Molecular dynamics simulations of metal nanostructures: dynamical strain, interaction with a substrate and environment effects

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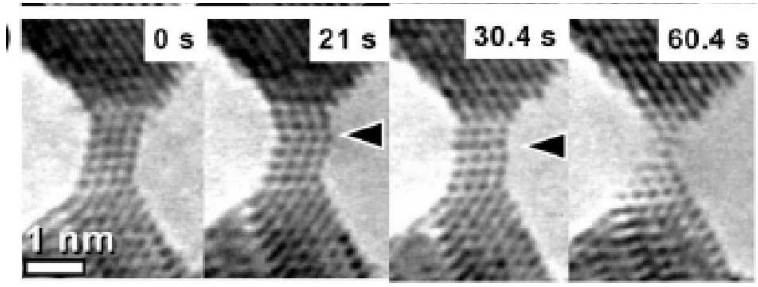
22th February 2012

Outline

1. Semiempirical description of metals

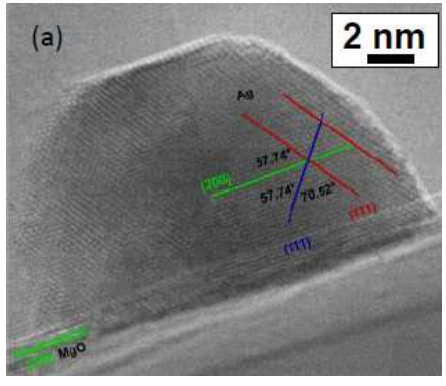
[Lagos, et. al. PRL **106** 055501 (2011)]

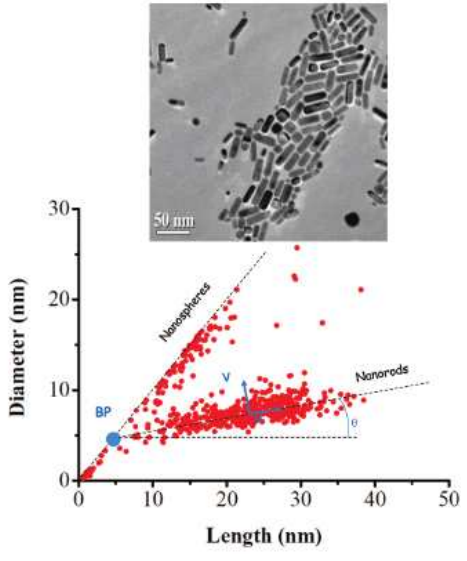


2. Stretched Au nanowires

[Stankic et.al. Nanoscale, in press]

3. Supported Ag nanoparticles





4. Au nanoparticles in solvation

[Hubert, et.al., Langmuir 26, 6887 (2010)]

5. Conclusive remarks

Ab-initio vs. semiempirical methods

- **Ab-initio:** accurate but computationally demanding.
- Restricted to systems of few hundred atoms.
- Timescale spans few picoseconds.

- **Semiempirical:** approximate, should be adapted to the case study.
- Able to handle systems of thousands (perhaps millions) of atoms.
- Timescale spans few nanoseconds.

Semiempirical: second-moment approximation (SMA) is appropriate to describe transition metals

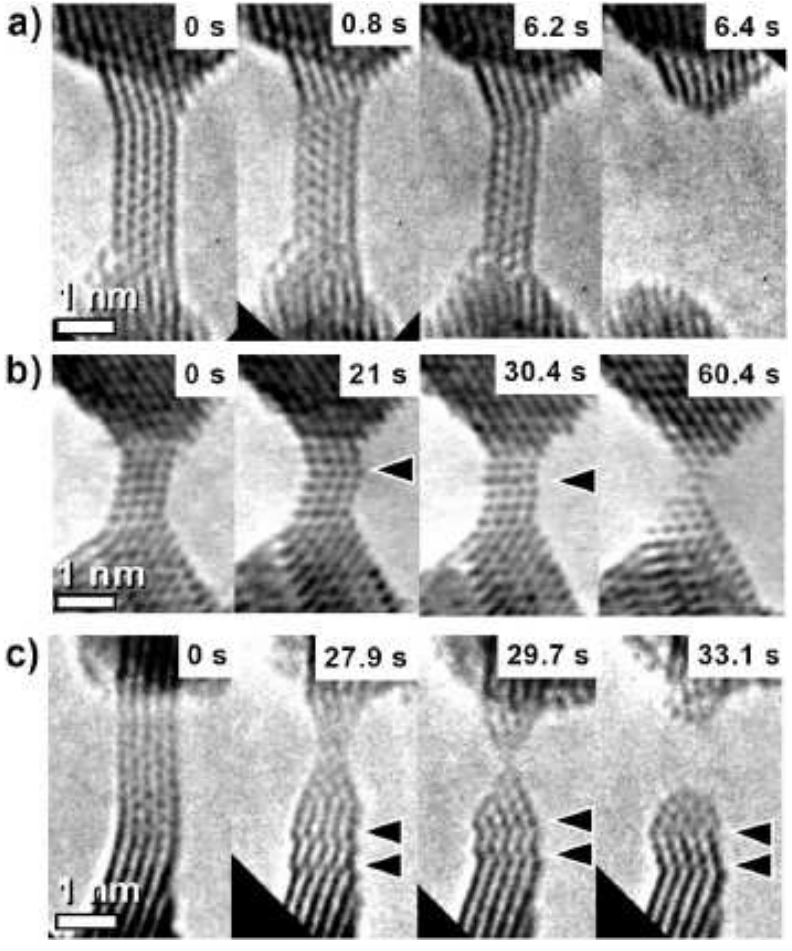
$$E_i = -\xi \sqrt{\sum_{j \neq i} \exp\left(-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right)} + A \sum_{j \neq i} \exp\left(-p\left(\frac{r_{ij}}{r_0} - 1\right)\right).$$

... and it contains the essential many-body physics information.

