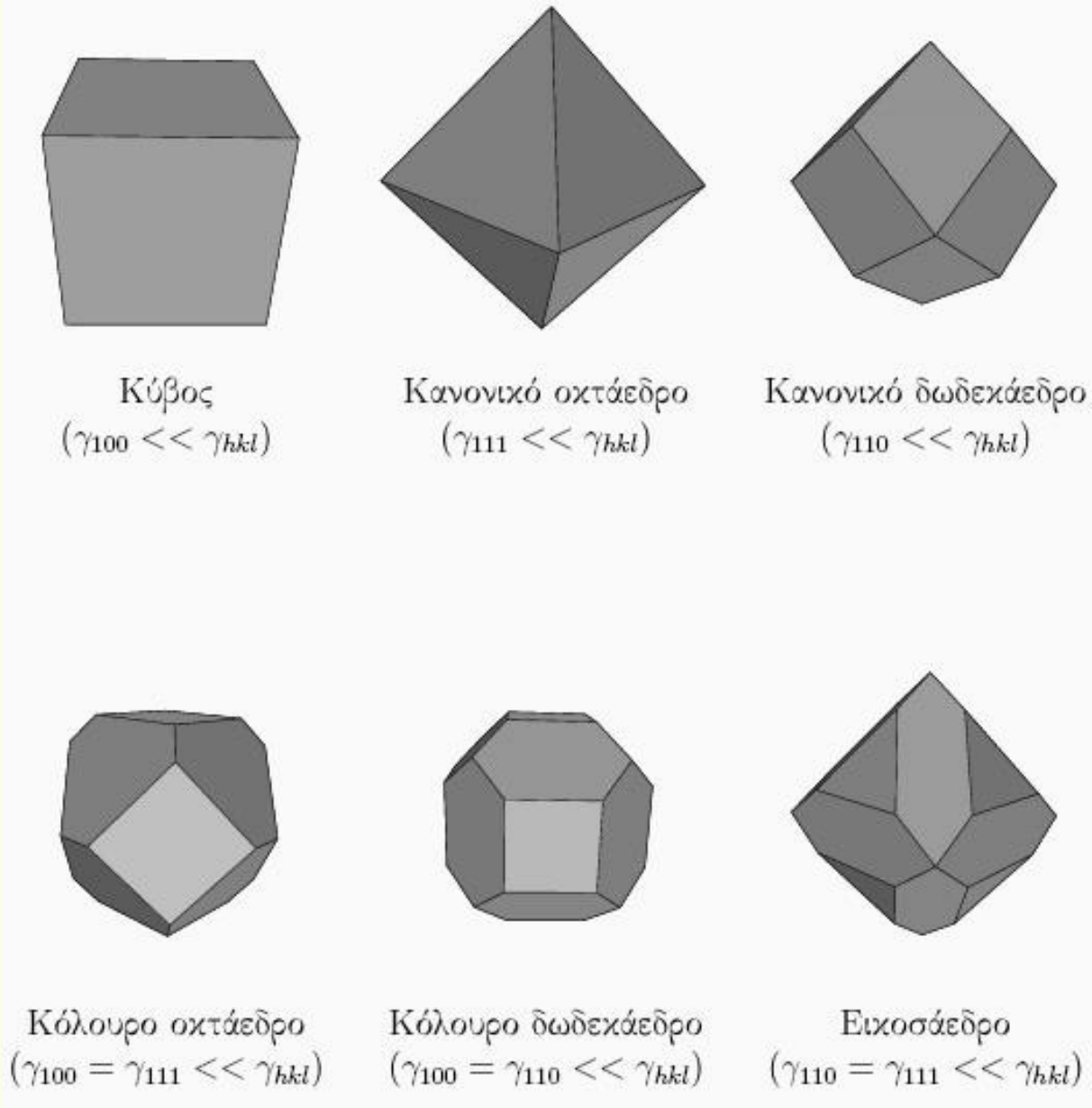


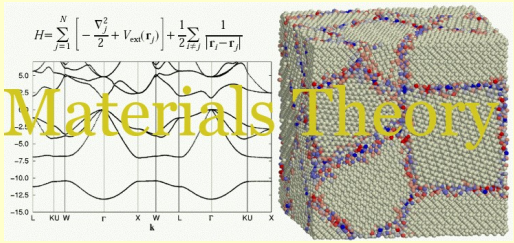


Examples of O_h polyhedra

- Symmetry is necessary (but not sufficient) condition that the system has reached equilibrium.

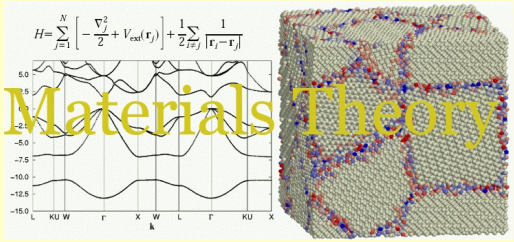
- A non symmetric (large) particle is most likely out of equilibrium.





Properties of equilibrium shape

- The shape depends on ratios between surface tensions.
- (*hkl*) planes with high surface tension (usually high-indexed ones) are less likely to appear in the equilibrium shape.
- Being steeper, high-index faces are usually hidden behind low-index ones, even if γ_{hkl} is low.
- The extra energy associated with the formation of edges between two surfaces is neglected.
- The Wulff polyhedron belongs to the same point group as the crystal structure of the material.



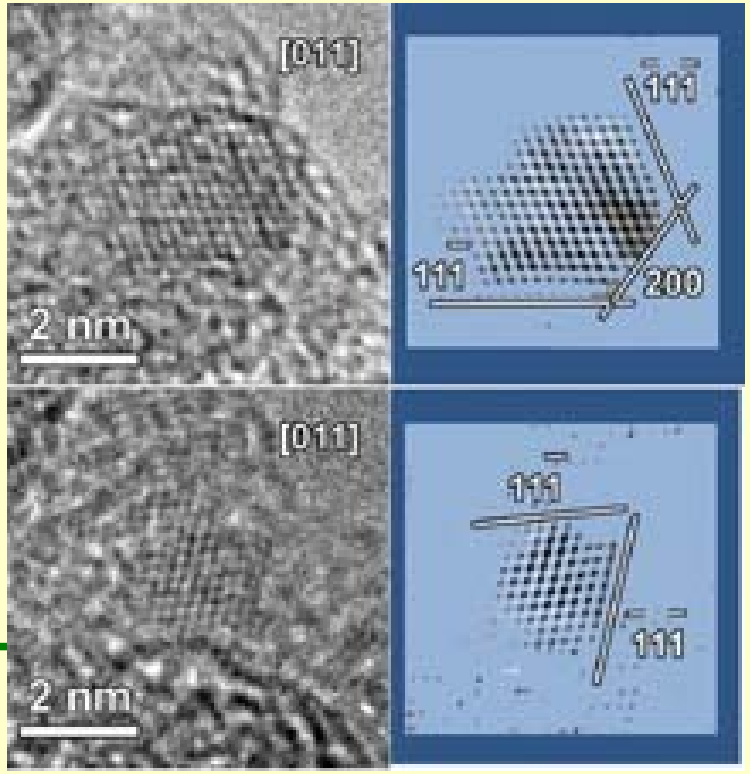
Equilibrium shapes in nature

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

Equilibrium shape: **minerals** (billions of years to equilibrate) or **nanoparticles** (small size).

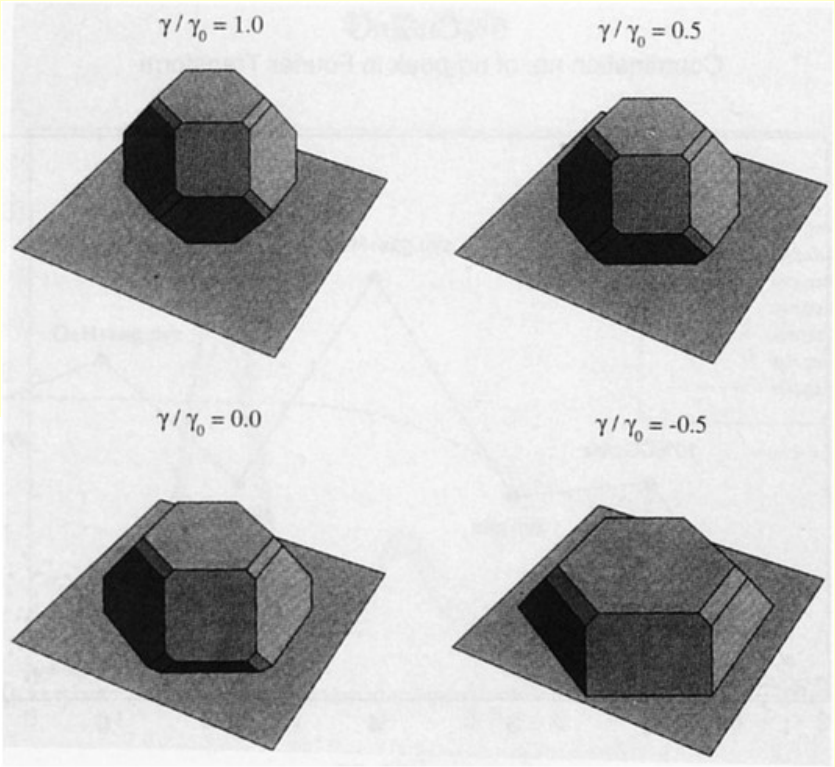
www.mindat.org

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



http://theory.materials.uoc.gr

Wulff's theorem and nanoparticles



Topics in Catalysis 1 (1994) 367–376

Wetting/non-wetting phenomena during catalysis: evidence from in situ on-line EXAFS studies of Cu-based catalysts

Bjerne S. Clausen [a], Jakob Schiøtz [b], Lars Gråbæk [a], Charlotte V. Ovesen [a], Karsten W. Jacobsen [b], Jens K. Nørskov [b] and Henrik Topsøe [a]

[a] *Haldor Topsøe Research Laboratories, DK-2800 Lyngby, Denmark*
[b] *Physics Department, Technical University of Denmark, DK-2800 Lyngby, Denmark.*

Wulff's theorem and nanoparticles

ELSEVIER

Surface Science 457 (2000) 229–253

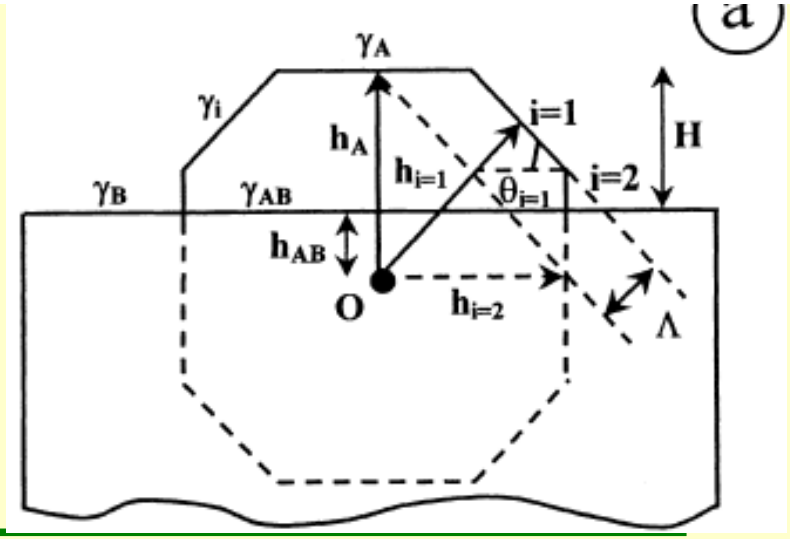
www.elsevier.nl/locate/susc

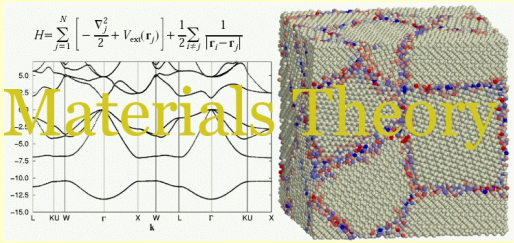
Equilibrium nano-shape changes induced by epitaxial stress (generalised Wulf–Kaishew theorem)

P. Müller *, R. Kern

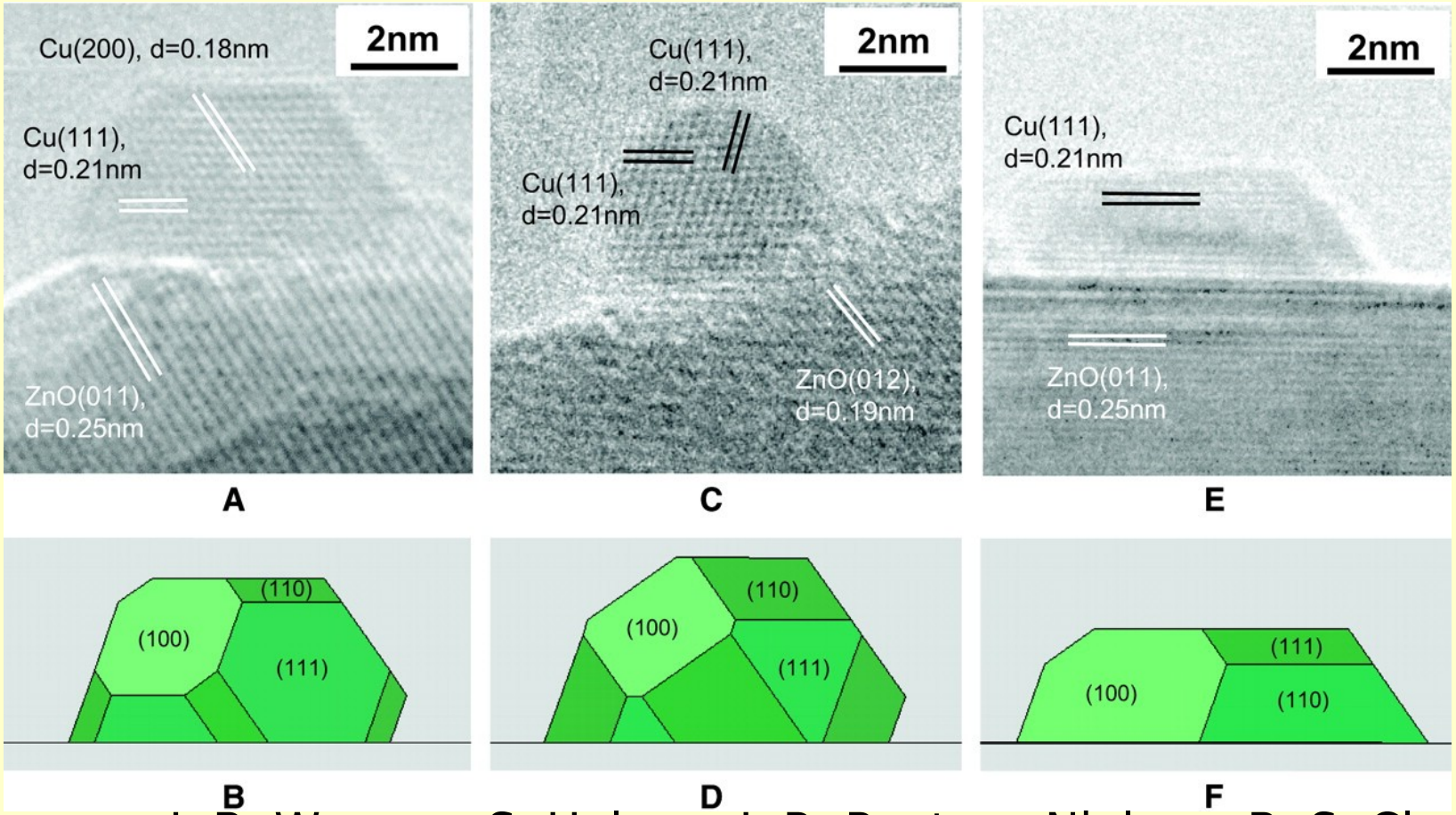
Centre de Recherche sur les Mécanismes de la Croissance Cristalline[1], CRMC2-CNRS, Campus de Luminy, case 913, F-13288 Marseille Cedex 9, France

