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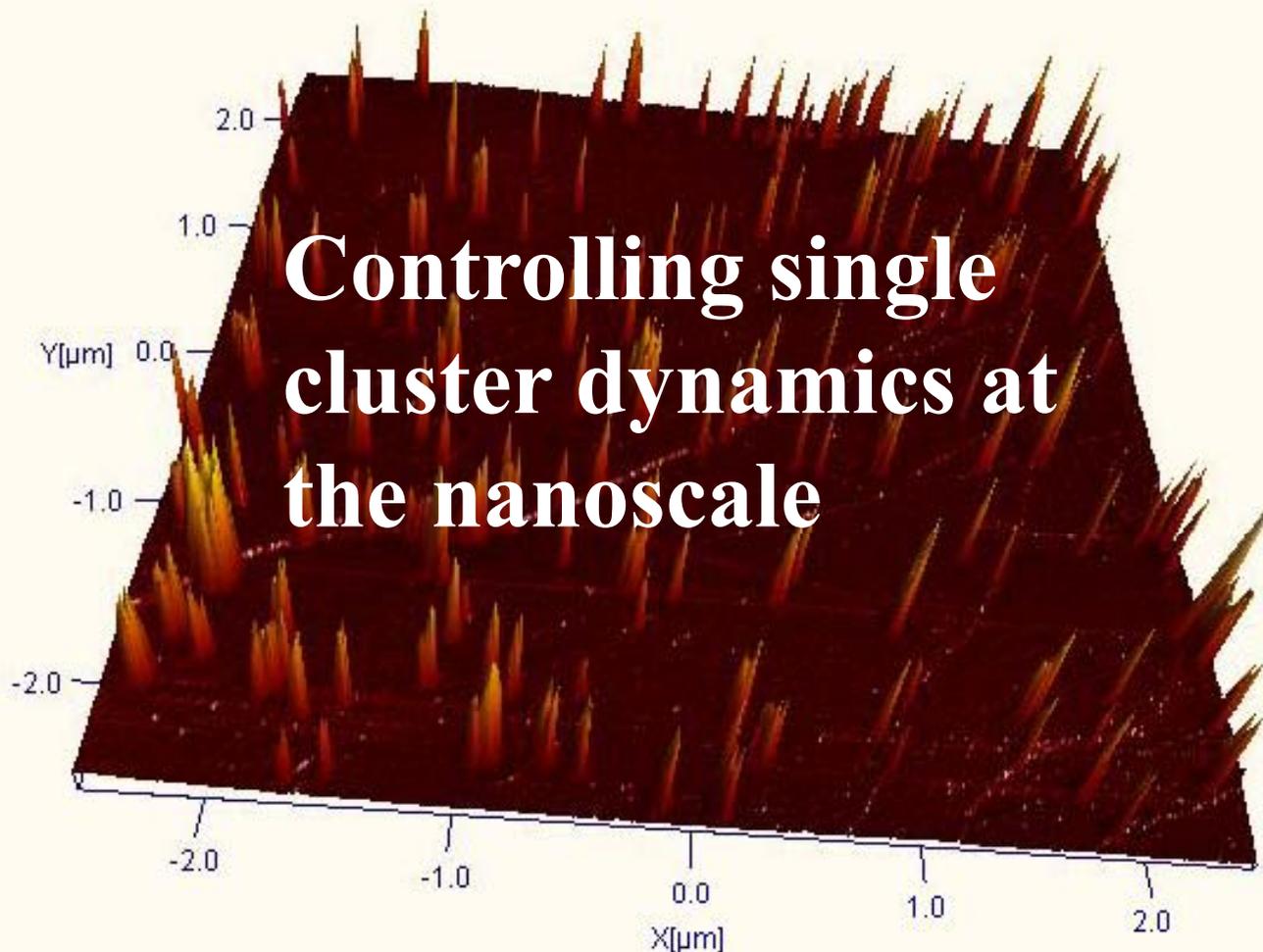
2063-5

ICTP/FANAS Conference on trends in Nanotribology

19 - 24 October 2009

Controlling single cluster dynamics at the nanoscale

PAOLICELLI Guido
*CNR INFN, National Research Center S3
Via Campi 213, 41100
Modena
ITALY*



Outline :

- Introduction
- Experimental method
- Detachments
- Movements
- Conclusions

Guido Paolicelli

Massimo Rovatti, Andrea Vanossi and Sergio Valeri*

- CNR-INFM Research Center on nanoStructures and bioSystems at Surfaces S3, Modena, Italia

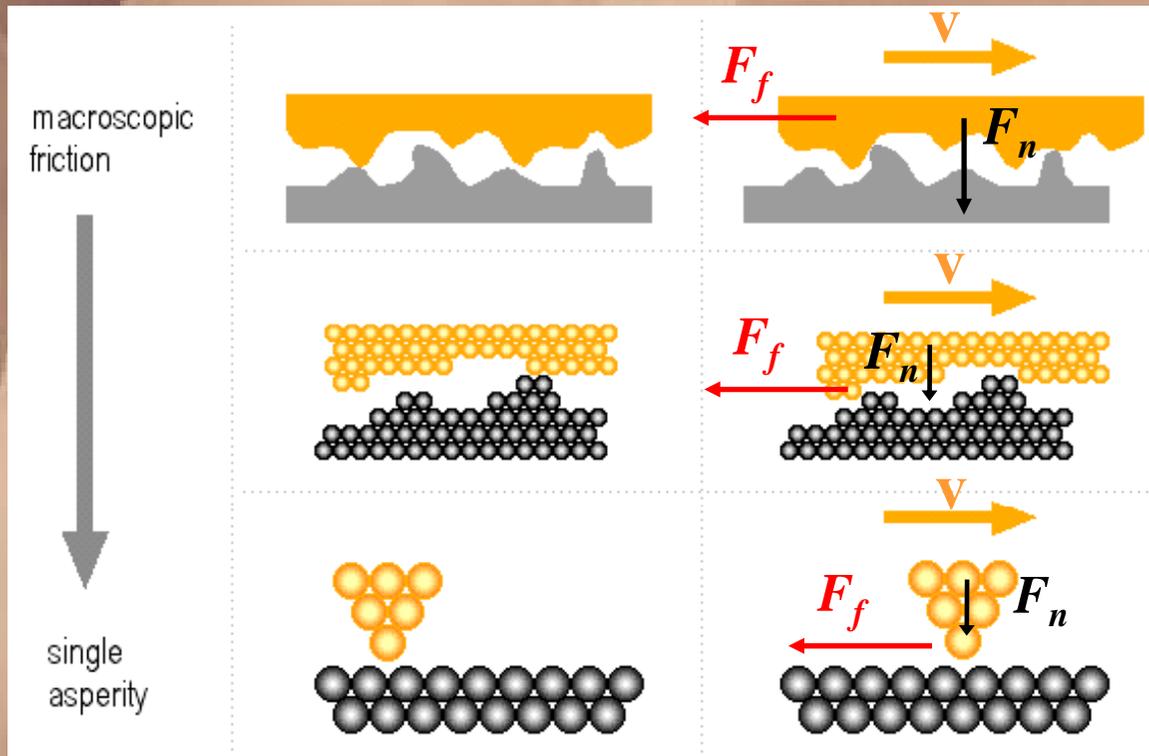
- Department of Physics University of Modena e Reggio Emilia, Modena, Italia