Stretched Au nanowires

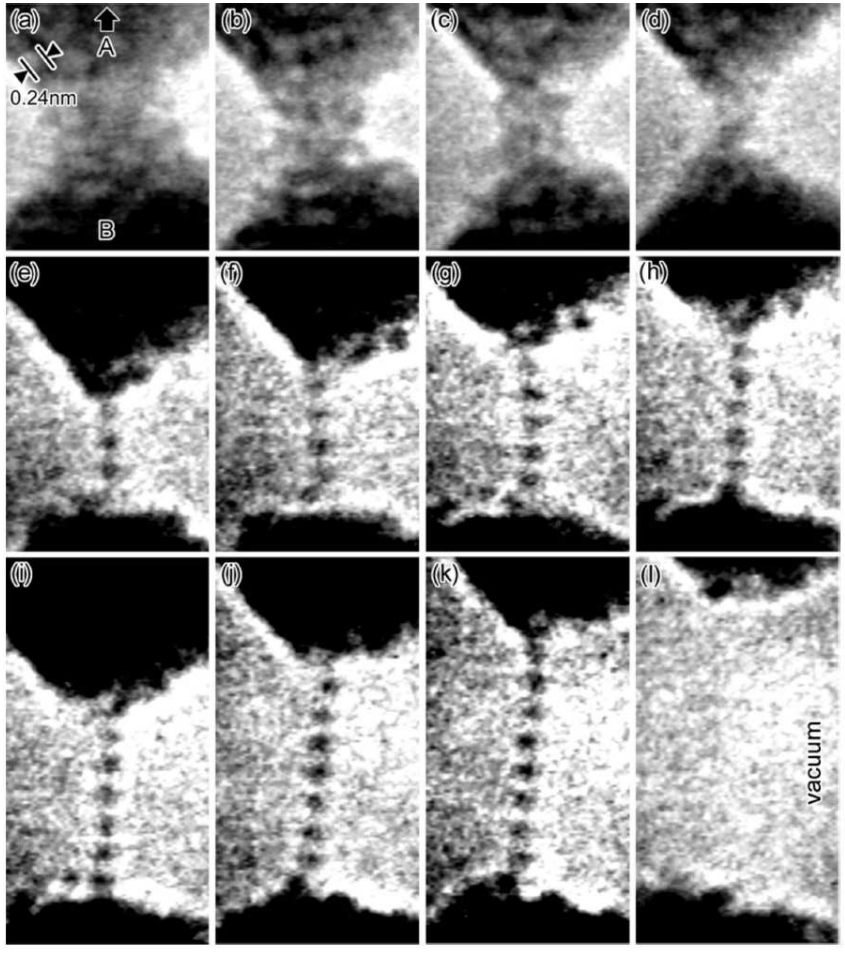
Planar defects at low temperature

[Lagos, et. al. PRL **106** 055501 (2011)]



Long atomic chains at room temperature

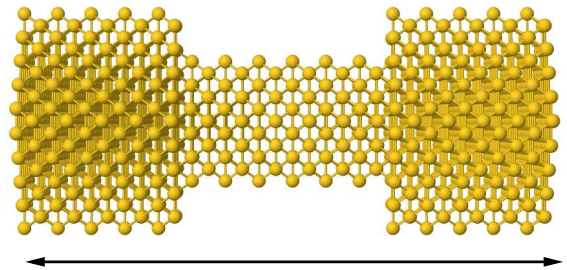
[Kizuka, PRB **77** 155401 (2008)]

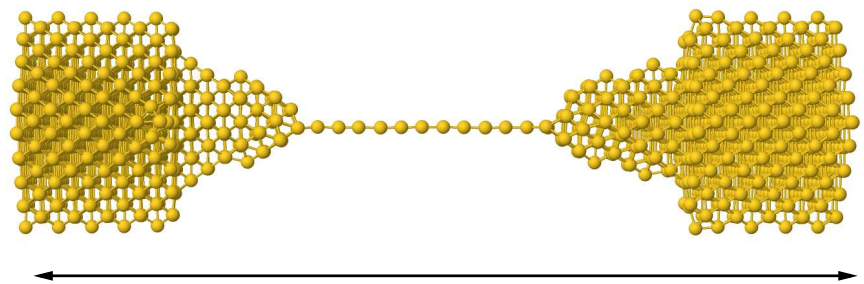


Simulation setup [Cortes-Huerto, Sondon and Saúl, submitted to PRB]

How do we introduce stretching?

1. Define degrees of freedom ($H_{l,m}\,, l, m = 1, 2, 3$) for the simulation cell.
2. Write the atomic coordinates as $\mathbf{r} = \underline{\mathbf{H}}\mathbf{s}$.
3. Define $H_{33} \equiv L_z(t)$.
4. Finally, add extra equation of motion: $L_z(t) = L_z(0) + v_{st}t$.