Received 25 October 1999; accepted for publication 15 February 2000

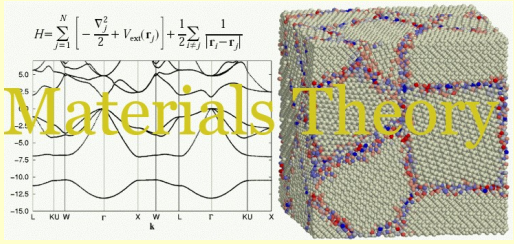




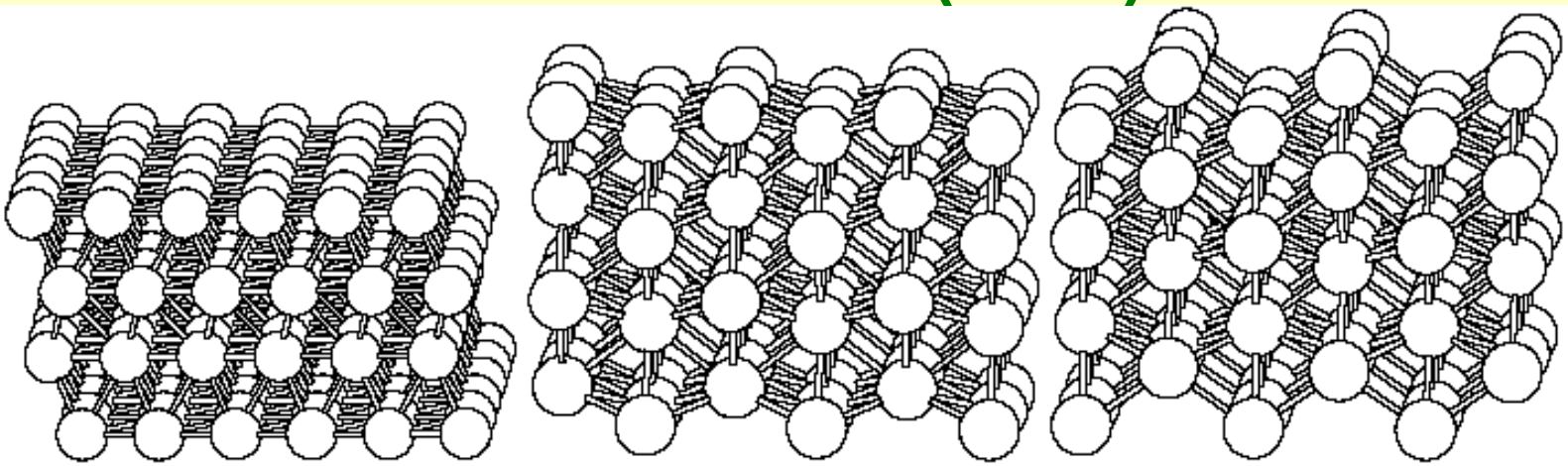
Wulff's theorem and nanoparticles



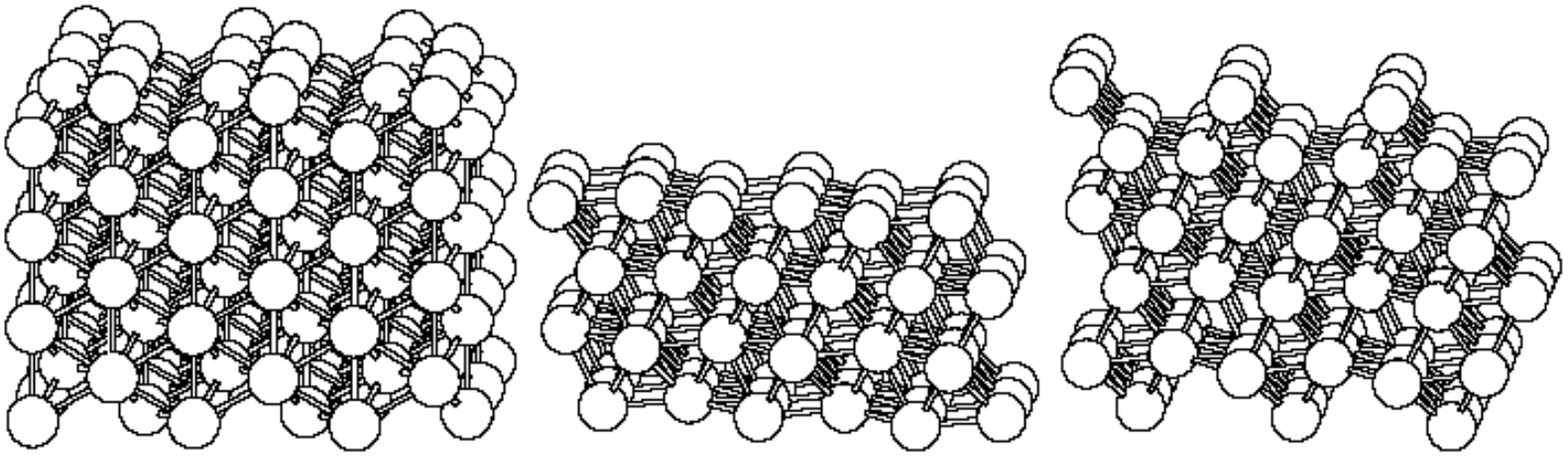
P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, H. Topsøe, *Atom-Resolved Imaging of Dynamic Shape Changes in Supported Copper Nanocrystals*, *Science* **295** 2053 (2002).



Surface tesion of Ru(hkl) from DFT

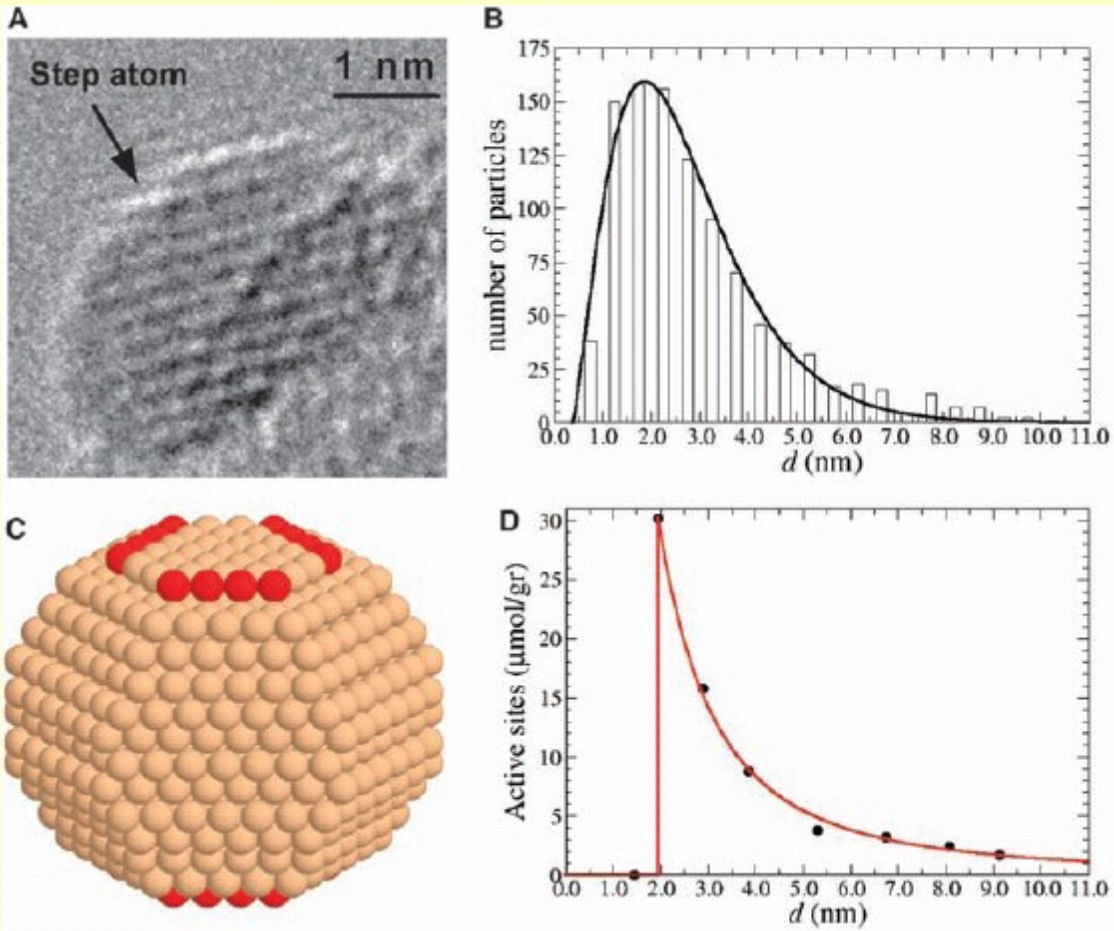


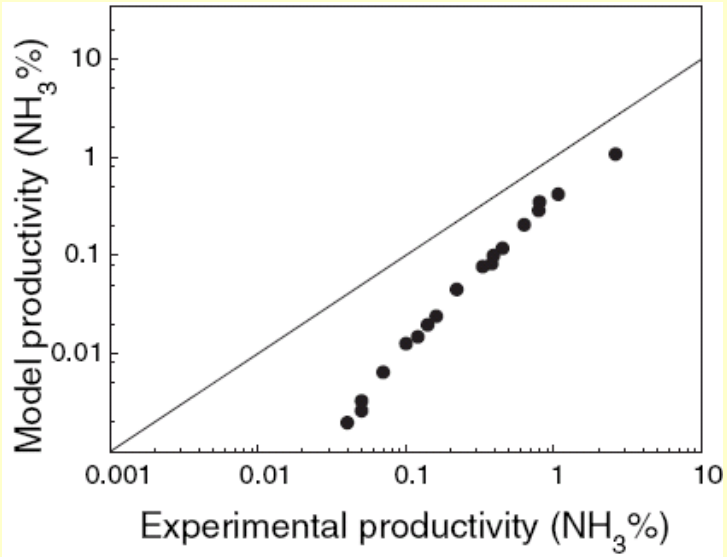
Ru(001); E_{surf}=2.76 J/m^2. Ru(100)$_A$; E_{surf}=3.07 J/m^2 Ru(100)$_B$; E_{surf}=3.71 J/m^2.



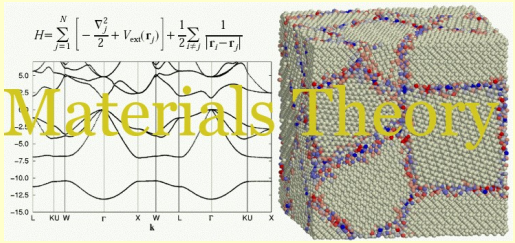
Ru(110); E_{surf}=3.45 J/m^2. Ru(101)$_A$; E_{surf}=3.15 J/m^2 Ru(101)$_B$; E_{surf}=3.63 J/m^2

