Ústav fyzikální chemie J. Heyrovského, ČAV,
Praha 8, Dolejškova 3

Scanning Probe Microscopy I
Basic Techniques

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Odd. elektrochemických materiálů

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Microscopic methods/resolutions

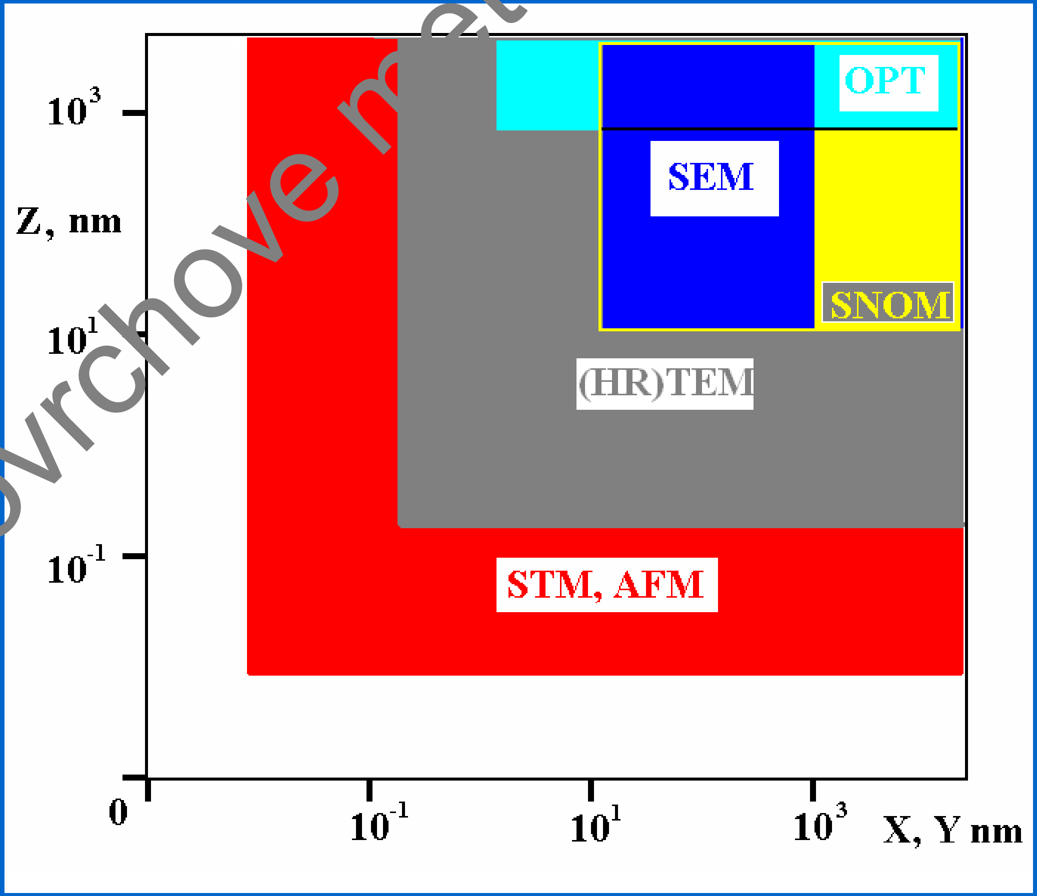
OPT: Optical Microscopy

SNOM: **S**canning **N**ear Field **O**ptical **M**icroscopy

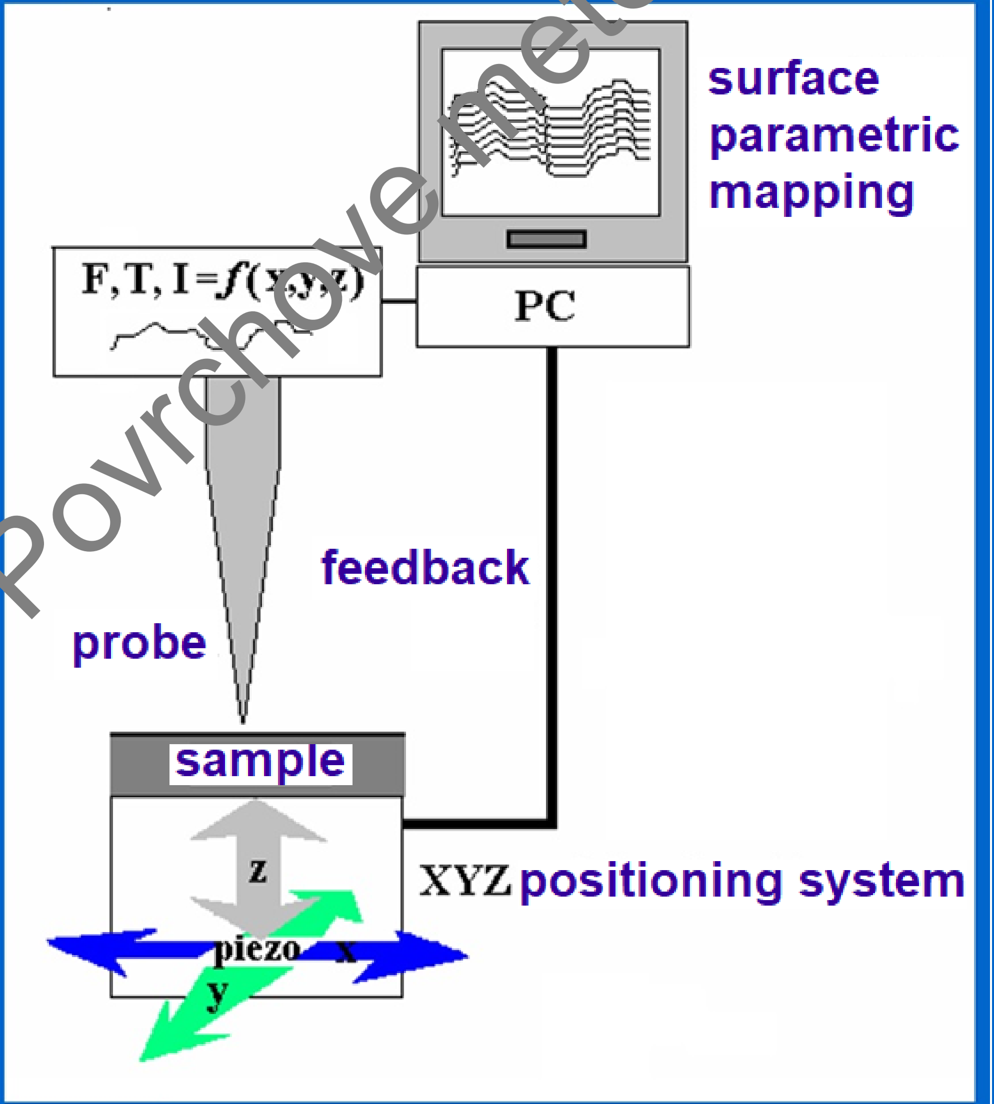
SEM: **S**canning **E**lectron **M**icroscopy

HRTEM: **H**igh **R**esolution **T**ransmission **E**lectron **M**icroscopy

STM, AFM:
Scanning **T**unneling **M**icroscopy,
Atomic **F**orce **M**icroscopy



Scanning Probe Microscopy



SPMs by information carriers

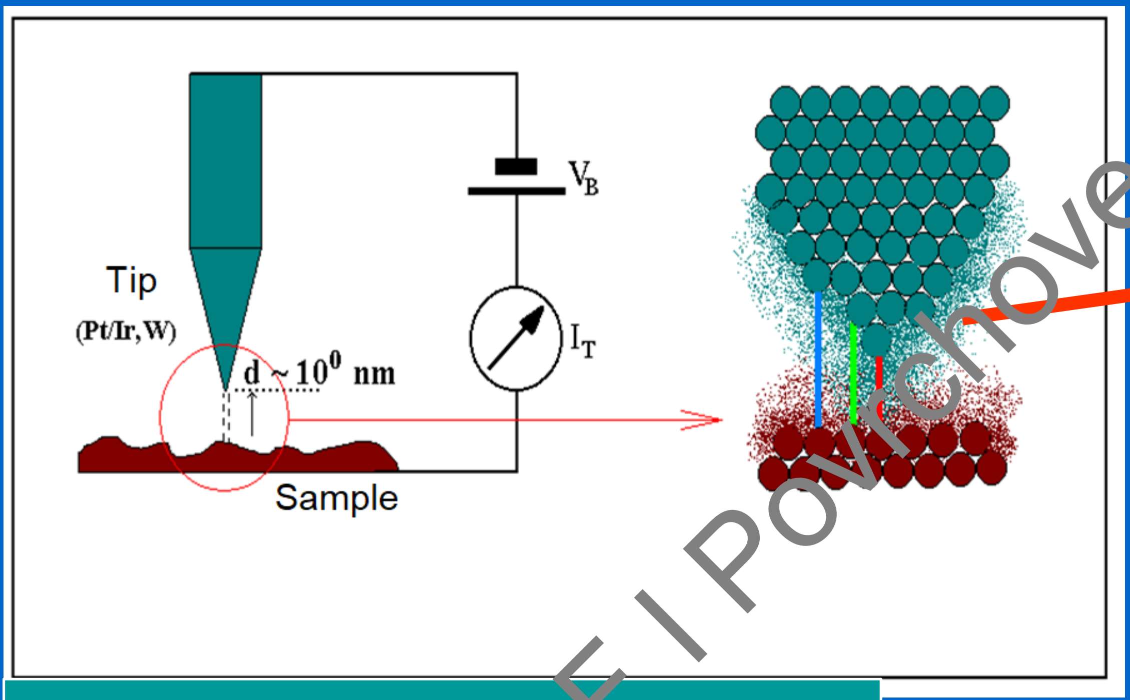
Electron - tunneling microscopy **STM/ECSTM,**
conductive AFM **CAFM (PFTUNA)**
Ion - electrochemical microscopy **EC STM/AFM**
Force interactions - atomic force microscopy **AFM/ECAFM**

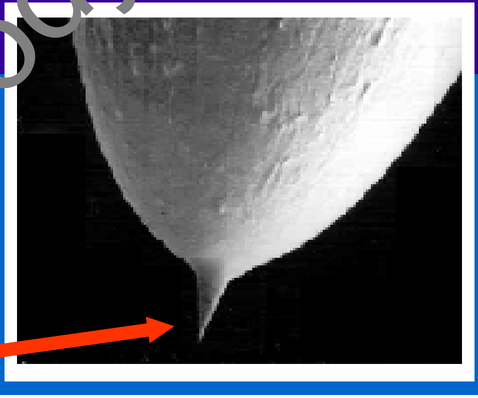
Electromagnetic (UV/Vis/IR light) - optical methods:
- **IR -** Thermal microscopy **ThM**
- **UV/Vis/IR – near-field** optical microscopy/spectr. **SNOM**
- Tip-Enhanced optical microscopy/spectr. **TERS/TEFS**

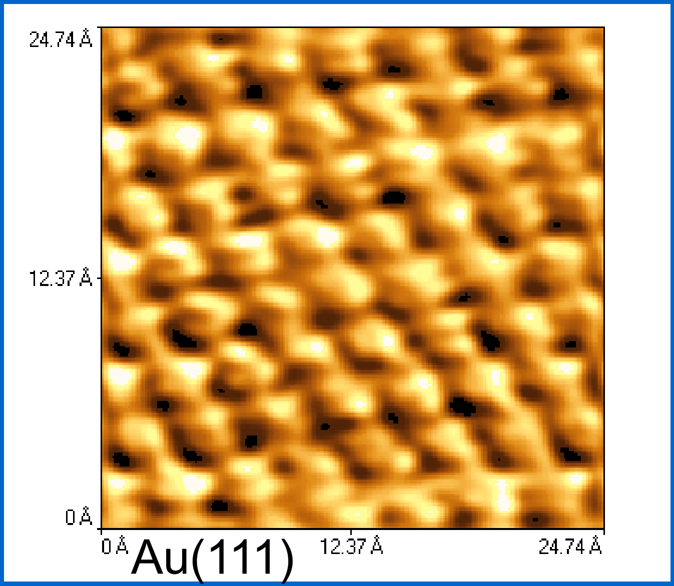
Electromag./electrostatic. field
- Kelvin probe microscopy **KPFM**/Surface Potential Microscopy

Tunneling Microscopy

Binning, Rohrer, IBM, 1981, Nobel Prize 1986







Approximation of tunneling current

$$I_T \sim V_B f_{mTS}(V_B) \exp[-2z\sqrt{(2m\Phi_{ST}/\hbar^2)}]$$

$\hbar = h/2\pi, f_{mTS}(V_B)$... reduced Planck.const.

$I_T(V_B)$ given by e-structure tip x sample,

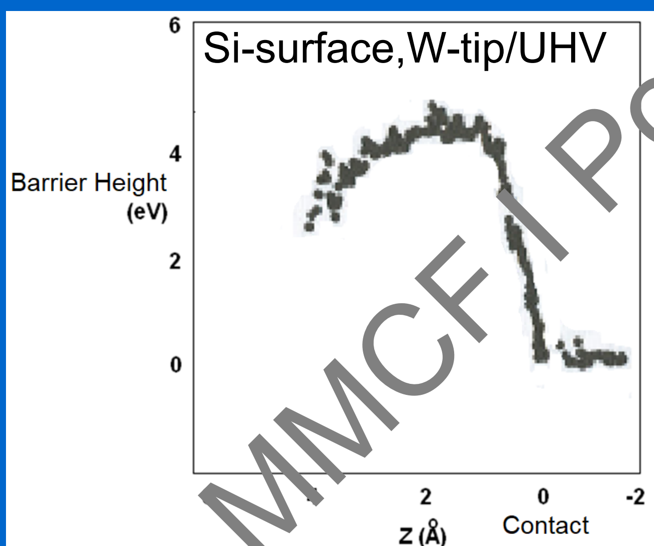
z...distance tip-sample (~ 10^{-1} nm), V_B up to ±1-2 V, I_T ~nA - pA

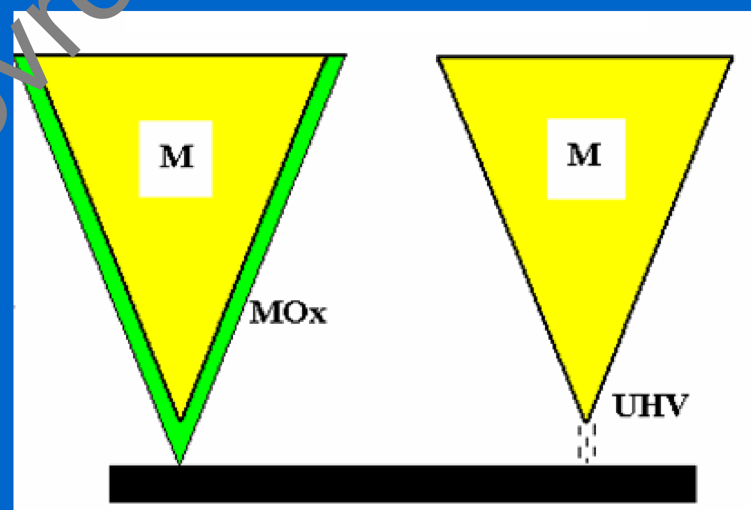
Tunneling barrier (distance) spectroscopy

Low bias V_B = const. : $(dI_T/dZ)/I_T \sim (2\sqrt{2m_e})/\hbar \sqrt{(\Phi_S + \Phi_T)}$

Φ_{Sample} , Φ_{Tip} local work function, I_T tunneling current,
Z tip-sample distance, m_e e-mass

Realization:
modulated axial distance (Z-axis) VVVVV, recording dI_T/dZ => $\Phi_{S,T}$
Considering Φ_{Tip} ≈ const. => lateral variation of barrier height ~ local Φ_S





D.A. Bonnel: Scanning Tunneling Microscopy and Spectroscopy
VCH 1993

Tunneling voltage spectroscopy

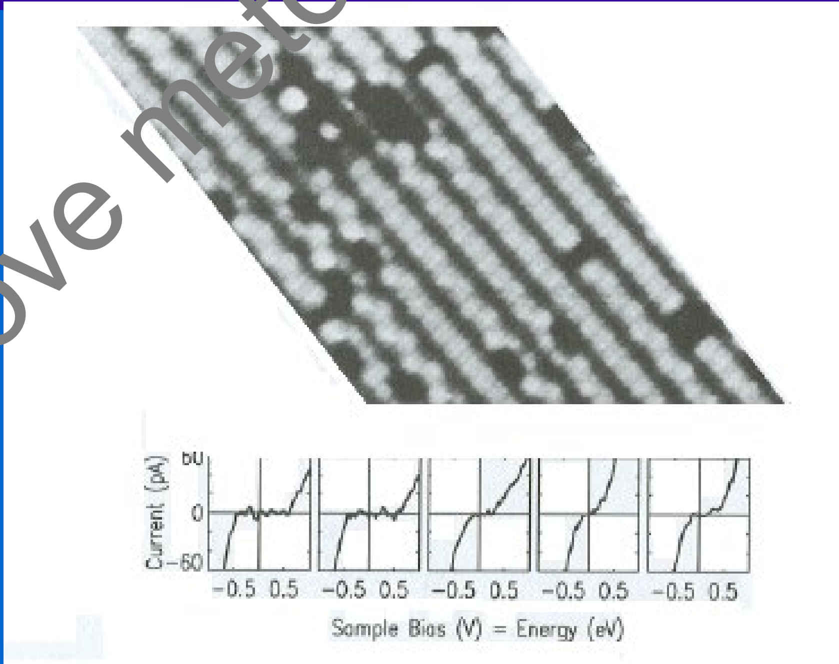
V_B < work function tip-sample (~10 mV)

dI_T/dV_B ≈ local surface density of states real or derived from internal band arrangement