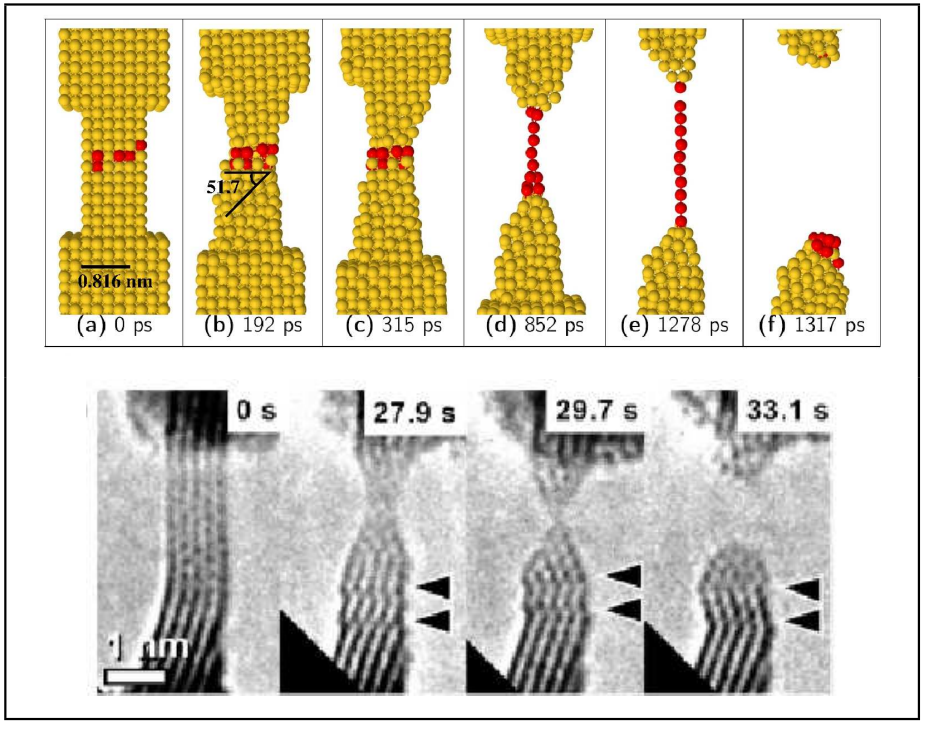




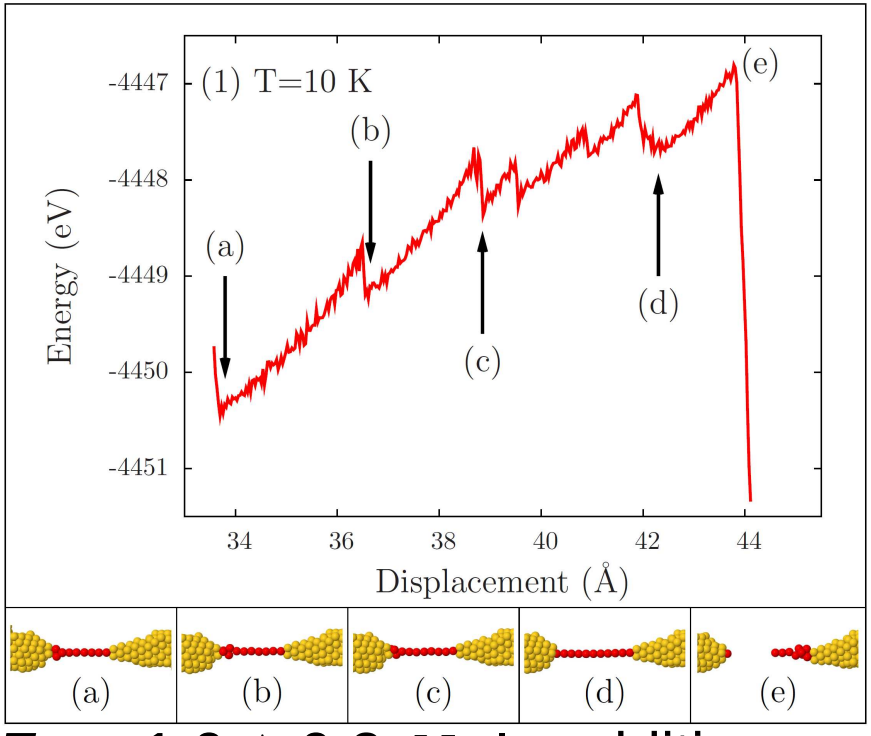
Range of temperatures 5-600 K. 50 initial configurations per temperature.

Temperature dependent stretching [Cortes-Huerto, Sondon and Saúl, submitted to PRB]

At T=150K, apparent formation of glide planes before formation of atomic chain.



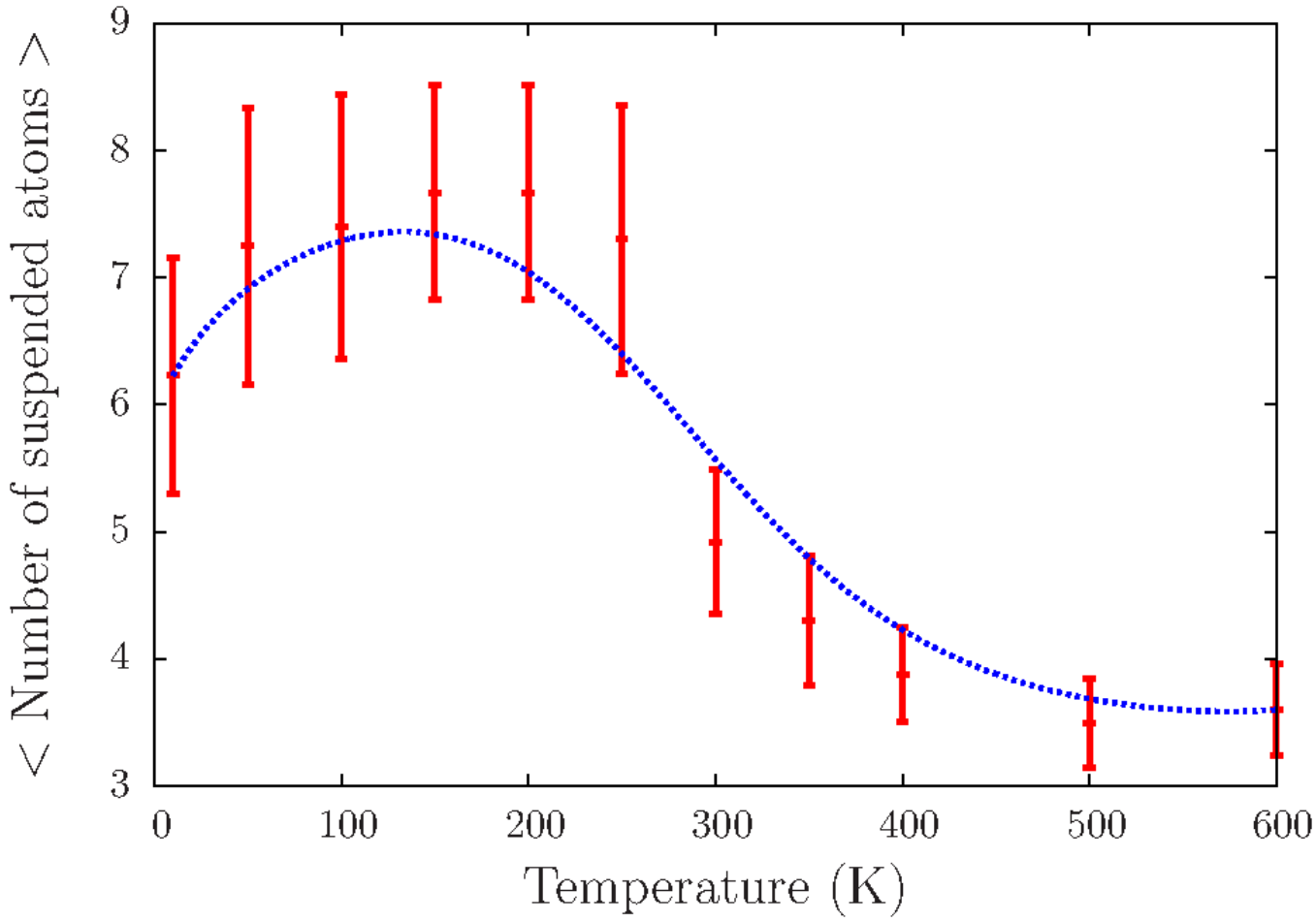
Evolution of an atomic chain upon stretching



$F_b = 1.0 \pm 0.2$nN. In addition, F_b independent of length and temperature [Kizuka, PRB **77** 155401 (2008)].

