Oberflächenphysik

Scanning Probe Microscopy

- **Friction Force Microscopy**
- Force Calibration
- Atomic Stick Slip
- Tomlinson Model
- Nano-manipulation
- **Atomic Force Microscopy**
- Short- and Long-Range Forces
- Kelvin Probe Force Microscopy
- Measurements on Semiconducting Devices
- Molecules on Insulating Surfaces

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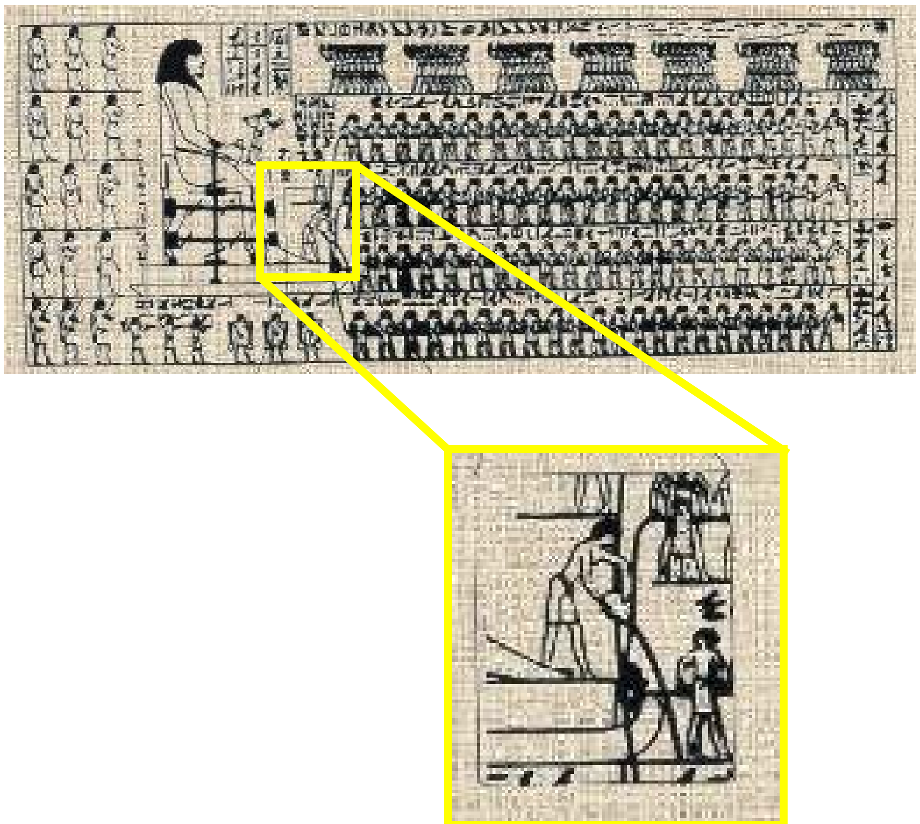
NANOlino Lab

Importance of Friction

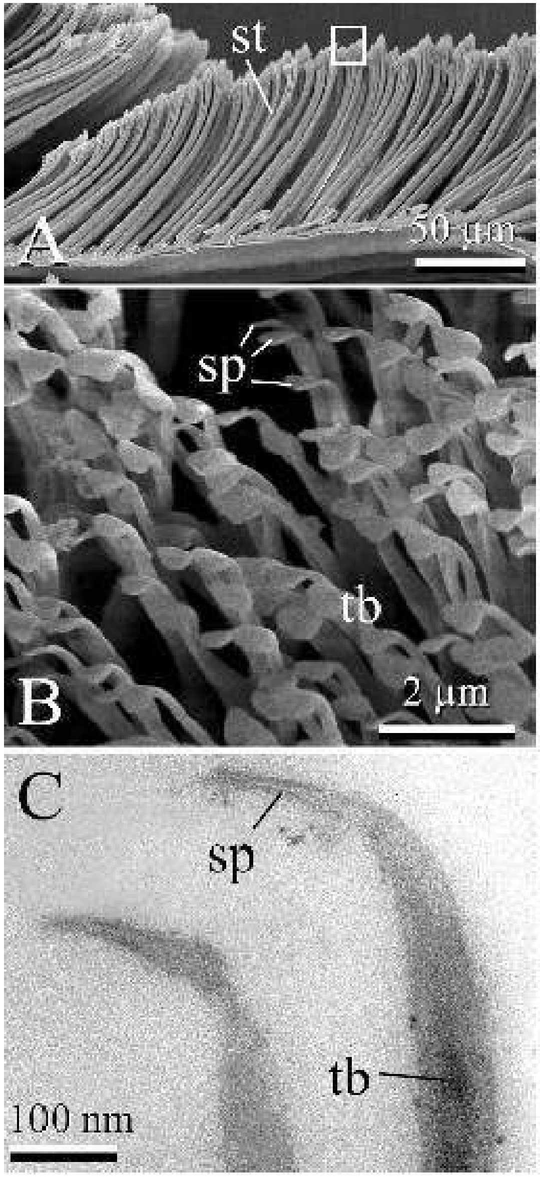
Long time ago...



Nowadays...

In all cases: It is higly desirable to reduce and <u>control</u> friction

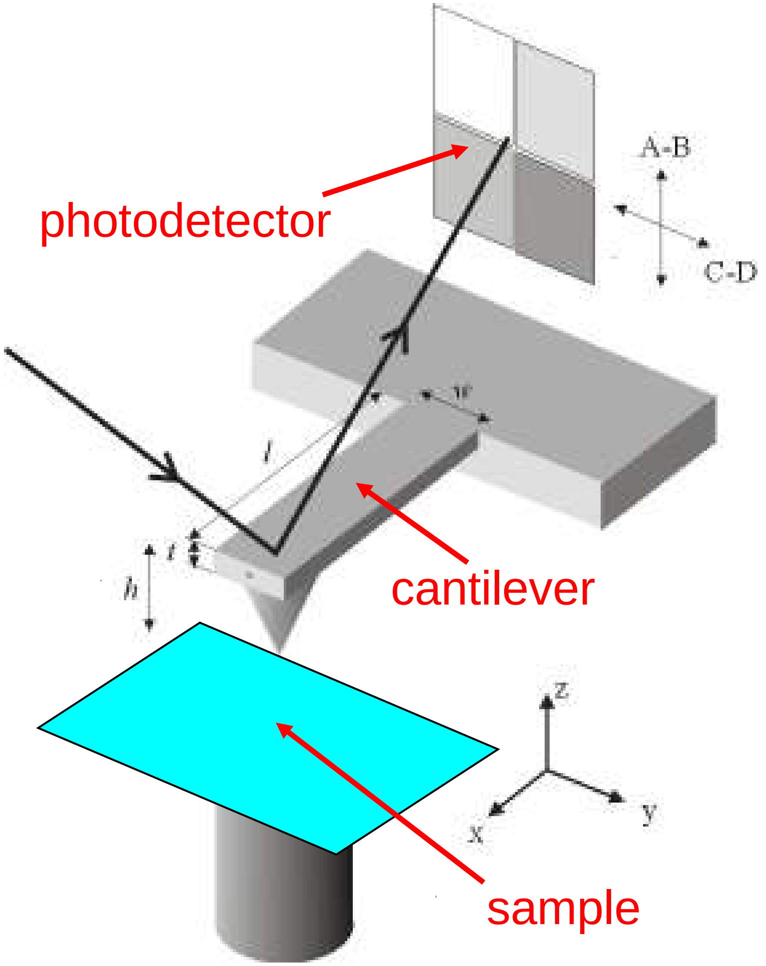
Gecko uses nanometer-sized contacts to climb walls



Gecko is able to control the
contact area on all length scales

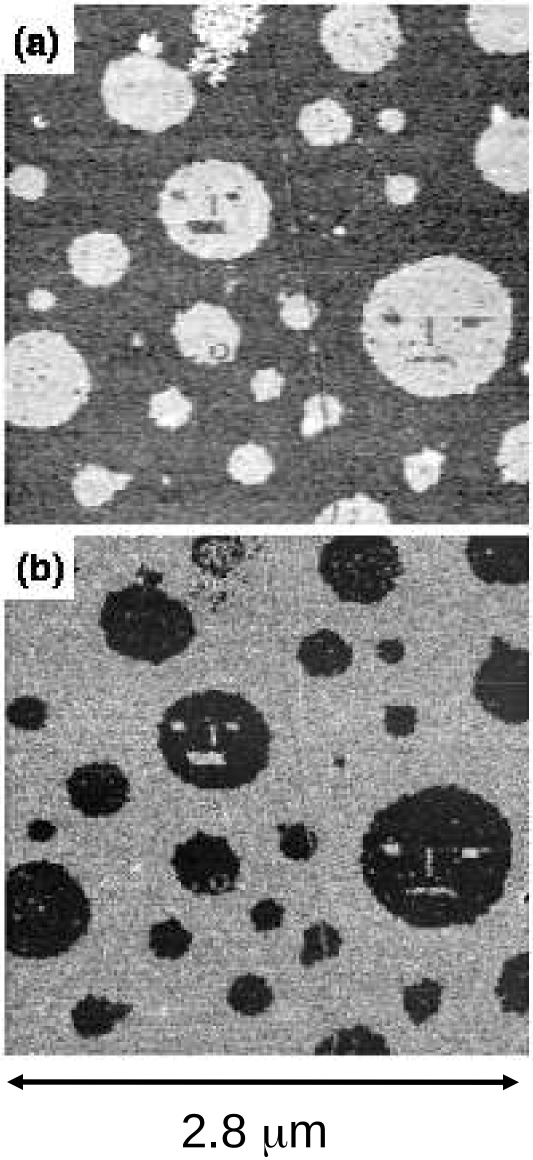
From B. Persson and S. Gorb
JCP, 119, 11437 (2003)

Atomic Force Microscopy (beam defelction)



- The normal and lateral forces on a sharp tip sliding on a surface are sensed using a laser beam
- Forces < 1 nN can be measured

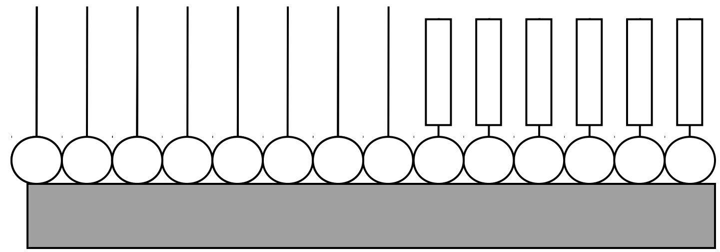
FFM on Langmuir-Blodgett films



Topo

Lat. Force

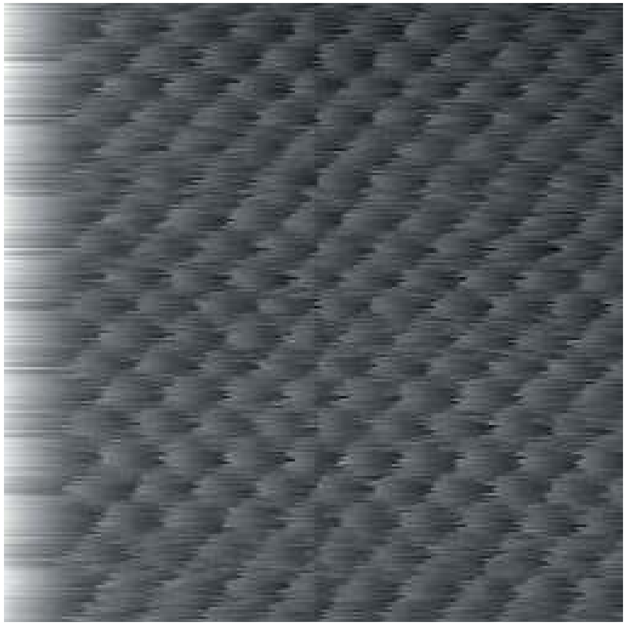
• **Material contrast** on mixed Langmuir-Blodgett films:

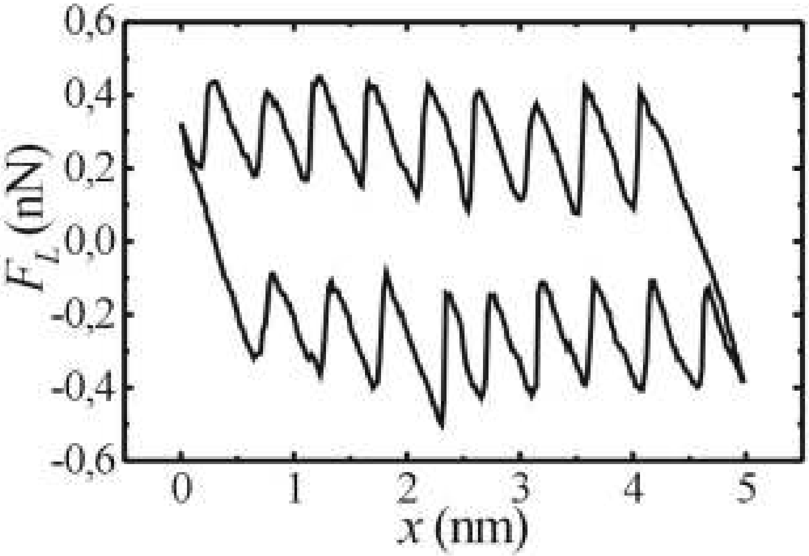


C-terminated

F-terminated

Atomic stick-slip

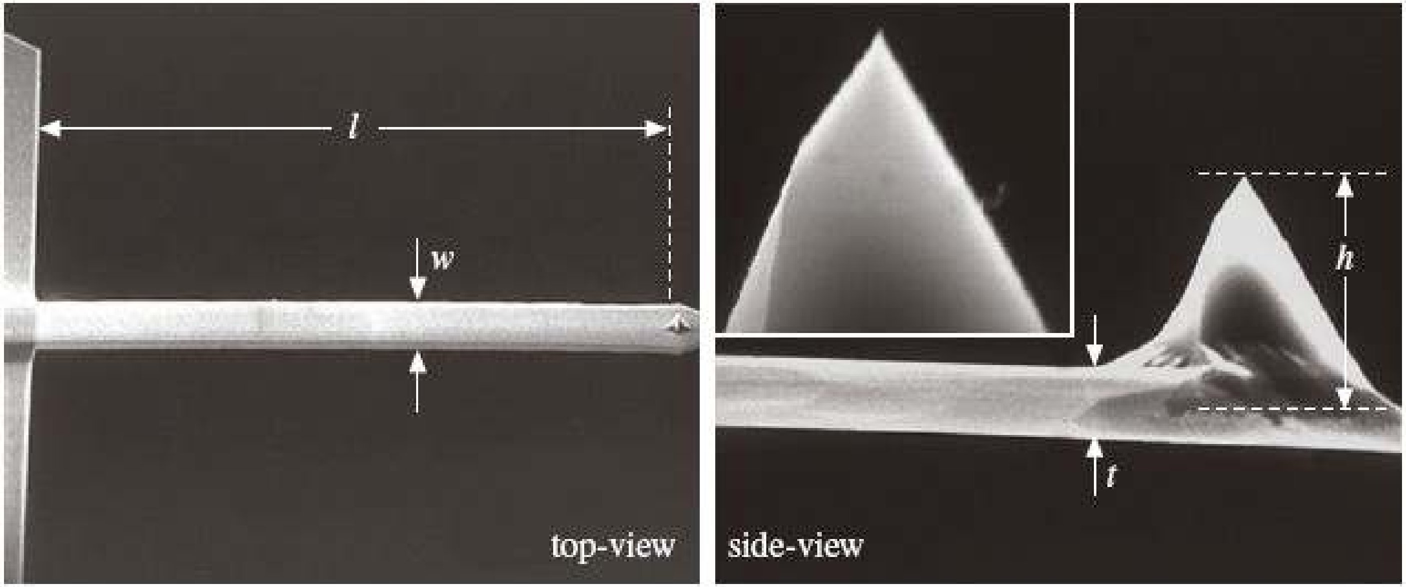




(friction map and friction loop on NaCl(100) in UHV)

Force Calibration

- Simple if **rectangular** cantilevers are used
- Cantilever width, thickness and length, tip height: from **SEM pictures**



Force Calibration

- Cantilever **thickness** also **from** the **resonance frequency**:

$$t = \frac{2\sqrt{12}\pi}{1.875^2}\sqrt{\frac{\rho}{E}}\, f_0 l^2$$

- ρ, E: density and Young (elastic) modulus

(Nonnenmacher et al., JVSTB 1991)

- For pure silicon:

$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

Force Calibration

- **Normal** and **lateral spring constants** of cantilever:

$$c_N = \frac{Ewt^3}{4l^3} \qquad c_L = \frac{Gwt^3}{3h^2 l}$$

- G: shear modulus
- For pure silicon:

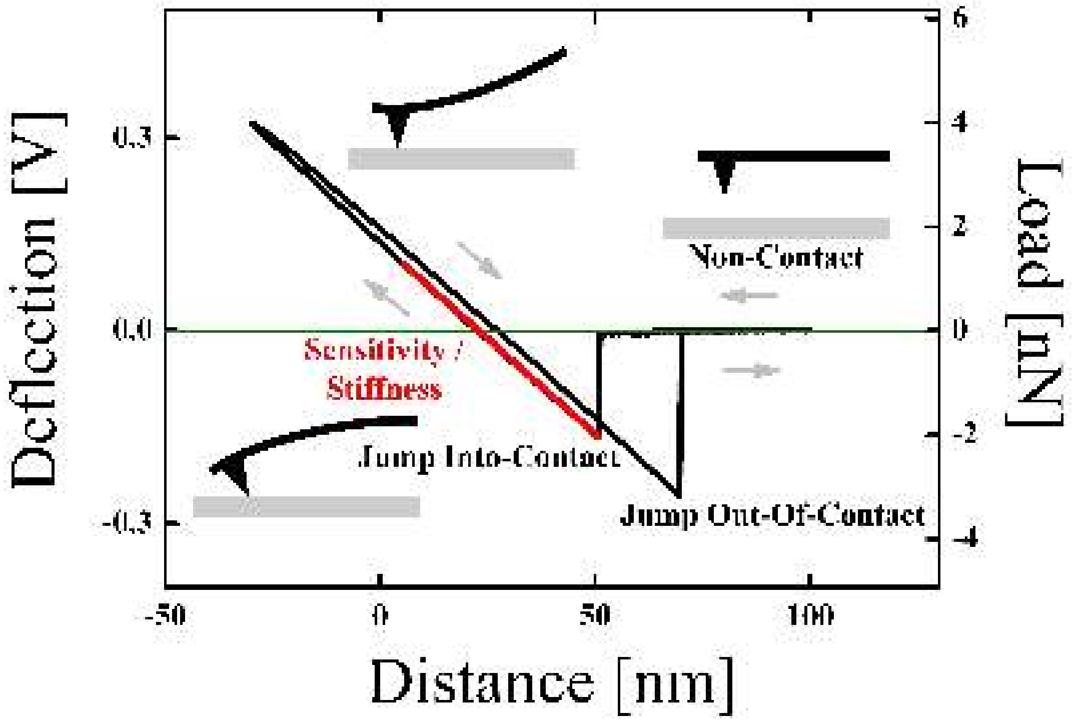
$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

$$G = 0.5 \cdot 10^{11} \text{ N/m}^2$$

Force Calibration

- Next step: **sensitivity of photodetector**
- Force-distance curves on hard surfaces (e.g. Al_2O_3):



- Scanner movement = cantilever deflection
- Slope → sensitivity

Force Calibration

- **Normal** and **lateral forces**:

$$F_N = c_N S_z V_N \qquad F_L = \frac{3}{2} c_L \frac{h}{l} S_z V_L$$

(if the laser beam is above the probing tip!)

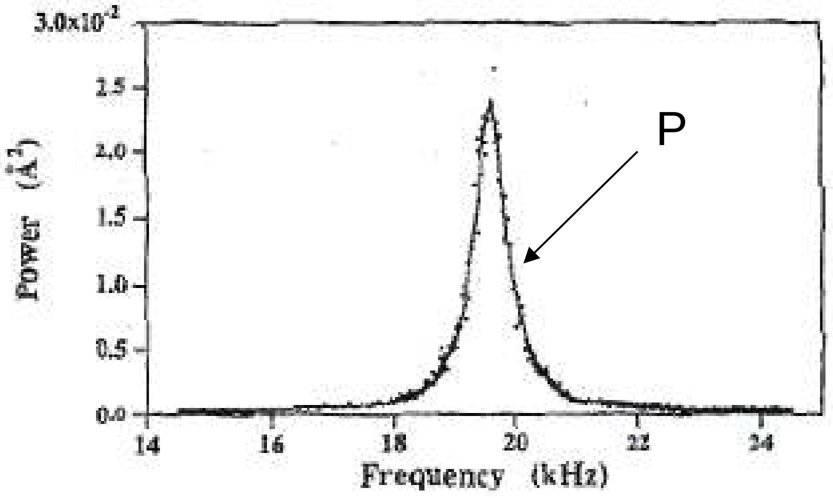
- V_N, V_L: normal and lateral signals

Force Calibration

- Alternative method: Spring constant **from thermal power spectrum** (Hutter et al., RSI 1993)

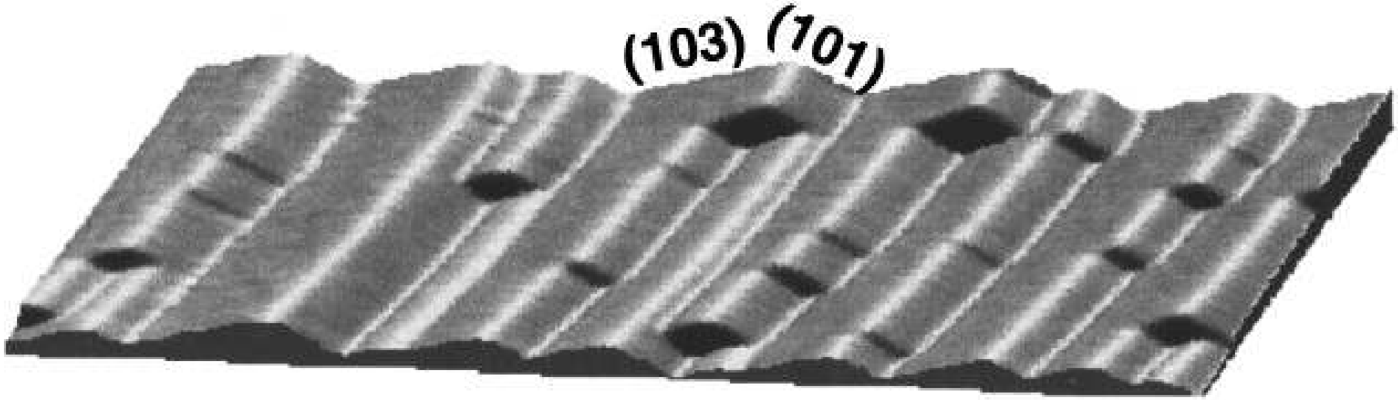
- Correct relation (Butt et al., Nanotech. 1995):

$$c_N = \frac{4k_B T}{3P}$$

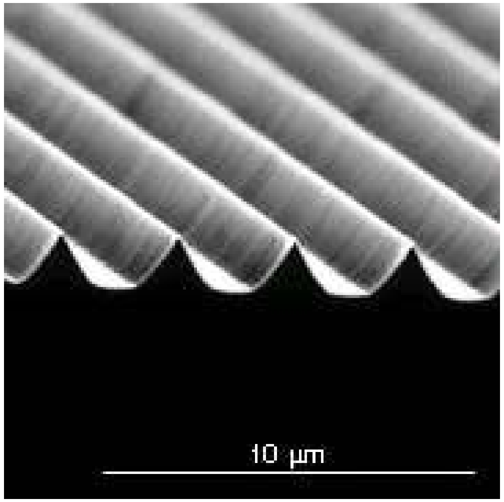


Force Calibration

• Alternative method: Scanning over profiles with **well-defined slope** (Ogletree et al., RSI 1996)



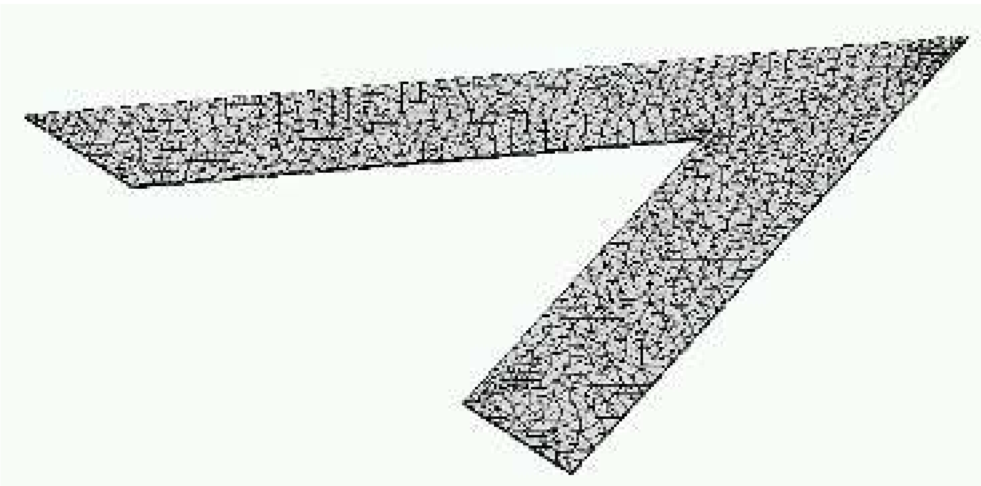
Commercially available grating:

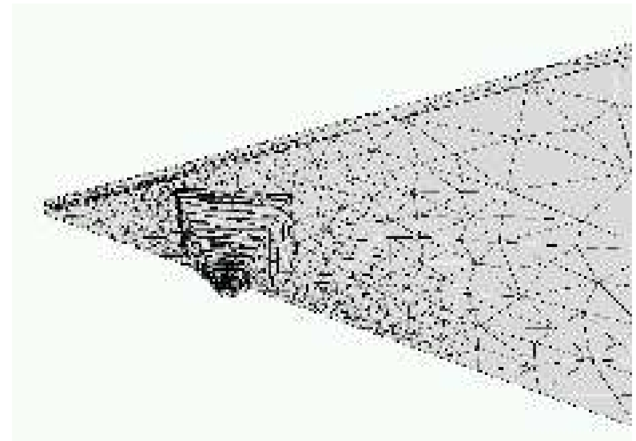


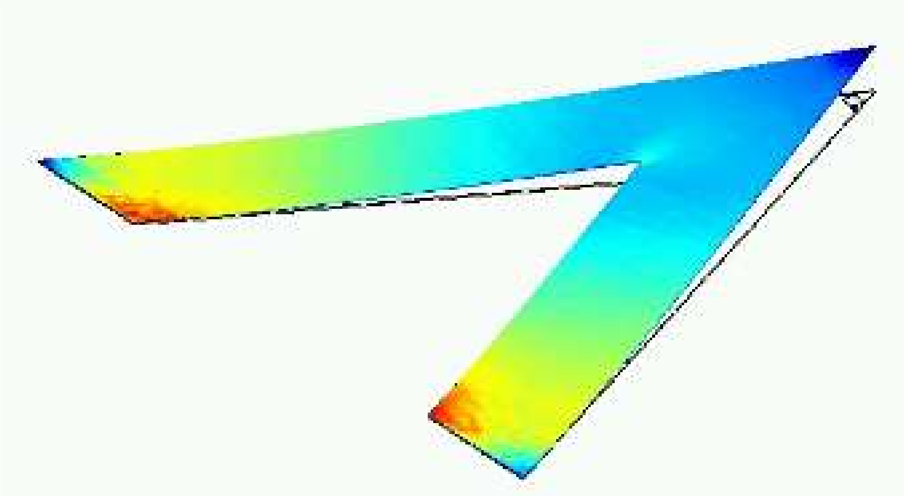
(TGG01, NT-MDT, Moscow)

Force Calibration

- Different shapes → **Finite elements analysis**



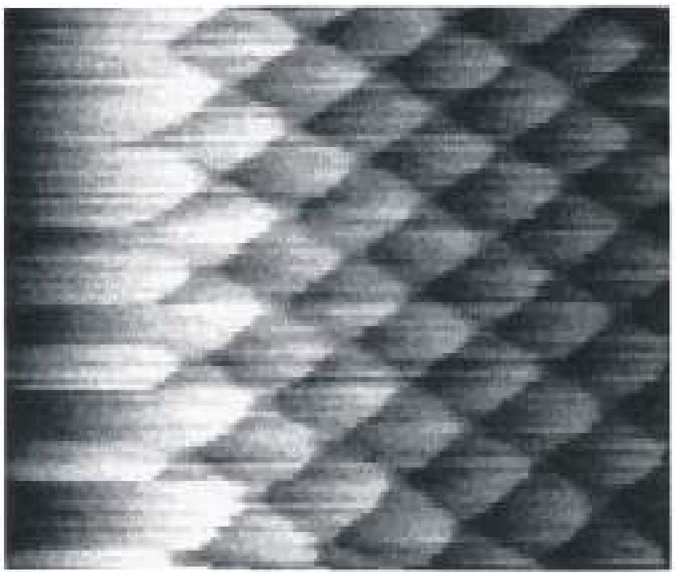




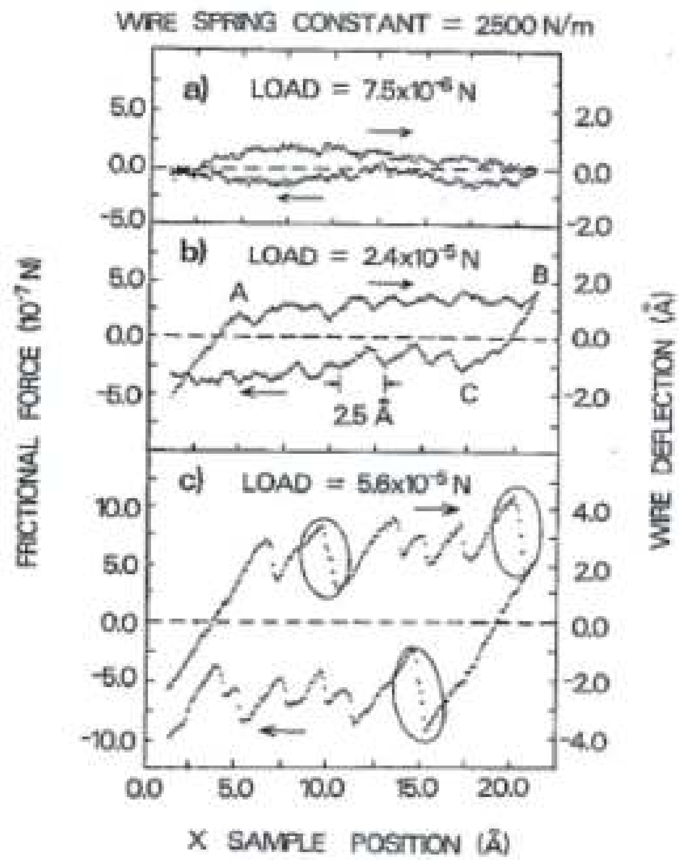
(Femlab™ 3.0)