Virtual catalyst for NH_3 synthesis

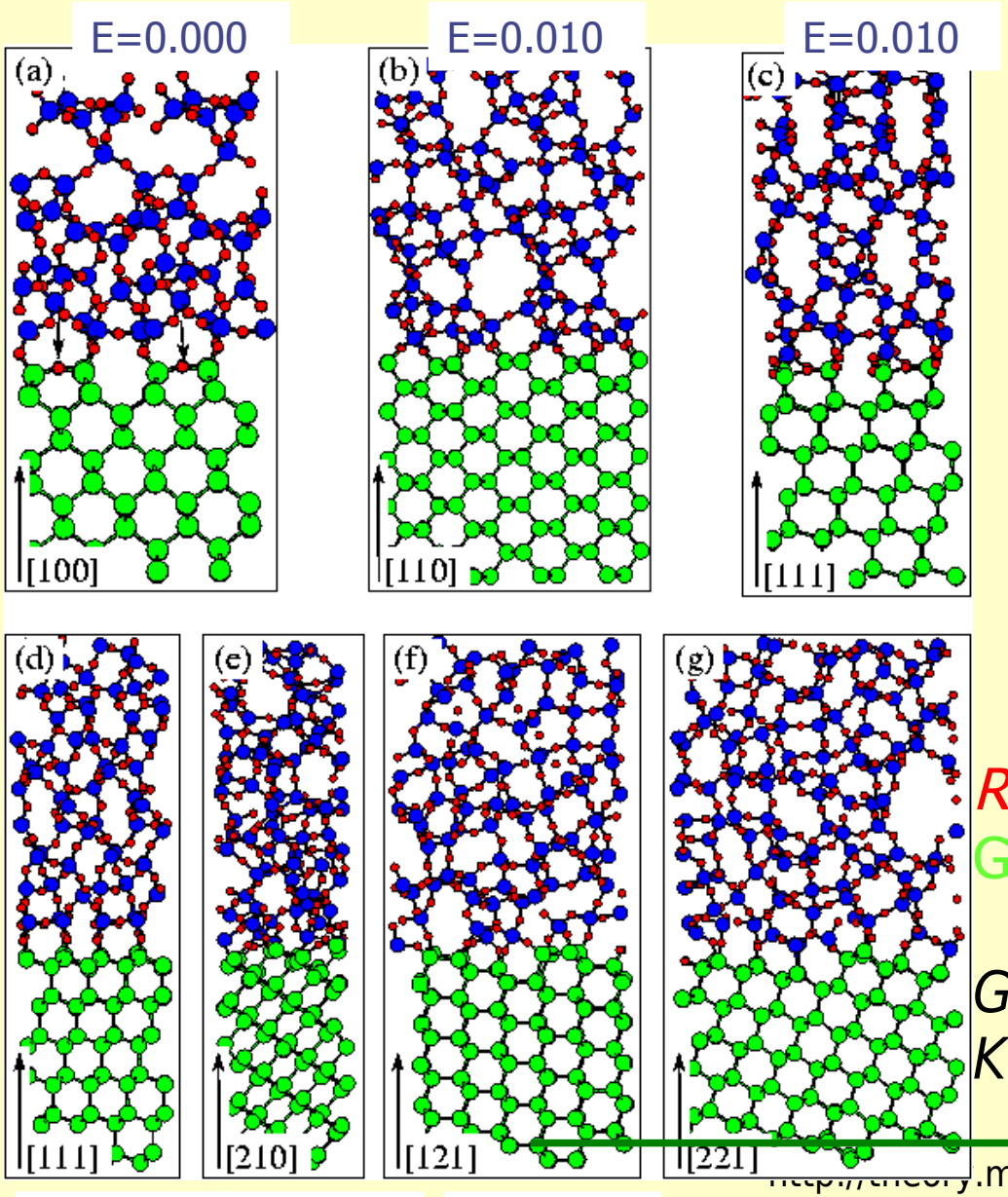


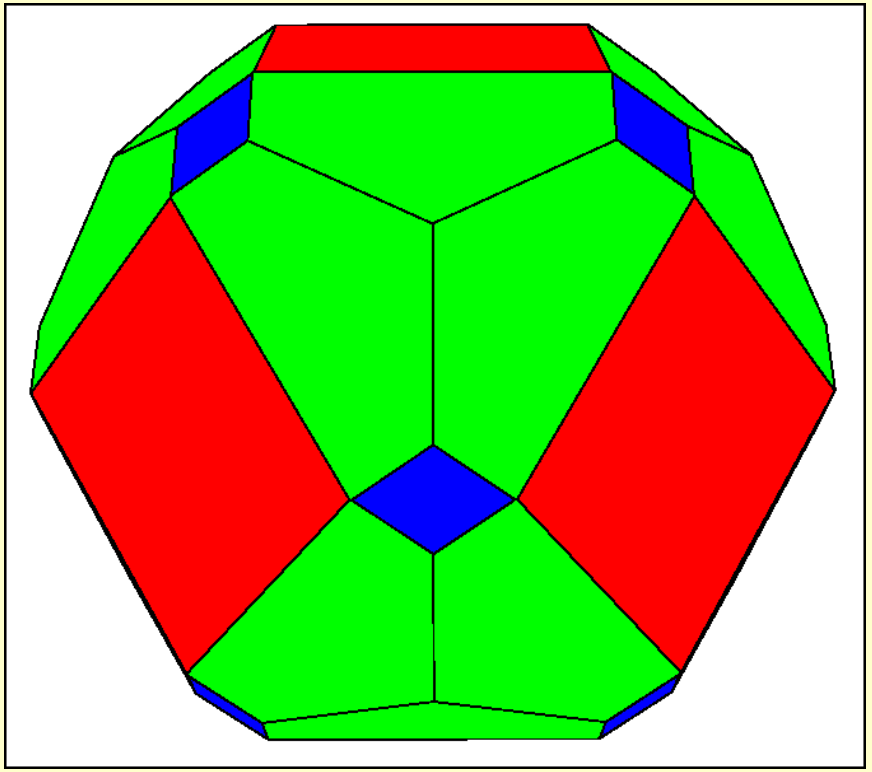


*K. Honkala, A. Hellman, I. N. Remediakis, A. Logadottir, A. Carlsson, S. Dahl, C.H. Christensen and J. K. Nørskov, Science, **307** 558 (2005); Surf. Sci., **600**, 4264 (2006); Surf. Sci., **603**, 1731 (2009).*



Si quantum dots in a-SiO_2

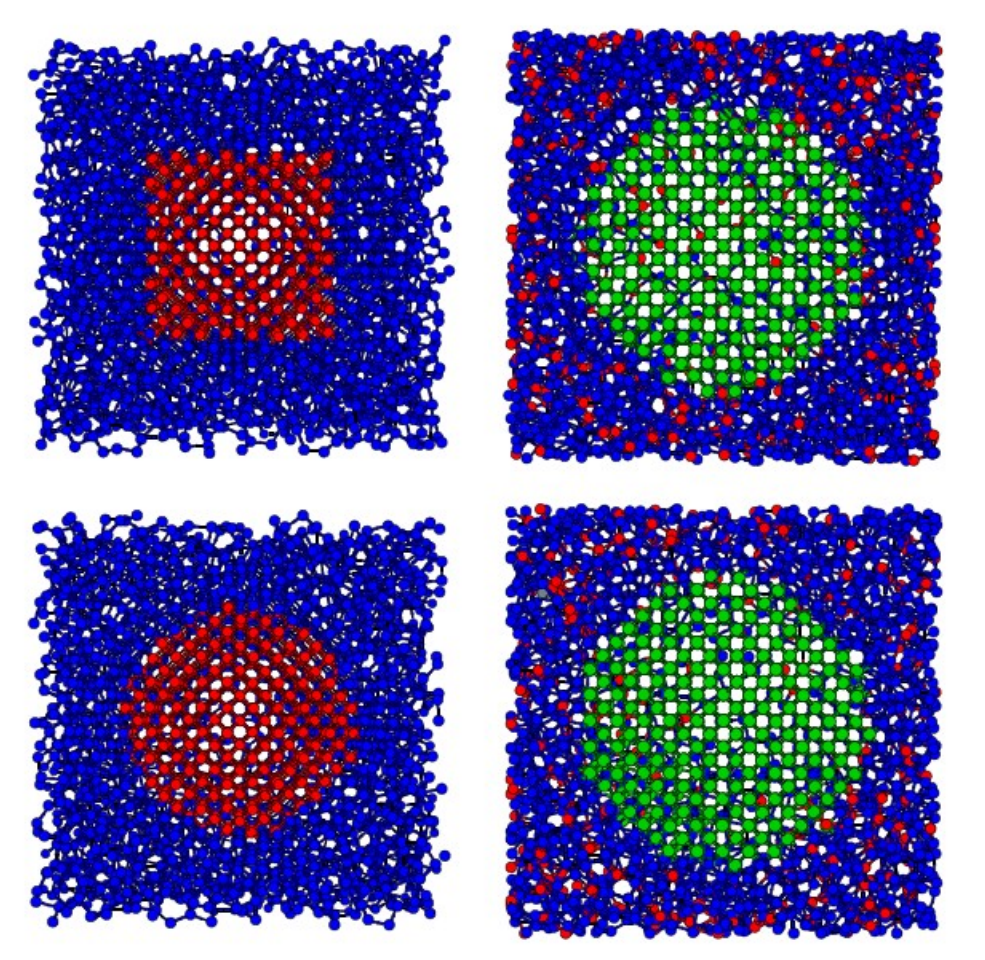




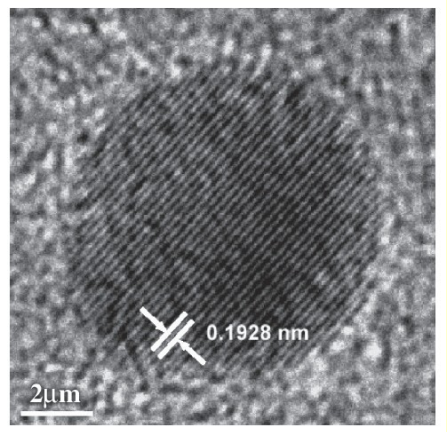
Red : {100} *Blue : {110}*
Green : {211}

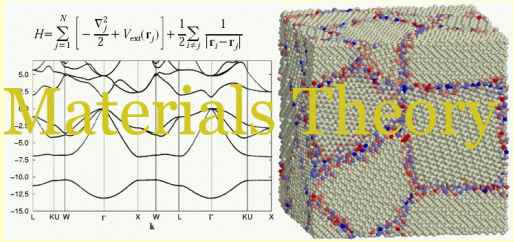
G. Hadjisavvas, I. N. Remediakis, P. C. Kelires, Phys. Rev. B ***74****, 165419 (2006).*

Shape of diamond nanocrystals in amorphous Carbon

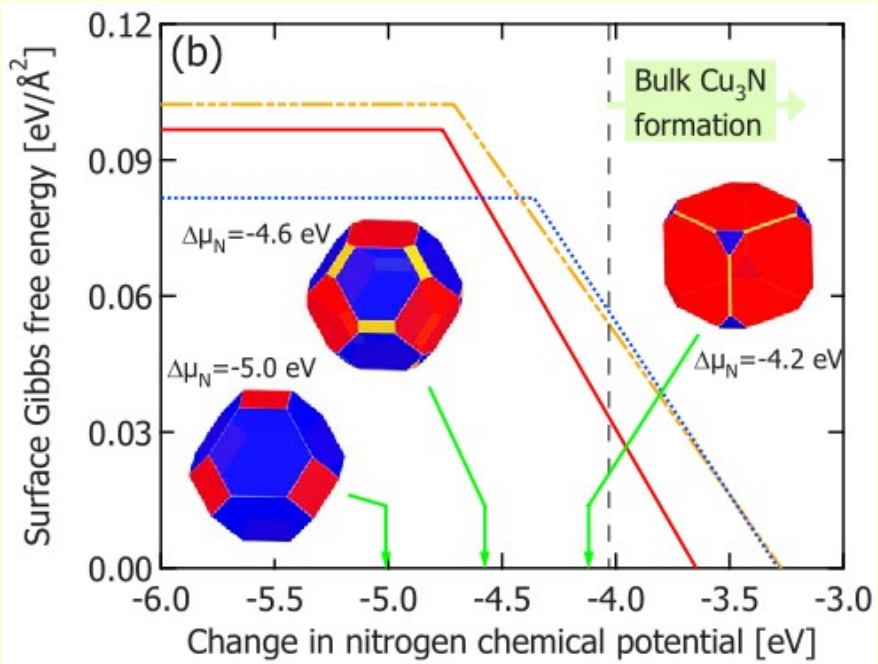


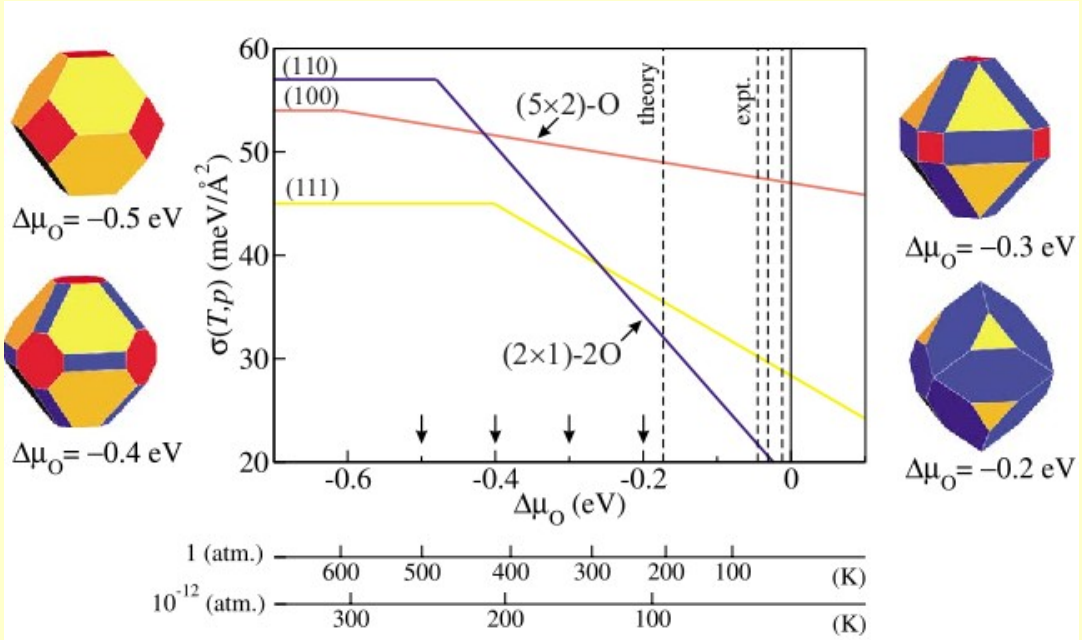
G. Kopidakis, I. N. Remediakis, M. G. Fyta and P. C. Kelires, Diam. Rel. Mater. ***16****, 1875 (2007).*





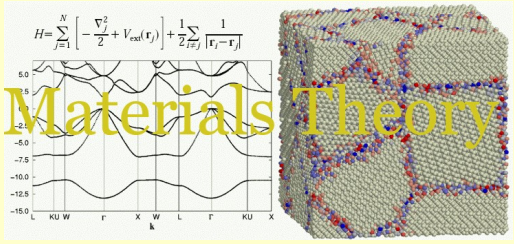
Cu (in N_2) and Au (in O_2)



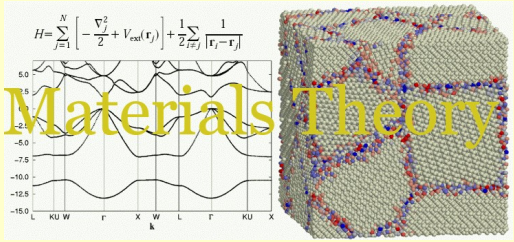


Left: *Morphology of copper nanoparticles in a nitrogen atmosphere: A first-principles investigation*, A. Soon, L. Wong, B. Delley, C. Stampfl, Phys. Rev. B **77**, 125423 (2008)

Right: *Shape and surface structure of gold nanoparticles under oxidizing conditions*, H. Shi and C. Stampfl, Phys. Rev. B **77**, 094127 (2008).



Au nanoparticles



Au nanoparticles

Catalysis, gas sensors, optoelectronics, bio-labeling, ...
Hybrid nanomaterials with unique properties.