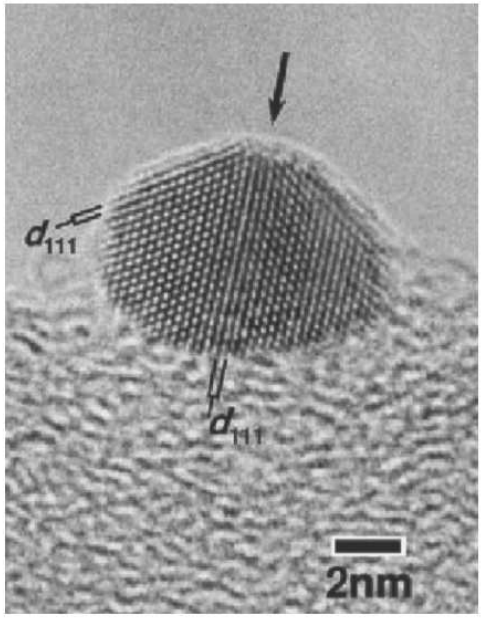
Take-home message [Cortes-Huerto, Sondon and Saúl, submitted to PRB]

Increasing temperature first helps to form long atomic chains, then destroys them.



Average number of suspended atoms has a maximum around 150 K.

Why nanoparticles?



Baletto, Ferrando, Rev. Mod. Phys. 77, 371 (2005)

1. Strongly size-dependent properties.
2. Large surface/volume ratio. Catalysis applications.
3. Plasmon resonance. Biological applications.

Metal nanoparticles manipulated since the roman empire!

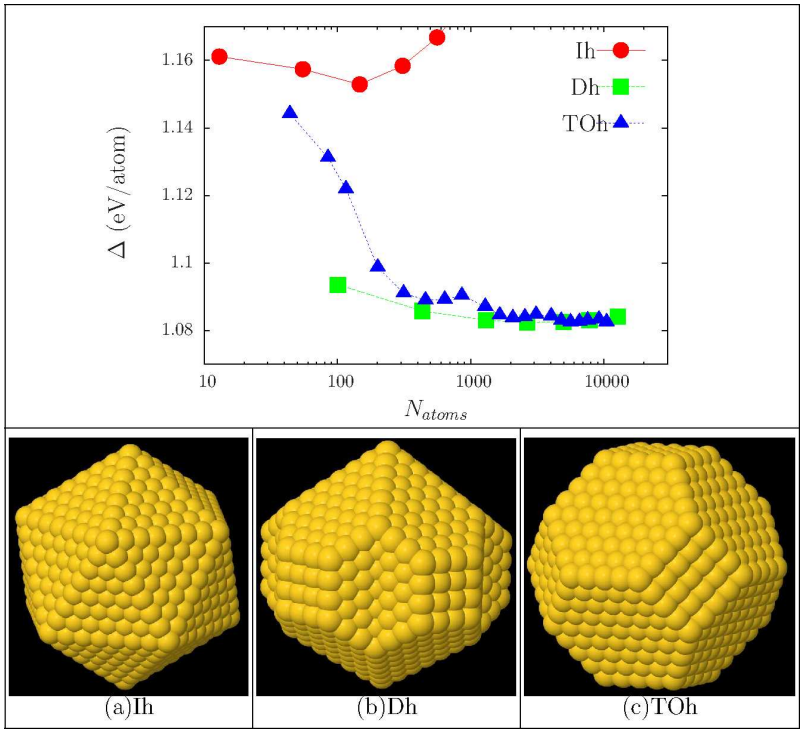
Lycurgus cup (290-325 AD). British Museum. *Photo courtesy C. Noguera.*

Supported Ag nanoparticles [Stankic et. al., Nanoscale, in press]

Model: Detailed description of cluster morphology while considering systems of thousands of atoms.

Metal-metal interaction

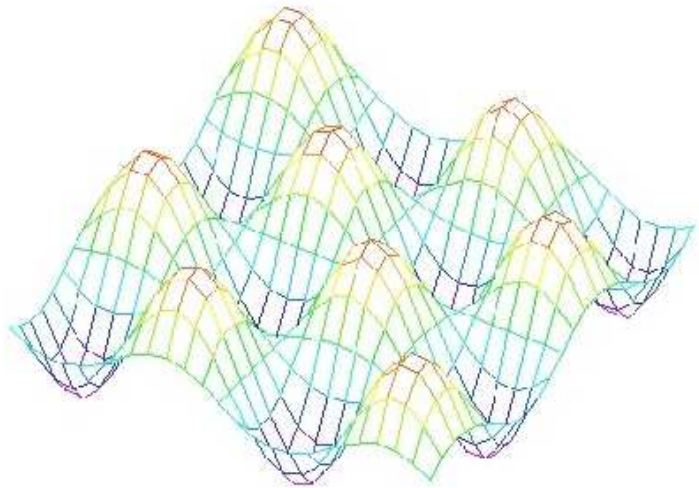
Second-moment approximation: $E_b \sim \sqrt{Z}$



Metal-MgO(100) interaction

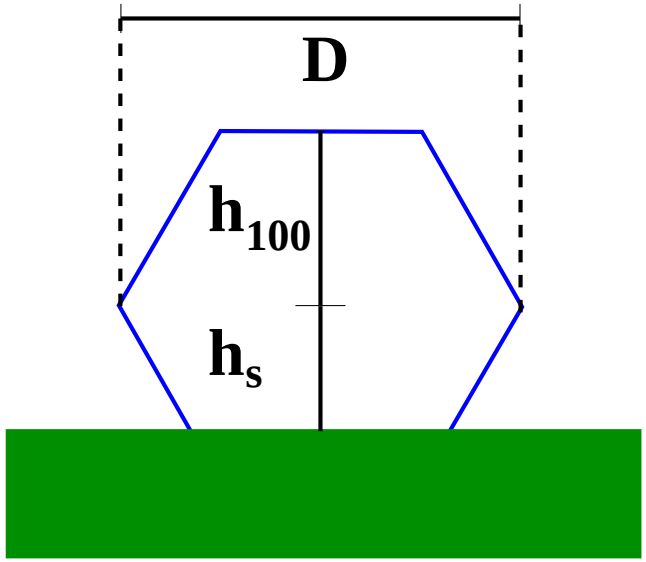
Many-body potential energy surface (PES)derived from ab-initio calculations

Vervisch, et.al., PRB 65, 245411 (2002).



