Nanotubes & Nanostructures 2001

Laboratori Nazionali di Frascati - Frascati - Italy

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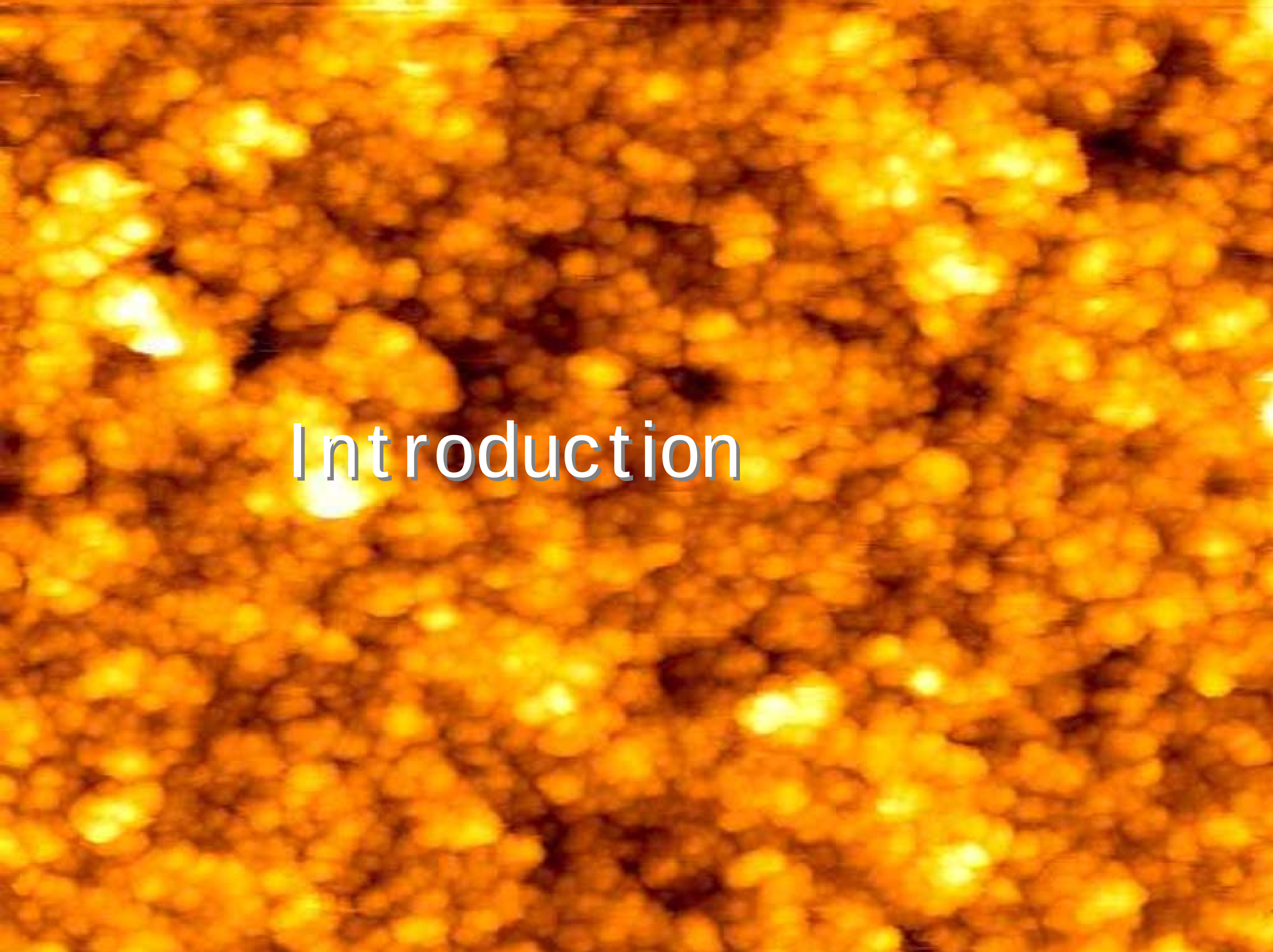
Ugo Valbusa (Dip.Fisica,Univ. Ge)
Valbusa@fisica.unige.it

Nanotribology of carbon based films

OUTLINE

- Introduction
- Nanostructured carbon films
- NCF friction and adhesion
- NCF mechanical properties
- Conclusions

Introduction



Macrotribology

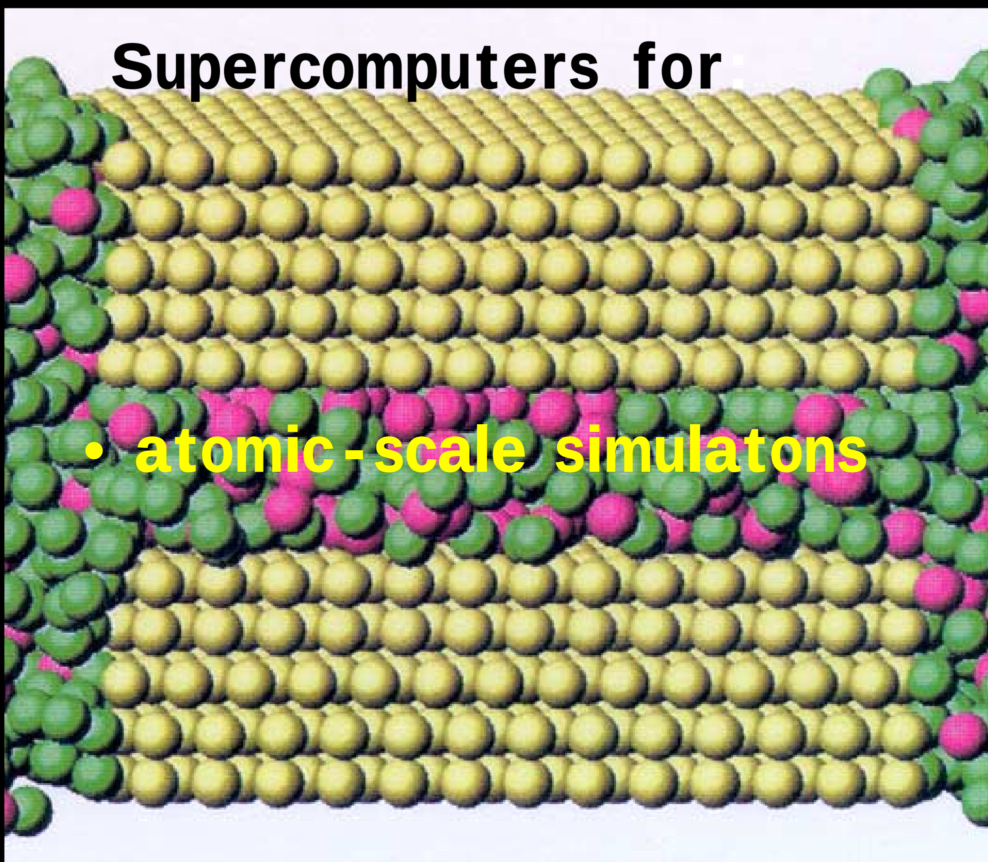
- Large mass (Gg,Mg)
- Heavy load (GN,MN)
- Wear
- Bulk

Micro/Nanotribology

- Small mass (μg,ng)
- Ligth load (μN,nN)
- No wear
- Surface

New techniques to measure:

- Surface topography
- Adhesion
- Friction
- Wear
- Lubricant film thickness
- Mechanical properties
- Lubricant molecules



Supercomputers for:

- atomic-scale simulatons

Tribology needs for future space and aeronautical systems

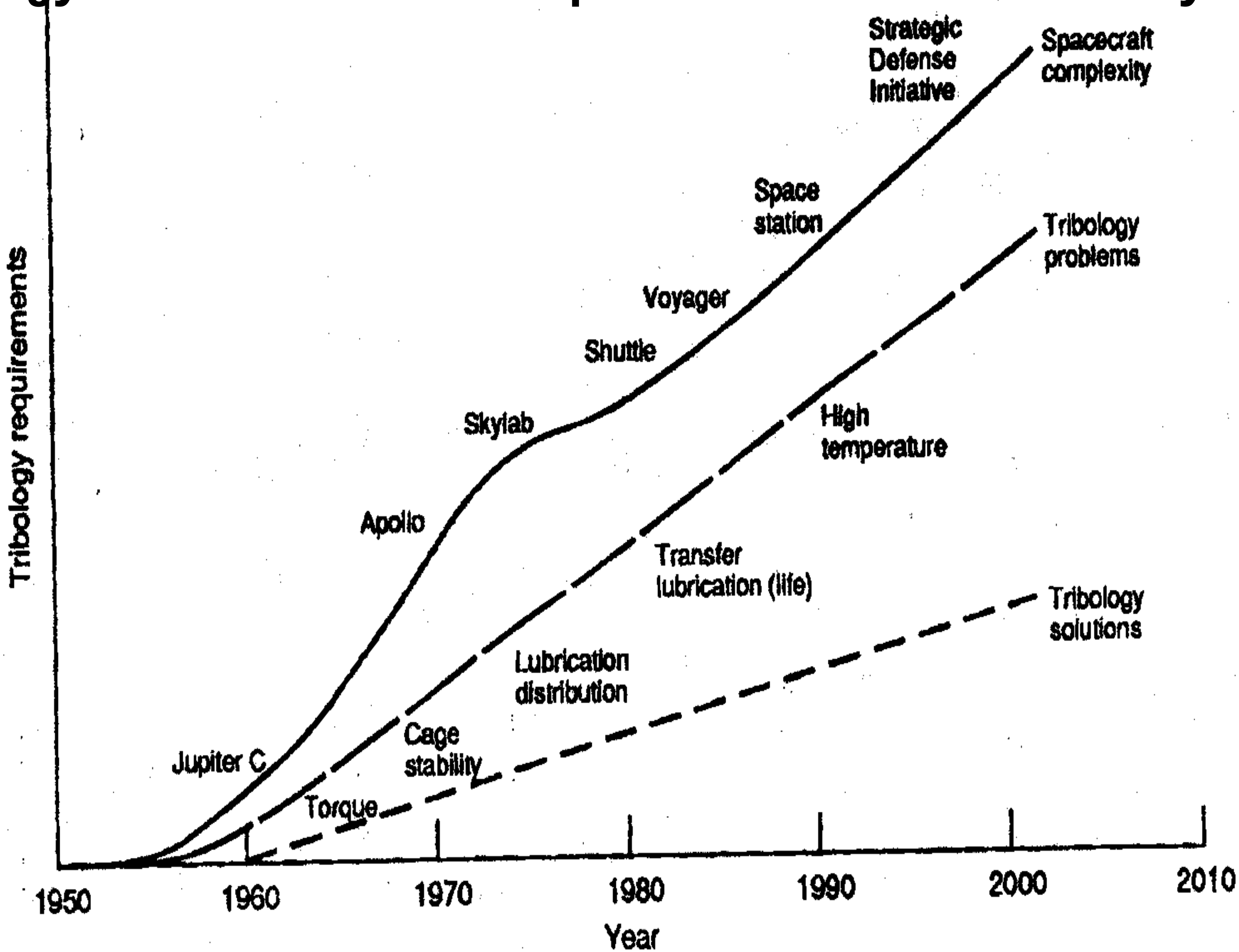
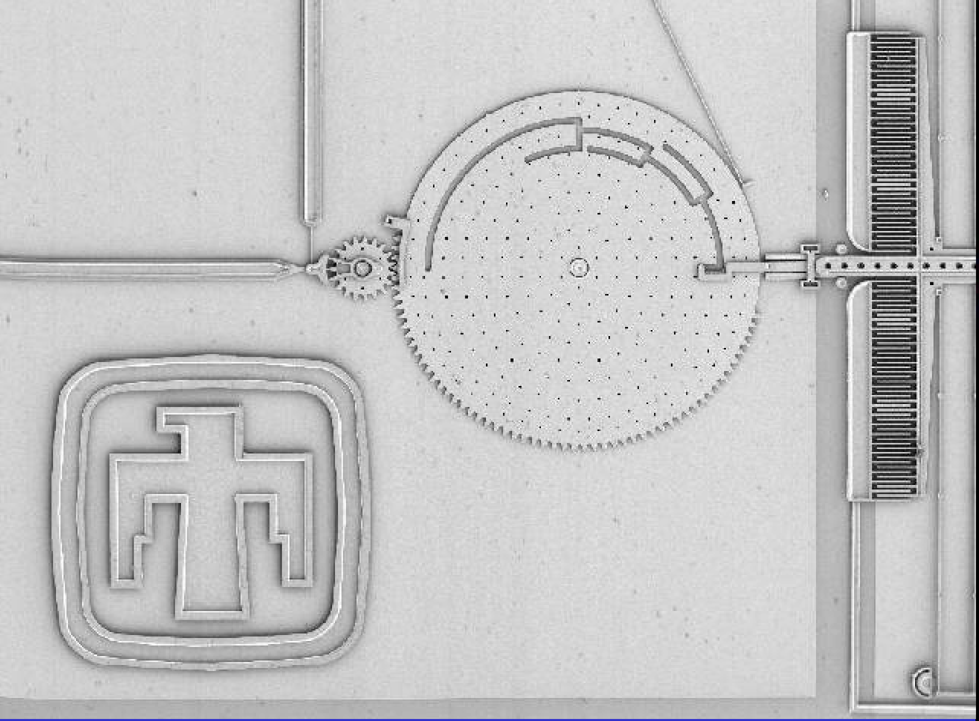


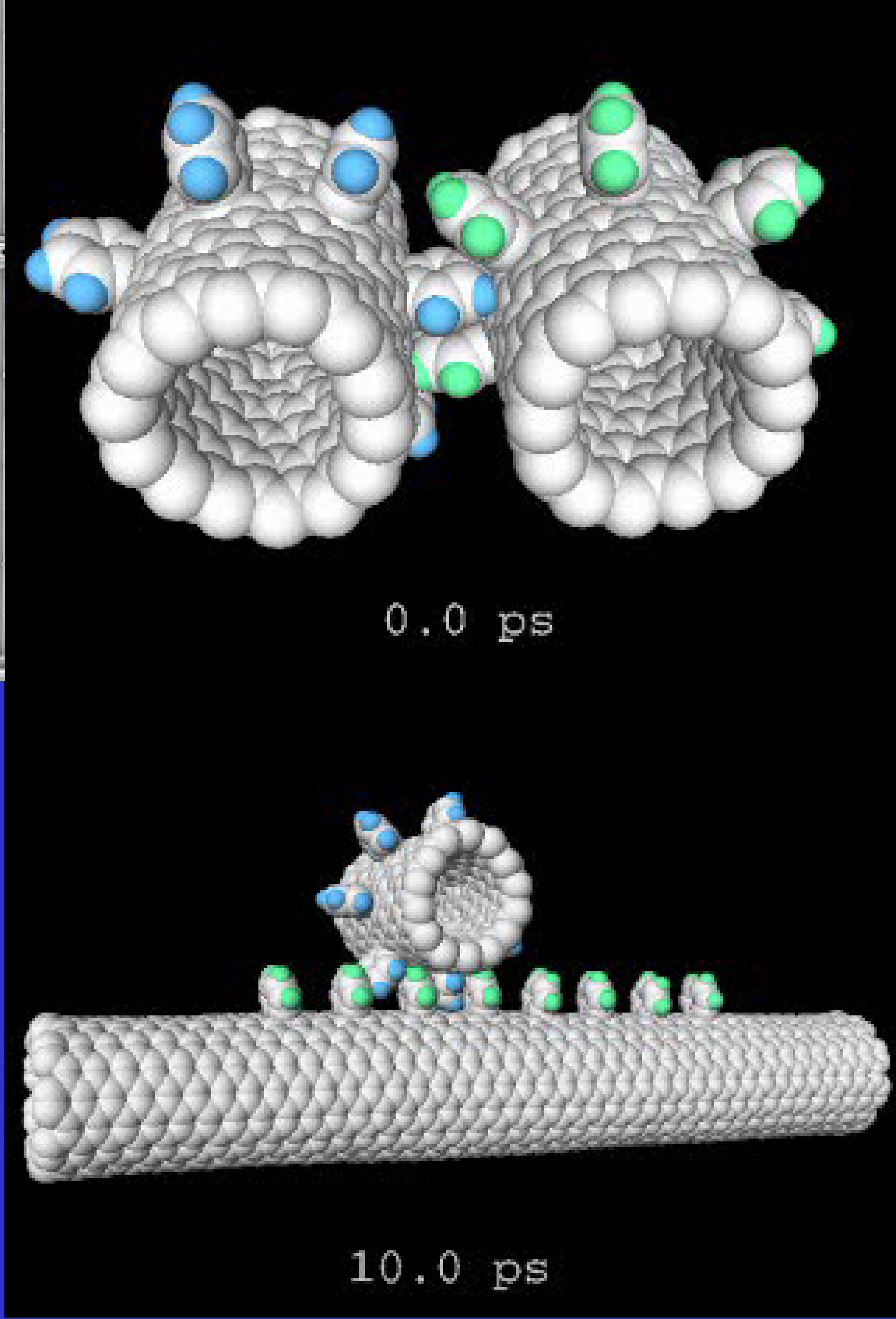
Fig. 5 Growth of tribology requirements with advances in space (Ref. 62).

R.Fusaro 1991NASA Technical Memorandum 104525

Problems & scientific challenges

- high temperatures
- low temperatures (-40°C aircraft flying at high altitude) (-170°C Mars, Moon)
- length of operation (up to 30 years)
- lubrication of vehicles and equipment's on Moon and Mars
- contamination or abrasion by dust
- ability to supply lubricant to the contact areas
- degradation due to atomic oxygen and radiation
- lack of oxygen in space





MEMS

NEMS

New materials

New methods for measuring friction at nanometer scale

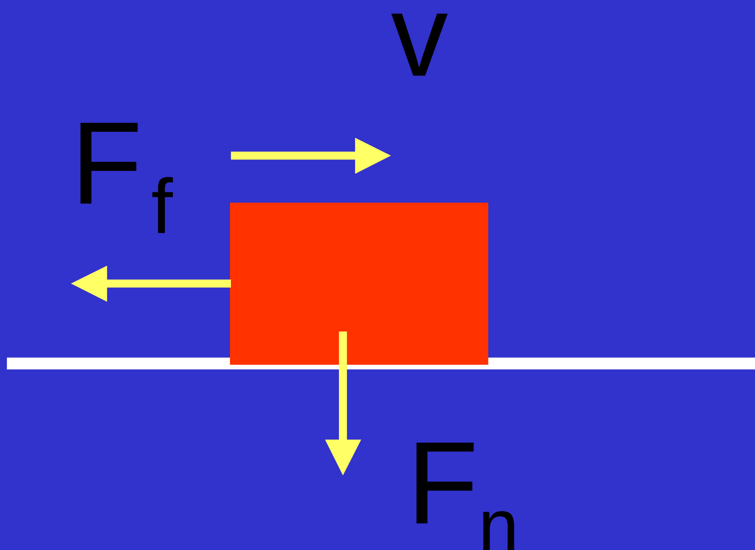
New methods for measuring mechanical properties at nanometer scale

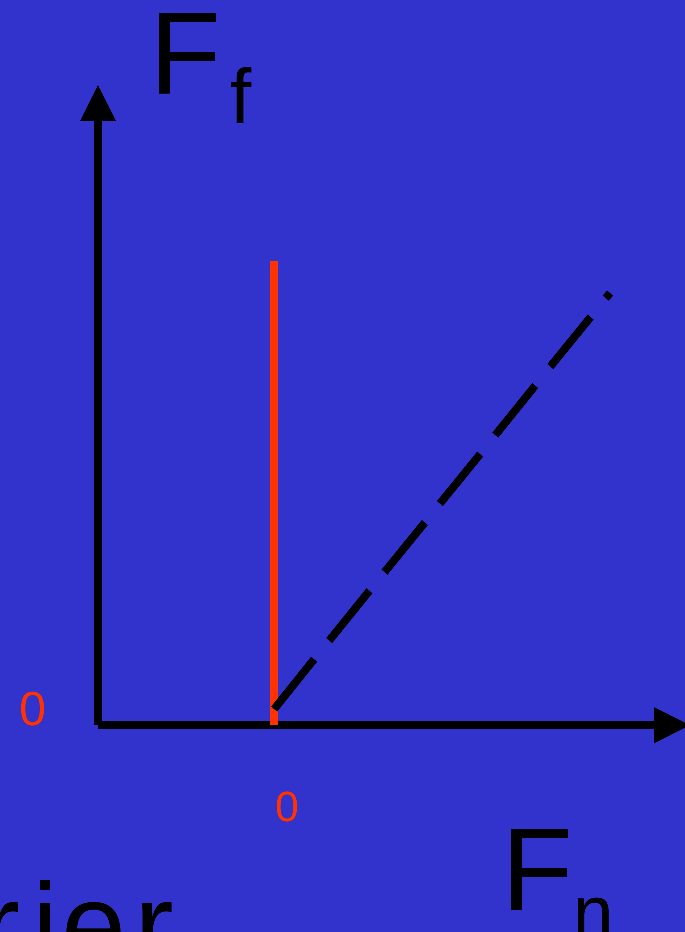
ns-C Preparation

ns-C are formed *via* cluster deposition, not *via* atom-by-atom deposition.