Atomic-Scale Measurements

- Atomic friction on **graphite**:



2 nm

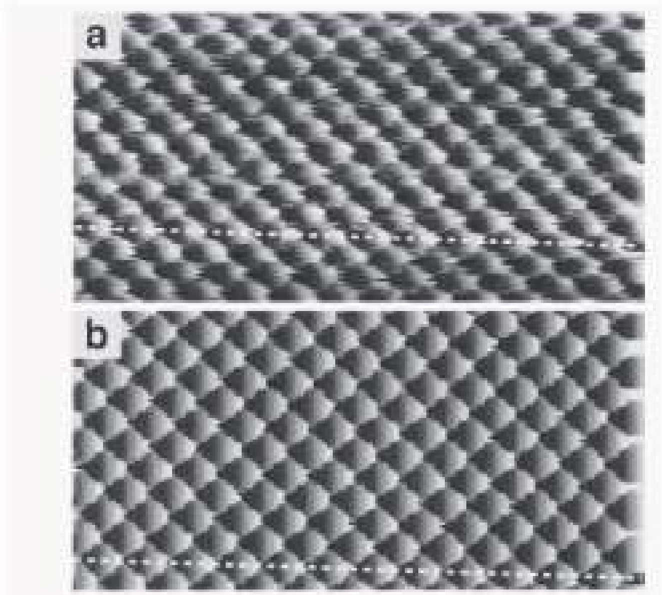


(Mate at al., PRL 1987)

Atomic-Scale Measurements

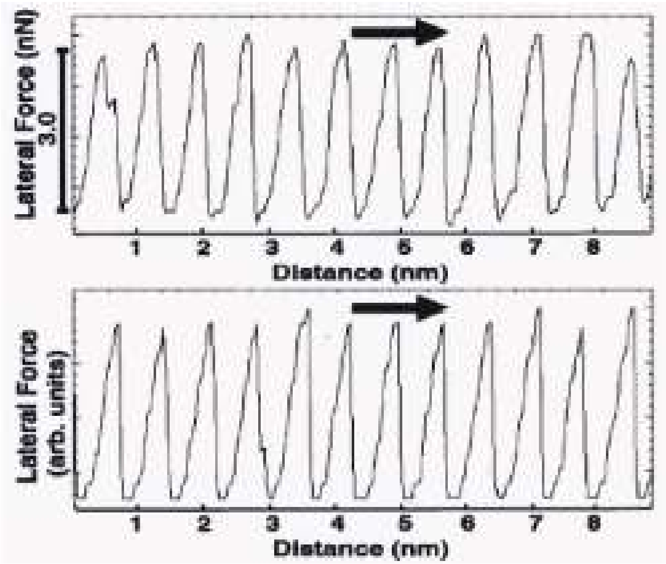
- Friction on **insulating surfaces** (Lüthi et al., JVSTB 1996):

KBr



Exp

Theo

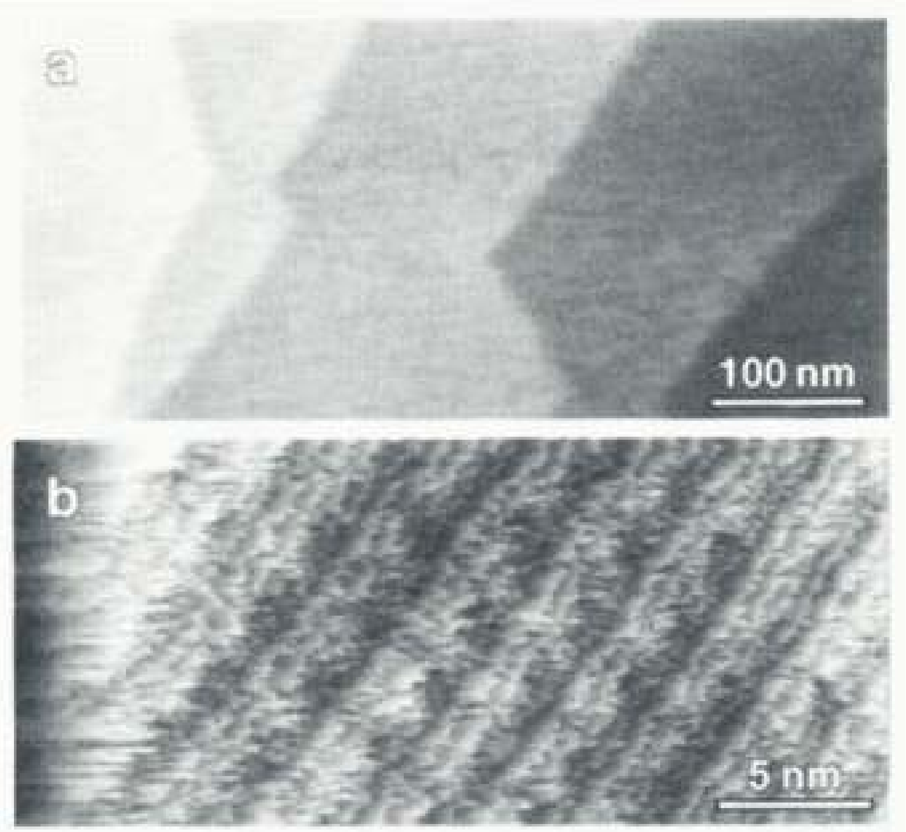


- No individual defects are observed

Atomic-Scale Measurements

- Friction on **semiconductors** (Howald et al., PRB 1995):

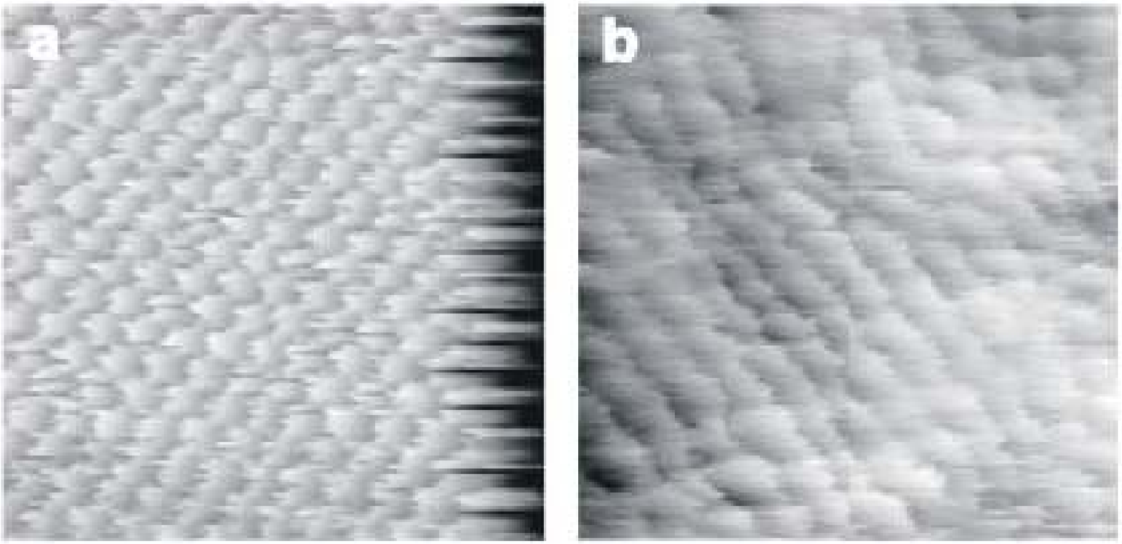
Si(111)7x7



(tip coated with PTFE)

Atomic-Scale Measurements

- Friction on **metal surfaces** (Bennewitz et al., Trib. Lett. 2001):

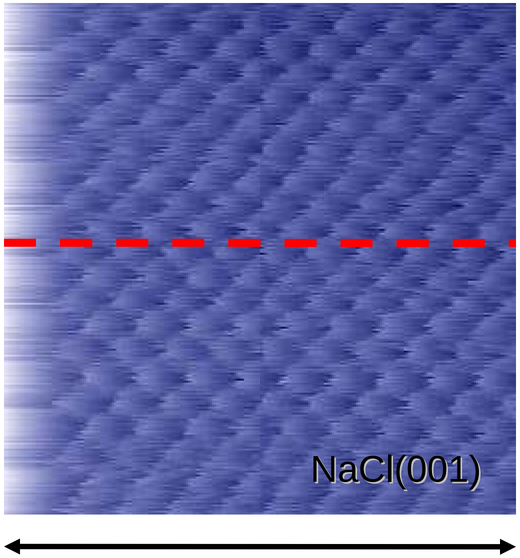


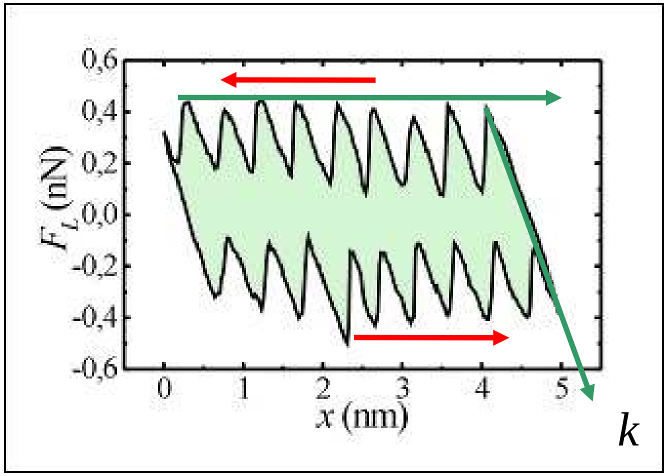
Cu(111) Cu(100)

Irregular features on the (100) surface (less packed!)

Atomic friction on crystal surfaces

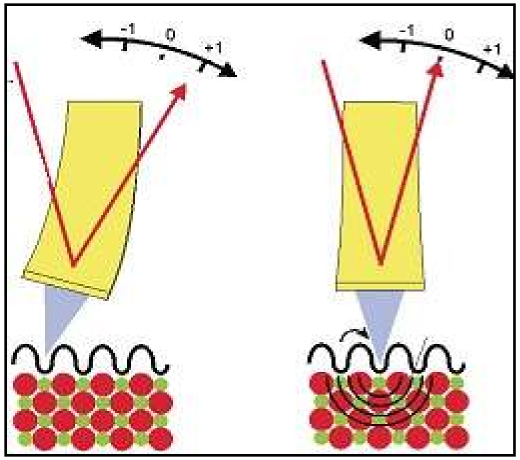
Our model systems: alkali halide surfaces (easy preparation, simple structure)





$$F_L^{\max} = \frac{2\pi V_0}{a}$$

Tomlinson model:
(Phyl. Mag. 1929)

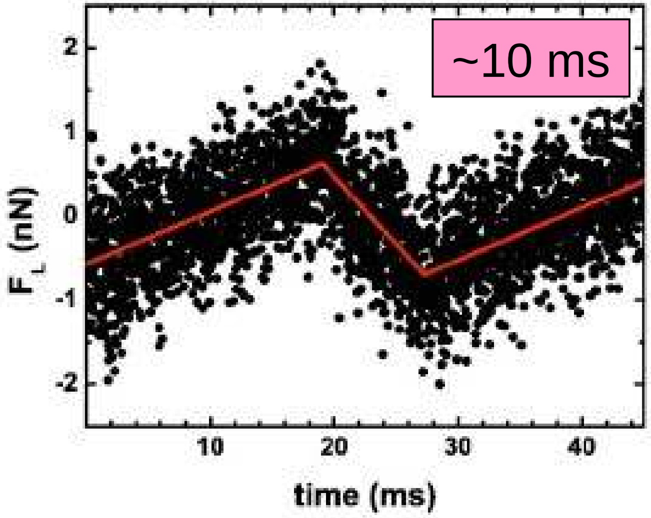


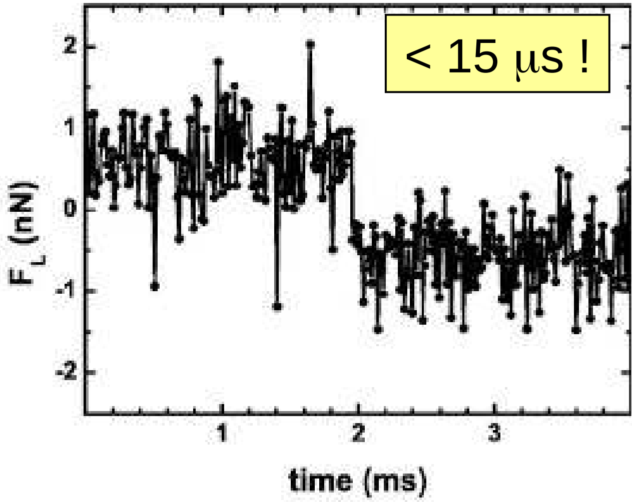
$V_0 \sim 1\,\mathrm{eV}$

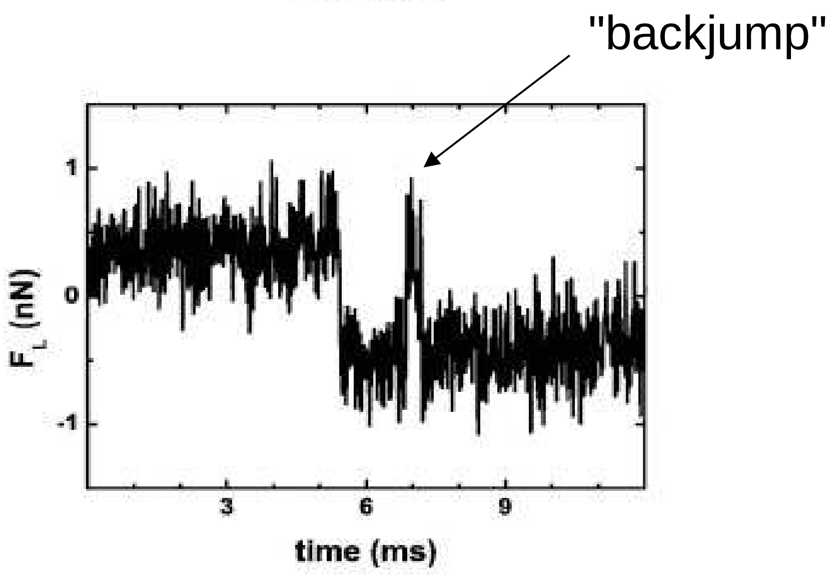
$k \sim 1\,\mathrm{N/m}$

Atomic-Scale Measurements

- Wide distribution of slip durations:







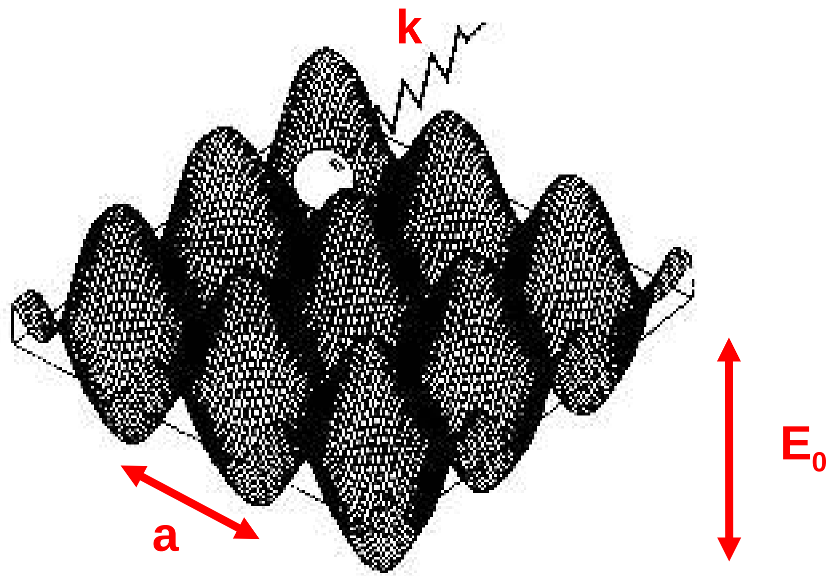
Why?

Modelling Atomic Friction

- The tip is subject to

1) periodic interaction with the underlying surface

2) elastic deformation of the cantilever



- In 1D the corresponding potential energies are represented by

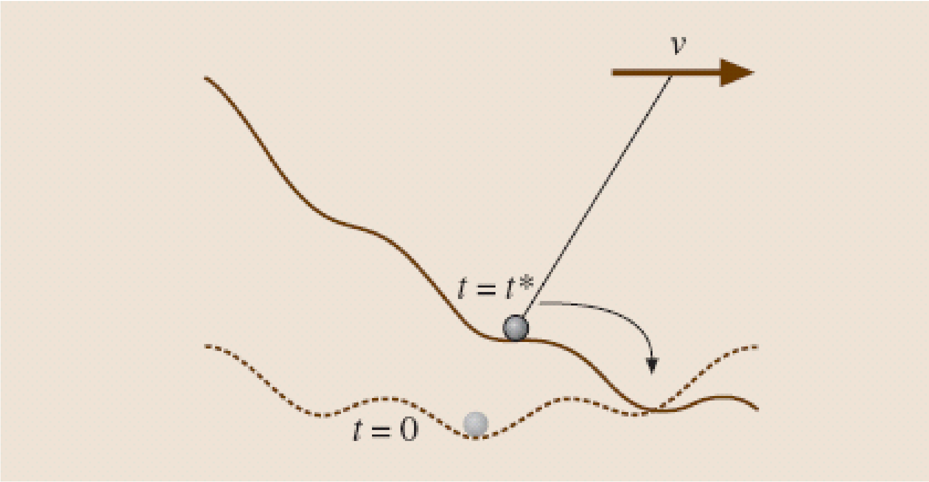
1) a sinusoid

2) a parabola

Modelling Atomic Friction

- Total energy of the system:

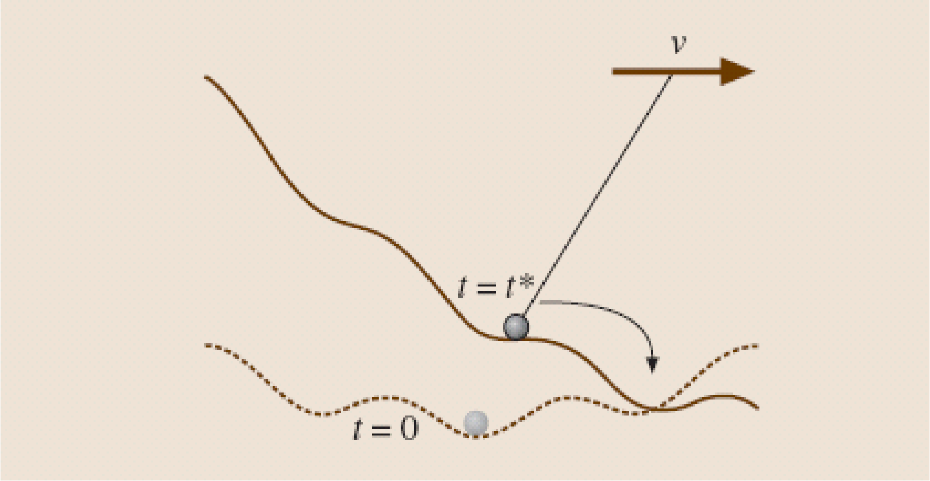
$$U_{\text{tot}}(x,t) = -\frac{E_0}{2}\cos\frac{2\pi x}{a} + \frac{1}{2}k_{eff}(vt - x)^2$$



- The tip can "stick" to the minima of the potential profile

Modelling Atomic Friction

- Tip position at a given time t: $$\frac{\partial U_{tot}}{\partial x} = \frac{\pi E_0}{a}\sin\frac{2\pi x}{a} - k_{eff}(vt - x) = 0$$

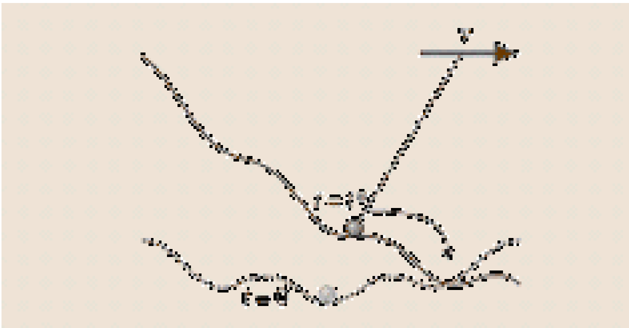


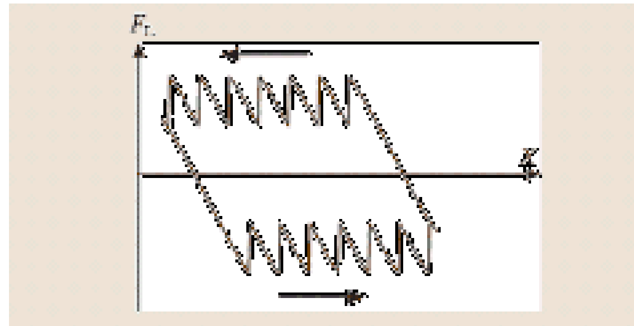
- Critical position (reached at t = t*):

$$x^* = \frac{a}{4}\arccos\left(-\frac{1}{\eta}\right) \qquad \eta = \frac{2\pi^2 E_0}{k_{eff} a^2}$$

- **Frictional parameter η** → tip-surface interaction vs. lateral stiffness

Modelling Atomic Friction



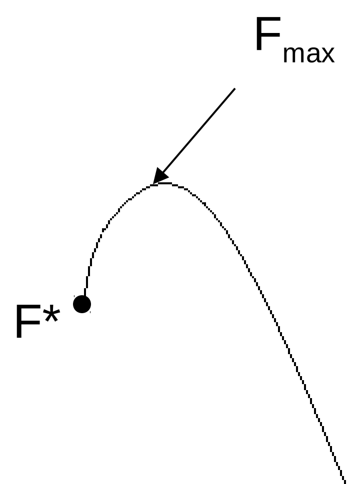


- Critical lateral force (at t = t*):

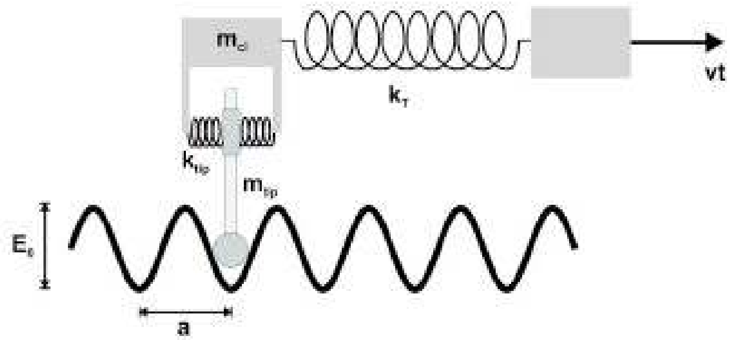
$$F^* = \frac{\pi E_0}{a}\sqrt{1 - \frac{1}{\eta^2}}$$

- Note that $F^* < F_{max}$!

$$F_{\max} = \frac{\pi E_0}{a}$$

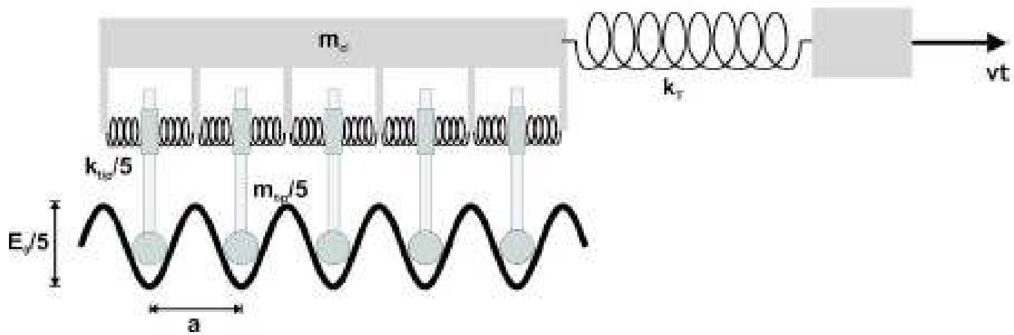


Modelling Atomic Friction



single contact

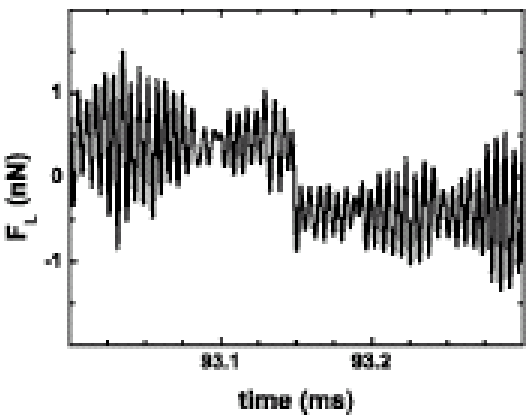
multiple contact



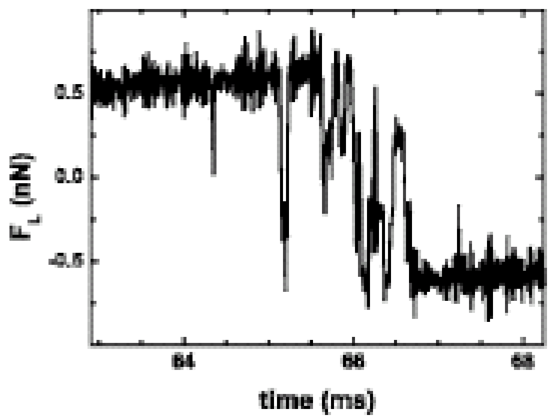
Modelling Atomic Friction

- Tip → Langevin equation (including thermal noise)
- Cantilever → Newton equation (without thermal noise)

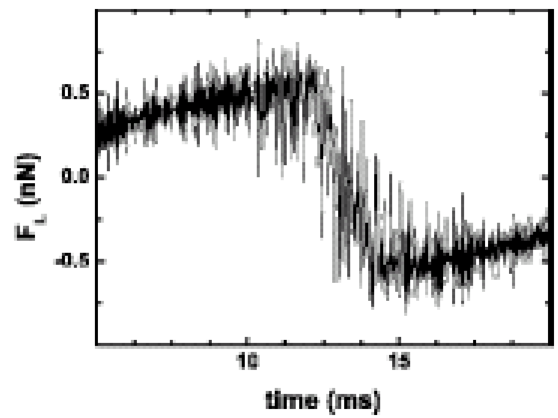
One tip



Three tips



Five tips



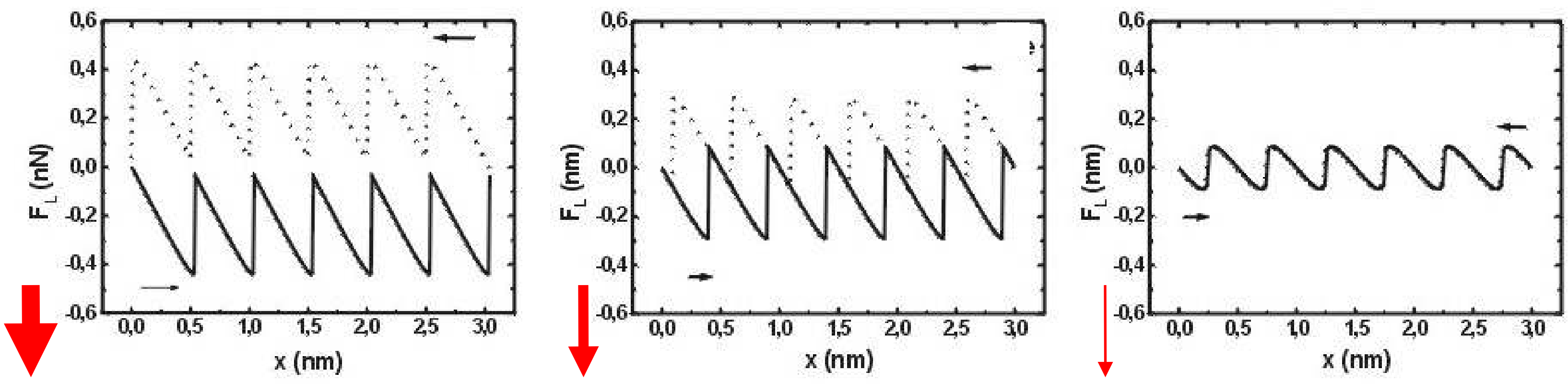
- Long slip times are found with multiple tips only

(Maier et al., PRB 2005)

Superlubricity

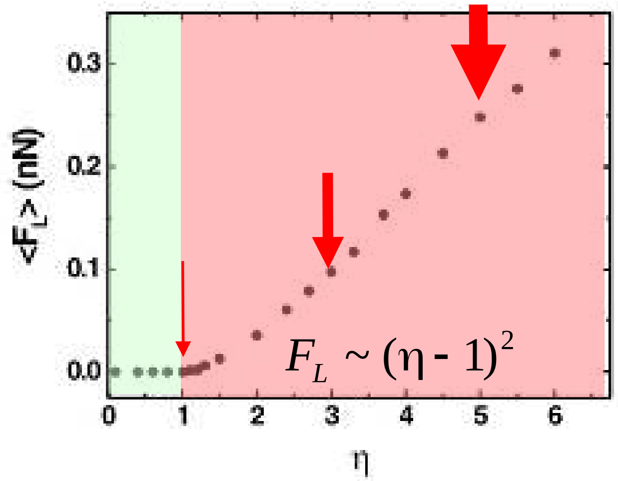
- From the Tomlinson model (without thermal activation):

η > 1 **η < 1**



$F_L \sim \eta$

superlubric regime



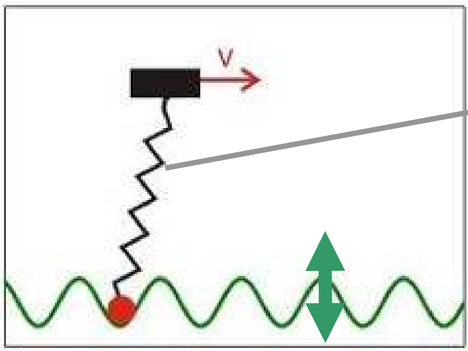
$F_L \sim (\eta - 1)^2$

stick-slip regime

A. Socoliuc et al., Phys. Rev. Lett. 92 (2004) 134301

"Dynamic superlubricity"

A third way to reduce friction: Tomlinson model with TIME modulation



$$V_{elas} = \frac{ka^2}{2}$$

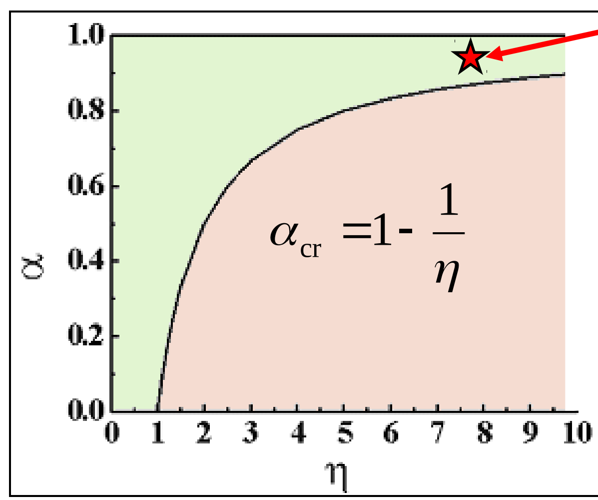
$$V_{int} = V_0 \cos\frac{2\pi x}{a}$$

$$\eta = \frac{(2\pi)^2 V_0}{ka^2}$$

$$V_0 \rightarrow V_0(1+\alpha\cos\omega t)$$

$$\eta_{eff} = \eta(1-\alpha)$$

Phase-diagram in the η-α plane:

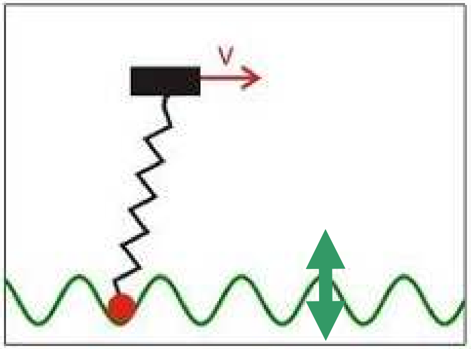


High loads
can be applied!