* Now at *SISSA* and CNR-INFM Democritos National Simulation Center, Trieste, Italia

Introduction

Experimental method

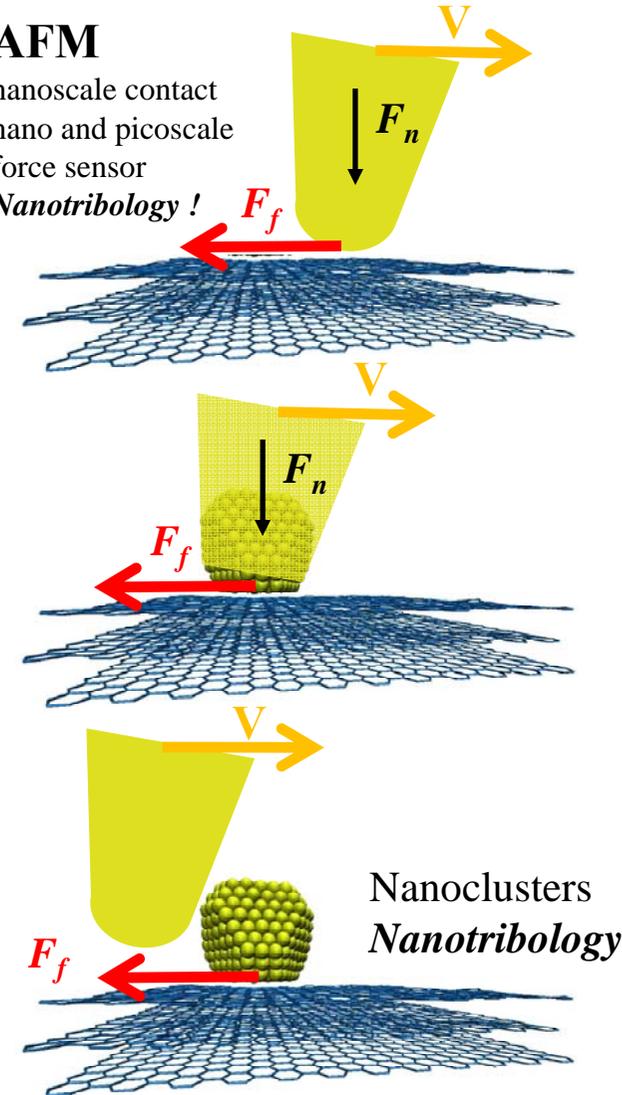
Tribology



Tribology at the atomic scale

AFM

nanoscale contact
 nano and picoscale
 force sensor
Nanotribology!



Nanoclusters
Nanotribology

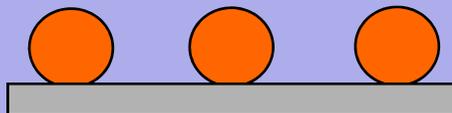
Introduction

Nanoclusters represent “specialised tool” to study friction at the nanoscale:

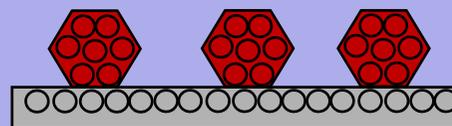
- *Controlled and variable contact size, range: 10- 200 nm*
- *Controlled and variable compositions at the contact interface*
- *Well defined cristalline interface*
- *Dynamical behaviour*



Defined contact areas at the nanometer scale can be obtained by using island deposited on surface.

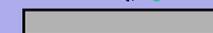


Statistical analysis may be performed on a uniform size clusters deposition

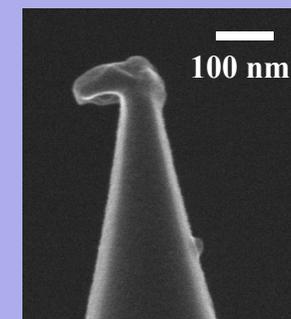


Commensurabilty effects on cristalline interface

AFM tip



Is difficult to control AFM tip shape during the microscope operation



System

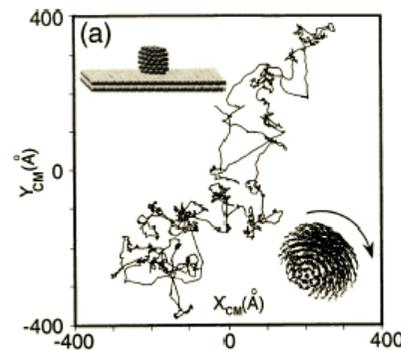
Gold /antimony nanoclusters on graphite (HOPG)
 possess peculiar dynamical characteristics:

-very high diffusion coefficient

L. Bardotti et al Phys. Rev. Lett. 74 (1995) 4694

- distinctive motion features :

- **pinnig effects**
- **Lévy flights**
- **rotation**



W.D. Luedtke and U. Landman Phys. Rev. Lett. 82 (1999) 3835

L. Lewis et al Phys. Rev. B 61 (2000) 16084

S. Pisov et al J.Phys.: Condes. Matter 19 (2007) 305015

superlubric translations

D. Dietzel et al

Phys. Rev. Lett. 101, 125505 (2008)

**Tribology interest
 at the nanoscale**

Experiment

CONDITIONS

- **Gold clusters \varnothing 10-50 nm**
- **Ambient conditions**
- **AFM induced translations**

OBJECTVES

- **controlled movements**
- **static friction versus contact area**

Experimental details

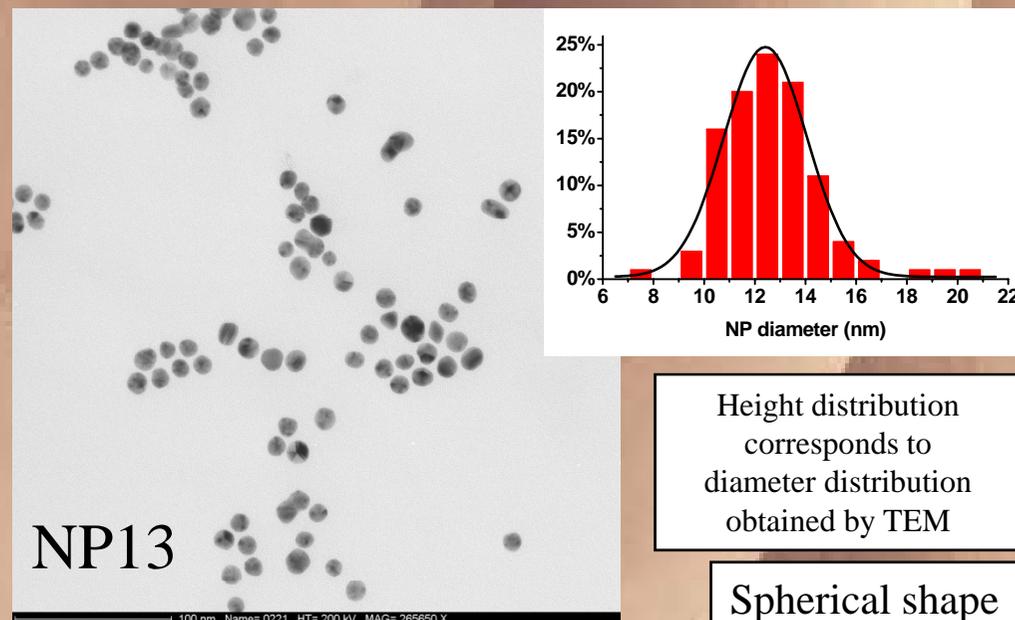
Three different cluster sizes were used :