Adhesion/friction Macroscopic scale

Slope µ
Friction coefficient

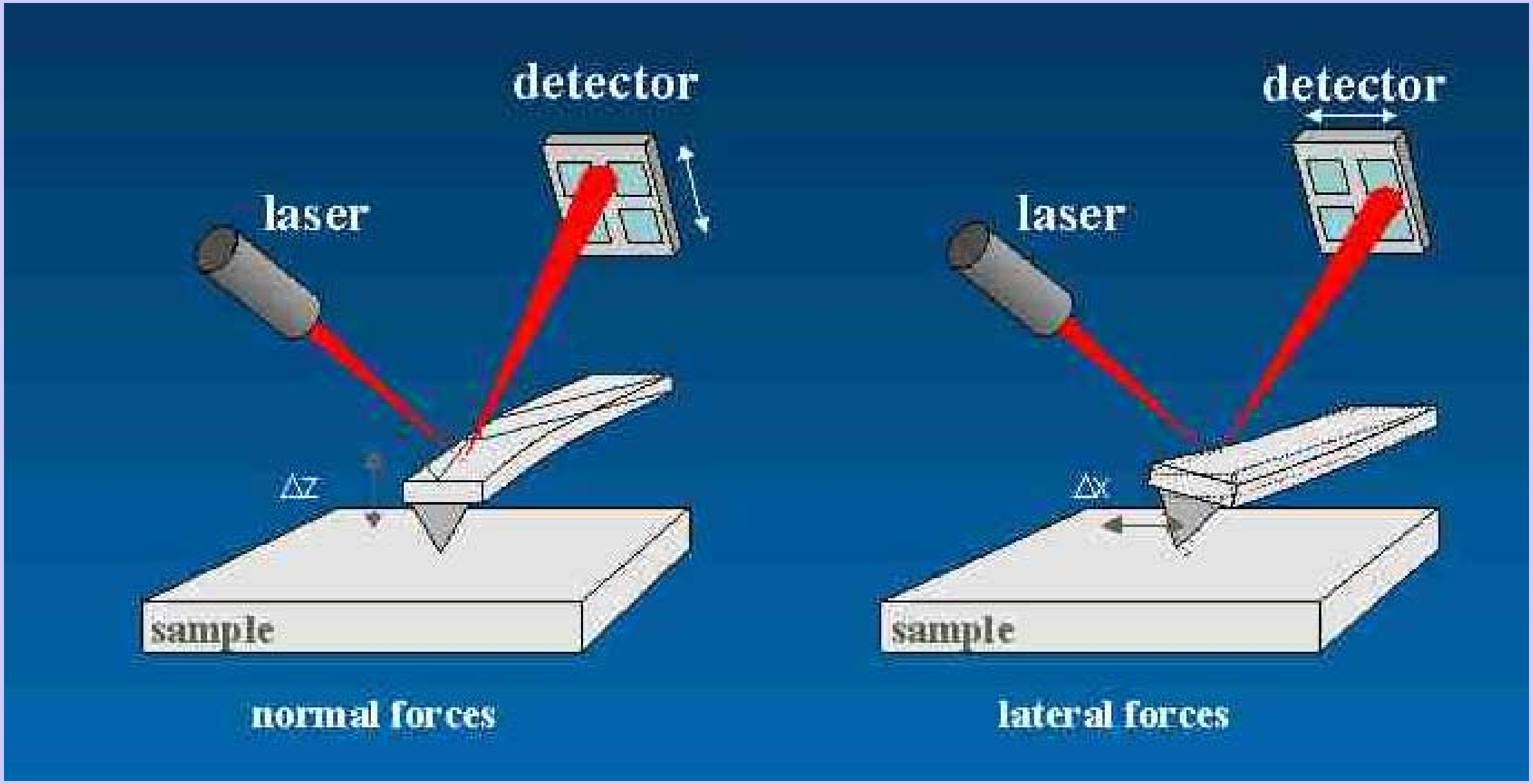




N&N2001 J.Chevrier

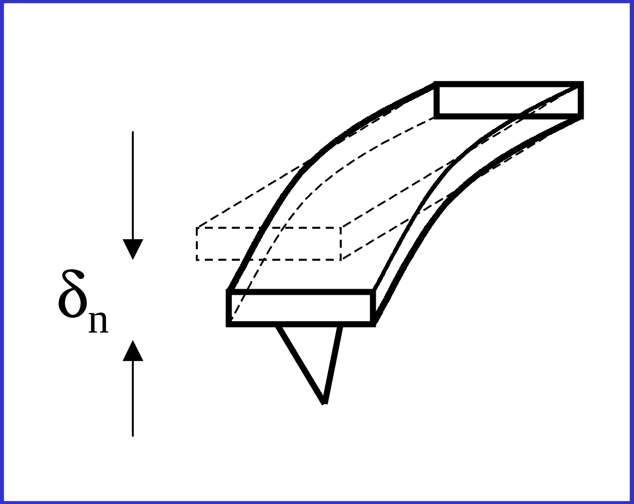
Friction measurements at the nanometer scale

Friction Force Microscope is an ideal instrument to study tribological properties at nanometric scale

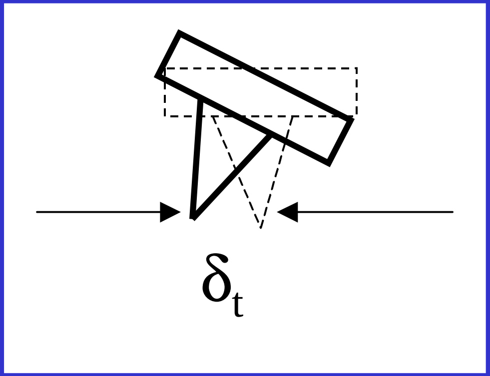


G. Mayer, N. M. Amer *Appl. Phys. Lett. 53, 1045 (1988)*

Friction/adhesion Nanoscale



Quantities measured in FFM experiments

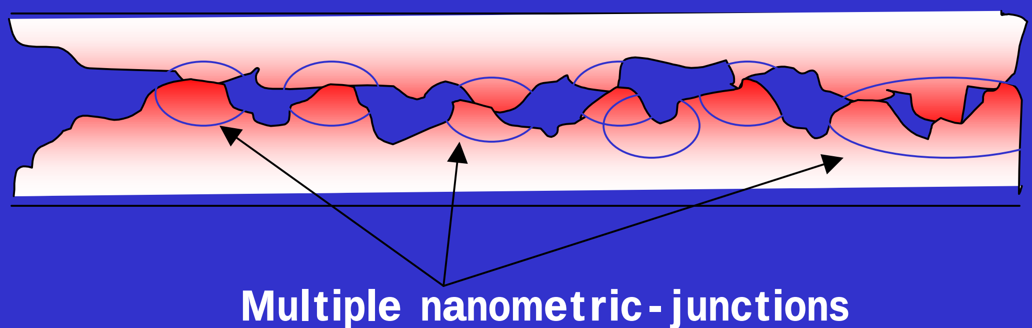


$$c_n = \frac{E}{4}\frac{wt^3}{L^3} \qquad c_{tor} = \frac{G}{3}\frac{wt^3}{Lh^2}$$

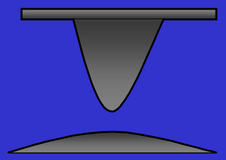
$$F_n = c_n \delta_n \qquad F_{lat} = \frac{3}{2} c_{tor} \frac{h}{L} \delta_t$$

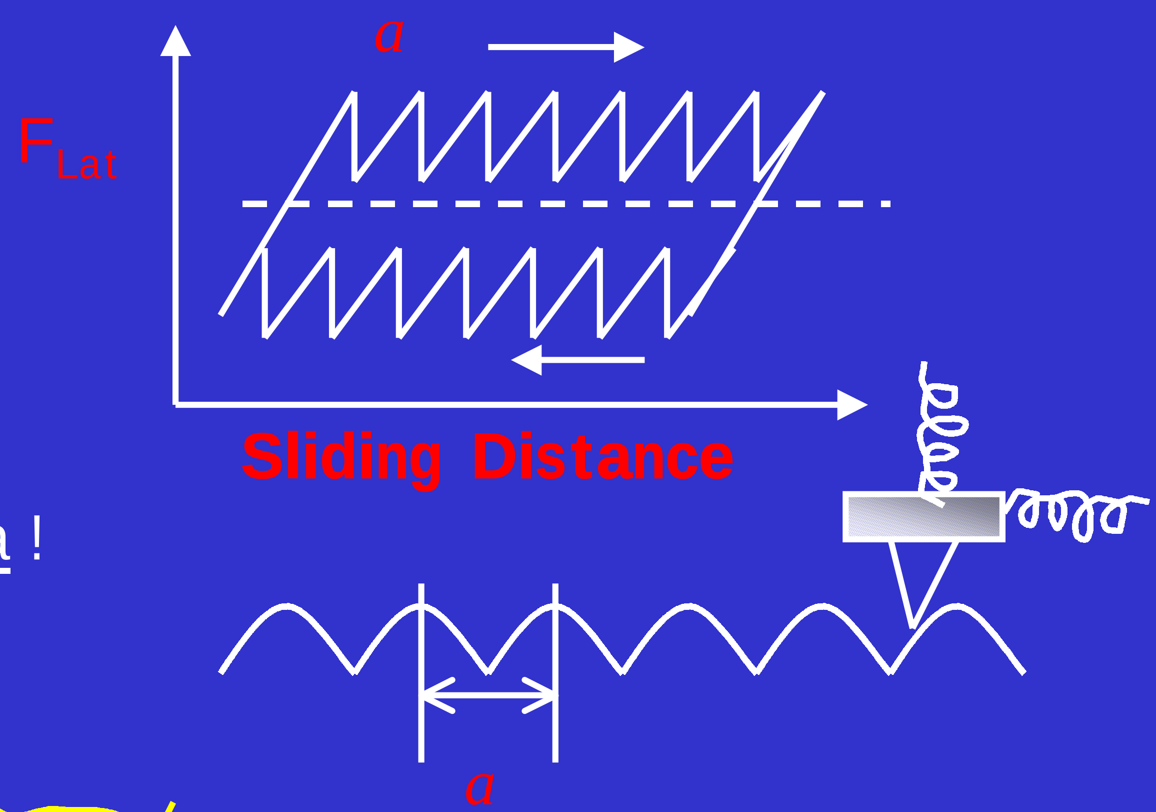
Macro vs Nano friction

Multi-asperity contacts: macro-world…the number of junctions increases on increasing load

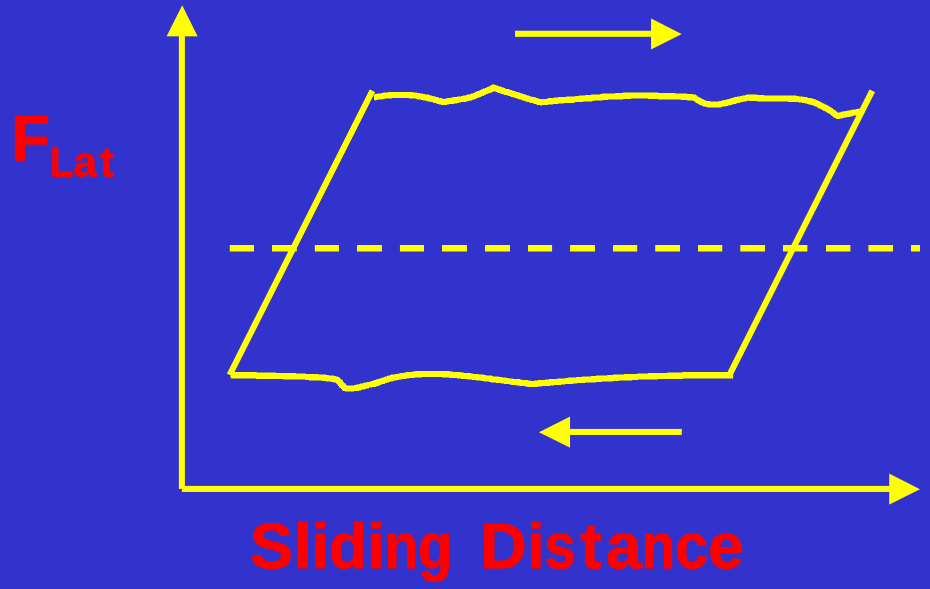


Single-asperity contact: nano-world ….. the area of the single contact increases on increasing load.

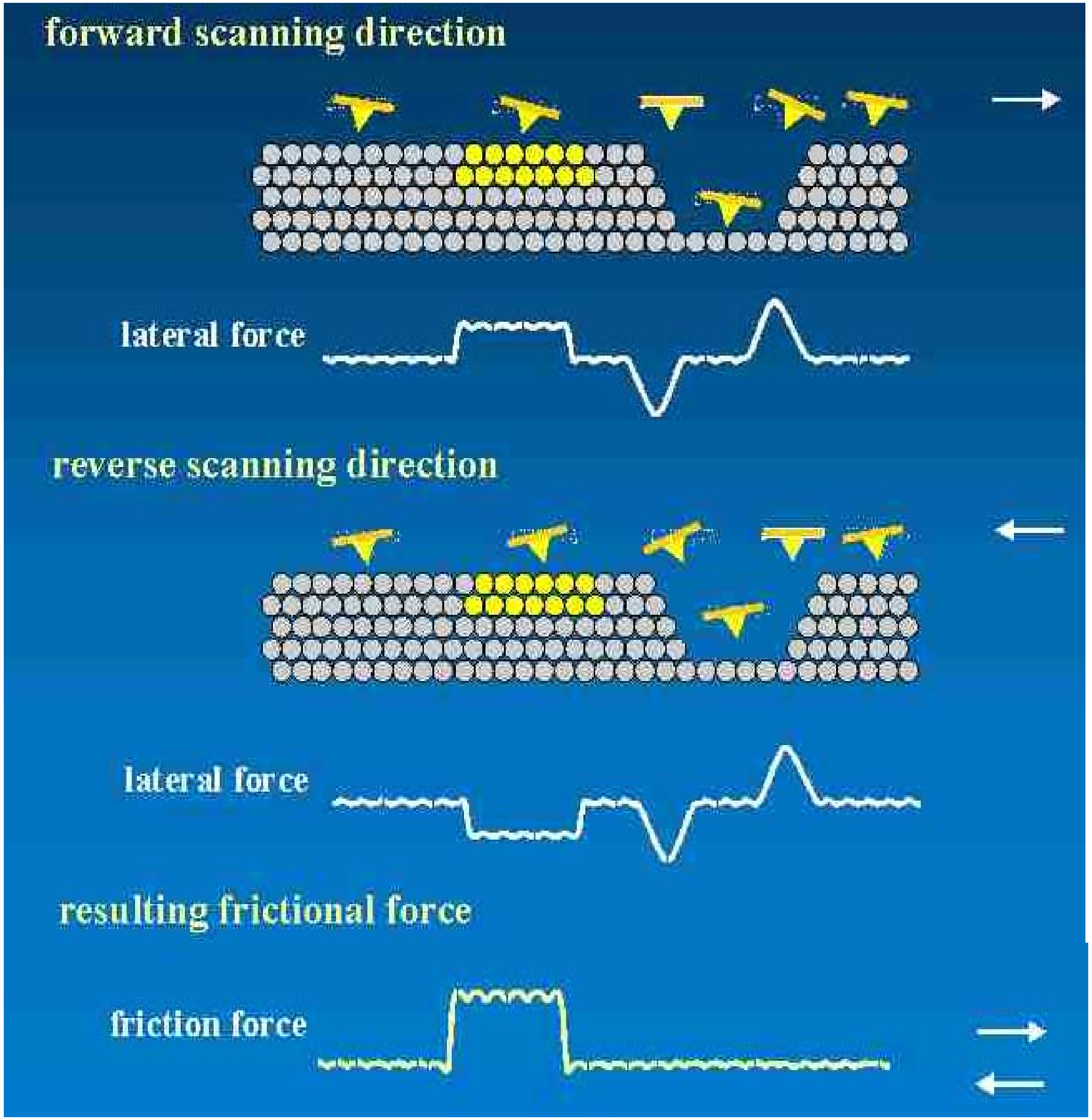




...but no information about <u>real contact area</u> !



Topographical effects on FFM measurements



Geometrical Effects

$$F_{Lat}^{Topo} \propto \frac{ds}{dx} F_{\perp}$$

$$F_{Lat}^{Friction} \propto \tau A \propto \tau \left(F_{\perp} + F_{off}\right)^{a}$$

Friction
(Bowden & Tabor)

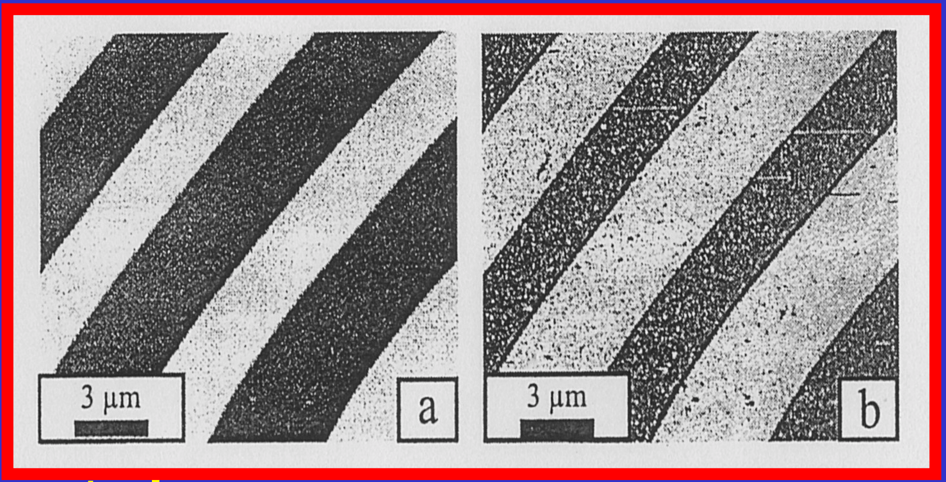
$a<1$

S.Sundararajan, B.Bhushan
J. Appl. Phys. 88, 4825 (2000)

Friction maps...FFM lateral resolution

Silicon oxides....Scandella et al. JVST B ***14****, 1255 (1989)*

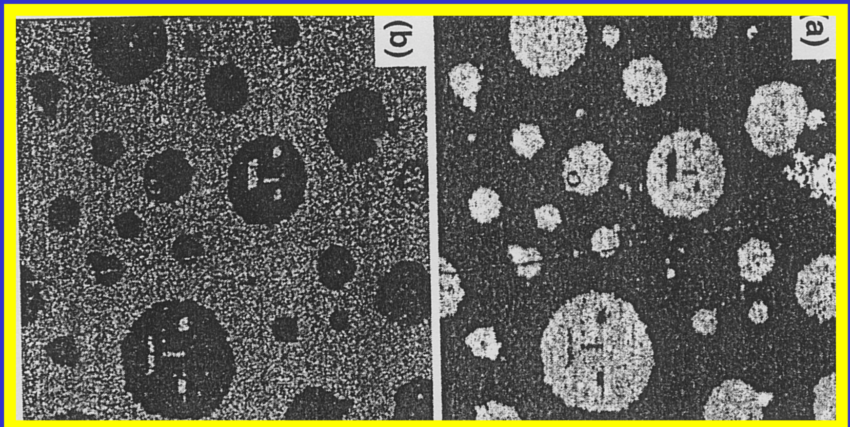
- Patterns di 150nm creati per fotolitografia su Si(110) ossidato SiO_2 chiaro, Si passivato ,scuro
- Immagine in lateral force, l' attrito è piu' alto nelle zone passivate



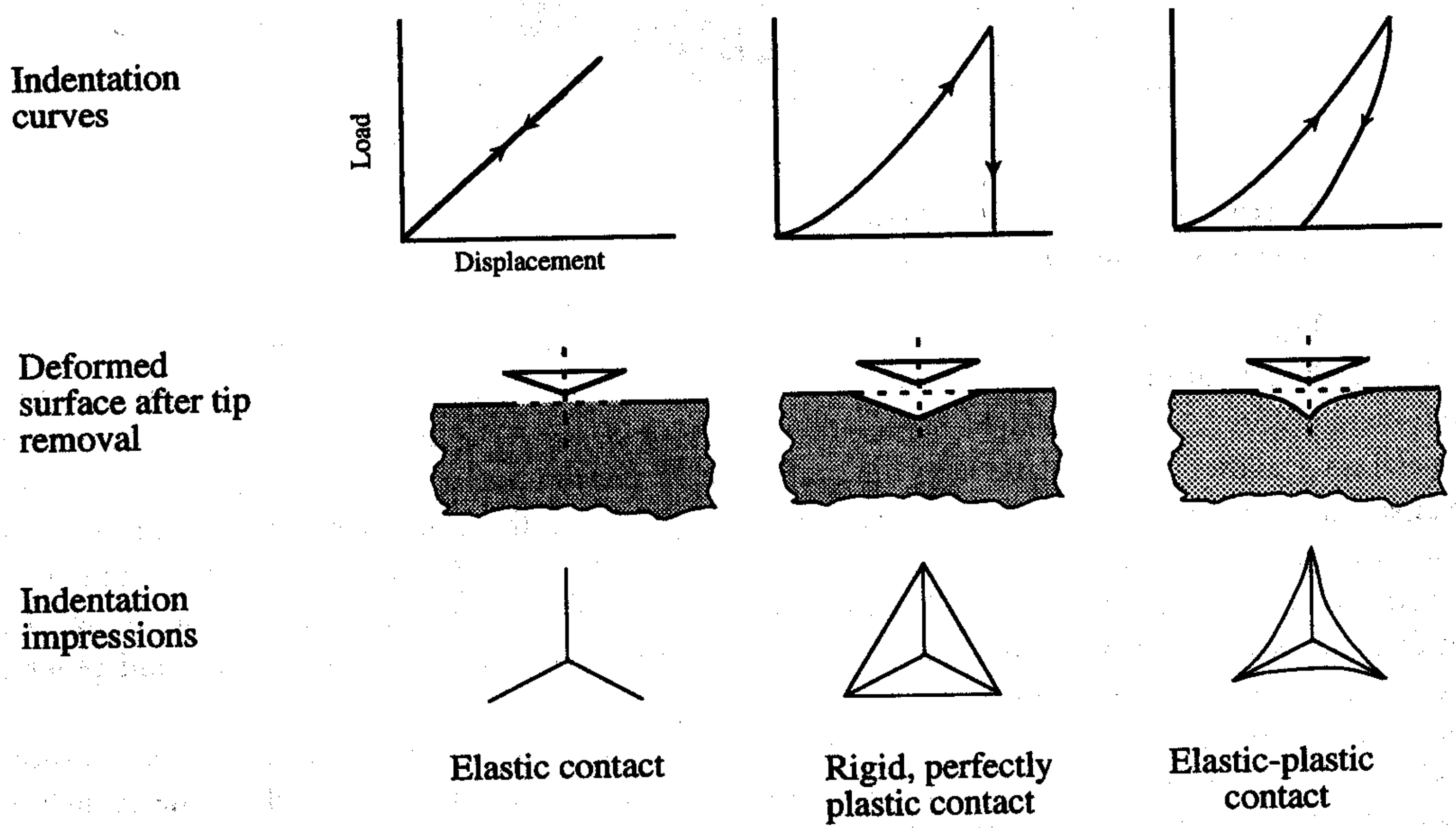
Langmuir-Blodgett films....Meyer et al.
Thin Solid Films 220, 132 (1992)

a) Immagine topografica che mostra come i domini degli idrocarburi (chiari) siano piu' alti del 'mare' di fluorocarburi.