Modulation VVVVV V_B, recording I_T-V_B curves

Output: d(log I_T)/d(logV_B) vs V_B

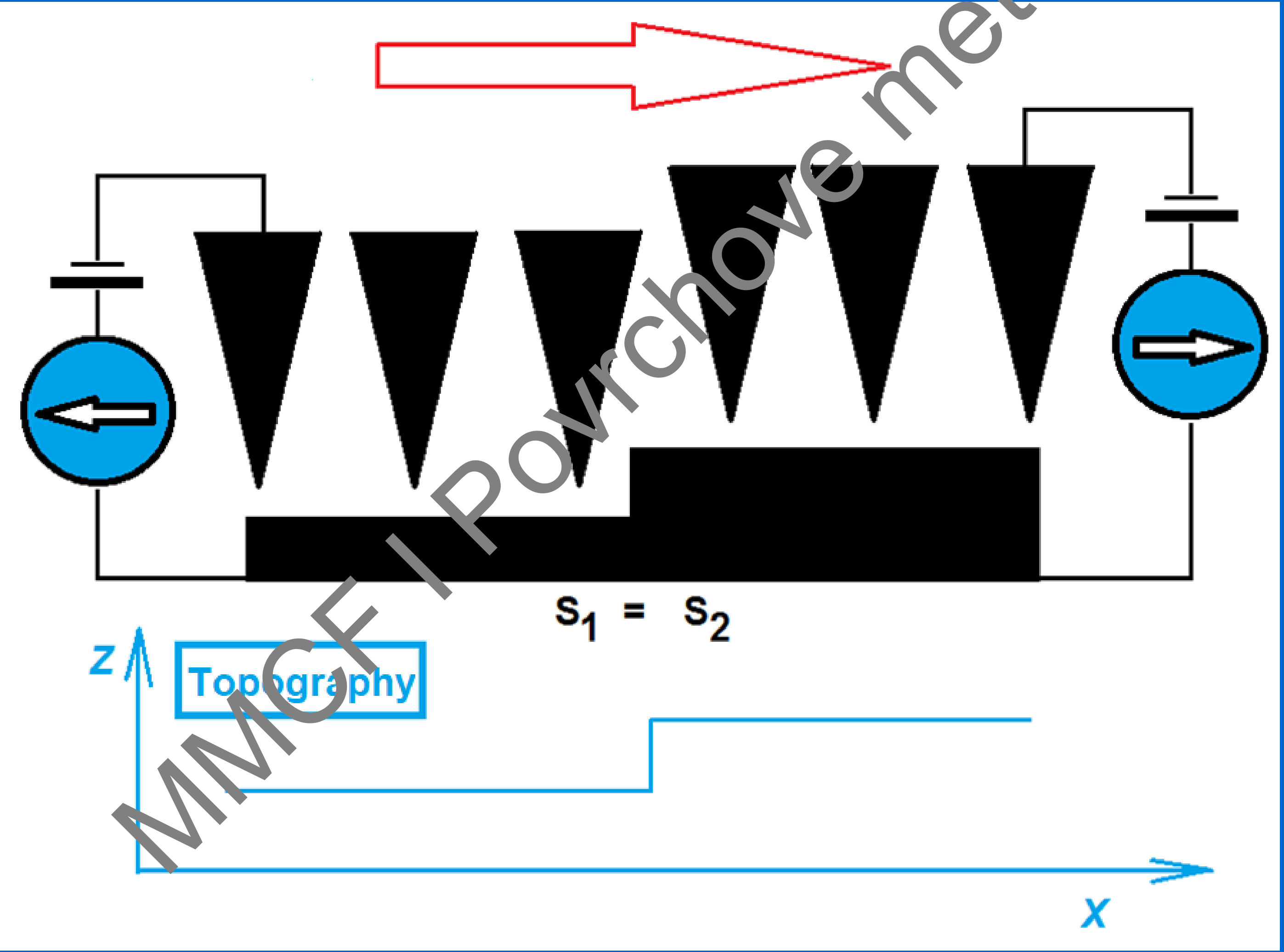
Yields: map of surface states (in UHV) shows filling of states, ad-atoms free (*dangling*) bonds...



I_T-V_B plots at single cryst. Si (UHV): STM Tip passing over defect
[*B. Persson, A. Baratoff, Phys.Rev.Lett. 59, 339*]

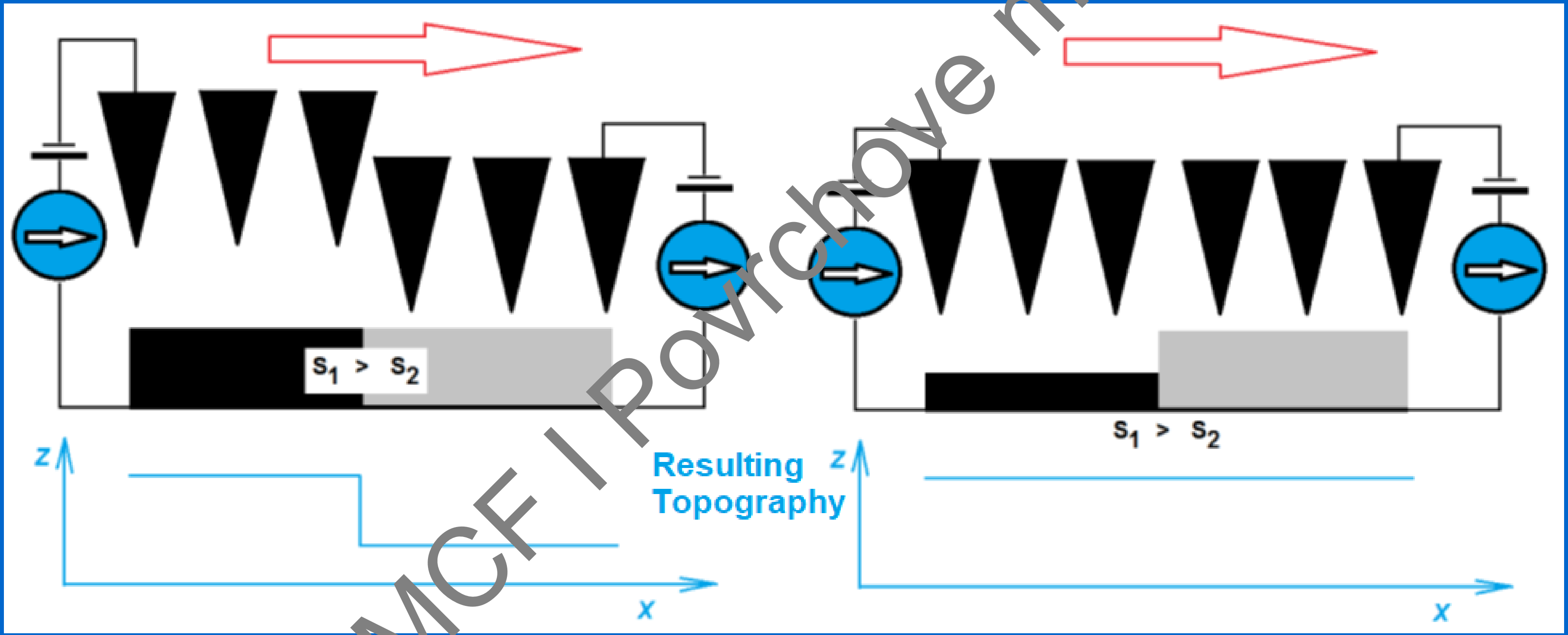
Frank, L. - Král, J., Ed., : Metody analýzy povrchů. Iontové, sondové a speciální metody Academia, Praha 2002

Tunneling microscopy – topography
uniform surface e-density



Tunneling microscopy – topography

nonuniform surface e-density => artefacts

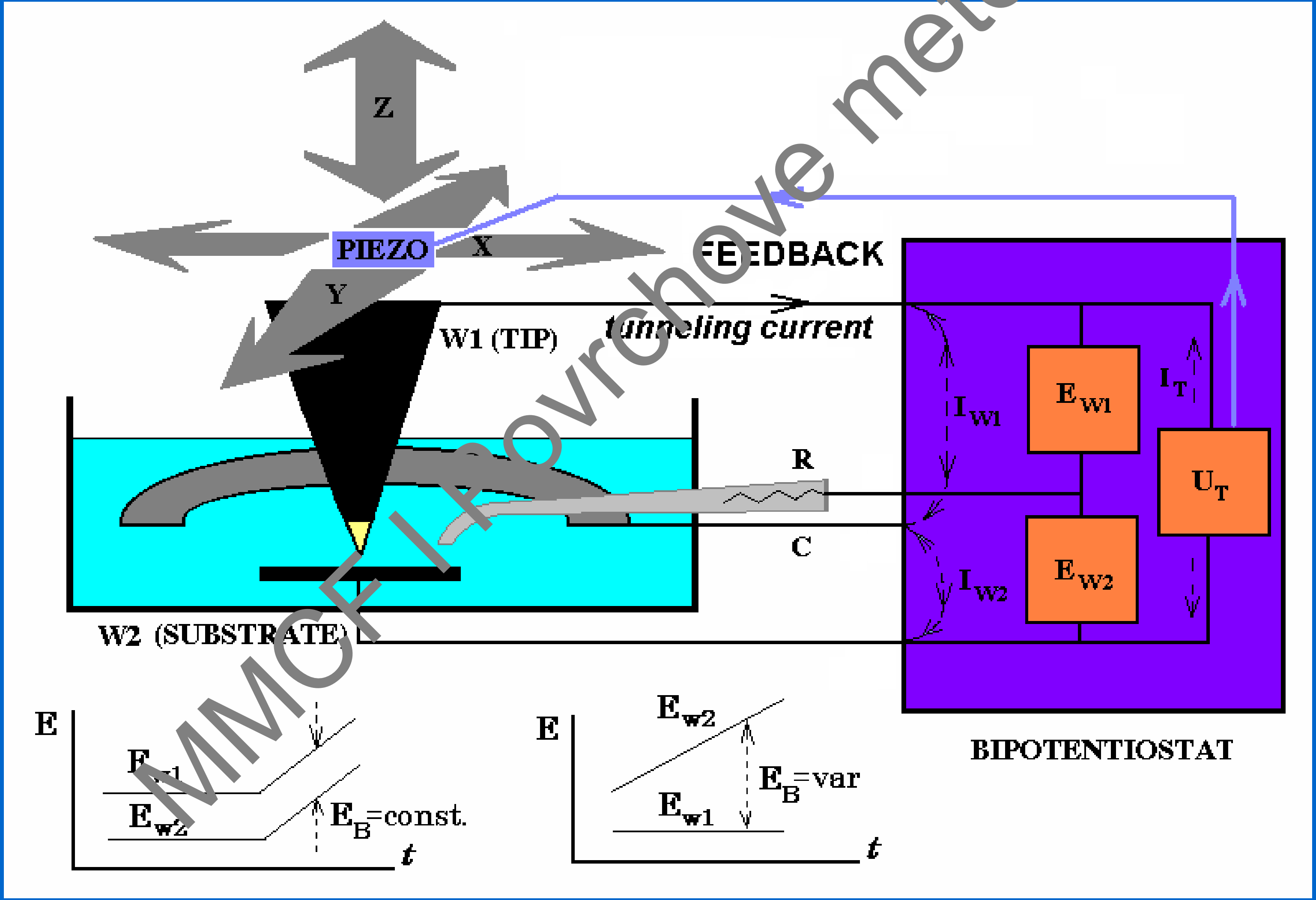


EC STM

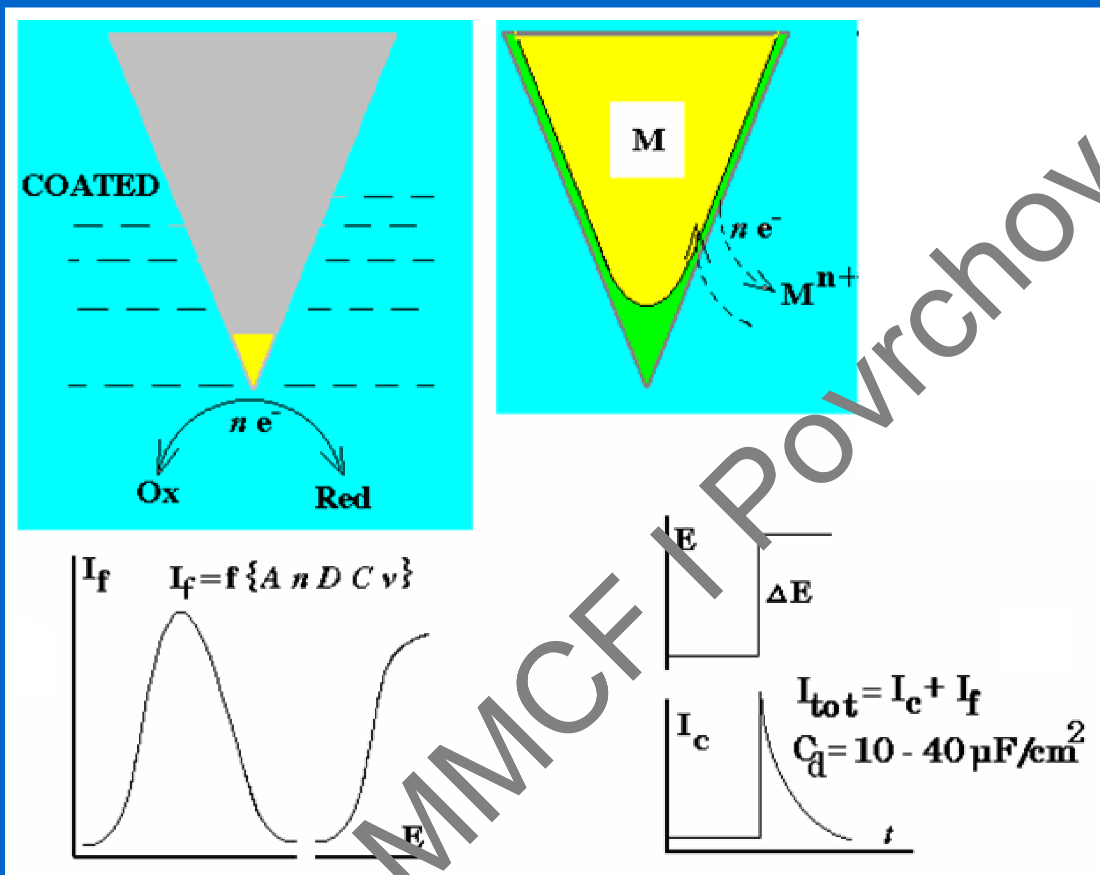
Electrochemical Scanning Tunneling Microscopy

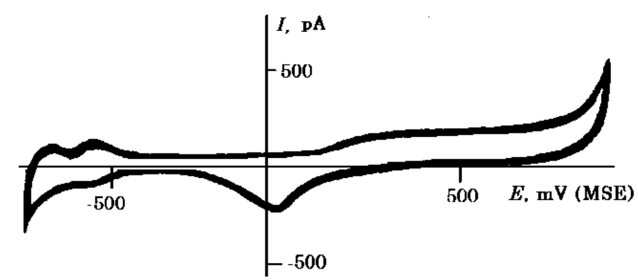
EC STM:

Detection of tunneling currents in EC experimental setting



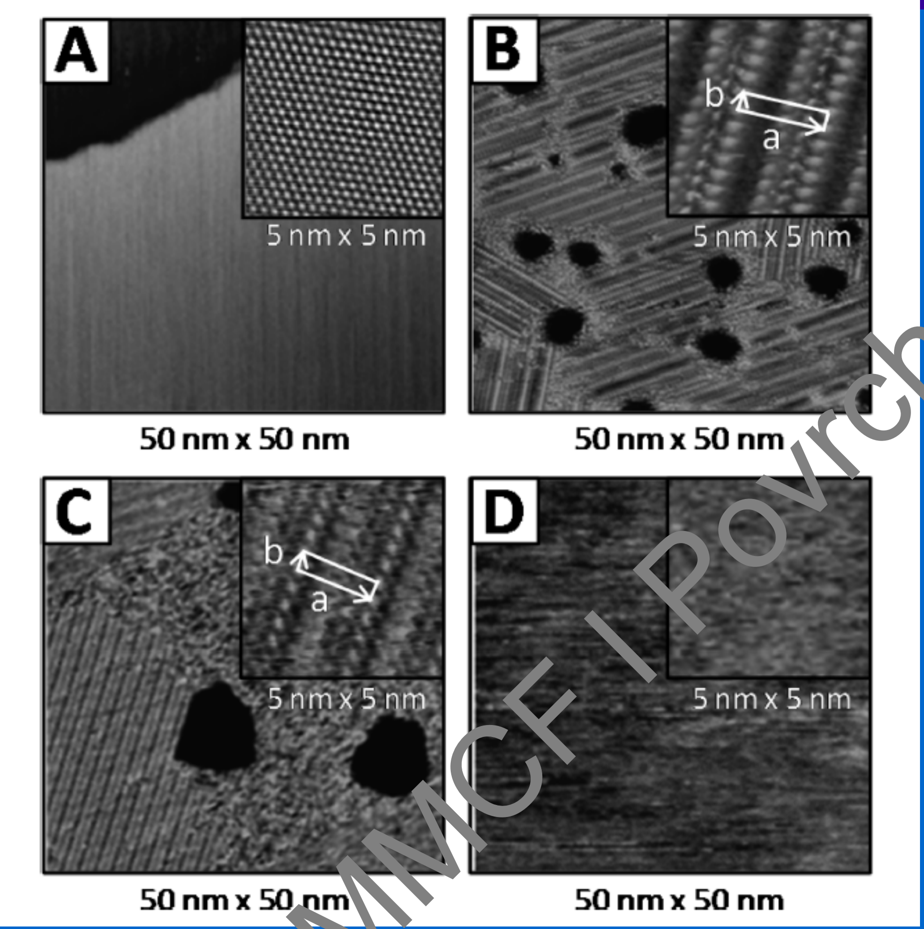
Probe/tip for EC STM





Voltammetry of Pt-Ir STM tip (polymer coated) in 0.1 M H_2SO_4 (deoxygenated) v = 200 mV/sec

