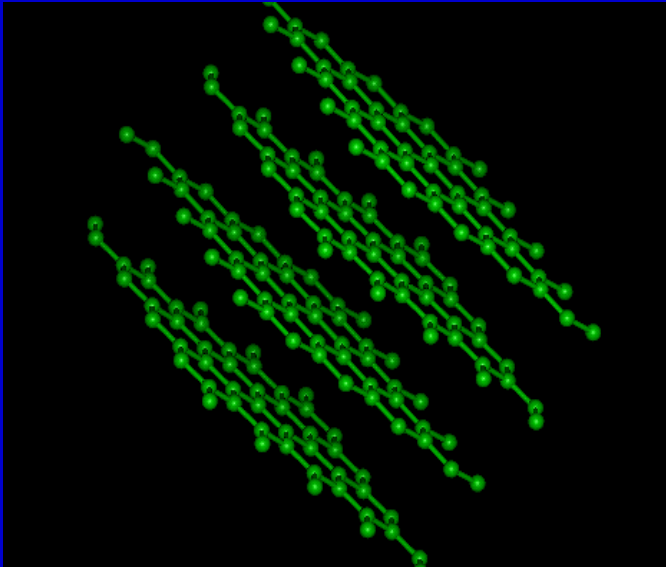


Solid Lubricants and Nanotribology

Fernando Lázaro Freire Jr.

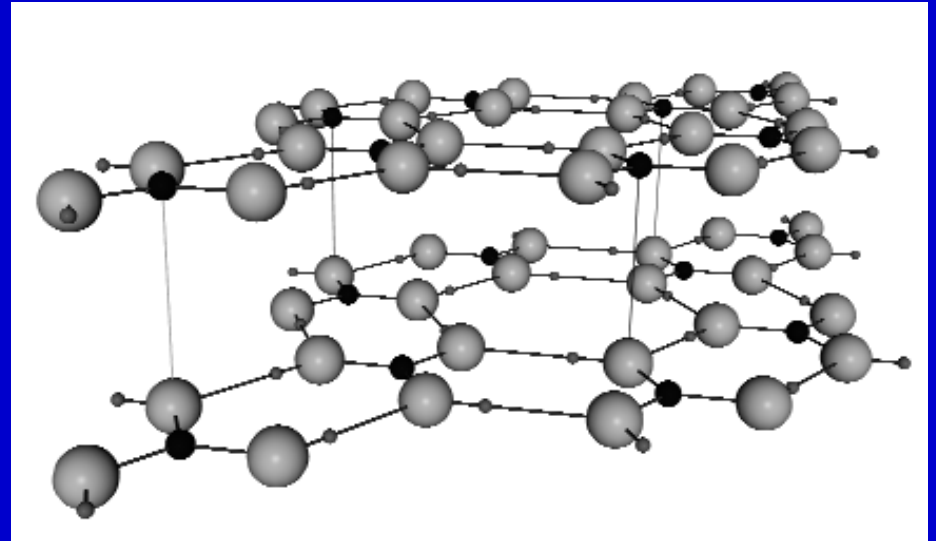
Departamento de Física, PUC-Rio

Solid Lubricants



C-C sp^2 → interatomic distance: 1.42 Å

Distance between planes: 3.35 Å

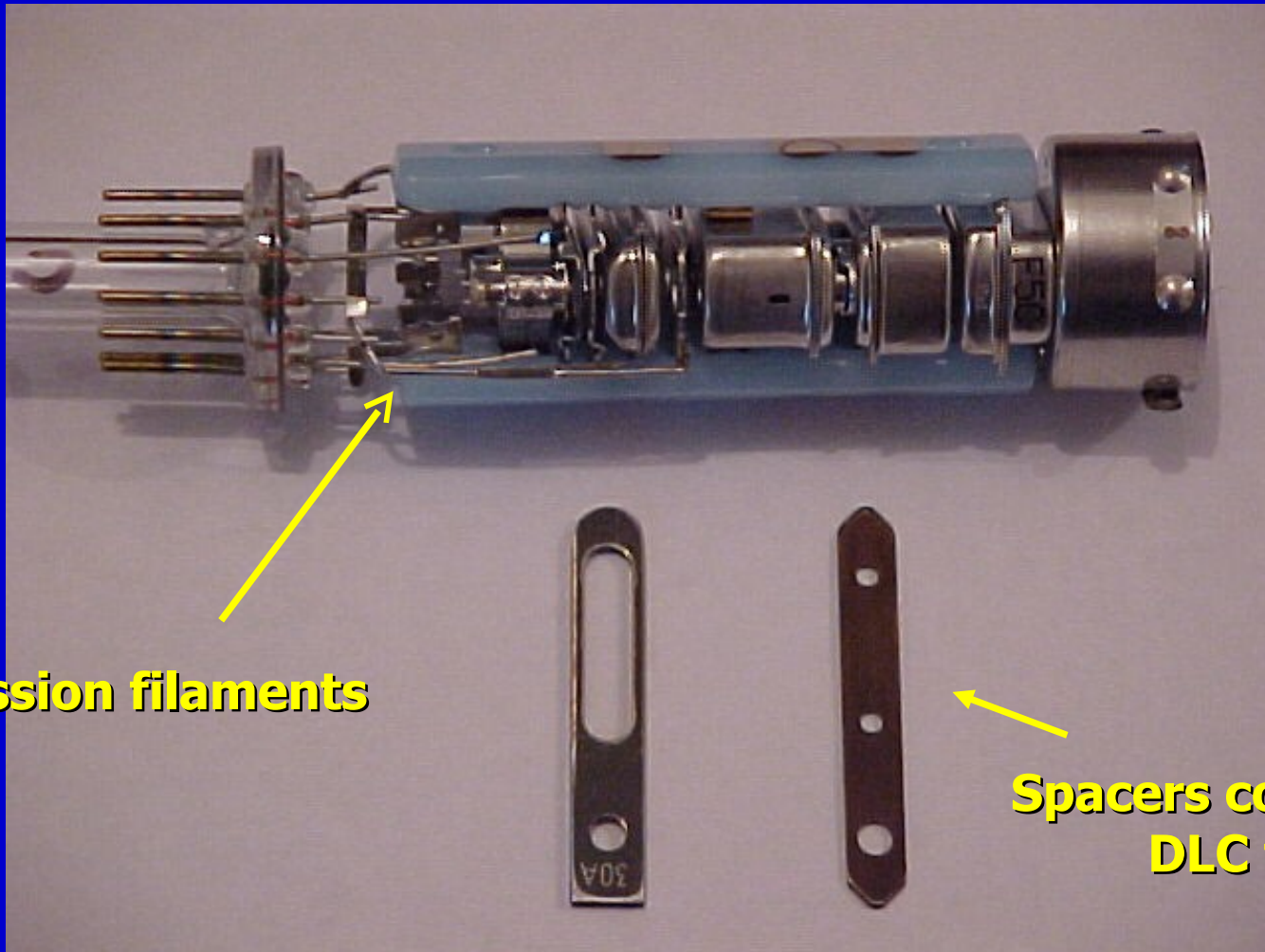


Boric acid: H_3BO_3

Distance between planes : 3.18 Å

Surf. Eng. **15**, 291 (1999)

Cathode rays tubes



Emission filaments

**Spacers coated with
DLC films**

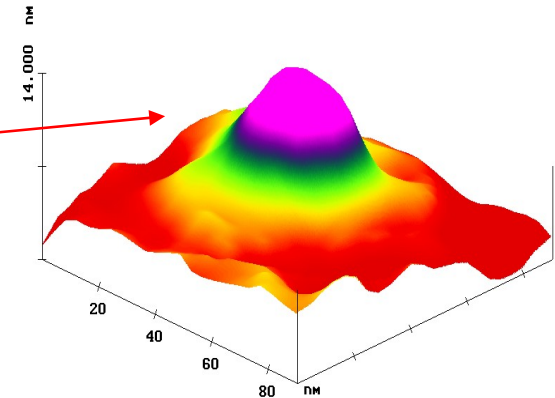
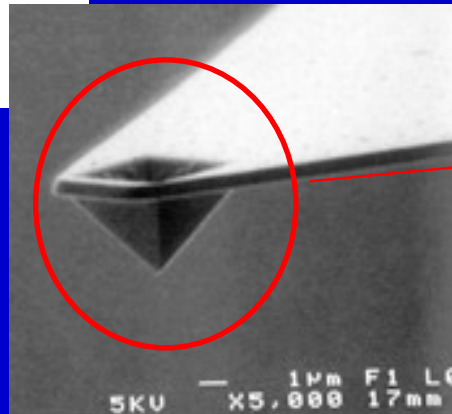
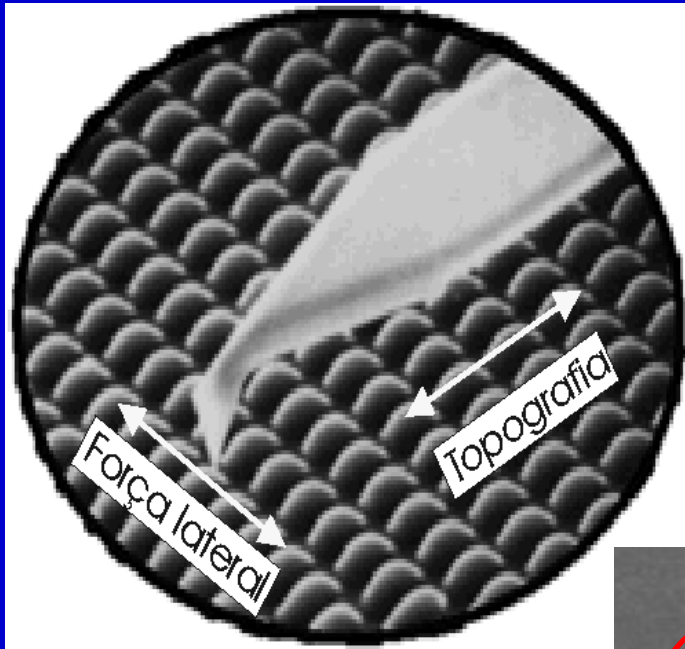
Macroscopic friction

AMONTON Laws (1698):

- Friction is independent on the contact area.
- Friction is independent on the velocity.
- Friction is proportional to the normal force

$$\mu = F_F / F_N$$

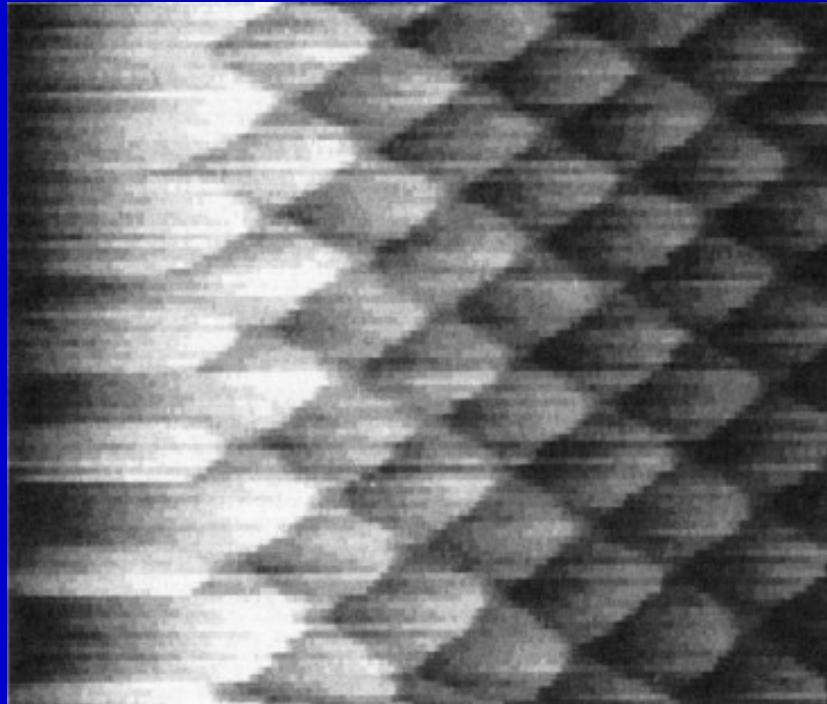
AFM: Nanotribology



Stick and slip

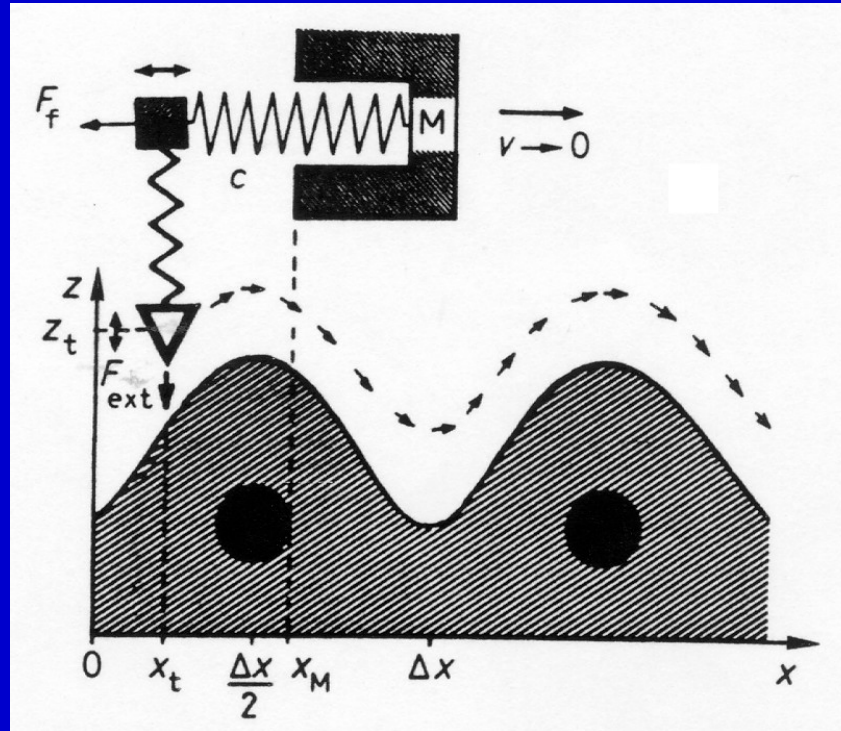
$2 \times 2 \text{ nm}^2$

Dark-light: $1.6 \mu\text{N}$



C.M. Mate *et al*, PRL 59 (1987) 1942

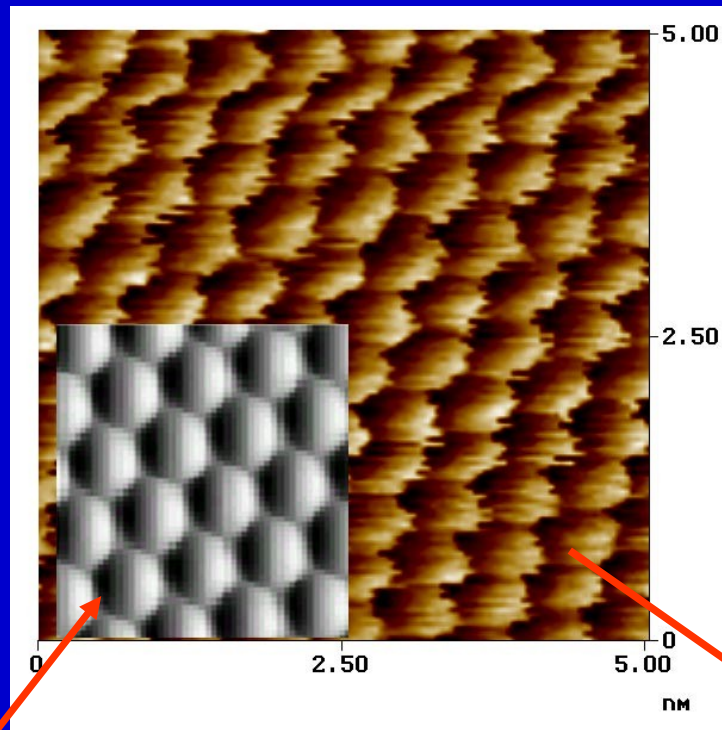
Tip movement



$$m \frac{\partial^2 x}{\partial t^2} = k_x(X - x) - \frac{\partial U_{BA}(x, y)}{\partial x} - \gamma \frac{\partial x}{\partial t},$$

$$m \frac{\partial^2 y}{\partial t^2} = k_y(Y - y) - \frac{\partial U_{BA}(x, y)}{\partial y} - \gamma \frac{\partial y}{\partial t},$$

$$U_{BA}(x, y) = U_0 \left[\cos\left(\frac{2\pi x}{a_x}\right) \cos\left(\frac{2\pi y}{a_y}\right) \right].$$