NP13 diameter = 13 ± 2 nm

NP24 diameter = 24 ± 3 nm

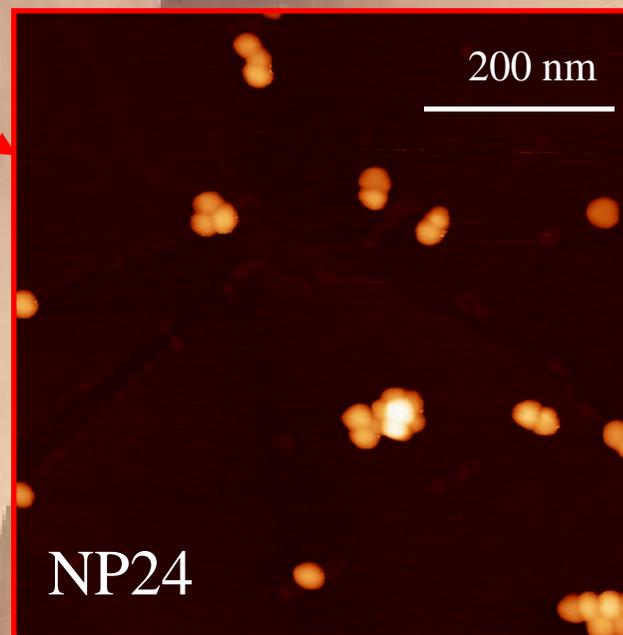
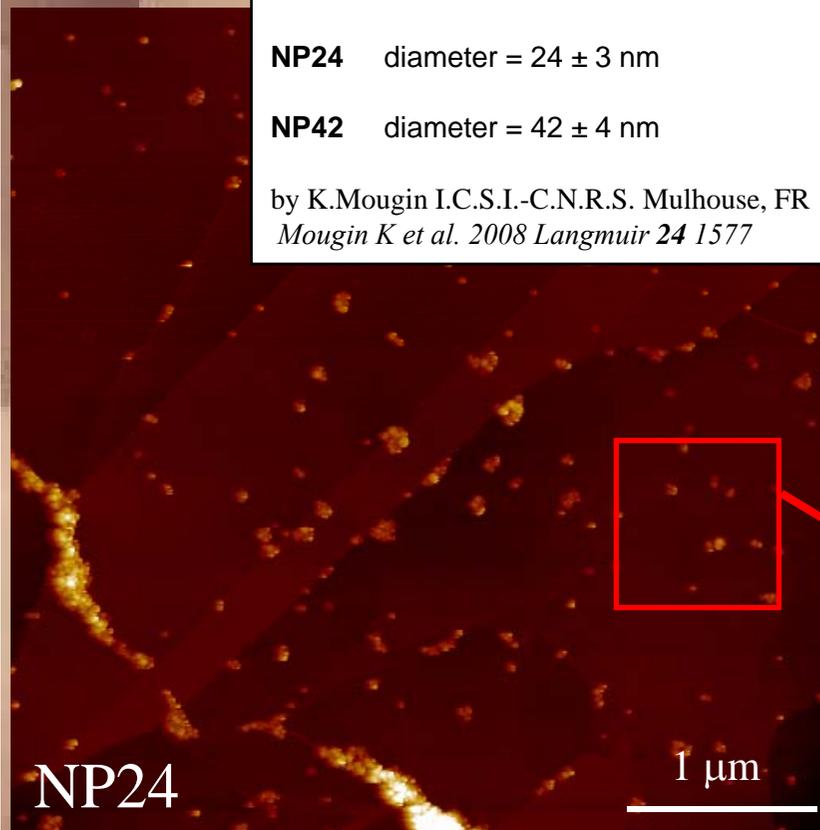
NP42 diameter = 42 ± 4 nm

by K.Mougin I.C.S.I.-C.N.R.S. Mulhouse, FR
Mougin K et al. 2008 Langmuir 24 1577



Height distribution
 corresponds to
 diameter distribution
 obtained by TEM

Spherical shape



Gold nanoclusters deposited on a freshly cleaved HOPG surface
 A droplet of suspension containing nanoclusters of well defined size is deposited onto the surface (air, RT) then dried with a nitrogen flux.

Experimental method

Contact AFM



substrate

- Torsional bending (ϕ)
- Force measurement
- Standard FFM

Dynamic AFM



substrate

- Amplitude oscillations
- Phase
- Frequency

➤ Damping effects

- Tip + cantilever + sample are in a **dynamic equilibrium state**.

$$\langle P_{dis} \rangle = \langle P_{in} \rangle - \langle P_0 \rangle$$

- The system is a **point mass driven oscillator with damping**
- actuator and tip oscillate like simple **sinusoidal waves**
- $\langle P_0 \rangle = \frac{1}{2} \alpha \omega^2 A^2$ $\alpha = \text{effective damping coefficient} = \frac{k}{Q\omega_0}$

$$\rightarrow \langle P_{dis} \rangle = \frac{1}{2} \frac{\omega k A}{Q} \left(Q A_d \sin \phi - A \frac{\omega}{\omega_0} \right)$$

At the resonance $\omega = \omega_0$, $A_0 = Q A_d$; normalised to the period T

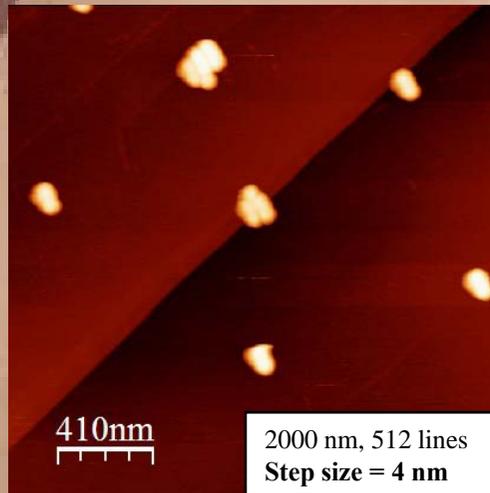
$$\rightarrow \langle E_{dis} \rangle = \frac{\pi k A^2}{Q} \left(\frac{A_0}{A} \sin \phi - 1 \right)$$