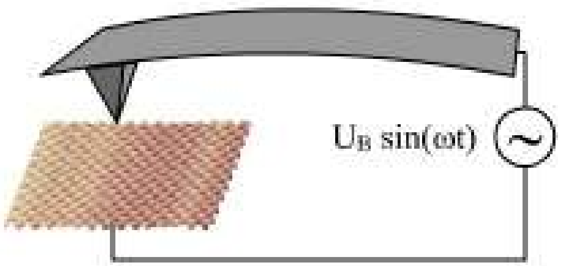
E. Gnecco et al., J. Phys.: Condens. Matt. a20 (2008) 354004

“Dynamic superlubricity”

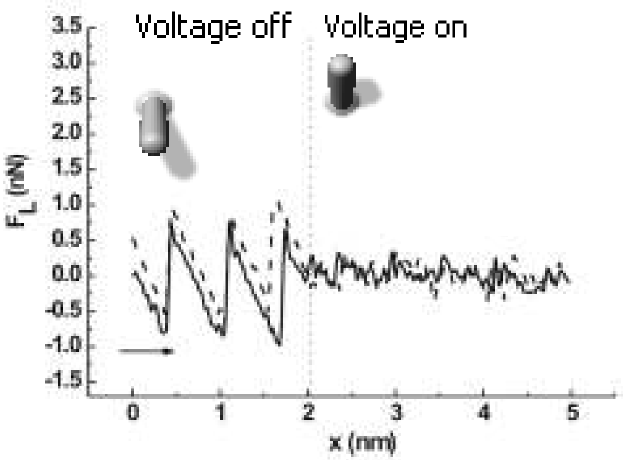
A third way to reduce friction: Tomlinson model with TIME modulation

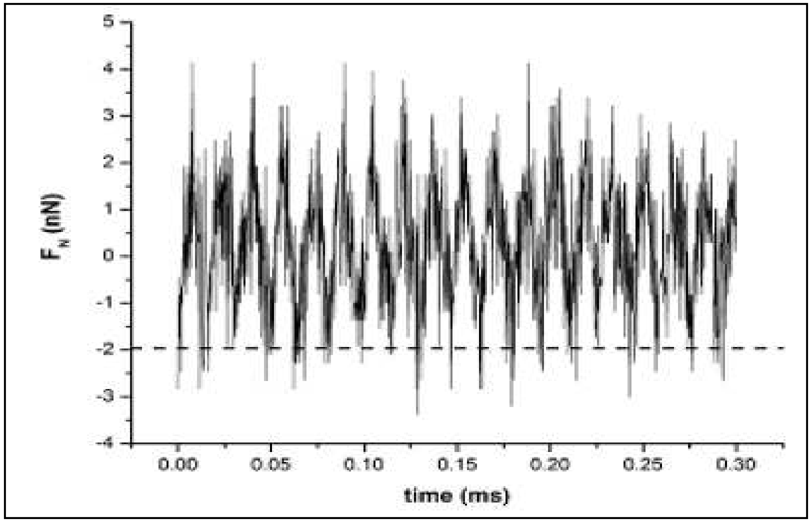


AC actuation
of the nanocontact:



NaCl(001)



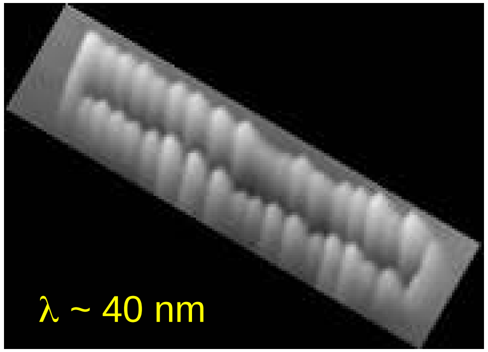


A. Socoliuc et al., Science 313 (2006) 207

Abrasion wear at the nanoscale

Ripples induced by localized abrasion:

Scratching single lines:

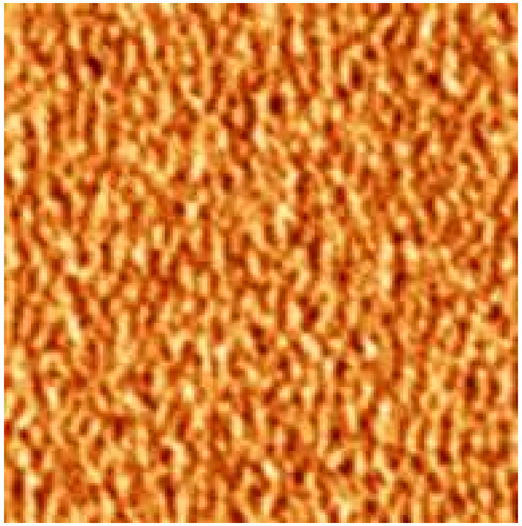


Analogies to waterjet cutting:

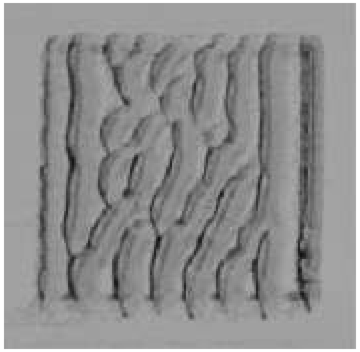
- Combined erosion and relaxation

Thermal activation of atomic-scale wear

Numerical analysis in progress



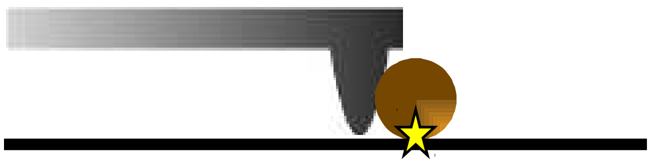
Scratching square areas:



Analogies to sand ripples:

A. Socoliuc et al.,a Phys. Rev. B 68 (2003) 115416

Manipulation of Nanoparticles

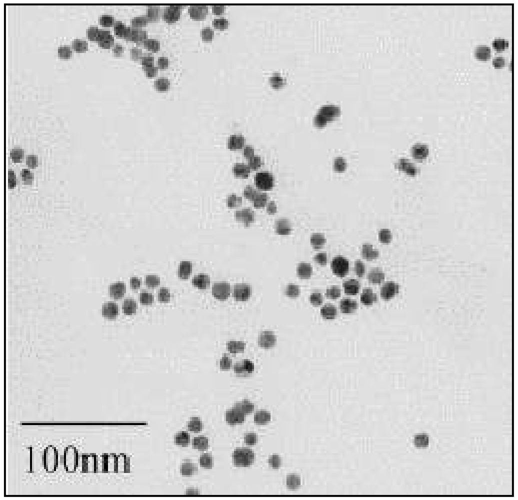


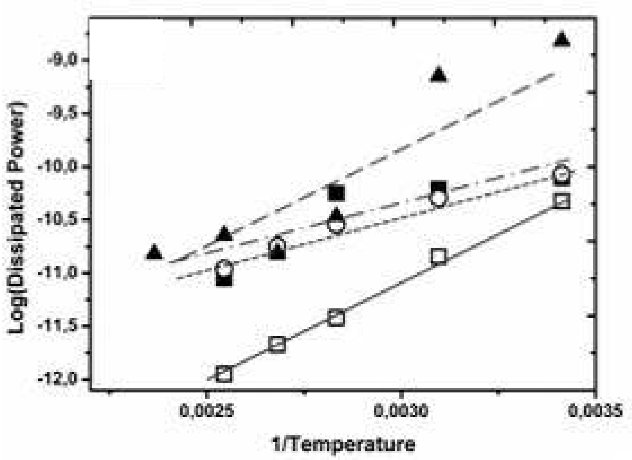
Power dissipation at onset of motion:

$$P_{\text{tip}} = \frac{1}{2}\frac{k\omega_0}{Q_{\text{cant}}}\left(Q_{\text{cant}} A_d A \sin\phi - A^2\right)$$

Thermal activation of the particle motion:

$$\log P_{\text{tip}} \sim \frac{1}{T}$$

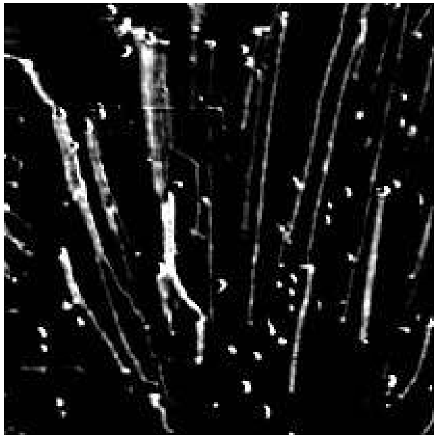


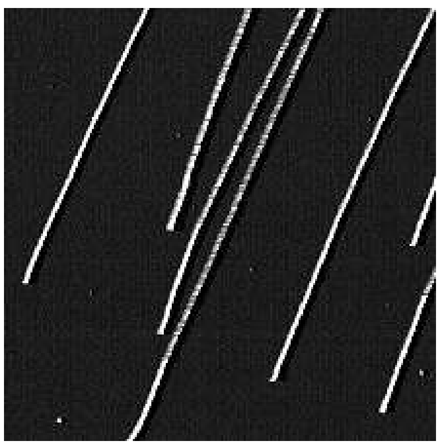


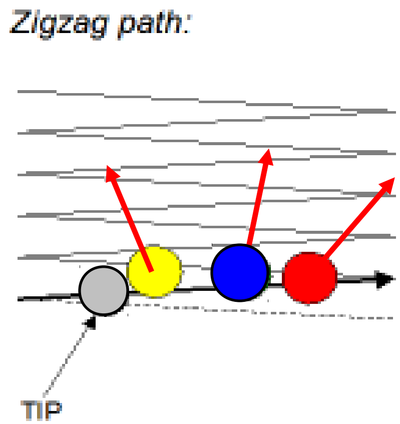
K. Mougin et al., Langmuir 24 (2008) 1577

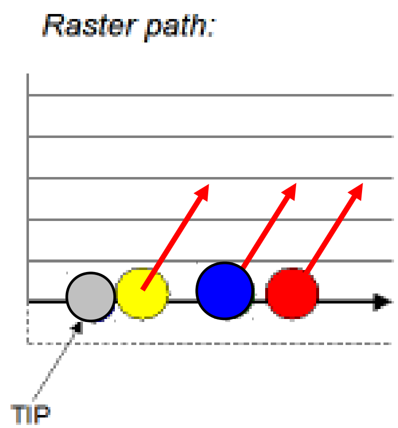
Manipulation of Nanoparticles

Nanoparticles can be “scattered” by the AFM tip:



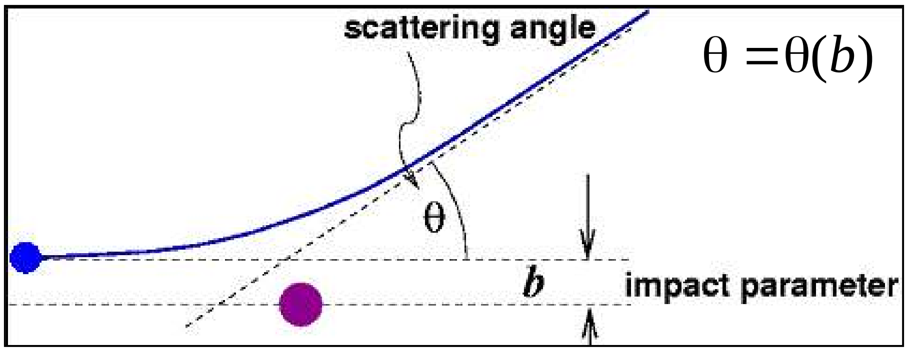


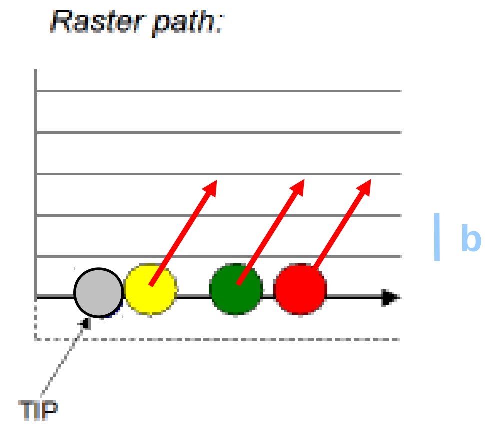




Manipulation of Nanoparticles

Analogy to classical scattering:



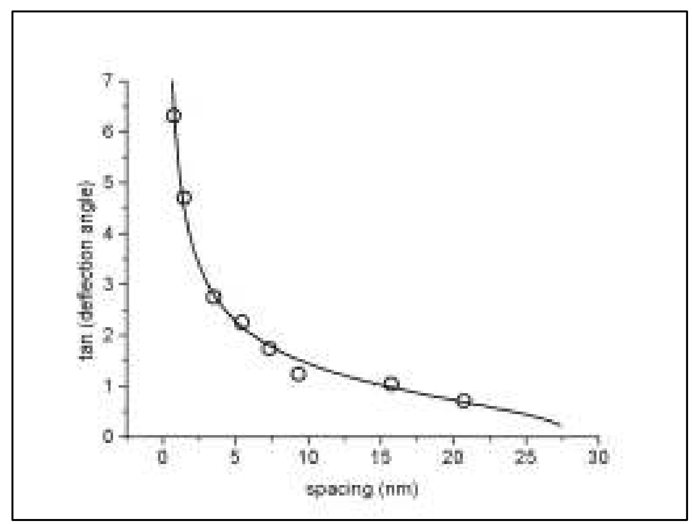


In tapping AFM:

$$\tan\theta = -\frac{b}{2R\left(\cos\alpha_0 + \log\tan\frac{\alpha_0}{2}\right)}$$

$$\alpha_0 = \arcsin\left(1 - \frac{b}{R}\right)$$

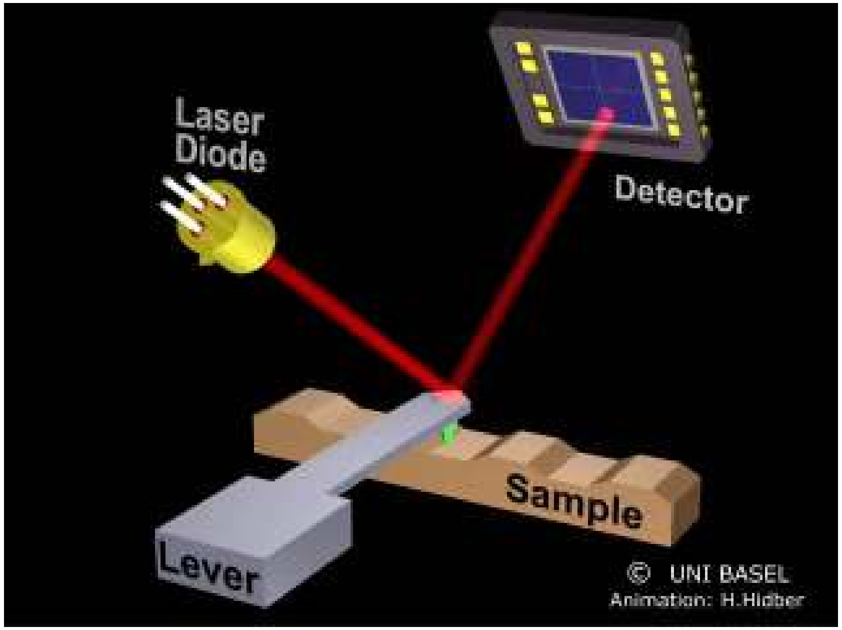
R ← tip and particle radii
b: spacing between consecutive scan lines



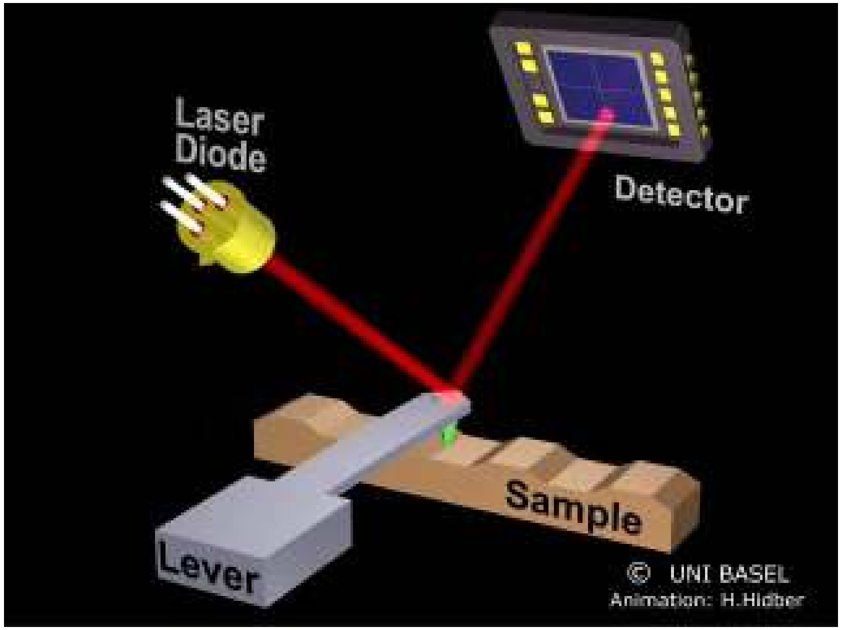
A. Rao et al., Nanotechnology 20 (2009) 115706

Atomic Force Microscopy

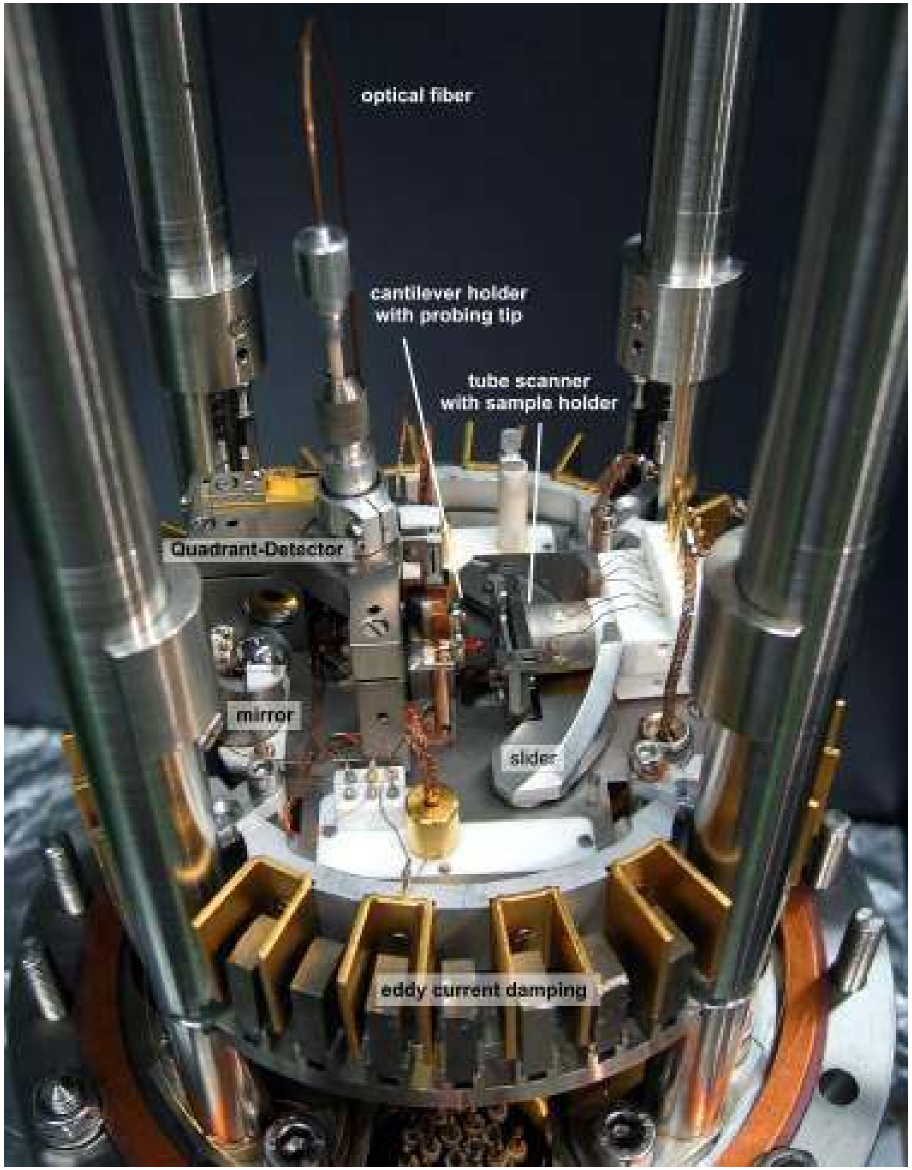
Kontakt AFM



Dynamisches AFM



Noncontact-AFM (nc-AFM)

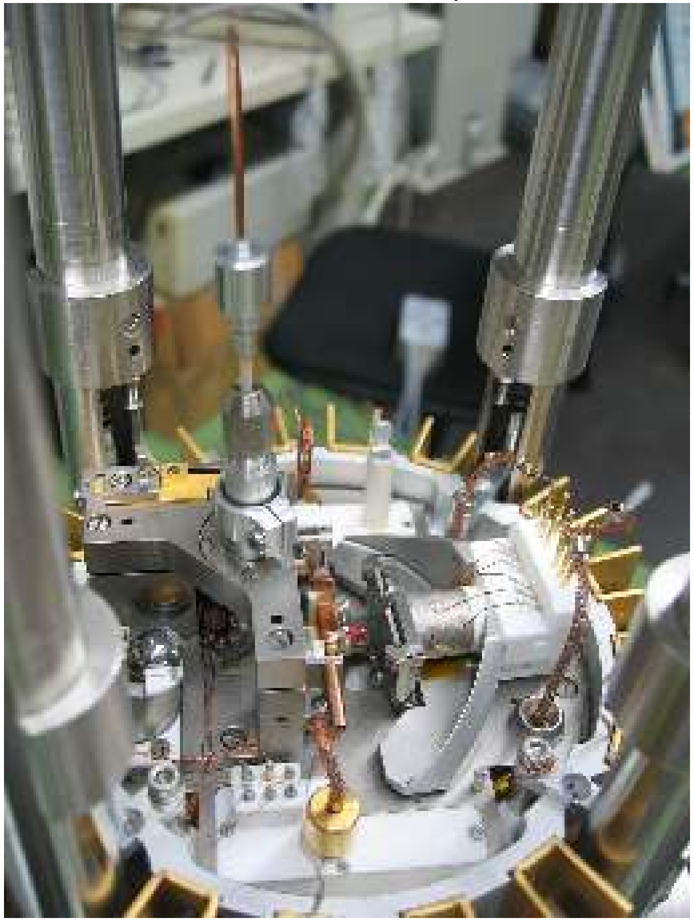


- UHV: Base pressure below $1x10^{-10}$ mbar
- Operation at room temperature
- Mixed mode: AFM/STM
- Beam deflection method
- Bandwidth of the photodetector: 3MHz
- Evaporation of molecules from a k-cell kept at 165ºC or 170ºC

Experimental Setup
AFM/STM

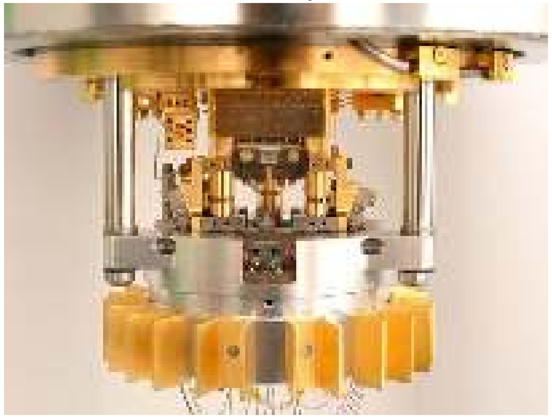
Nanosurf, ambient AFM (Flex-AFM)

home-build RT-AFM, UHV



Multimode AFM

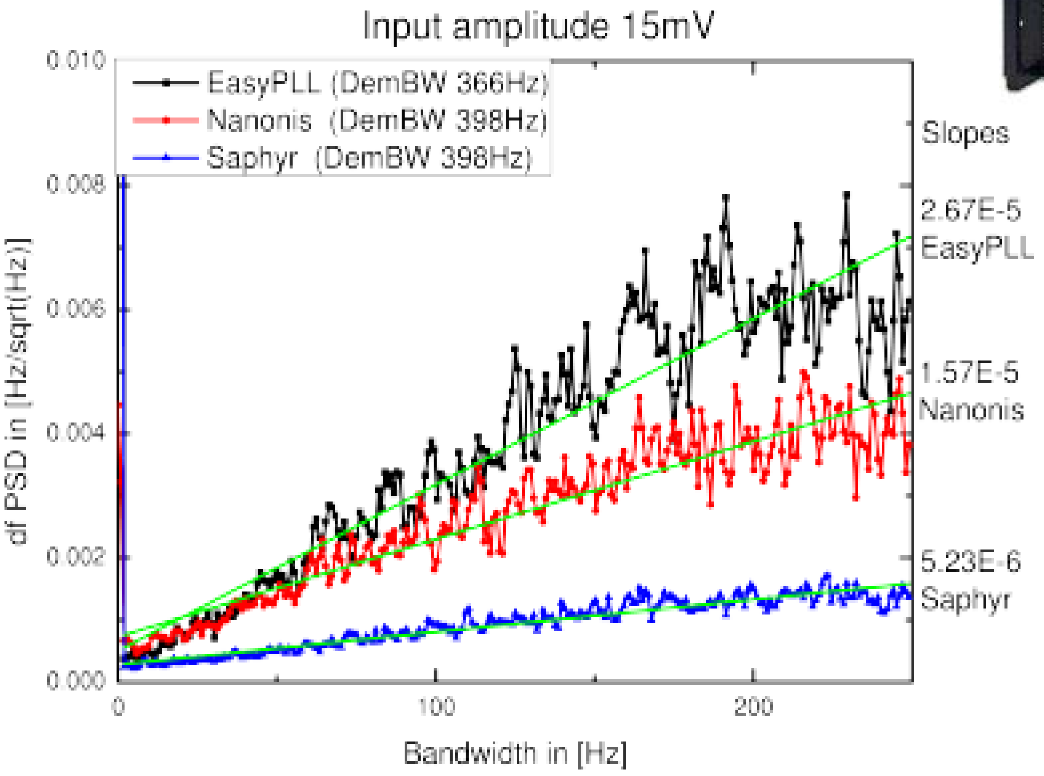
LT-STM/AFM, Omicron



Electronics Development (Saphyr)