EC STM: Imaging Self-Assembled Monolayers on immersed surface



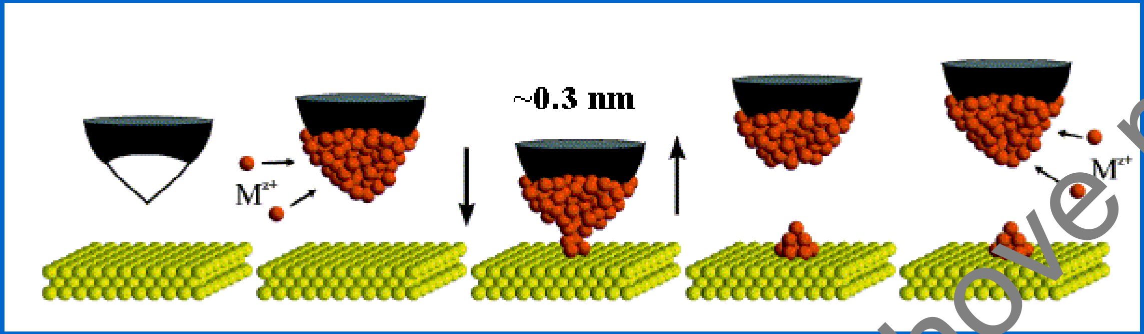
Aq. 0.1M Na_2HPO_4, pH 6

SAM - molecular ad-layer: mercaptopropionic acid (MPA) on Au111,
U_B= 300 mV/I_T = 100 pA

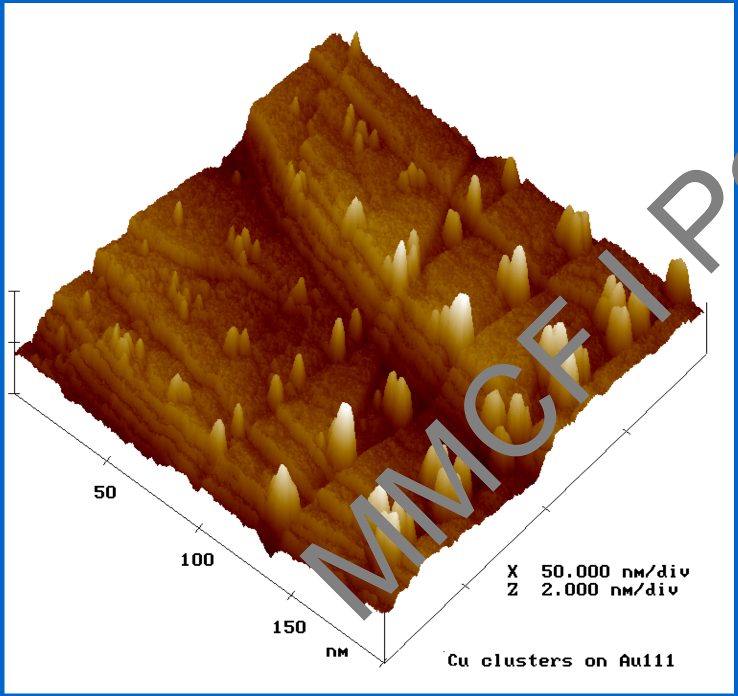
V. Climent et al:
J. Phys. Chem. C 2014, 118, 15754−15765

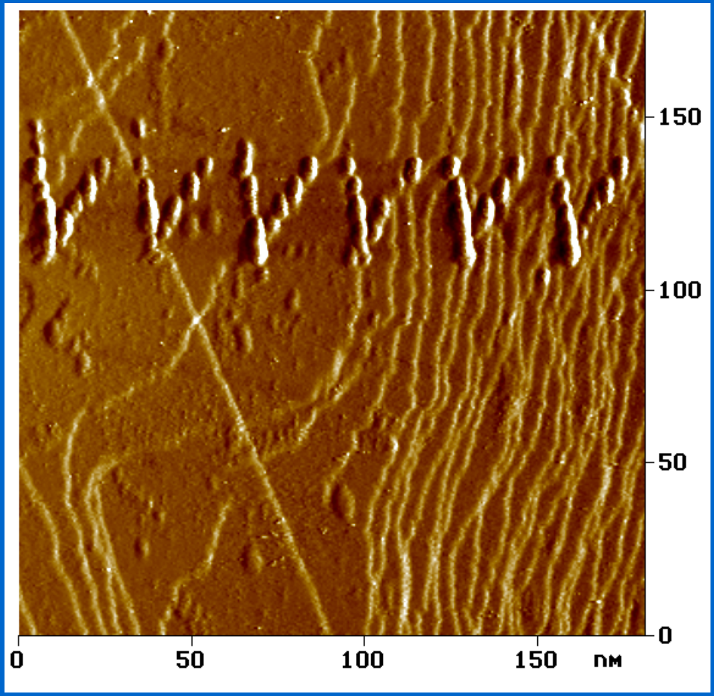
Tip-assisted „nanoprint“

STM tip-deposited nanoparticles Cu $d \geq 8$ nm, $h < 1$ nm



Aqueous 0.1M H_2SO_4 + 10^{-3} $CuSO_4$





Atomic Force Microscopy

and force-based techniques

AFM

Force Interactions
Range/mode

Long - magnetic, coulombic - **noncontact**

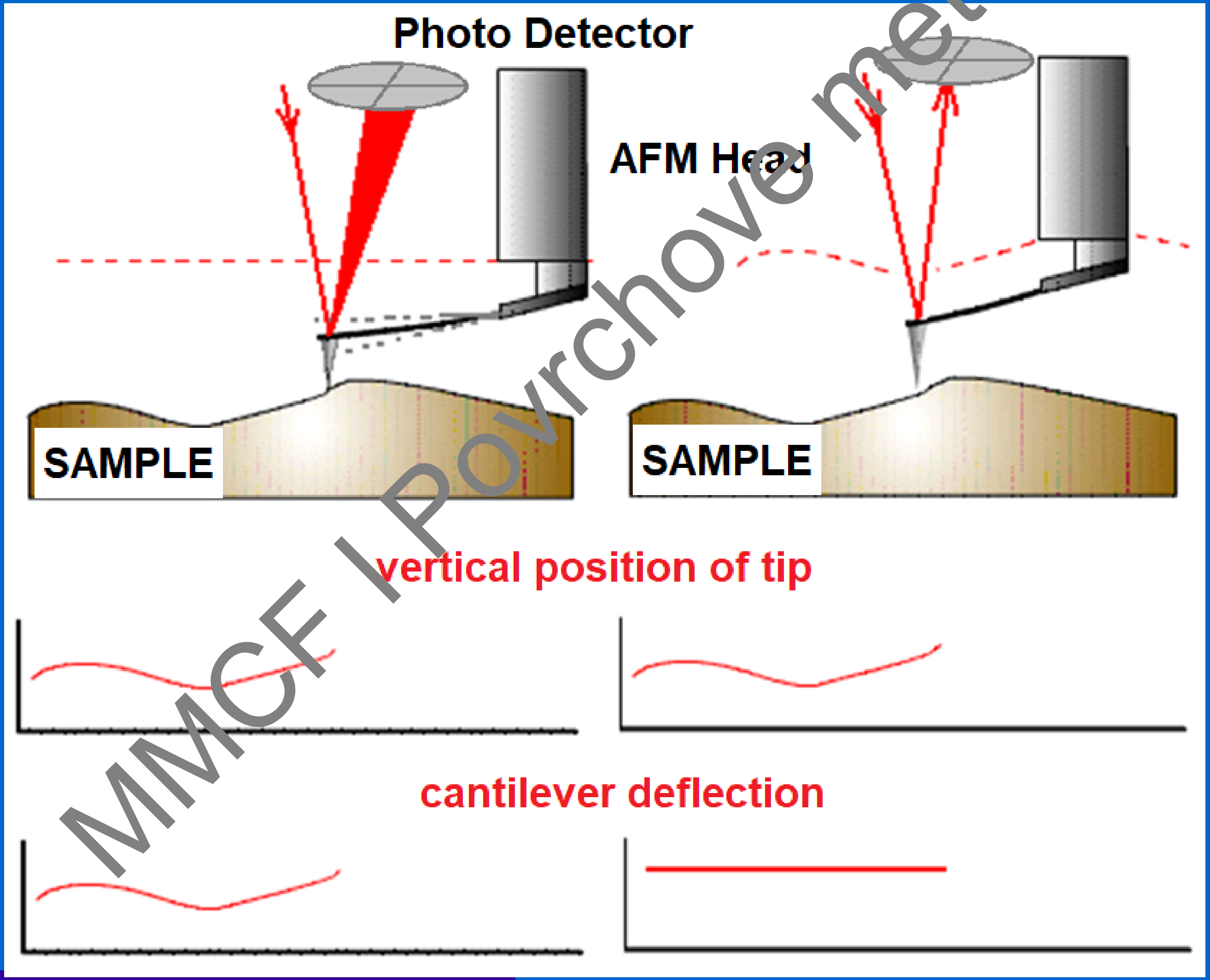
Medium - van der Waals (dipol-dipol, induced - dipol-nonpolar) **semicontact**

Short - binding (attractive) interactions, repulsive (deformation) – **„contact“**

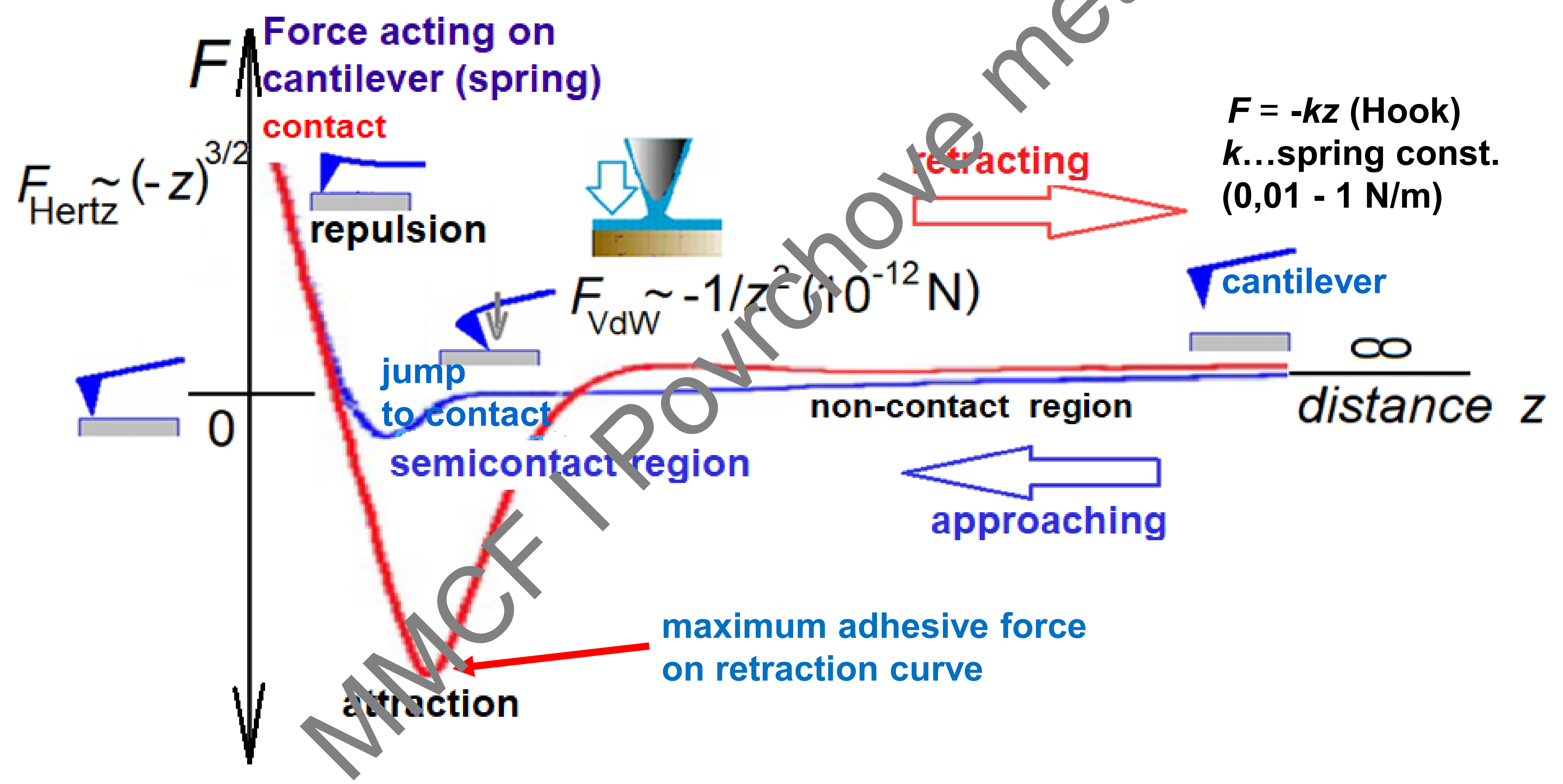
„Derived AFM techniques“ ex-situ / in fluids

Conductive AFM (CAFM) - conductivity meas., Tunneling AFM (TUNA) (!)
Electrochemical AFM (EC AFM) – AFM imaging during EC experiments
+ tip-assisted „electro-lithographic“ techniques
Scanning Electrochemical Microscopy (SECM) – imaging based on
charge transfer reactions/Faraday currents (feedback)

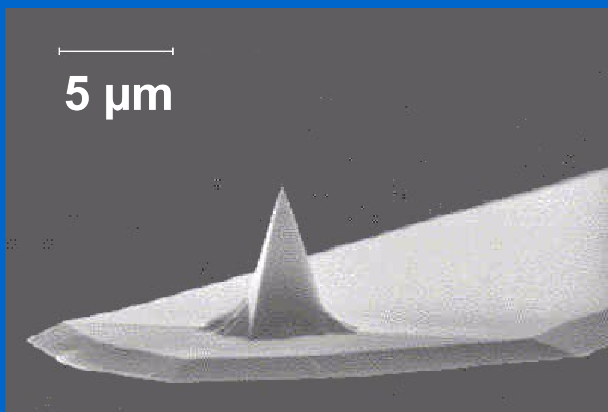
AFM fundamentals

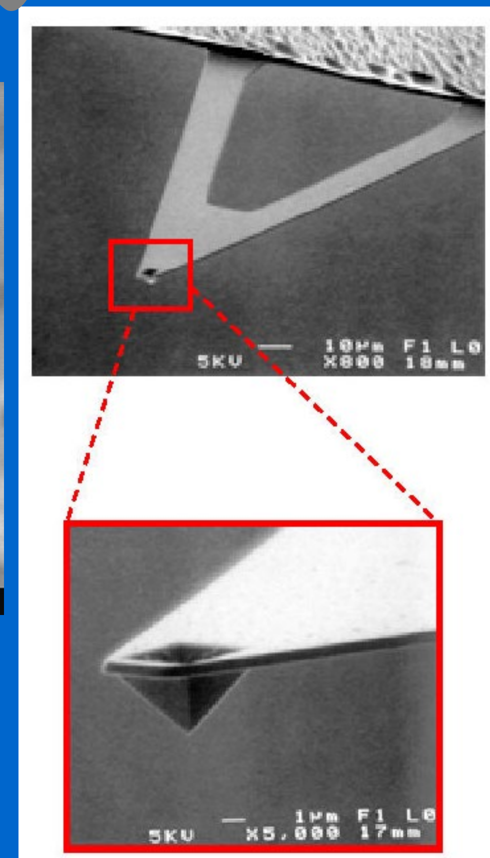


AFM fundamentals – force curve



AFM Probe:
Tip and spring (*cantilever*)

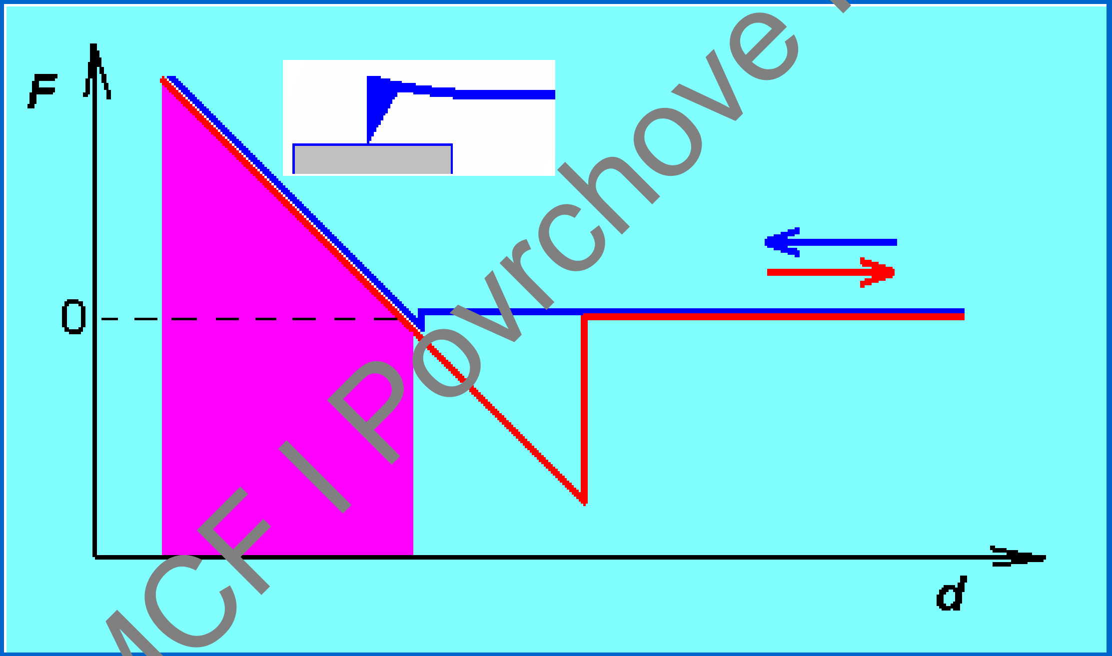




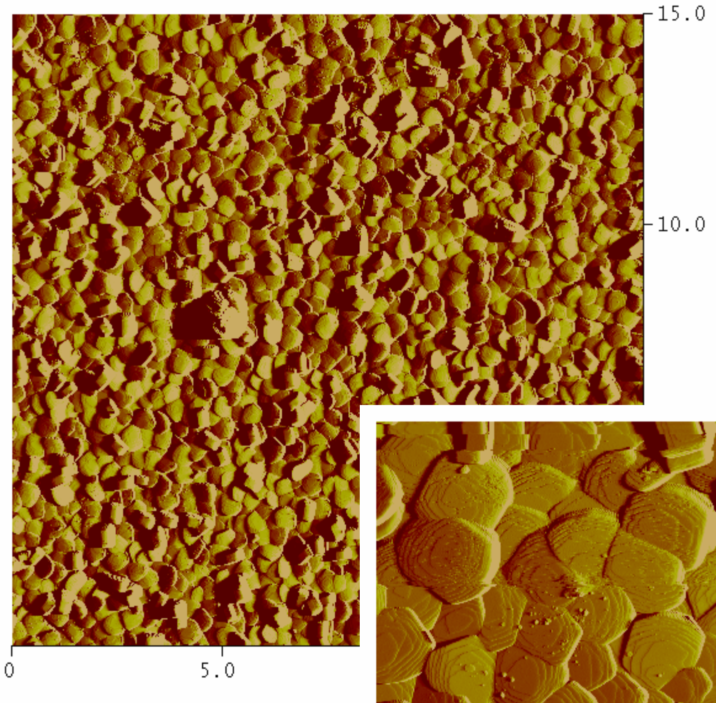
material of tip and cantilever: Si, Si_3N_4