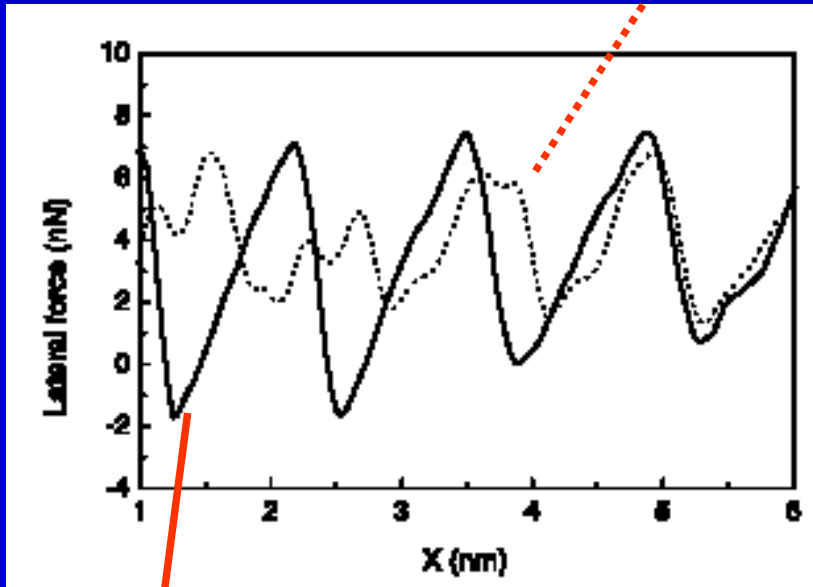


simulation

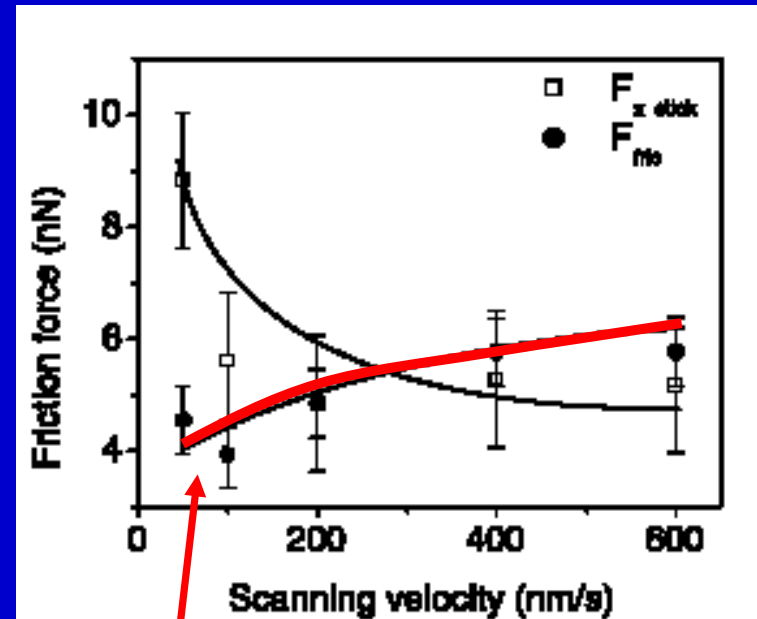
friction force map

A.R. Rivas, R. Prioli, R.M. Zamora, Ultramicroscopy 97 (2003) 315
Stick and slip amorphous surfaces

500 nm/s



50 nm/s



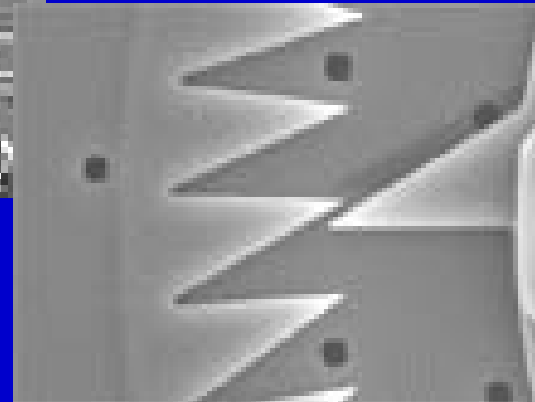
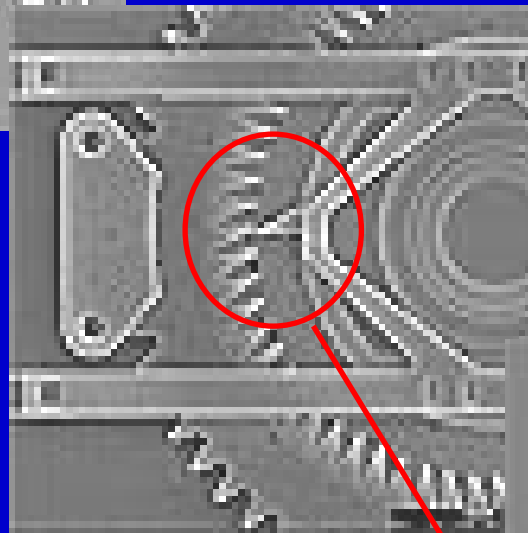
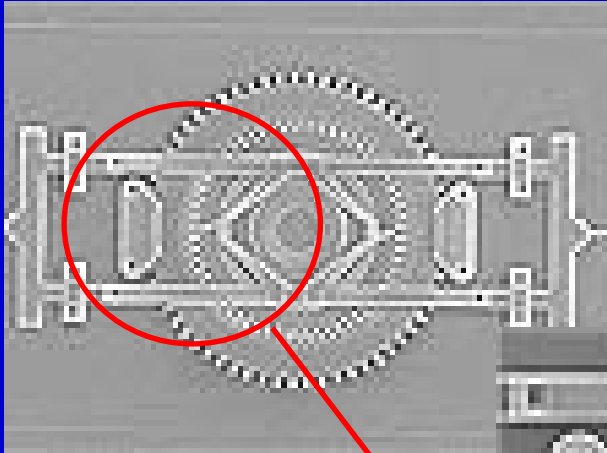
$$F_F = (F_x^{\max} + F_x^{\min})/2$$

R. Prioli, A.R. Rivas, F.L. Freire Jr., Appl. Phys. A 76 (2003) 565
Dependence with velocity and normal force

Nanotribology applications

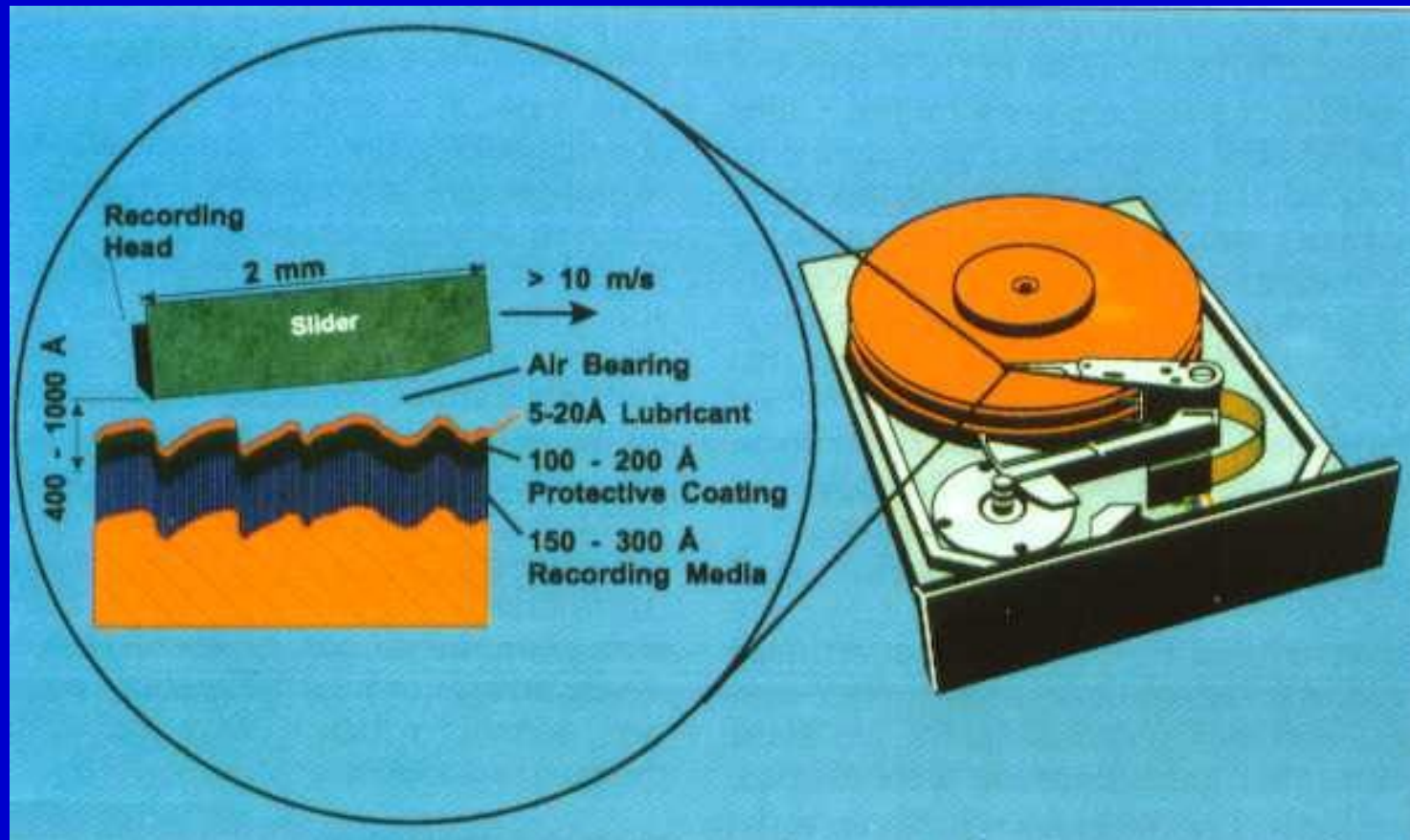
Energy dissipation processes

Adhesion forces

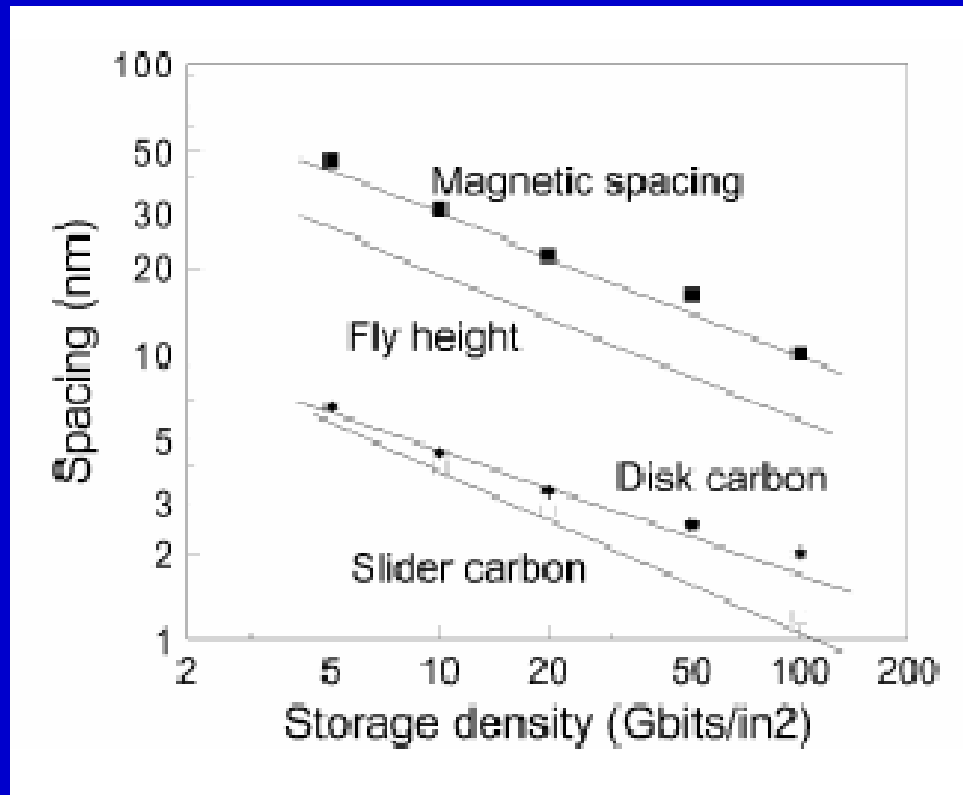


MEMS and NEMS

Hard magnetic disks

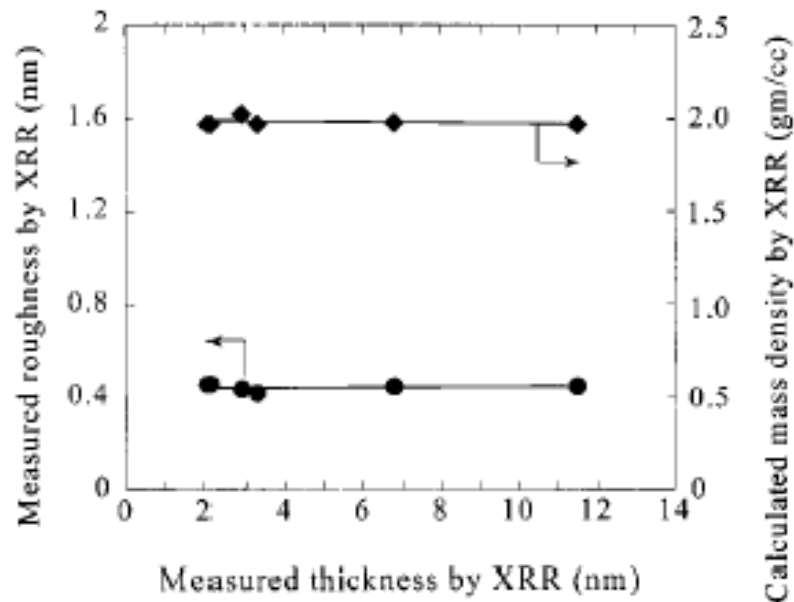


Hard magnetic disks: road map



<http://www.almaden.ibm.com/st/projects/lubricants/>

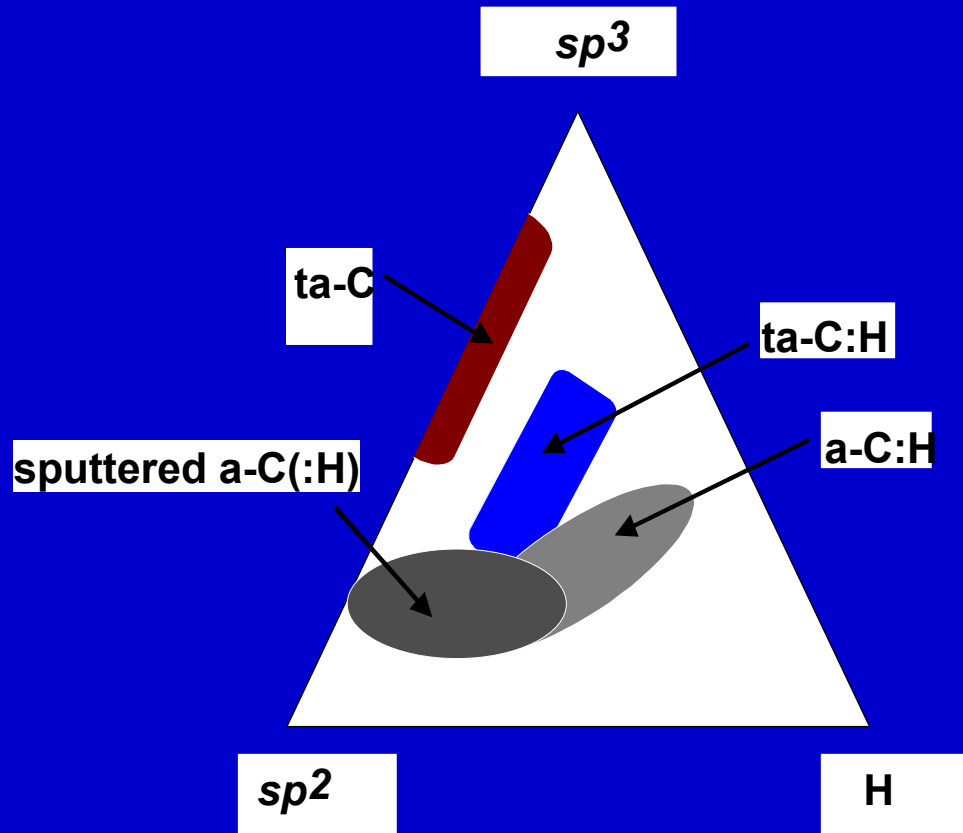
Metrology of 1–10 nm thick CN_x films: Thickness, density, and surface roughness measurements