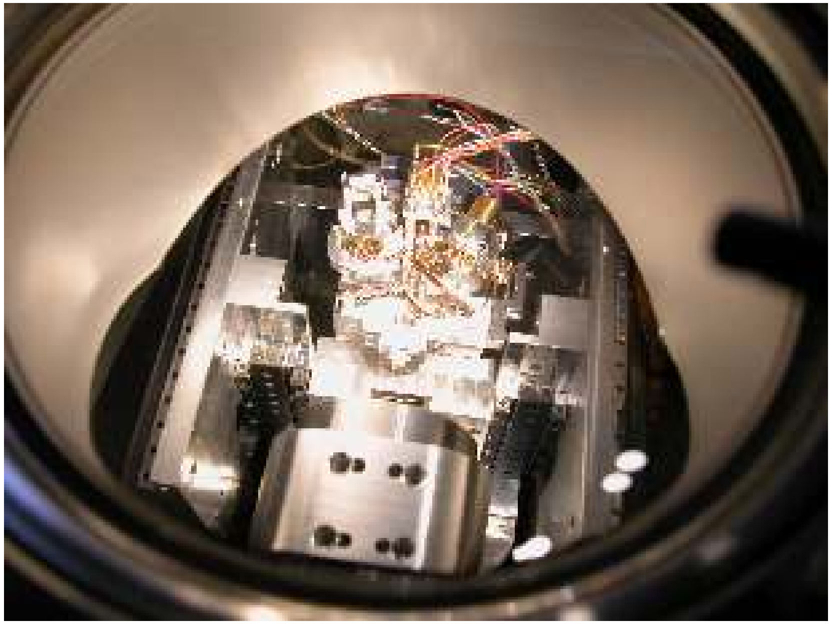
FPGA based multi-PLL system

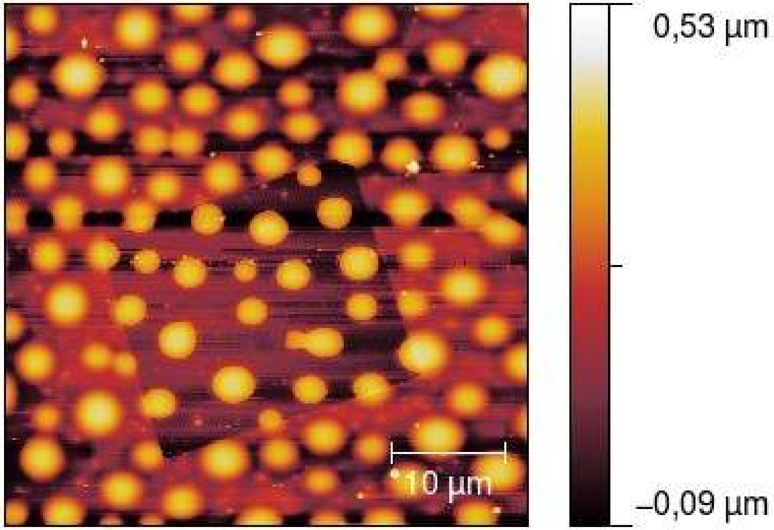
Collaboration with Nanosurf, Liestal, Switzerland



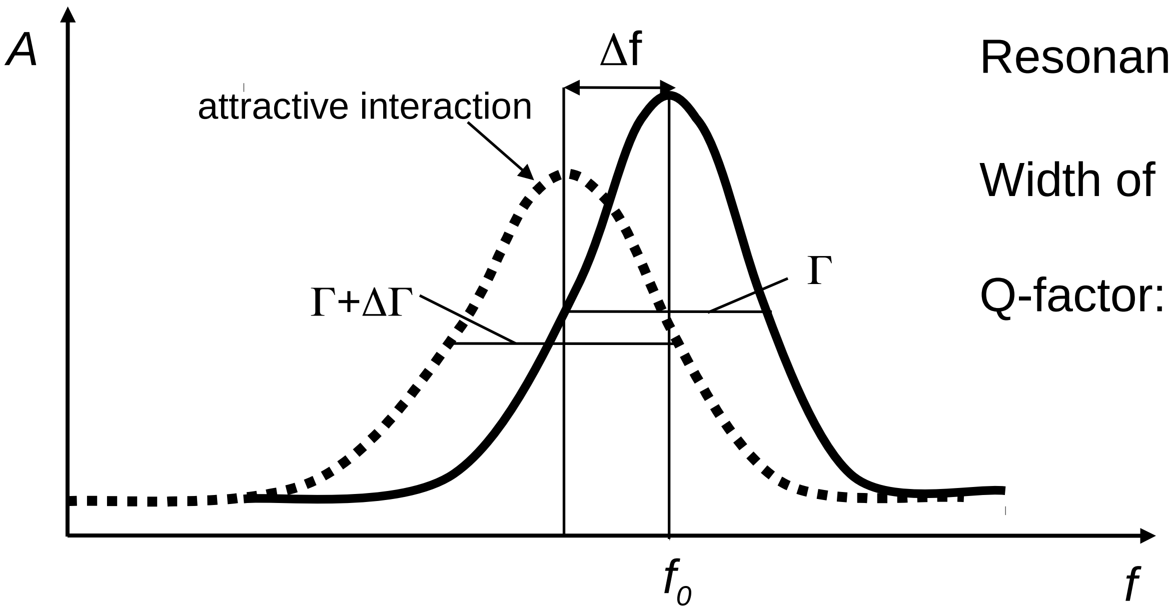
SIMS-SPM Hardware development

Collaboration with Ferrovac, Zurich, Switzerland
and T. Wirtz Lippmann Institute, Luxembourg





Quantitative understanding of nc-AFM



Resonance frequency: f_0

Width of resonance curve (FWHM): Γ

Q-factor: $Q = \frac{2\pi \cdot f_0}{\Gamma}$

Conservative forces ⇒ shift of resonance curve Δf
Dissipative forces ⇒ broadening of curve $\Delta\Gamma$

Forces in nc-AFM

Frequency modulation: $f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$ $\Delta f = -\frac{f_0}{2k}\frac{\partial F_{tot}}{\partial z}$

⇒ measured topography = surface of constant $\frac{\partial F}{\partial z}$

$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

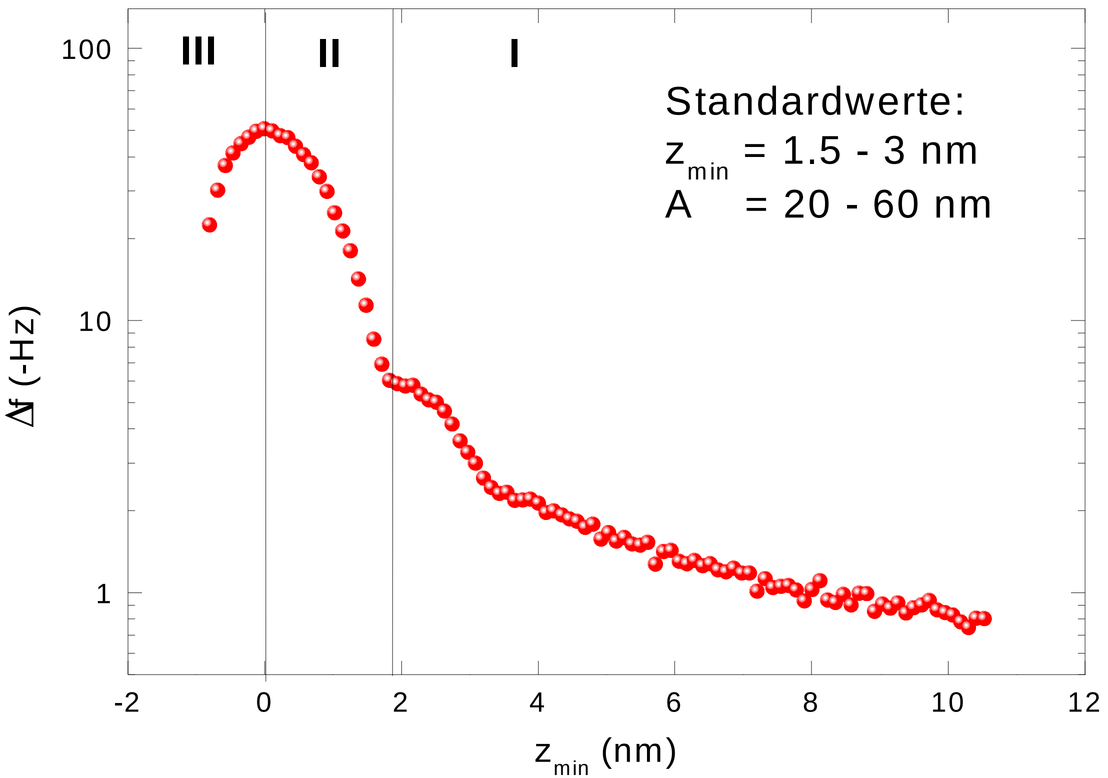
bonding between tip and sample atoms (only for d < 5 Å)

only for magnetically sensitive tips

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2$$

$$F_{vdW} = -\frac{HR}{6d^2}$$

Dynamic Mode, non-contact

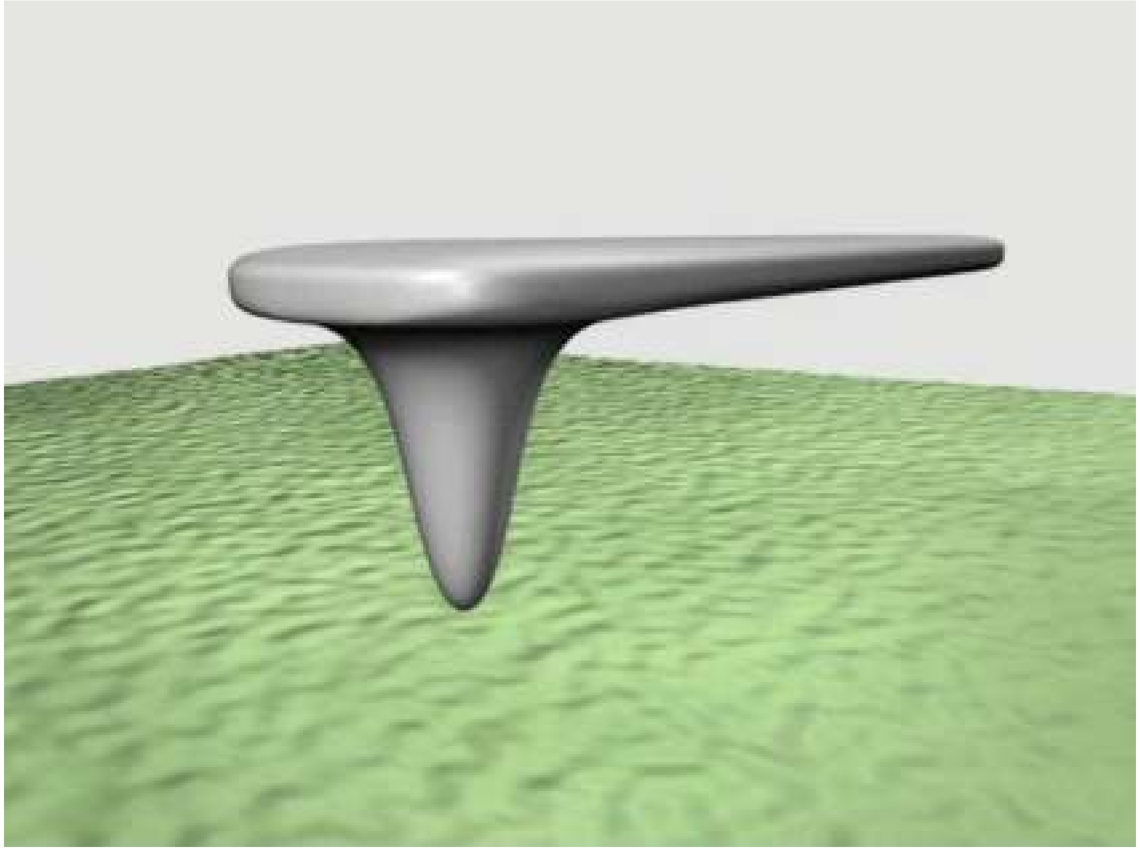


region I:
attractive forces
non-contact mode

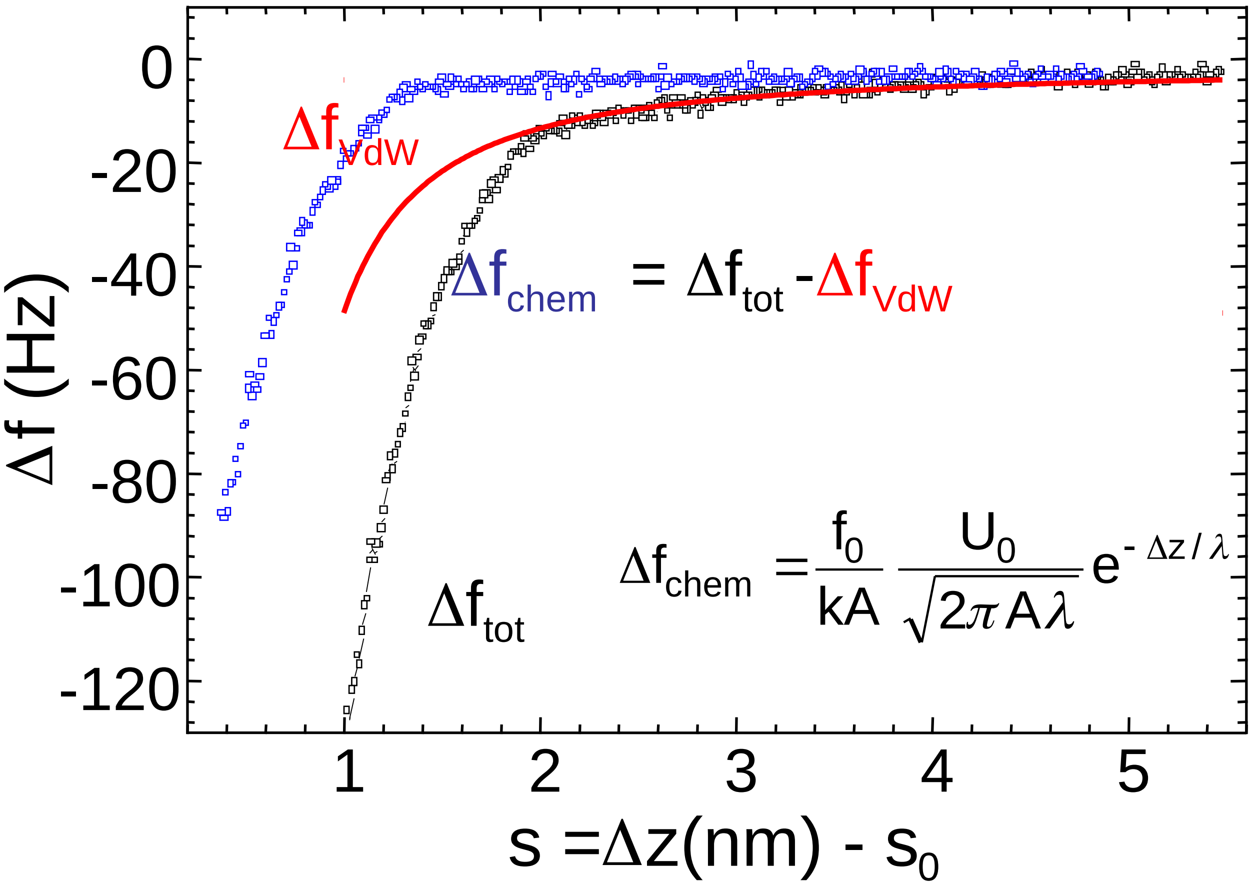
region II:
attractive forces
atomic resolution

region III:
repulsive forces
tapping mode

nc-AFM scheme



Short range interaction

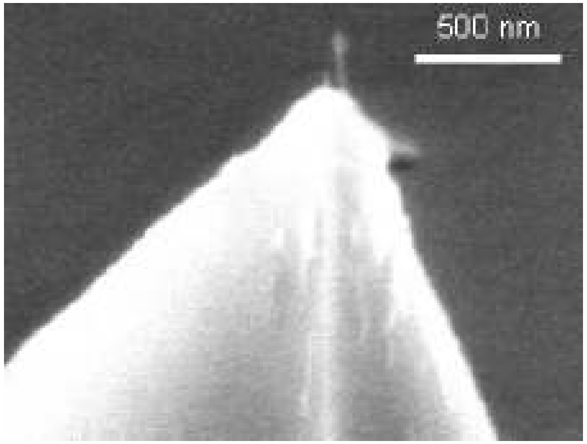


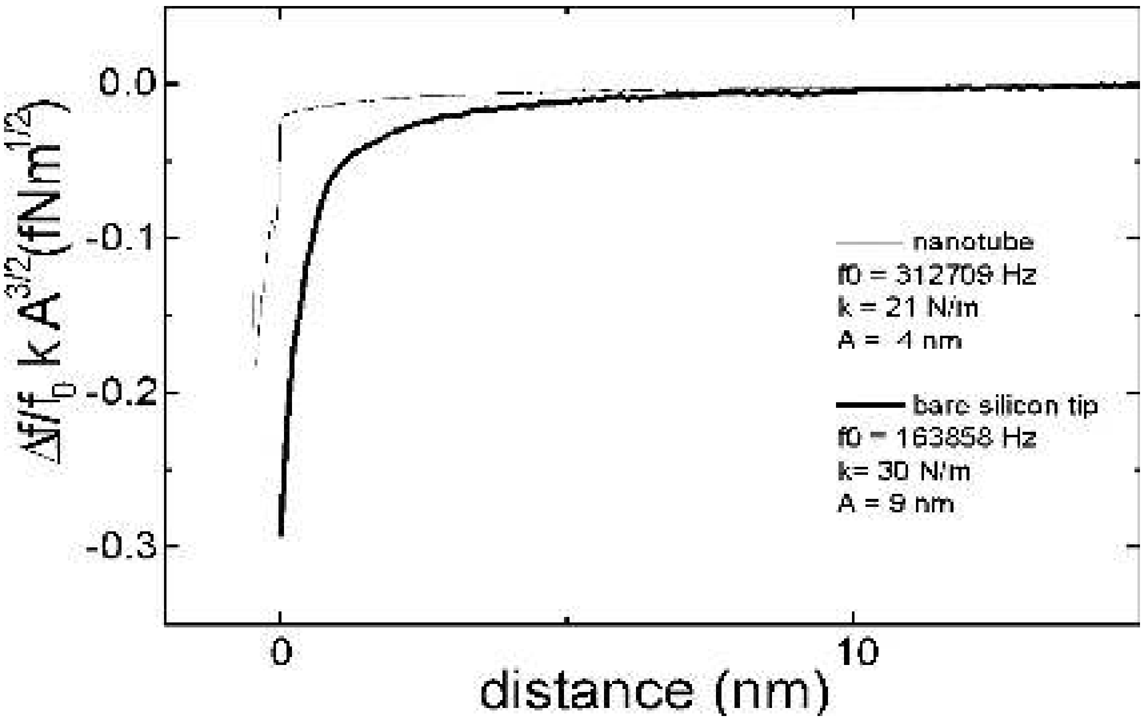
λ = 0.35 nm

U_0 = -4.7 eV

s_0 = 0.45 nm

Carbon nanotubes as probing tips for nc-AFM

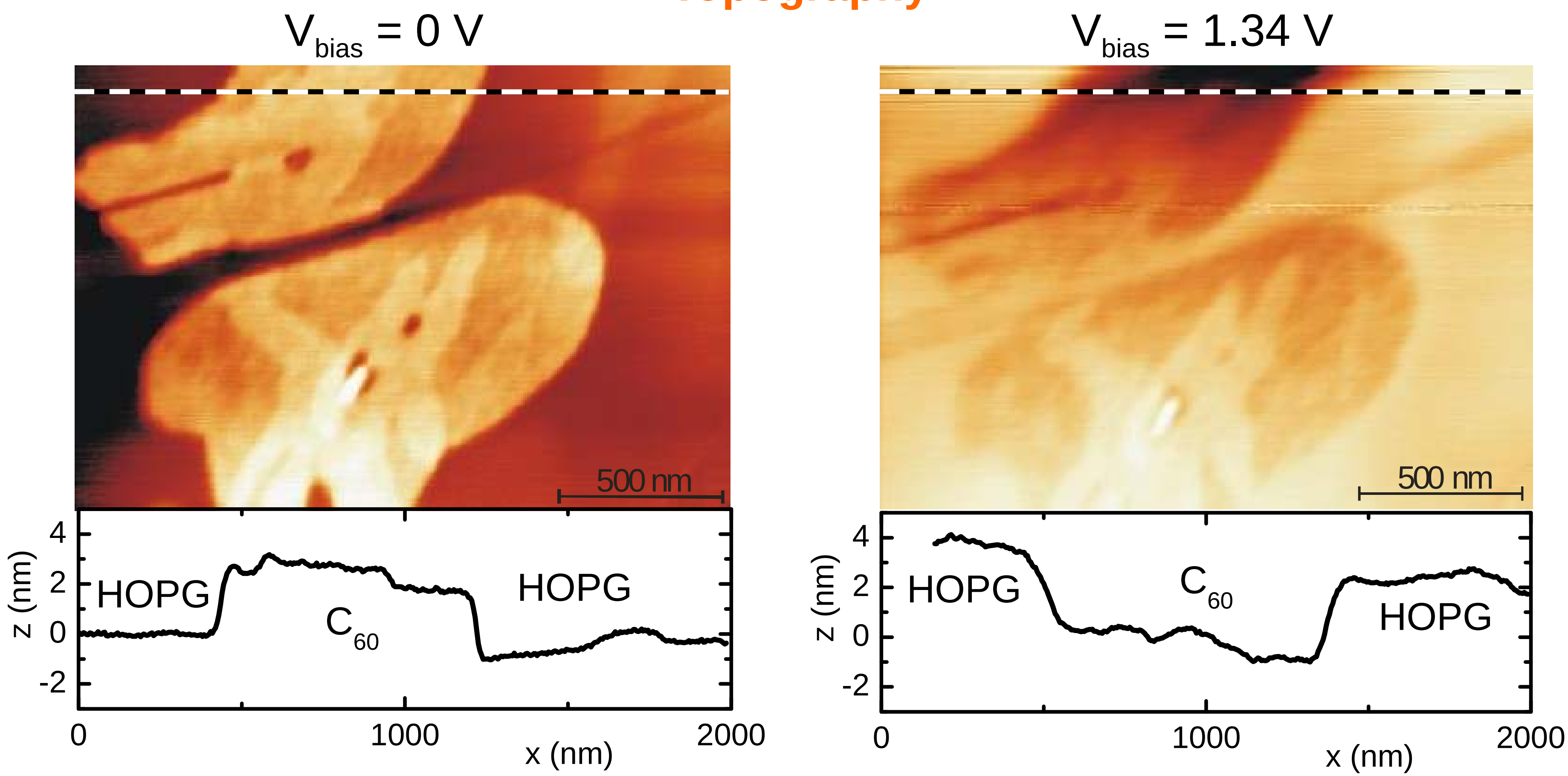




⇒ Long-range forces are reduced

inhomogeneous sample: HOPG + ½ monolayer C60

Topography

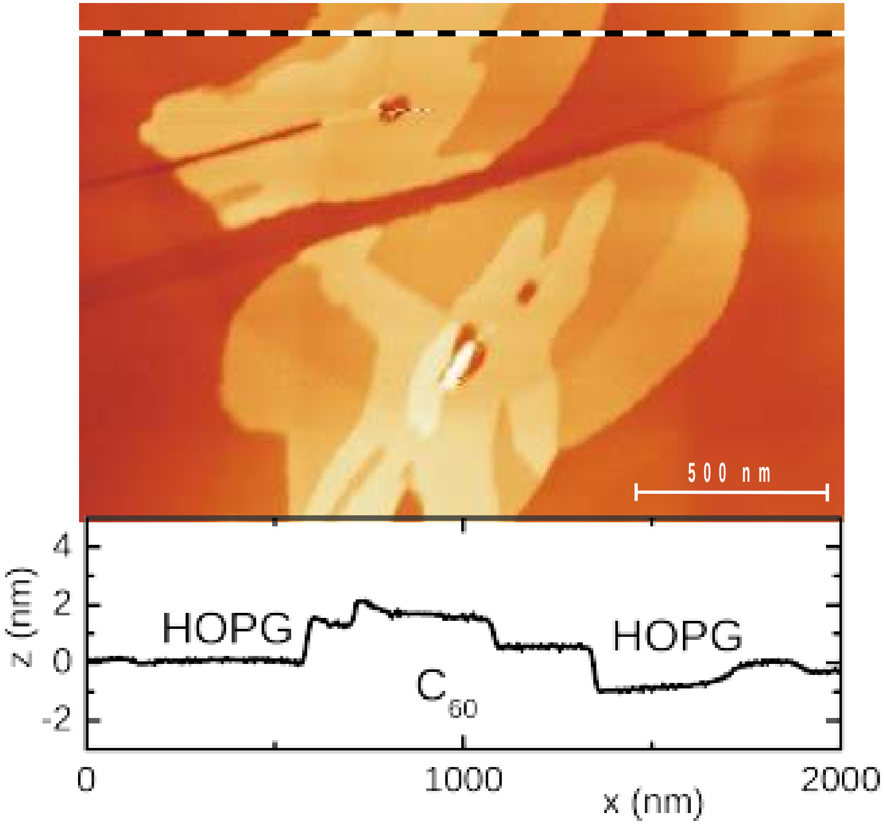


→ contrast inversal: HOPG ↔ C_{60}

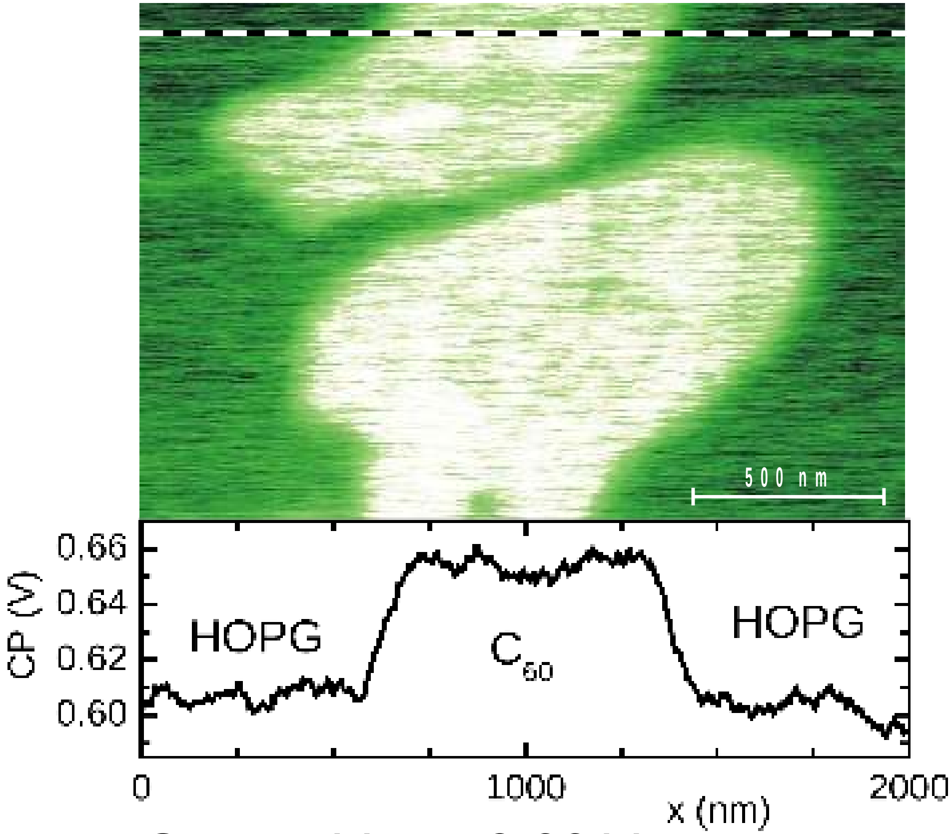
S. Sadewasser et al., PRL 91 266101 (2003)

inhomogeneous sample: HOPG + ½ monolayer C60

topography



contact potential



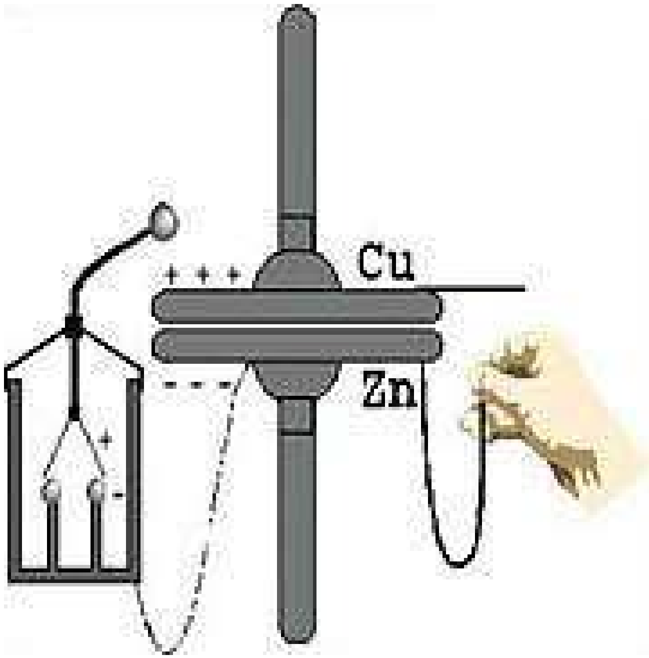
HOPG: $V_{CP} \cong 0.61$ V

C_{60}: $V_{CP} \cong 0.66$ V

⇒ NC-AFM: residual electrostatic force for fixed V_{bias}

Makroskopische Kelvin-Sonde

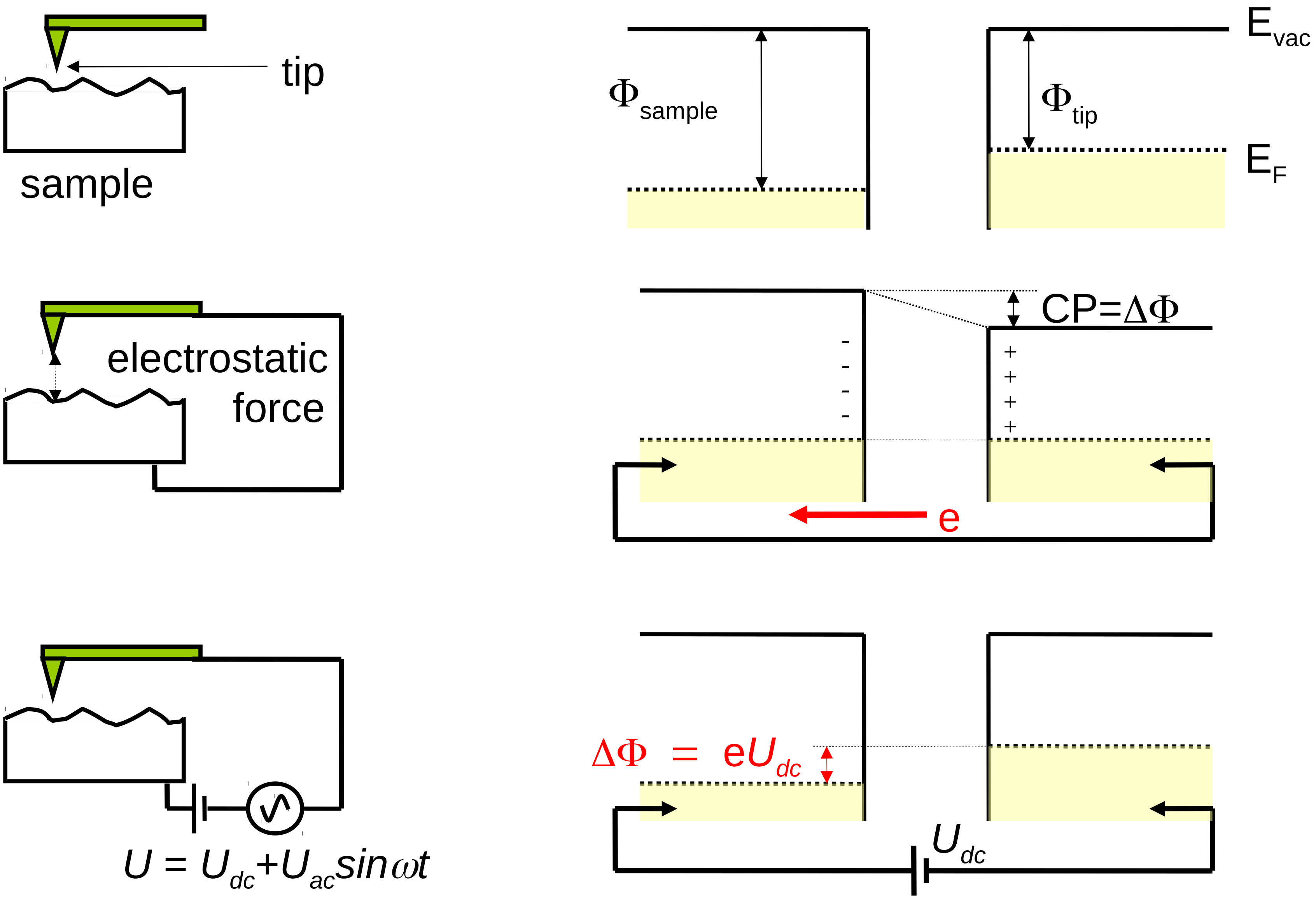
Lord Kelvin 1861



Verschiebestrom

$I(t) = (U_{dc} - U_{CPD})\, f\ \Delta C \cos \omega t.$

Kelvin Principle



Electrostatic Forces in nc-AFM

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 \quad \Rightarrow \quad F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}\left(V_{bias} - V_{CP}\right)^2$$