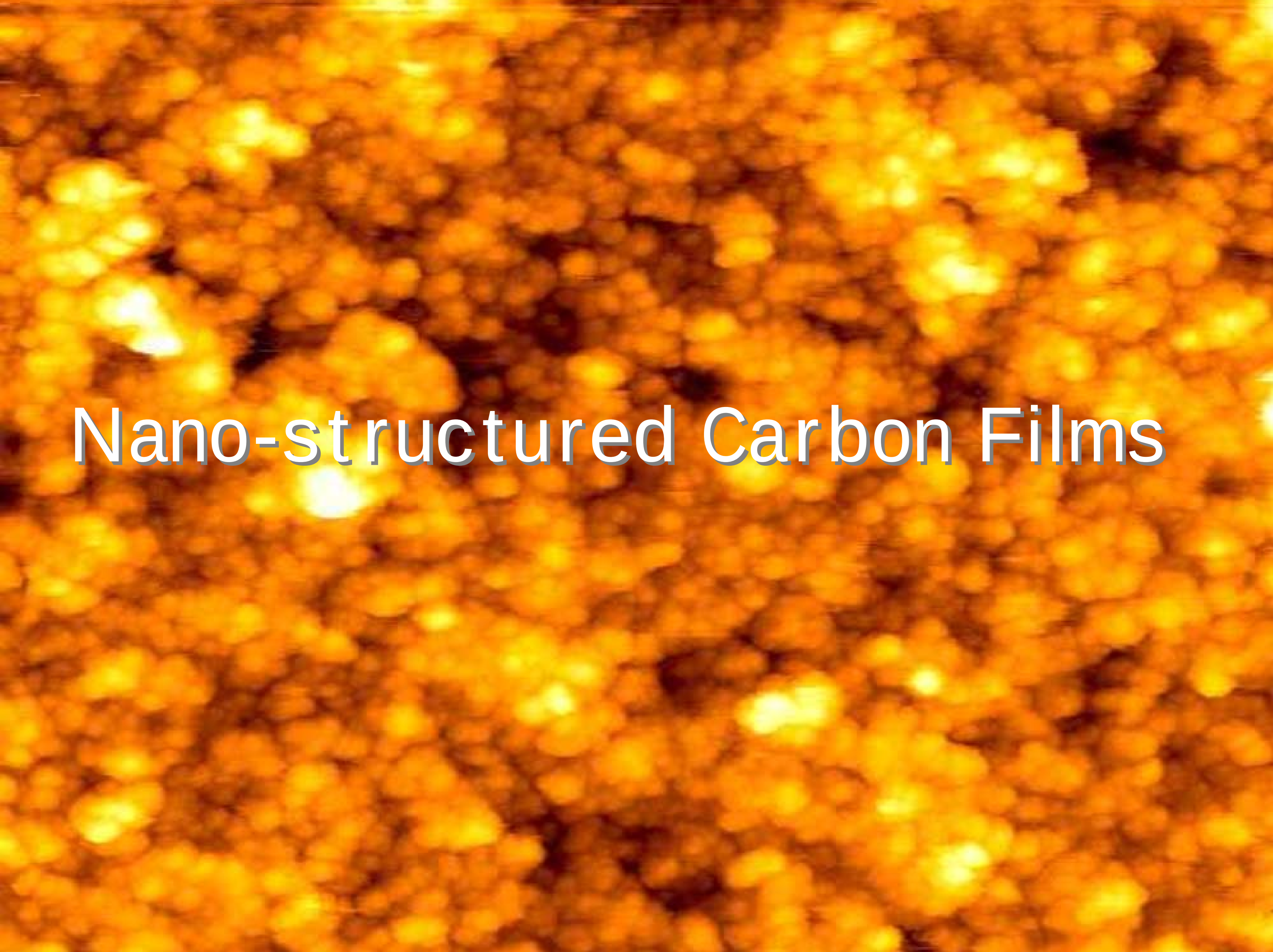
b) Lateral force mostra che gli idrocarburi hanno un attrito inferiore rispetto ai fluorocarburi.



Indentation curves

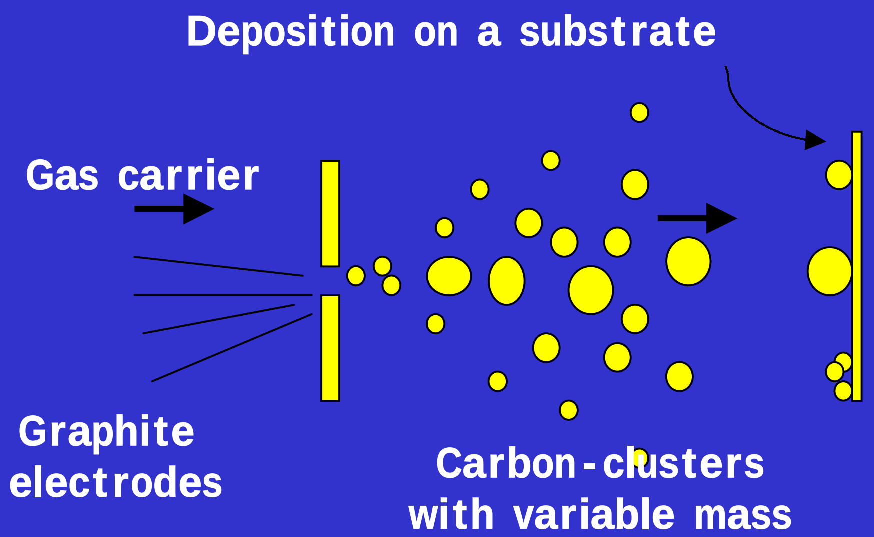


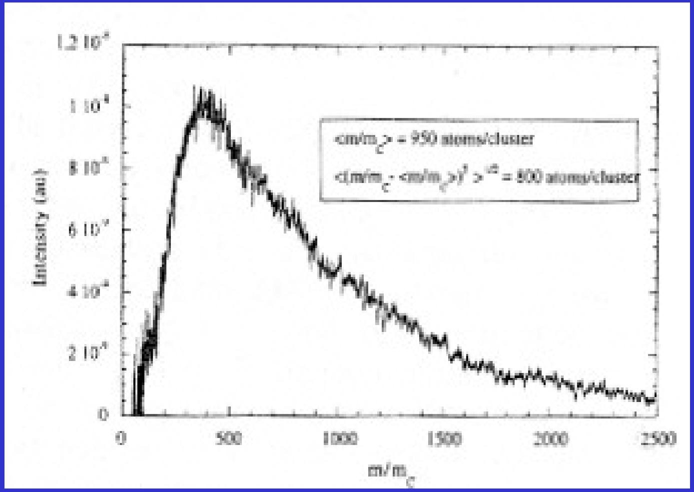
Nano-structured Carbon Films



ns-C Preparation

ns-C are formed *via* <u>cluster deposition</u>, not *via* atom-by-atom deposition.





P.Milani *et al. J. Appl. Phys.* ***82****, 5793 (1997)*

Surface morphology and mechanical properties depend on the nature of primeval clusters

NSCF have been produced by a micro-pulsed cluster beam source (P.Milani et al. Surface Sci.1998)

A. Libassi et al. / Surface Science 402–404 (1998) 441–444

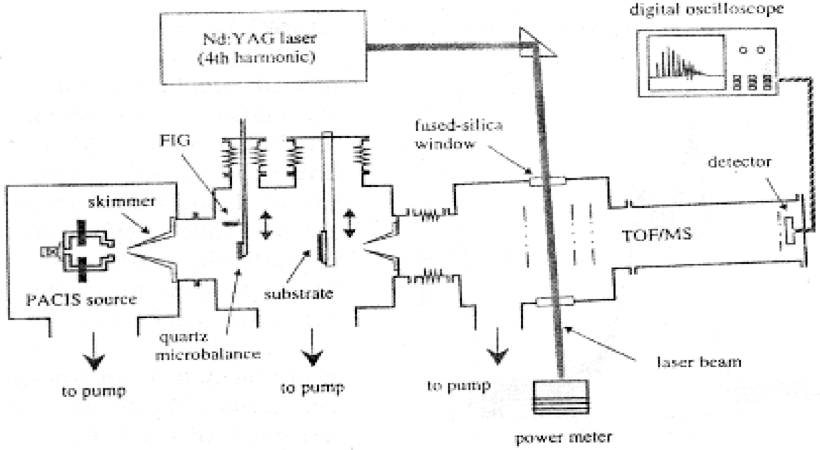
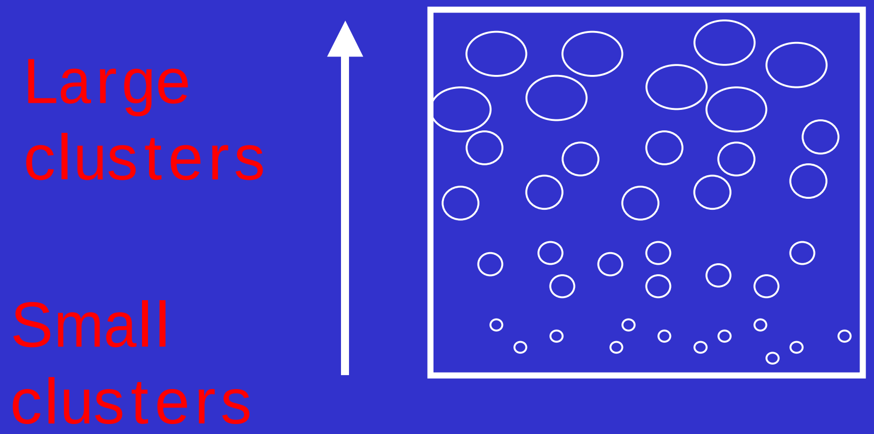
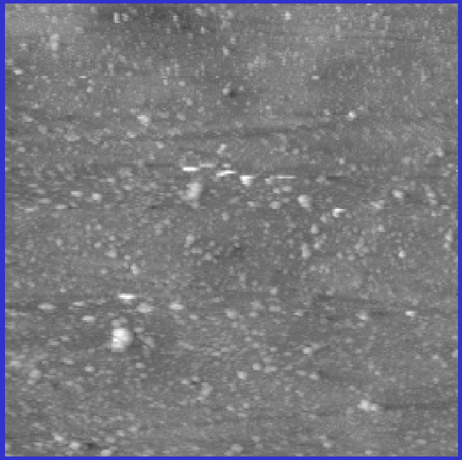


Fig. 1. Schematic view (not to scale) of the experimental apparatus used for thin film deposition.

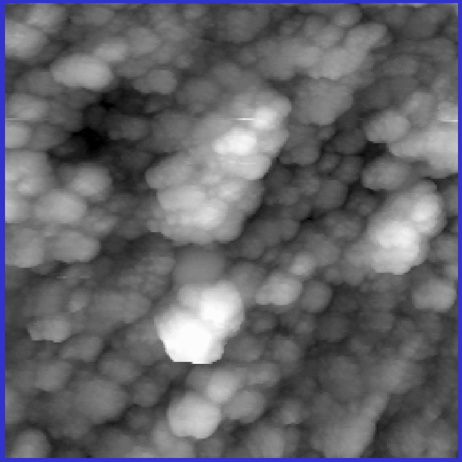
Samples having a gradient in the cluster size (dynamical focussing effect)



Samples with different thickness
-> for a constant flux, different deposition times

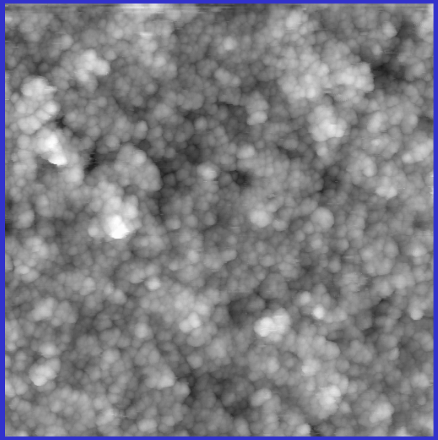


15 x 15 μm^2

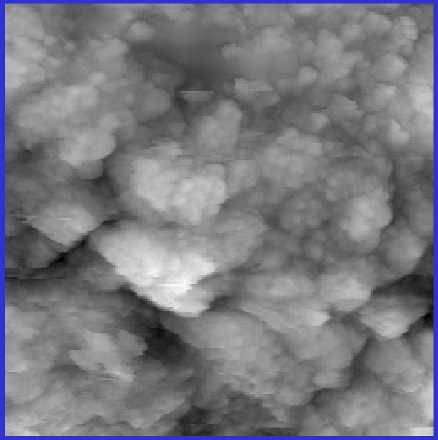


2.5 x 2.5 μm^2

Small clusters

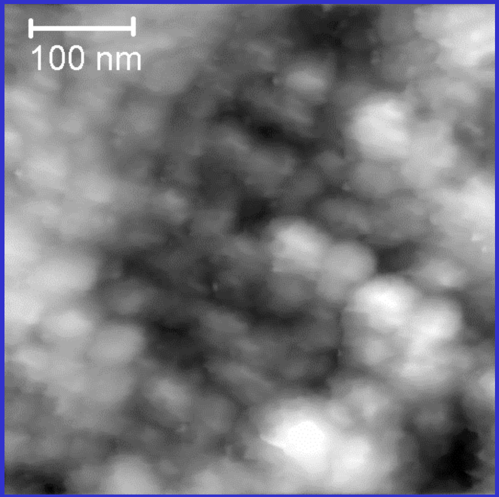


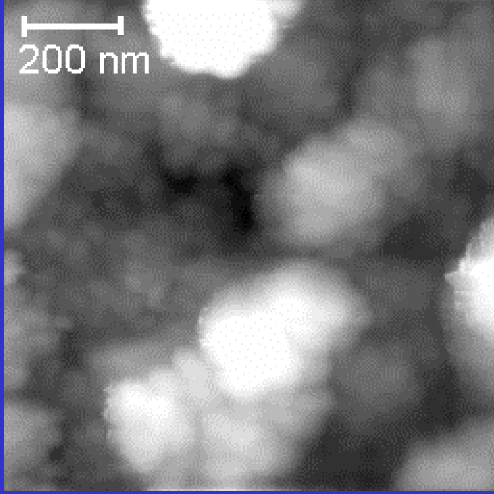
15 x 15 μm^2

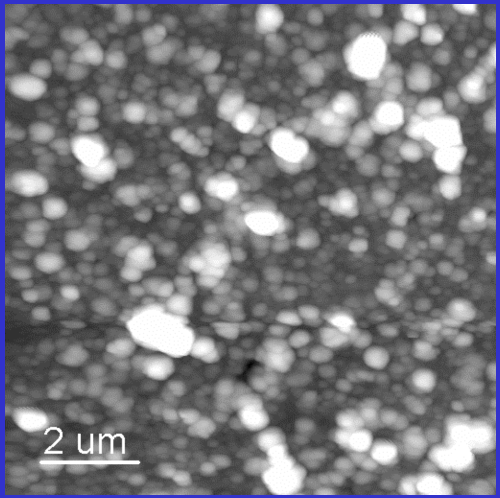


2.5 x 2.5 μm^2

Medium clusters







Big cluster

Morphological quantities

$$Height \quad of \quad the \quad interface \qquad z(\mathbf{r},t)$$

$$Mean \quad height \qquad \langle z(t,L)\rangle = \frac{1}{L^2}\int d\mathbf{r}\, z(\mathbf{r},t)$$

$$Roughness \qquad w(t,L) = \left\{ \frac{1}{L^2}\int d\mathbf{r}\left[z(\mathbf{r},t) - \langle z(t,L)\rangle\right]^2 \right\}^{1/2}$$

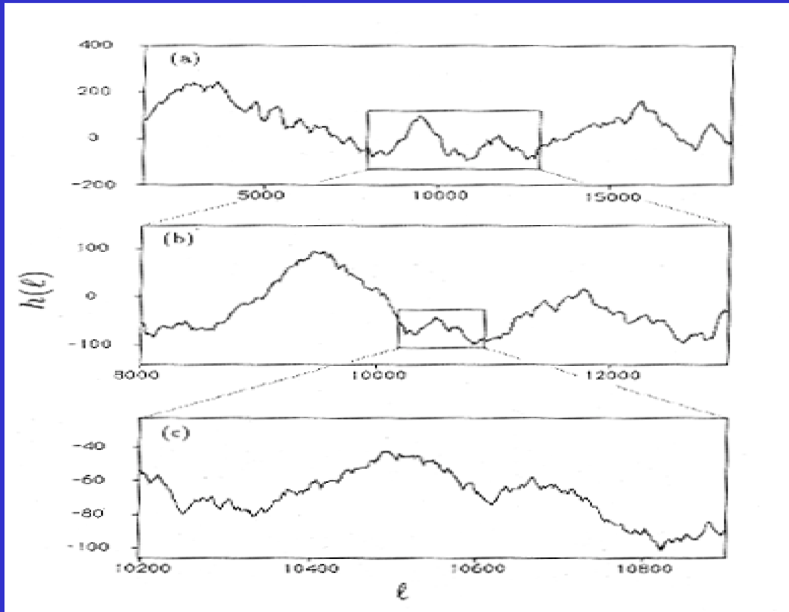
$$Height-Height \;\; Corr. \quad G(\mathbf{r},t) = \left\langle (z(\mathbf{r},t) - z(0,t))^2 \right\rangle$$

$$Lateral \;\; Correlation \;\; Lenght \qquad \xi$$

A self-similar interface is statistically invariant for isotropic scale transformations:

$$\text{If} \quad \mathbf{r}' = b\,\mathbf{r}$$
$$\text{then} \quad z' = b\,z$$

A self-affine interface is statistically invariant for anisotropic scale transformations:



$$\text{If} \quad \mathbf{r}' = b\,\mathbf{r}$$
$$\text{then} \quad z' = b^{\alpha}\,z$$

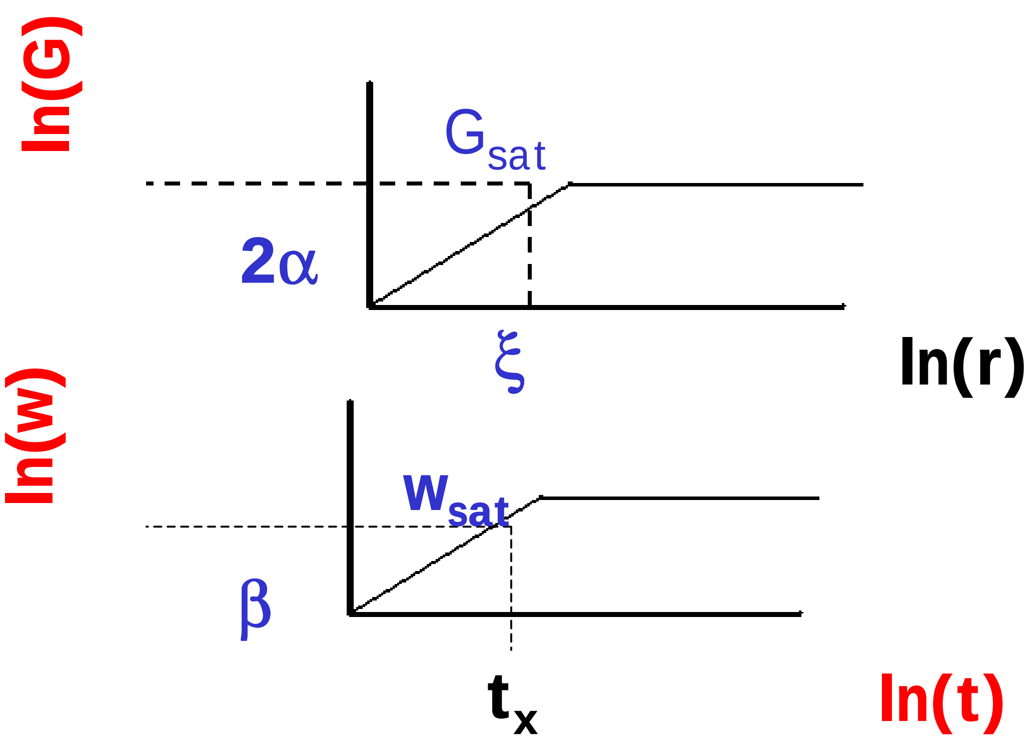
Self-affine interface and scaling laws

α is the roughness exponent

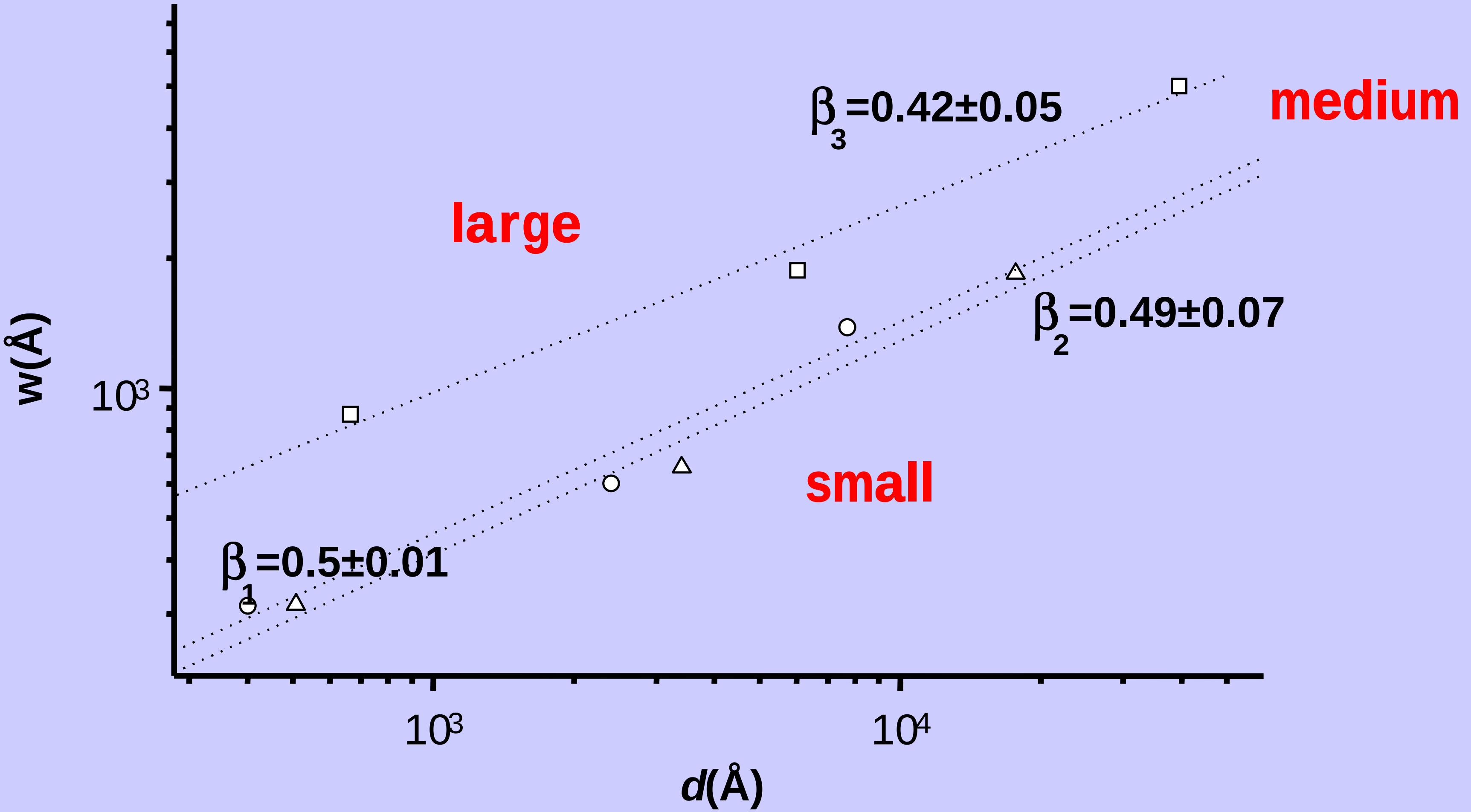
ξ is the lateral correlation length

β is the growth exponent

$$G(\mathbf{r}) \propto r^{2\alpha} \quad \text{if } r << \xi << L$$
$$G(\mathbf{r}) \propto G_{sat} \quad \text{if } r >> \xi$$