- T. Trevethan *et al.* Phys Rev. Lett. **98**, 028101 (2007)
- R. Garcia *et al.* Nature Materials **6**, 405 (2007)
- H. Hölscher Appl. Phys. Lett. **89**, 123109 (2006)
- N.F. Martinez and R. Garcia Nanotechnology **17**, S167 (2006)
- R. Garcia *et al.* Phys Rev. Lett. **9**, 016103 (2006)
- B. Anczykowski *et al.* Appl. Surf. Science **140**, 376 (1999)

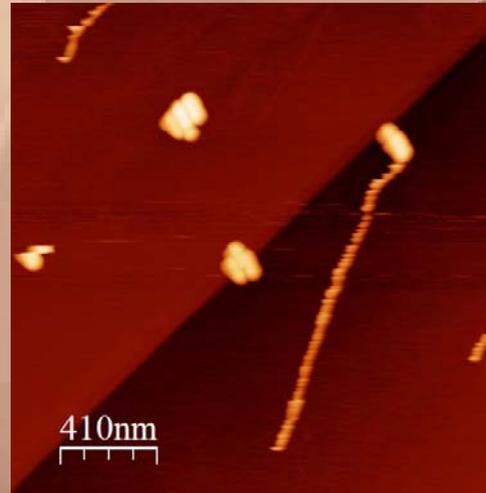
Amplitude Modulation - AFM *Tapping mode*

NP 42

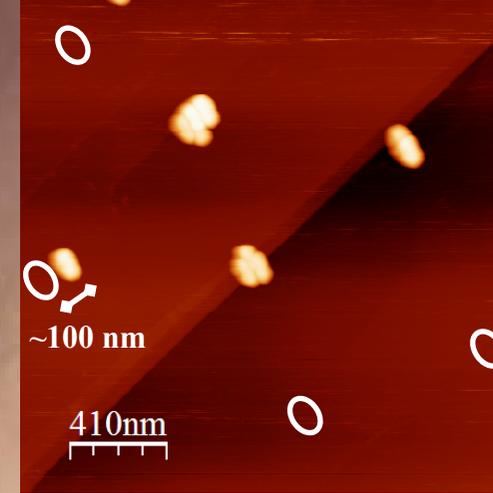
Initial image, topography
 $A_0 = 13 \text{ nm}$, $A = 10 \text{ nm}$



Manipulation scan, topography
 $A_0 = 15 \text{ nm}$, $A = 10 \text{ nm}$



Final image, topography
 $A_0 = 13 \text{ nm}$, $A = 10 \text{ nm}$



Tip and cantilever act as external excitation sources and they may induce clusters detachments and movements

Movements are intentionally induced using a tip amplitude oscillation A_0 larger than that optimised for imaging purpose.

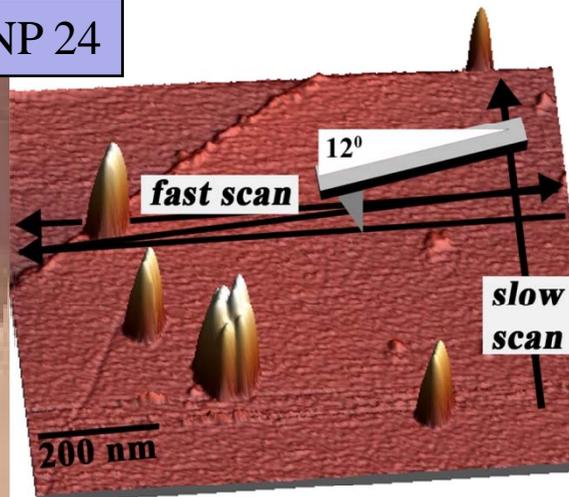
Controlling parameter is the energy dissipation signal measured on clusters

$$\langle E_{diss} \rangle = \frac{\pi k A^2}{Q} \left(\frac{A_0}{A} \sin \phi - 1 \right)$$

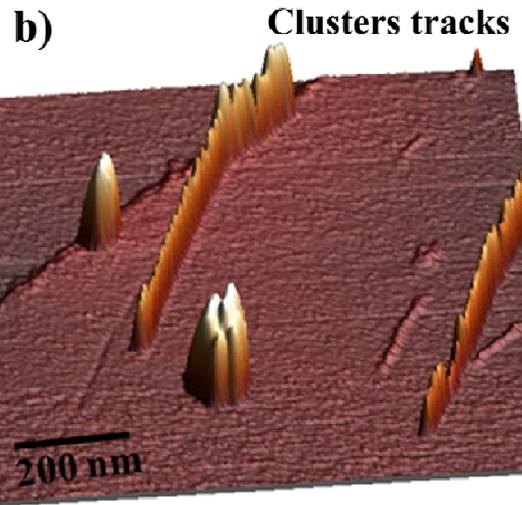
- G. Paolicelli *et al.* Appl. Phys. Lett. **95**, 143121 (2009)
- A. Rao, *et al.* Nanotechnology **20**, 115706 (2009)
- G. Paolicelli *et al.* J.Phys.:Condens. Matter **20**, 354011 (2008)
- K. Mougín *et al.* Langmuir, **24**, 1577 (2008)
- C. Ritter *et al.* Phys. Rev. B **71**, 085405 (2005)

cluster –substrate properties

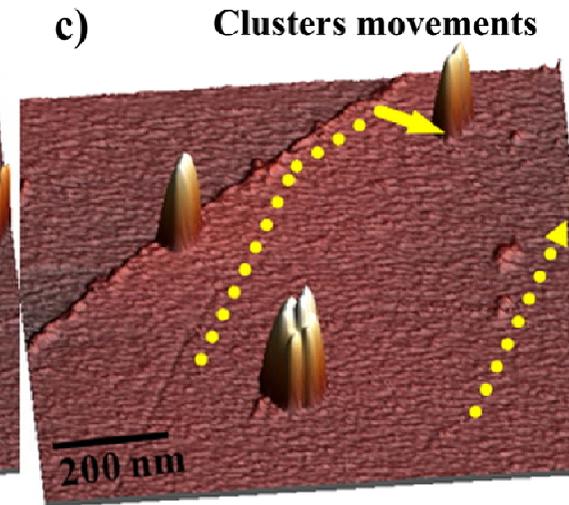
NP 24



Initial imaging $A_0 = 23,4 \text{ nm}$



Manipulation $A_0 = 29.3 \text{ nm}$



Imaging $A_0 = 23.4 \text{ nm}$

Clusters initially sitting on a graphite step remain pinned on their positions

Typical behaviour of surface defects

Clusters move towards the slow scan direction by small steps

Clusters usually do not cross the steps and trajectories are modified on their proximity