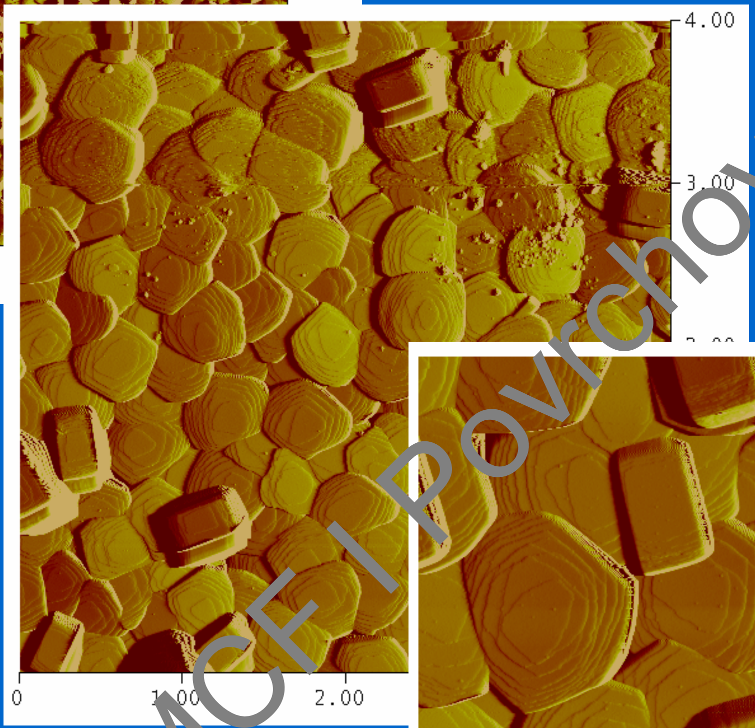
Scanning in selected regions of force curve

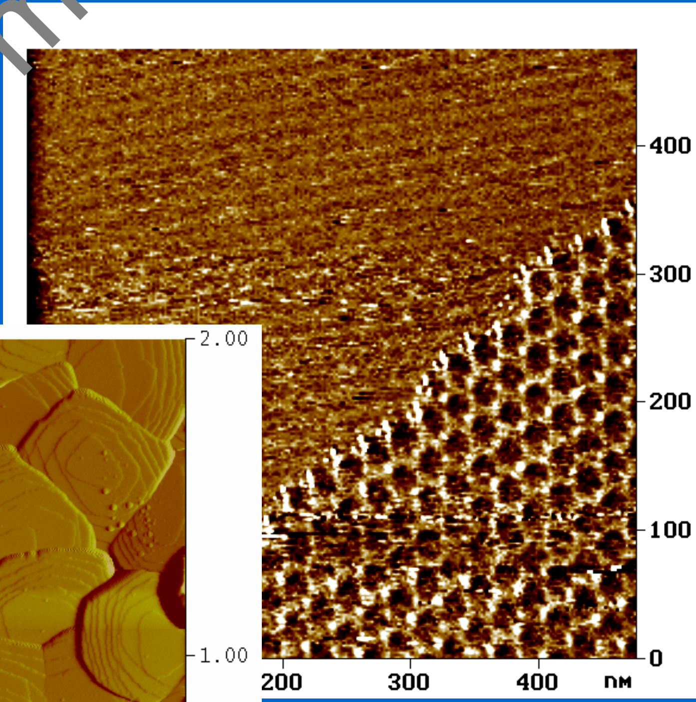
AFM in repulsive forces: Contact Mode

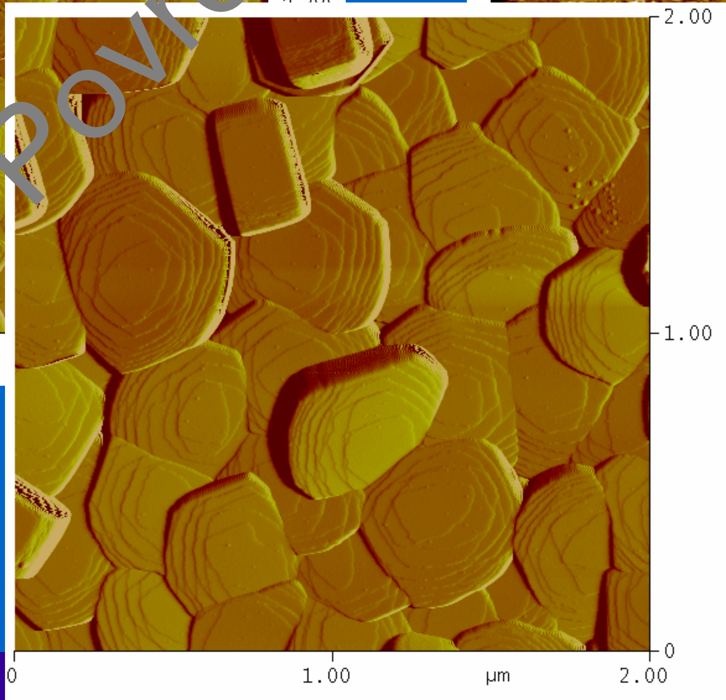


AFM imaging in contact mode



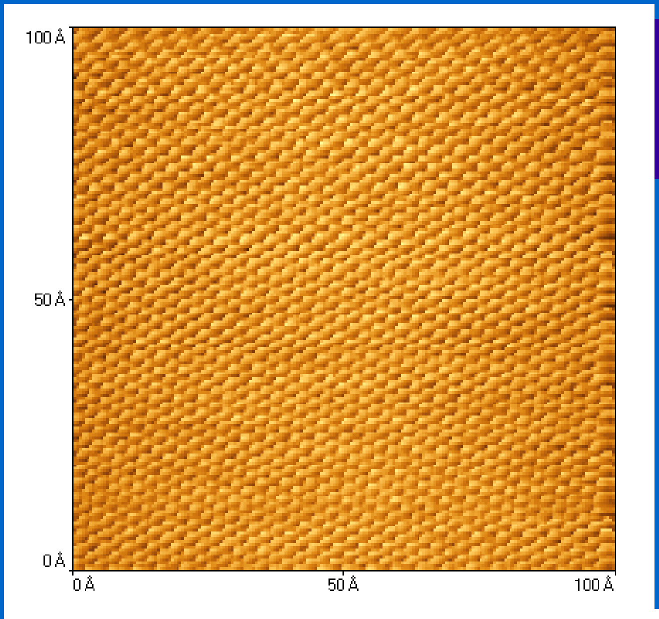




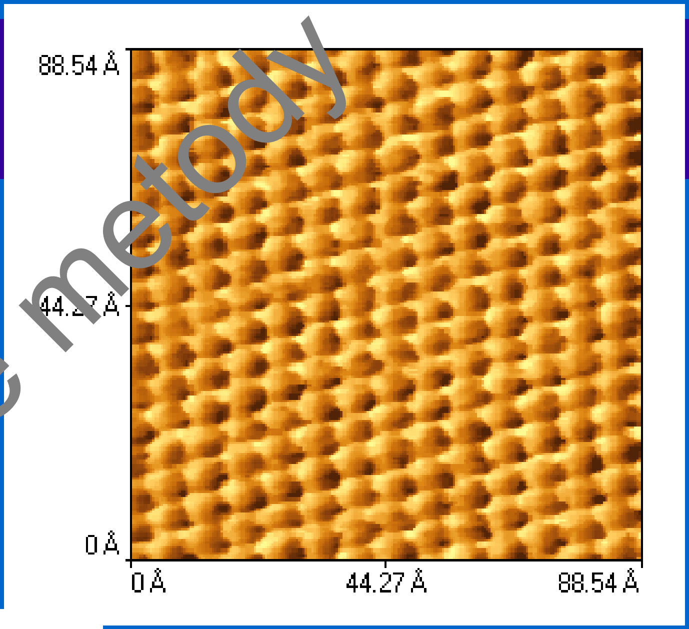


Zeolite crystals

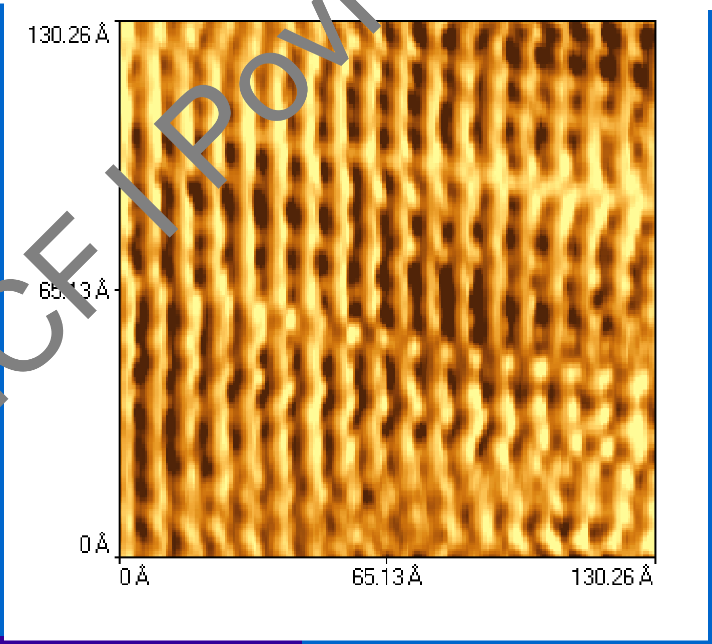
AFM imaging in contact mode



Graphite - HOPG

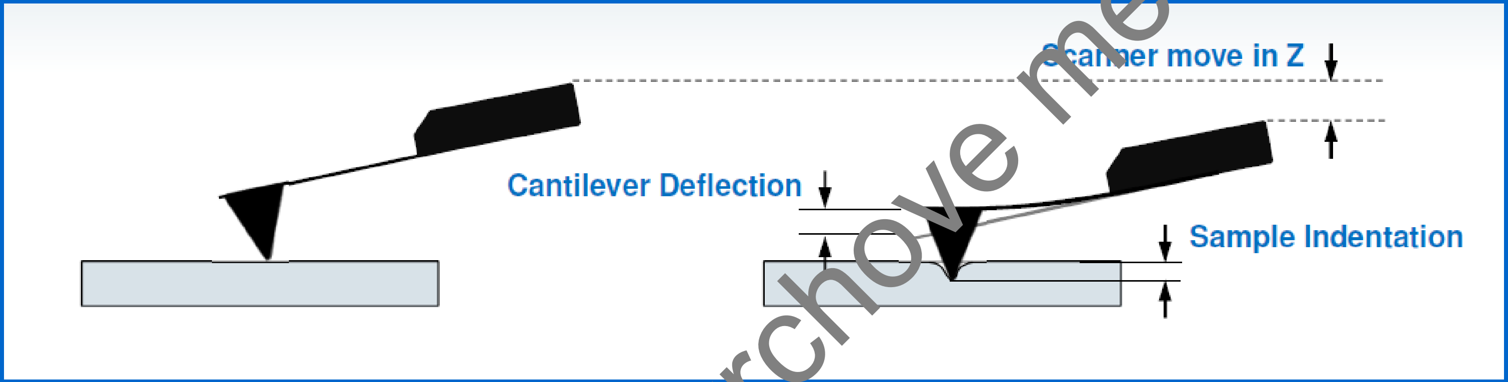


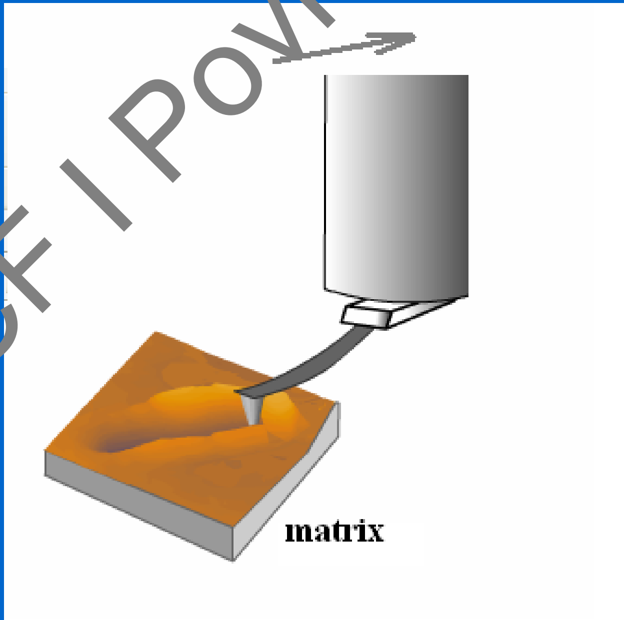
Mica - muscovite



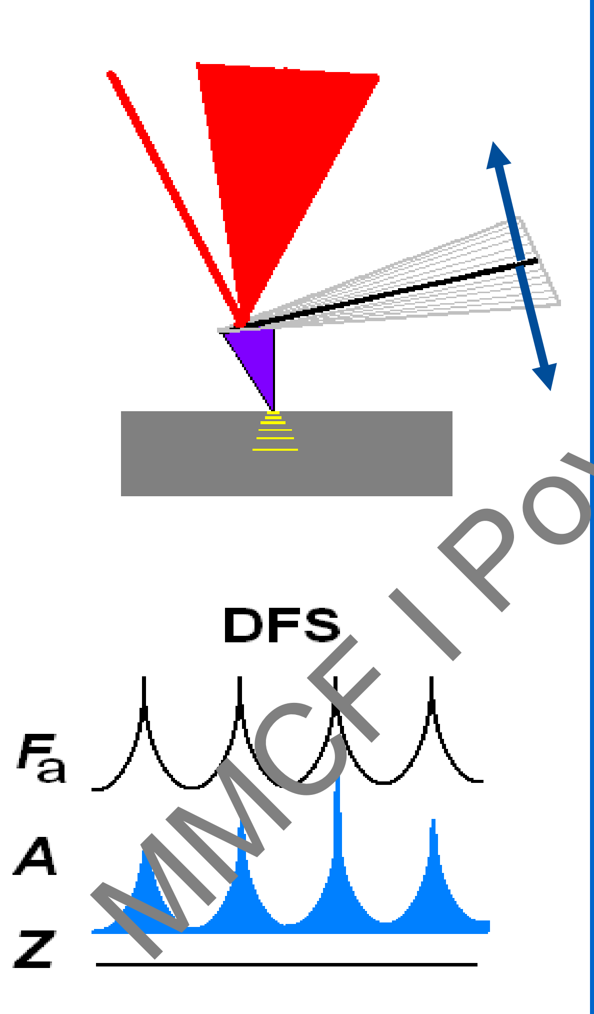
Oriented PTFE molecules on Si wafer

Contact mode AFM - repulsive forces – indentation, nano-lithography





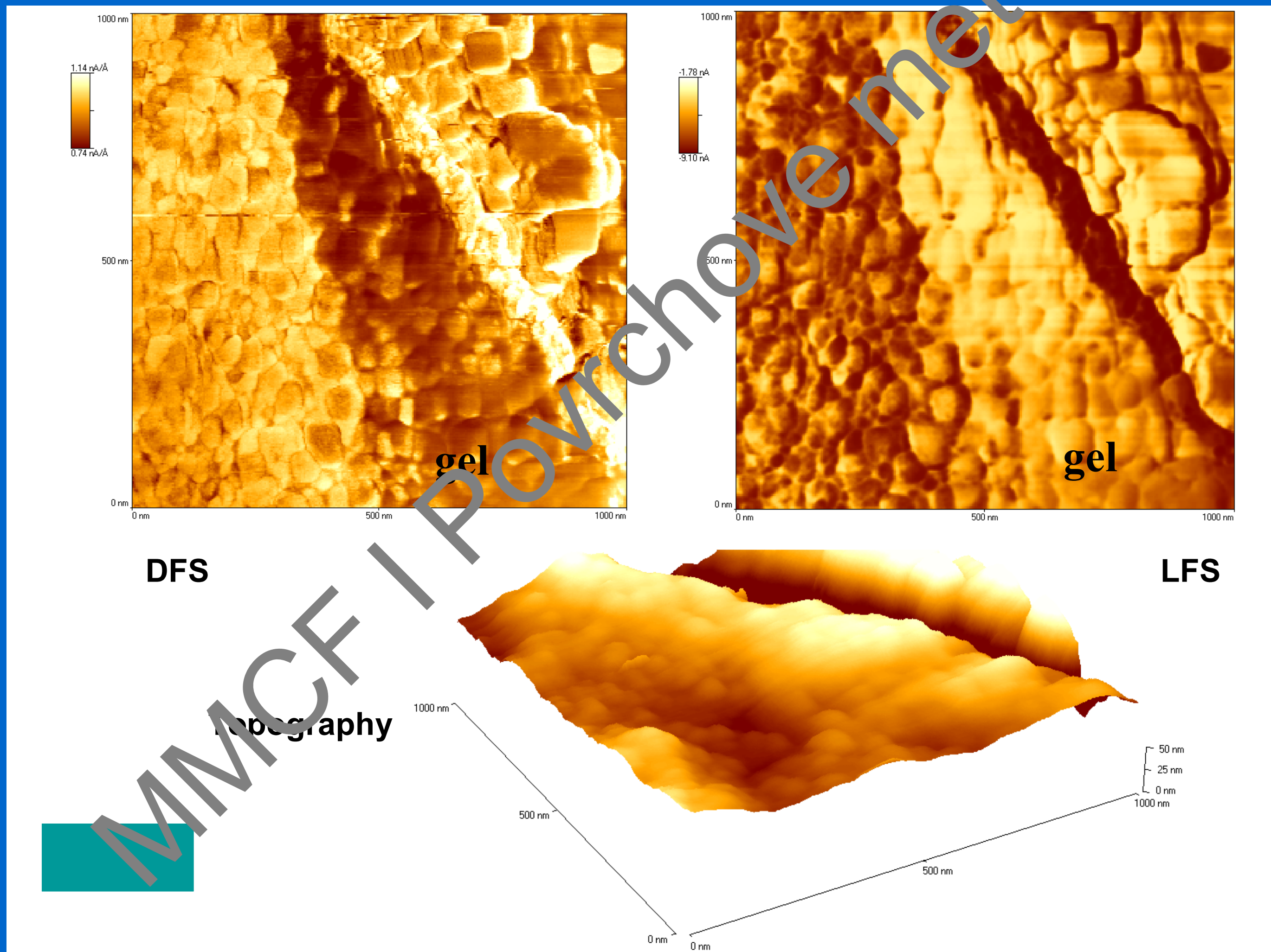
Contact mode AFM – Dynamic Force Microscopy/Spectroscopy (DFM/S)