**a- CN_x films deposited by
pulsed dc magnetron
sputtering**

**Dejun Li, Yanfeng Chen, Yip-Wah Chung, F. L. Freire Jr.
J. Vac. Sci. Technol. A 21 (2003) L19**

Carbon-based films:



Influence of humidity and velocity

- AFM calibration.**
- hidrofilic and hidrofobic surfaces.**
- results.**

**R. Prioli, M.E. H. Maia da Costa, F.L. Freire Jr. , Tribology
Letters 15 (2003) 177**

**R.M.R. Zamora, C. S. Tasayco, R. Prioli, F.L. Freire Jr., Phys.
Stat. Sol. A 201 (2004) 550; Surface Science (submitted)**

Influence of surface wettability

- Hydrophobic films

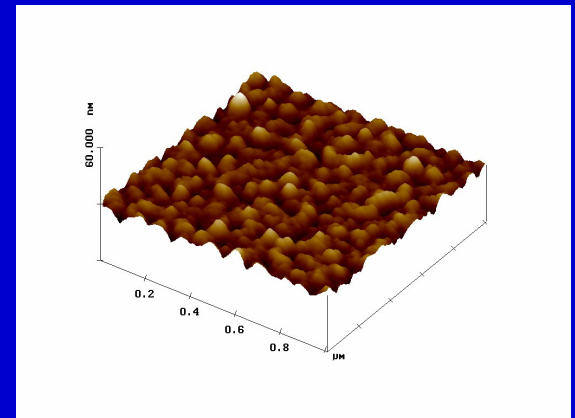
Amorphous carbon films Contact angles (°)

a-C:F

70 - 95

a-C:H:N

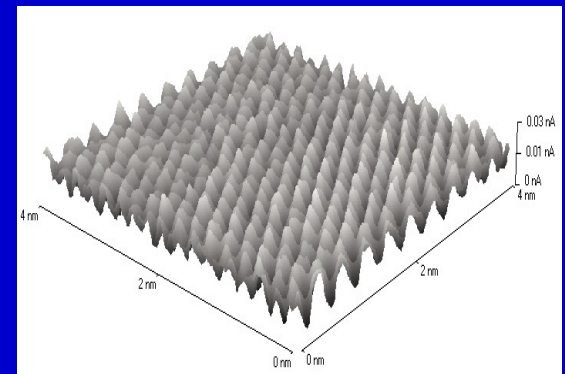
60 - 78



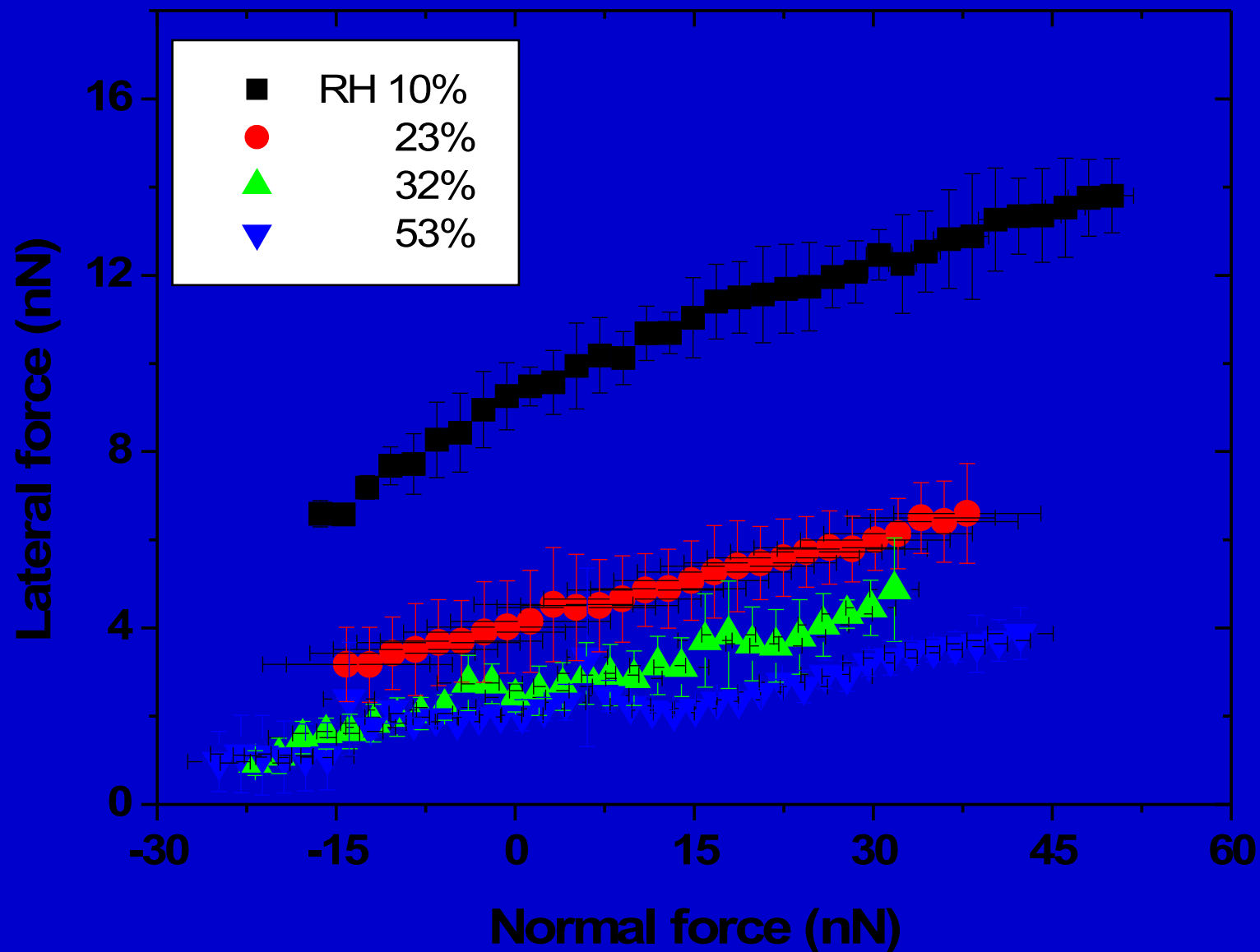
Hydrophilic surfaces

mica

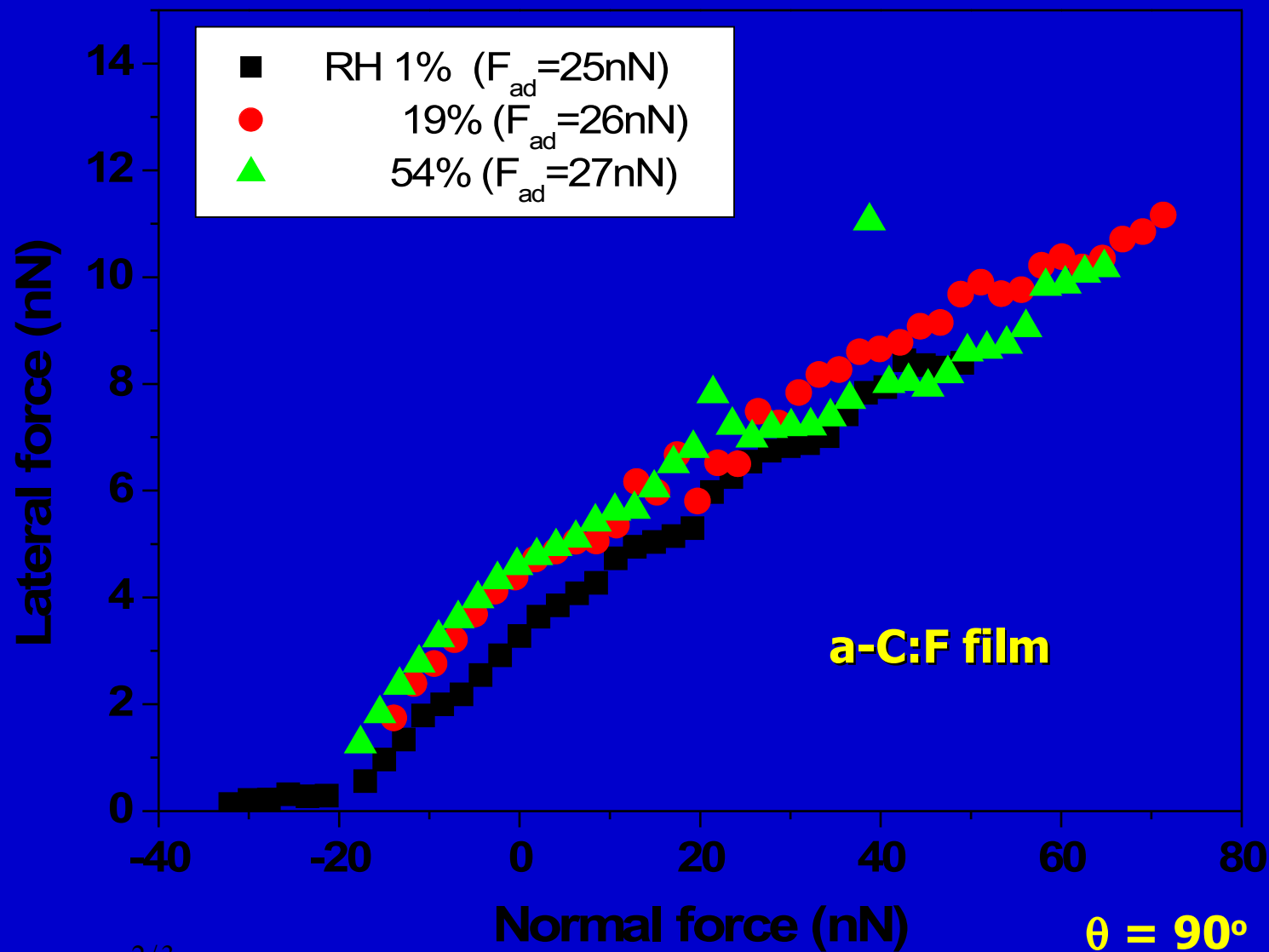
5 - 10



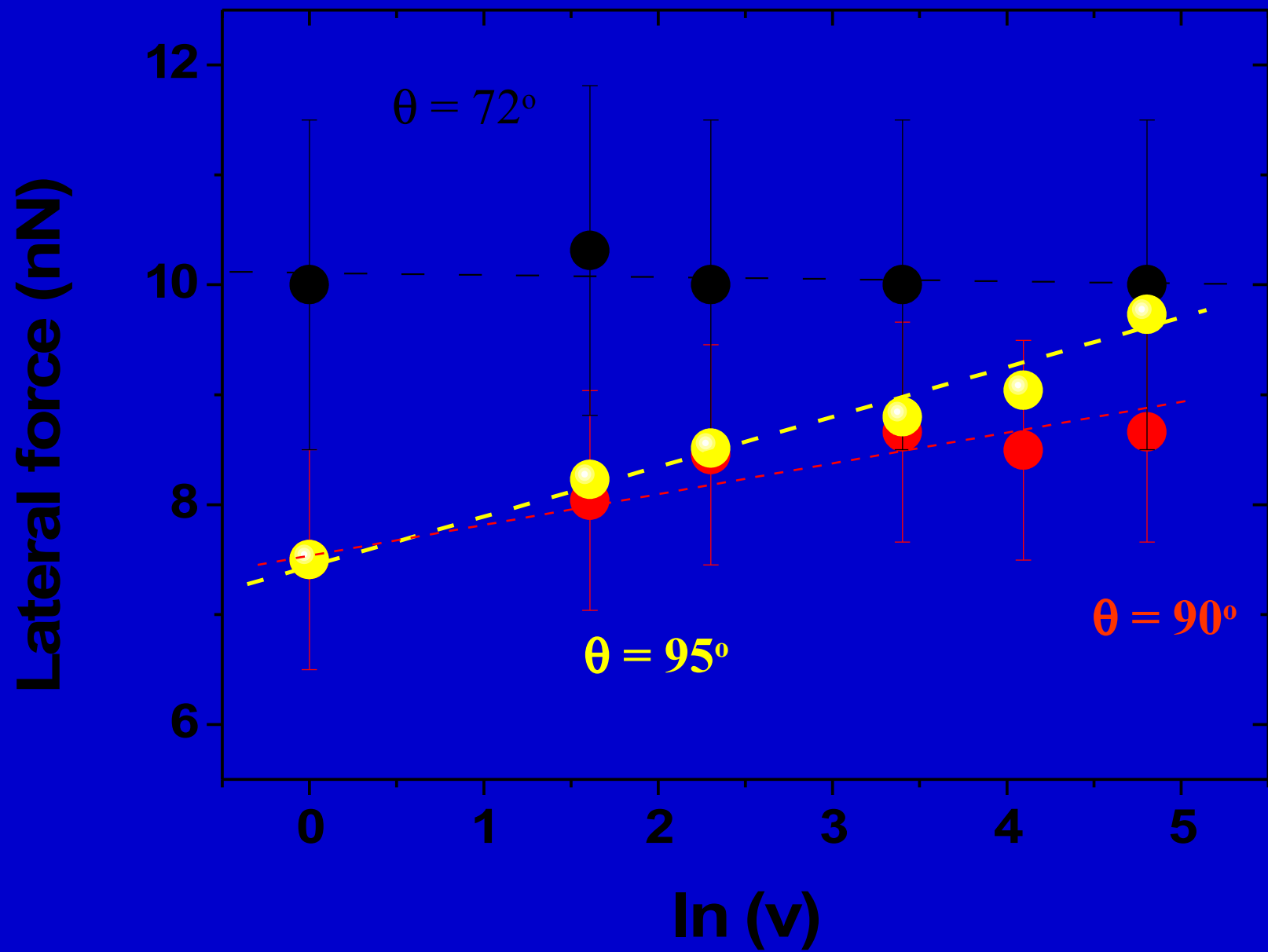
Hydrophilic mica



Hydrophobic amorphous carbon



$$F_L = CF_N^{2/3} + \alpha F_N$$



Friction model

VOLUME 88, NUMBER 18

PHYSICAL REVIEW LETTERS

6 MAY 2002

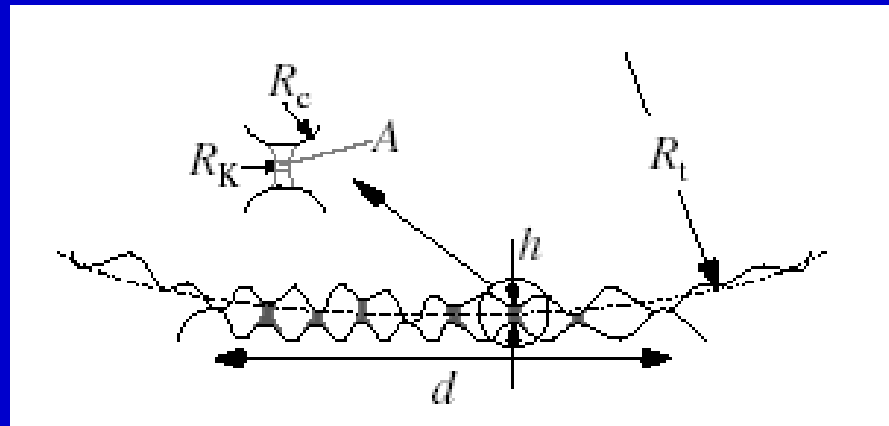
Kinetics of Capillary Condensation in Nanoscopic Sliding Friction