We have found few large jumps

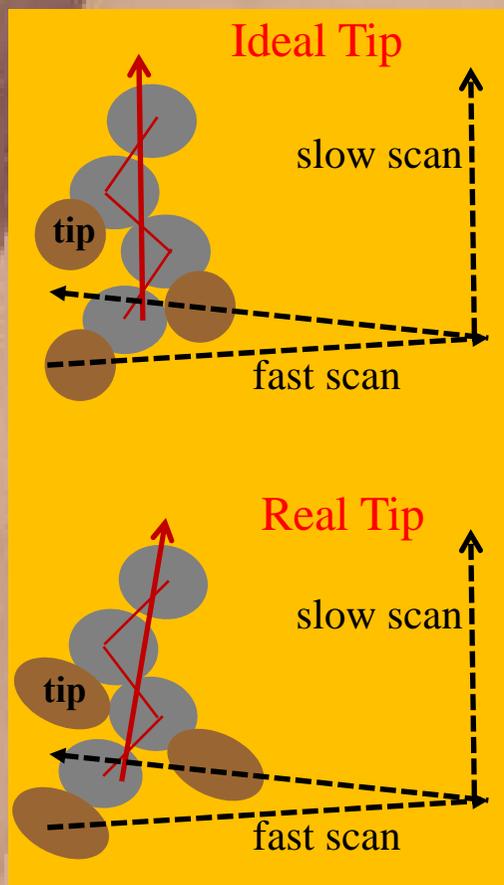
*Our results seem to agree with recent measurements by D. Dietzel et al. (Phys. Rev. Lett. **101**, 125505 (2008)) who observed, by contact AFM, superlubric translations of antimony island on HOPG graphite.*

Appl. Phys. Lett. **95**, 143121 (2009)

Interaction mechanisms ?

Quantitative measurements ?

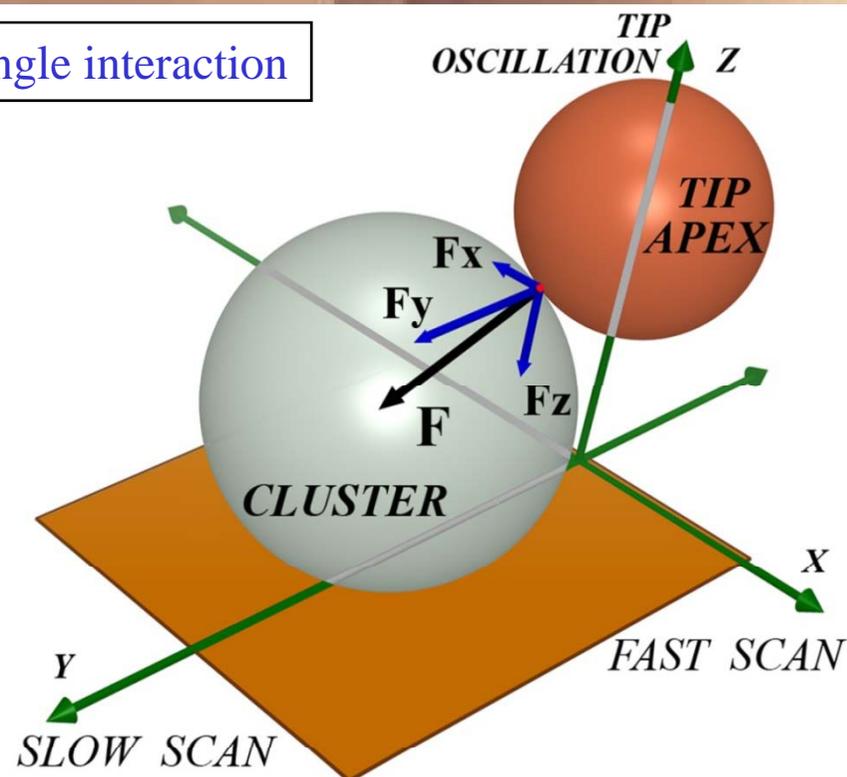
Trajectory



- Comparable tip and clusters dimensions
- Scan step smaller than tip and cluster diameter

A. Rao, E. Gnecco, D. Marchetto, K. Mougou, M. Schöenberger, S. Valeri, and E. Meyer
 Nanotechnology **20**, 115706 (2009)

Single interaction

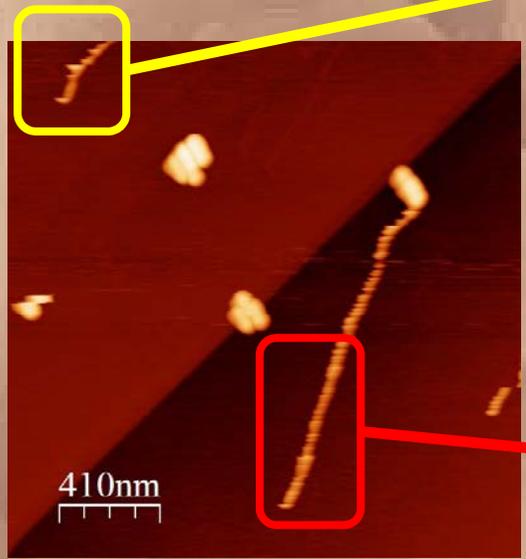
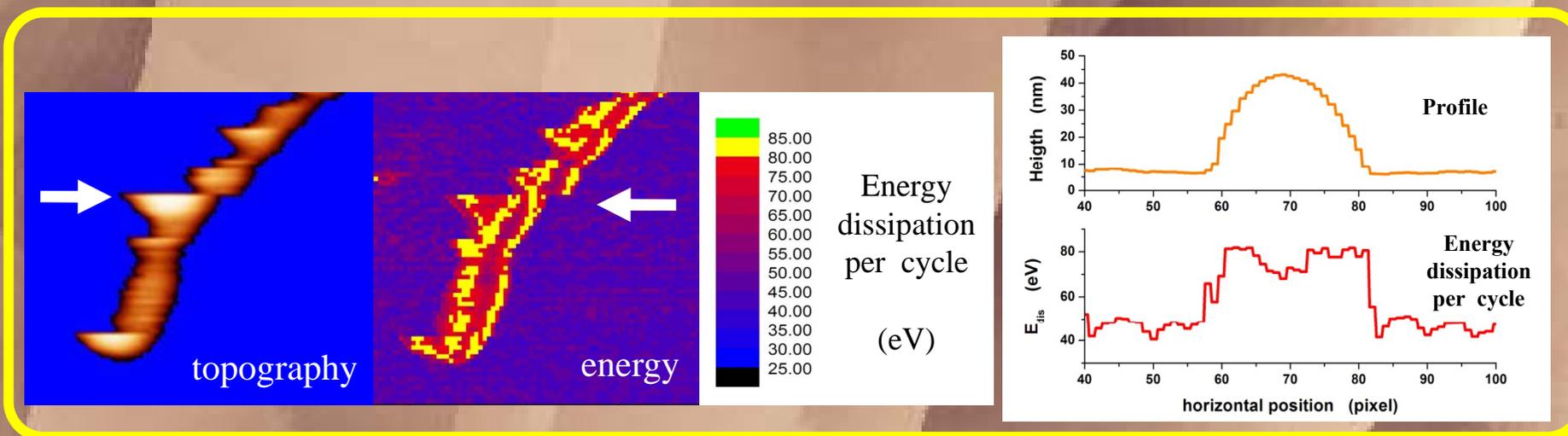


- Consider only the final repulsive force acting during the contact F
- Spherical shape for both the cluster and tip apex,

Then the force scheme becomes intrinsically anisotropic respect to the substrate surface normal and sensitive to the force components F_x, F_y coplanar to the graphite surface.