Energy dissipation - "probe defectoscopy": elasticity (Y_M), plasticity

Tip in contact, oscillating cantilever
f_{drive} => $A_{drive}/A_{response}$

AFM DFS material analysis - Zr/Nb/ZrO_2

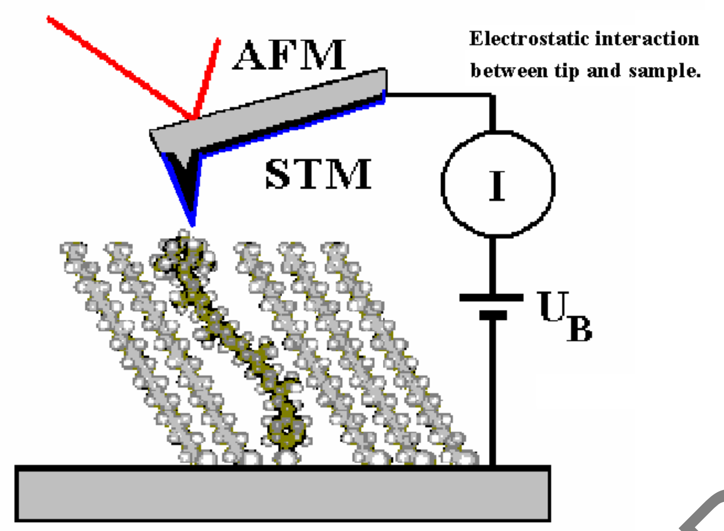


Techniques combining AFM and e-conductivity

Contact mode:
Conductive Force Microscopy (CFM)

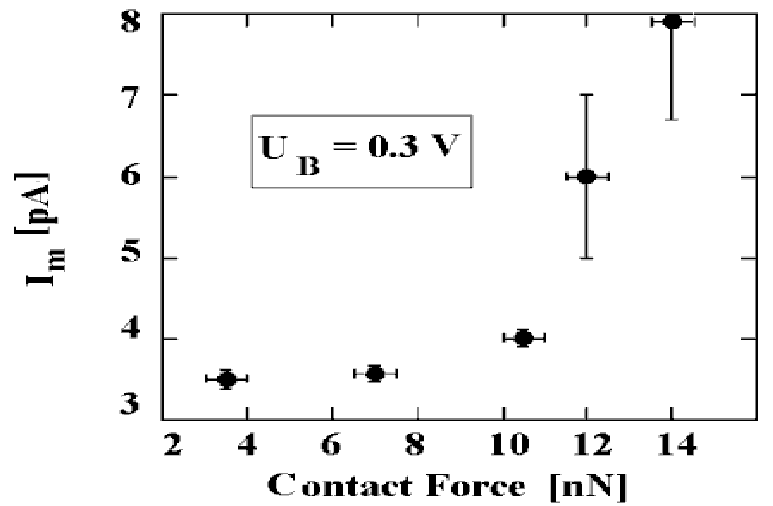
Non-contact mode (!):
Tunneling AFM (TUNA)

Conductive Force Microscopy (CFM)
Tunneling AFM (TUNA)



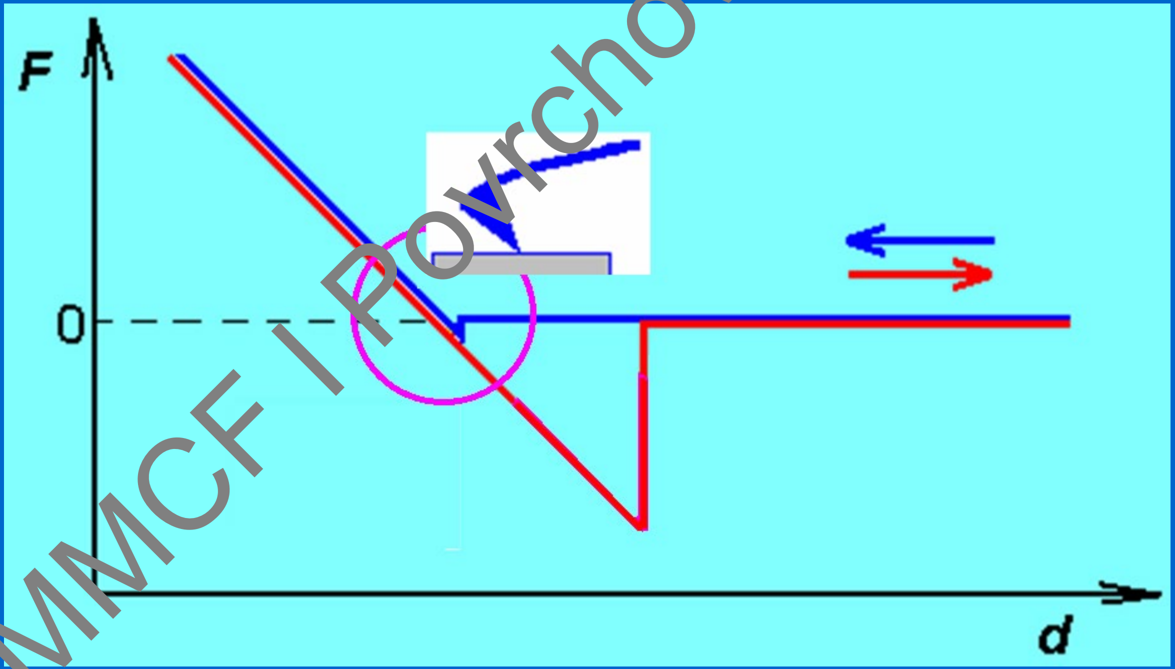
Carotenoid embedded in 1-docosanethiol attached to Au.
Current measured between biased Pt-coated AFM cantilever and Au substrate.
Maximum current (I_m) vs. contact force.

[J. Phys. Chem. B 103 4006-4010 (1999)]

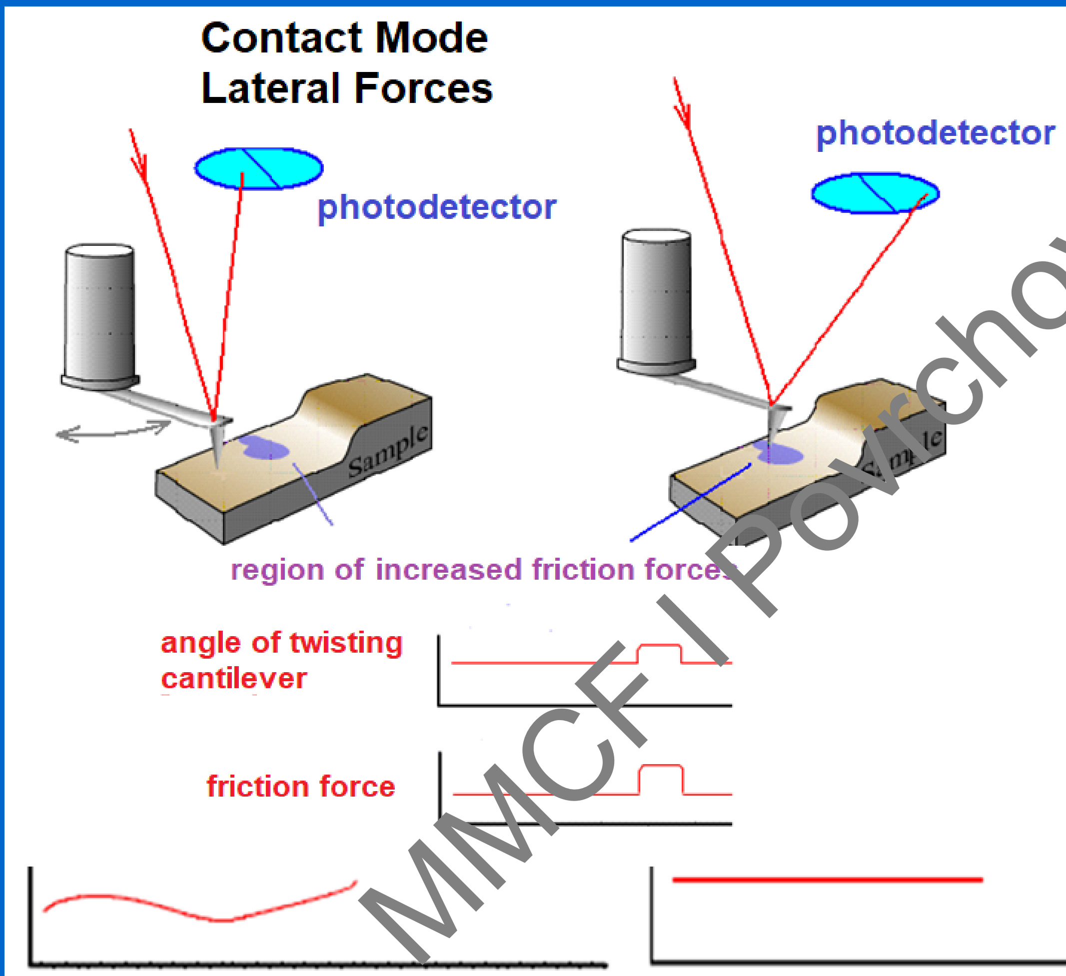


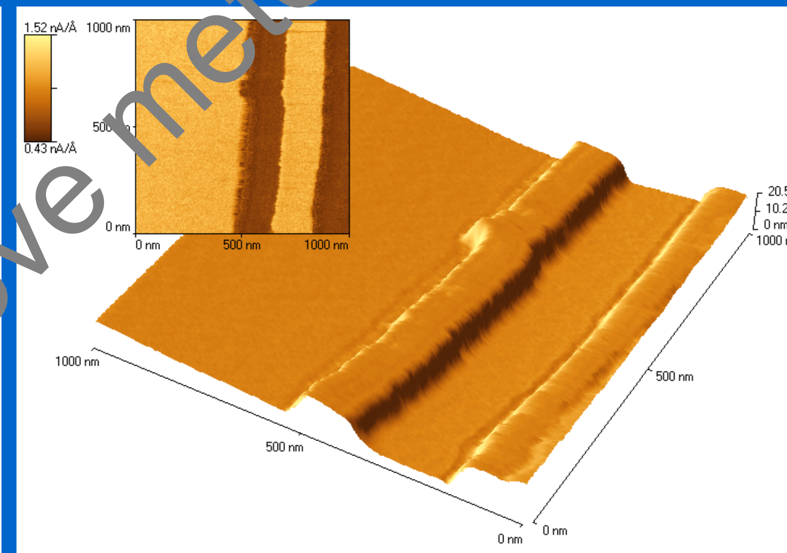
Contact mode AFM – attractive forces:

Adhesion
Friction



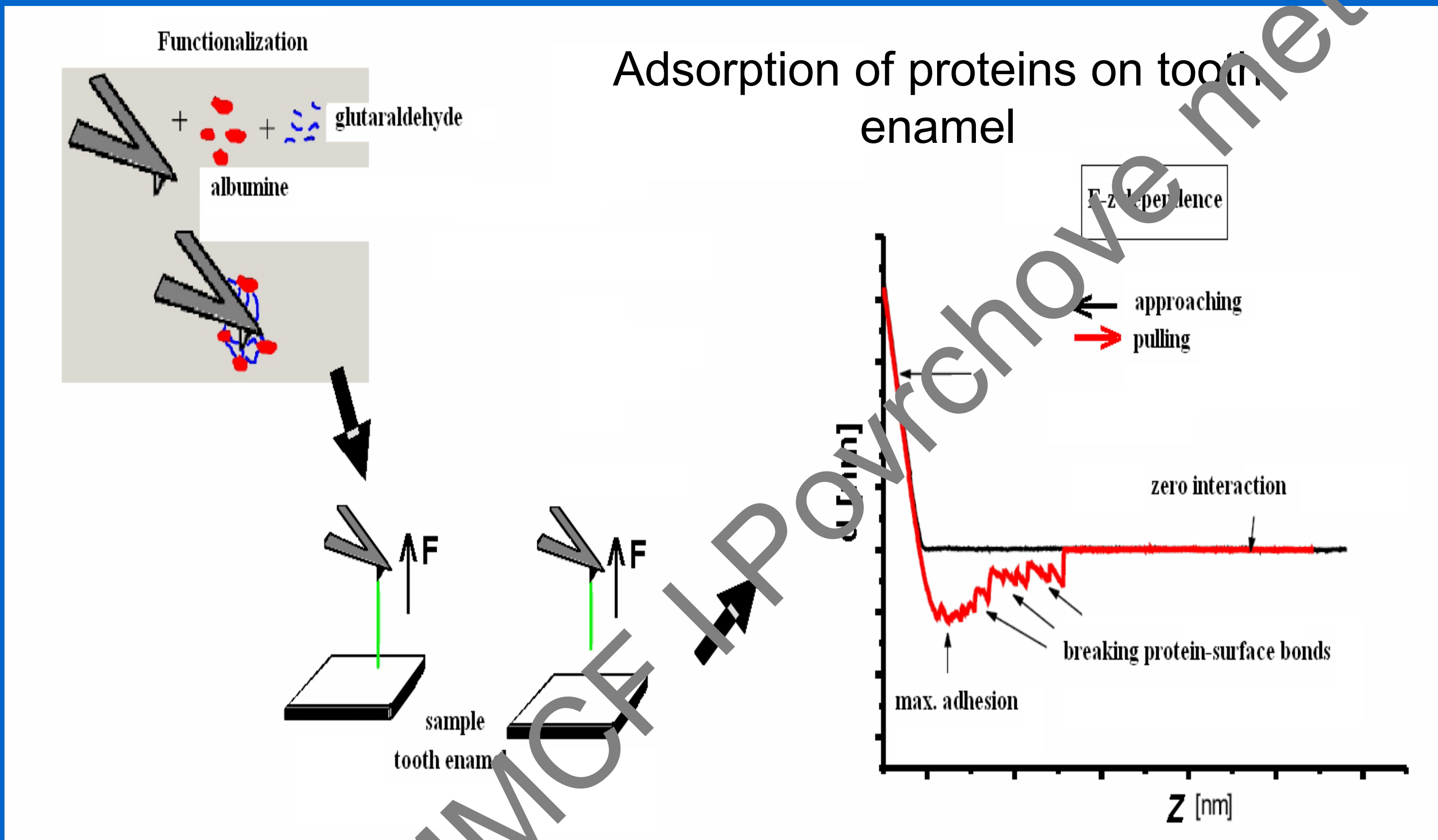
Attractive Lateral Forces (friction) for material analysis (LFM)

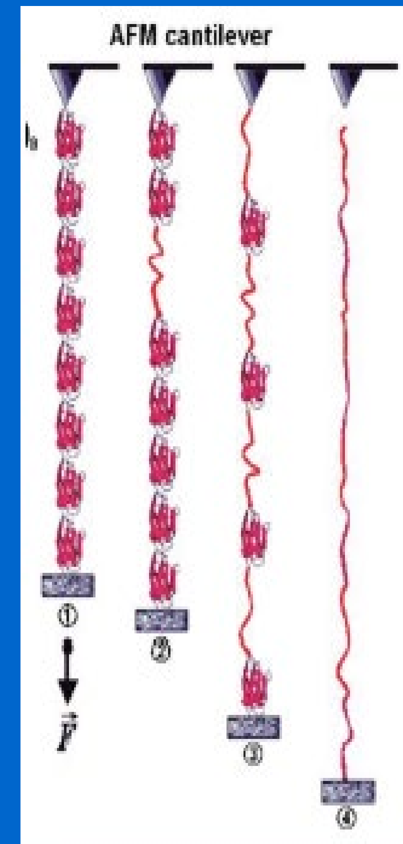




PTFE film on glass
-topography
-map of lateral forces (friction)

Attractive axial forces for „chemical“ analysis





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University of Kaiserslautern, Department of Operative Dentistry and Periodontology, Saarland University

PeakForce Tapping QNM:

Complete force curve for 3D imaging and surface Quantitative Nanoscale Mechanical analysis

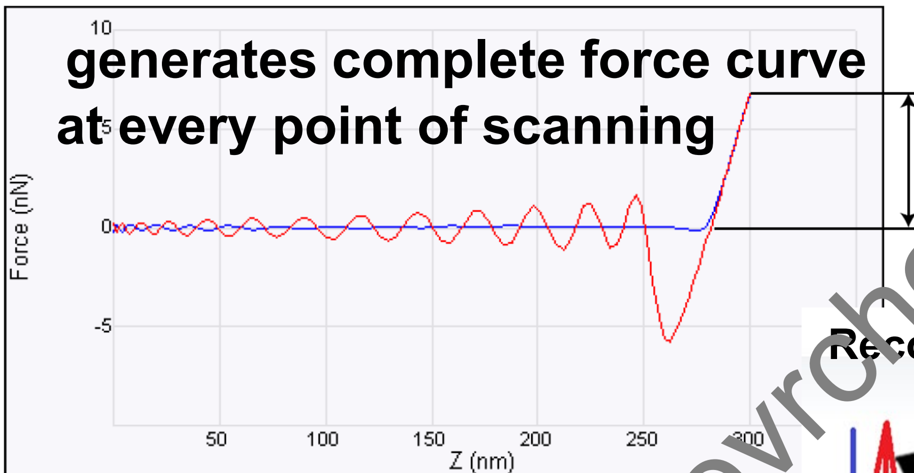
Force curve is collected at each point of scan

For
- 3D Topography (contact, height) at Peak Force
- Quantitative Nanoscale Mechanical analysis - mapping surface nanomechanical properties (adhesion, stiffness/Y_M, deformation, dissipation) extracted from various regions of force curve.