Elisa Riedo,¹ Francis Lévy,² and Harald Brune¹

¹*Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

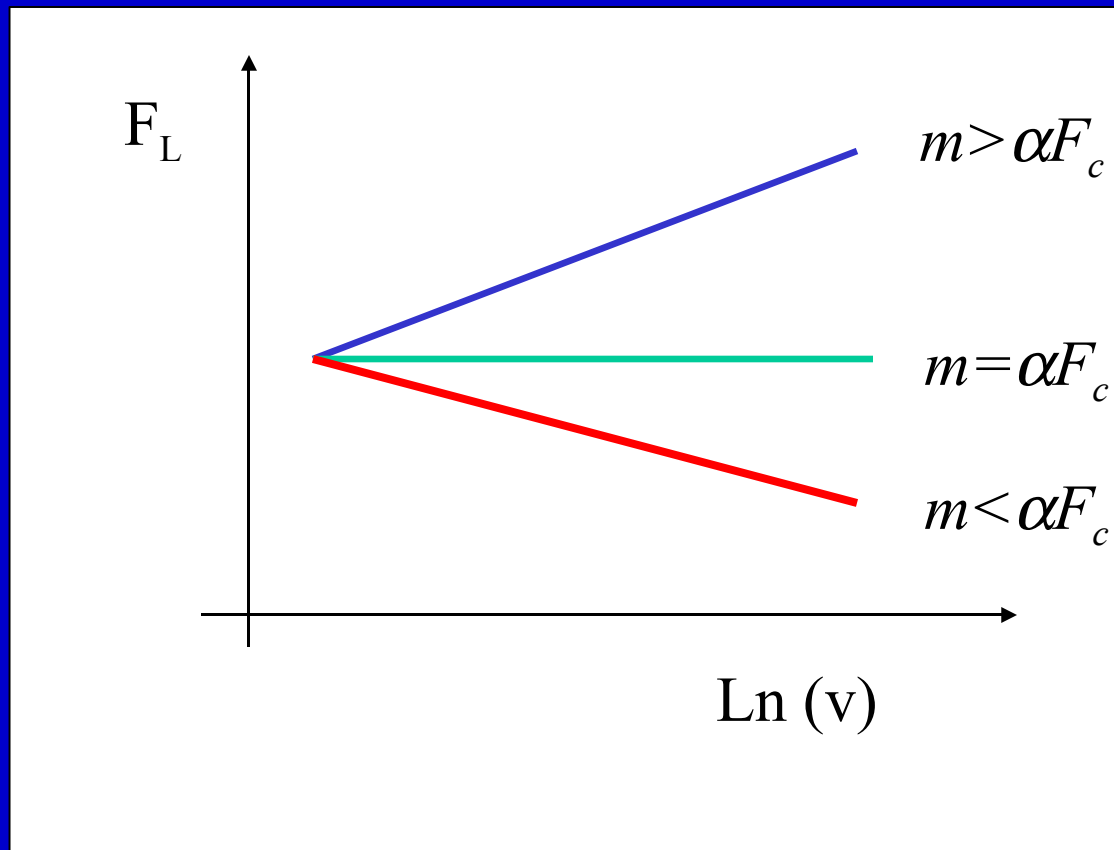
²*Institut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

(Received 20 December 2001; published 18 April 2002)

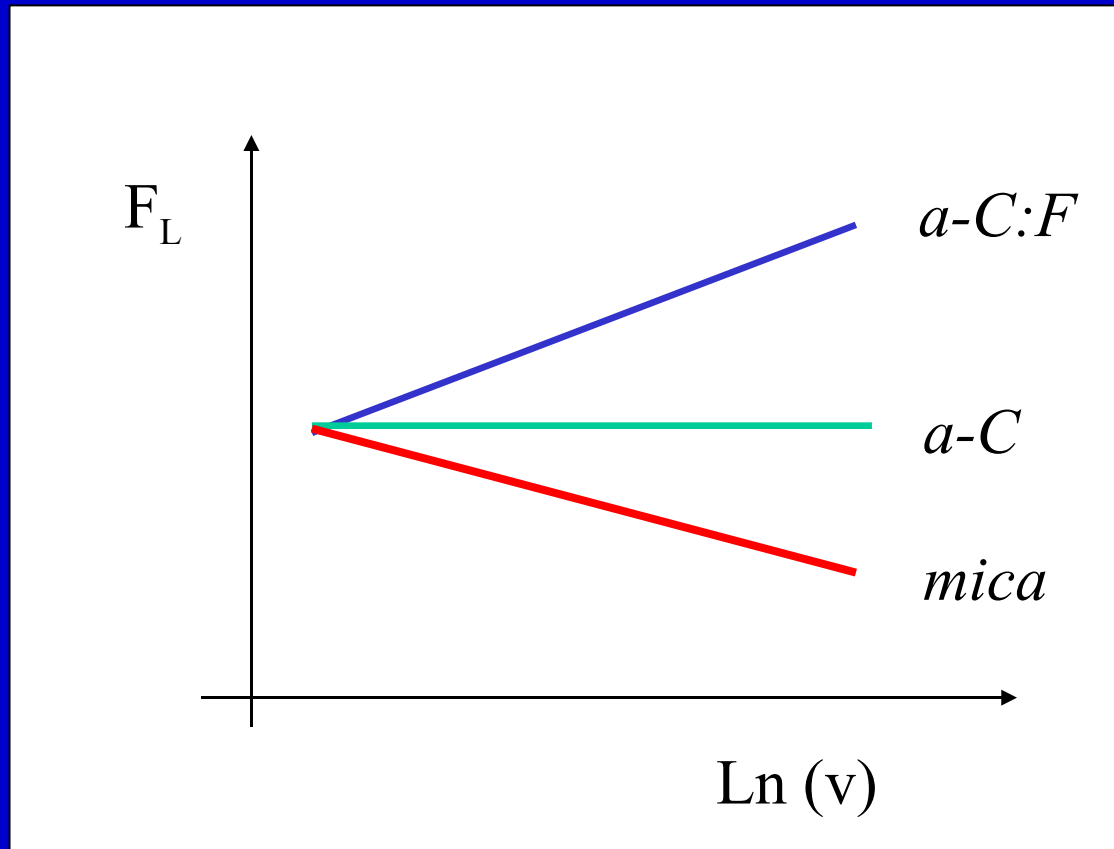


$$\begin{aligned}
 F_F &= \mu(F_N + F_{ss}) + \mu[F_c f(t)] + m \ln\left(\frac{v}{v_B}\right) \\
 &= \mu(F_N + F_{ss}) - \mu[2\pi R_t \gamma (\cos\theta_s + \cos\theta_t)] \\
 &\quad \times \left(\frac{1}{\lambda A \rho} \frac{1}{\ln \frac{p_s}{p}}\right) \ln \frac{v}{v_A} + m \ln\left(\frac{v}{v_B}\right),
 \end{aligned}$$

$$F_L = \mu F_N + [m - \alpha F_C] \ln(v)$$



$$F_L = \mu F_N + [m - \alpha F_C] \ln(v)$$



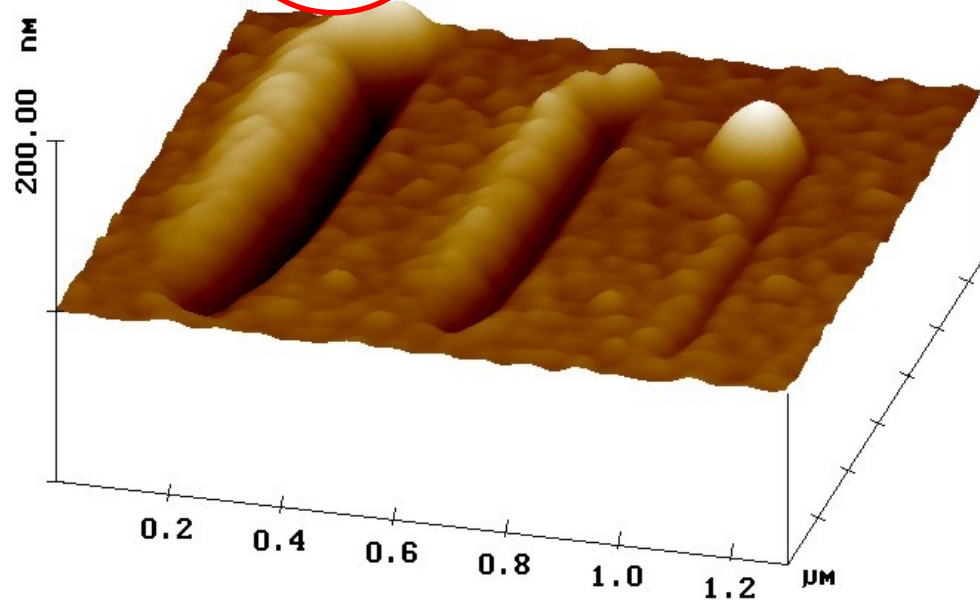
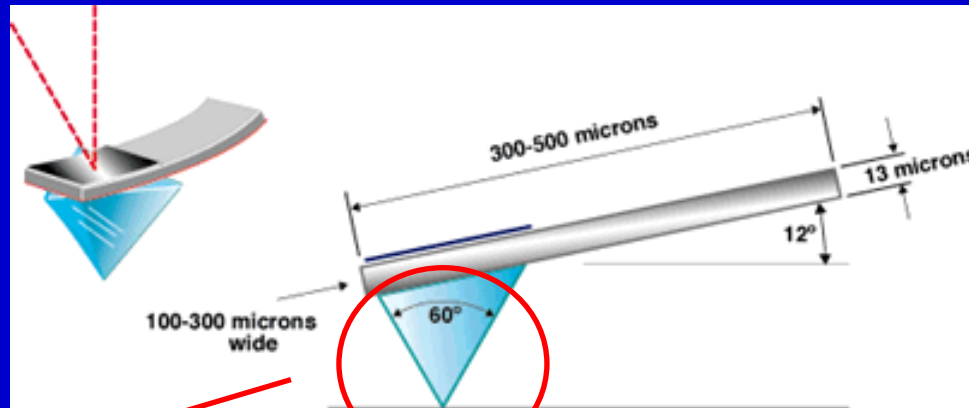
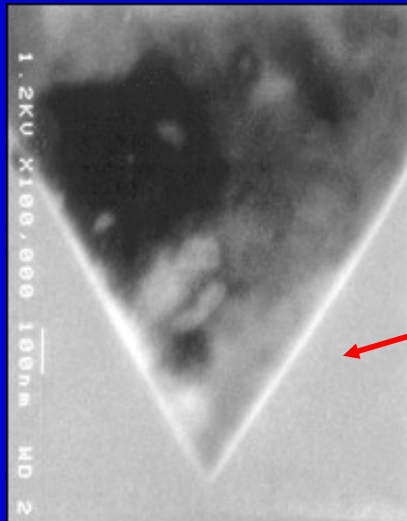
Conclusions:

- **The velocity dependence of friction is strongly influenced by the capillary condensation of water.**



- **The friction can be correlated with the surface hydrophobicity.**

Wear at nanometer scale



Films:

→ deposited by PECVD in $\text{C}_2\text{H}_2\text{-CF}_4$ atmosphere: a-C:H and a-C:F

a-C:H Hardness → 20 GPa; $\text{sp}^3/\text{sp}^2 \sim 1$; H = 20 at.%

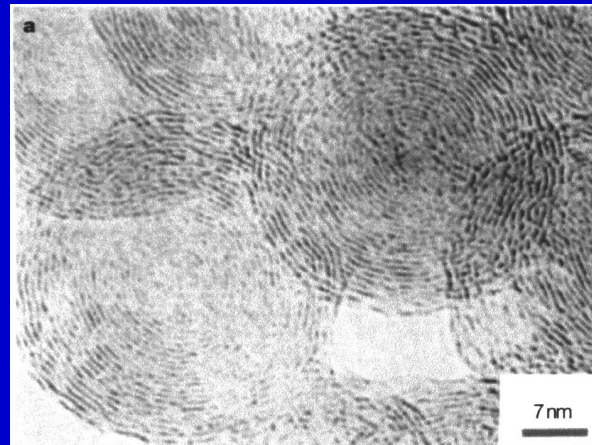
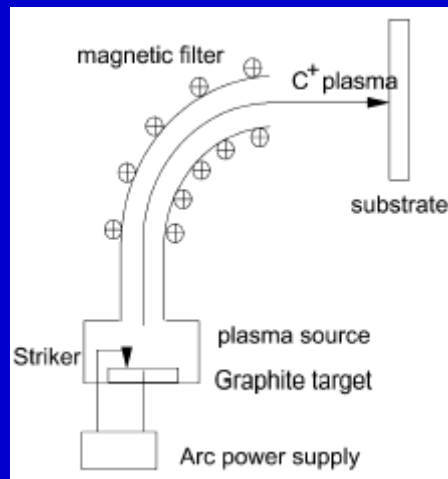
a-C:F Hardness → 5 GPa; F = 23 at.%