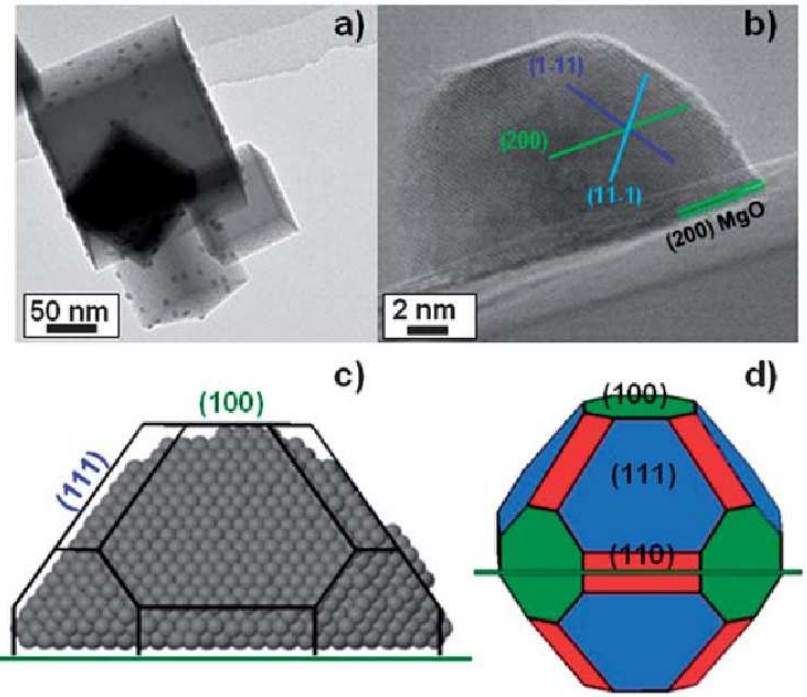
Ag cluster on MgO(100) flat surface [Stankic et. al., Nanoscale, in press]

Wulff-Kaishev theorem: how to compute adhesion energy β by looking at the nanoparticle.



$$\frac{\beta}{\sigma_{100}} = \frac{h_{100} - h_s}{h_{100}}$$

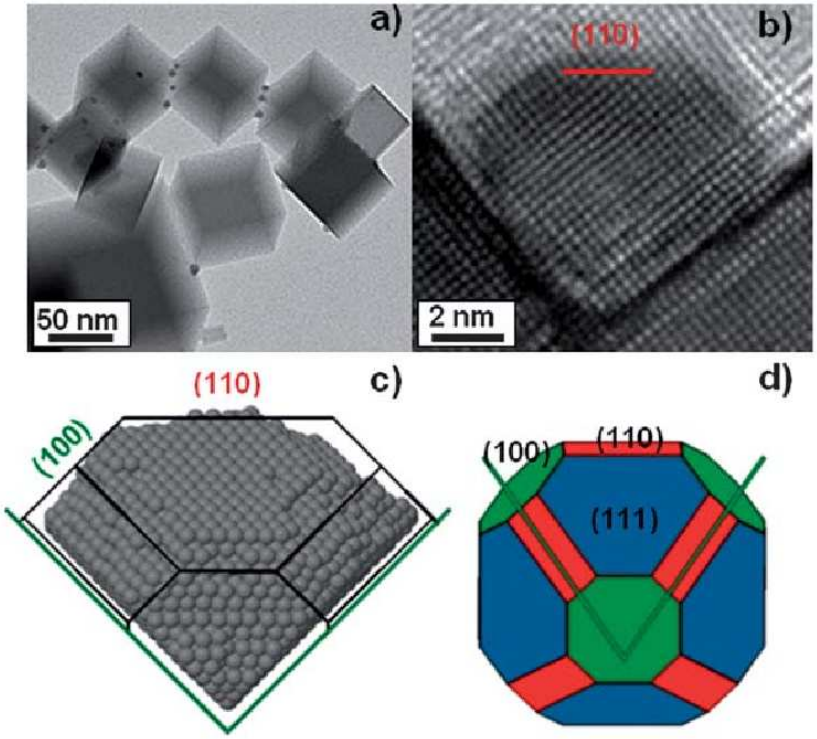
a) TEM of Ag clusters on MgO crystallites. b) HRTEM of Ag cluster showing (111) and (100) facets.



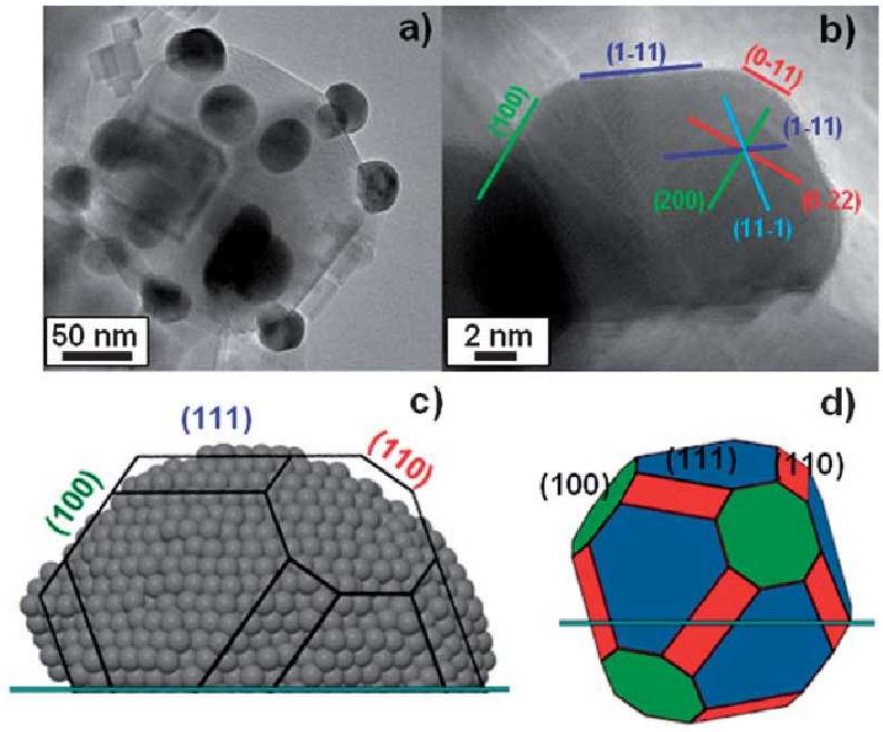
c) MD simulation of Ag cluster on flat MgO surface. d) Wulff construction indicating (111), (100) and (110) exposed facets.