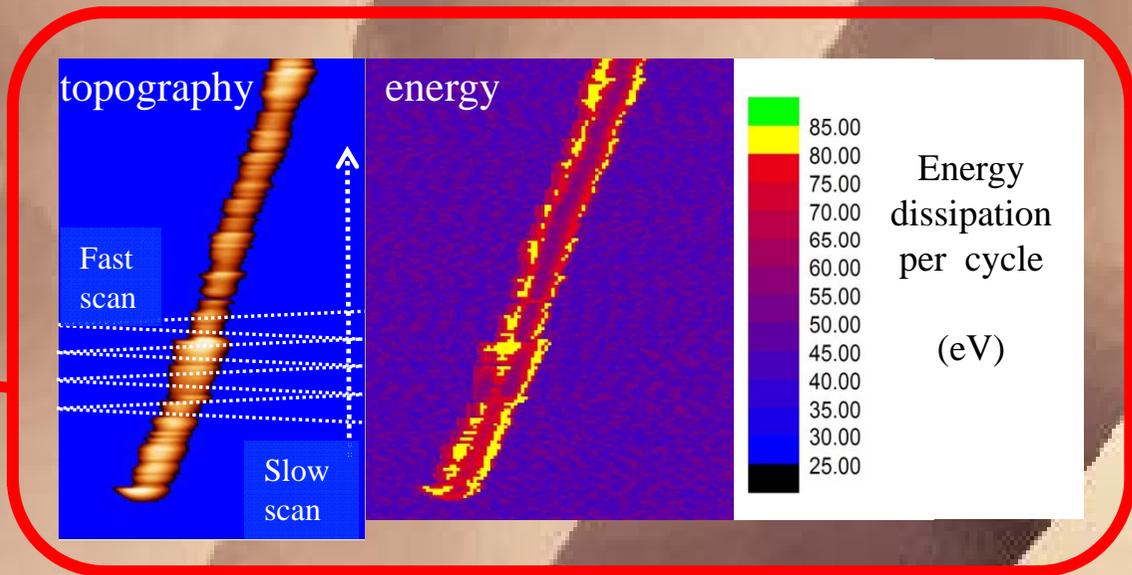
M. S. Marcus, R. W. Carpick, D. Y. Sasaki, and M. A. Eriksson,
 Phys. Rev. Lett. **88**, 226103 (2002).

D. A. Aruliah, M. H. Muser and U. D. Schwarz Phys. Rev. B **71**
 085406 (2005)



Manipulation scan
 $A_0 = 15 \text{ nm}$, $A = 10 \text{ nm}$

NP 42



Clusters detachments

We explore an equivalent area of about **10 μm^2**
 for **NP13**, **NP24** and **NP42** systems

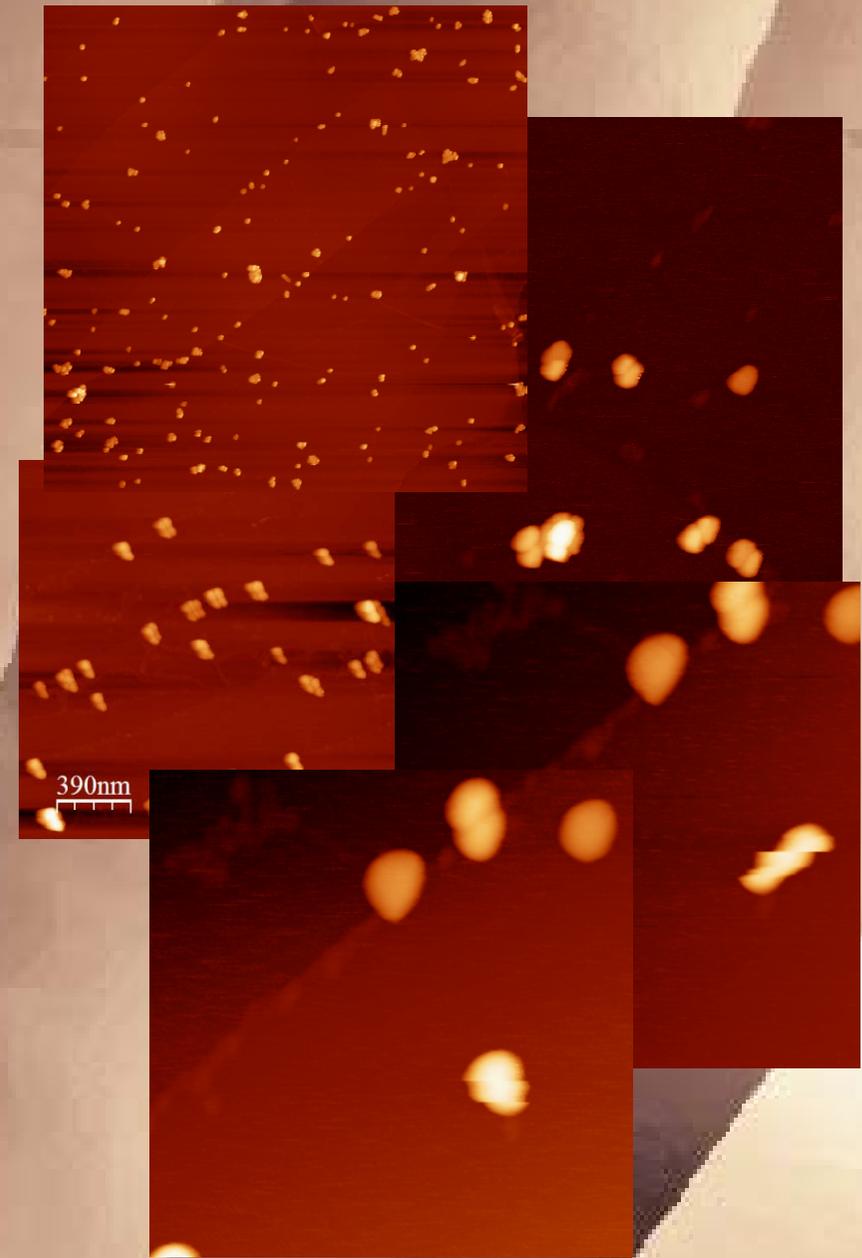
Each equivalent area contains a total amount of
 about
140 clusters.