→ deposited by filtered arc: ta-C and nanostructured carbon films

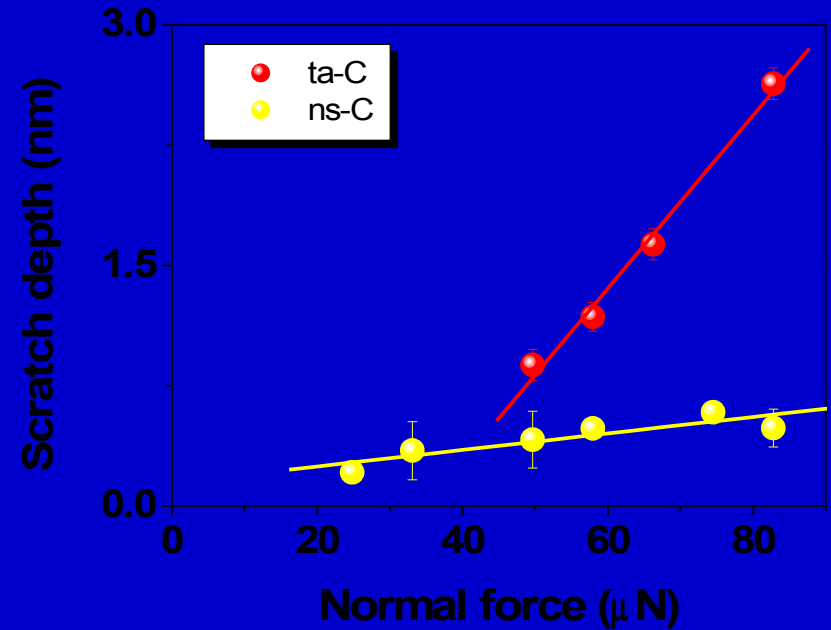
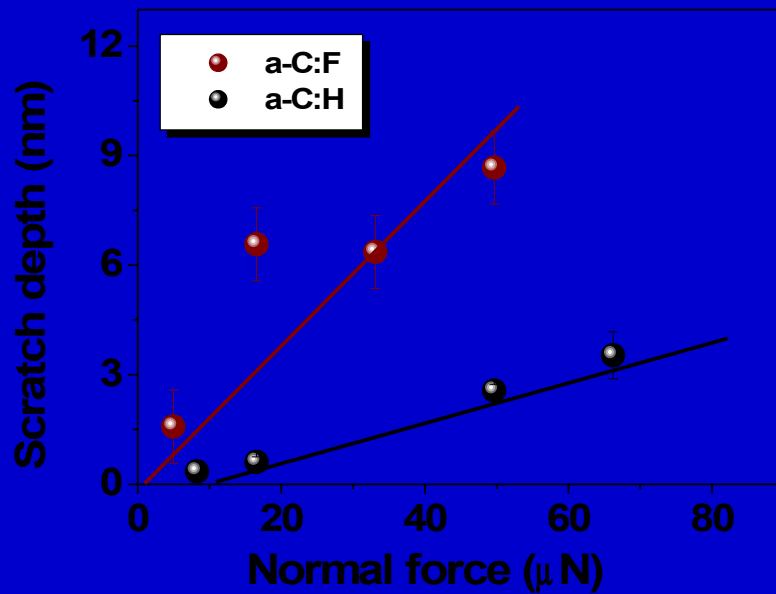
ta-C Hardness → 80 GPa; $\text{sp}^3/\text{sp}^2 \sim 4$

ns-C Hardness → ? (high elastic recovery); $\text{sp}^3/\text{sp}^2 \sim 0$

F.L. Freire Jr., R. Prioli, M. Chowala, Diamond and Related Materials, 12 (2003) 2195

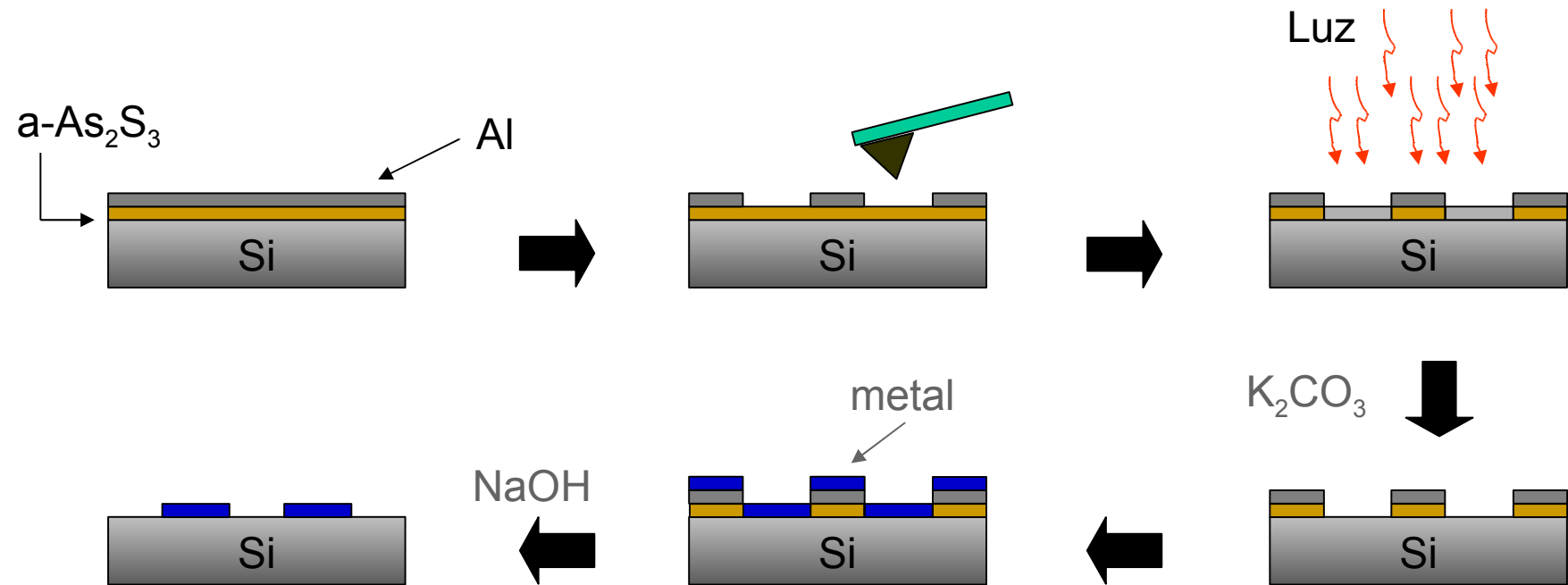


Scratch test

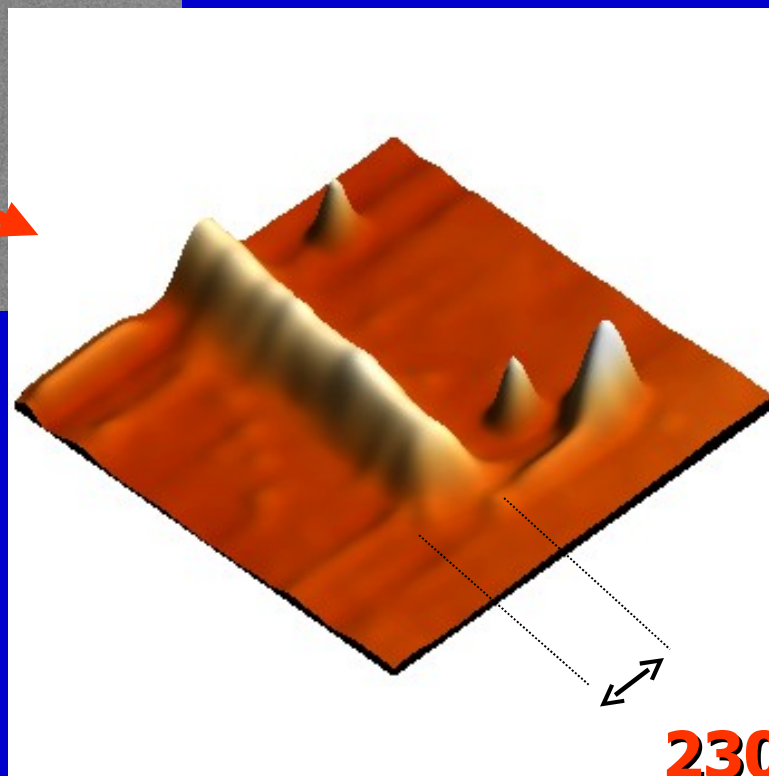
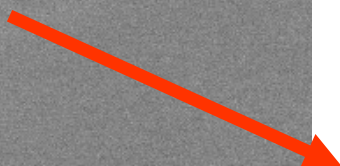
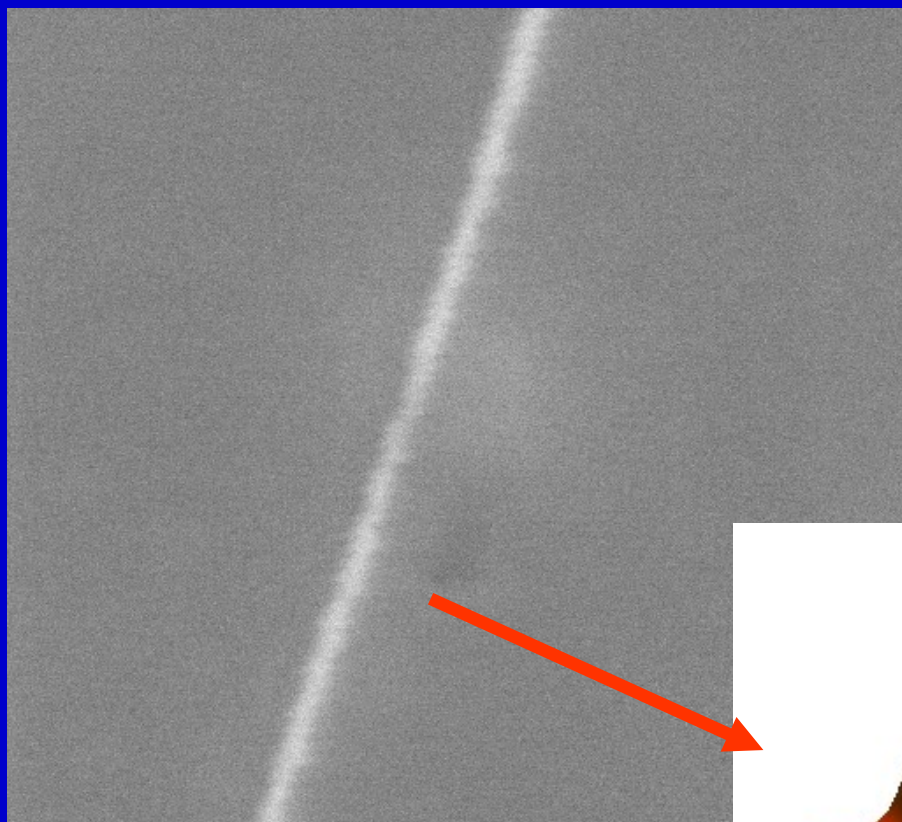


F.L. Freire Jr., R. Prioli, M. Chowala, *Diamond and Related Materials*, 12 (2003) 2195

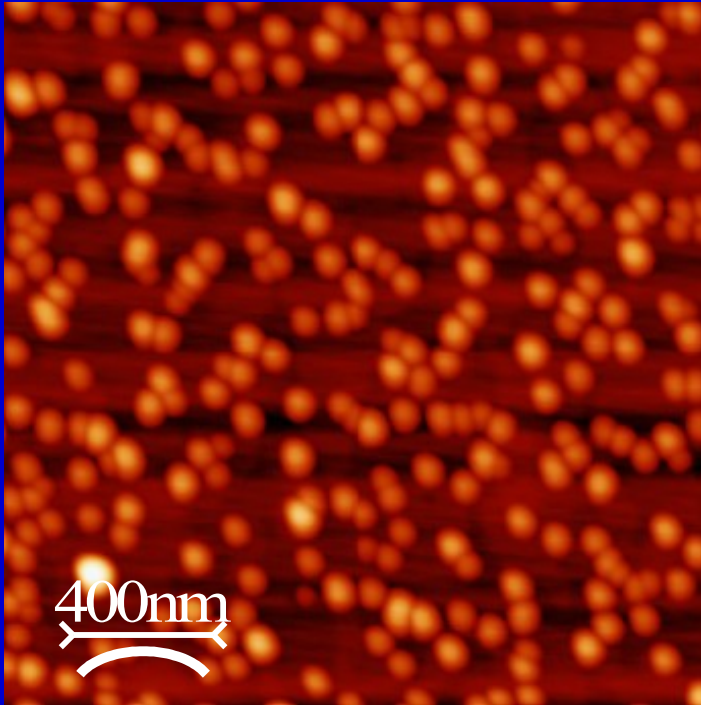
nanolithography



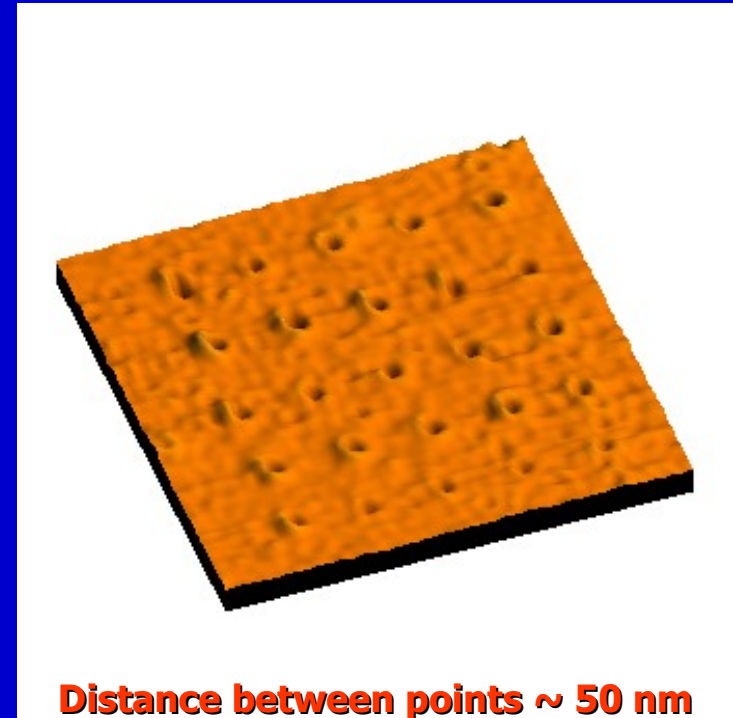
scheme



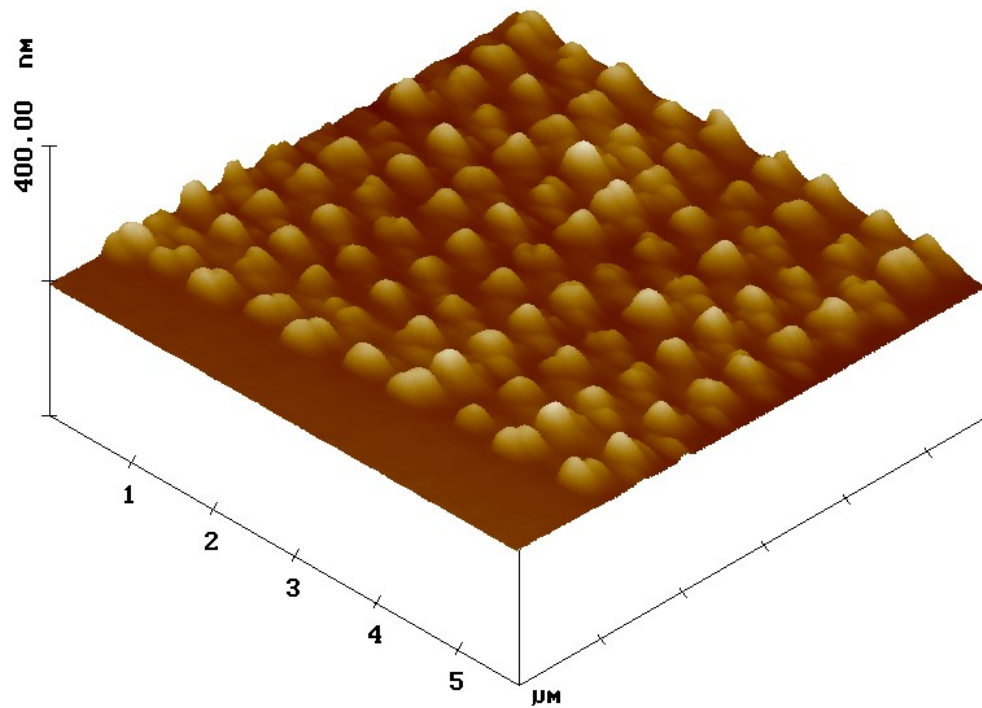
230 nm



**Atomic force microscopy of InAs
on InP**



**Defects induced by AFM tip on the
surface of InP**



InAs quantum dots grown onto InP

Prof. Rodrigo Prioli

Dra. Valéria Nunes

PHd students:

Marcelo Eduardo H. Maia da Costa

Robert Zamora

Henrique Fonseca Filho

Cristiano Camacho

Paola Ayala

Carlos Sanchez Tasayco

M

MSc student:

Clara Muniz

Collaborators:

Prof. Gino Mariotto (Università di Trento, Italia)

Prof. Manish Chowala (Rutgers University, USA)

Prof. Yip Wah Chung (Northwestern University, USA)