Ag cluster on complex MgO surfaces [Stankic et. al., Nanoscale, in press]

Orientation of the top facet follows average orientation of MgO surface.



Ag clusters grown along the contact line between two stacked MgO crystallites.

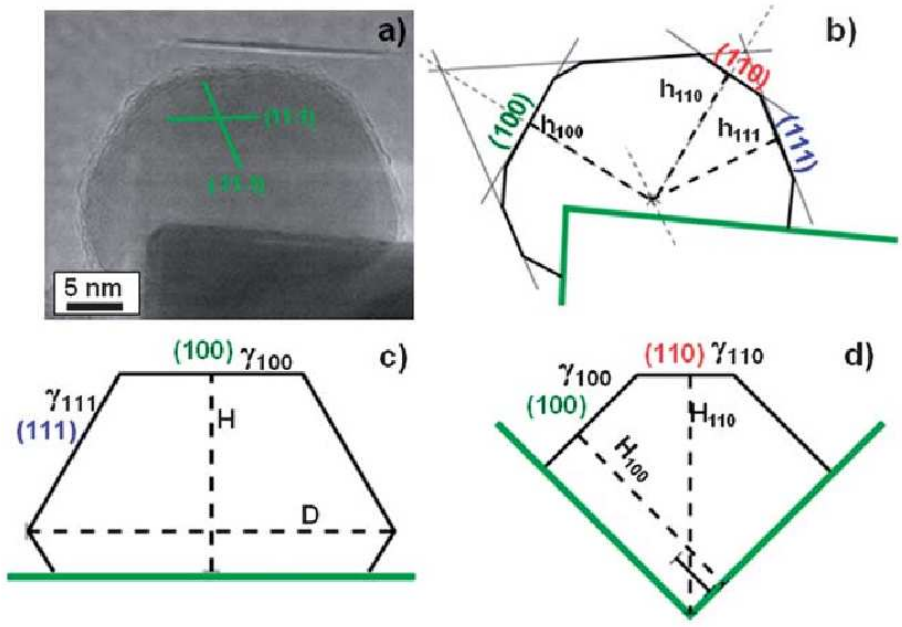


Ag clusters grown on multiatomic steps of MgO crystallites.

Simulation suggests nanoparticles are in local equilibrium.

Take-home message [Stankic et. al., Nanoscale, in press]

Combination of TEM experiments and atomistic simulations to study Ag nanoparticles supported on complex MgO surfaces.

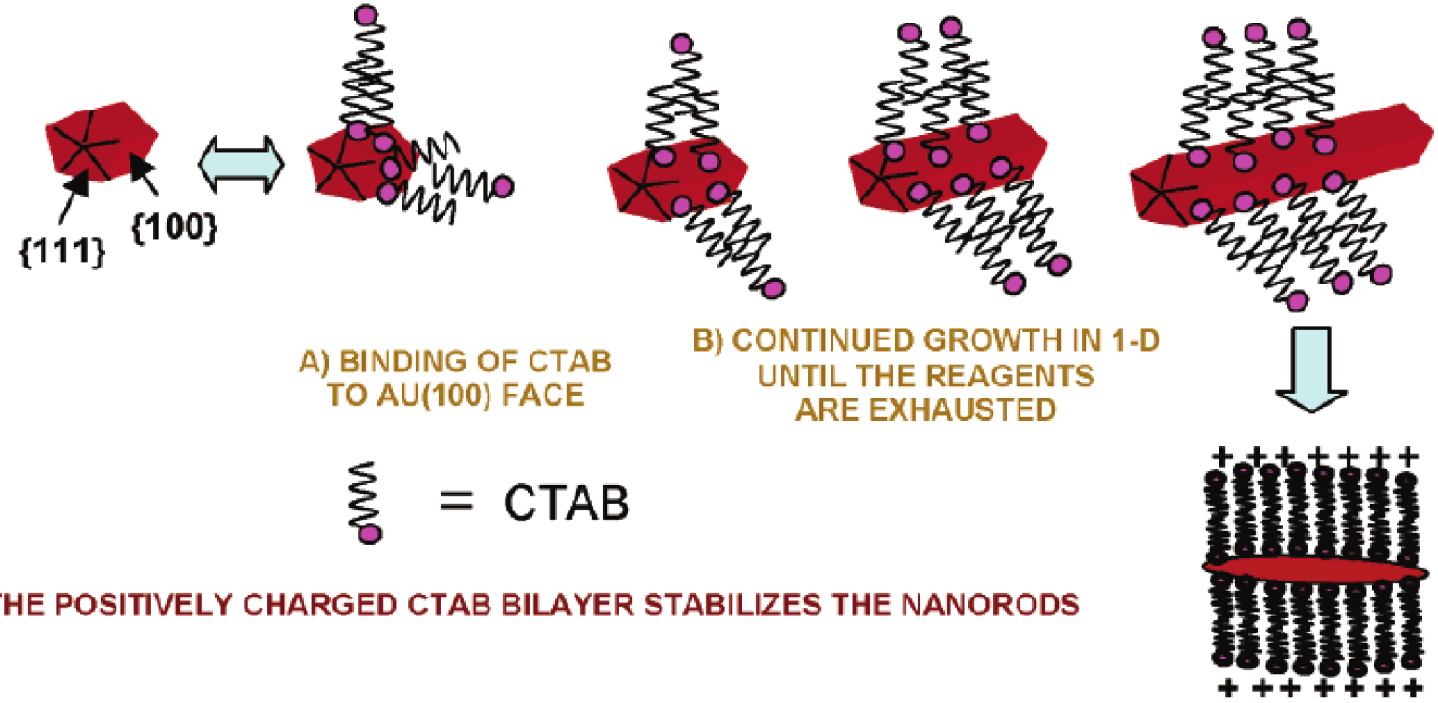


Unambiguous evidence of the occurrence of open (110) facets in equilibrium shape of Ag clusters. Evaluation of the ratio $\sigma_{110}/\sigma_{100}$.