About **18 different tips** were used each of them
 calibrated according to :
Sader et al. Rev. Sci. Instrum. 70 (1999) 3967

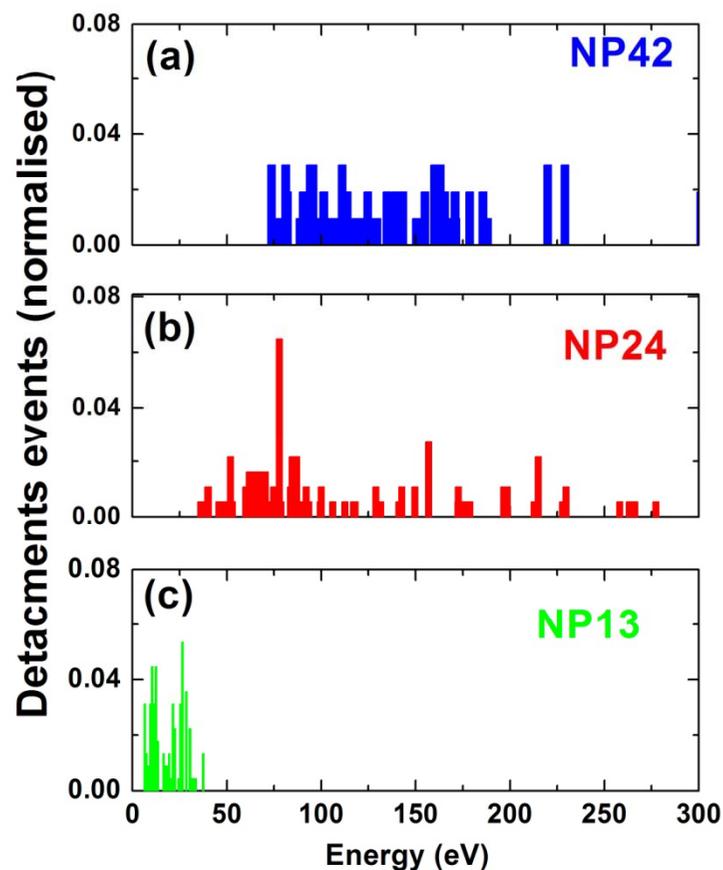
Two kinds of tips (*nominal values*) :

K=3 N/m f=75 kHz

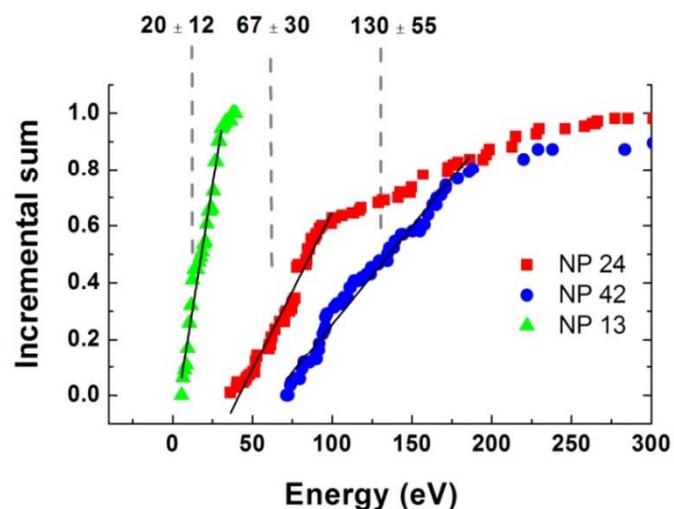
K=40 N/m f=300 kHz



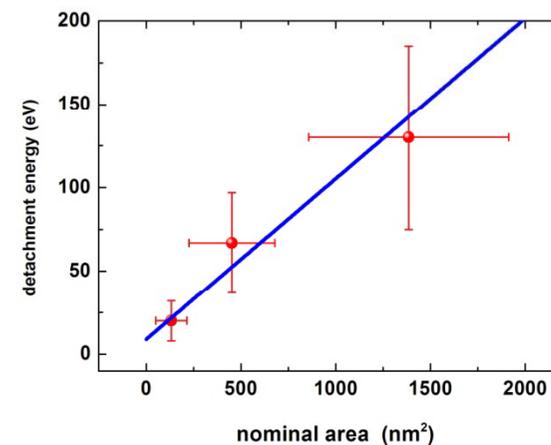
Clusters detachments



Panel (a), (b) and (c)
 Number of detachment events (normalized to the total number of single clusters) and their associated detachment energy sorted by increasing energy.

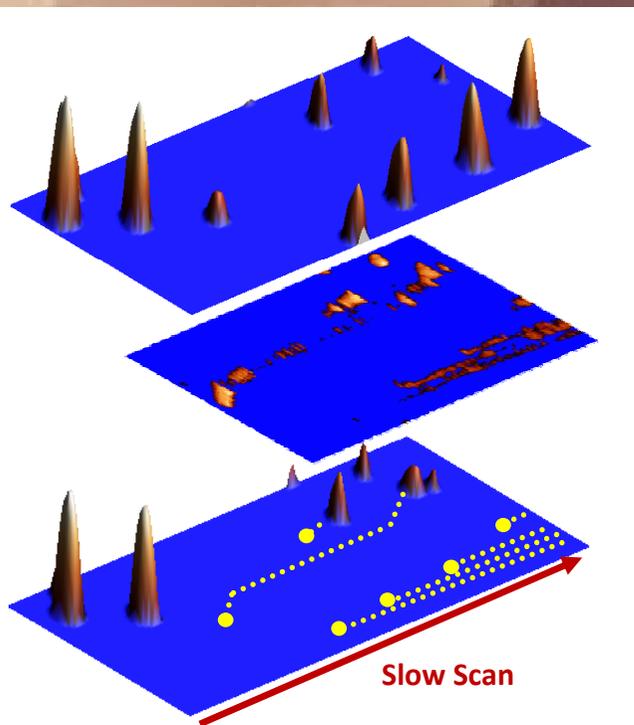
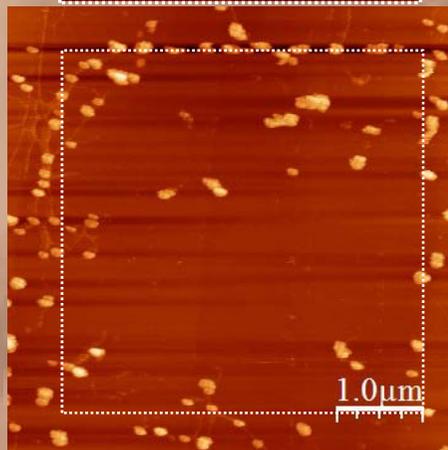
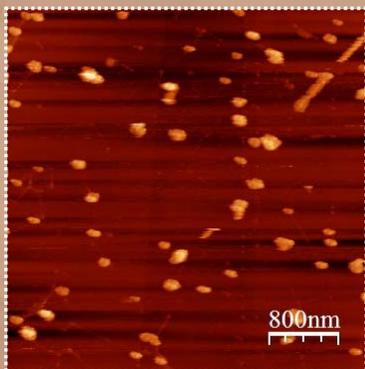


Incremental sum of detachments events. The linear increase represents regions where detachment occurrence has random uniform probability. Energy thresholds are located in the centre of these regions, while their width fix the maximum associated errors.



Clusters selection

Deposition of a suspension containing both 24 and 42 diameter particles obtained by stirring equal volumes of the two original liquids.