Feedback set by Peak Force (contact)Tapping

AFM PFQNM – Peak Force tapping

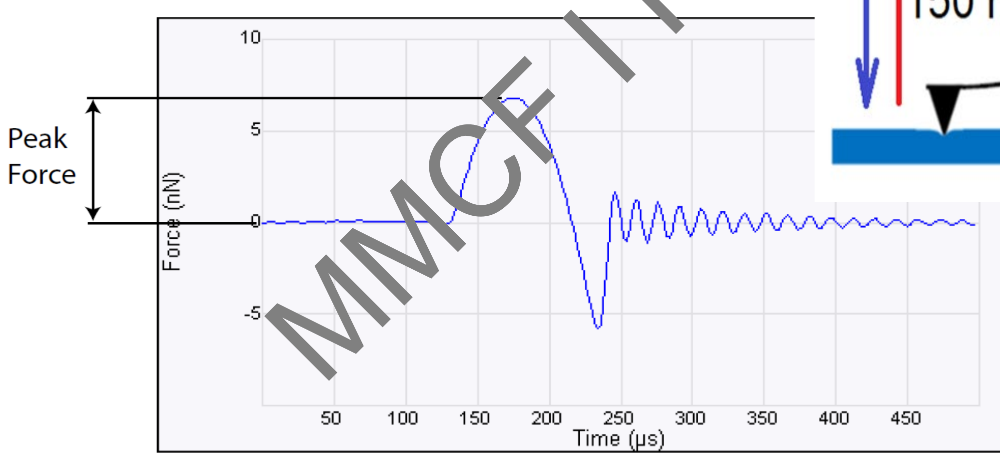
Figure 2.5f Force curve, Force vs. distance



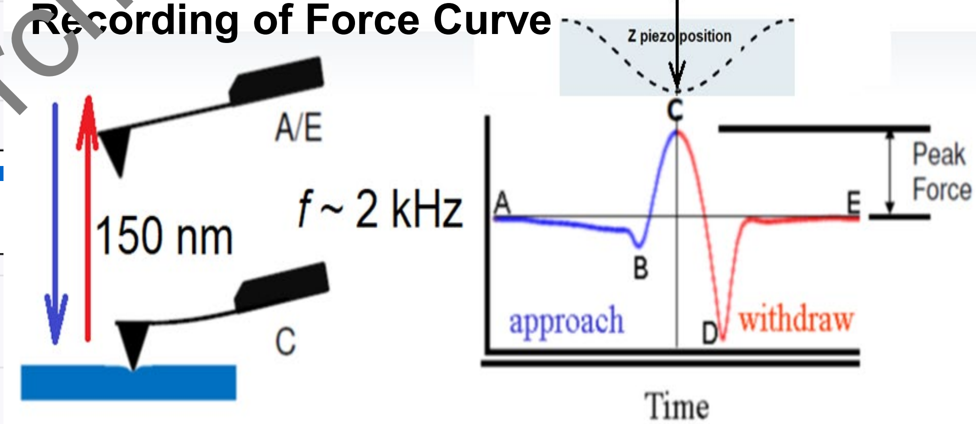
generates complete force curve at every point of scanning

Periodic contact with surface - contact 3D (height) images

Figure 2.5e The “heartbeat,” Force vs. Time

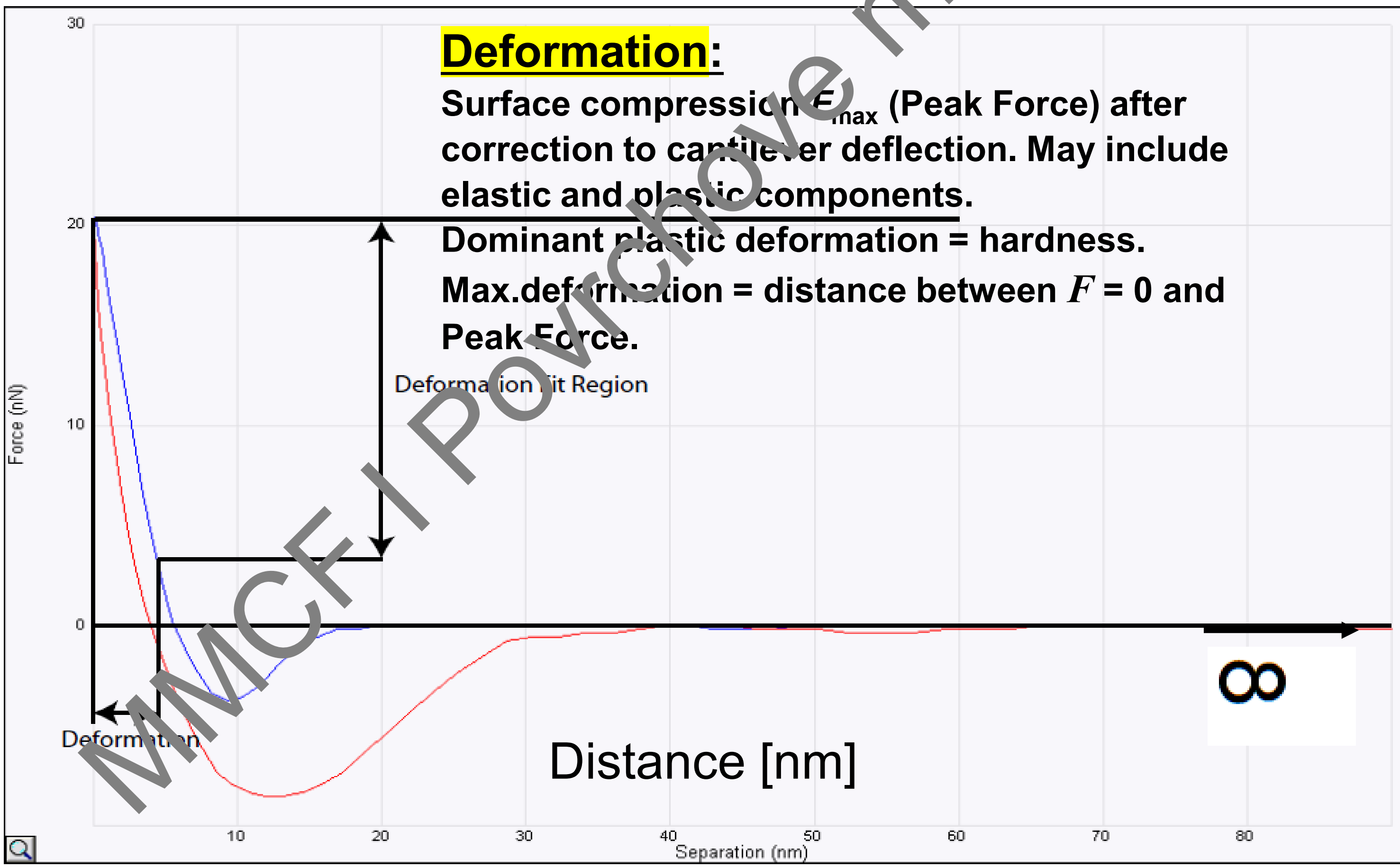


Recording of Force Curve



AFM PFQNM –interpretation of force curve: Deformation

Figure 2.5j Deformation



Deformation:

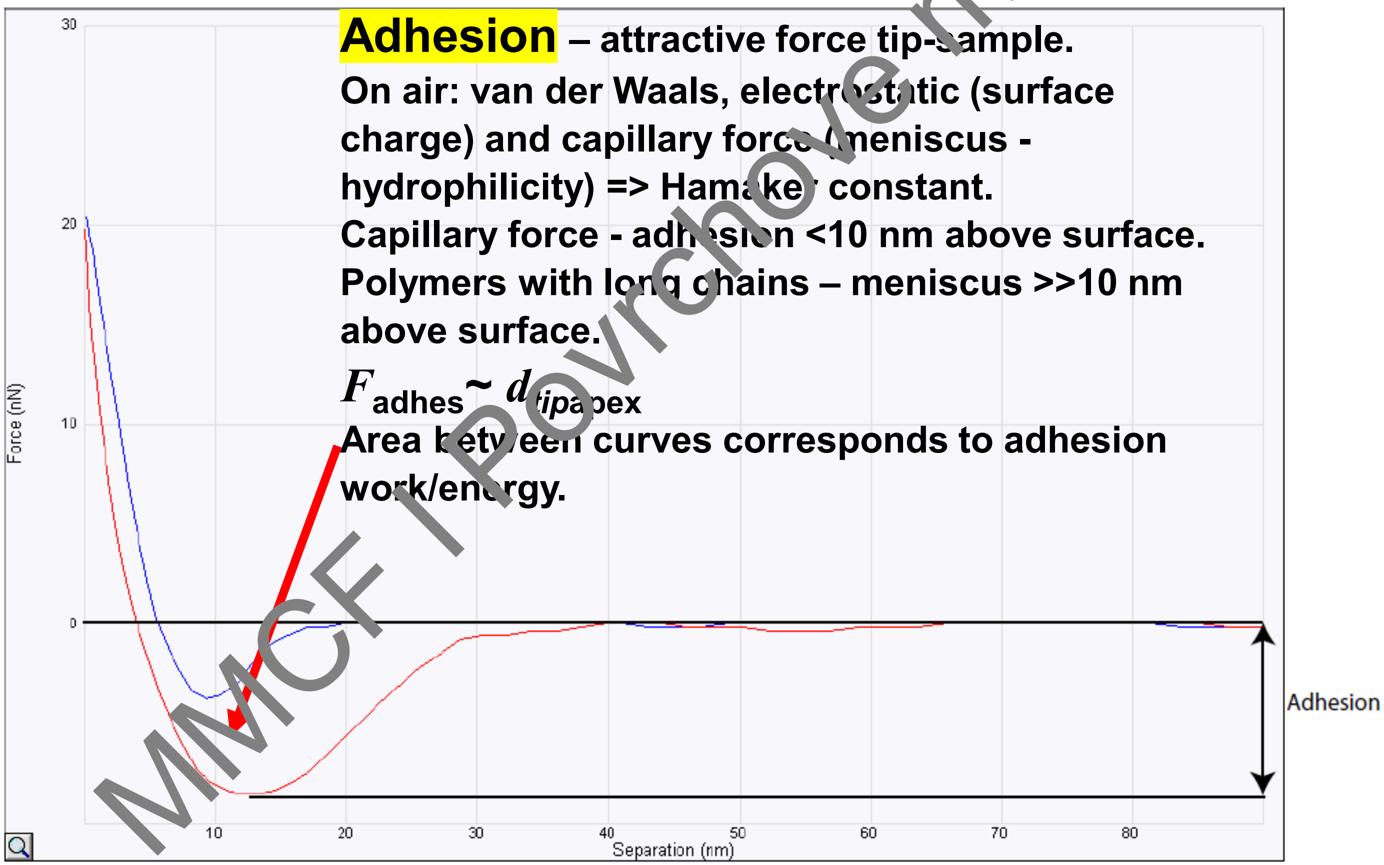
Surface compression F_{max} (Peak Force) after correction to cantilever deflection. May include elastic and plastic components.

Dominant plastic deformation = hardness.

Max.deformation = distance between F = 0 and Peak Force.

AFM PFQNM –interpretation of force curve: Adhesion

Figure 2.5c Adhesion on a PS+LDPE blend



Adhesion – attractive force tip-sample.

On air: van der Waals, electrostatic (surface charge) and capillary force (meniscus - hydrophilicity) => Hamaker constant.

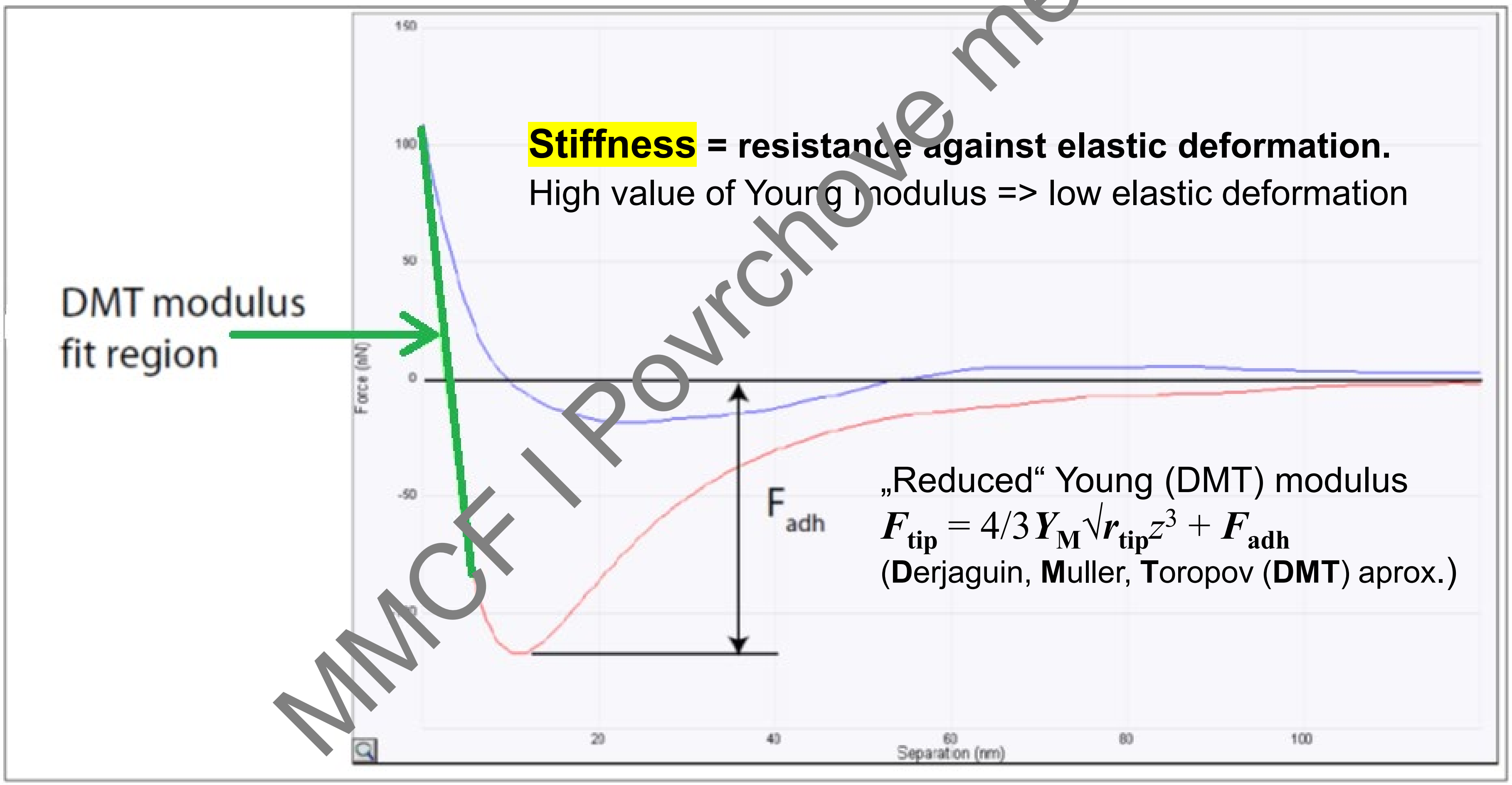
Capillary force - adhesion <10 nm above surface.

Polymers with long chains – meniscus >>10 nm above surface.

$F_{\text{adhes}} \sim d_{\text{tip apex}}$

Area between curves corresponds to adhesion work/energy.