$$V_{CP} = 1/e \cdot \left(\Phi_{tip} - \Phi_{sample}\right)$$

contact potential

Φ - work function

apply bias: $$V_{bias} = V_{dc} + V_{ac} \cdot \sin(\omega t)$$

Kelvin Probe Force Microscopy

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 = F_{dc} + F_{\omega} + F_{2\omega}$$

$$F_{dc} = -\frac{\partial C}{\partial z}\left[\frac{1}{2}\left(V_{dc} - V_{CP}\right)^2 + \frac{V_{ac}^2}{4}\right]$$

$$F_{\omega} = -\frac{\partial C}{\partial z}\left(V_{dc} - V_{CP}\right)V_{ac}\sin(\omega t)$$

$$F_{2\omega} = \frac{\partial C}{\partial z}\frac{V_{ac}^2}{4}\cos(2\omega t)$$

AM-KPFM

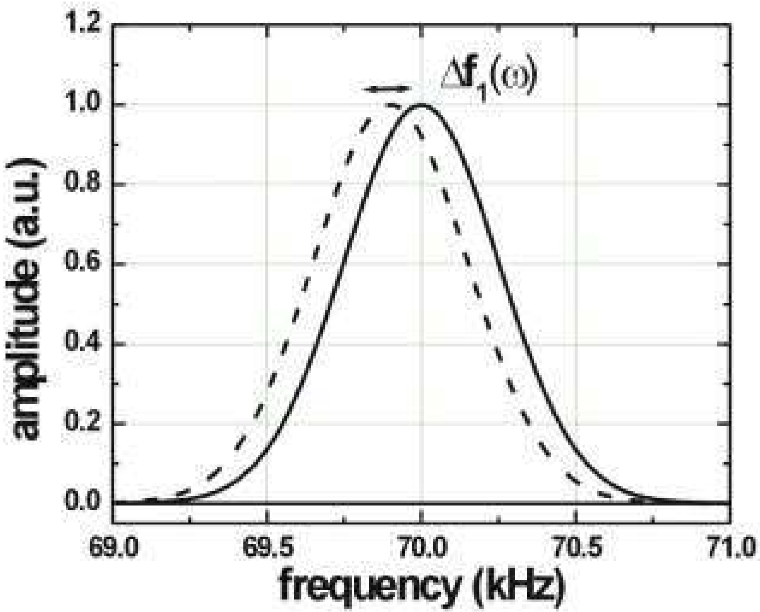
Amplitude Modulation

FM-KPFM

Frequency Modulation

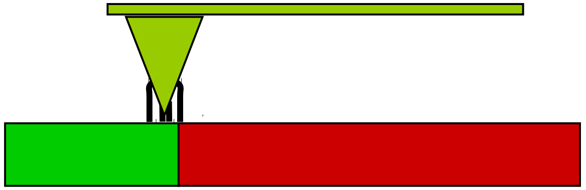
FM – KPFM
Frequency Modulation Detection

$$\Delta f(\omega) \propto \frac{\partial F_{el}}{\partial z} \propto \frac{\partial^2 C}{\partial z^2}\left(V_{dc} - V_{CP}\right) V_{ac} \sin(\omega t)$$



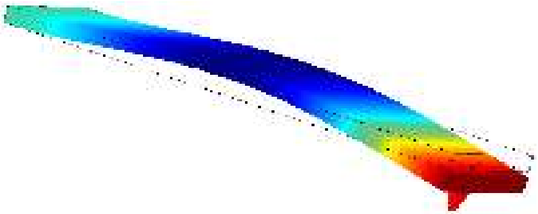
- frequency ω of V_{ac} between 1-3 kHz
- detection of the oscillation of $A(\Delta f_1)$ with a lock-in
- limiting factor: bandwidth of the FM-demodulator / PLL

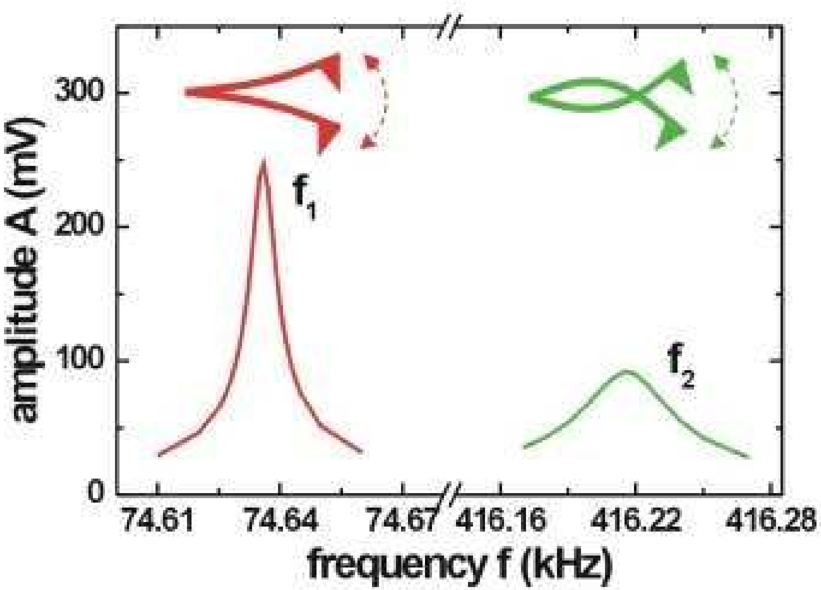
$$A(\Delta f_1) \propto \partial F_{el}/\partial z$$



AM – KPFM
Amplitude Modulation Detection

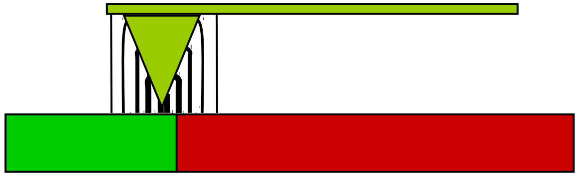
$$F_\omega = -\frac{\partial C}{\partial z}\left(V_{dc} - V_{CP}\right)V_{ac}\sin(\omega t)$$



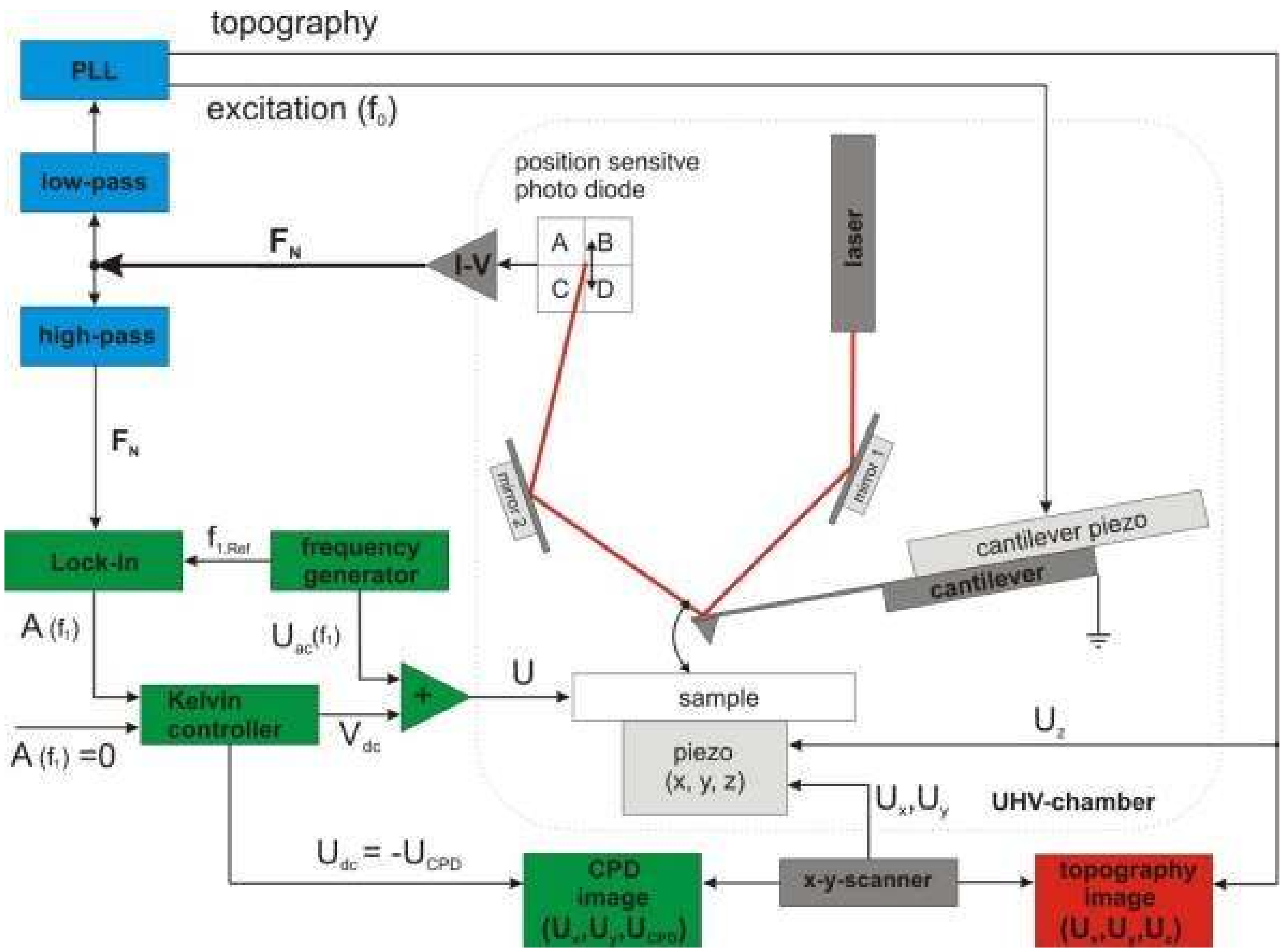


- tune ω to the second resonance f_2
- detection of the oscillation amplitude A_ω with a lock-in
- limiting factor: bandwidth of the photodiode

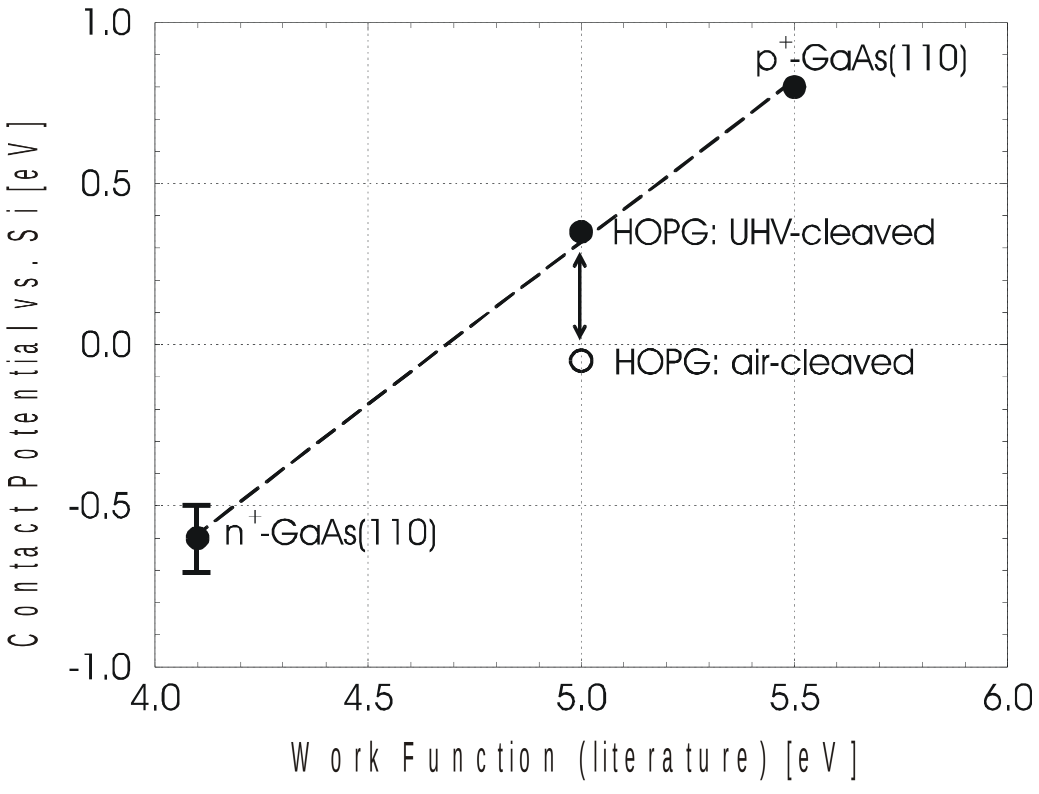
$$A_\omega \propto F_\omega$$



Experimental Setup
nc-AFM & AM-KPFM



KPFM calibration and absolute work function



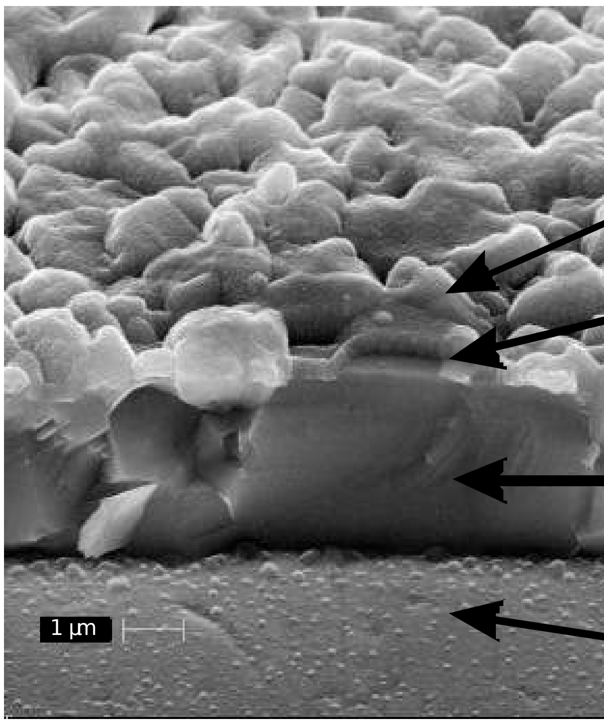
Φ-Si-Cantilever = 4.70 (±0.1) eV

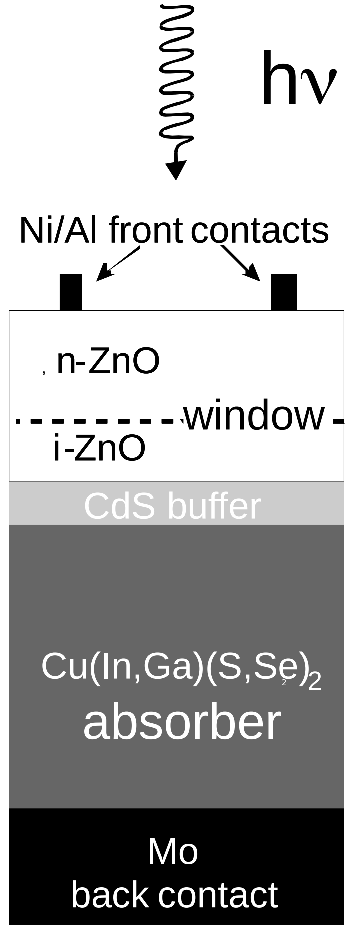
U_{ac} = 100 mV

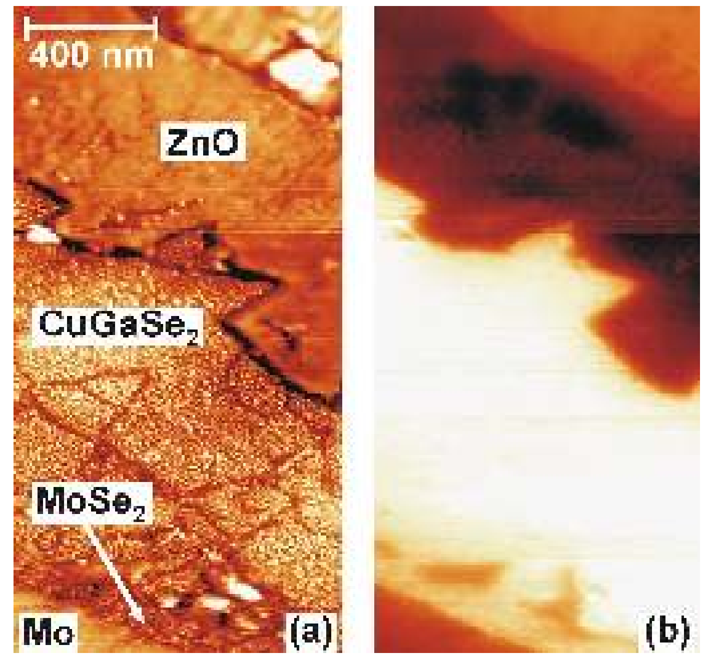
→ absolute and quantitative work function determination

Kelvin Probe Force Microscopy (KPFM)

chalcopyrite thin film solar cells







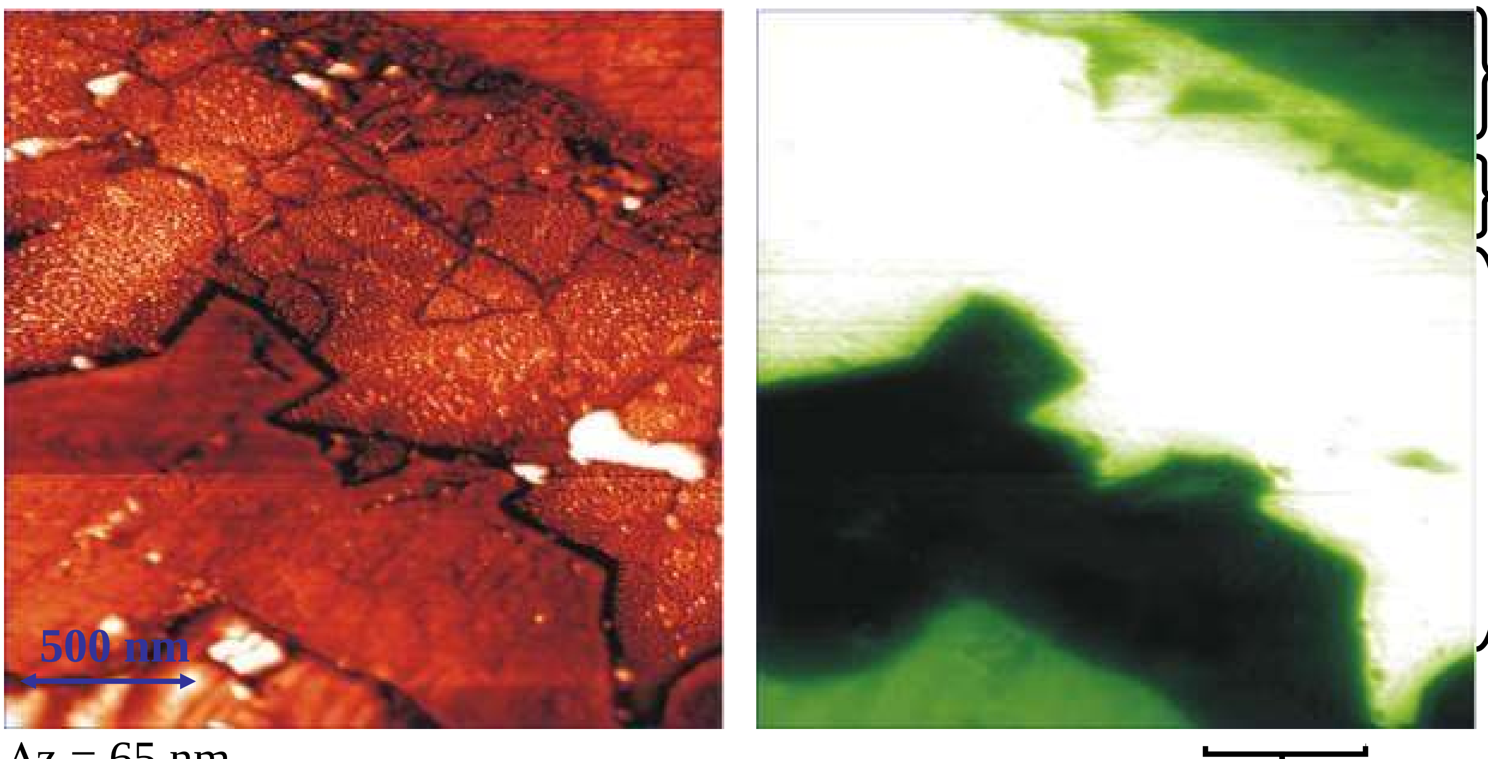
work function (Φ = 3.92-4.86 eV)

Th. Glatzel et al., APL 81, 2017 (2002),
D. Marron et al., APL 85, 3755 (2004).

Polished Cross Section of a $CuGaSe_2$ Solar Cell

$CuGaSe_2$ solar cell device: V_{oc} = 820 mV, η = 4.6 %

polished and Ar-ion sputtered cross section



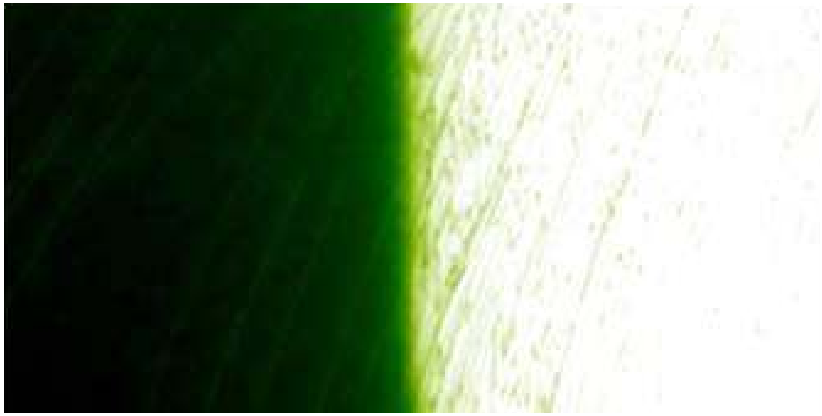
Glatzel *et al.*, APL **81**, 2017 (2002)

AM-KPFM measurement on GaP pn-junction

n-type GaP wafer with p-type GaP layer, $\sim 10^{18}$ cm^{-3}, UHV cleavage along (110) surface

topography

work function



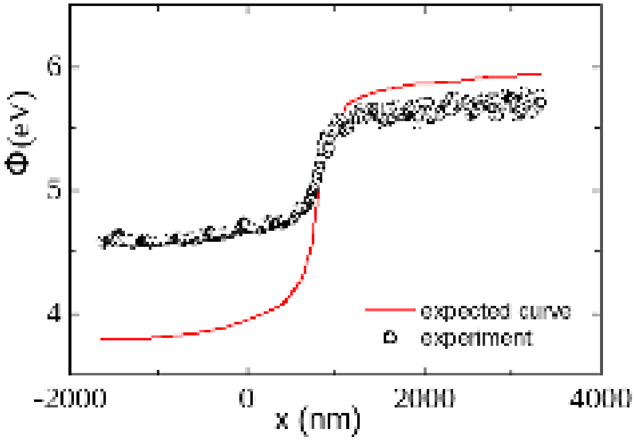
Δz = 4.5 nm 2.5×5 μm^2 Φ = 4.56 - 5.77 eV

most III-V semiconductors:

no surface states on the (110) surface

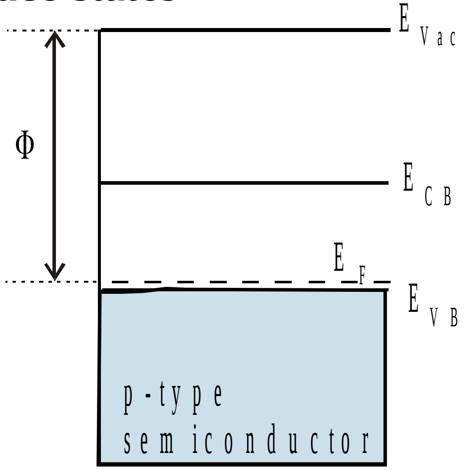
☜ GaP does show surface states

⇒ discrepancy of Φ_{exp} to Φ_{theo} due to surface states!