Possible extension to other fcc metals.

Surfactant-driven growth of metal nanorods

1. Thermodynamic effects (Dh particles)

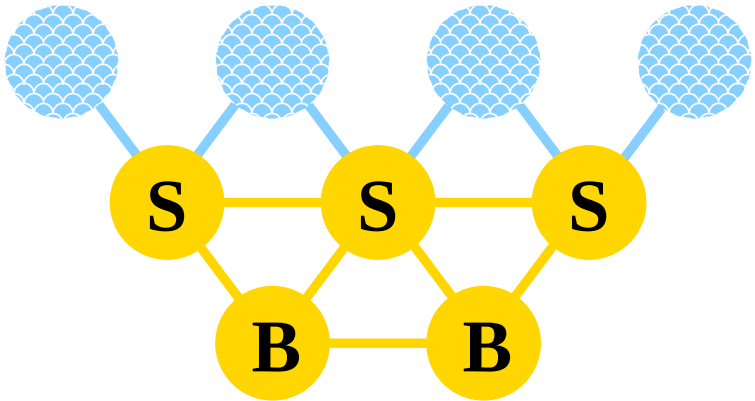


2. Symmetry breaking and kinetic effects (fcc particles)

Adapted from [Murphy, et.al., J. Phys. Chem. B 109, 13857 (2005)]

Our model [Cortes-Huerto, Goniakowski and Noguera, *to be submitted*]:

Atoms of the environment represented implicitly.



Schematic representation of surface (S) and bulk (B) Au atoms interacting with an environment of virtual atoms (blue spheres).

We suppose environment species bind to Au atoms via free-surface bonds.

In other words:

$$E_i = E_i^{SMA} + E_i^{M-E} \, ,$$

where

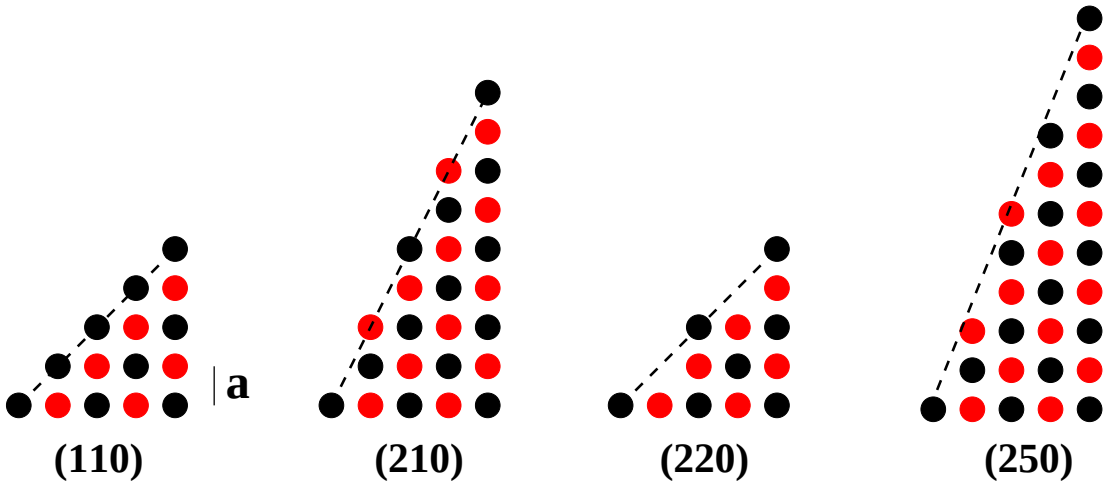
$$E_i^{M-E} = -\epsilon (Z_B - Z_i)^p \, .$$

Only two parameters:
$0 < \epsilon < 0.01$ (eV/atom) and
$0 < p < 2.5$.

Net effect of the M-E contribution is to stabilise systems with low-coordinated atoms.

Surface energy [Cortes-Huerto, Goniakowski and Noguera, *to be submitted*]

Schematic contruction of (hk0) surfaces of fcc lattice.