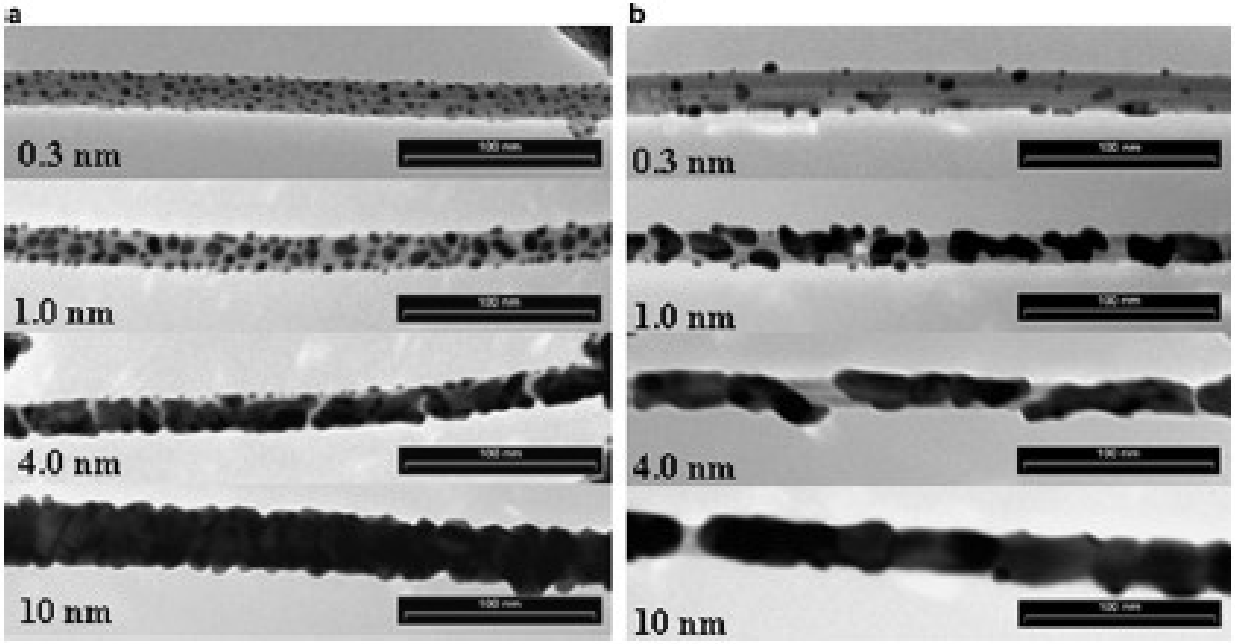
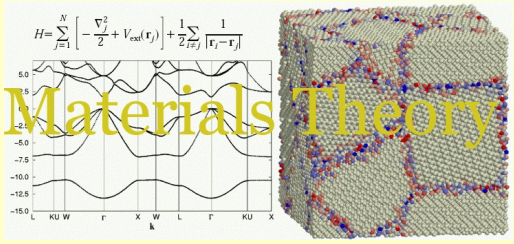
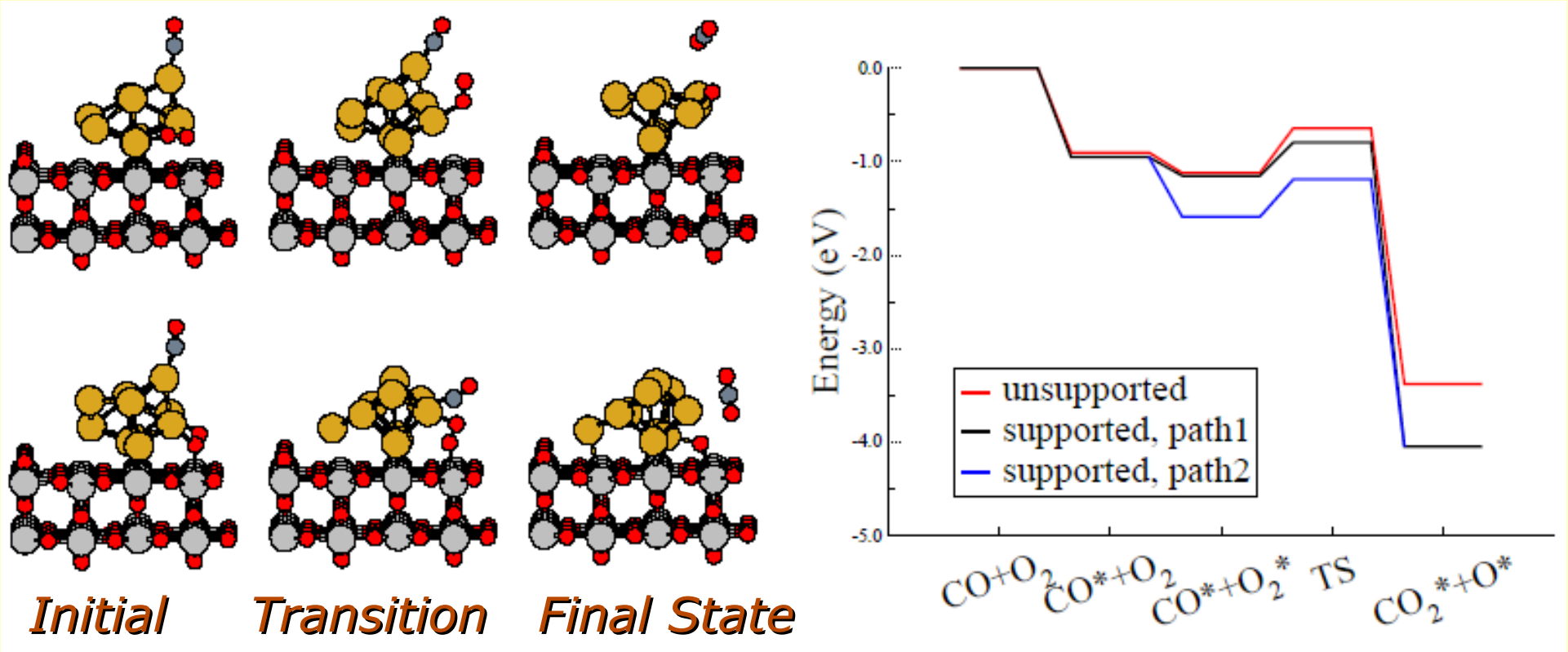


Fig. 4. TEM micrographs of different gold coating on MWCNTs (a) oxygen plasma-treated and (b) pristine.

Au@(C nanotubes): *C. Bittencourt et al., Chem. Phys. 328 (2006) 385.*



CO oxidation @ room T

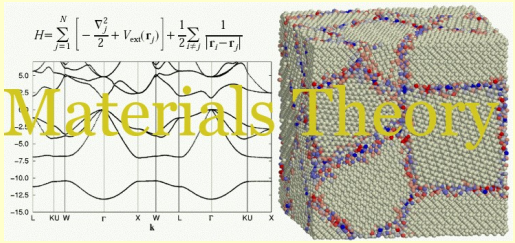


Gold-only (top) and Gold-oxide interface path (bottom).

CO oxidation barrier: 0.36-0.40 eV (calculation), 0.36 or 0.38 (experiment)

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

Appl. Catal. A ***291*** *13 (2005).*

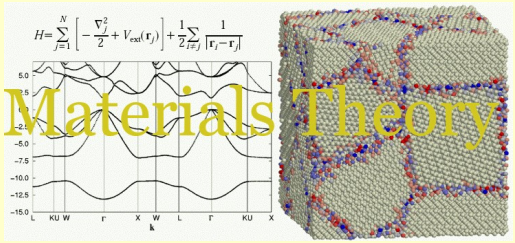


Equilibrium shape of Au nanoparticles from first principles

- Using Density Functional Theory, we calculate the surface tension of different Au surfaces.

- Using Wulff construction, we find nanoparticles with minimum energy.

- Novel approach: take into account interactions of nanoparticle with its environment.



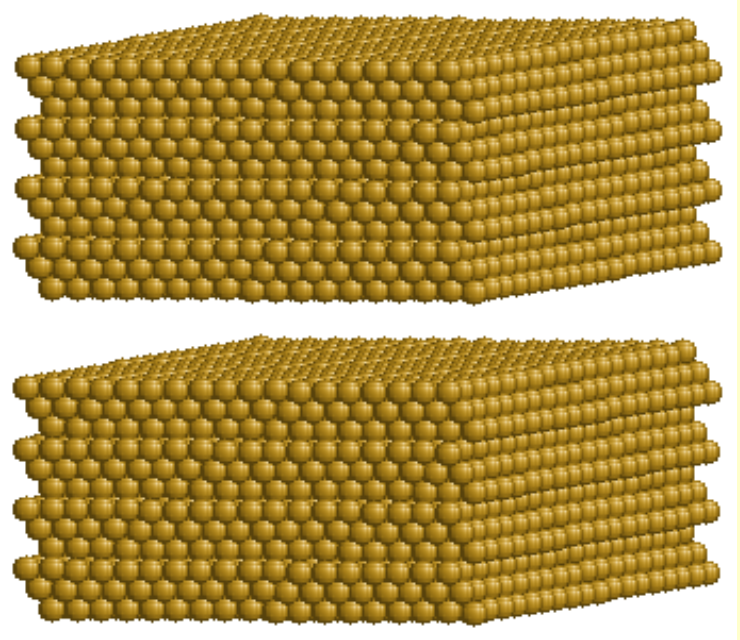
Modeling Au surfaces with DFT

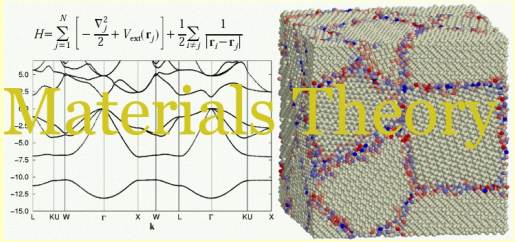
- Slab model.

- Parameters chosen for convergence of surface tension within 0.01 J/m^2.

- Calculate total energy of slab and bulk Au.

- $E_{slab} = N\,E_{bulk} + 2A\gamma$





Surface tensions, equilib. shapes

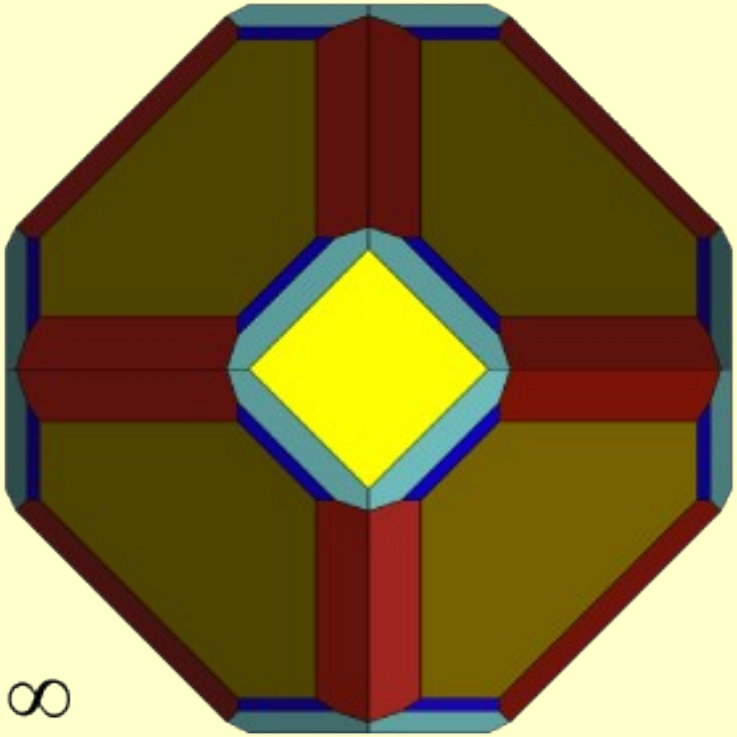
	This work	Other[a]	Other[b]
γ_{111} (J/m^2)	0.69	0.640	1.385
$\gamma_{100}/\gamma_{111}$	1.23	1.11	1.15
$\gamma_{110}/\gamma_{111}$	1.22	1.24	1.22
$\gamma_{210}/\gamma_{111}$	1.33	1.31	1.29
$\gamma_{211}/\gamma_{111}$	1.17	1.19	1.18
$\gamma_{221}/\gamma_{111}$	1.13	1.16	1.15
$\gamma_{310}/\gamma_{111}$	1.31	1.28	1.28
$\gamma_{311}/\gamma_{111}$	1.26	1.24	1.22
$\gamma_{320}/\gamma_{111}$	1.35	1.30	1.28
$\gamma_{321}/\gamma_{111}$	1.25	1.26	1.23
$\gamma_{322}/\gamma_{111}$	1.11	1.13	1.12
$\gamma_{331}/\gamma_{111}$	1.18	1.21	1.19
$\gamma_{332}/\gamma_{111}$	1.07	1.11	1.11
$\gamma_{410}/\gamma_{111}$	1.32	1.25	1.26
$\gamma_{411}/\gamma_{111}$	1.27	1.23	1.22
$\gamma_{421}/\gamma_{111}$	1.32	1.29	1.26
$\gamma_{430}/\gamma_{111}$	1.34	1.29	1.27
$\gamma_{431}/\gamma_{111}$	1.27	1.27	1.25
$\gamma_{432}/\gamma_{111}$	1.19	1.20	1.18
$\gamma_{433}/\gamma_{111}$	1.09	1.09	1.09
$\gamma_{441}/\gamma_{111}$	1.22	1.22	1.21
$\gamma_{443}/\gamma_{111}$	1.06	1.09	1.08

$\gamma_{hkl} \sim N_{hkl}$; $N_{hkl}=2h+k$ or $4h+2k$.