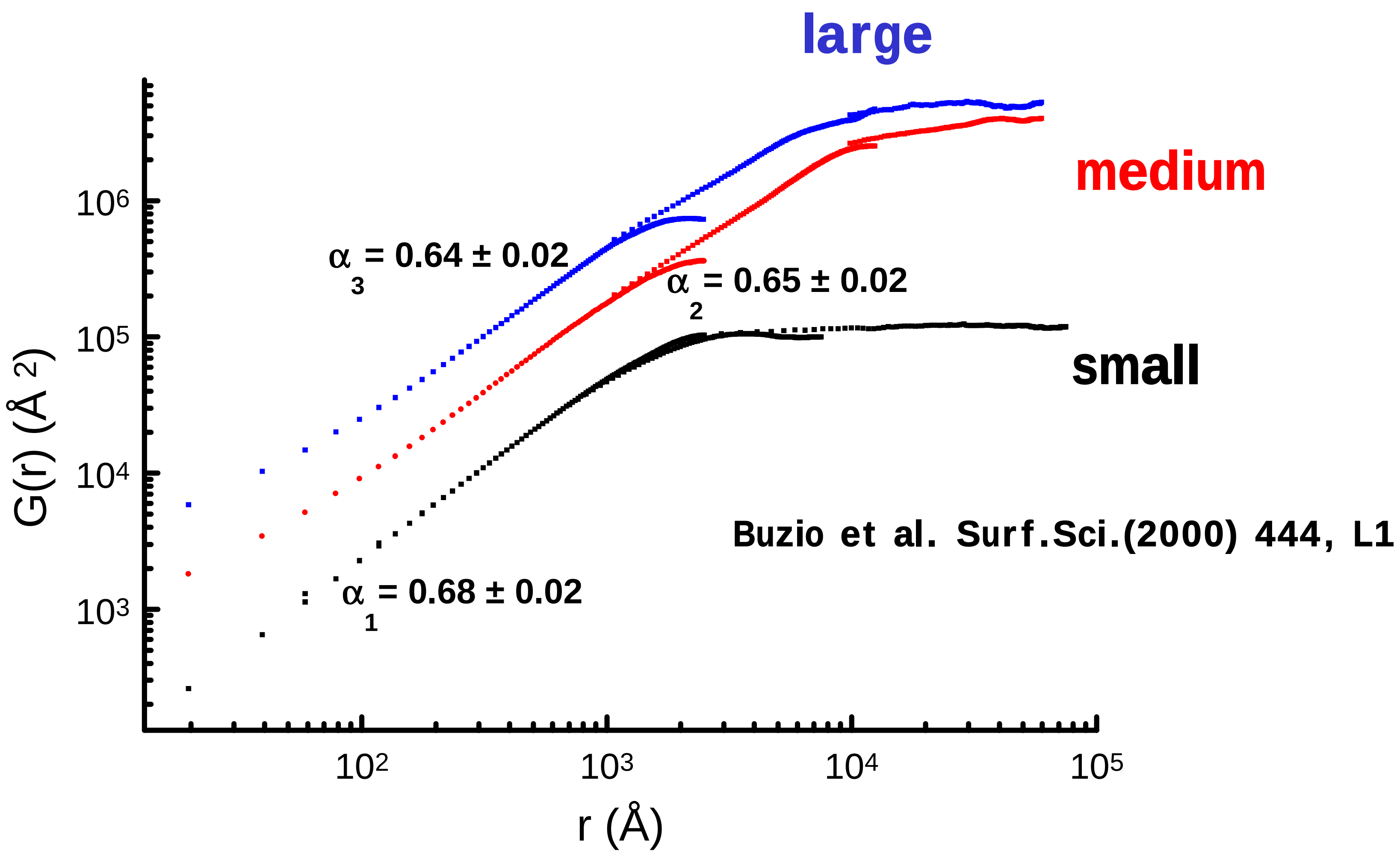


$$w(t, L) \propto t^{\beta} \quad \text{if } t << t_x$$
$$w(t, L) \propto w_{sat} \quad \text{if } t >> t_x$$



The β coefficient does not change with the primeval cluster size

Scaling laws



The α coefficient does not change with the primeval cluster size

Fractal dimension of NSCF

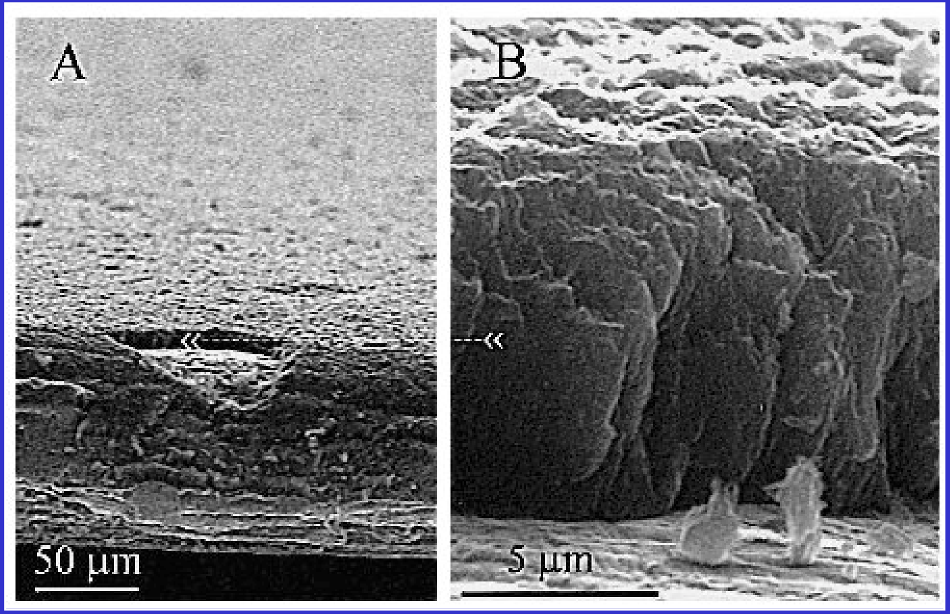
An alternative method to calculate the α parameter is *via* the fractal dimension, following the algorithm of Dubuc et al. (1989)

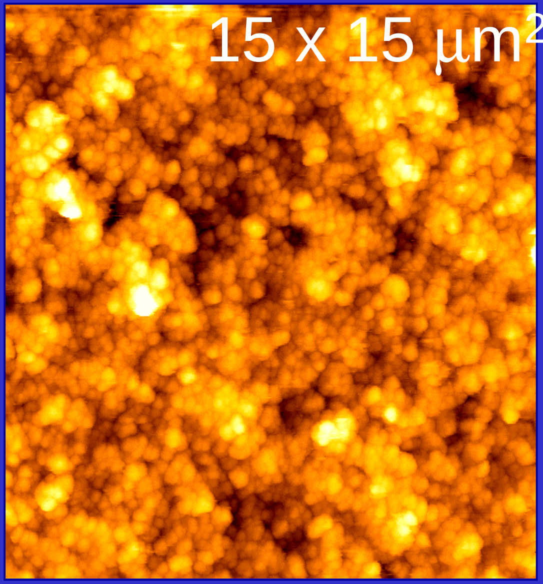
If D is the fractal dimension of a 2-dimensional structure ->

$$D = 3 - \alpha$$

➡ An independent way to calculate α

ns-C Morphology

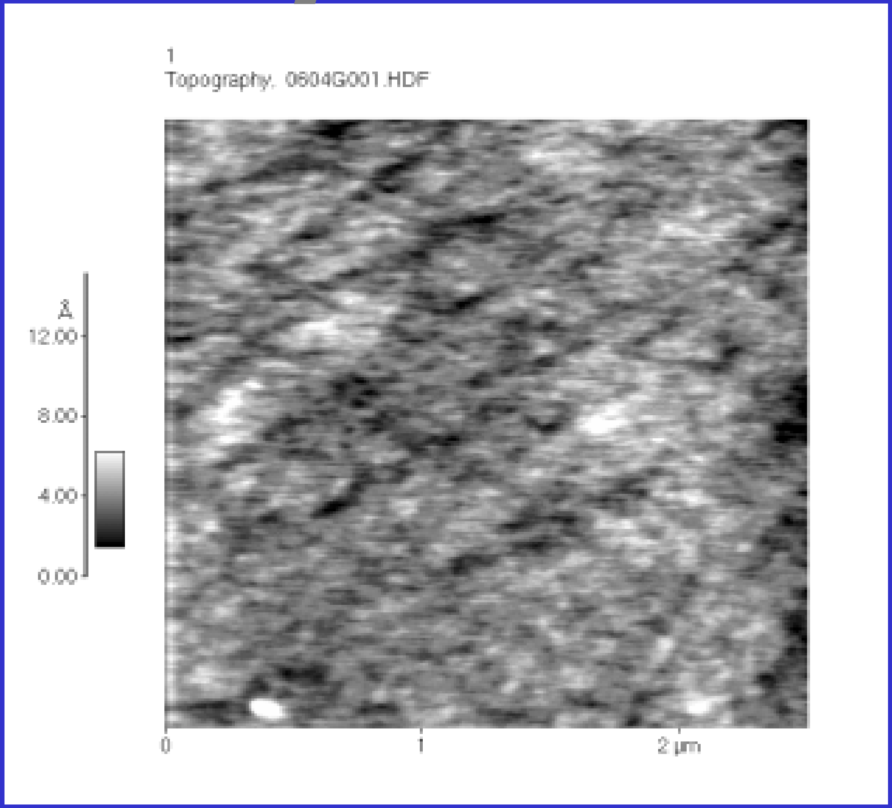




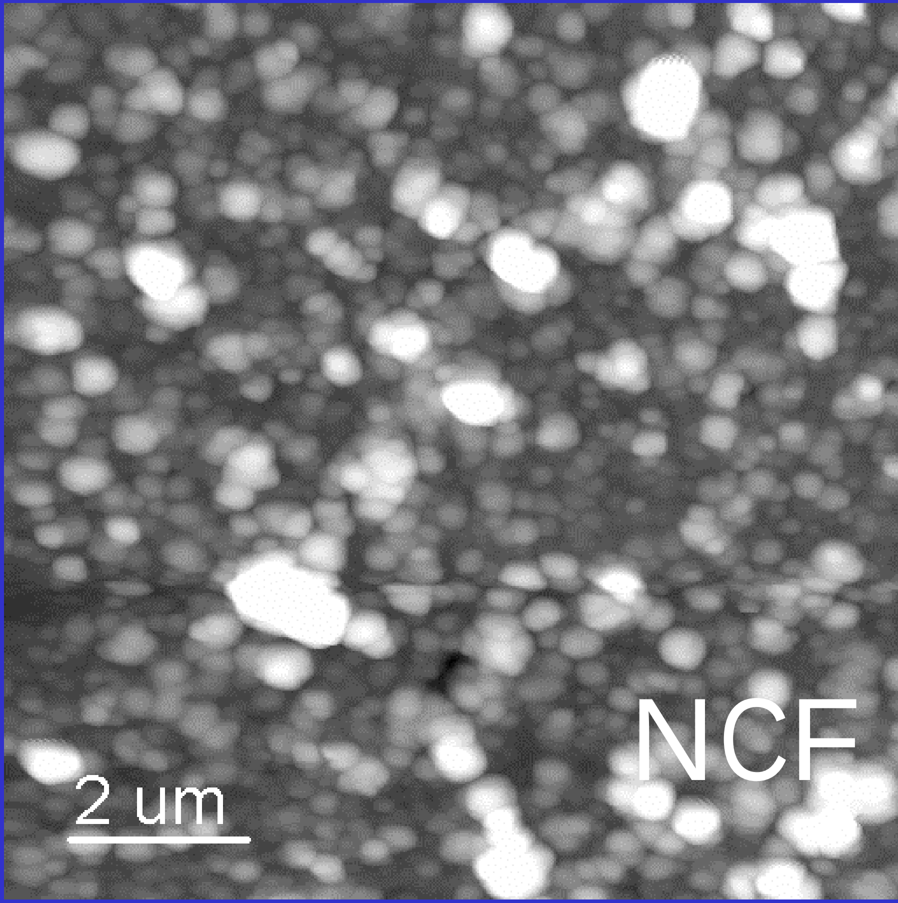
R.Buzio *et al. Surf.Sci.* ***444***, *L1 (2000)*

Surface morphology has been characterised by AFM measurements operated in IC-AFM in air; <u>ns-C films are self-affine</u> from nanometric to micrometric scale.

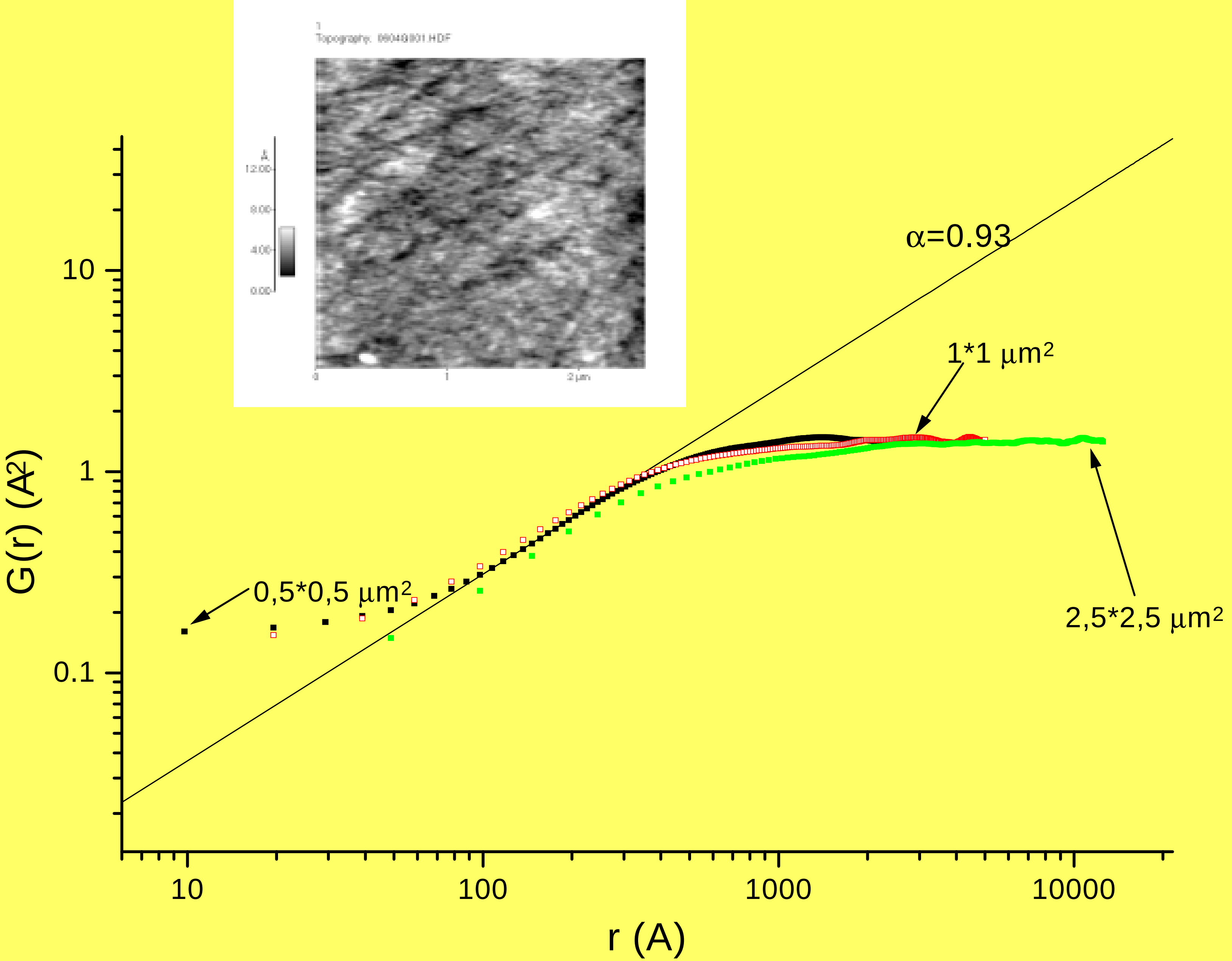
Comparison with other C films



Morphology of Carbon films grown by Laser Ablation (E.Riedo -ESRF)

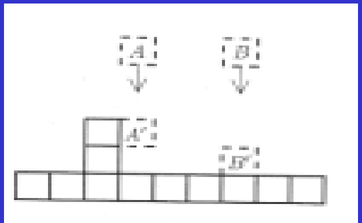


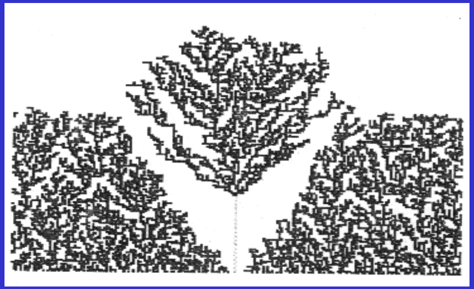
roughness is very low (≈ 5 A) and there is not evidence of nano-structures



Laser ablation Riedo et al.

Balistic deposition -> coral reef

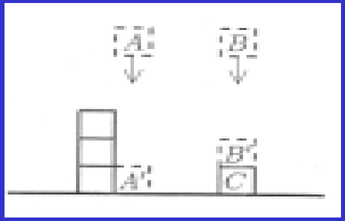


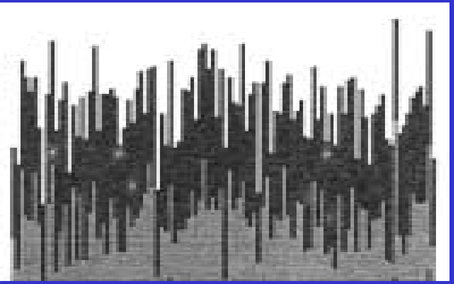


$\alpha \sim 0.33 \div 0.35$

$\beta \sim 0.21 \div 0.24$

Random deposition

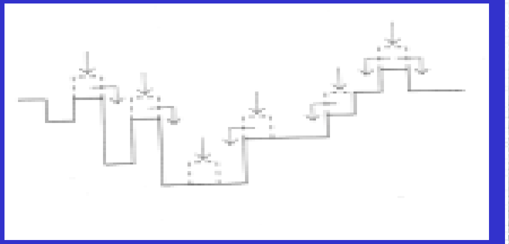


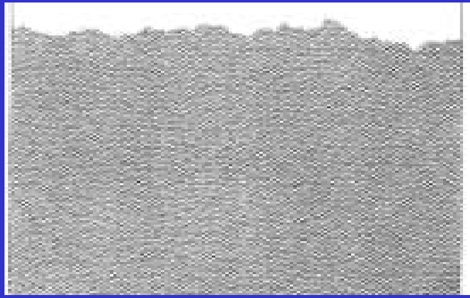


$\alpha \to \infty$

$\beta = 0.5$

Random deposition with relaxation





$\alpha = 0$

$\beta = 0$

Quenched noise

liquid fronts advancing inside porous media

propagation of burning fronts

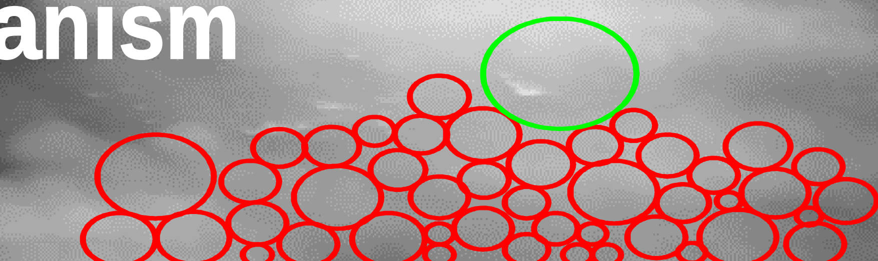
widespread impurities of the medium *locally* pin the interface of the fluid *(quenched noise)* and force As a consequence, the propagation of the interface is slowed or even stopped.