AFM PFQNM –interpretation of force curve: Stiffness (Y_M/DMT)

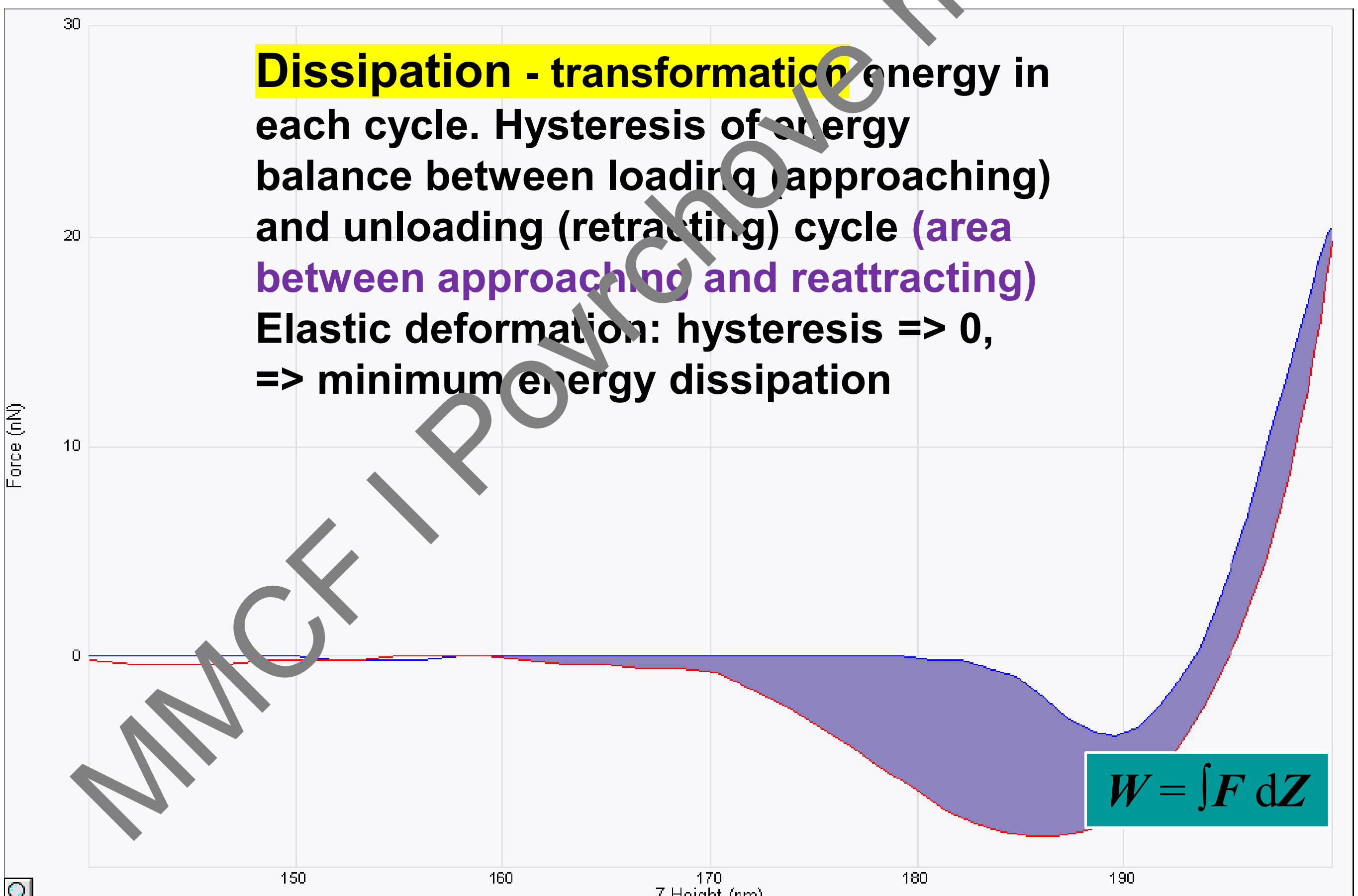


Stiffness = resistance against elastic deformation.
High value of Young modulus => low elastic deformation

„Reduced“ Young (DMT) modulus
$F_{tip} = 4/3\, Y_M \sqrt{r_{tip} z^3} + F_{adh}$
(**D**erjaguin, **M**uller, **T**oropov (**DMT**) aprox.)

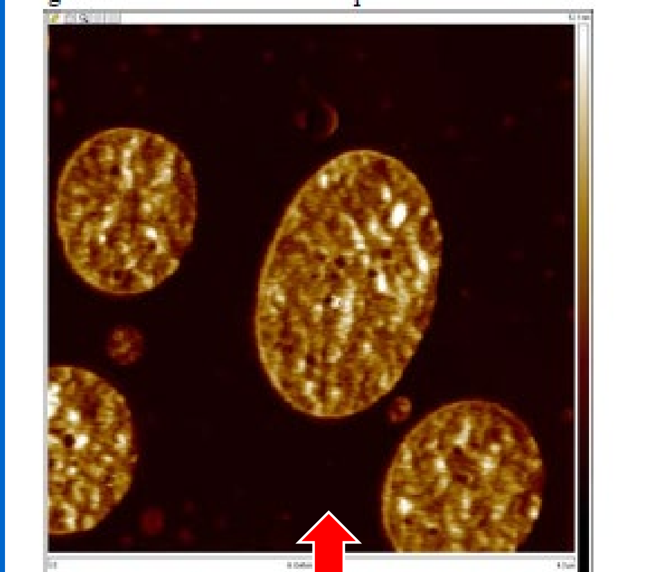
AFM PFQNM – interpretation of force curve
Dissipation

Figure 2.5h Dissipation (shaded area) in a polystyrene (PS) and Low-density polyethylene (LPDE) blend



Dissipation - transformation energy in each cycle. Hysteresis of energy balance between loading (approaching) and unloading (retracting) cycle (area between approaching and reattracting)
Elastic deformation: hysteresis => 0,
=> minimum energy dissipation

$$W = \int F \, dZ$$



Composite
PS/LDPE
(Y_{PS}~3GPa/Y_{LDPE}~0.3GPa)

AFM PFQNM - interpretation of force curve

Figure 2.5d Adhesion map of a PS+LDPE blend

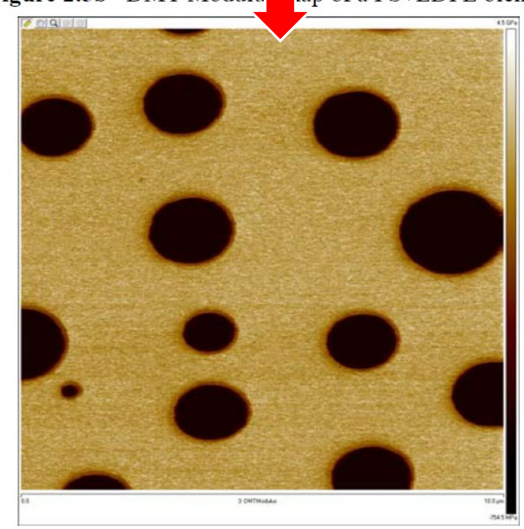
Deformation

Adhesion

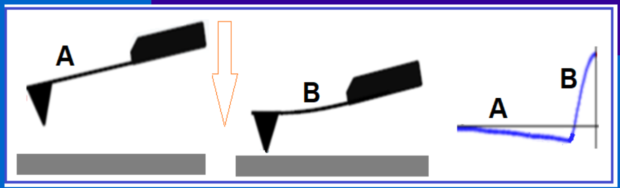
Dissipation

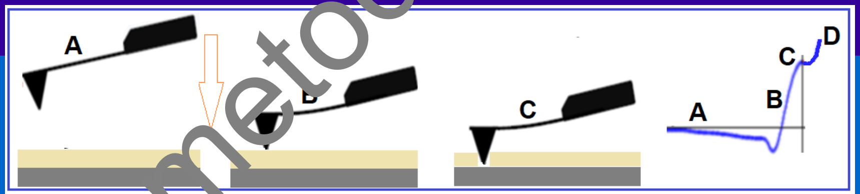
Stiffness (Y_M, DMT-approx.)

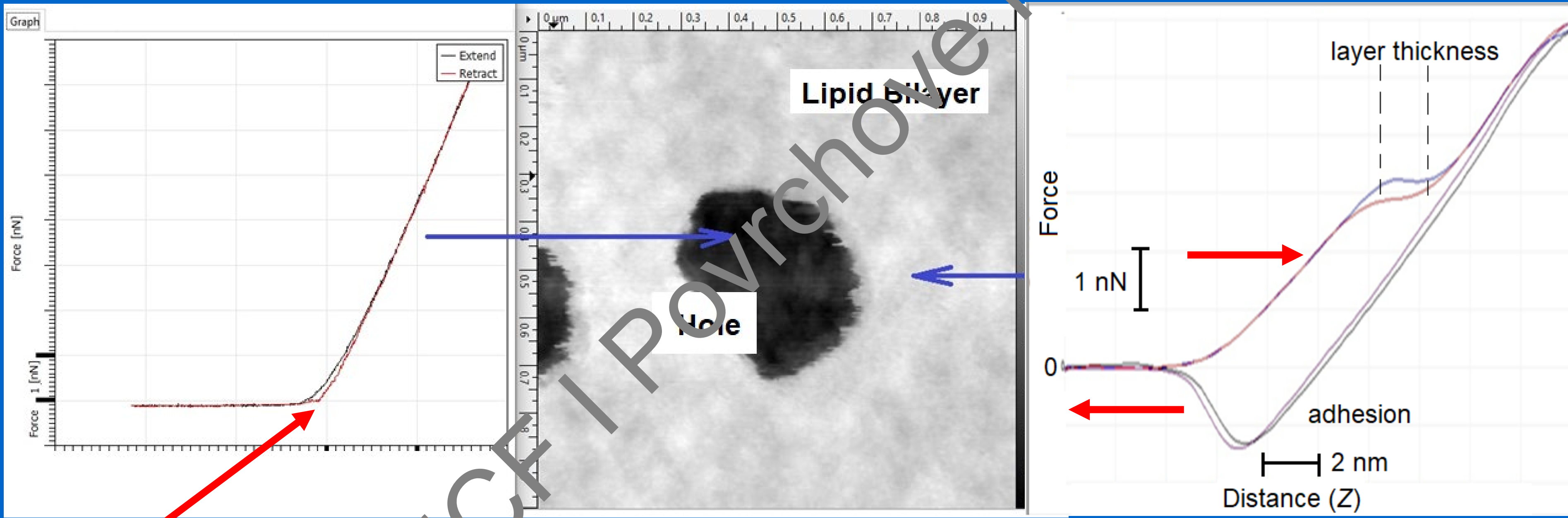
Figure 2.5b DMT Modulu ap of a PS+LDPE blend



PFQNM on soft layers - interpretation of force curve



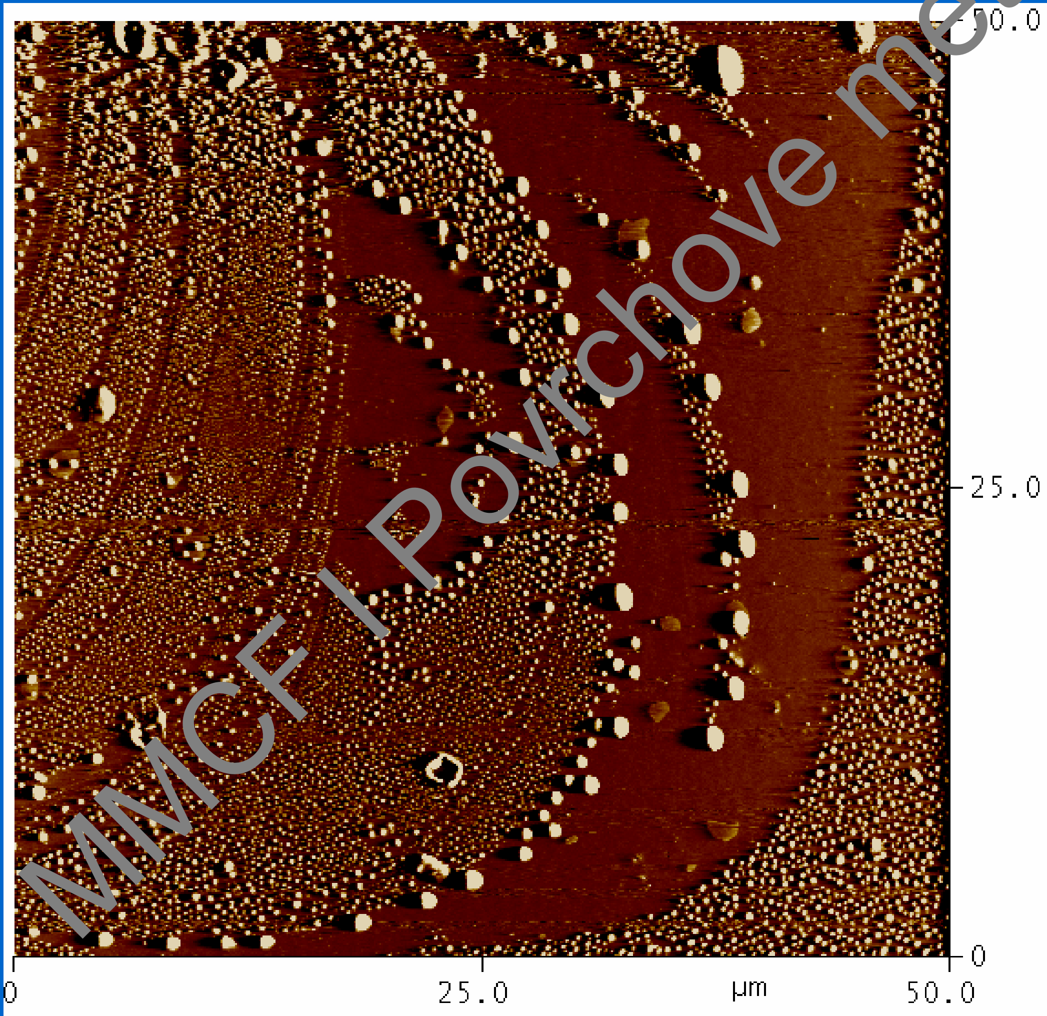




No adhesion to clean Si-wafer (water-immersed)

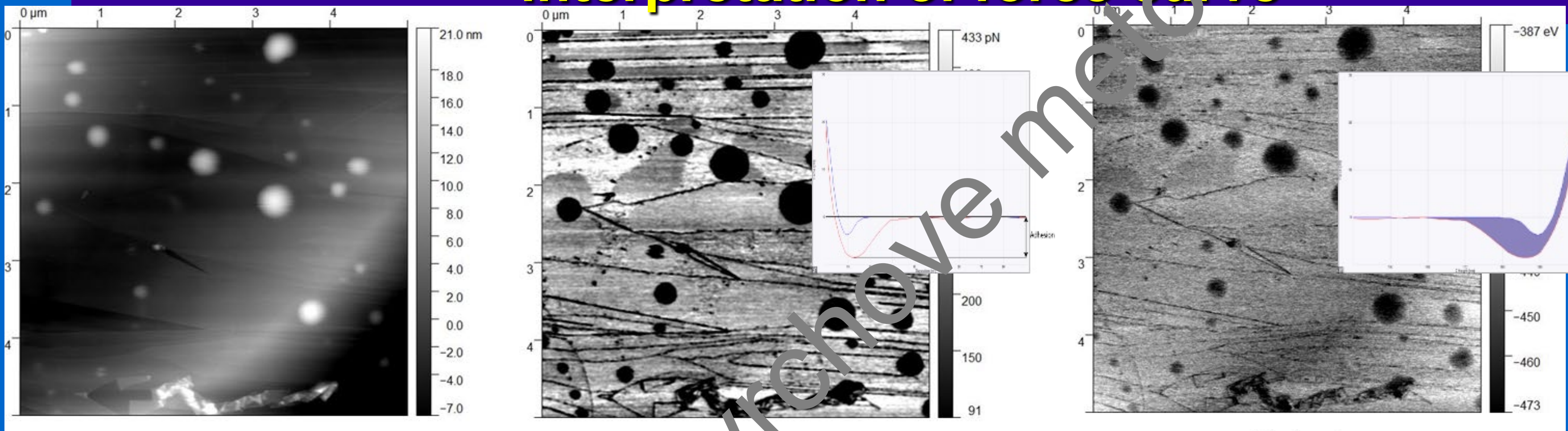
Lipid bilayer on Si-wafer immersed in aqueous media – delay on rising part of force curve: compression, penetration resistance (PFQNM)

AFM imaging of zero-mass nano-objects: Gaseous nanobubbles on immersed surfaces



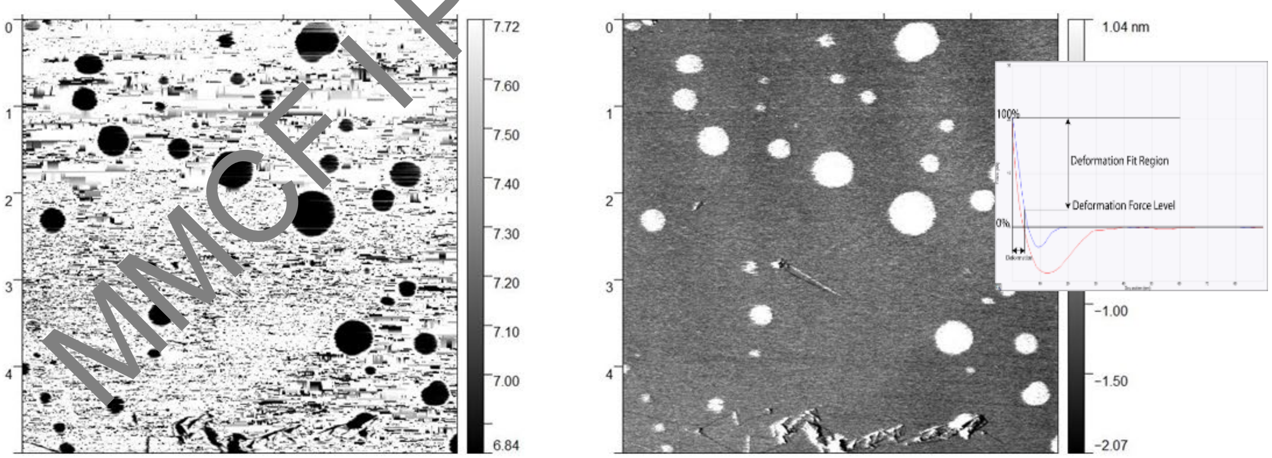
In-situ AFM *tapping*, amplitude image Hydrophilized tip and cantilever