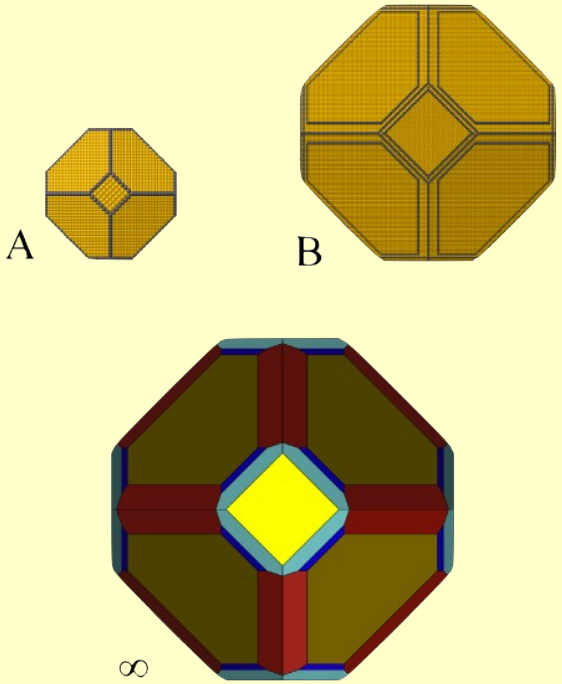
(Mackenzie et al., J. Phys. Chem. Solids (1962))

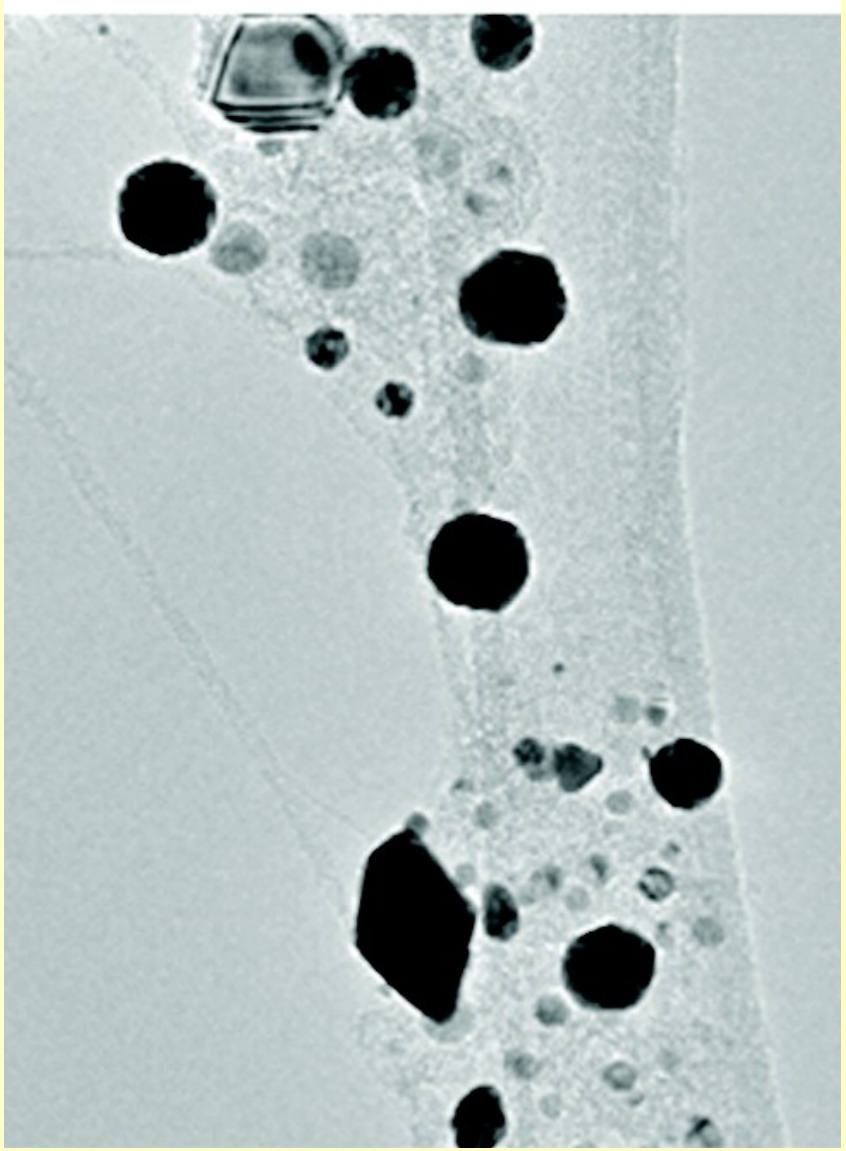
[a]: *MAEAM, Wen & Zhang, (2007);*

[b]: *LMTO+Mckenzie, Galanakis et al. (2002).*



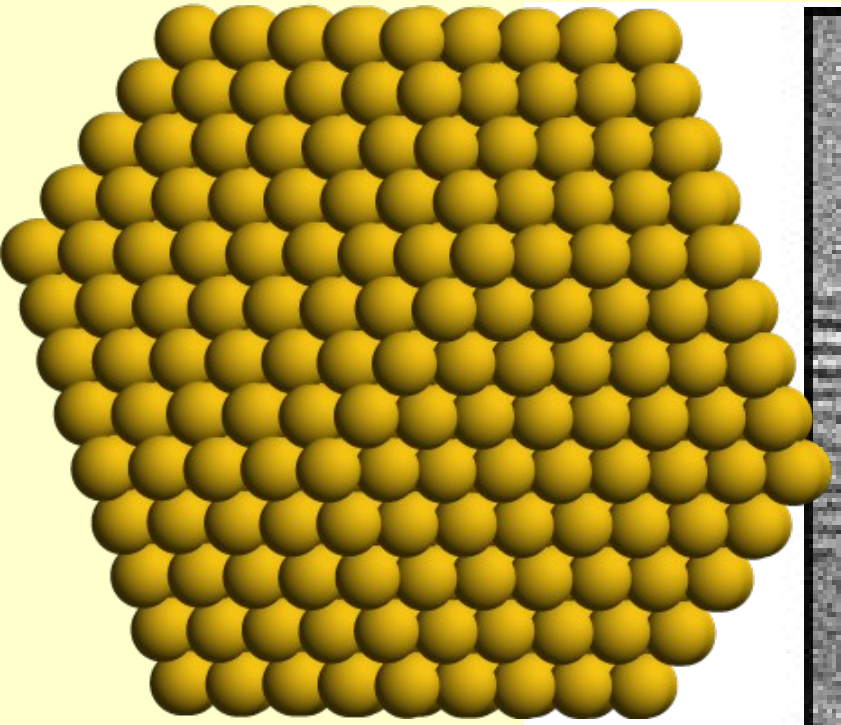
Equilibrium shapes





Quintana et al., ACS nano 4 (2010) 6105

Equilibrium shapes



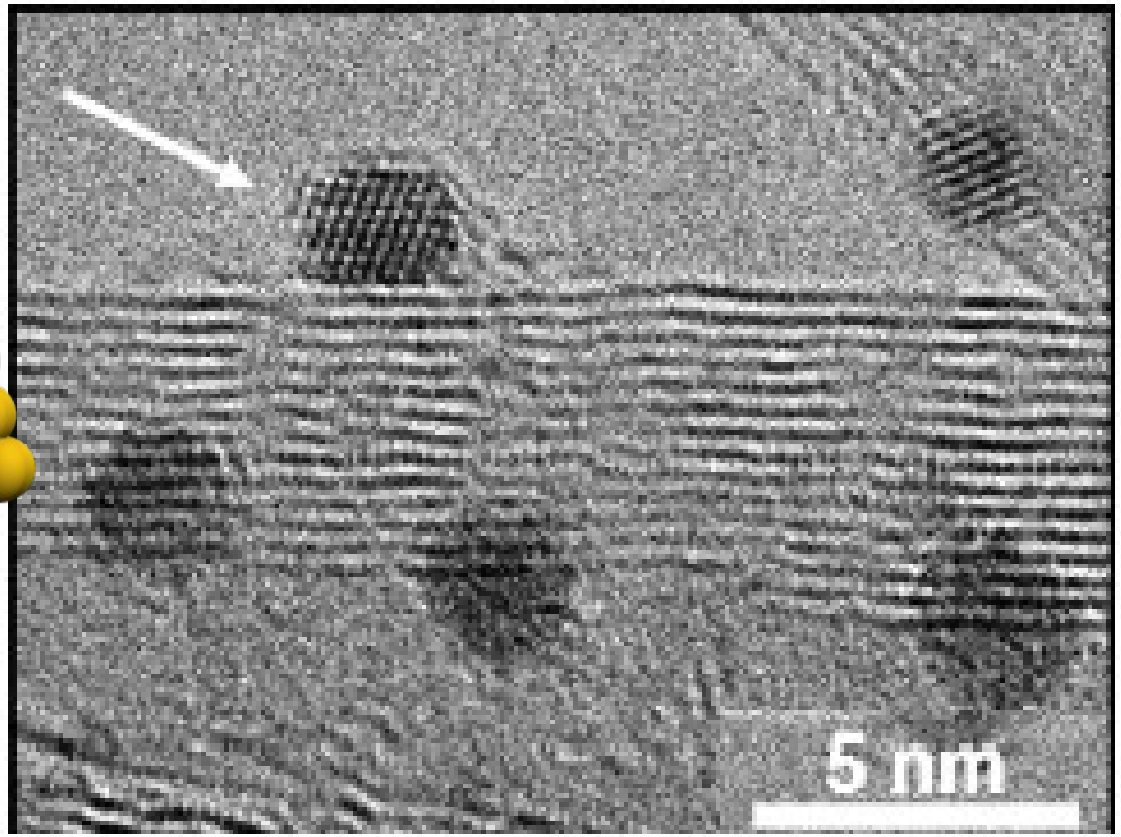
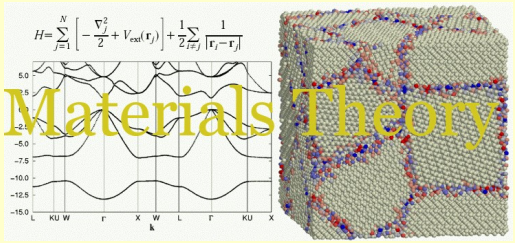
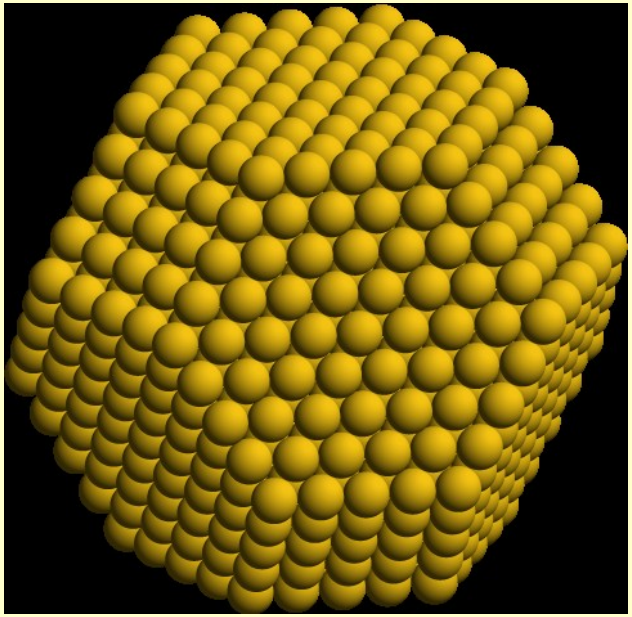


Fig. 2. HREM image of gold coating on oxygen plasma treated arc-discharge MWCNTs. The gold particles formed at the tube surface present a strong tendency for epitaxial relationship between the graphene layers and the (111) planes of gold.

Bittencourt et al., Surf Sci. 601 (2007) 2800



Equilibrium shapes



- Predicted nanoparticles match observations even at small sizes.

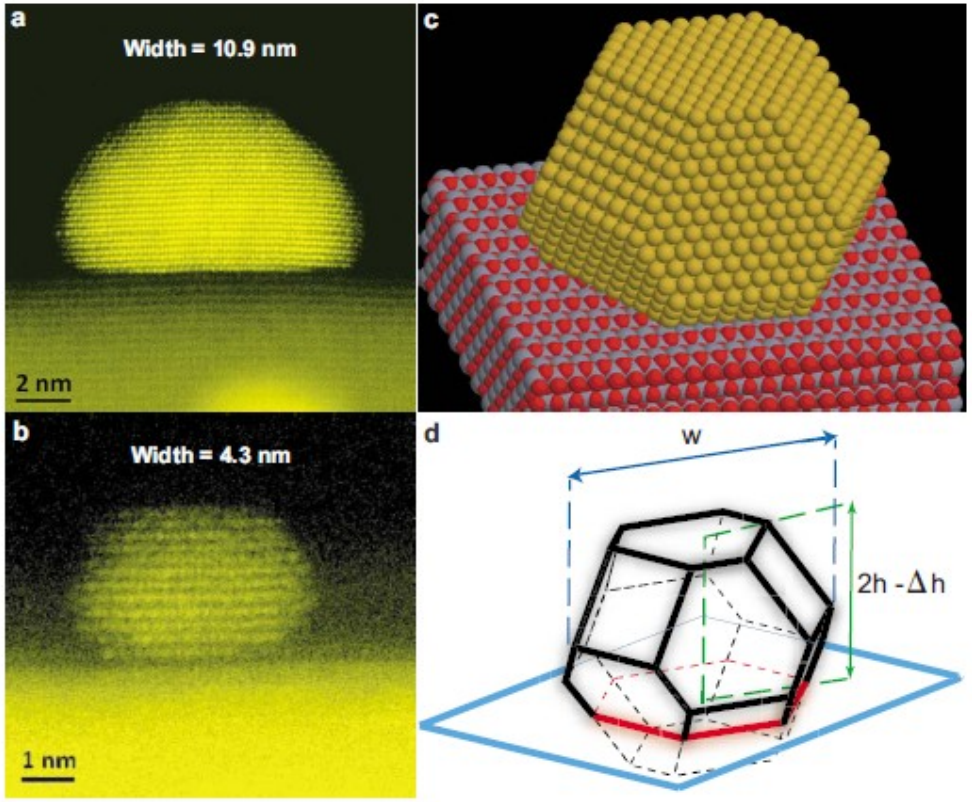


FIG. 3. (Color online) (a) 10.9 nm Au NC, (b) 4.3 nm Au NC, (c) model of Au NC, and (d) schematic of Au NC shape showing measurements of NC dimensions.