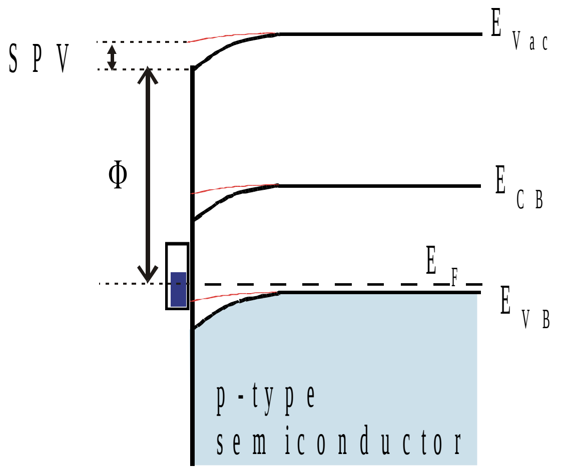


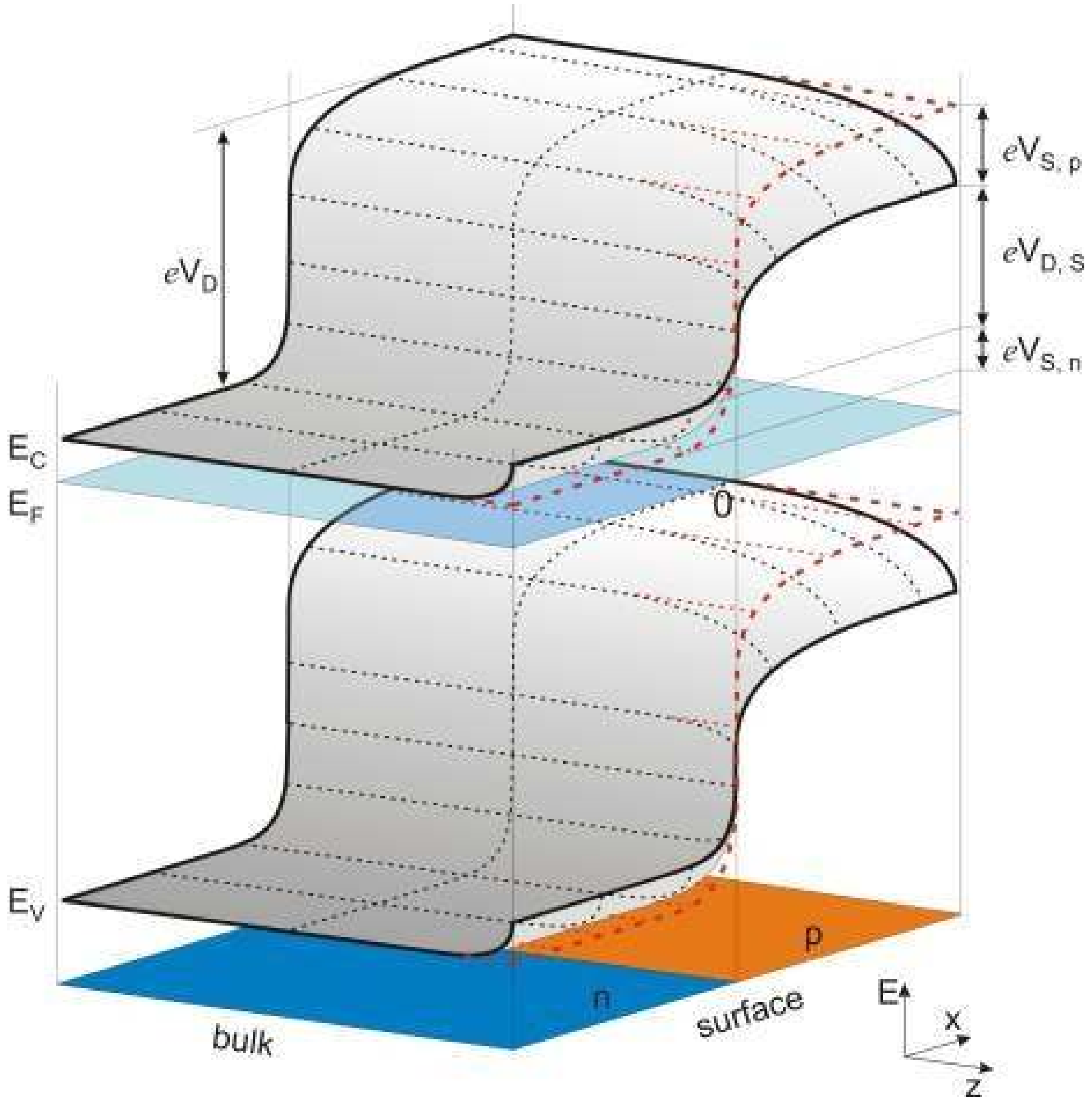
Surface Effects

no surface states



surface states

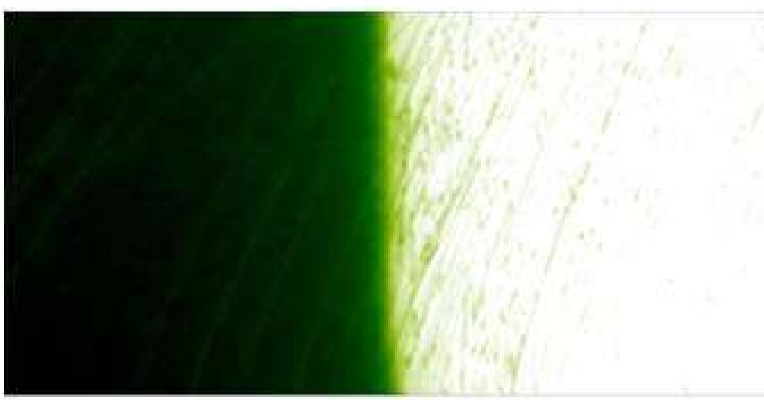




Surface Photovoltage
GaP pn-Interface

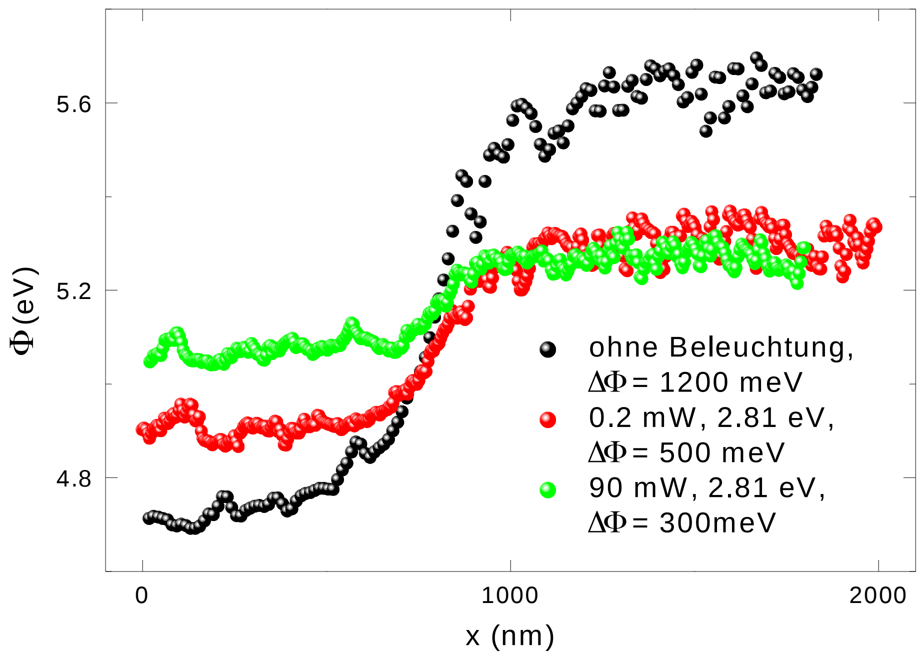
n- GaP p- GaP

Δz = 4.5 nm (5000x2500 nm)

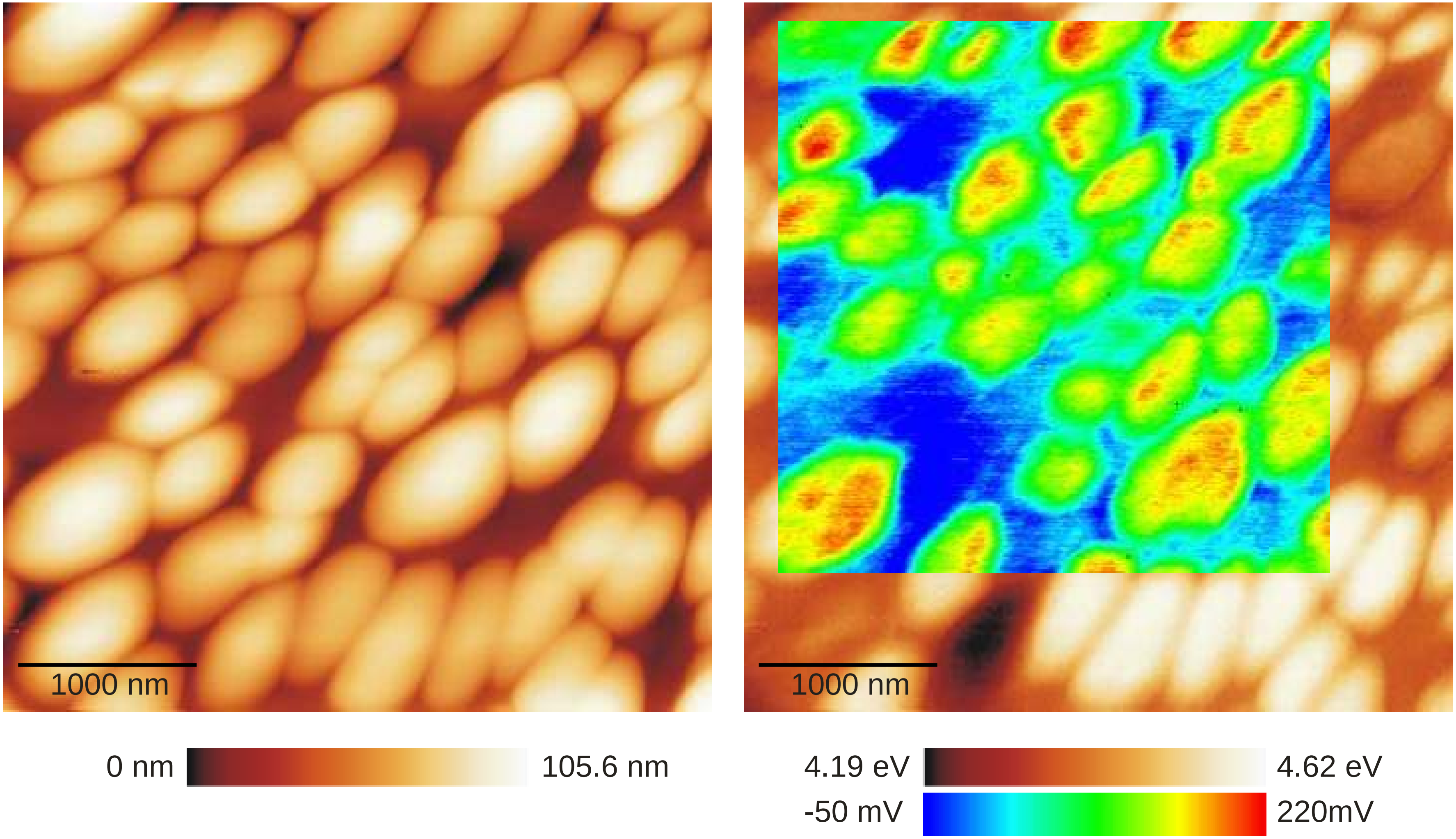


Φ = (4.56 - 5.77)eV

n- GaP p- GaP

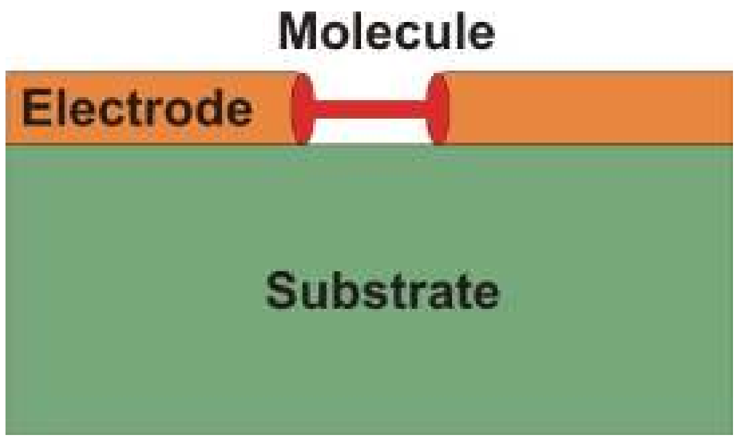


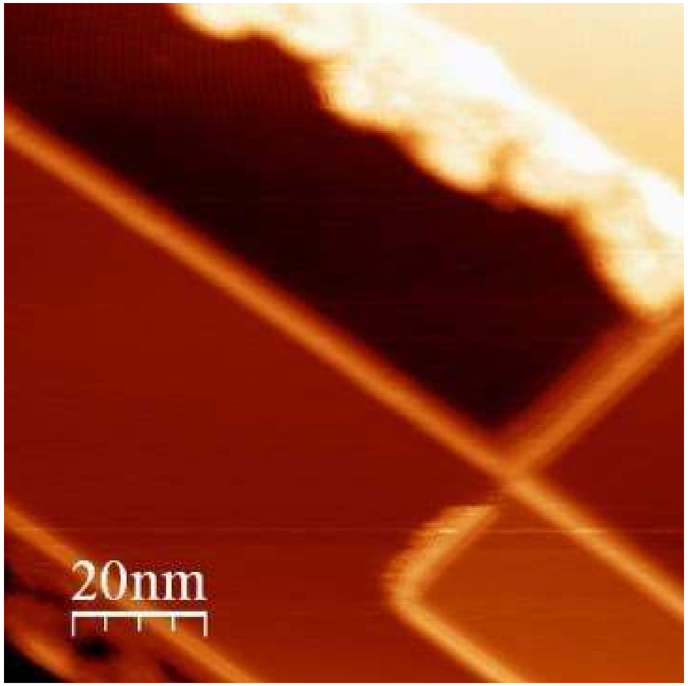
Surface Photovoltage
MDMO-PPV/PCBM – 675nm



Motivation

Molecular electronics



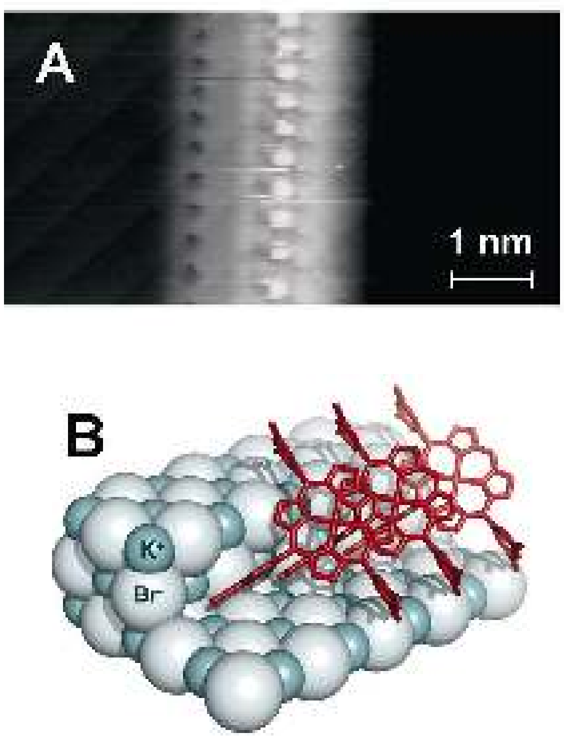


Molecules on Insulators:

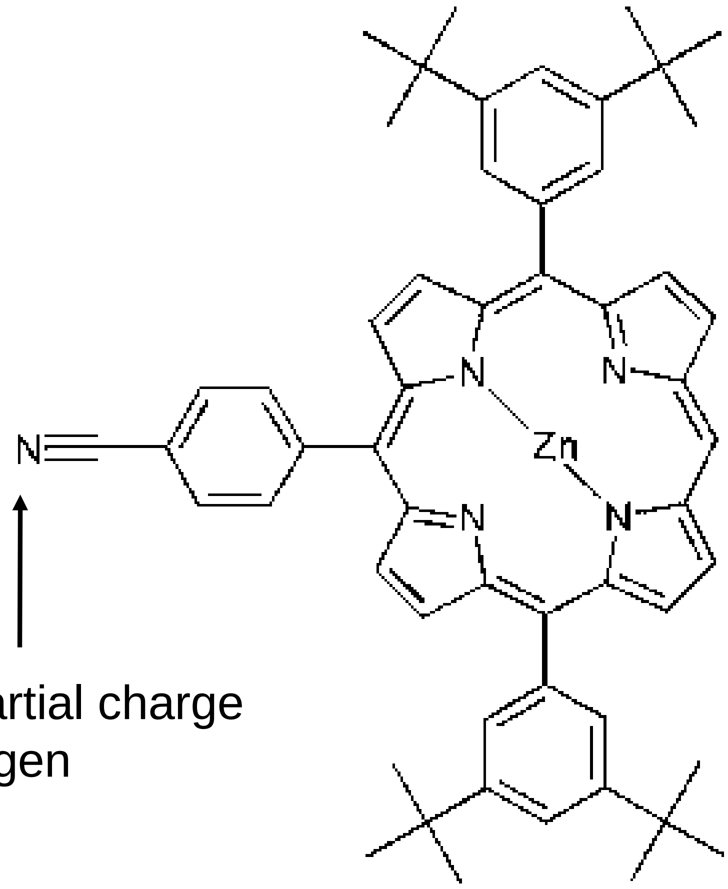
- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not so easy to find applications

Asymmetric Cyano-Porphyrins

Natural light harvesting complexes



S. Meier et al., Small, 2008, 4, 1115



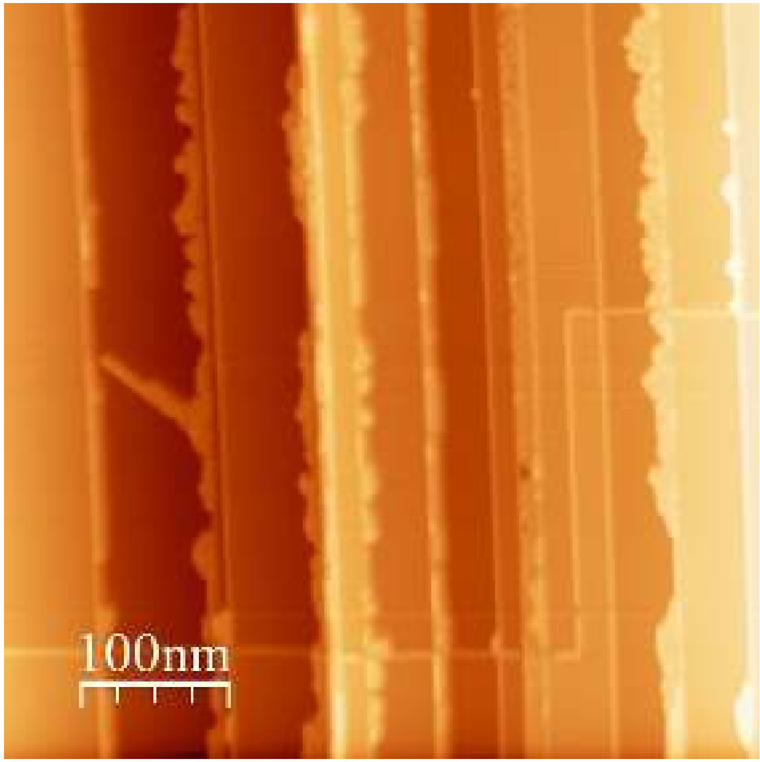
Negative partial charge on the nitrogen

Balaban et al., *Acc. Chem. Res.* **2005**, 38, 612 – 623

Wire Formation

Decoration of step edges on KBr(100)

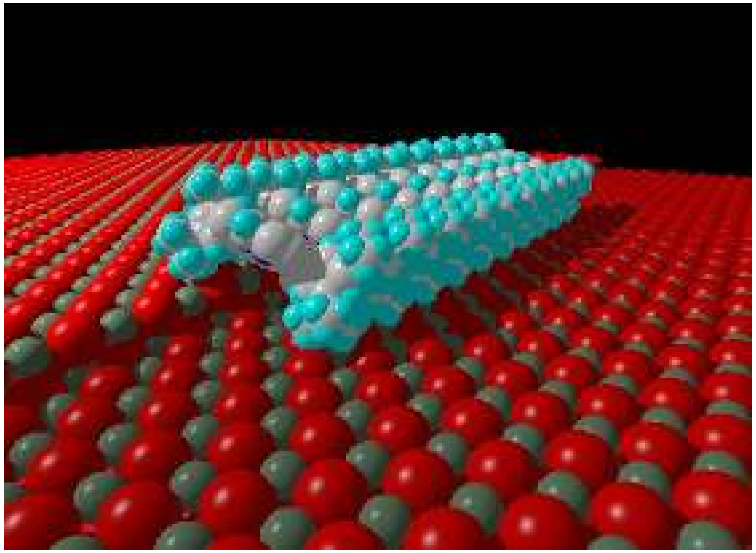
- In situ cleaved KBr with 0.5 ML of molecules
- Steps (< 1nm) are decorated with monowires
- Higher steps act as nucleation sites for structure growth across terraces

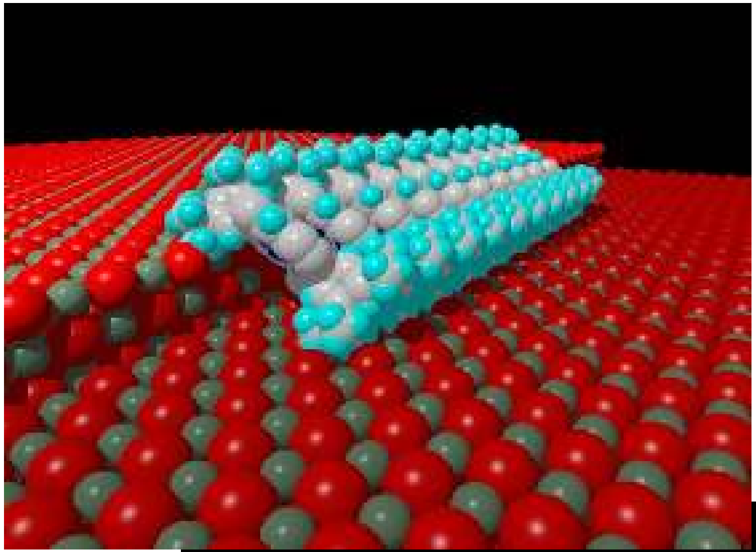


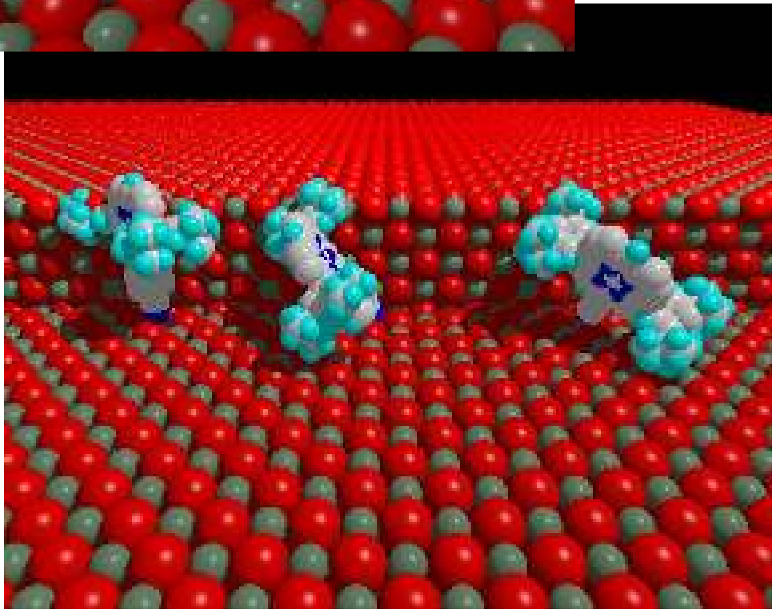
L. Zimmerli et al., J. Phys.: Conf. Ser., 2007, 61, 1357

Wire Formation

Structural model



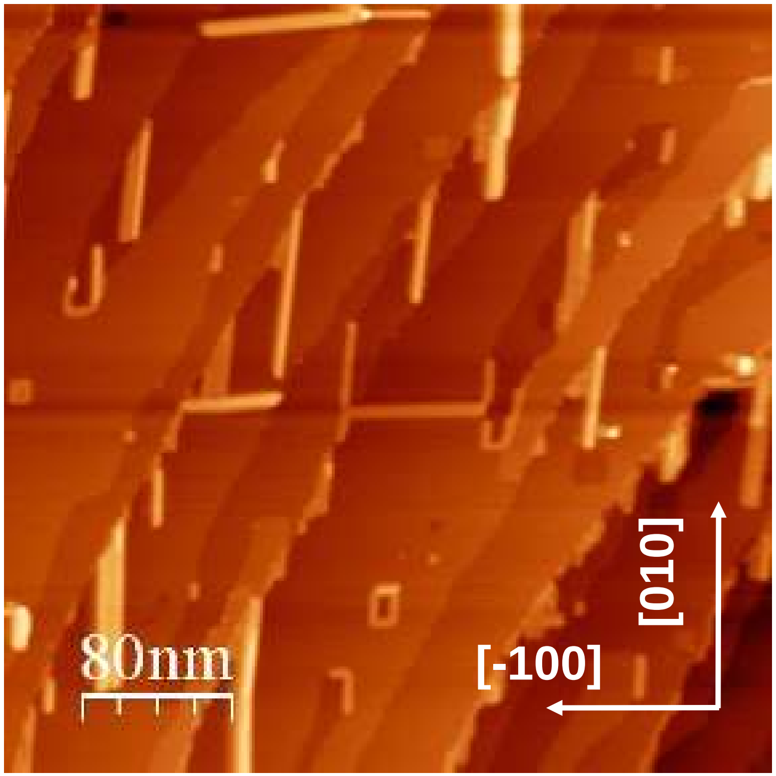




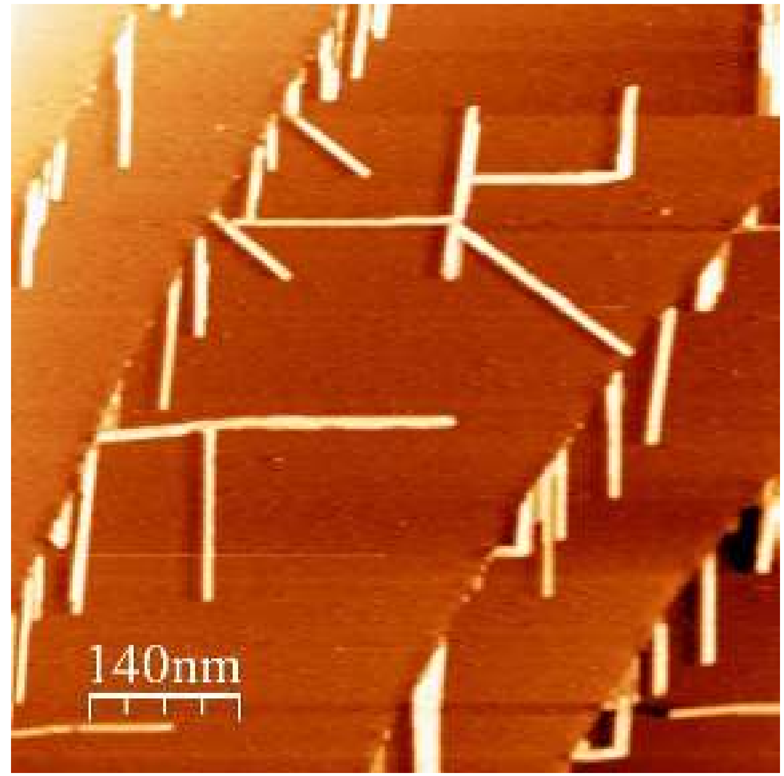
- The tilt angle of the molecules is determined by the side groups, the π-π stacking and the step height.
- Steps higher than 3 ML prevent a π-π stacking.

Molecular Assemblies

Molecular wires on NaCl



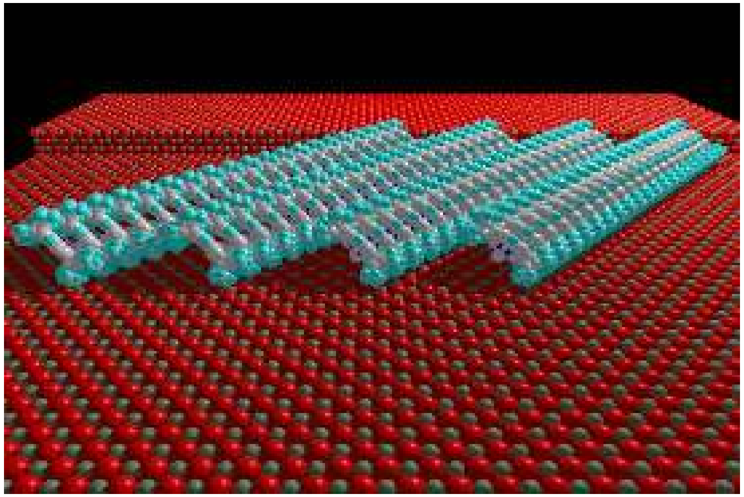
$f_0 \approx 170992 Hz, \Delta f = -9.5 Hz, Q = 15k, A = 40 nm$

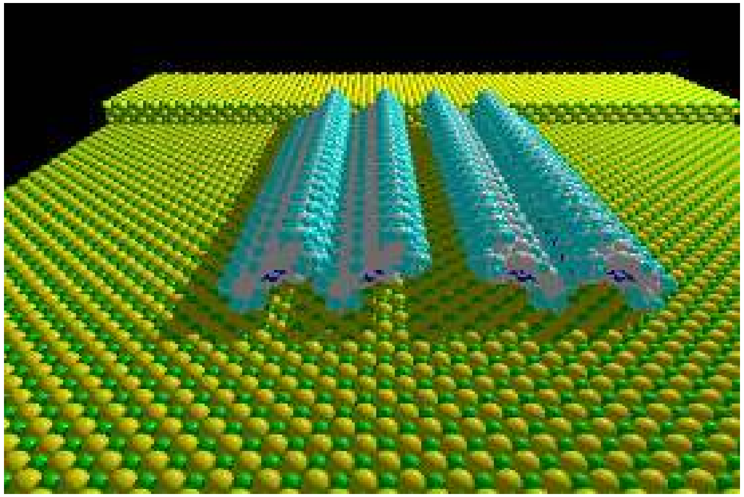


$f_0 \approx 170992 Hz, \Delta f = -11 Hz, Q = 15k, A = 40 nm$

Molecular Assemblies

Structural model

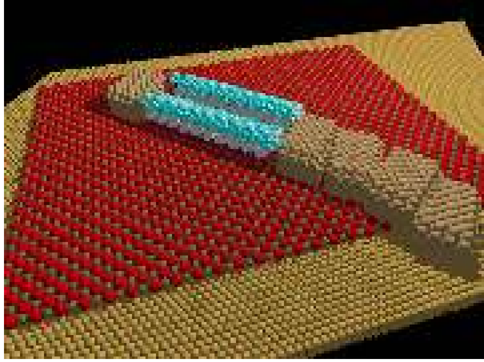


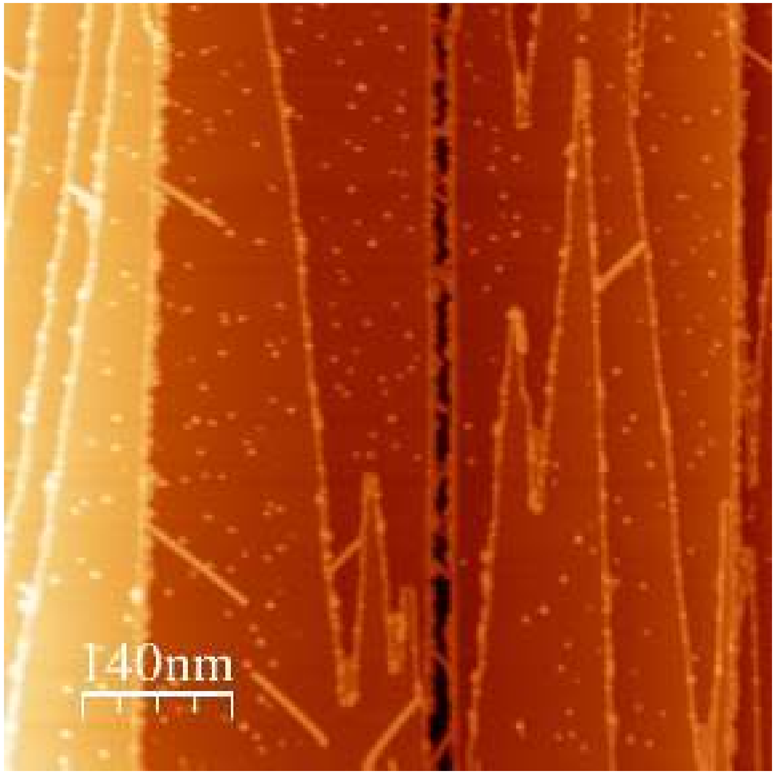


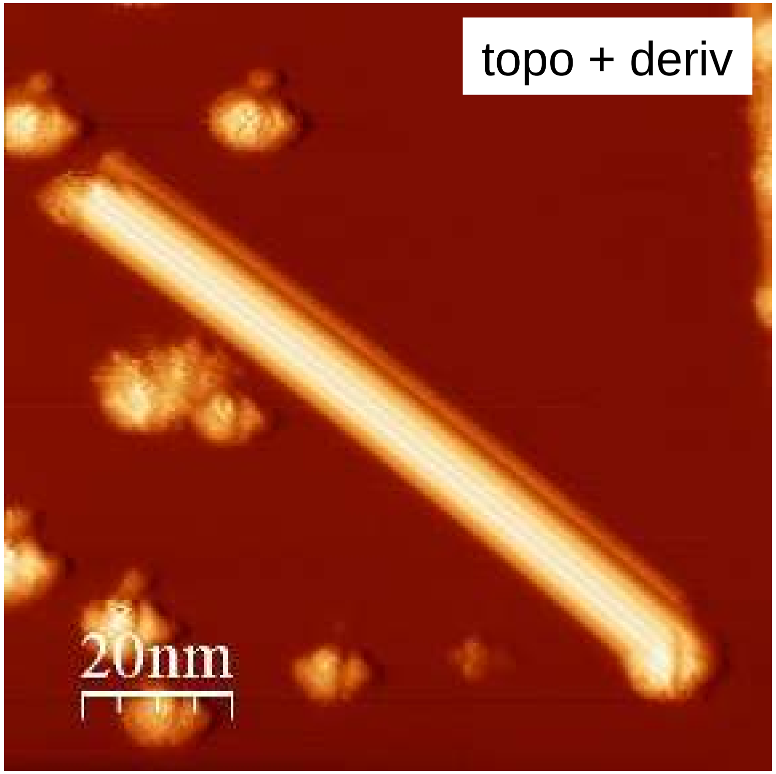
- Intermolecular equilibrium separation ~ 5.7 Å
- Directed growth by the substrate

Contacting Molecular Assemblies

Au-Molecules-Au







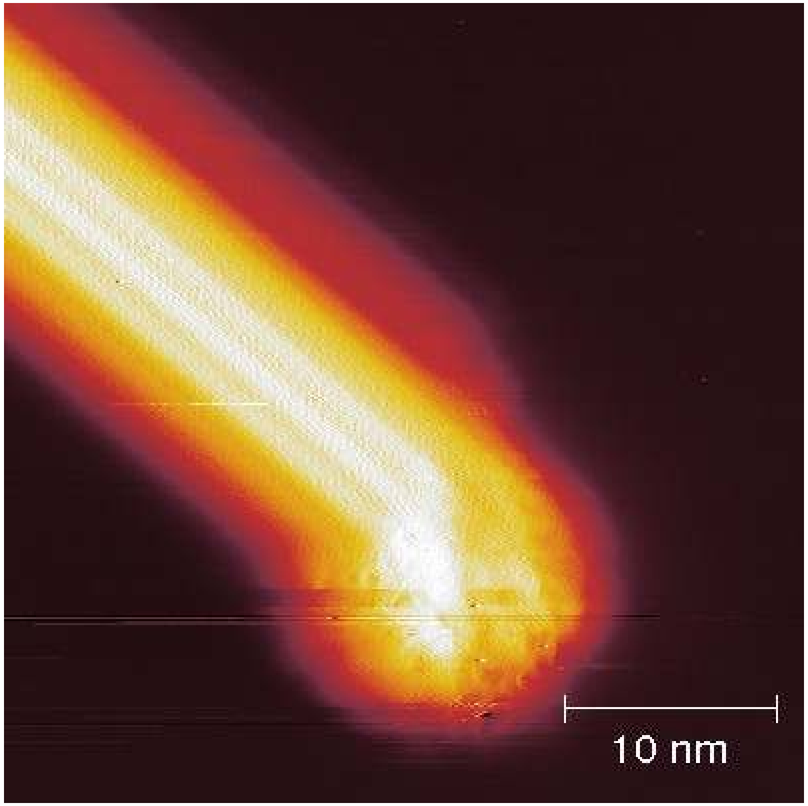
- Molecules arrange at steps and across terraces
- The growth is started/stopped at gold clusters.