R.Buzio et al. Surface Science 444 (2000) L1–L6

- NSCF are self-affine

- The $\alpha \approx 0.7$ a $\beta \approx 0.4$ parameters do not depend on cluster size

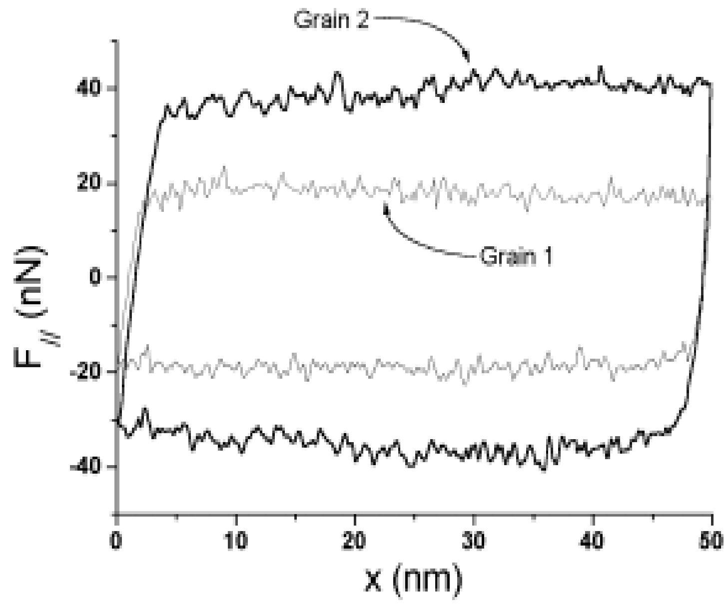
- NSCF grow *via* a quenched-noise mechanism



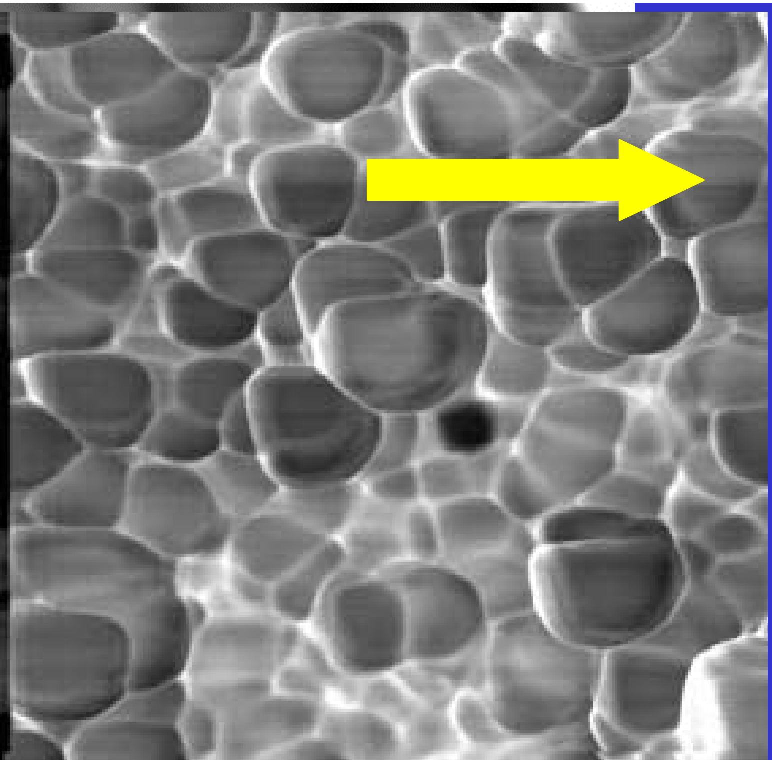
Outline

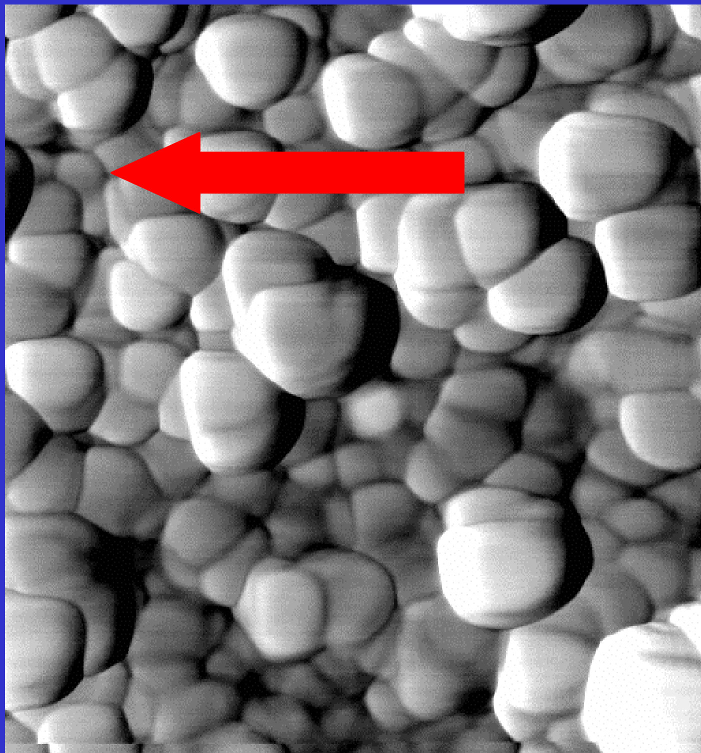
- Nanostructured carbon-based films (ns-C).
- Friction Force Microscopy for tribological investigations: single asperity friction in wear-less regime.
- FFM measurements on ns-C films : influence of morphology and cluster size on the frictional response.
- Comparison of ns-C, a-C and HOPG frictional performance.

Lateral Force Maps

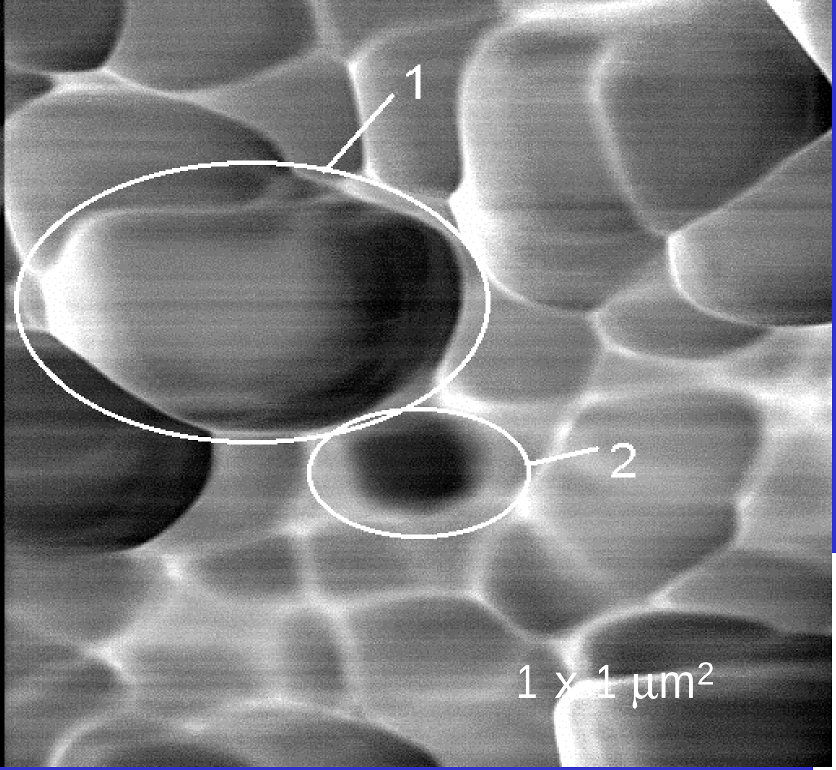


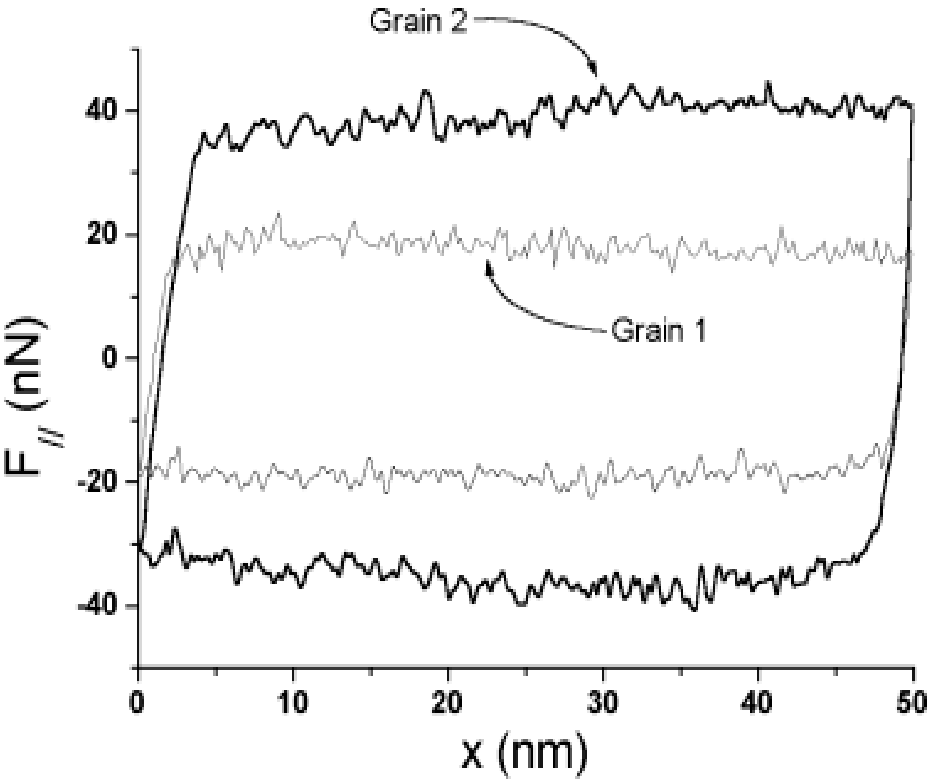
2 x 2 μm^2

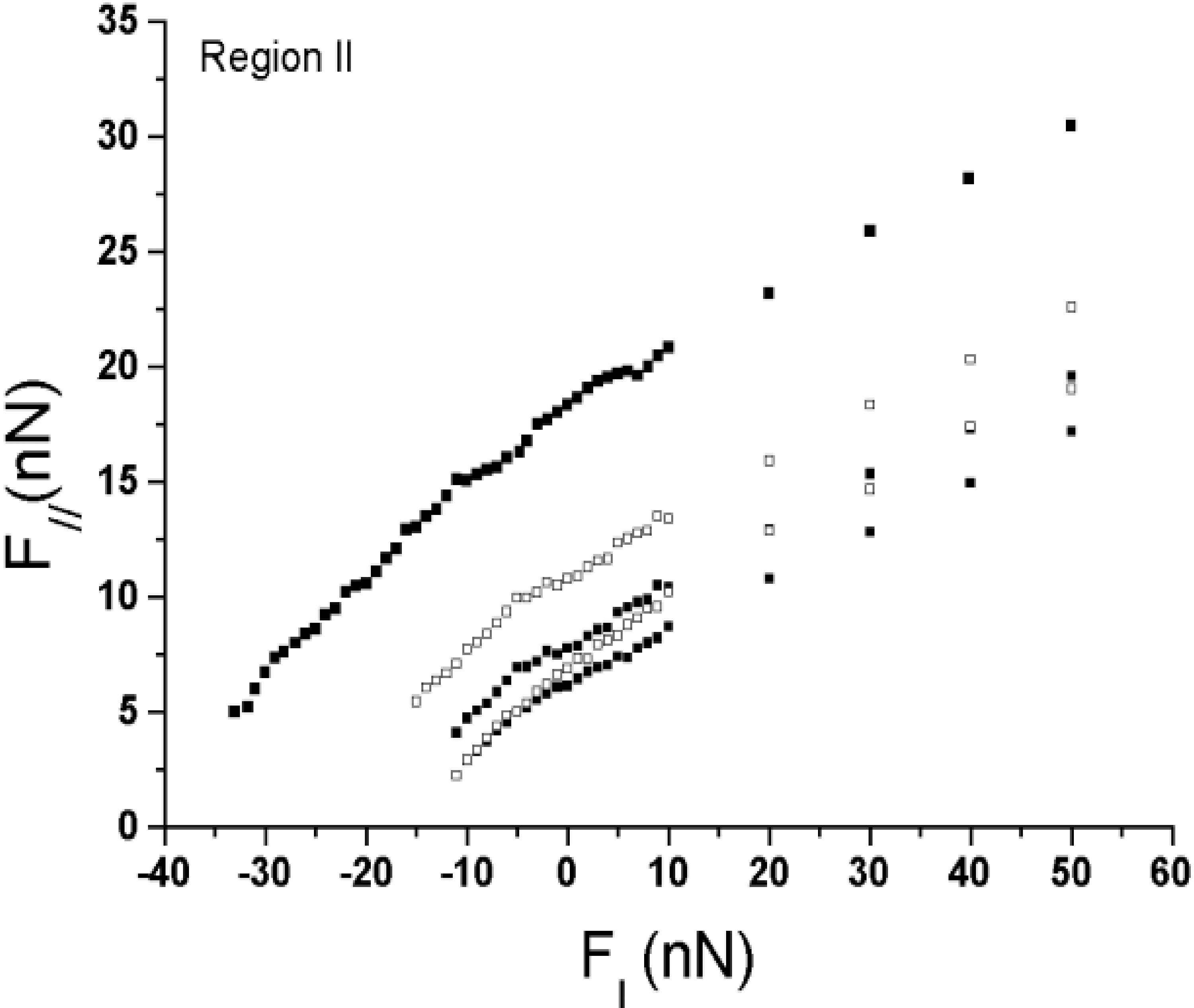




Friction-loop amplitude depends on surface location





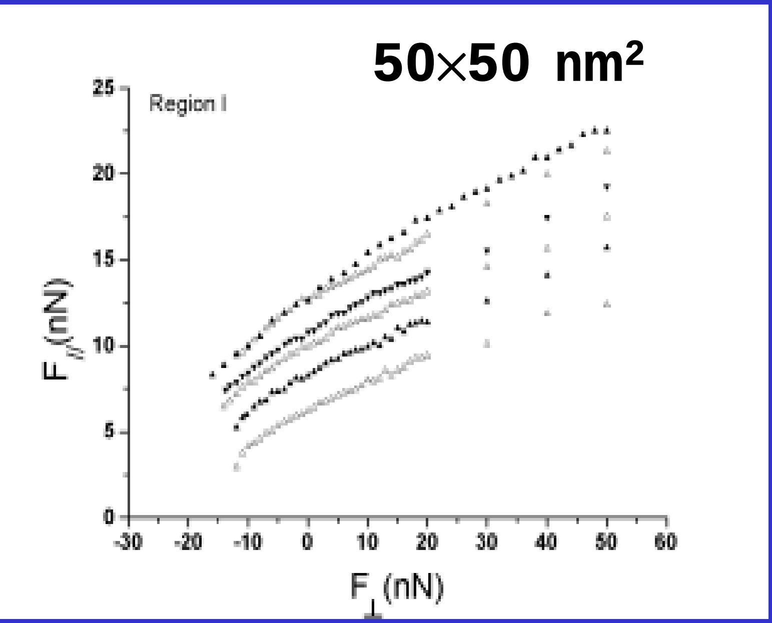


Region II
35
30
25
20
15
10
5
0
-40
-30
-20
-10
0
10
20
30
40
50
60
$F_{//}$(nN)
$F_{\perp}$ (nN)

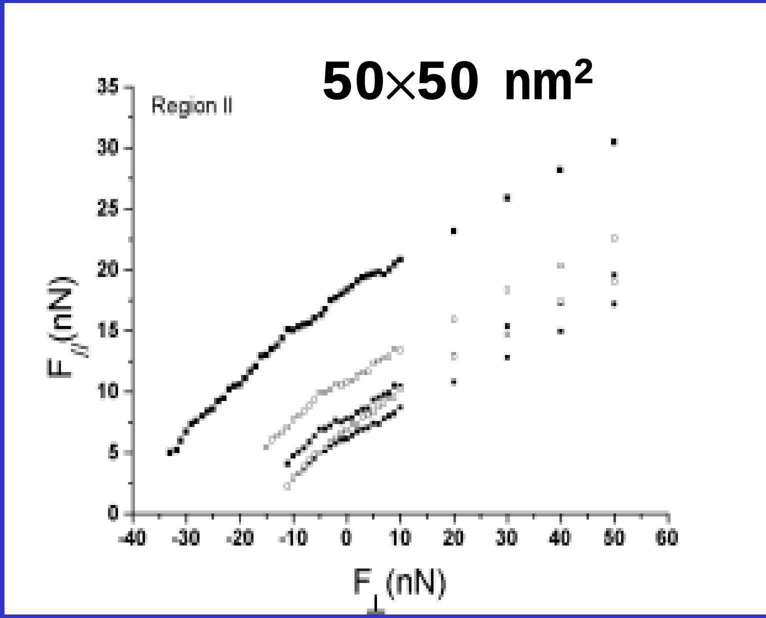
mean friction-loop amplitude vs the normal load and ns-C composition. scan-area

Small

Big



mass size



a) There is a non-linear dependence of lateral force from the normal load as expected in the single-asperity regime

b) The scattering of experimental curves reflects that adhesion varies on changing the specific location were frictional properties are tested (the particular grain on which the tip is located).

Experimental results on ns-C films

a) The non-linear dependence of lateral force from the normal load is fitted by the Hertzian-plus-offset model (DMT theory)...

$$F_{//} = \pi\tau\left(\frac{R}{K}\right)^{2/3}\left(F_{\perp} - F_{off}\right)^{2/3} = C\left(F_{\perp} - F_{off}\right)^{2/3}$$

α C films*	0.45
HOPG*	0.0012
Diamond*	0.26
ns-C films Region I	0.10
ns-C films Region II	0.14

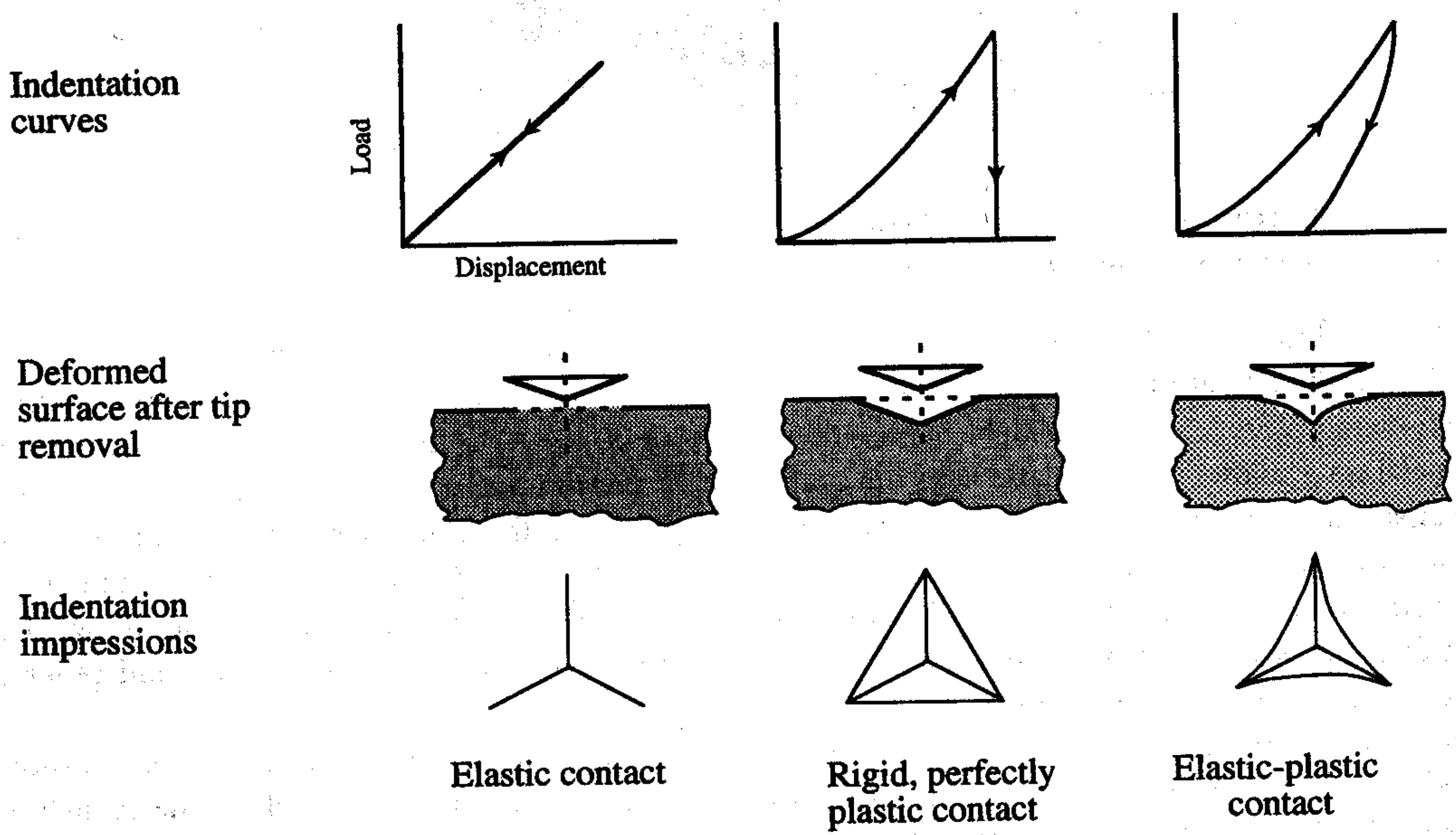
R.Buzio et al. Carbon 2001

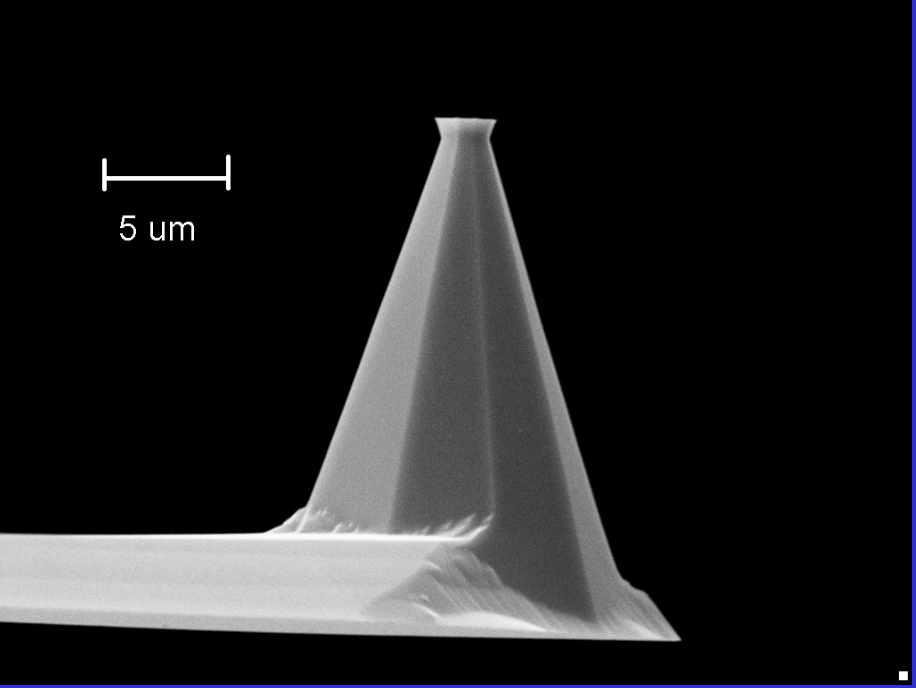
Conclusions

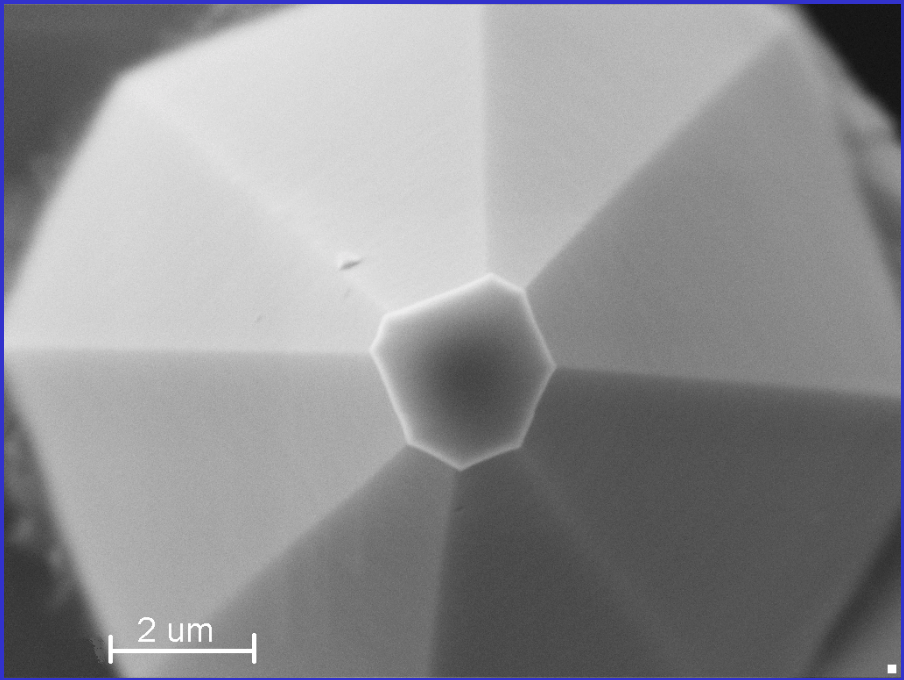
Friction on ns-C films at the nanometric scale is influenced by the local cluster size, morphology and hydrofilicity, *i.e. it is a size-dependent property of these materials.*