PHYSICAL REVIEW B **82**, 195421 (2010)

Equilibrium shapes and triple line energy of epitaxial gold nanocrystals supported on TiO_2(110)

Shankar Sivaramakrishnan,[1,2,*] Jianguo Wen,[2] Michael. E. Scarpelli,[1,2] Benjamin J. Pierce,[1,2] and Jian-Min Zuo[1,2]
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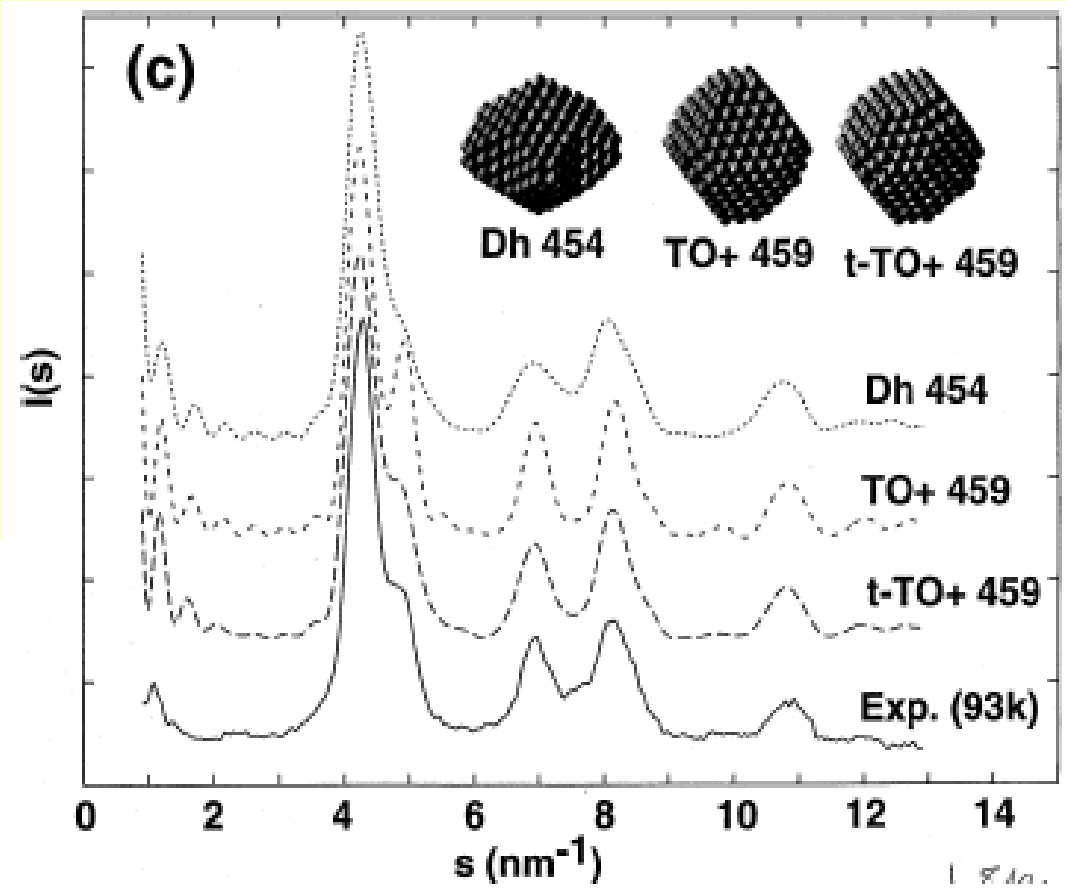
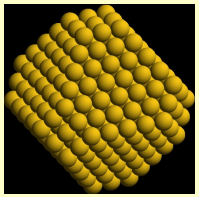
[2]*Frederick Seitz Materials Research Laboratory, University of Illinois–Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801, USA*

Equilibrium shapes

- Predicted nanoparticles match observations even at really small sizes. (459 atoms, 2.5 nm)





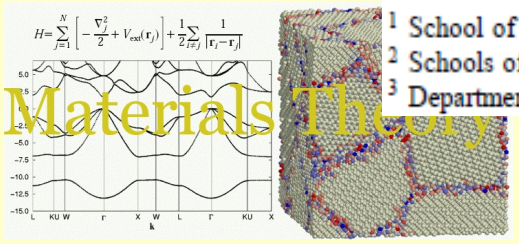
Z. Phys. D 40, 503–508 (1997)

ZEITSCHRIFT FÜR PHYSIK D

Structural evolution of larger gold clusters

Charles L. Cleveland[1], Uzi Landman[1], Marat N. Shafigullin[2], Peter W. Stephens[3], Robert L. Whetten[2]

[1] School of Physics & Center for Computational Materials Science, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA
[2] Schools of Physics & Chemistry, and Microelectronics, Research Center, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA
[3] Department of Physics, State University of New York, Stony Brook, NY 11794, USA



Simple formula for interfacial tension

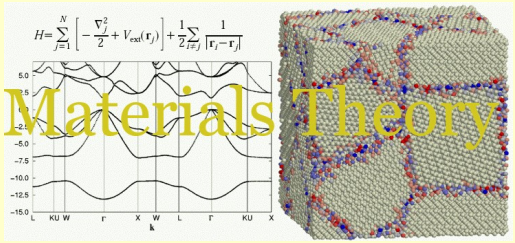
- When nanoparticles form in a reactive environment, some molecules may attach to gold surfaces, lowering thus the surface tension.

- For a slab of Au within a reservoir of molecules a:

$$E_{tot}=N_{Au}E_{Au}+N_aE_a+2\gamma_{int}A$$

- $E_{ads}=E(slab+a)-E(clean\ slab)-E_a$ after some math:

$$\gamma_{int}=\gamma+N_{ads}E_{ads}/A$$



Environment-dependent shape

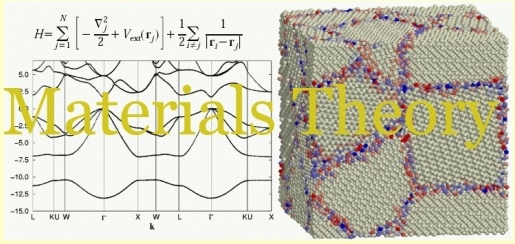
- $\gamma_{int}=\gamma+N_{ads}E_{ads}/A$

- γ_{int} is very close to γ for weak interaction (low E_{ads}) or low concentration (N_{ads}/A).

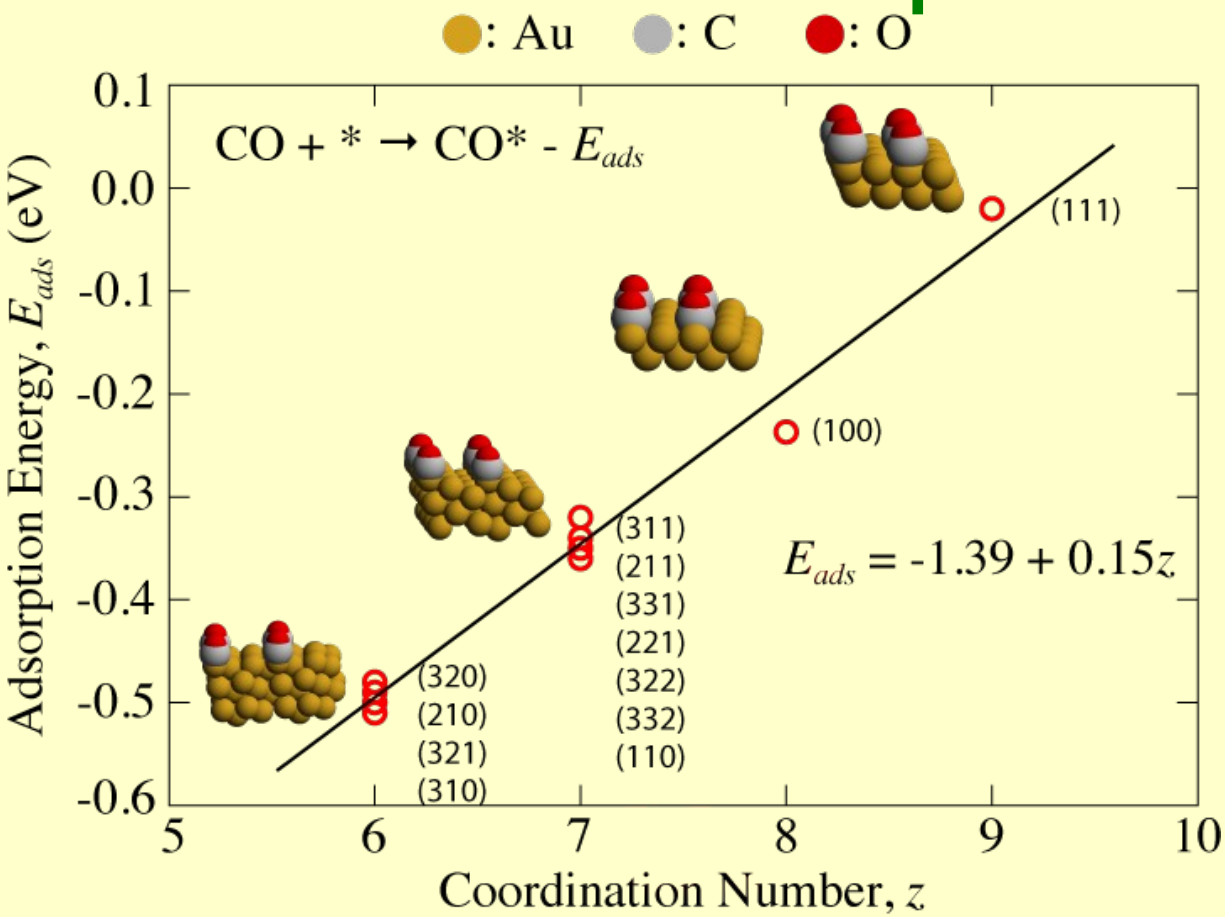
- As a result, the equilibrium shape of nanoparticles in most cases is similar to the equilibrium shape in vacuum.

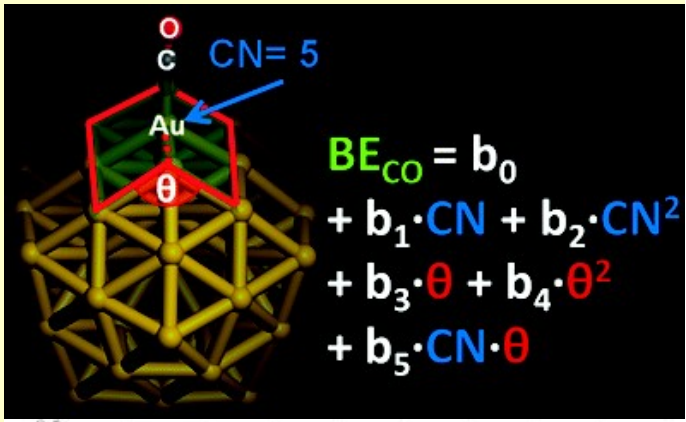
- Exception: very strong bindind AND high concentration.

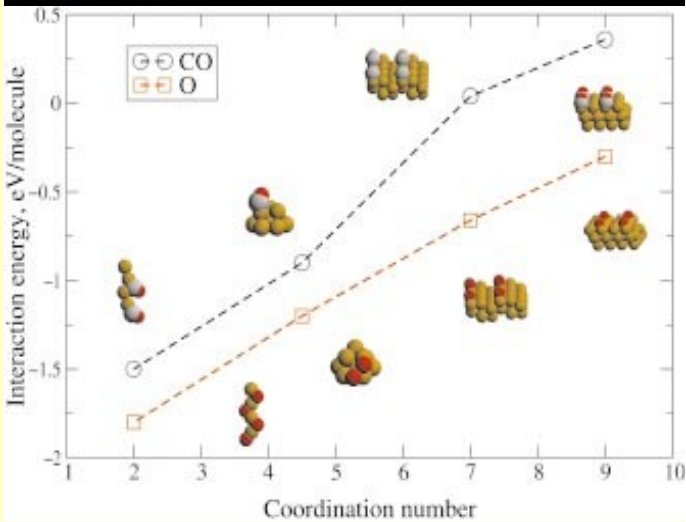
- Case study: CO.



CO Adsorption on Au







The first calculation of CO on every Au(hkl).

Barmparis and INR, PRB 2012.

G. Mpourmpakis, A. N. Andriotis, D. G. Vlachos, Nano Lett. ***10,*** *1041 (2010) ; S. R. Bahn, N. Lopez, J. K. Nørskov, and K. W. Jacobsen, Phys. Rev. B* ***66****, 081405 (2002)*

Au nanoparticles in CO gas

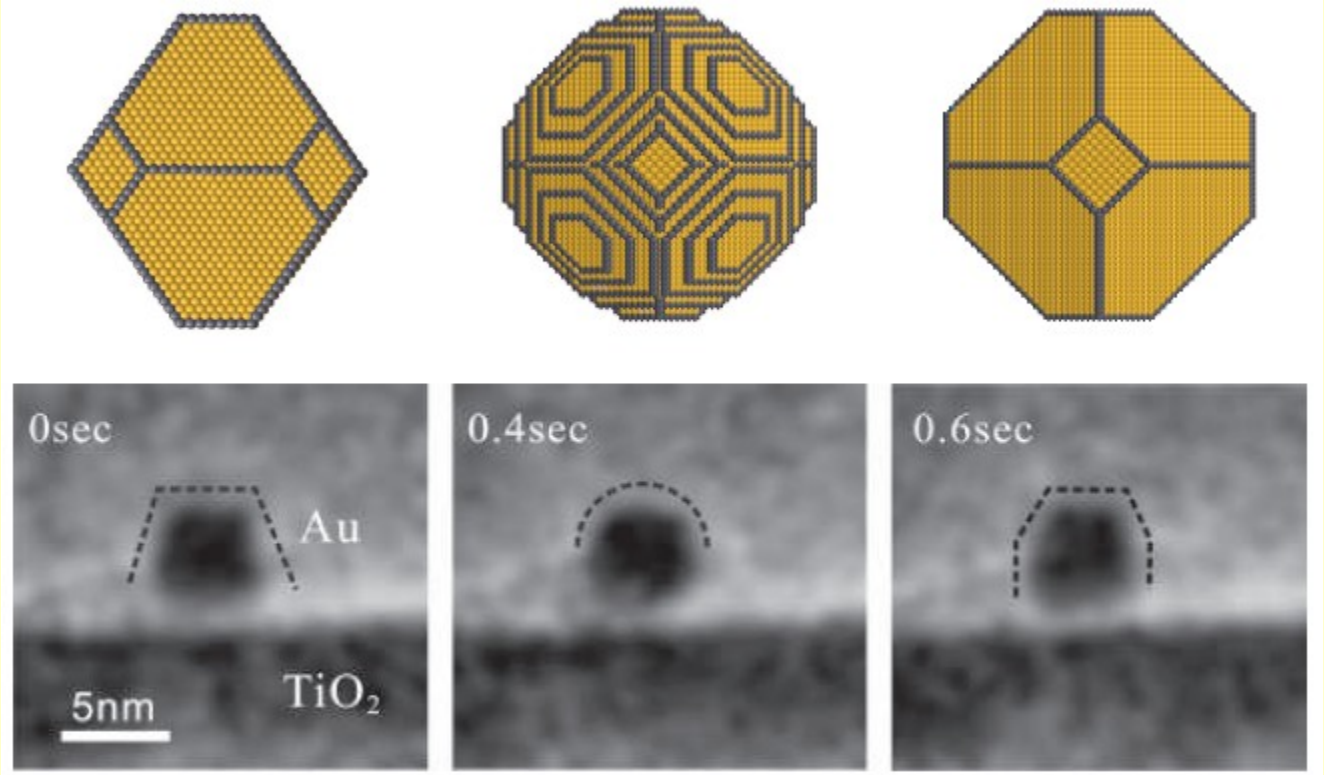
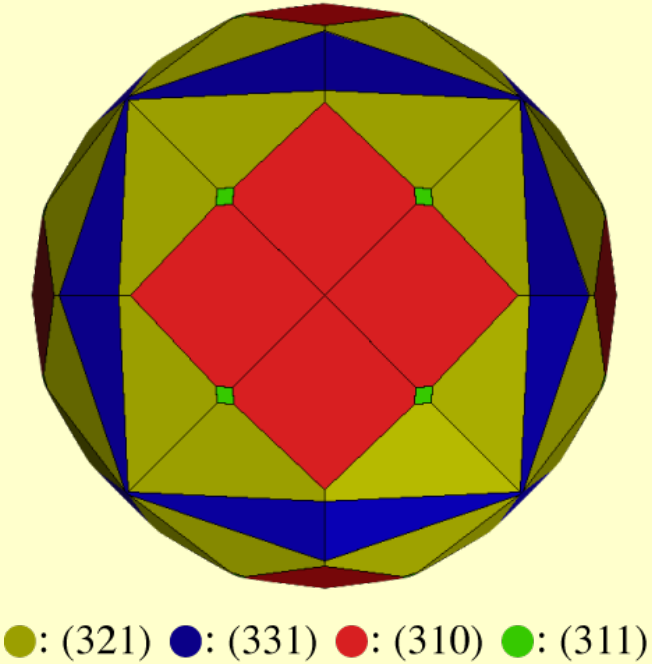
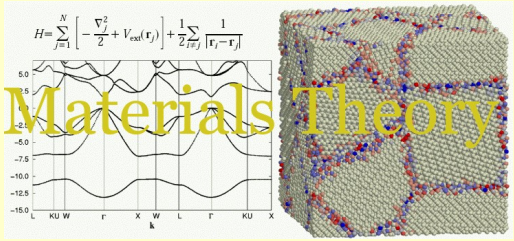