CNPq, CAPES and FAPERJ

In order to fit our experimental data with Riedo's model we need to calculate or measure the parameters ν_a , ν_b , m , P_s , P etc.

$$\nu_a = \frac{2a}{t_a} \quad \begin{array}{l} \text{(contact diameter)} \\ \text{(time to built up a capillary bridge 25 } \mu\text{s)} \end{array}$$

a is obtained with the use of the Johnson-Kendal-Robertson

$$F_{ad} = -\frac{3}{2}\pi RW_{12}$$

$$\frac{1}{E} = \frac{(1-\nu_{tip}^2)}{E_{tip}} + \frac{(1-\nu_s^2)}{E_s}$$

$$a^3 = \frac{R}{E} \left[F + 3\pi RW_{12} + \sqrt{6\pi RW_{12}F + (3\pi RW_{12})^2} \right]$$

Calibração de Força Lateral

	μ MICA	μ HOPG
PUC	0.062	0.009
LIU [1]	0.095	0.011
ELISA [2]		0.009
RUAN [3]		0.006
LABARDI [4]	0.027	0.013
WARMACK [5]	0.086	
Average	0.068	0.01
σ	0.034	0.002

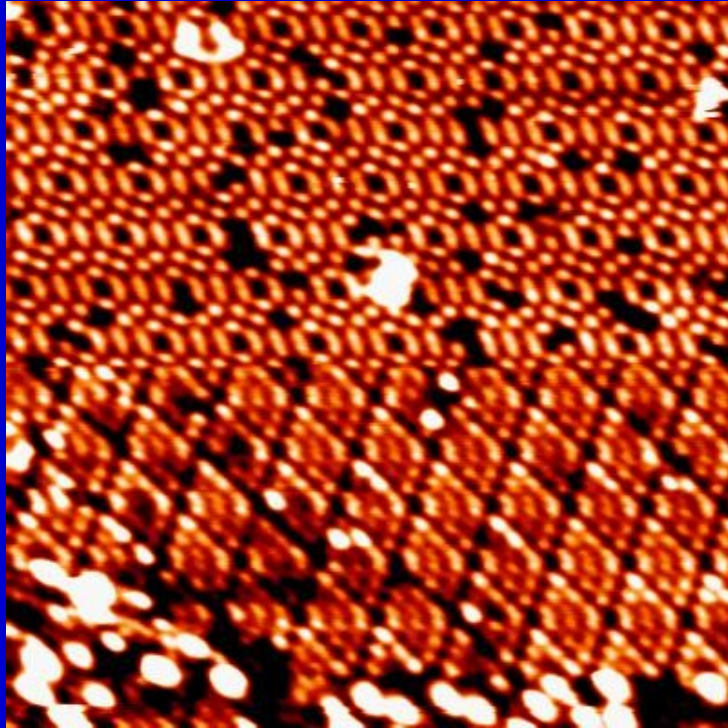
[1] - E.Liu et.al., Wear 192,141 (1996)

[2]- E.Riedo et. al., Surface Sci. 477, 25 (2001)

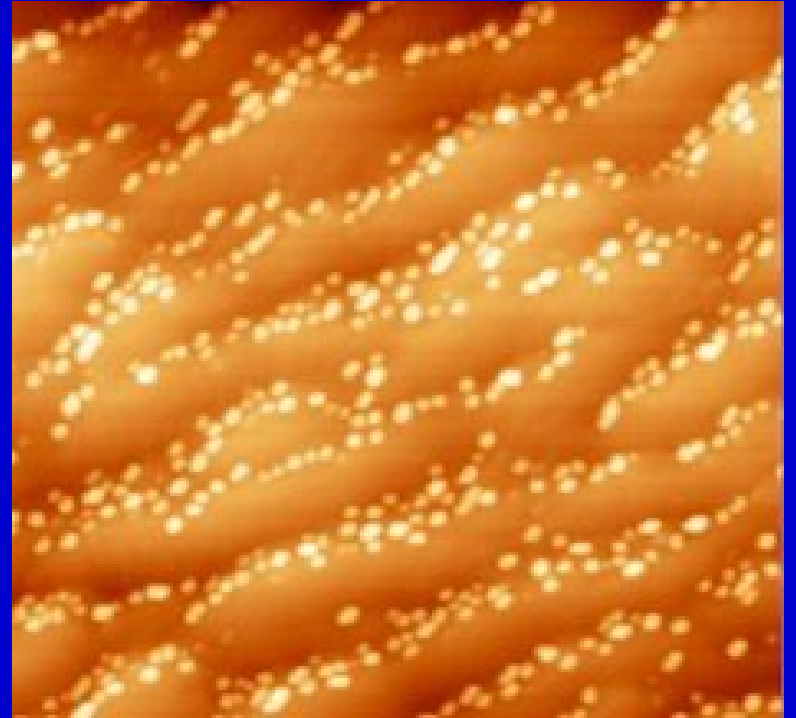
[3] - J.A.Ruan et. al., J. of Tribology 116, 378 (1994)

[4] - M.Labardi et.al., Appl. Phys. A 59, 3 (1994)

[5] - R. J. Warmack et. al., Rev. Sic. Instrum. 65, 394 (1994)