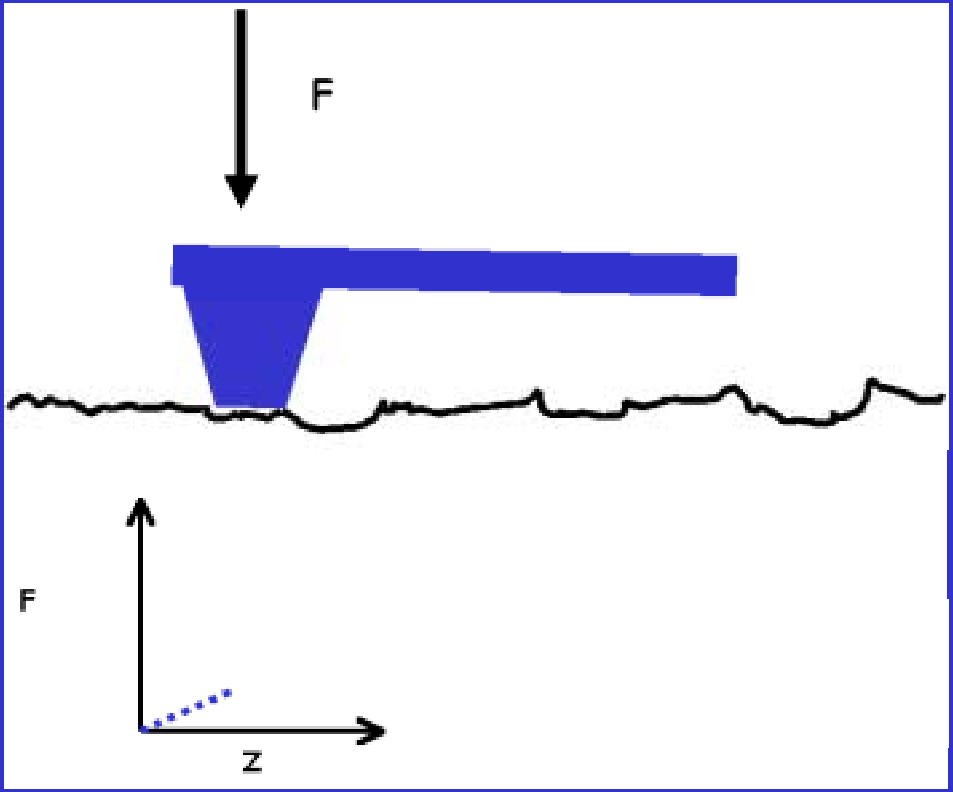
The value of the coefficient of friction shows that ns-C are not self-lubricant as HOPG even if their composition is similar: however ns-C frictional performance is better than that of a-C films.

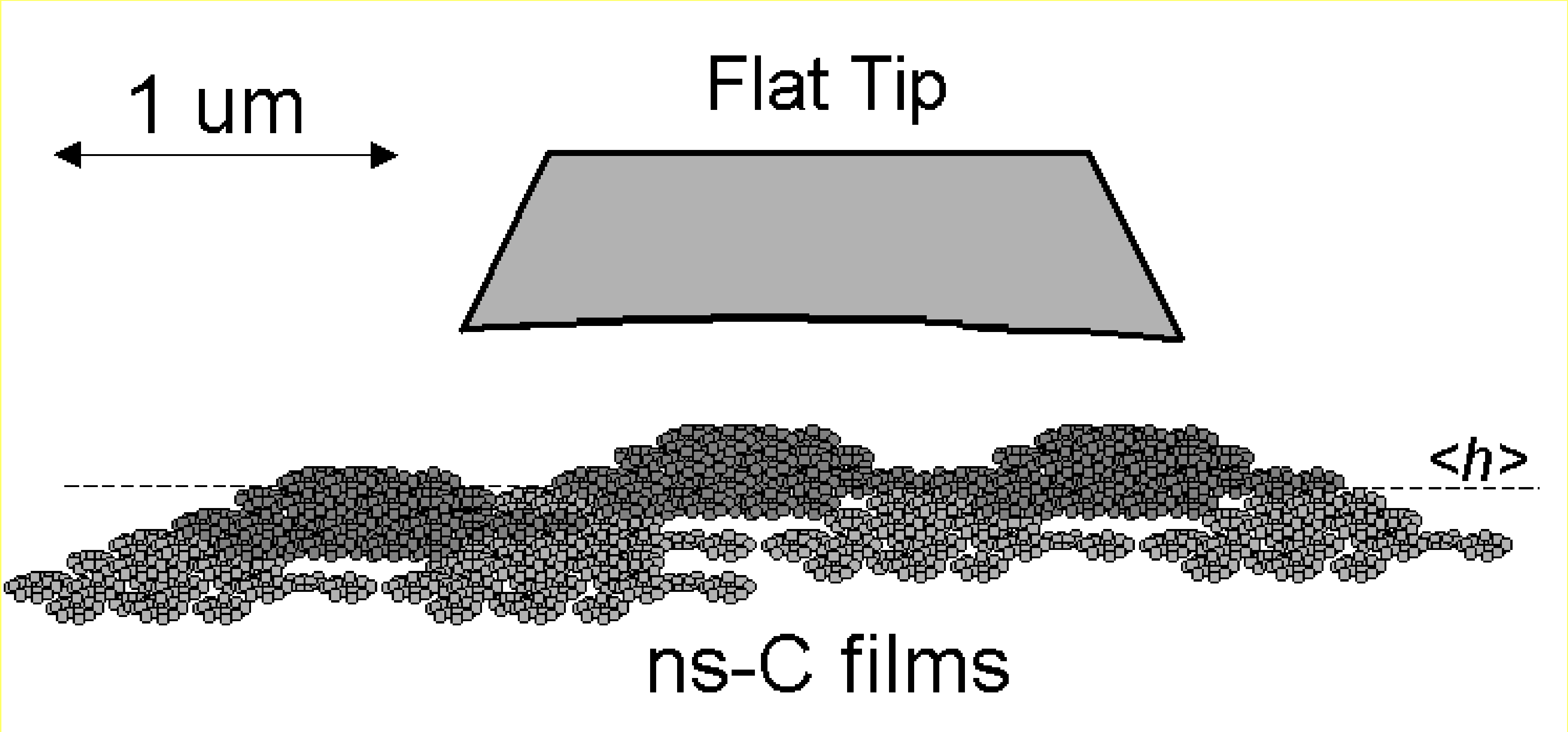
Indentation Curves

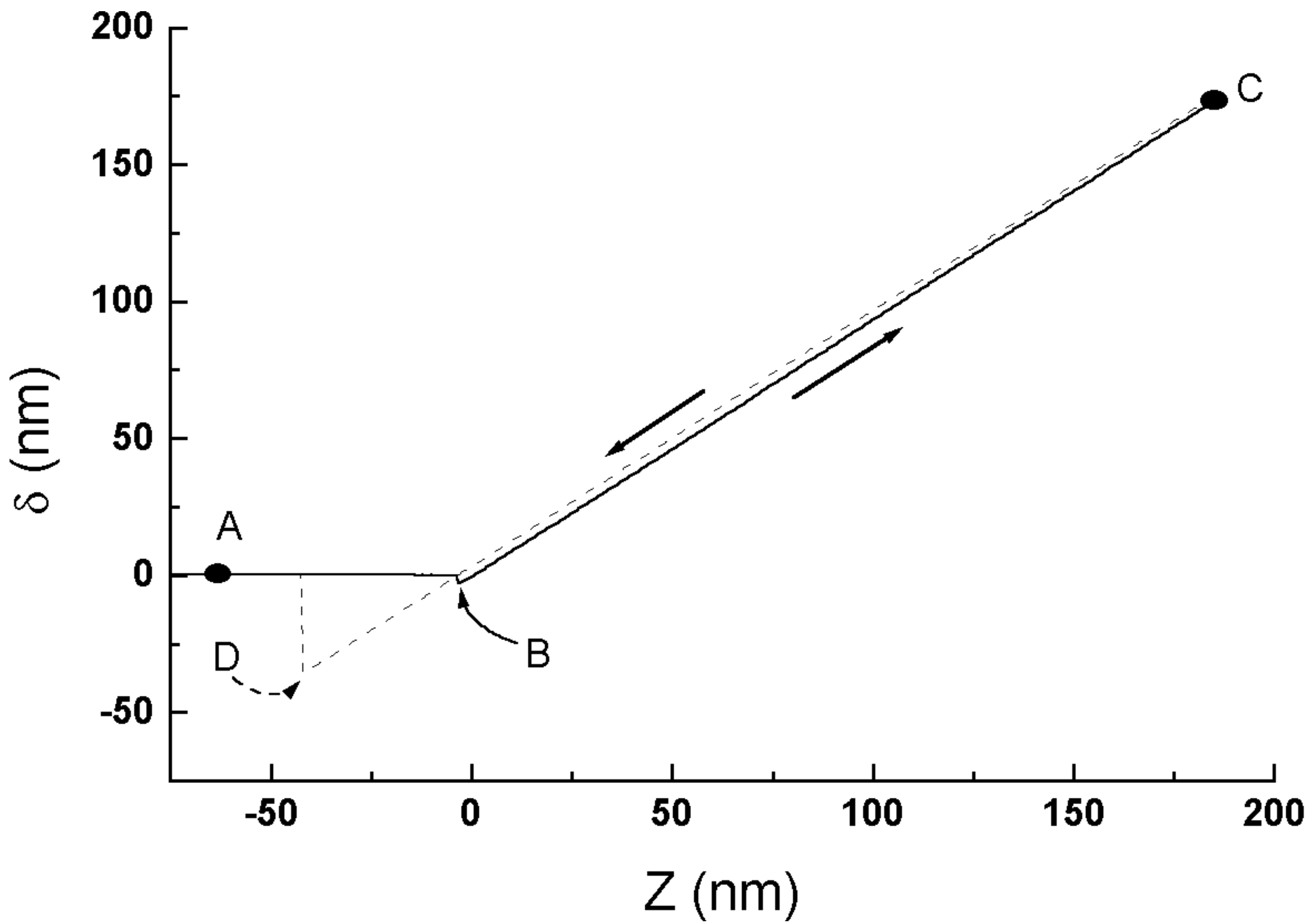


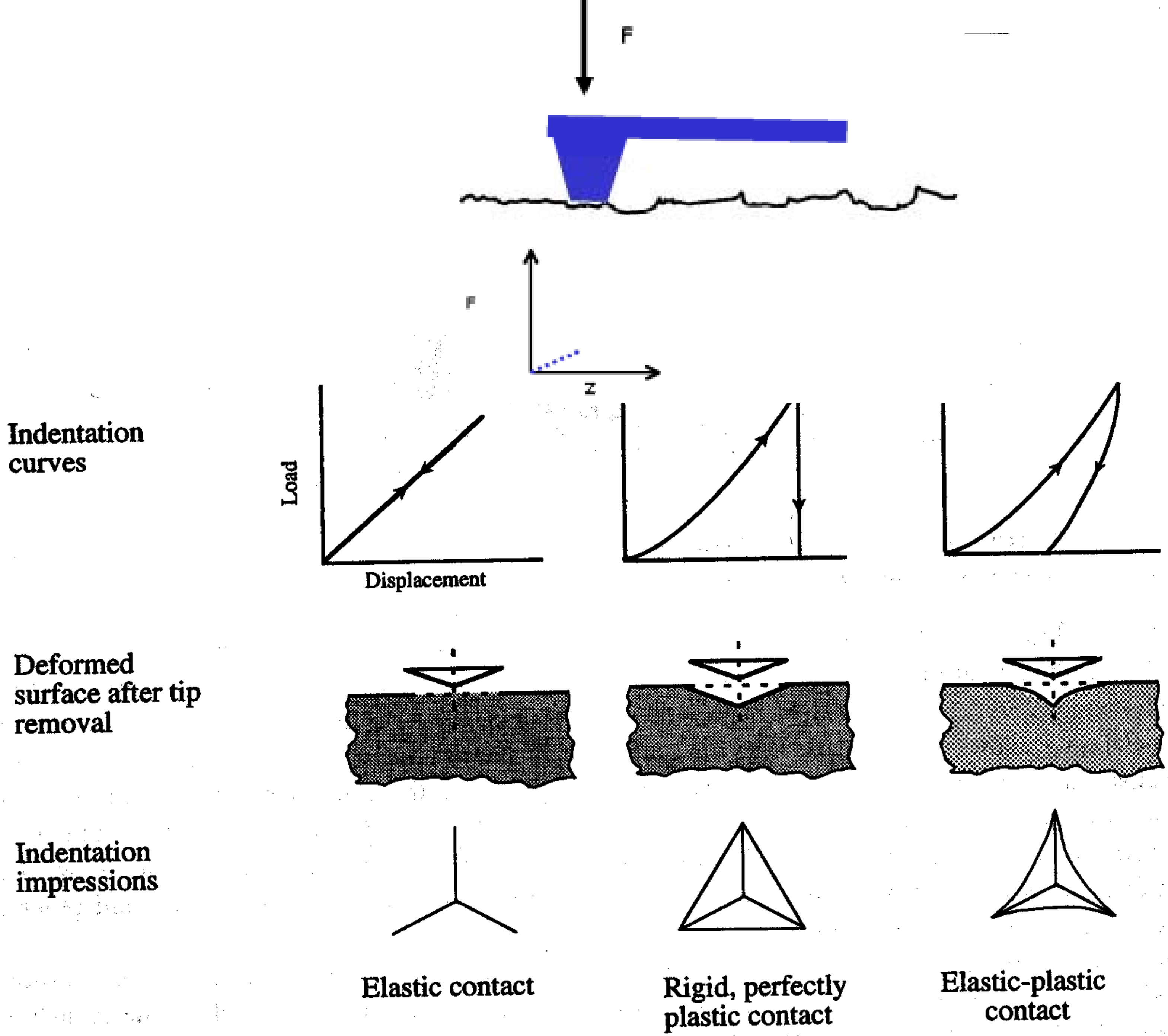

5 um


2 um

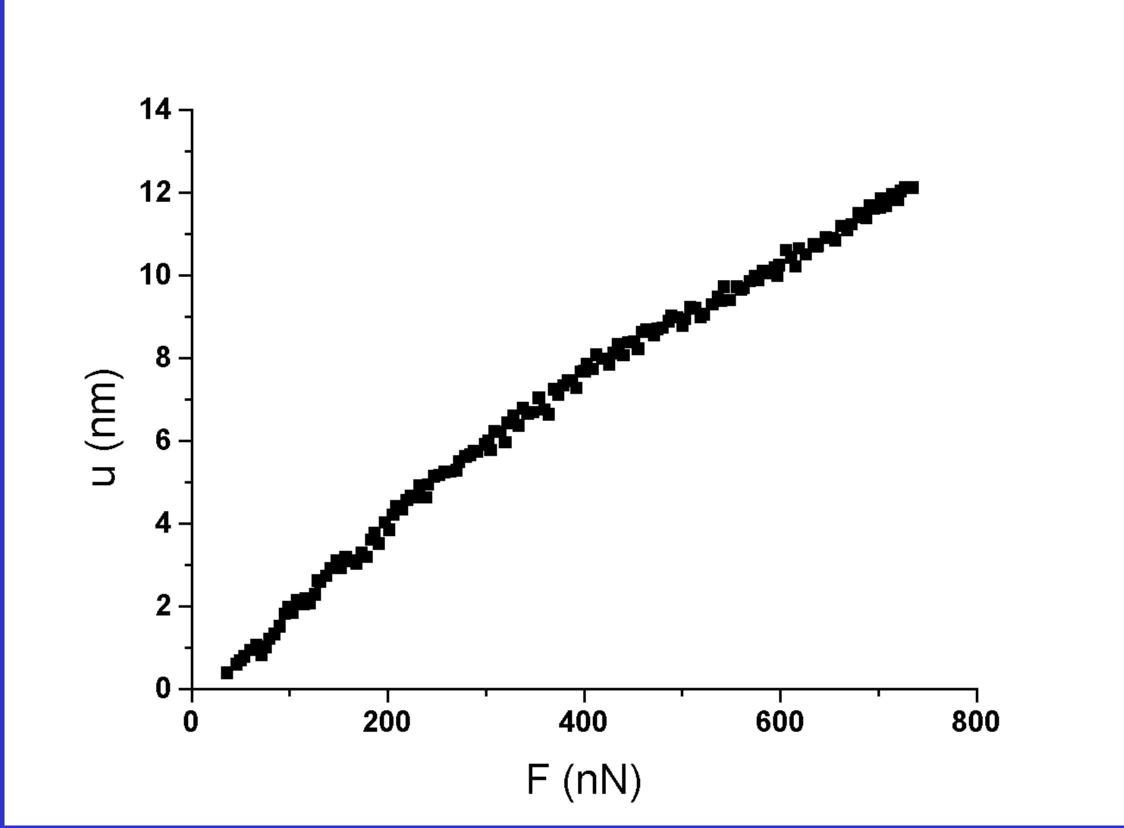

F
F
z

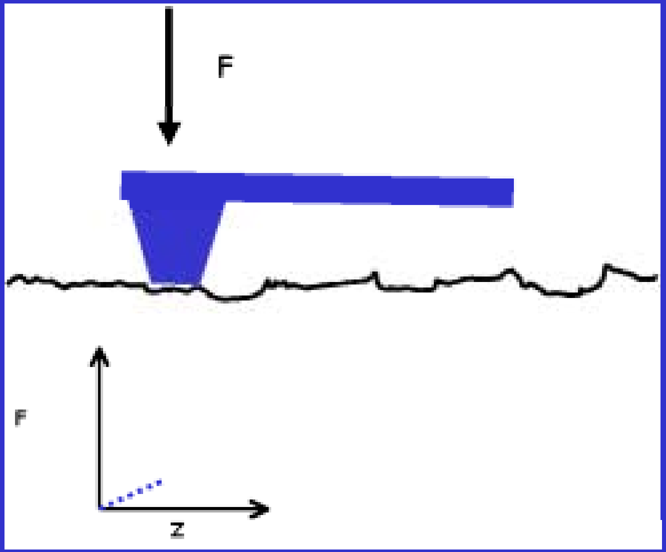

Flat Tip
1 um
<h>
ns-C films


200
150
100
50
0
-50
δ (nm)
-50
0
50
100
150
200
Z (nm)
A
B
C
D

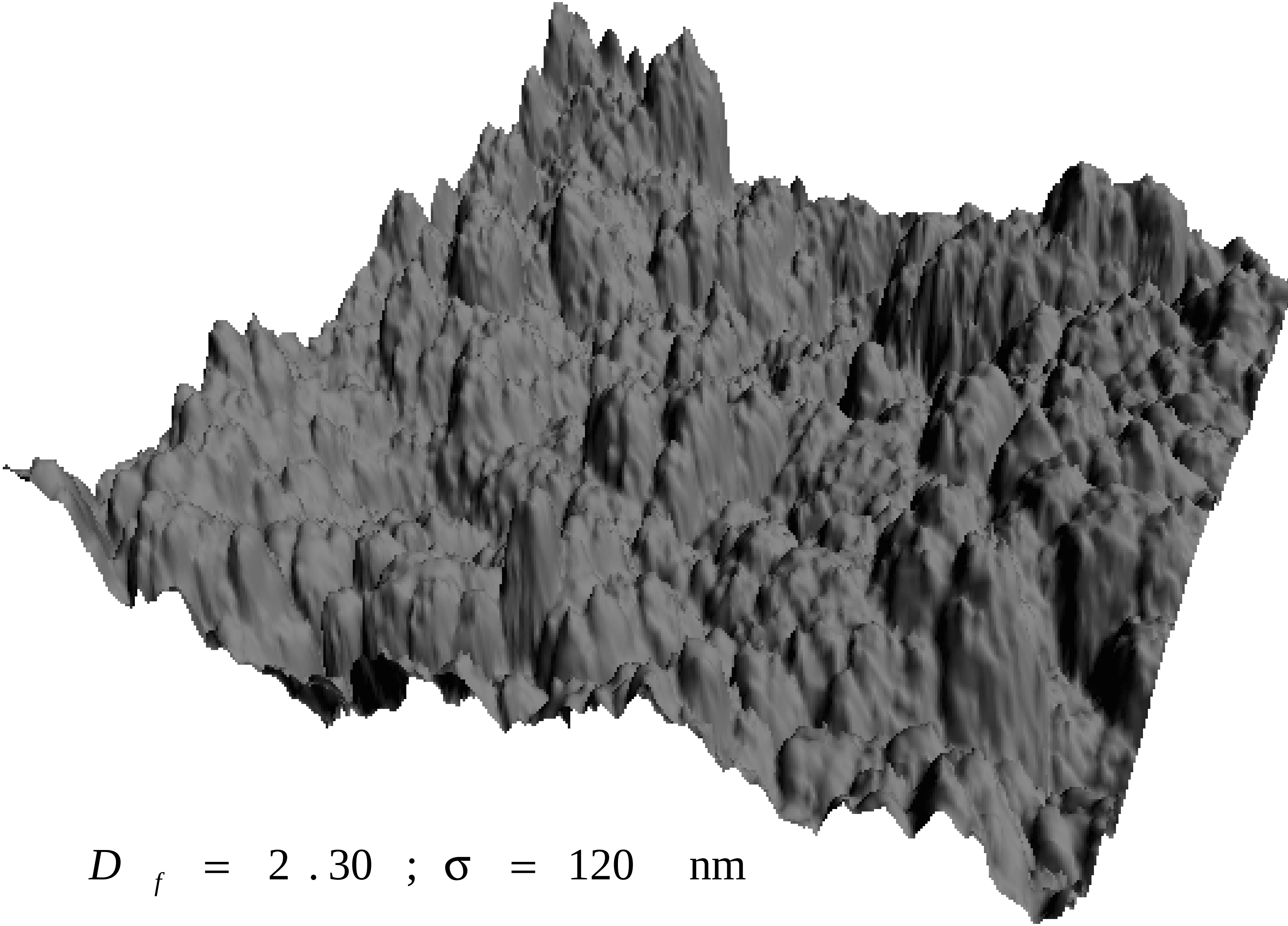

F
F
z
Indentation curves
Load
Displacement
Deformed surface after tip removal
Indentation impressions
Elastic contact
Rigid, perfectly plastic contact
Elastic-plastic contact