Figure 3. Shape change of gold nano-particles during oxidation (surrounding gas is CO (1%) in dry air at about 1180 Pa).



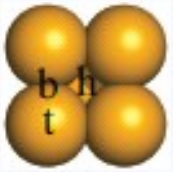
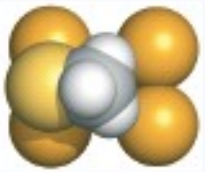
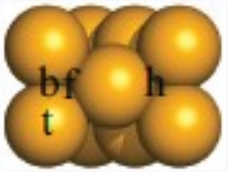
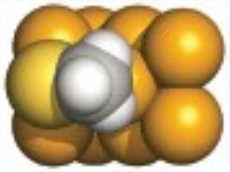
$$\gamma_{int}=\gamma+\theta E_{ads}/A_{at}$$

TEM by K. Ueda, T. Kawasaki, H. Hasegawa, T. Tanji and M. Ichihashi, Surf. Interf. Anal. ***40****, 1725 (2008).*



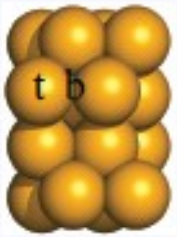
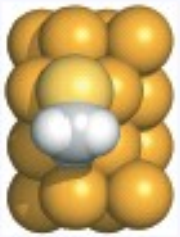
CH_3S- on Au(hkl)

Planar surfaces.

Surface	Microfacet notation	A	z	Configuration	E_{ads} (eV)	d_{Au-S} (Å)	d_{S-C} (Å)	Adsorption Sites	Relaxed configuration
100	-	35.62	8.0	b-t-t	-0.57	79.7	1.85		
				b-t-a	-0.52	2.47	1.85		
				h-t-p	-0.20	2.67	1.86		
				t-t-a	0.06	2.39	1.84		
110	-	37.78	7.0	b-t-a	-0.71	2.46	1.85		
		50.37		b-t-a	-0.709	2.45	1.85		
		50.37		b-t-t	-0.708	2.44	1.84		
		50.37		t-t-t	-0.23	2.35	1.84		
111	-	30.85	9.0	b-t-a	-0.153	2.52	1.85		
				b-t-t	-0.146	2.52	1.85		
				t-t-t	0.12	2.40	1.83		
				h-t-p	0.13	2.61	1.87		

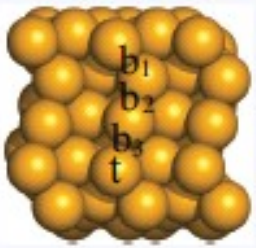
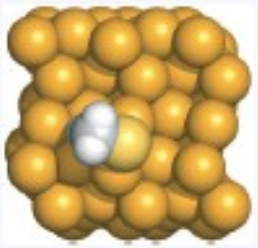
CH_3S- on Au(hkl)

Stepped n(100)x(111) surfaces.

Surface	Microfacet notation	A	z	Configuration	E_{ads} (eV)	d_{Au-S} (Å)	d_{S-C} (Å)	Adsorption Sites	Relaxed configuration
311	2(100)x(111) or 2(111)x(100)	59.06	7.0	b-l-t	-0.75	2.43	1.84		
				b-l-a	-0.71	2.43	1.85		
211	3(111)x(100)	43.62	7.0	b-l-t	-0.75	2.44	1.84		
		43.62		b-l-a	-0.73	2.43	1.85		
		43.62		b-u-t	-0.72	2.44	1.85		
		43.62		t-l-a	-0.19	2.37	1.84		
		87.24		b-l-t	-0.81	2.45	1.84		
322	5(111)x(100)	73.43	7.0	b-l-t	-0.79	2.43	1.84		
				t-l-t	-0.17	2.35	1.84		

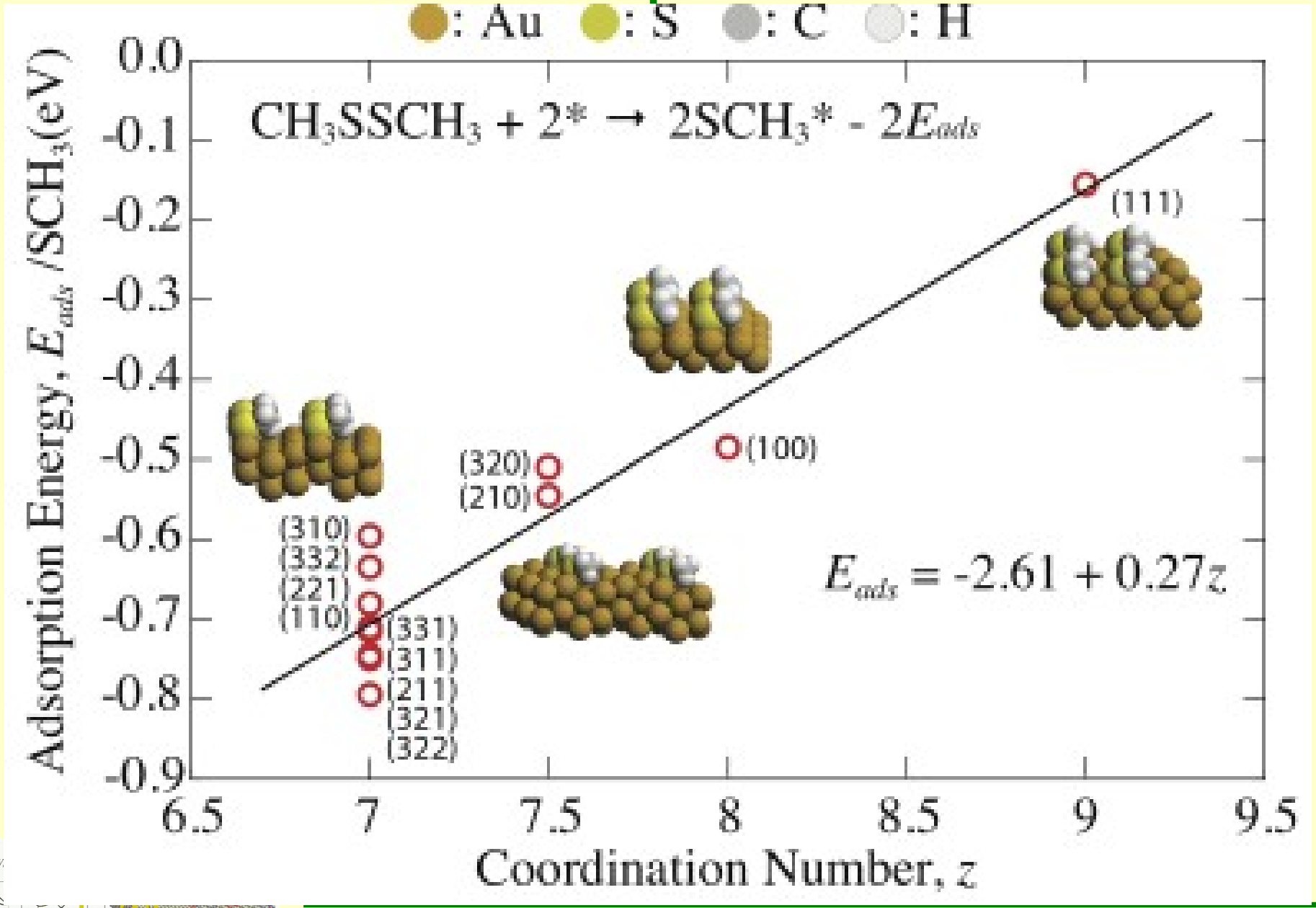
CH_3S- on Au(hkl)

Kinked surfaces.

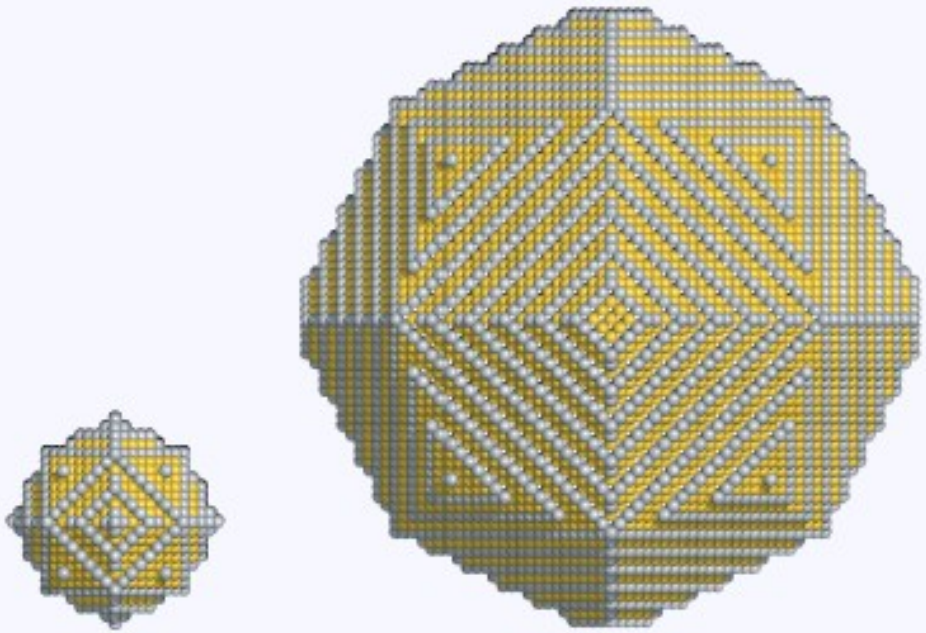
Surface	Microfacet notation	A	z	Configuration	E_{ads} (eV)	d_{Au-S} (Å)	d_{S-C} (Å)	Adsorption Sites	Relaxed configuration
321	-	99.95	7.0	b2-l-t	-0.75	2.45	1.84		
			7.0	b1-l-t	-0.66	2.47	1.84		
			6.0	t-l-t	-0.32	2.34	1.85		
421	-	81.61	6.5	b3-l-t	-0.79	2.44	1.84		
			7.0	b1-l-t	-0.65	2.47	1.84		

Barmparis, Honkala, Remediakis, submitted to J. Chem. Phys.

Thiol adsorption on Au



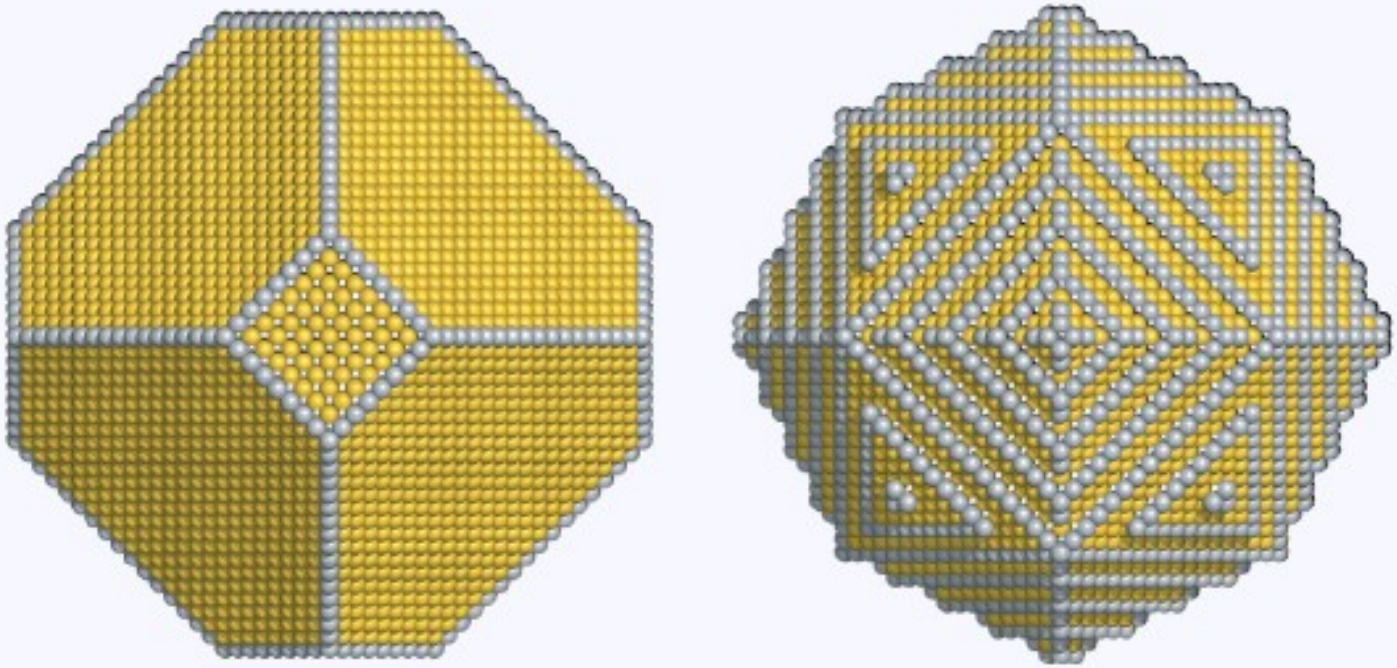
Thiol-protected Au nanoparticles



Atomistic Wulff construction for thiolate-covered gold nanoparticles at 5.0 and 14.2 nm respectively.