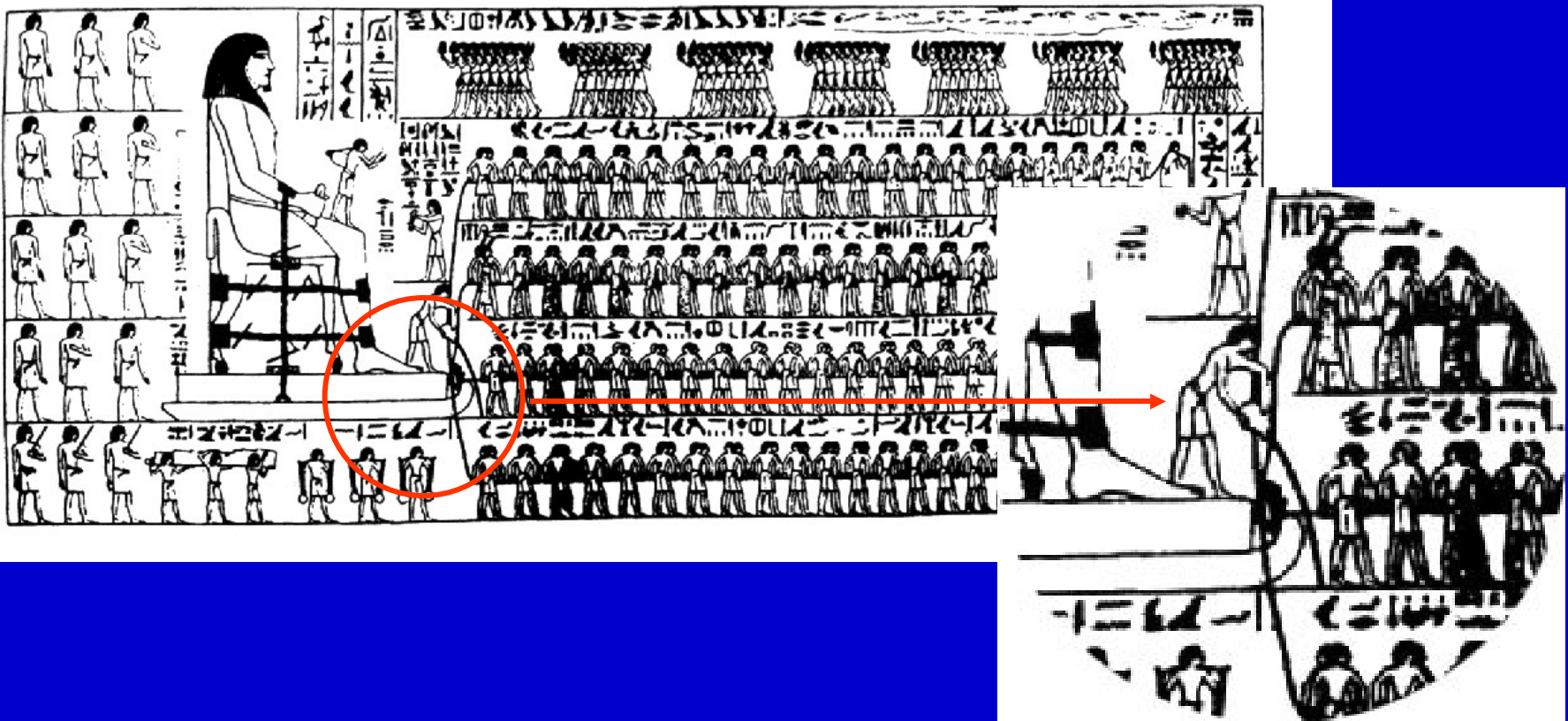


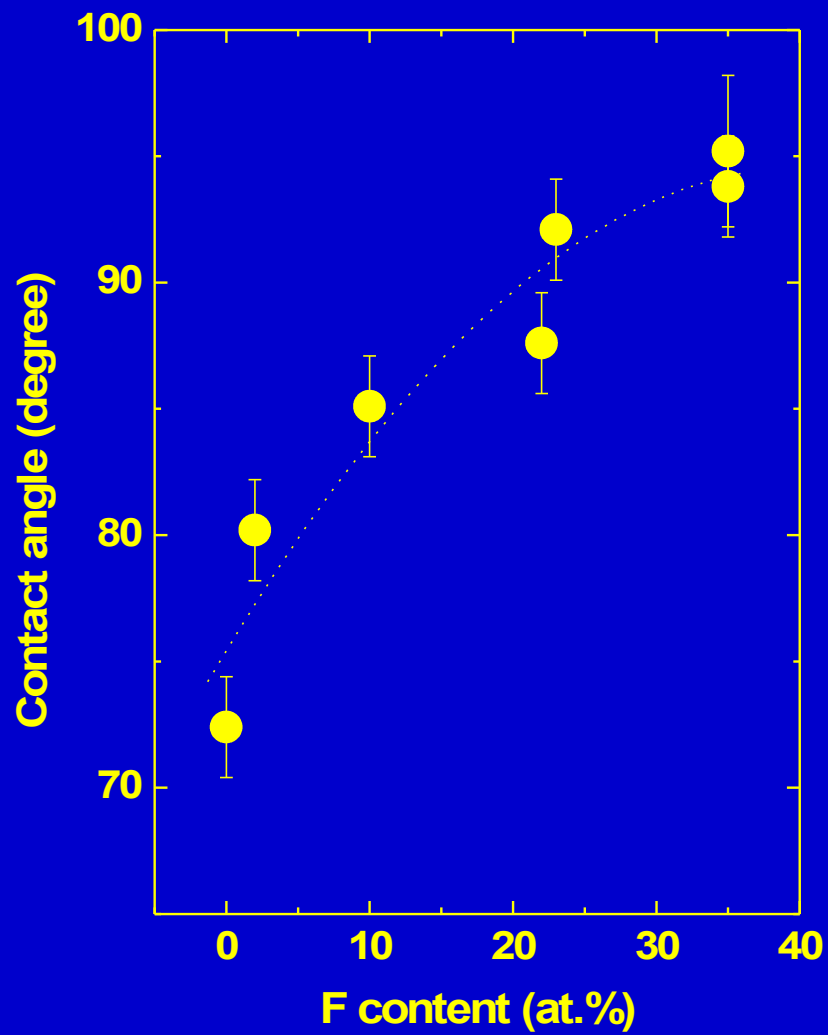
STM –UHV Si reconstructed 7x7



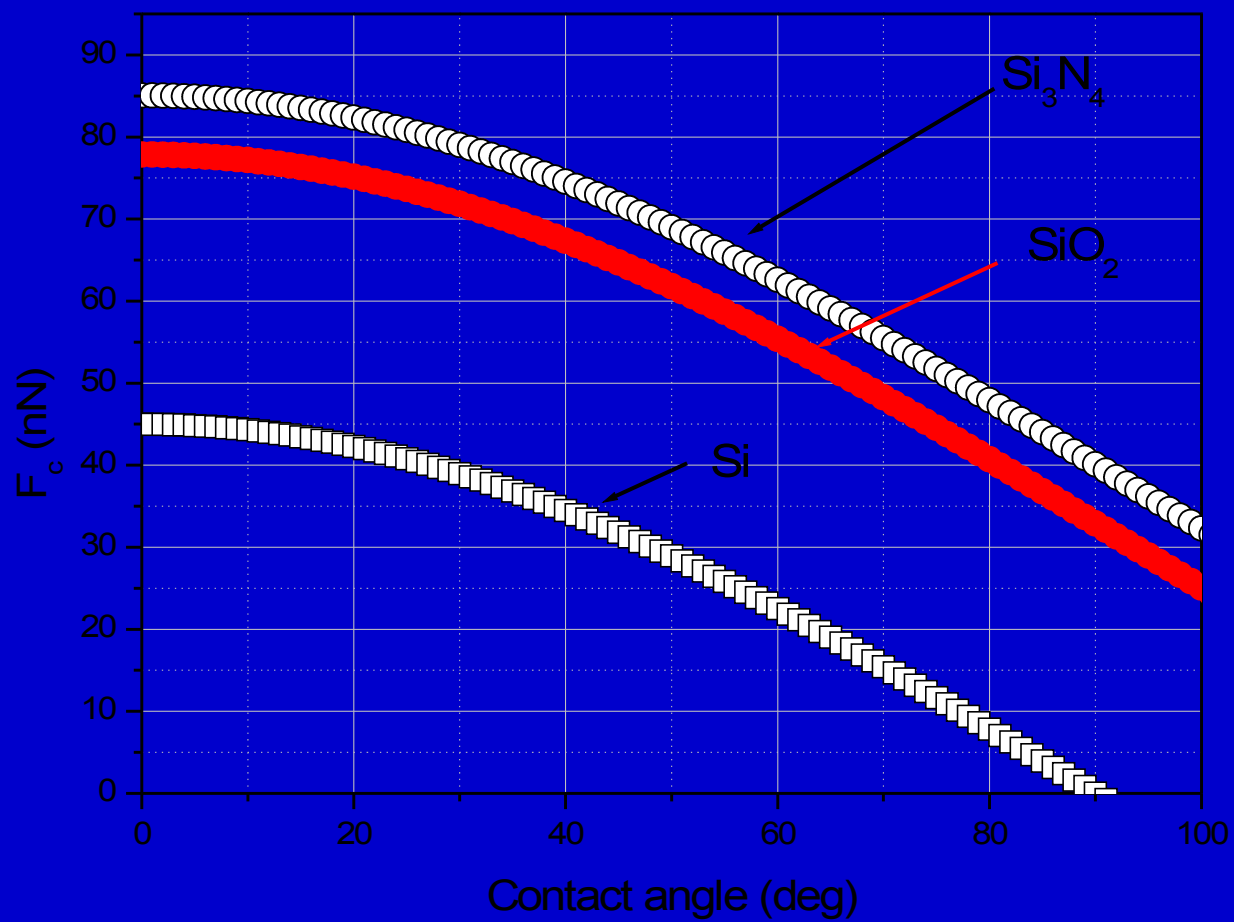
AFM dots

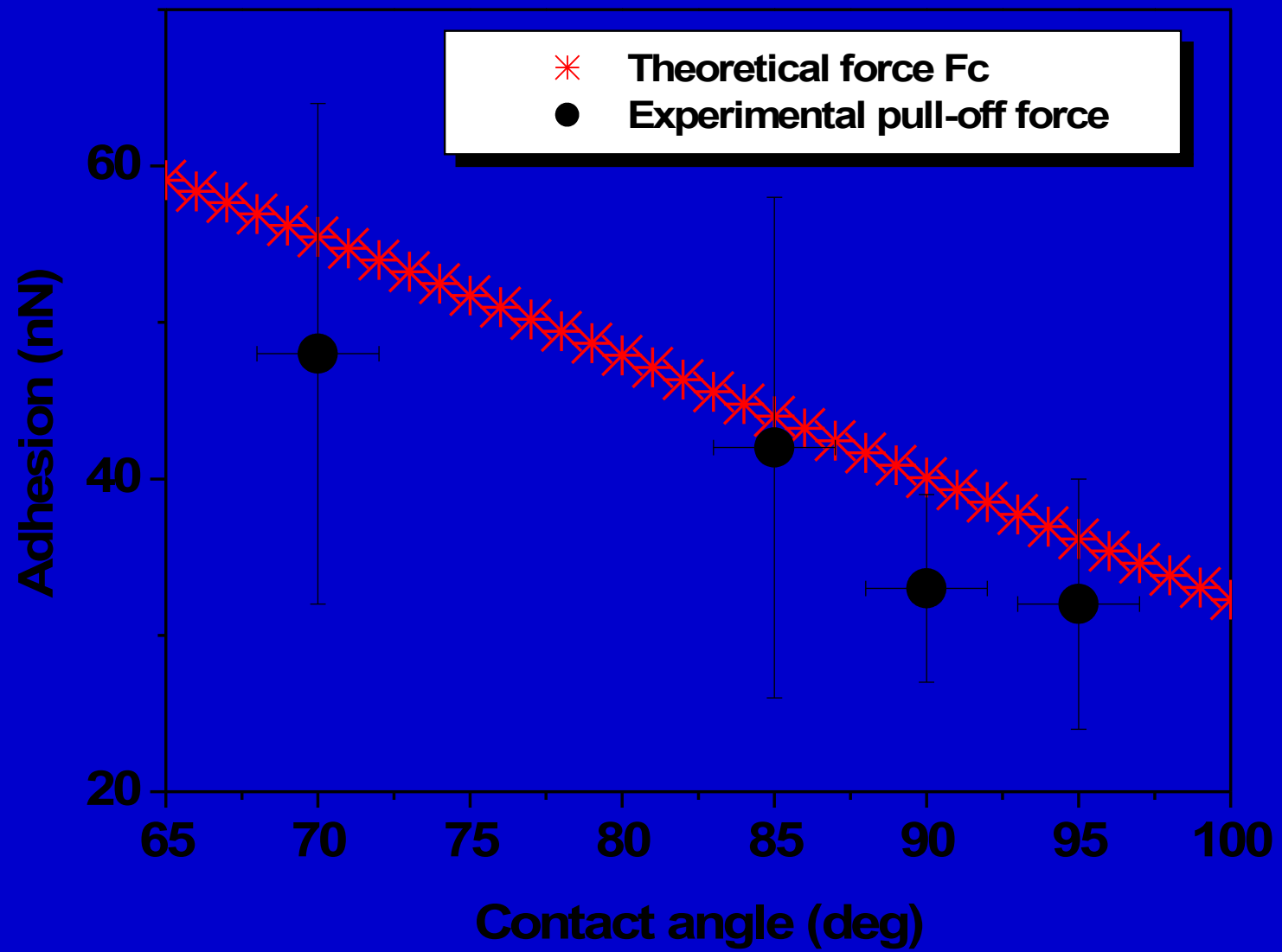
Tribologia

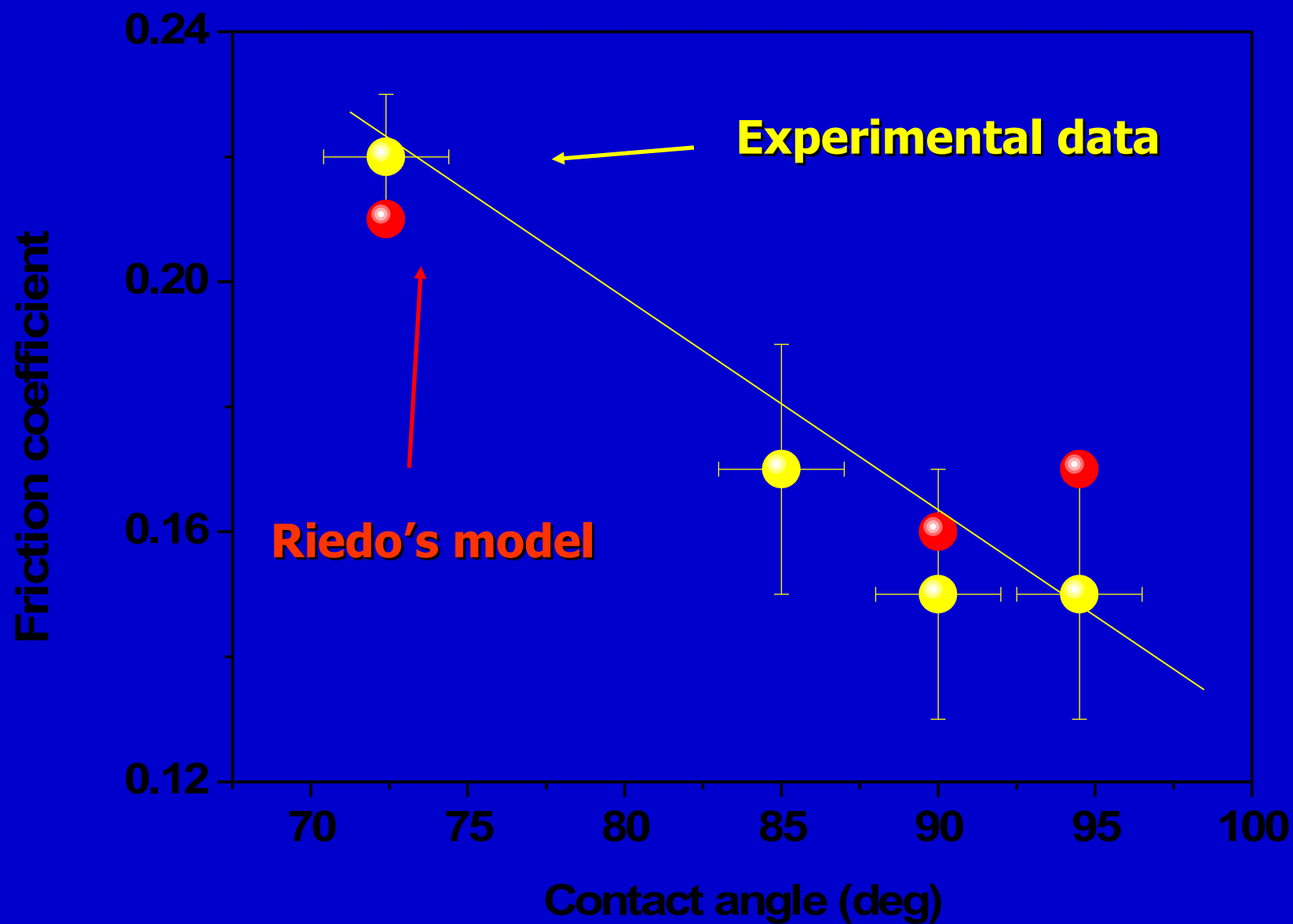




$$F_c = 2\pi R_t \gamma_L (\cos(\theta_s) + \cos(\theta_t))$$



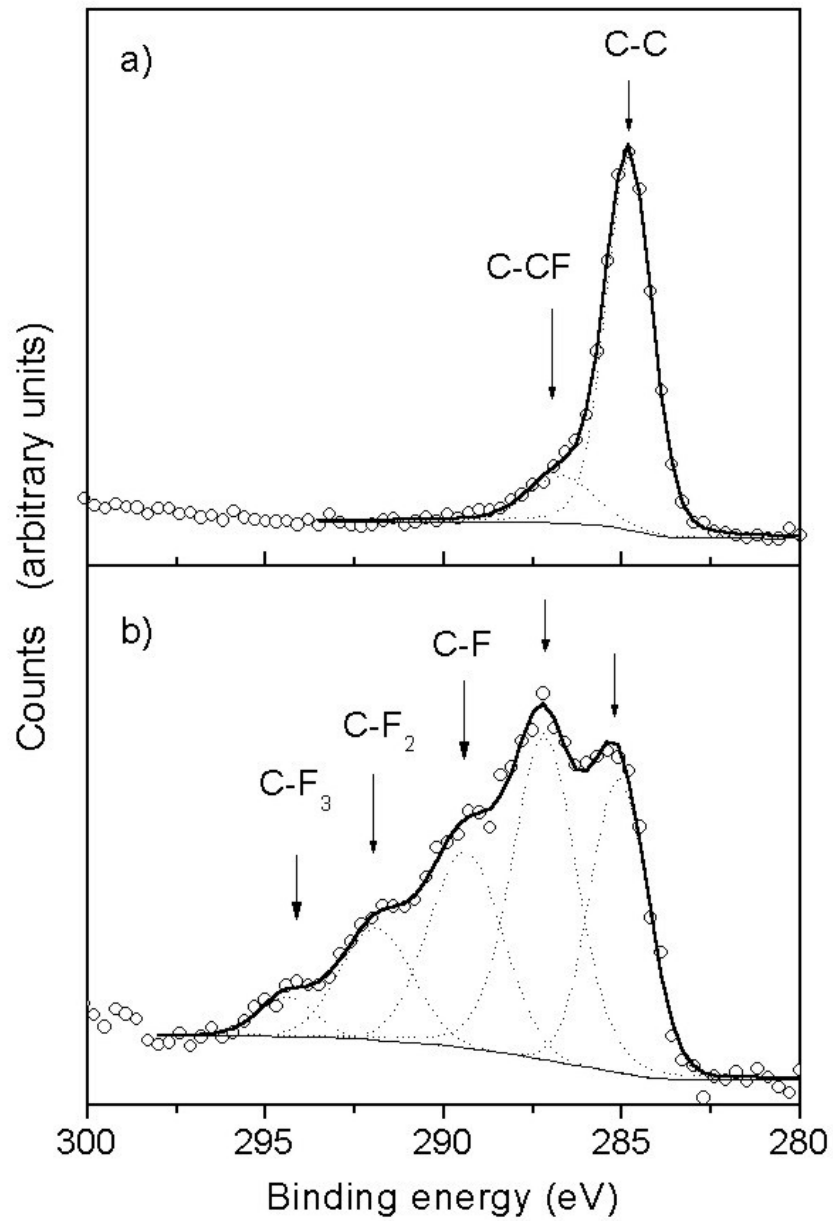




Films deposited by rf-PECVD using C₂H₂-CF₄ mixtures

C₂H₂ partial pressure (%)	Composition (at.%)				Atomic density (10²³ atoms/cm³)
	C	H	F	O	
100	77	22	0	1	1.3
90	76	21	2	1	1.2
77	74	15	10	1	1.1
50	73	4	22	1	0.9
33	70	2	23	5	0.7
25	60	2	35	3	0.6
20	60	2	35	3	0.7

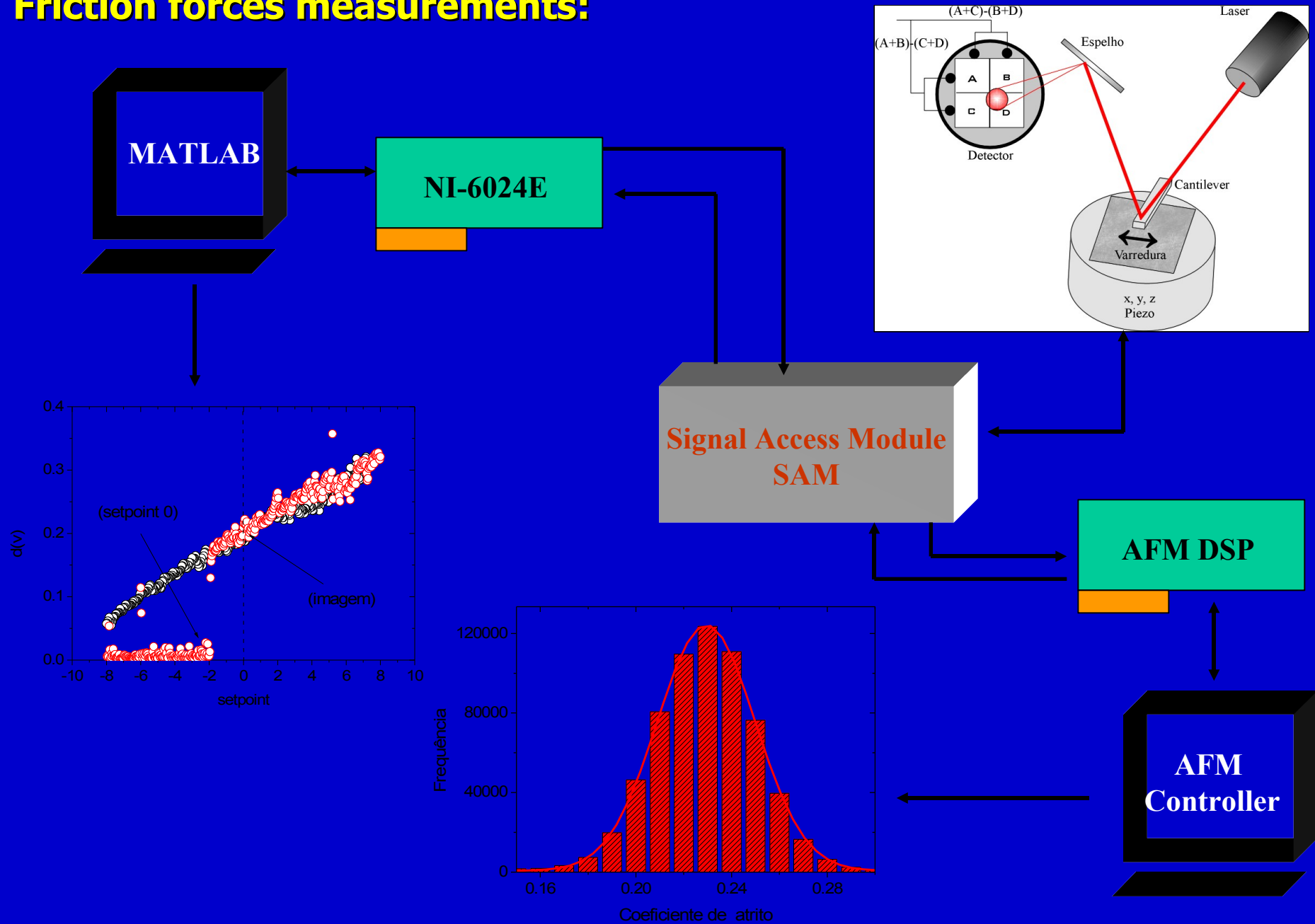
Chemical composition and atomic density by IBA



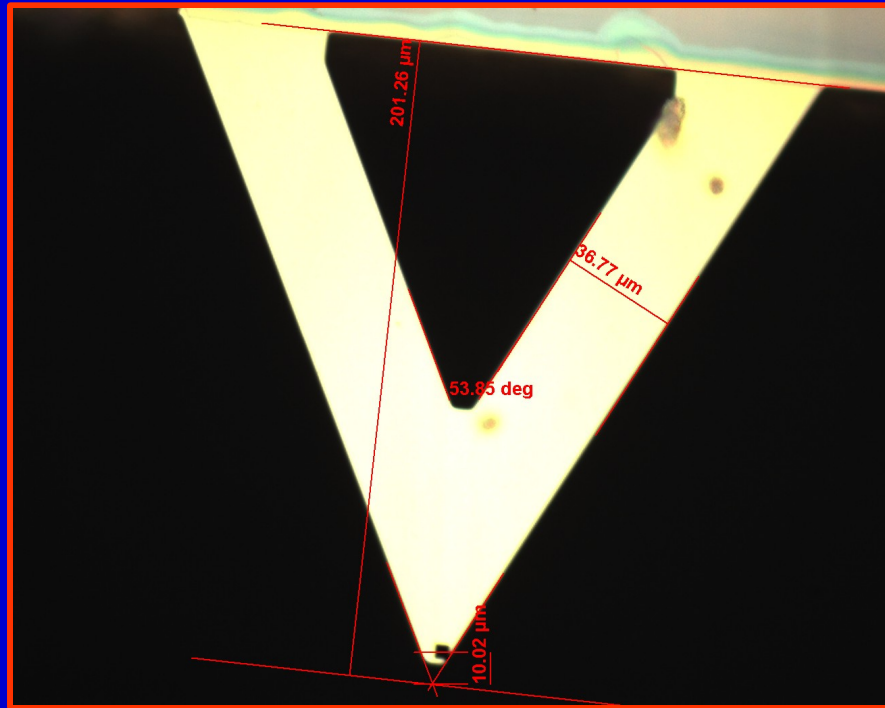
← **F = 10 at.%**

← **F = 35 at.%**

Friction forces measurements:



Cantilever calibration



EAFM Van de Graaff

File Method Help

Tip Material
☐ Si ☒ Si₃N₄

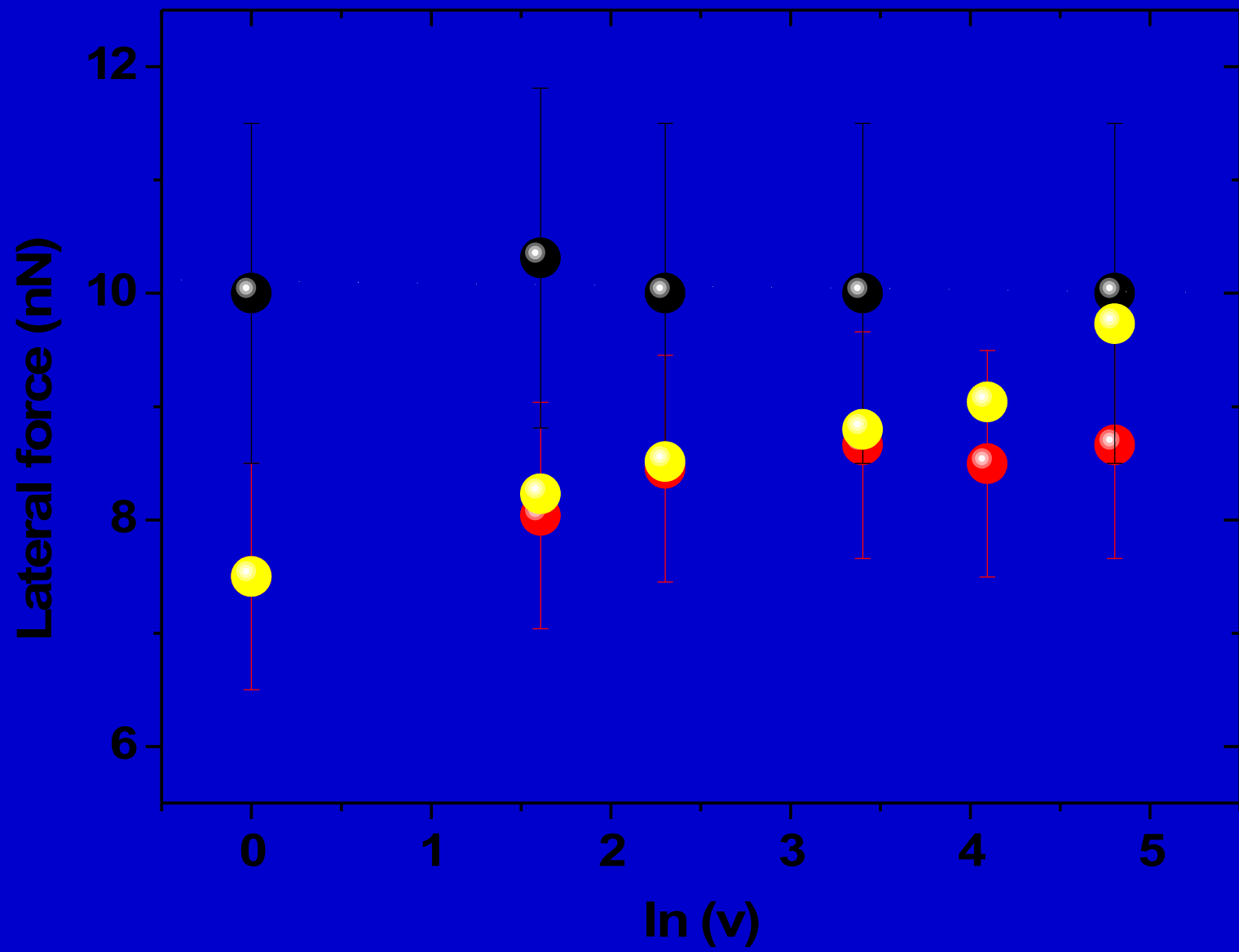
L (um)	190,7
h (um)	3,3
t (um)	0,72
w (um)	26,03
a (deg)	26,68
d (um)	9,68

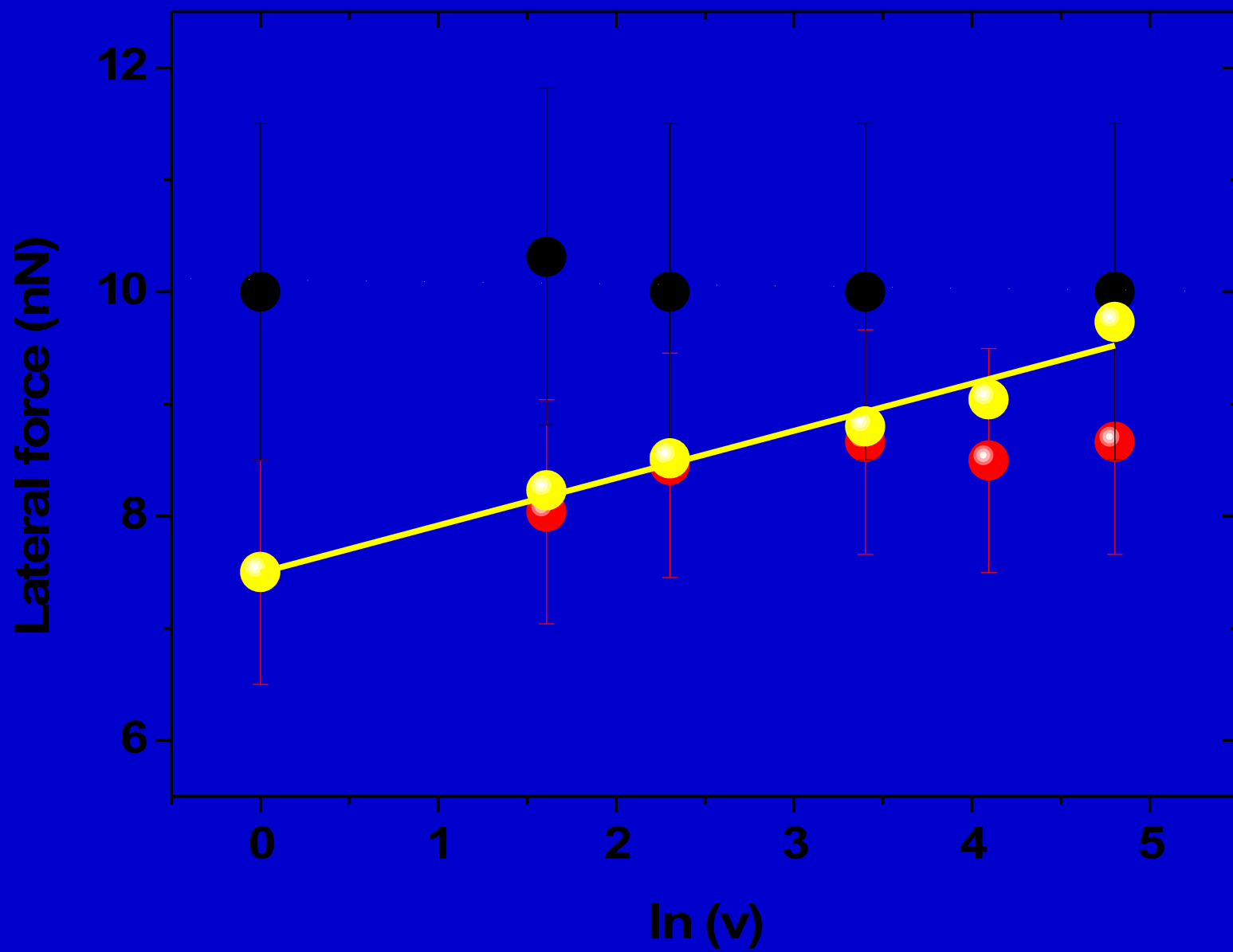
Constants Values (N/m)
Ky : 215,274
Kz : 0,06267
Cn : -11,5205

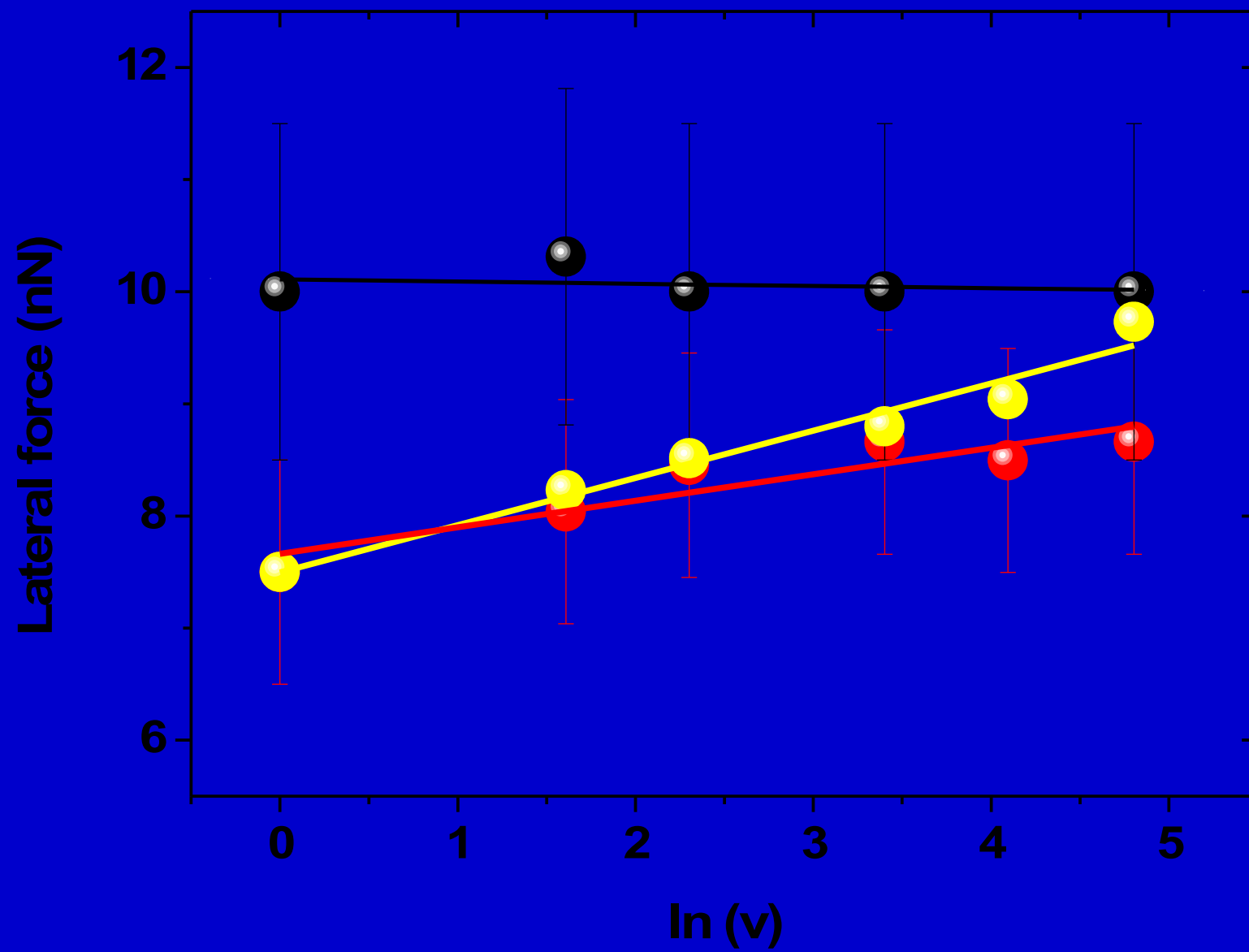
Reset Source Table

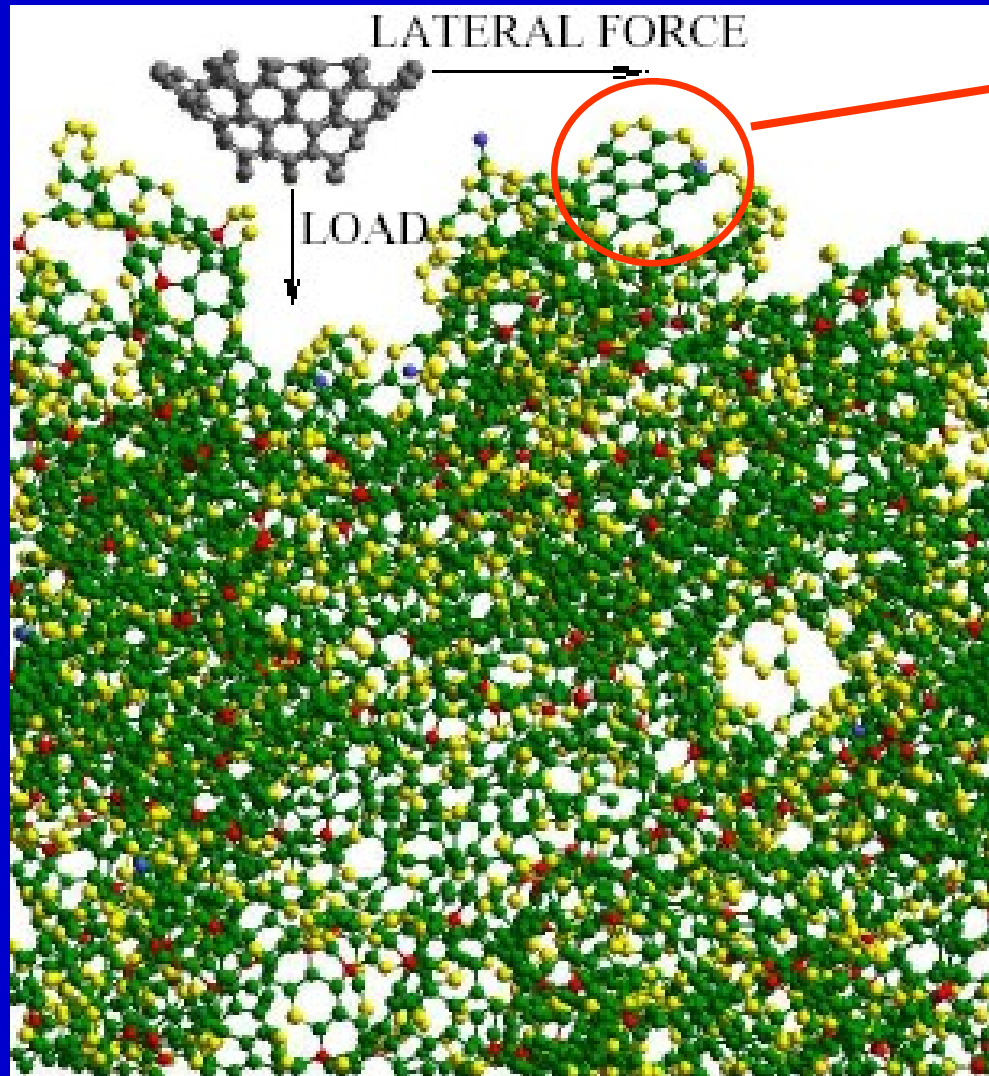
Calculate Constants

E. Liu, B. Banplain, J.P. Celis, Wear 192 (1996) 141









Cluster sp^2