Glatzel et al., Appl. Phys. Lett., **2009**, 94, 063303

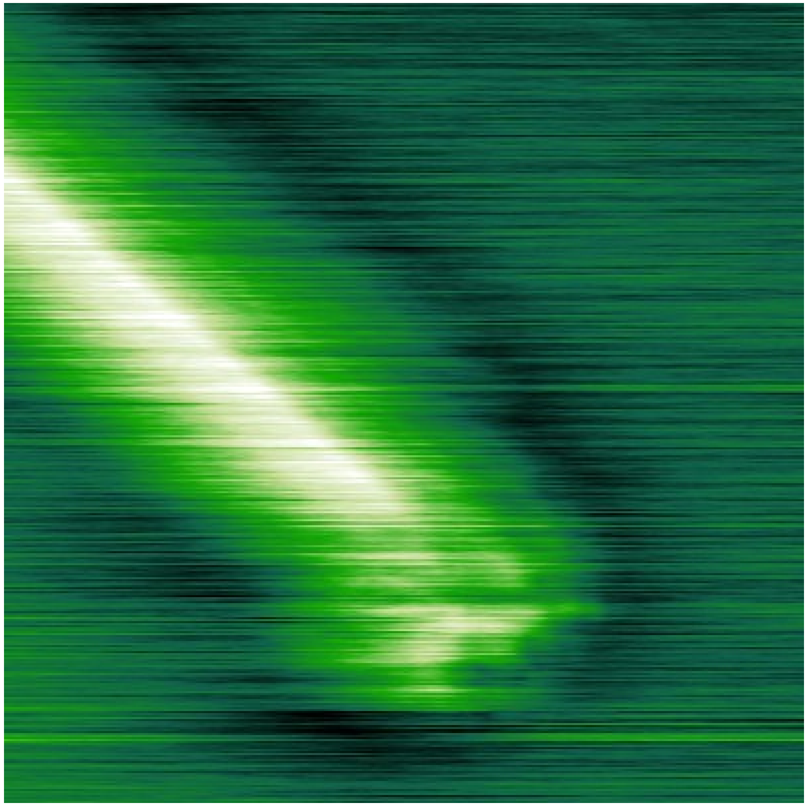
Contacting Molecular Assemblies

KPFM

Topography



LCPD

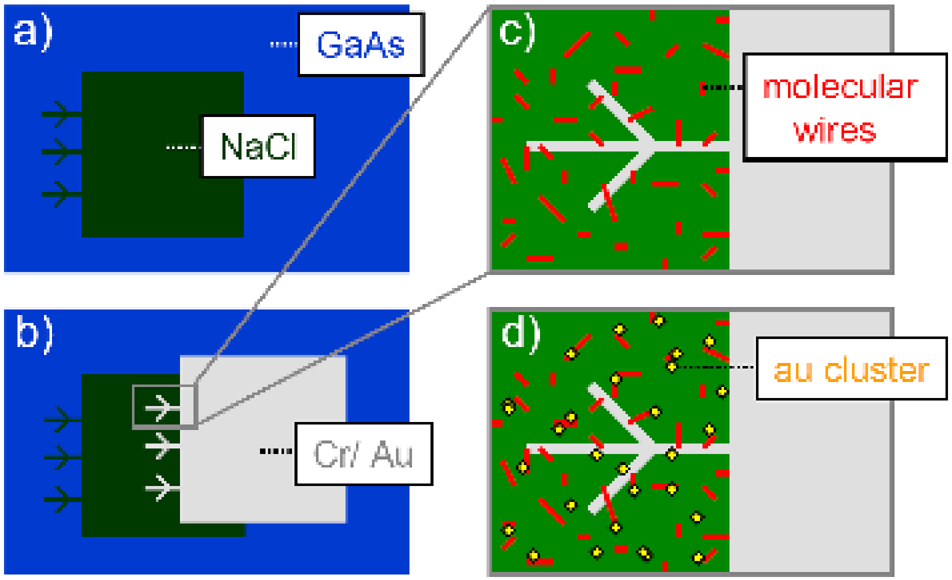


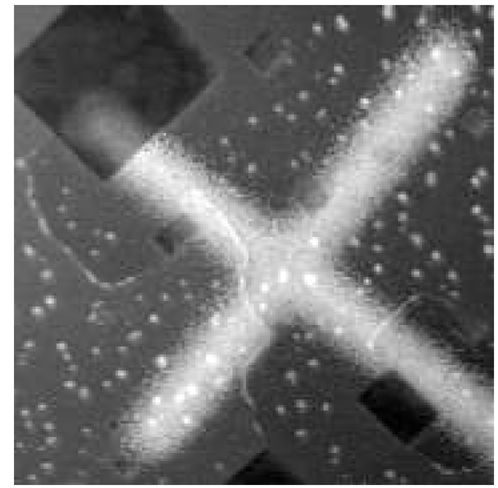
LCPD= -0.5...0.2eV

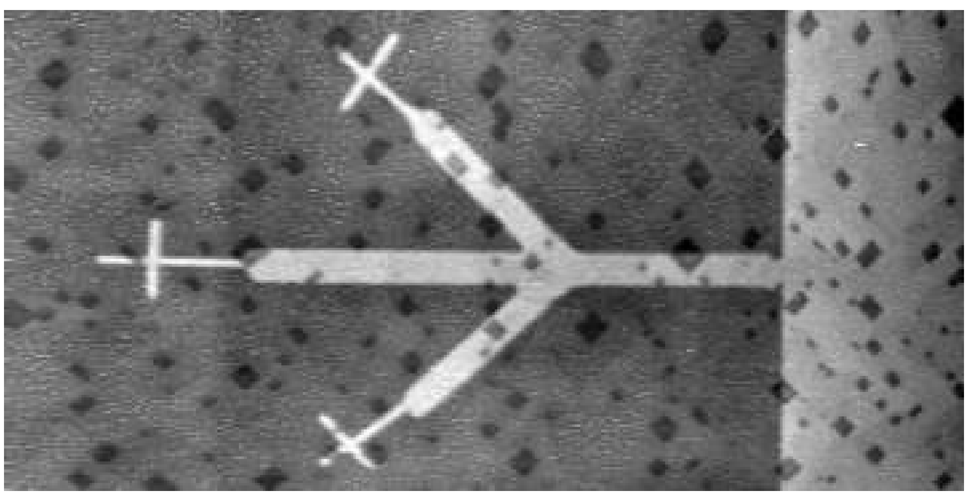
Glatzel et al., Appl. Phys. Lett., **2009**, 94, 063303

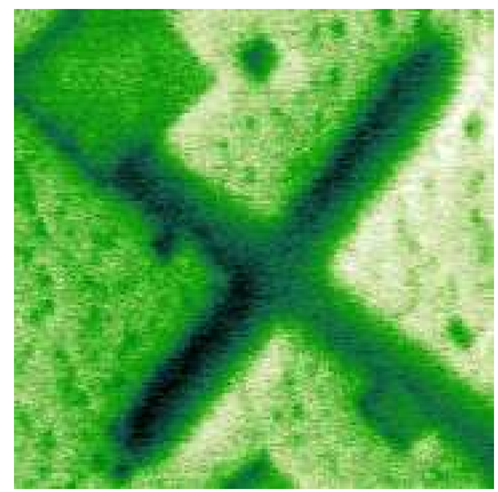
Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)



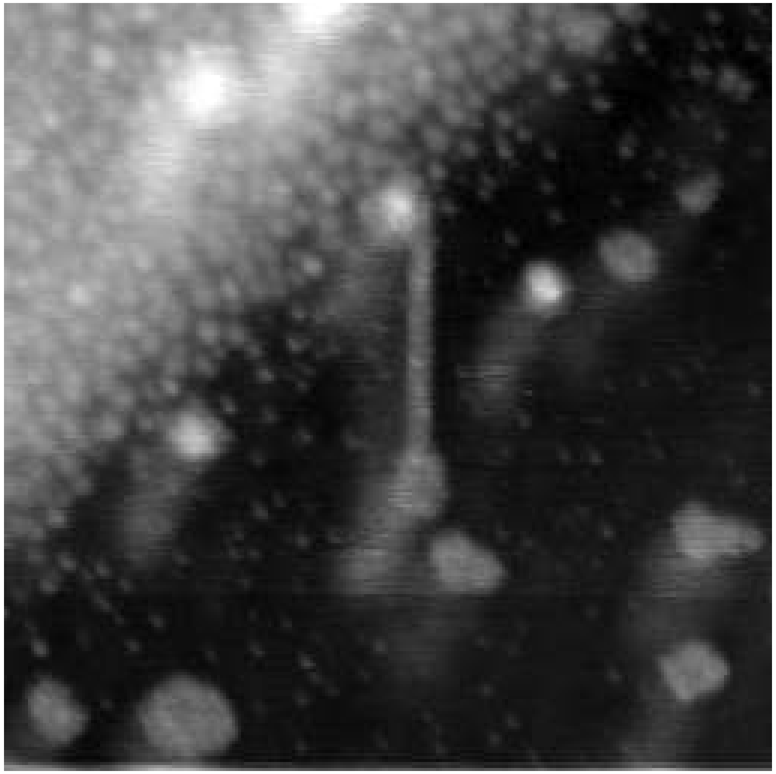




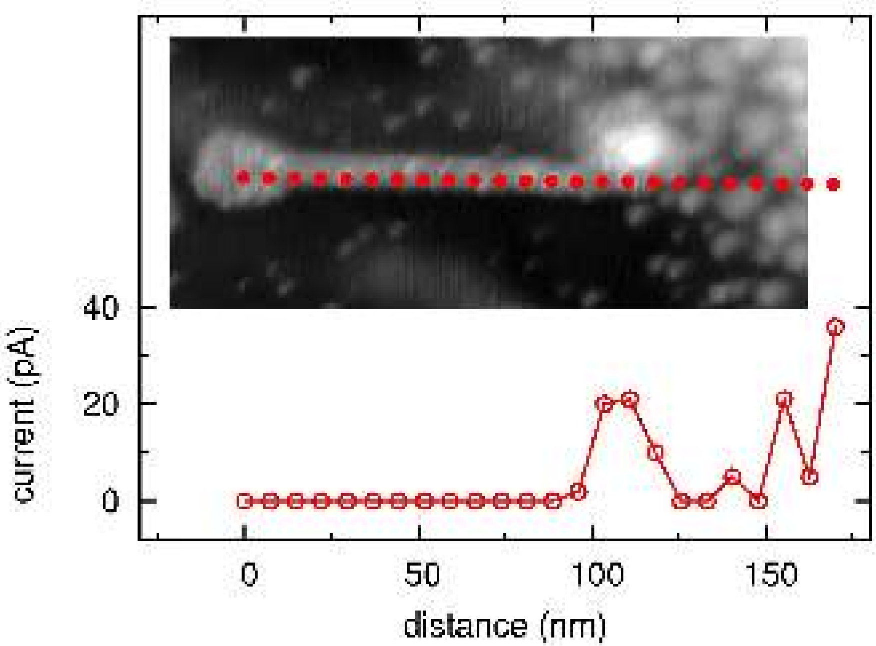


Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)

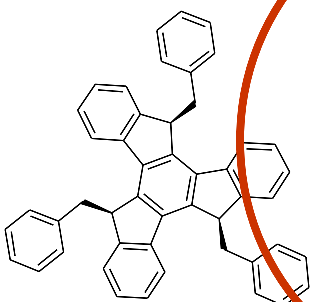


300x300nm^2

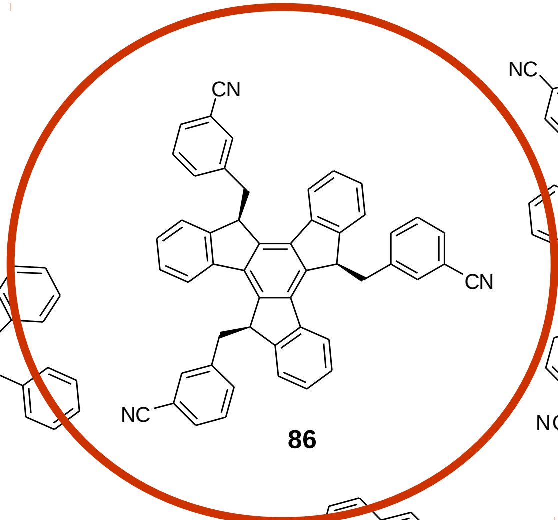


Functionalized Truxenes

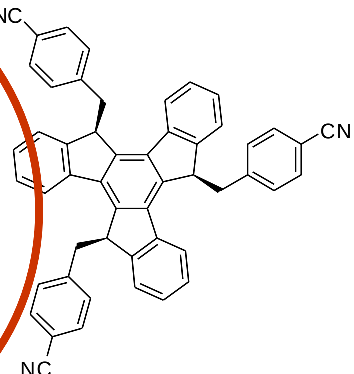
Structure



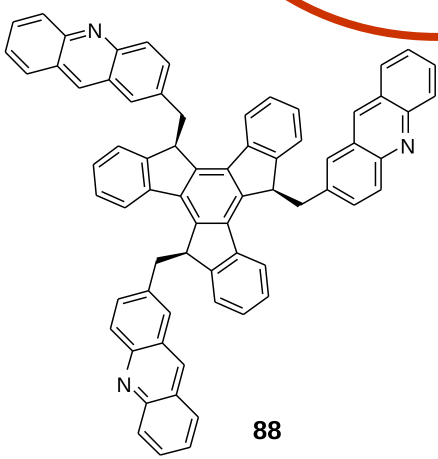
85



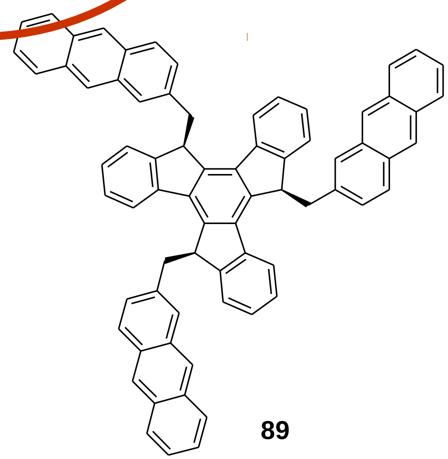
86



87



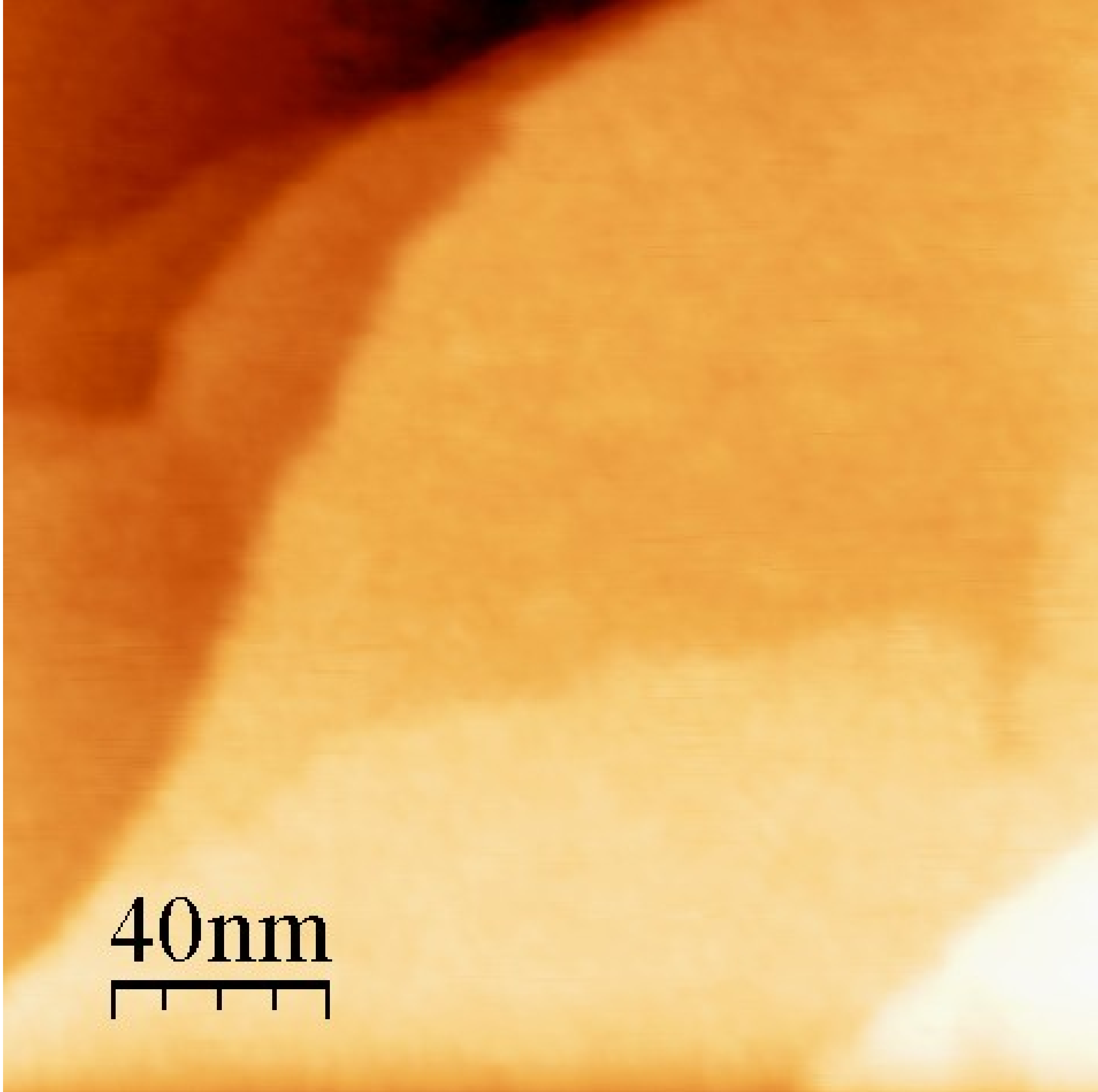
88



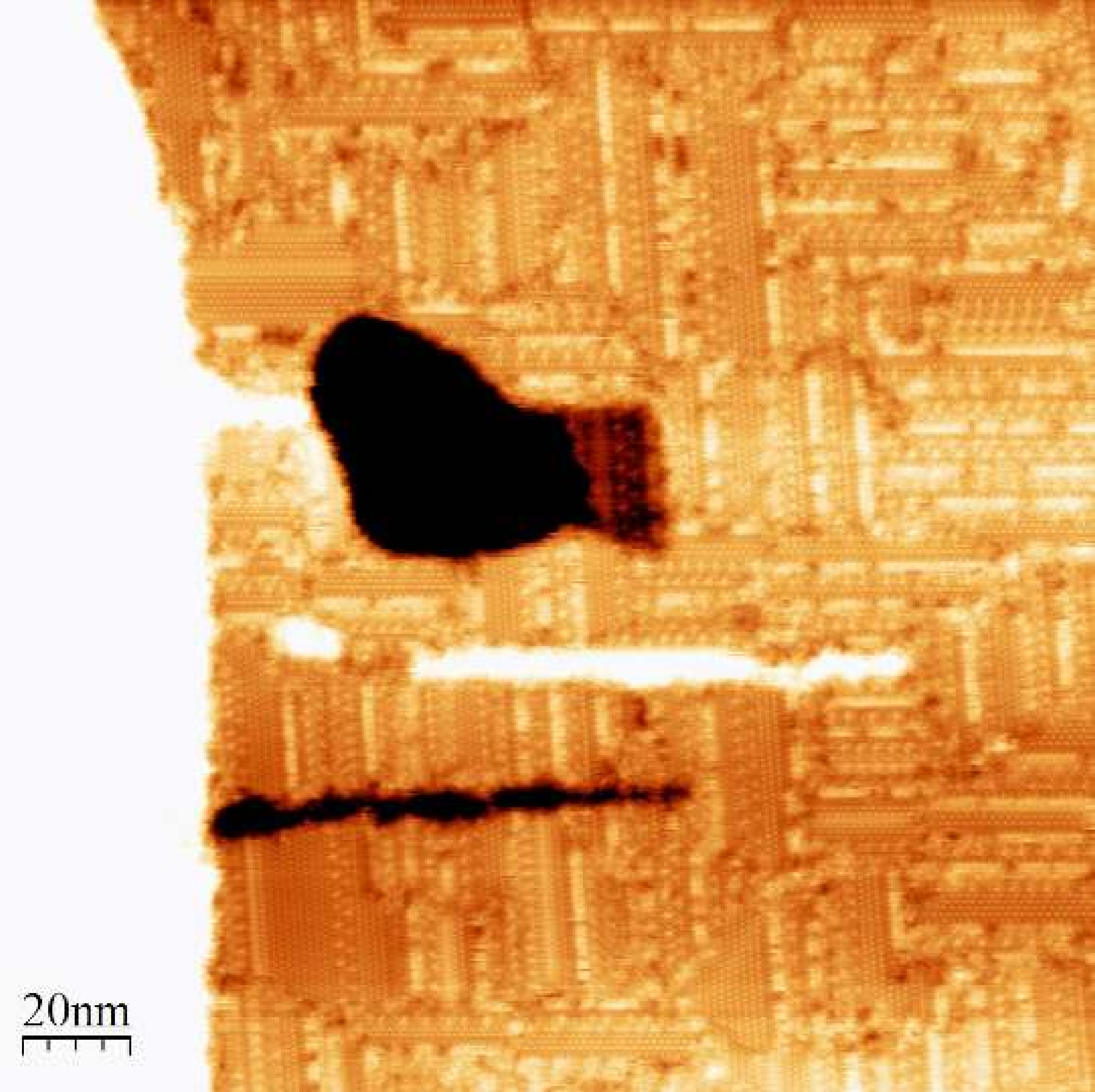
89

O. de Frutos et al., Chem. Eur. J. 8(13), 2879 (2002)

evaporation onto
the sample at RT

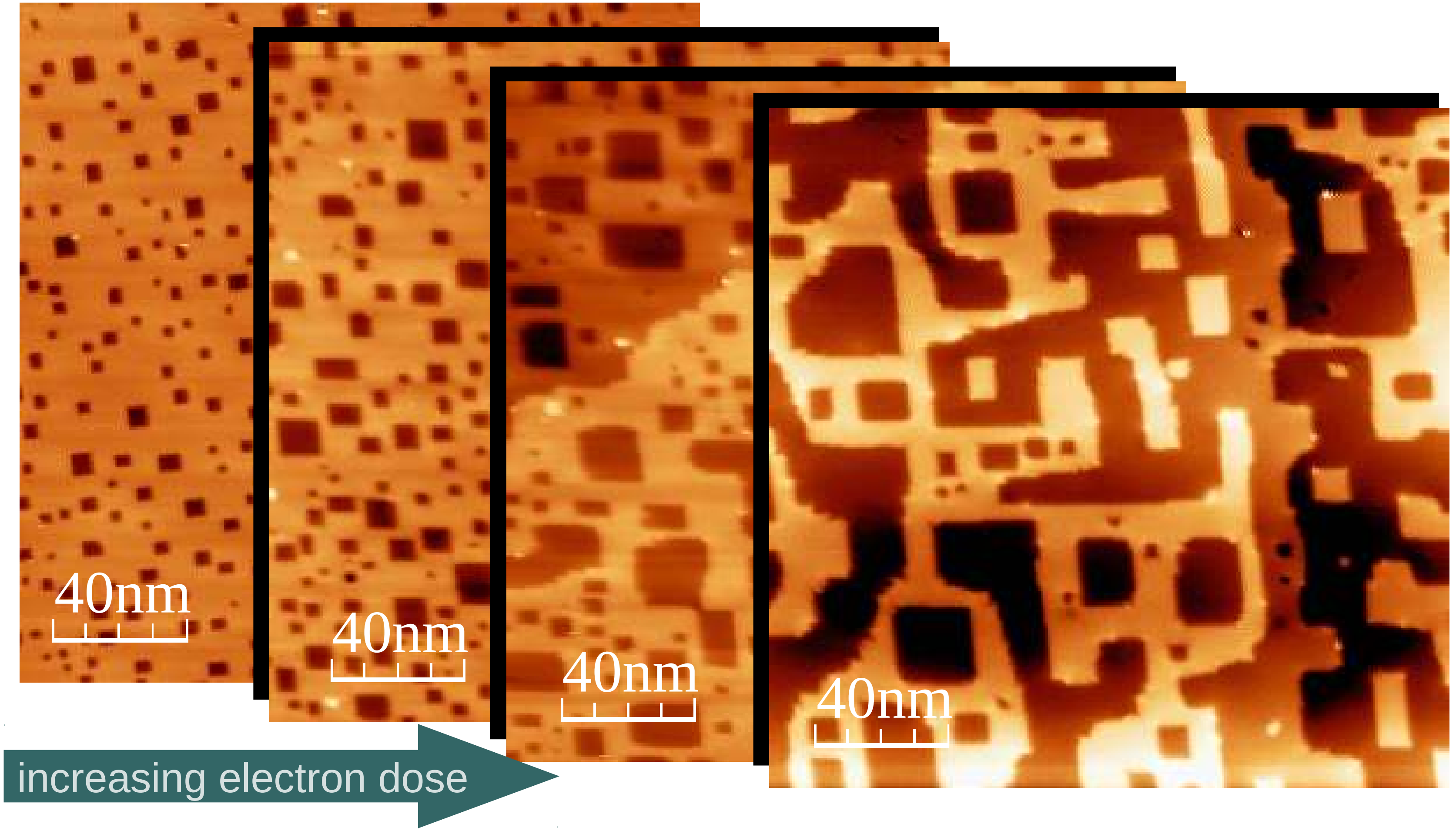


and the result of
post annealing at
155 C for 15 mins



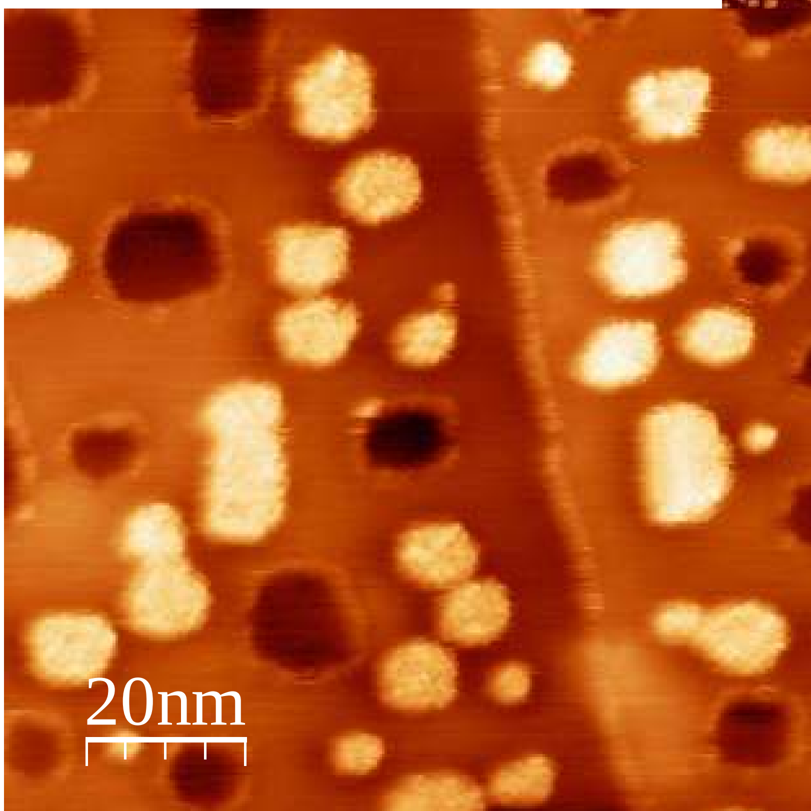
Single Crystal KBr

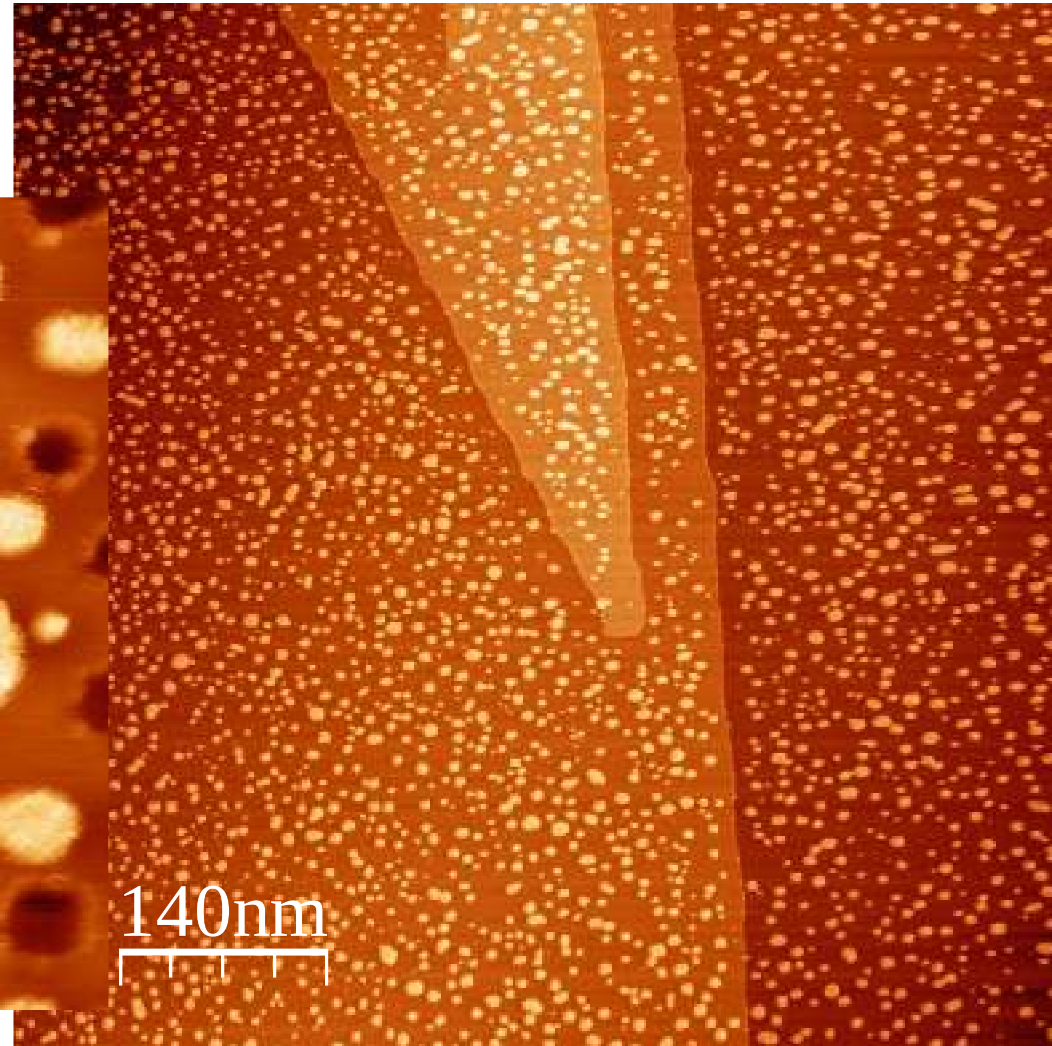
Substrate patterning by electron irradiation