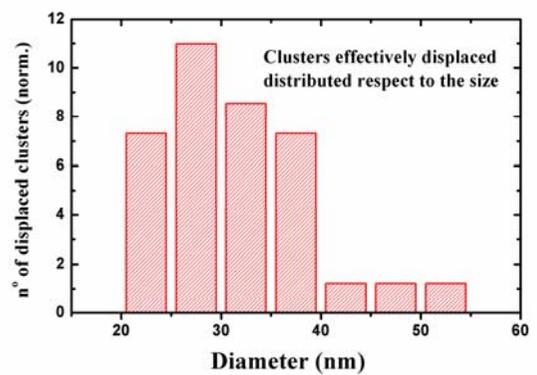


Initial : two **large clusters** , more than **40 nm high**, located on left corner plus eight **smaller clusters**, between **15 and 30 nm high**. Blue plane is a 10 nm cut-off introduced for graphical reason.

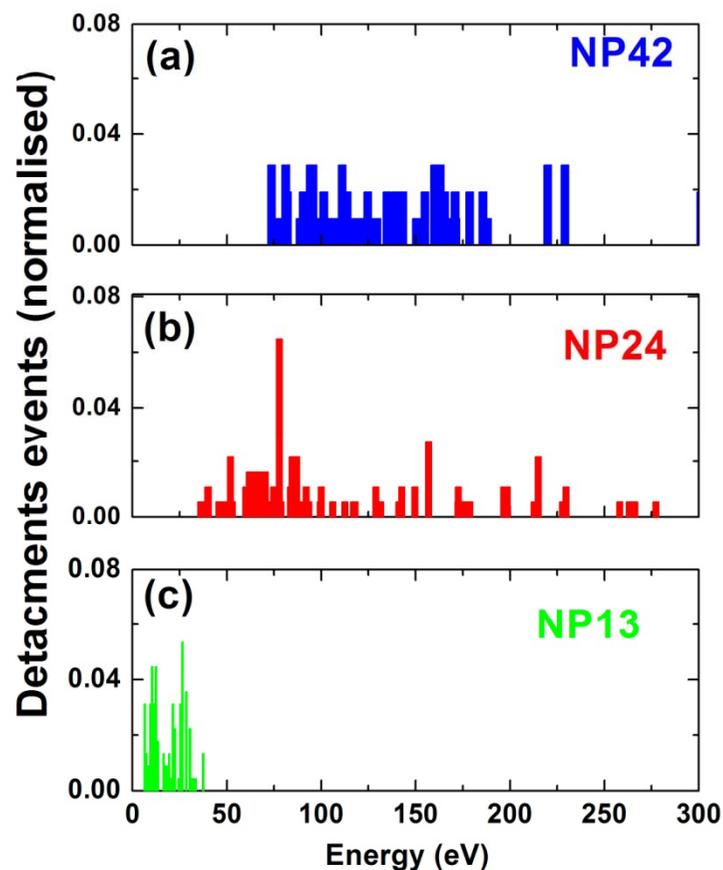
Central : clusters **movements**, induced using an oscillation energy just above the E_{24} detachment threshold, are shown in the central image.

Lower : the **selection effect** and the trajectories, deduced from the central image, aligned along the slow scan direction.

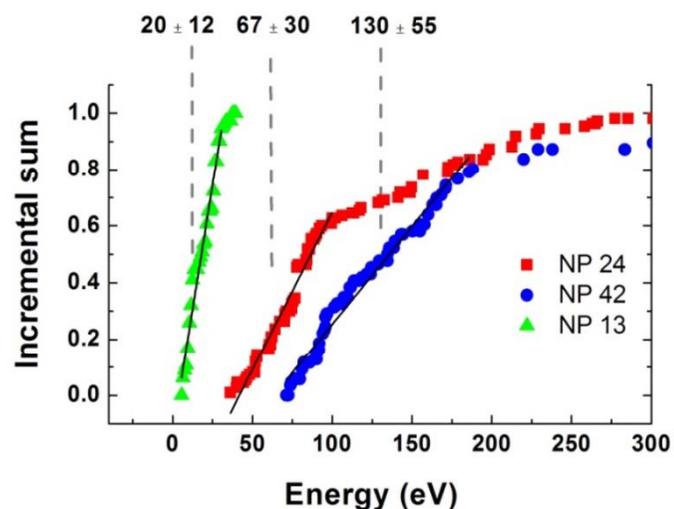
Appl. Phys. Lett. **95**, 143121 (2009)



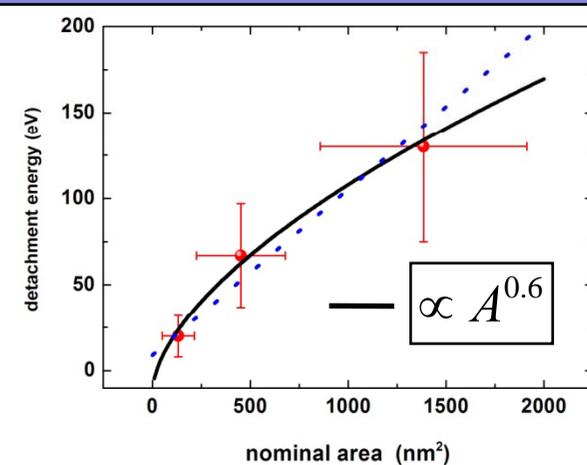
Clusters detachments



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 Number of detachment events (normalized to the total number of single clusters) and their associated detachment energy sorted by increasing energy.



Incremental sum of detachments events. The linear increase represents regions where detachment occurrence has random uniform probability. Energy thresholds are located in the centre of these regions, while their width fix the maximum associated errors.



Conclusions

• Nanotribology :

Different effects governing nanoclusters forced trajectories can be evaluated and measured using the **AFM with Amplitude Modulation feedback and monitoring the phase shift signal.**

Localised high friction areas like the graphite steps or preferred sliding directions are put in evidence by trajectories analysis.

The method we present allow to distinguish and **measure the energy detachment threshold** for cluster size down to the tenth-nanometer scale.

Results are in qualitative agreement with those of D.Dietzel *et al* (PRL.101 (2008) 125505) but represent a step forward to the direction of measuring nanometer mechanical properties because the corresponding contact areas are two order of magnitude smaller.

• Controlled movements :

Two different gold nanocluster sizes, 24 ± 3 and 42 ± 4 nm of diameters respectively, deposited on HOPG graphite, have been **selectively detached and moved** in a controlled way using the **AFM with Amplitude Modulation feedback.**

Control is obtained by tuning the interaction strength between the oscillating tip and clusters. This parameter can be continuously adjusted **varying the amplitude oscillations and monitoring the phase shift signal.**

The existence of a **unique controlling parameter, expressed in terms of energy**, is the key point of this method and allow very reproducible and easily exportable results.

Acknowledgements

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- **Luca Marzani**

- **Luca Incerti**

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Institutions

CNR-INFM, S3 National Research Center on nanoStructures and bioSystem at Surfaces



Dipartimento di Fisica,
Università di Modena e Reggio Emilia



Project



Net-Lab *SUP&RMAN*



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