- 1st layer, - 2nd layer

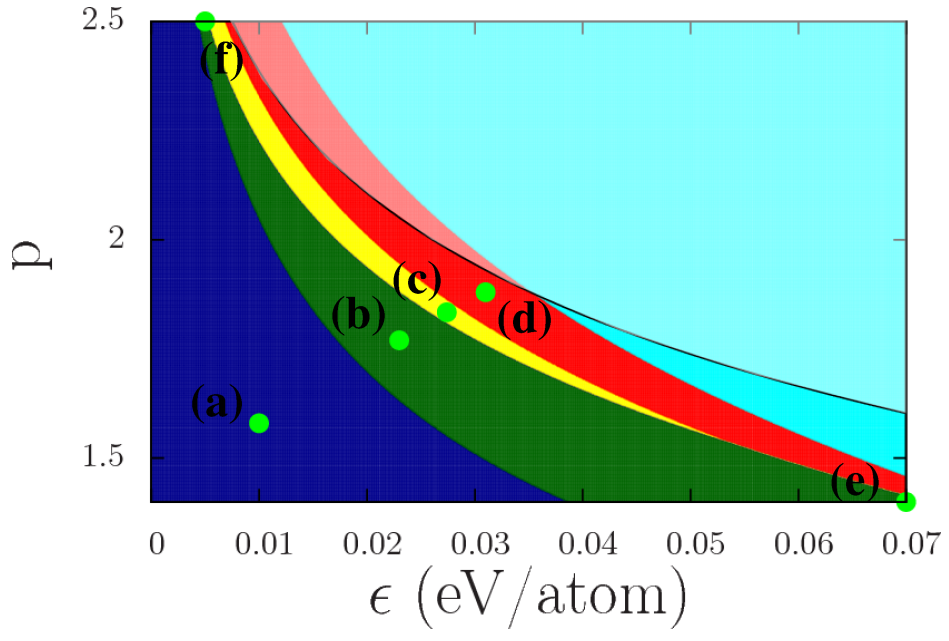
We compute

$$\sigma_{env} = \sigma_{vac} + \delta\sigma \,,$$

with

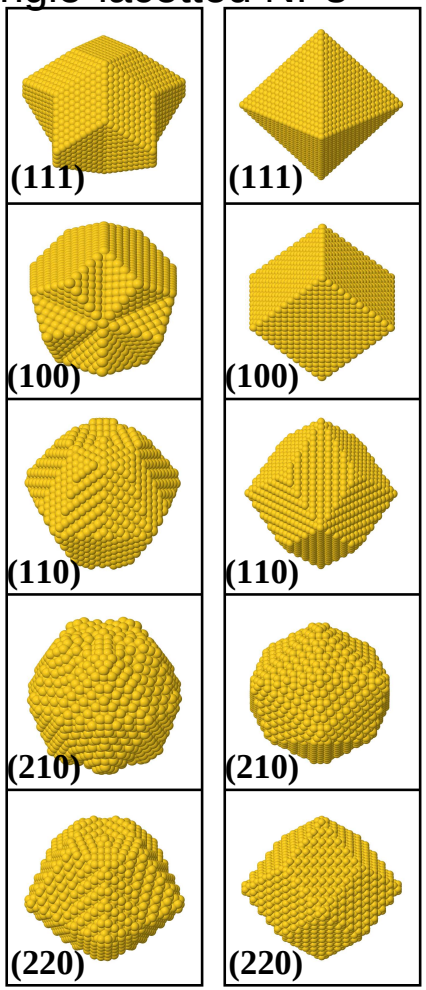
$$\delta\sigma = -\frac{\epsilon}{A}\sum_i (Z_B - Z_i)^p \,.$$

Code: (111), (100), (210), (220).



Relative stability of NPs [Cortes-Huerto, Goniakowski and Noguera, *to be submitted*]

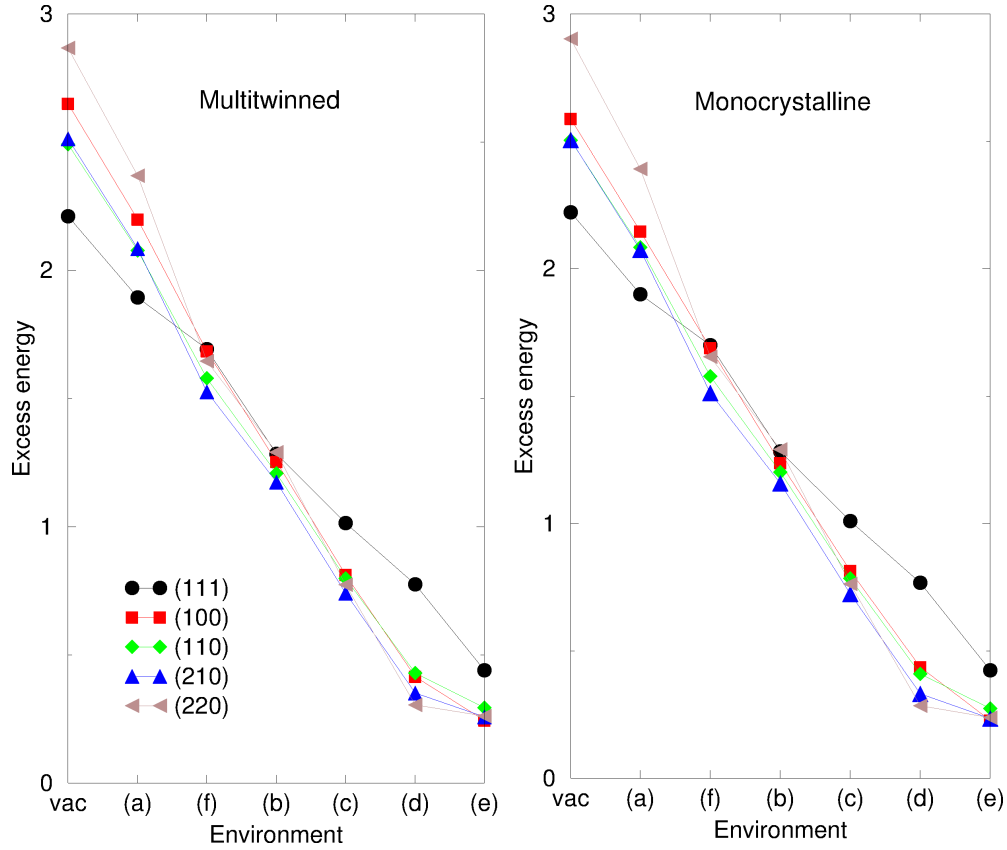
Single-facetted NPs



(a) MT (b) MC

Excess energy:

$$\Delta(N) = \frac{E_{\text{clus}} - NE_{\text{coh}}}{N^{2/3}} .$$



1. For a given size: excess energy decreases when going from vacuum to strongly interacting environment.
2. Dispersion of excess energy decreases.
3. Inversion of stability for different facets and also between MT and MC particles.
4. For a given environment: relative stability depends on size.

Take-home message

- Promising efficient, simple and generic (two-parameter) model to study metallic nanoparticles in solvation.
- Potentially wide range of application by considering different pairs of parameters.
- Avoid description of complex processes at the interface, instead provides trends.
- **Work in progress:** full motif optimisation and growth simulations.

Conclusive remarks and acknowledgments

We have presented three extensions of SMA intended to understand and complement experimental data for three different model systems.

- **Stretched nanowires**: Andres Saúl (CINaM-Marseille) and Tristana Sondón (ICMAB-Barcelona). ANR-08-NANO-PO56-36 SUD.
- **Supported nanoparticles**: Slavica Stankic, Jacques Jupille and Jacek Goniakowski (INSP-Paris).
- **Nanoparticles in solvation**: Jacek Goniakowski and Claudine Noguera (INSP-Paris). ANR-11-BS10-006 MIGRANI.