Wulff construction for thiolate-covered gold nanoparticle.
Sphericity: 95%

Adsorption increases reactivity.

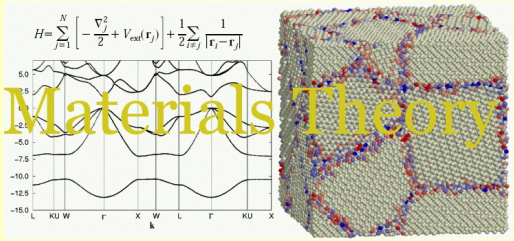


Left: Model of a typical Au nanoparticle (d ~10 nm, ca. 22750 atoms) in non-interacting environment (sphericity = 89%, N_{act} =78 μmol/g)
Right: a same size thiolate-protected gold nanoparticle (sphericity = 95%, N_{act} = 299 μmol/g)

Barmparis, Honkala, Remediakis, submitted to J. Chem. Phys.

Spectroscopic signature of nanoparticles

- The nanoparticle shape affects the electronic structure.
- As a first step, we consider a free electron inside a nanoparticle.
- Cube: $$E_{n1n2n3} = \frac{\hbar^2 \pi^2 (n_1^2 + n_2^2 + n_3^2)}{2 m a^2}$$
- Sphere: $$E_{nlm} = \frac{\hbar^2 x_{nl}^2}{2 m r^2}$$



Can one measure the shape of a nanoparticle?

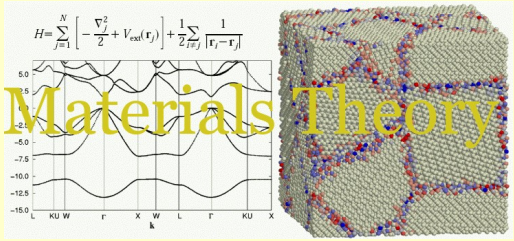
CAN ONE HEAR THE SHAPE OF A DRUM?

MARK KAC, The Rockefeller University, New York

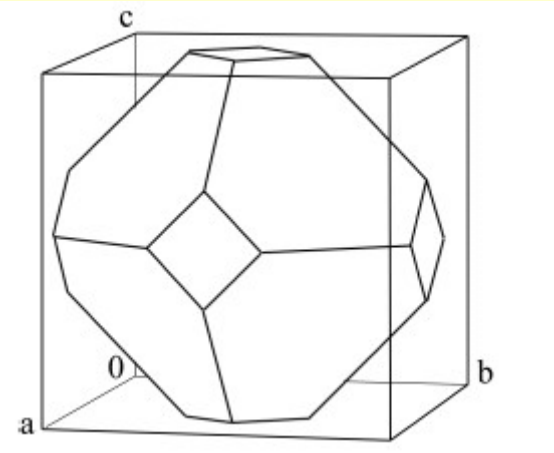
To George Eugene Uhlenbeck on the occasion of his sixty-fifth birthday

3. Before I go any further let me say that as far as I know the problem is still unsolved. Personally, I believe that one cannot "hear" the shape of a tambourine but I may well be wrong and I am not prepared to bet large sums either way.

Source: *The American Mathematical Monthly*, Vol. 73, No. 4, Part 2: Papers in Analysis (Apr. 1966), pp. 1–23

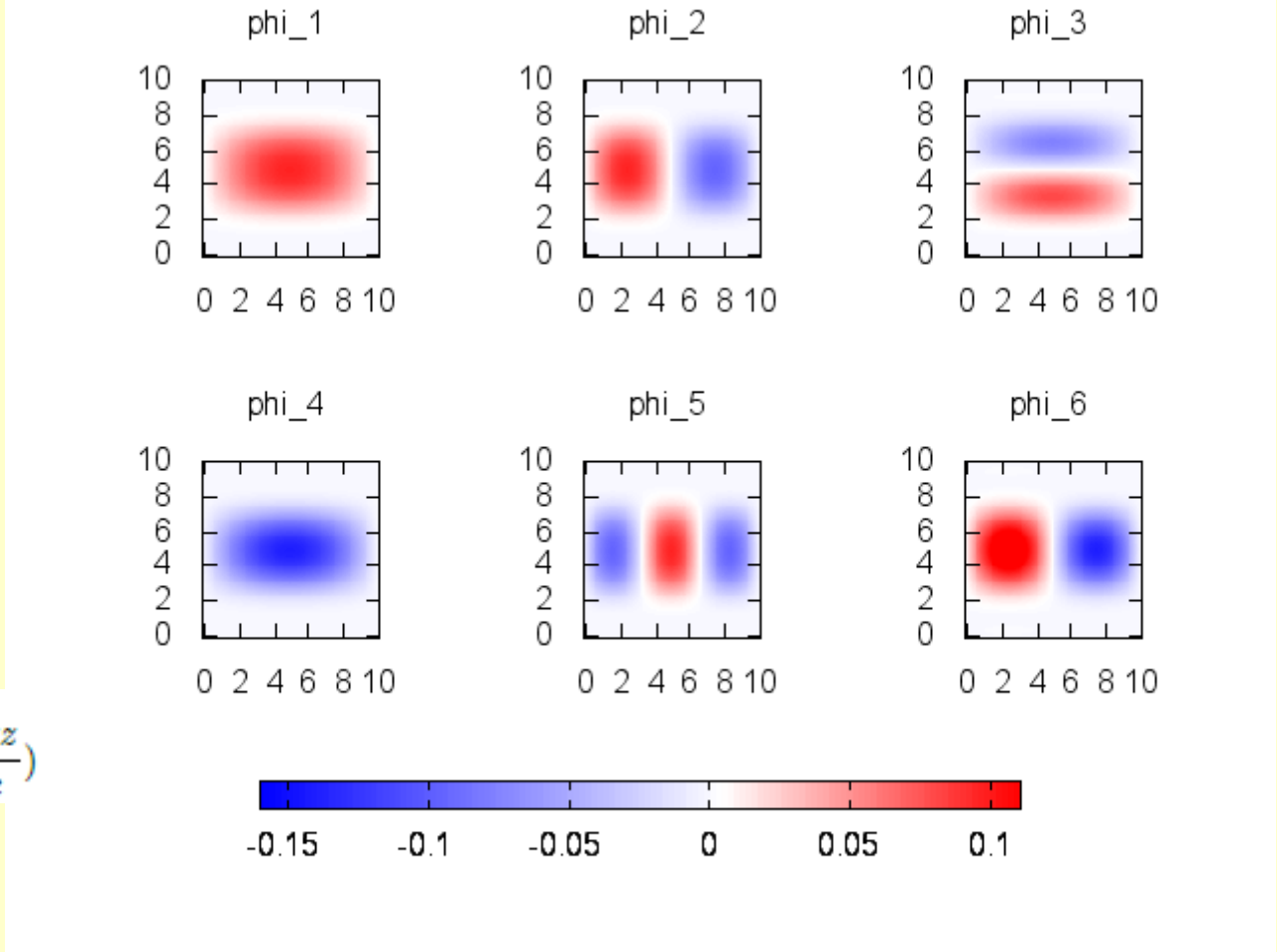


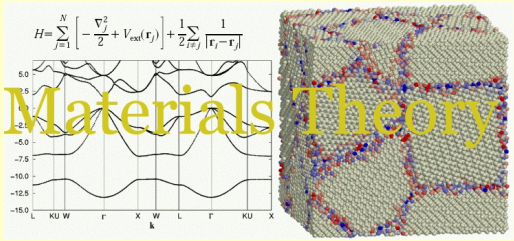
Wave functions in a Au nanoparticle



$$\psi_i(x,y,z) = \sum_{n,m,l} c_{i,n,m,l}\phi_{n,m,l}(x,y,z)$$

$$\phi_{n,m,l}(x,y,z) = \sqrt{\frac{8}{abc}} sin(\frac{n\pi x}{a}) sin(\frac{m\pi y}{b}) sin(\frac{l\pi z}{c})$$



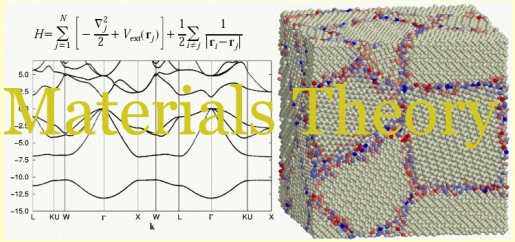


Shape-dependent energy levels

Energies in eV $nm^{2/3}$, (scaled to correspond to identical volume).

The first step towards spectroscopic identification of shapes?

n	Sphere	CO	SCH3	Clean	Cube
0	0.00	0.00	0.00	0.00	0.00
1	2.10	2.14	2.18	2.21	2.26
2	2.14	2.14	2.18	2.21	2.26
3	2.14	2.14	2.18	2.21	2.26
4	4.79	4.80	4.78	4.37	4.51
5	4.79	4.80	4.78	4.37	4.51
6	4.80	4.80	5.03	5.44	4.51
7	4.82	4.89	5.03	5.44	6.02
8	4.85	4.89	5.03	5.44	6.02
9	6.11	6.14	6.24	6.06	6.02



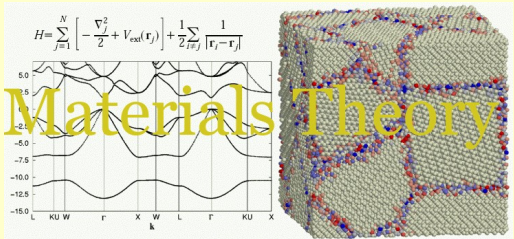
Conclusions

Quantum mechanical simulations can be used to derive accurate equilibrium shapes for metal, semiconductor and insulator nanoparticles.

Nanoparticles in weakly interactive environments have similar shapes.

Nanoparticles increase their sphericity upon exposure to reactive environment.

Energy levels can be used as a probe of shape.



Acknowledgements

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- G. Barmparis.
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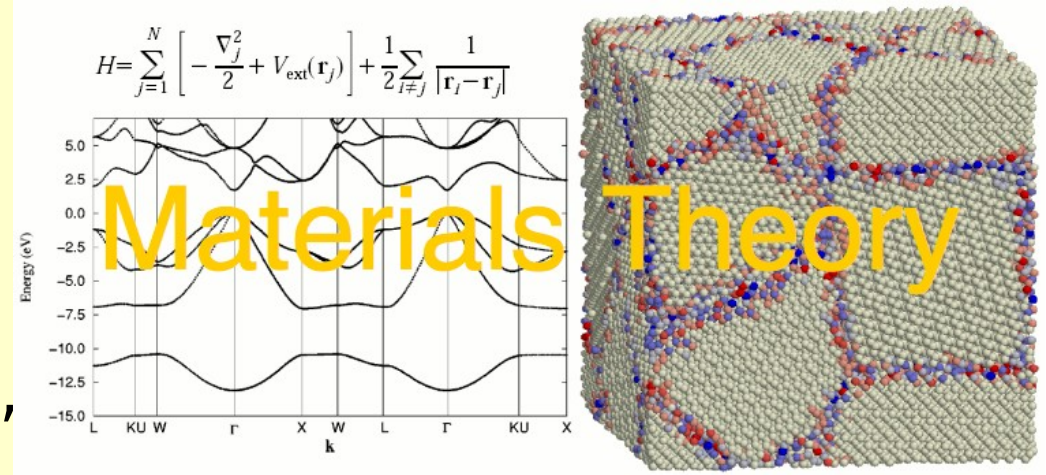
- K. Honkala (Jyväskylä University, Finland).



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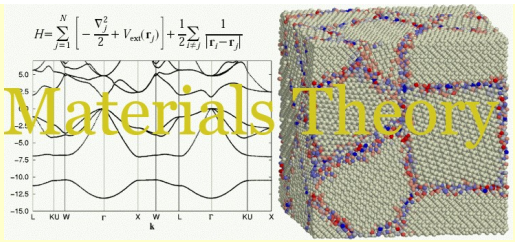
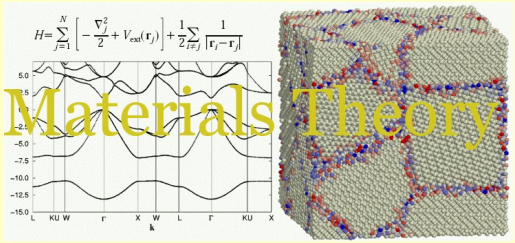


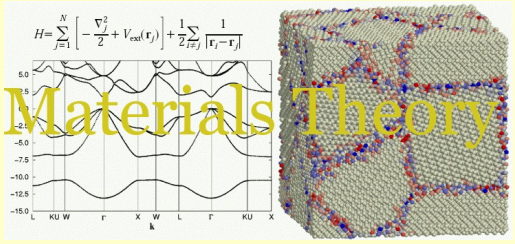
Materials Theory Group

C. Motsanos (graduated), N. Galanis, C. Mathioudakis, G. Kopidakis, I.Remediakis, E. Tylianakis, G. Barmparis, S. Stamatiadis

Not shown in this picture: K. Moratis (graduated), A. Maniadaki, E. Pantoulas (graduated), G. Kotsopoulou, V. Markoulaki.

Computer Support: S. Stamatiadis & Computer Center (D. Counalakis).




$H=\sum_{j=1}^{N}\left[-\frac{\nabla_j^2}{2}+V_{ext}(\mathbf{r}_j)\right]+\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$
5.0
-2.5
-5.0
-7.5
-10.0
-12.5
-15.0
L KU W Γ X W L Γ KU X
k
Materials Theory