Truxenes on patterned surface

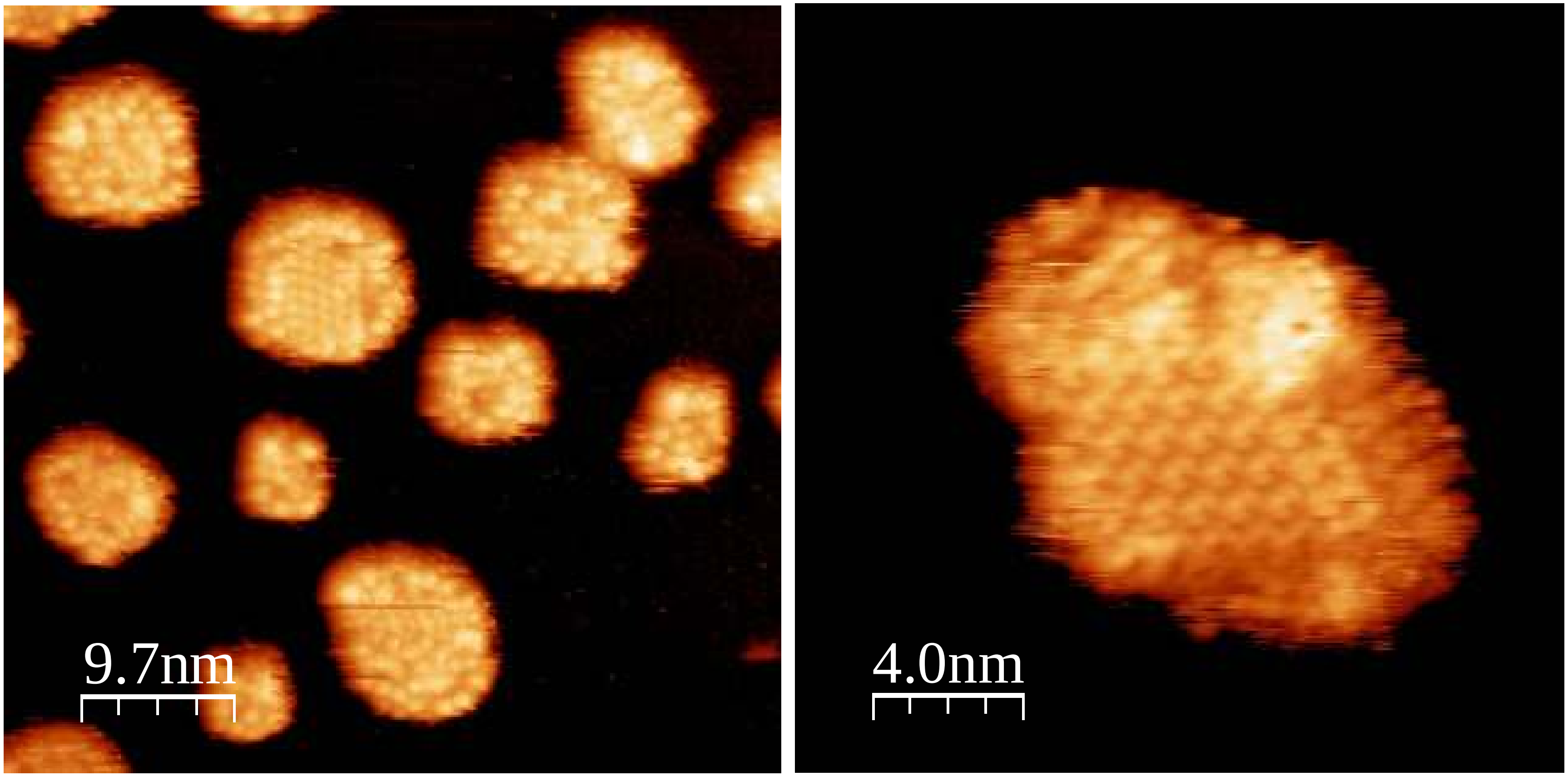
Filled and unfilled pits





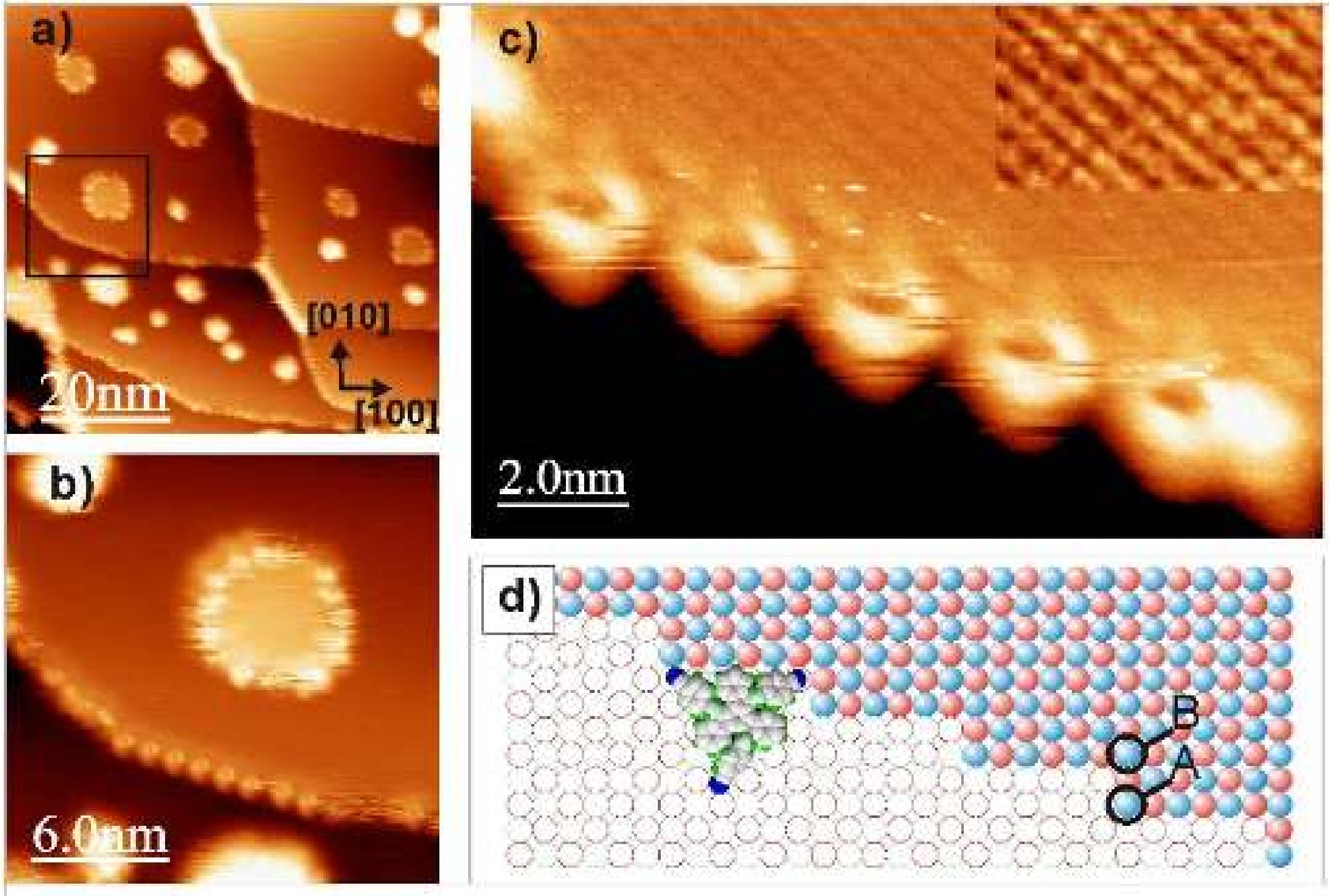
Truxenes on patterned surface

Organization within the pits



Imaging a Single Molecule

Measurements at RT

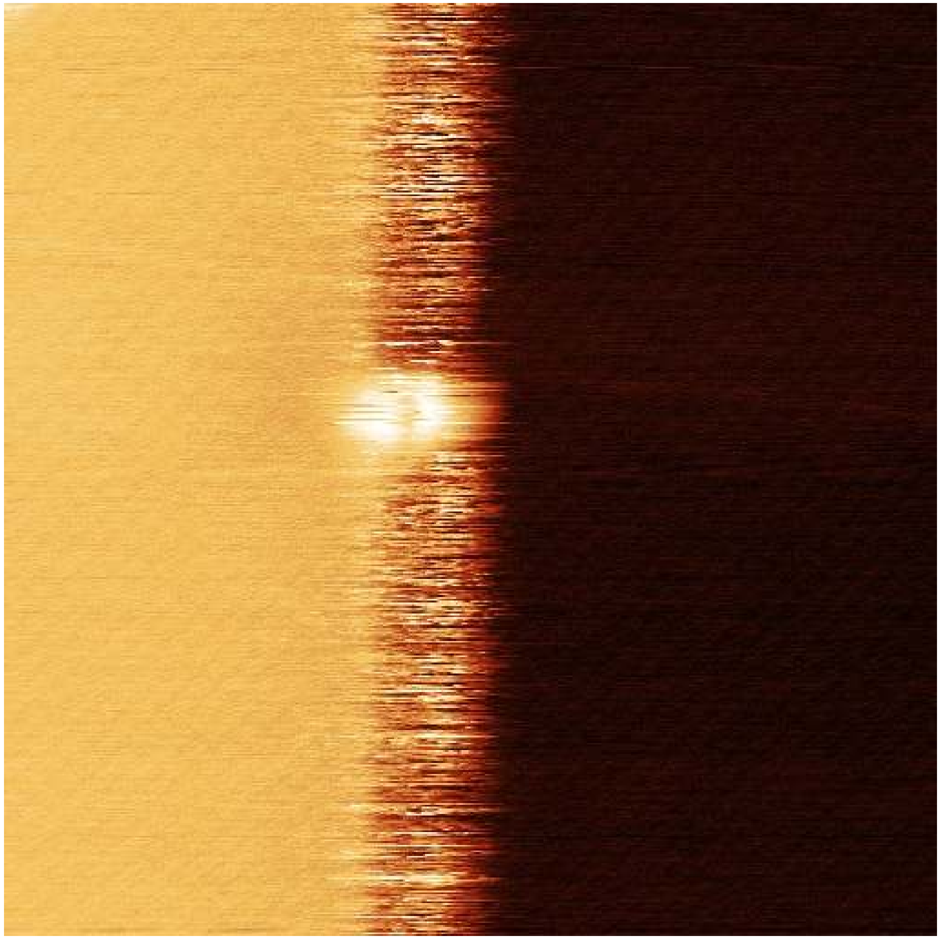


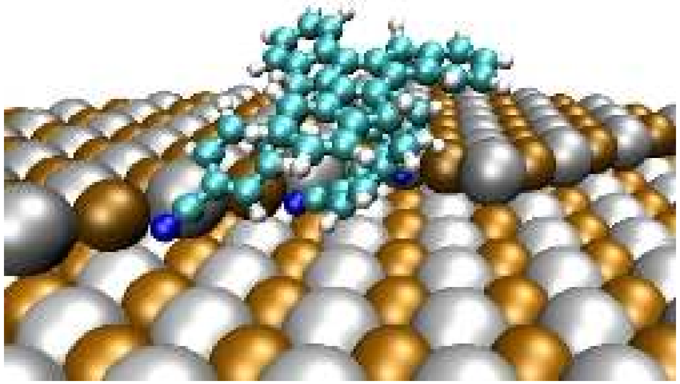
- Re-arrangement of the substrate, edges are running in the [-3 1 0] direction
- no chemical interaction with the surface
- adsorbed on K or Br terminated double atomic kink

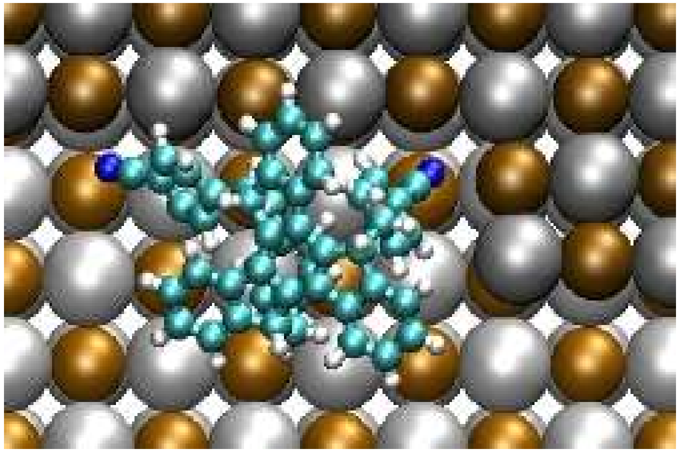
Imaging a Single Molecule on KBr

Measurements at RT and Quantum Chemical Calculations

Collaboration with A. Echavarren, Tarragona, Spain
and A. Shluger, UCL, London, UK



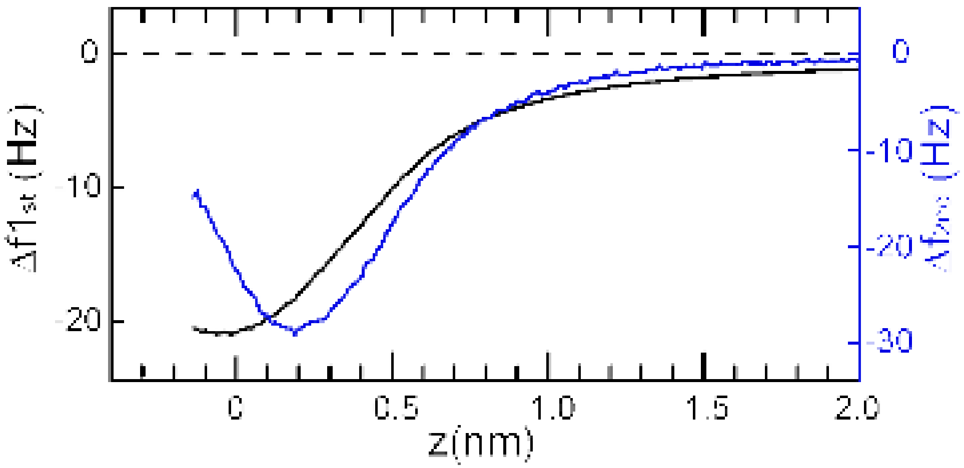


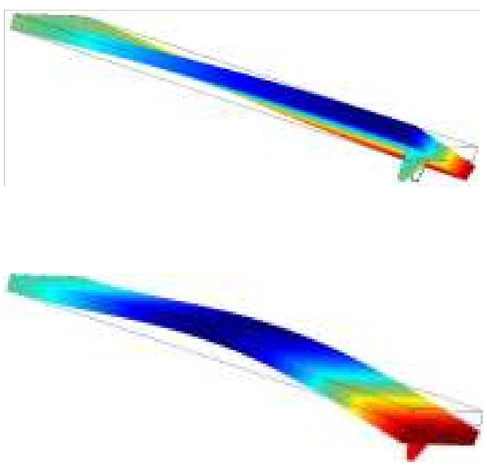


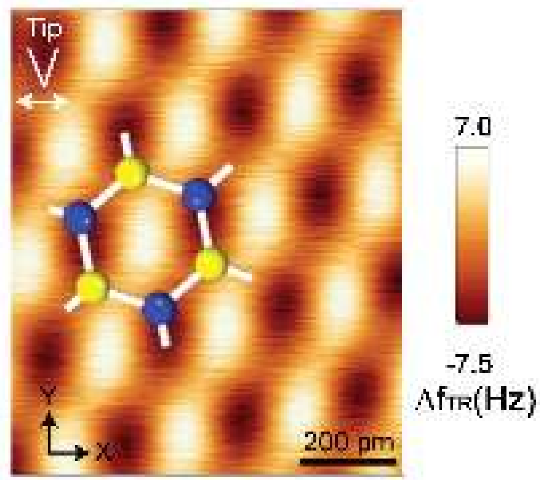
B. Such, Th. Glatzel et al. ACS Nano, 4, 3429-3439, (2010).

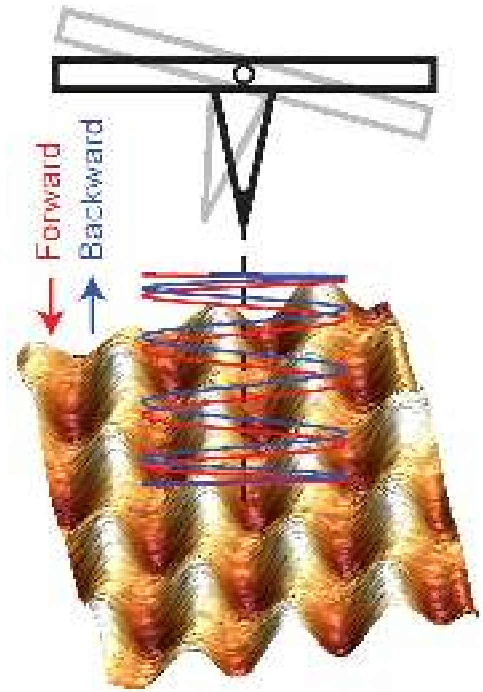
Bimodal Dynamic Force Microscopy

increased sensitivity and stability







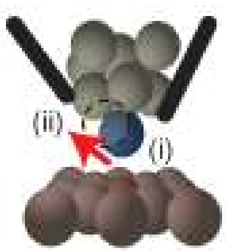


S. Kawai & Th. Glatzel et al.,

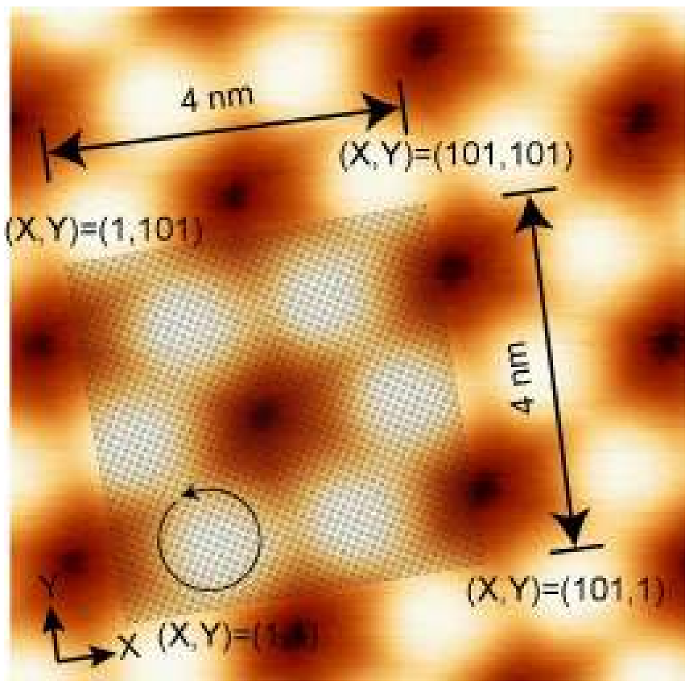
PRB 81, 085420, (2010),
PRB 80, 085422, (2009),
PRL 103, 220801, (2009).

3D Force Fields

atomic and molecular scale



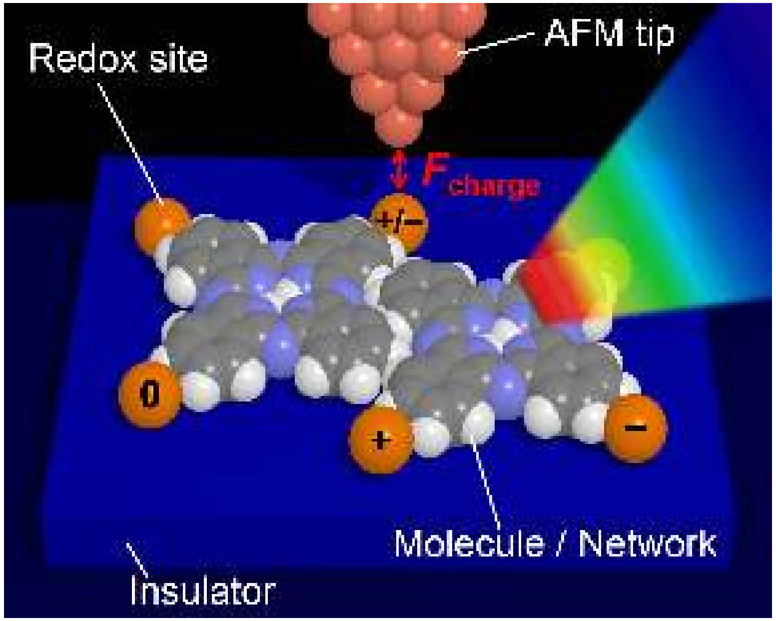
Collaboration with SPECS-Nanonis, Berlin, Germany

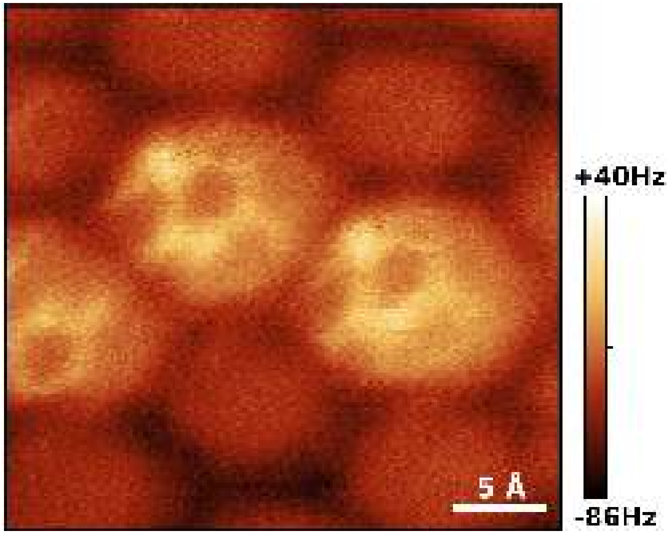


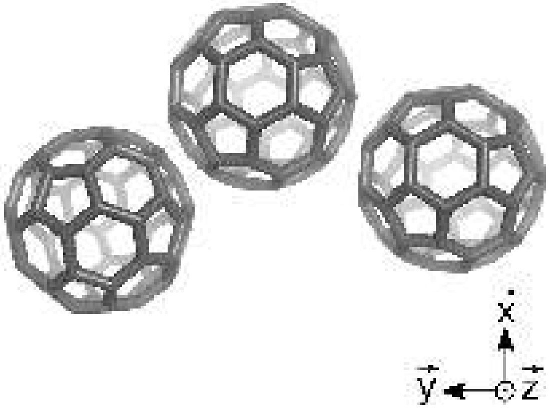
$A_{TR} = 50\,\text{pm}$

Motivation

Molecular Electronics



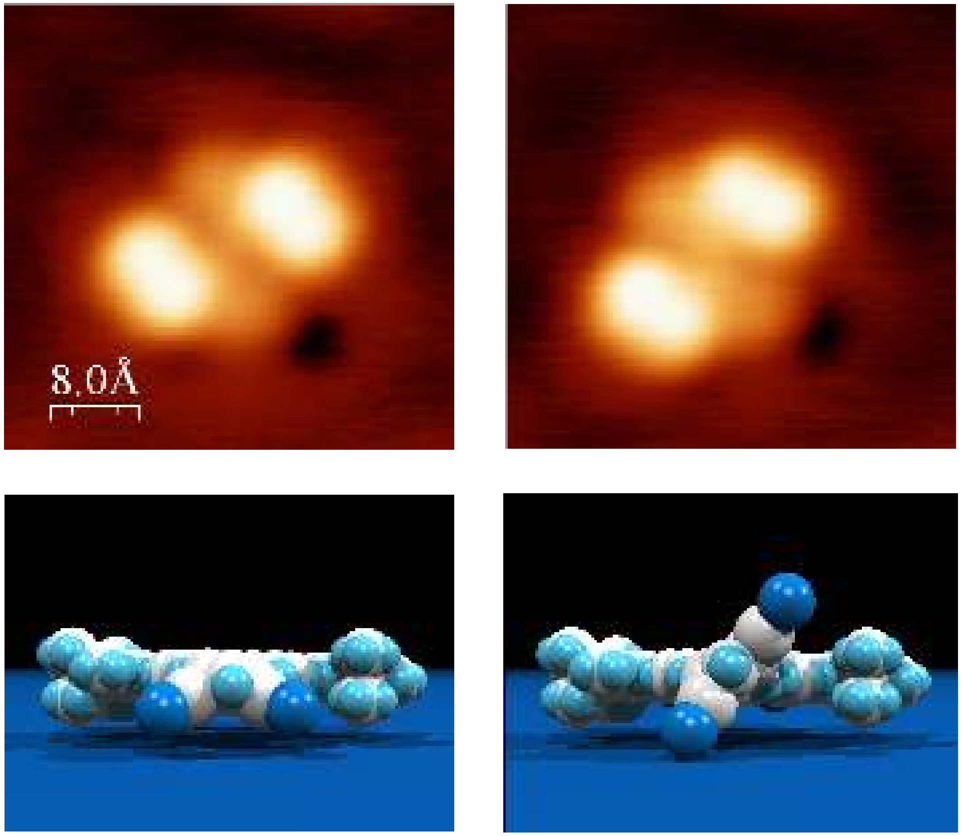




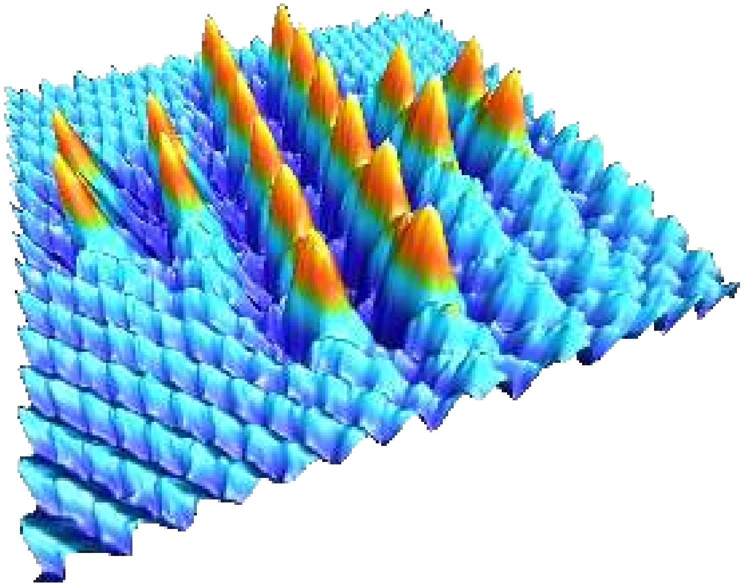
- 2D and 3D spectroscopy
- Combination of optical excitation and high resolution
- Transfer to solar cell devices?

Meyer & Glatzel, Science, 2009, 324, pp1397

Molecular Manipulation
at room temperature and 5K



Porphyrin on Cu(111) at 5K



Br adsorbates on KBr at room temperature manipulated by nc-AFM