Indentation curve

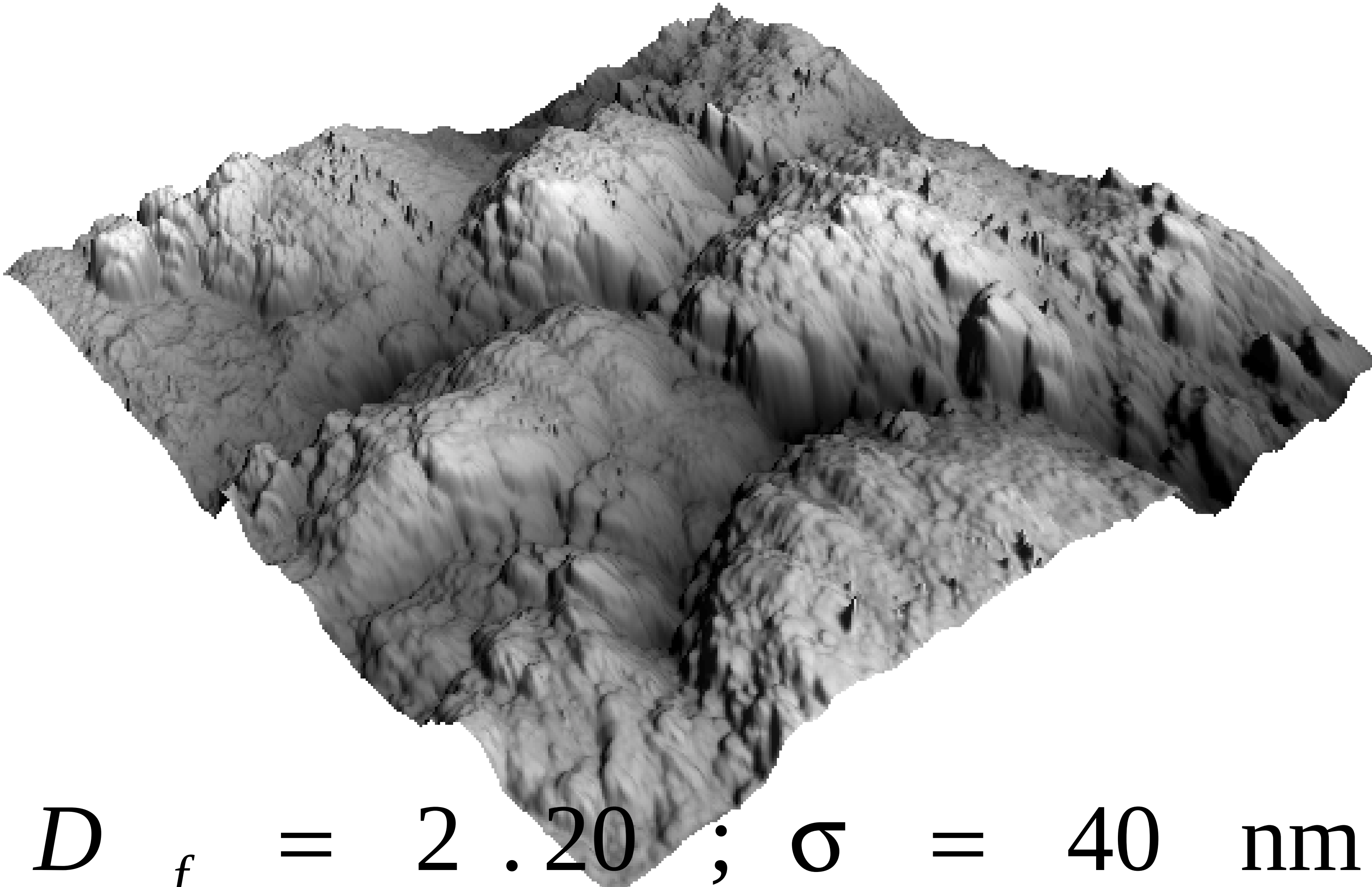




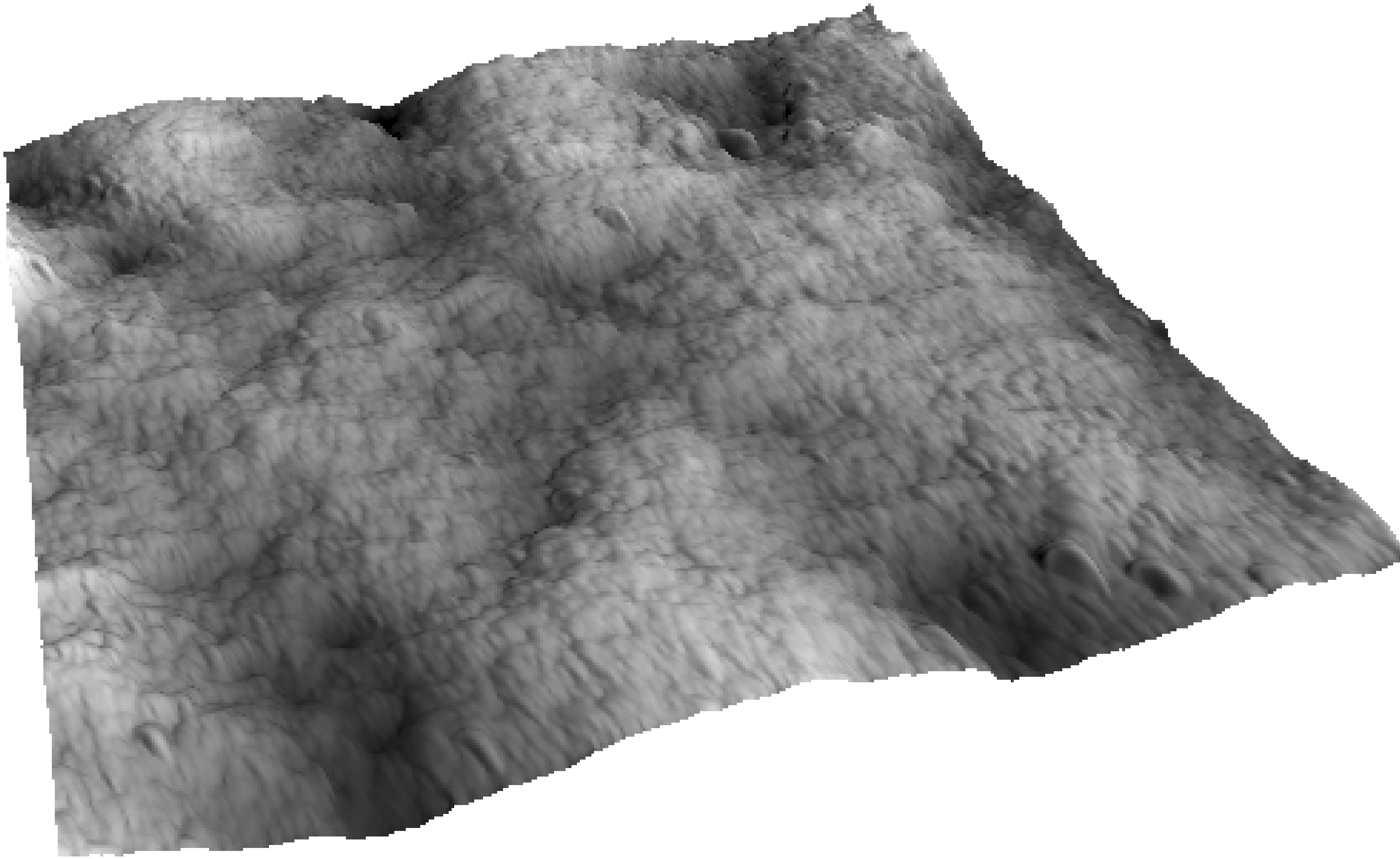
$$F = H \times A$$



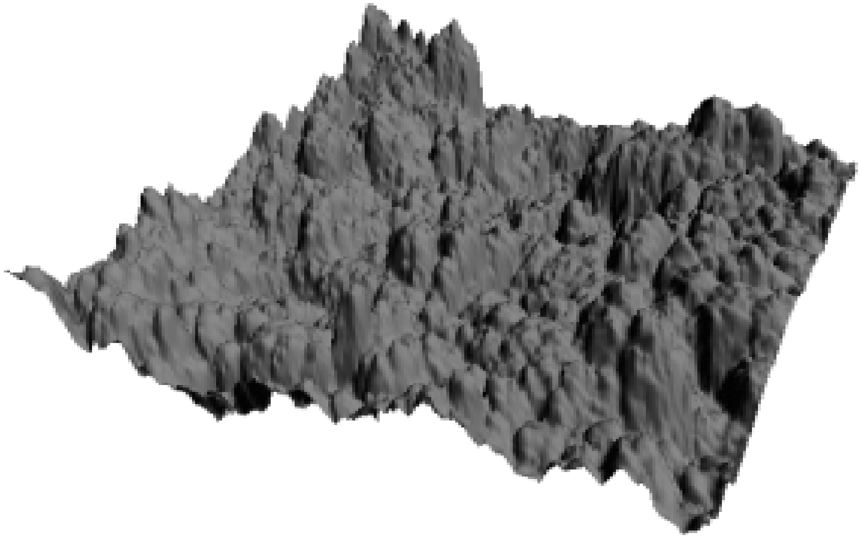
$D_f = 2.30$; $\sigma = 120$ nm



$D_f = 2.20$; $\sigma = 40$ nm

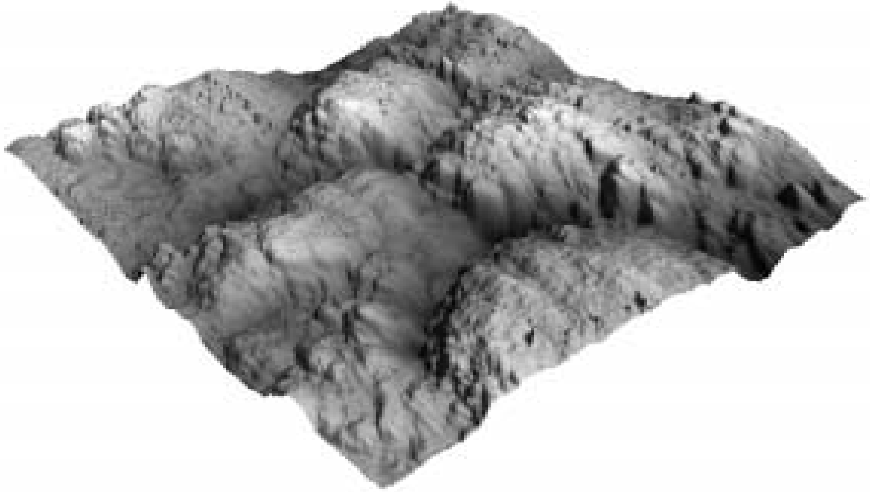


$D_f = 2.10$; $\sigma = 20$ nm

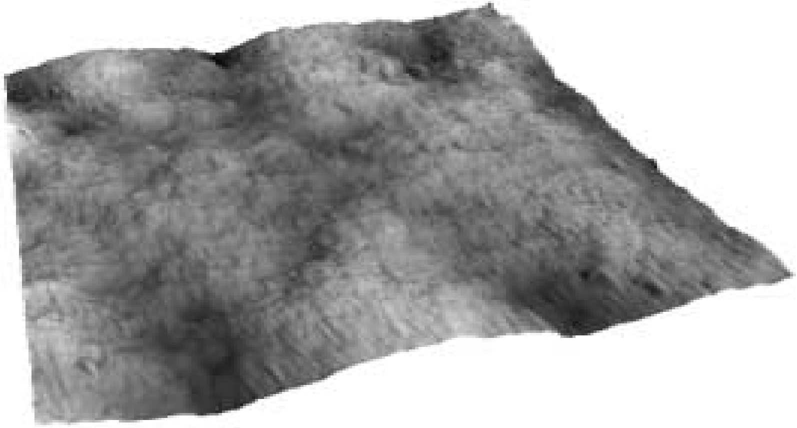


$D_f = 2.30$; $\sigma = 120$ nm

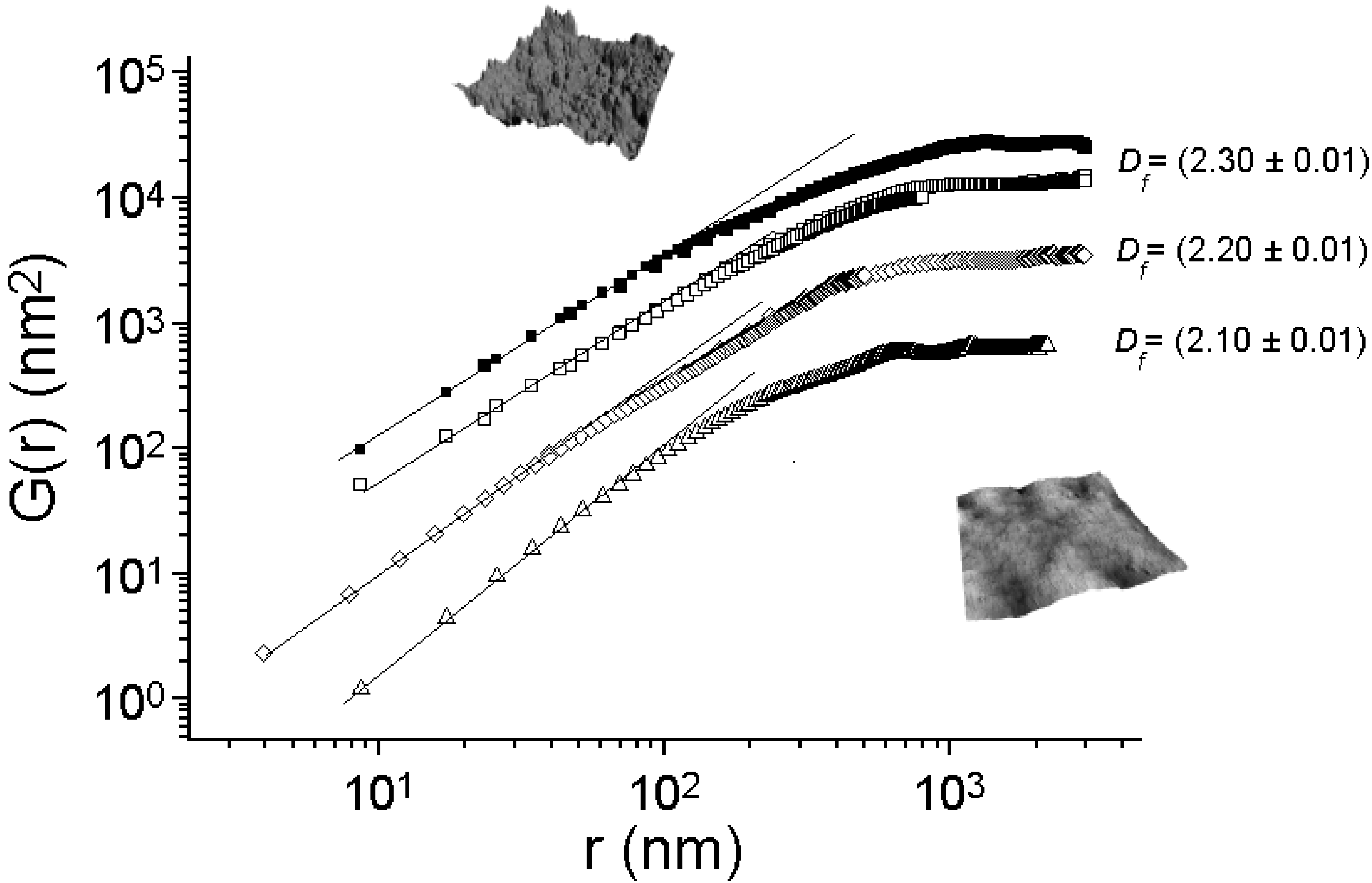
$D_f = 2.30$; $\sigma = 80$ nm



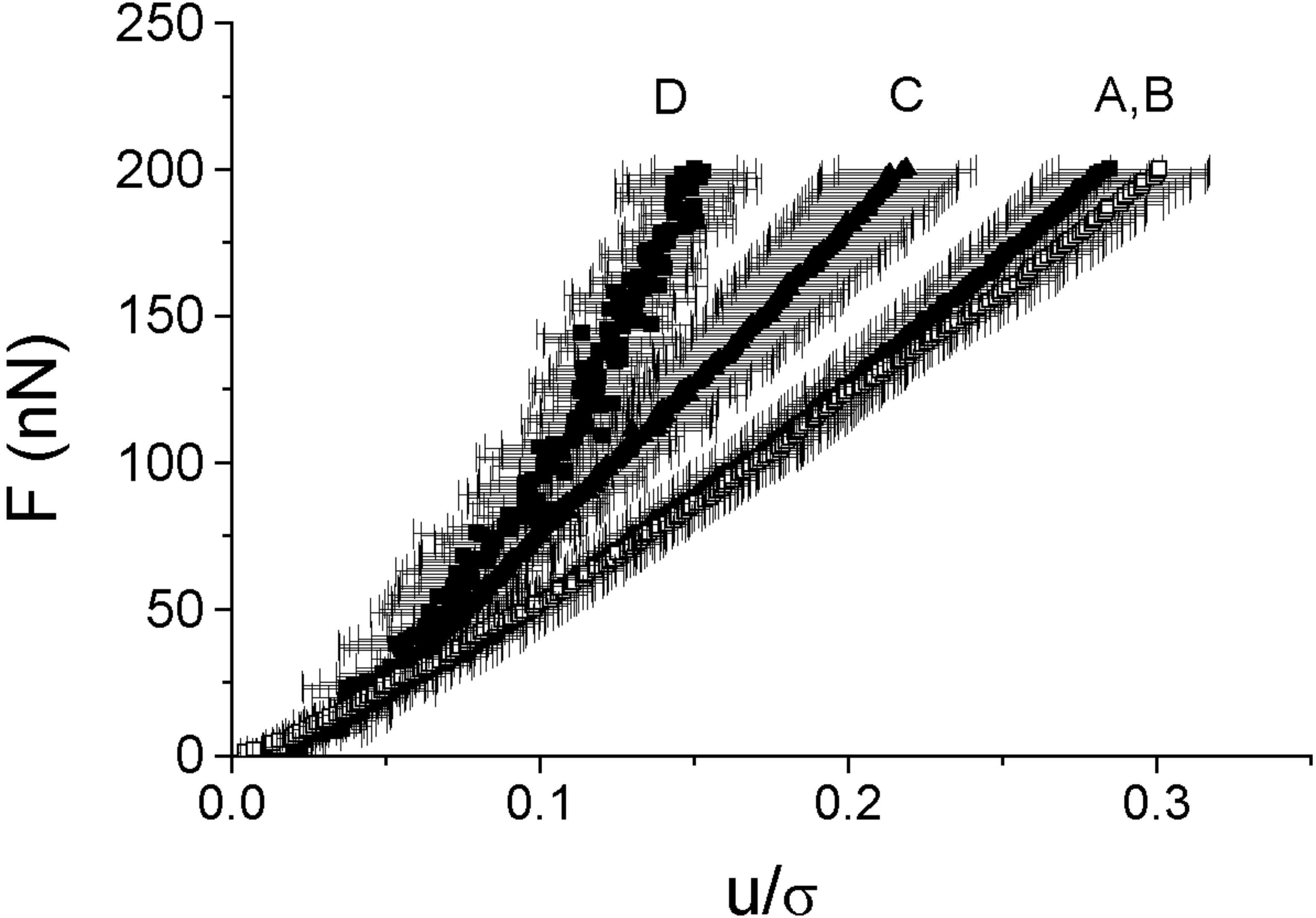
$D_f = 2.20$; $\sigma = 40$ nm



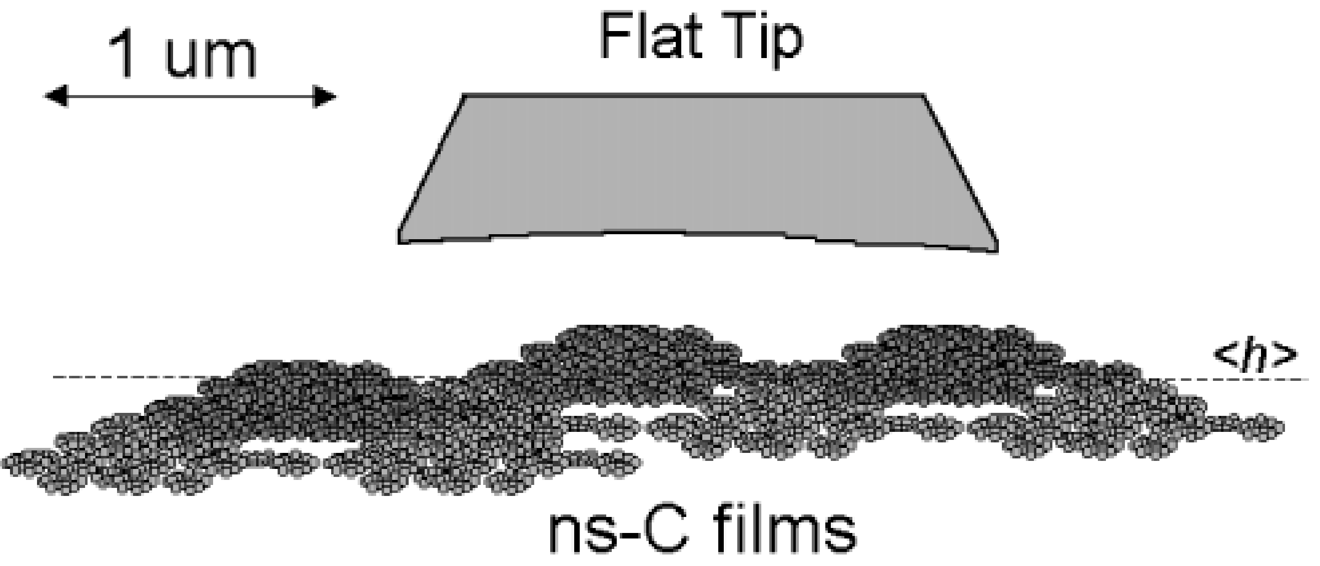
$D_f = 2.10$; $\sigma = 20$ nm

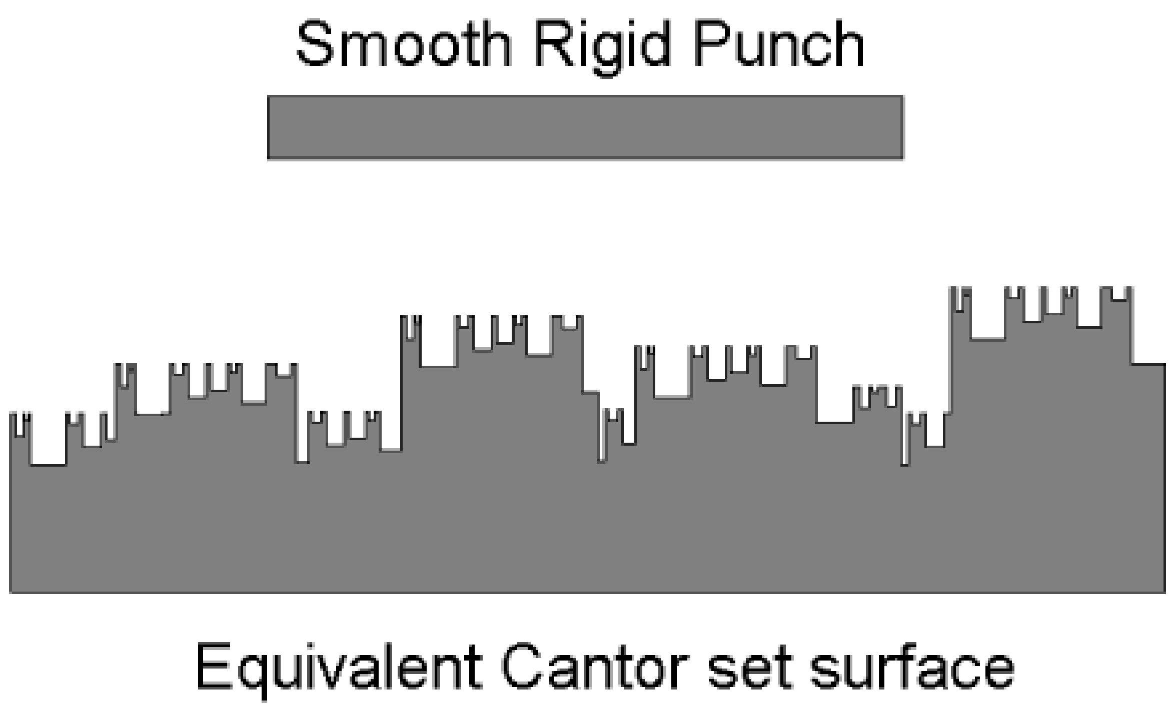


10^5
10^4
10^3
10^2
10^1
10^0
G(r) (nm^2)
10^1
10^2
10^3
r (nm)
D_f = (2.30 ± 0.01)
D_f = (2.20 ± 0.01)
D_f = (2.10 ± 0.01)



D
C
A,B
F (nN)
250
200
150
100
50
0
0.0
0.1
0.2
0.3
u/σ

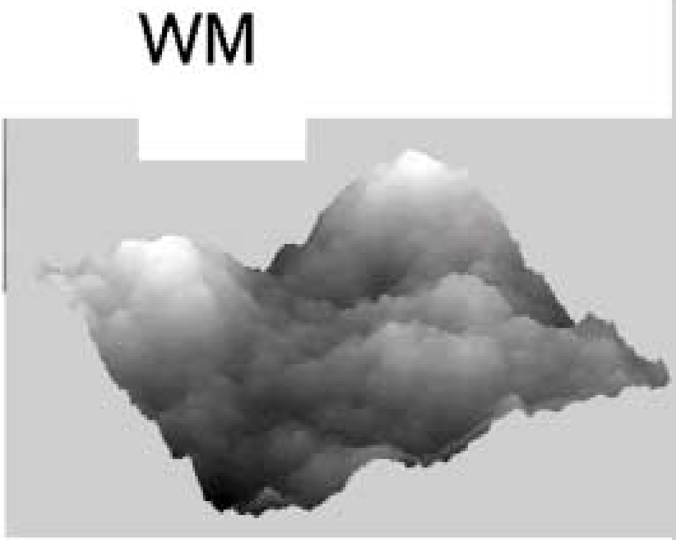

1 um
Flat Tip
<h>
ns-C films

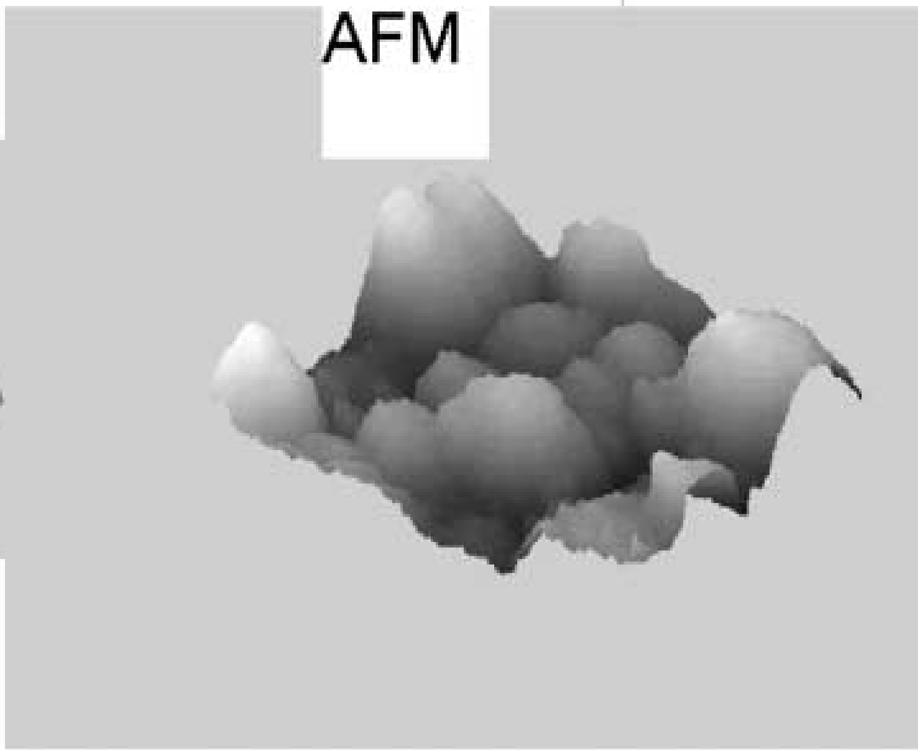

Smooth Rigid Punch
Equivalent Cantor set surface

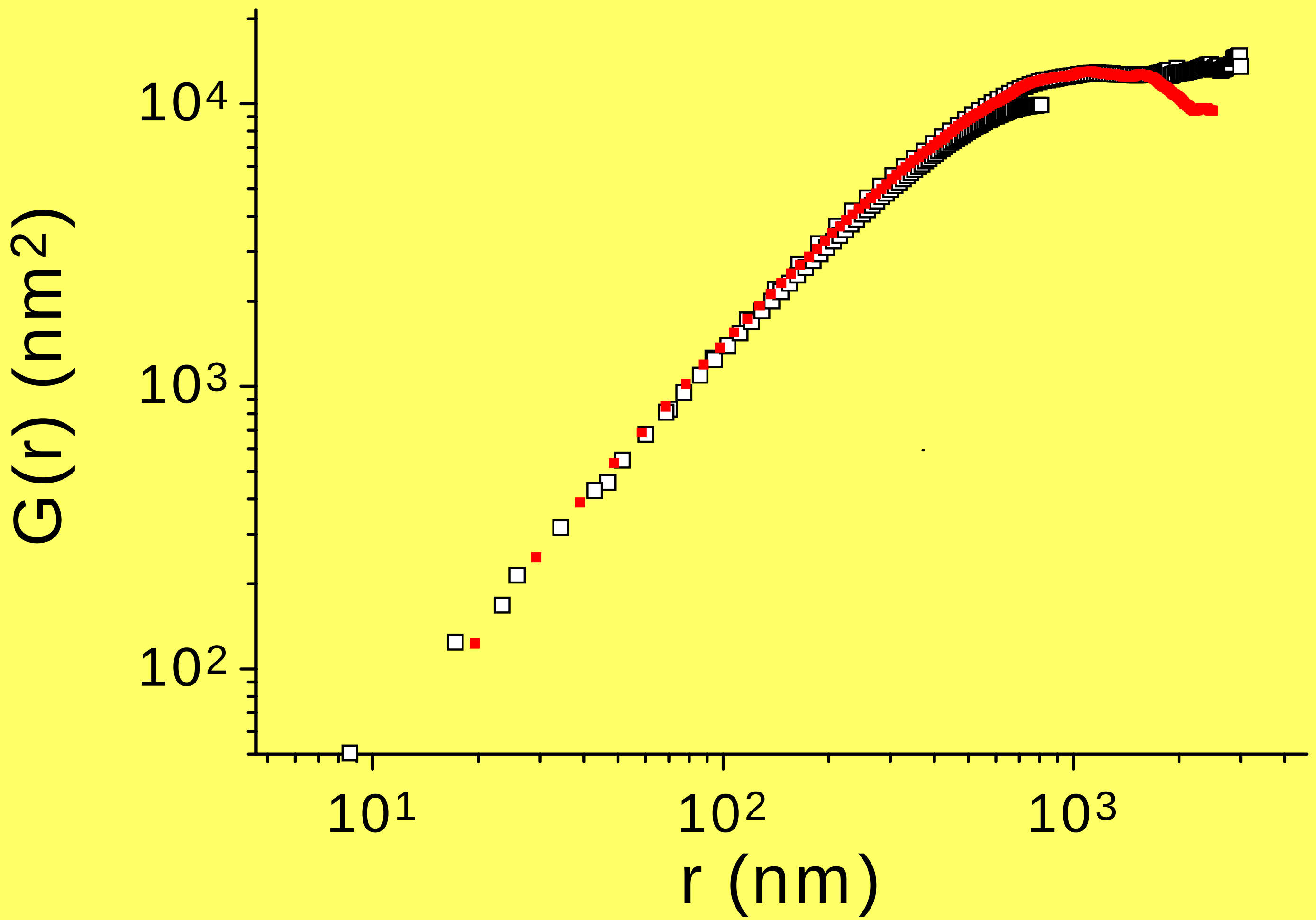
$D_F = 2.30 \pm 0.01.$

$\sigma_{sat} \approx 80$ nm.

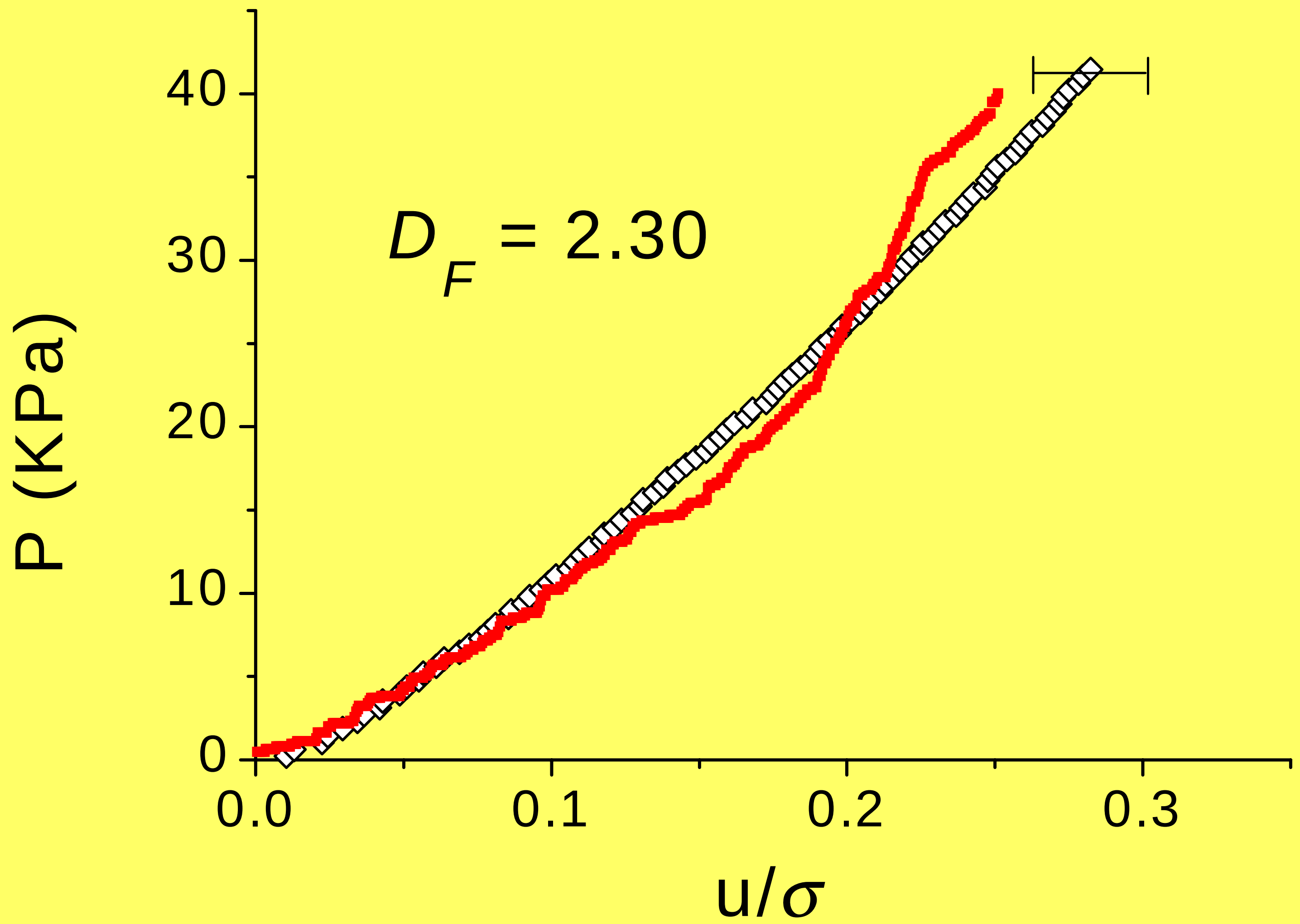
$\xi \approx 800$ nm.



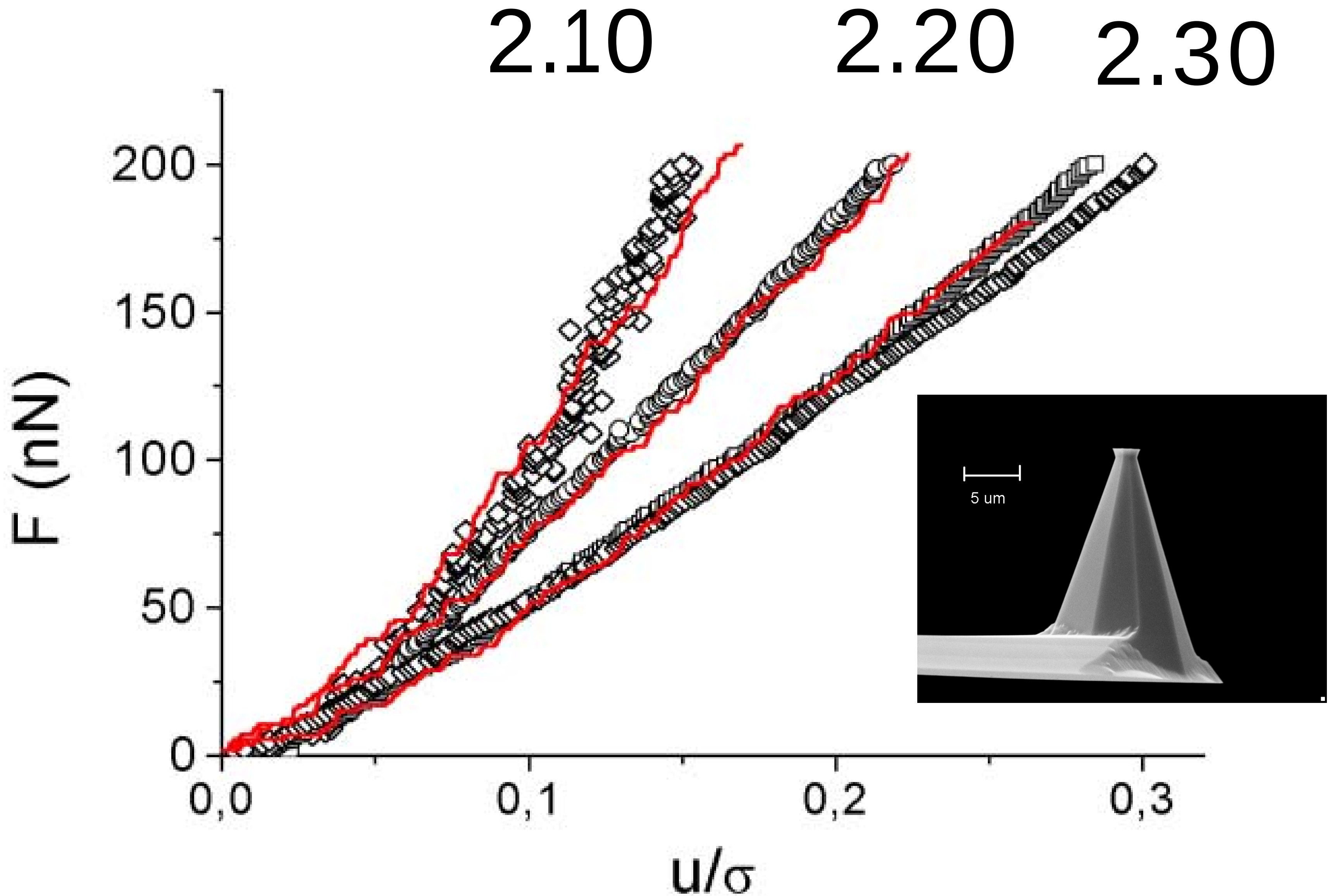




G(r) (nm2)
10^4
10^3
10^2
10^1
10^2
10^3
r (nm)



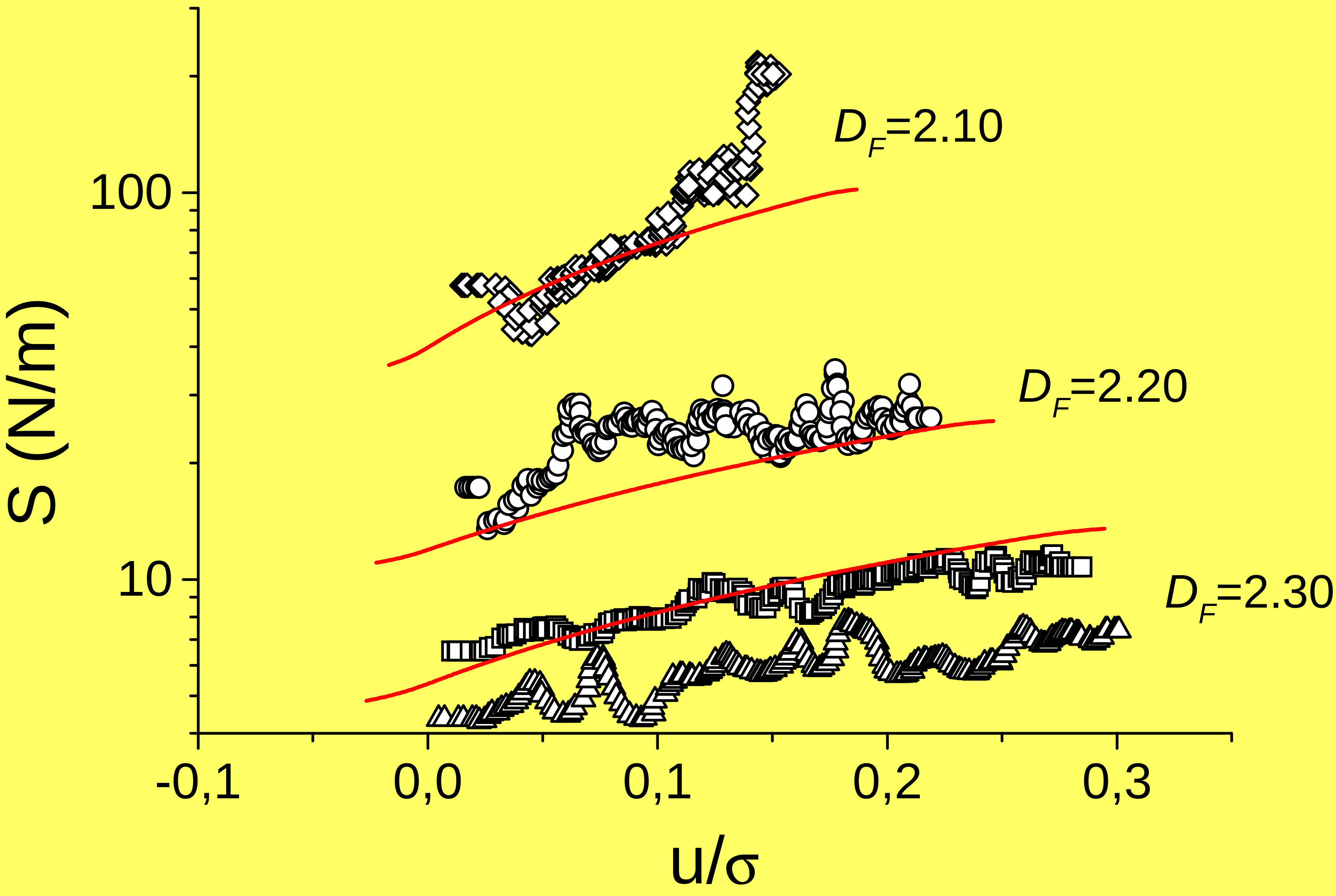
40
30
20
10
0
P (KPa)
$D_F = 2.30$
0.0
0.1
0.2
0.3
u/σ



2.10
2.20
2.30
F (nN)
200
150
100
50
0
0,0
0,1
0,2
0,3
u/σ
5 um

Stiffness

$$S = H \times dA/dz$$



S (N/m)
100
10
-0,1
0,0
0,1
0,2
0,3
u/σ
D_F=2.10
D_F=2.20
D_F=2.30

Fractal nature of stiffness

C.Boragno
R.Buzio
E.Gnecco
F.Buatier
U.Valbusa

INFM Unità di Genova
Dipartimento di Fisica
Università di Genova
Via Dodecaneso 33 16136
Genova Italy
PRA CLASS
ASI Contract