AFM-PFQNM of gaseous nanodomains - interpretation of force curve



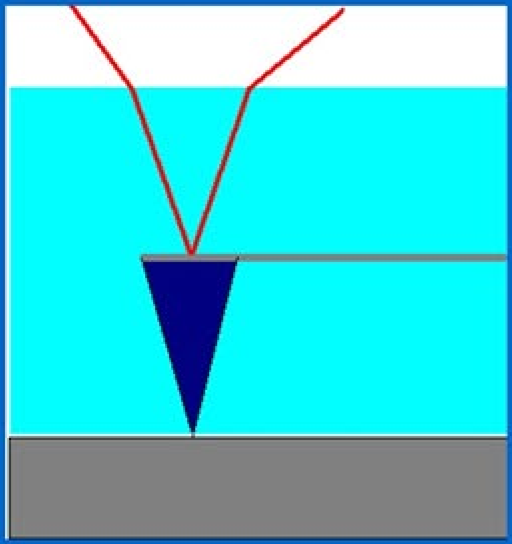
Height Adhesion Dissipation

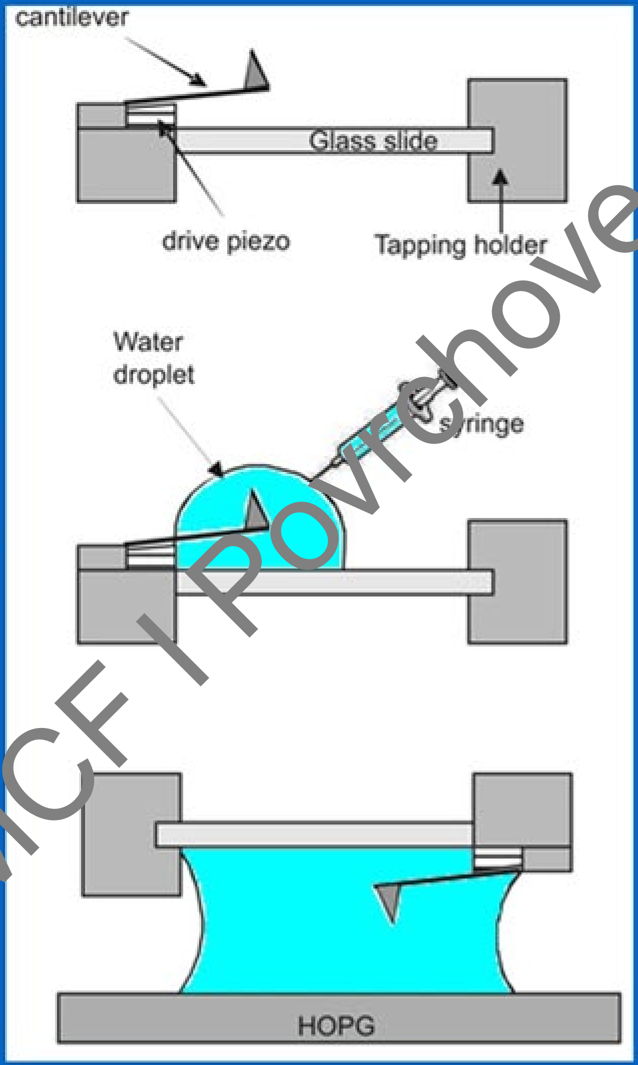
Gaseous nanodomains on water-immersed surface – hydrophilized tip

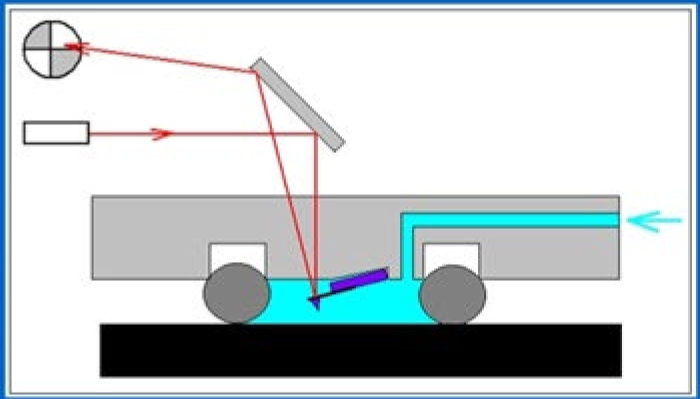


LogStiffness Deformation

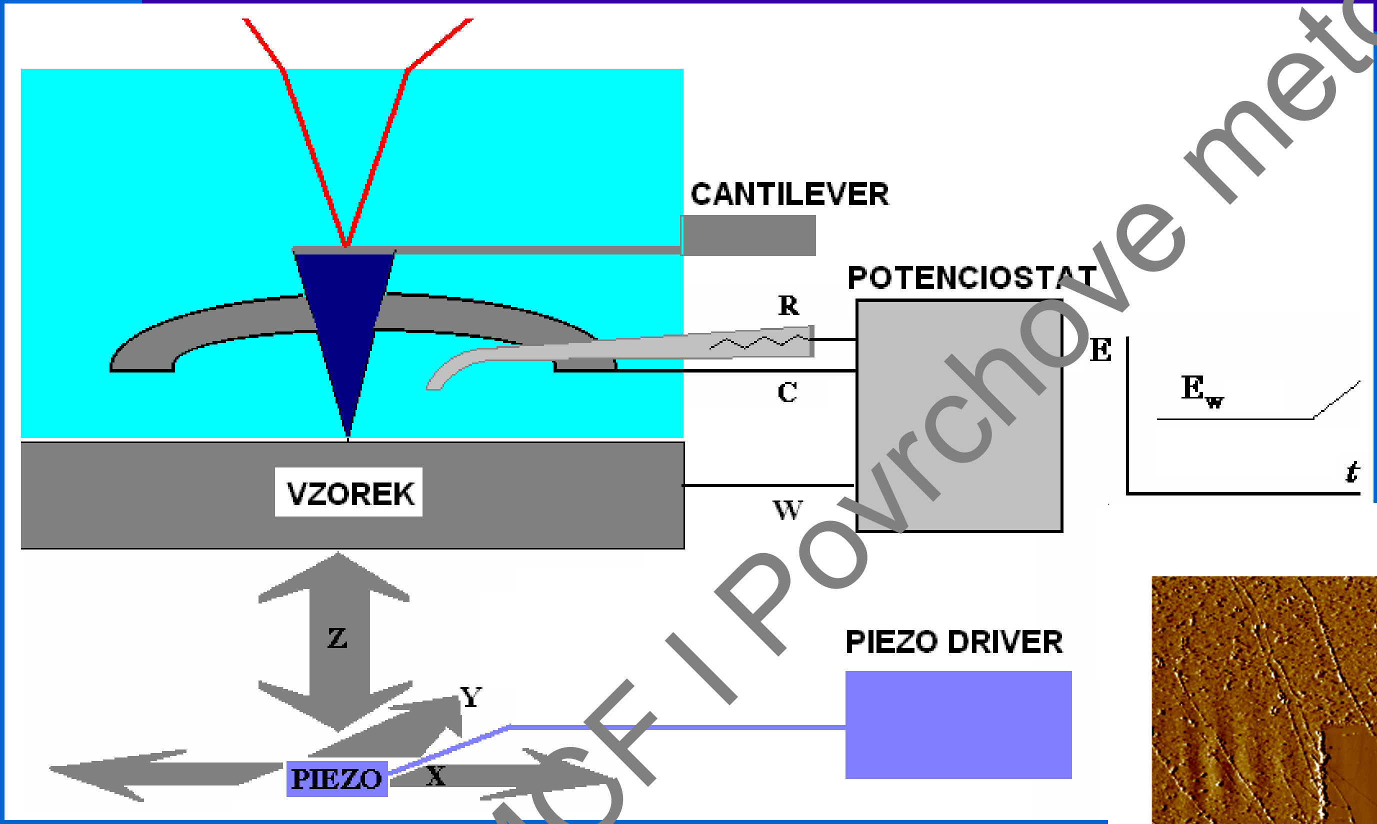
AFM in liquids

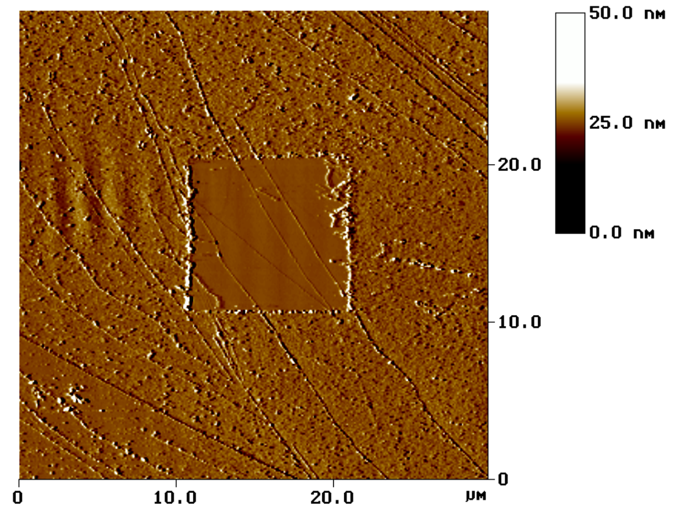






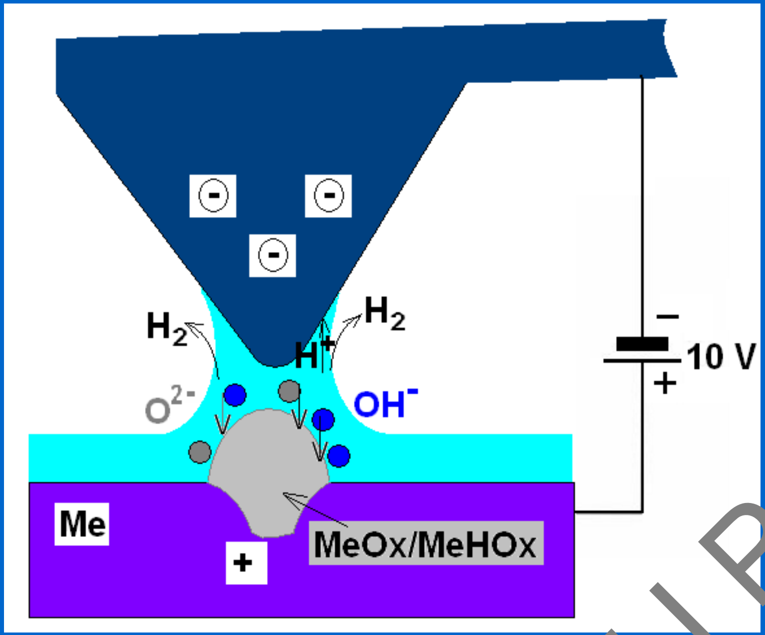
AFM in EC: AFM imaging *in situ*





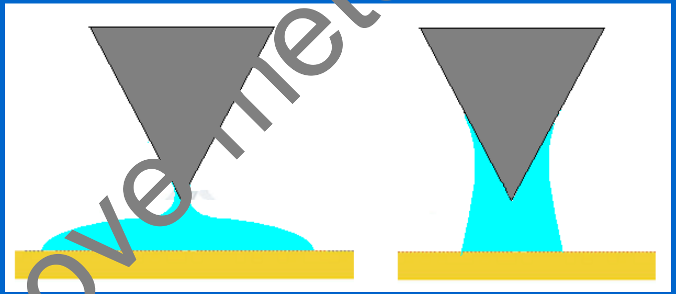
Cu deposit on HOPG basal plane removed by SPM tip

ECAFM/lithography: tip-assisted local electrochemical deposition/dissolution of oxide

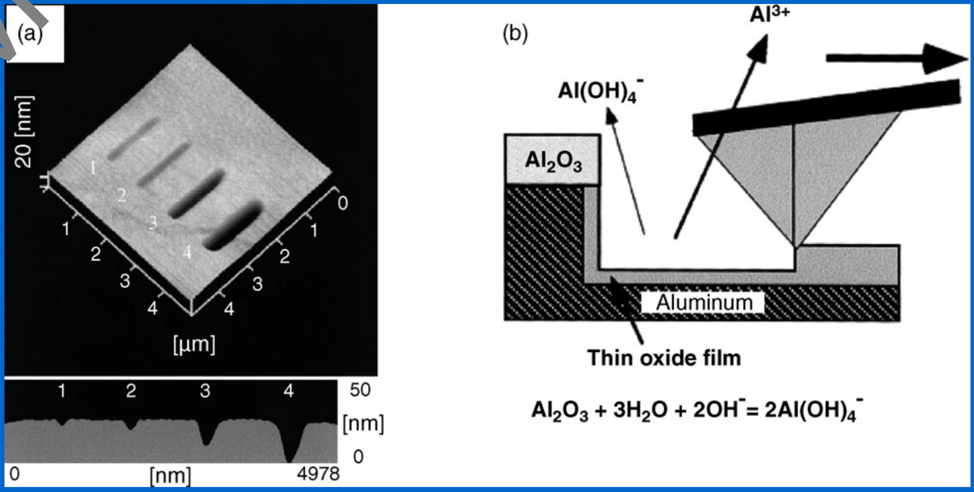


Field intensity 10^7 V/cm =>
water dissociates H_2O => OH^- + H^+

2-electrode system



Water meniscus on hydrophilic and hydrophobic substrate



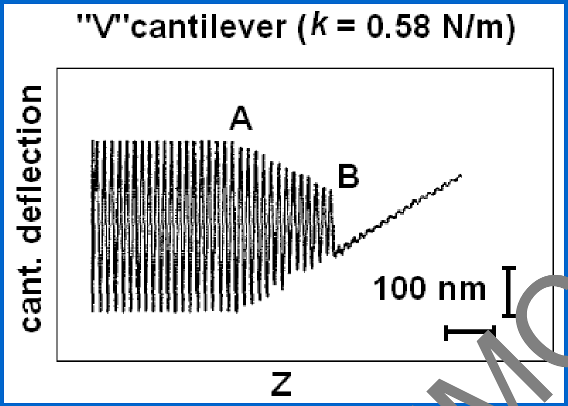
TSENG, Ampere A. Tip-Based Nanofabrication Fundamentals and Applications. Springer New York Dordrecht Heidelberg London 2011. ISBN 978-1-4419-9898-9.

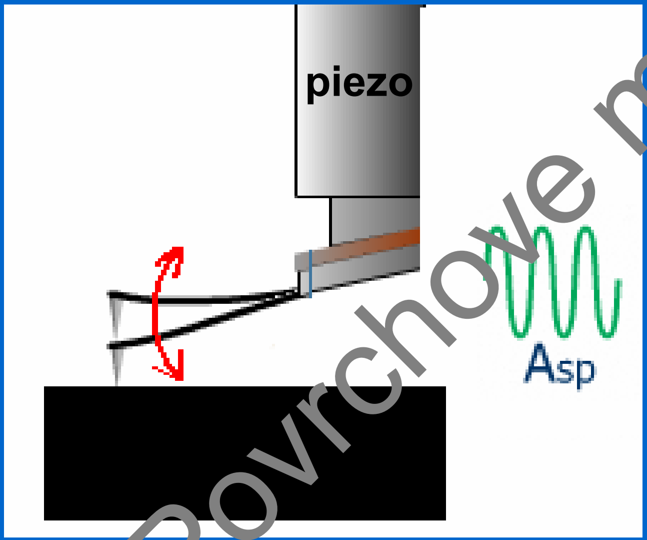
Semi(contact) mode - tapping

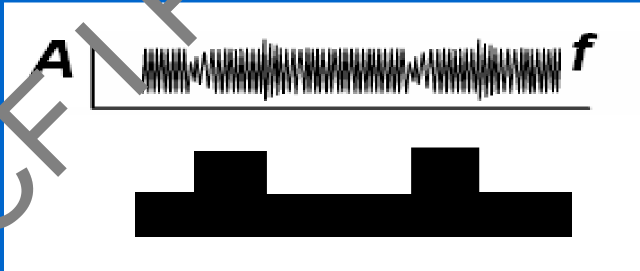
Acoustic/mgt. drive

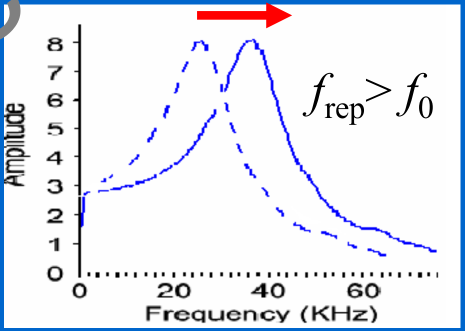
Mechanical oscillator
oscillation in resonance
input parameters:
f_{rez} A_{sp} **(~ 20 nm)**

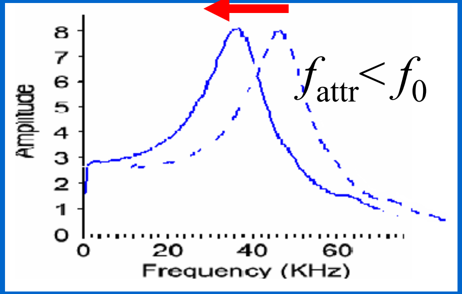
output parameters
A, Δf, $\Delta\theta$, d *(deflect.)*

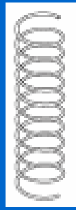












$$md^2z/dt^2 = \underbrace{-kz}_{\text{Hook}} \underbrace{-(m\omega_0/Q)dz/dt}_{\text{Dissipation (dumping)}} + \underbrace{F_{tip\text{-}sample}}_{\text{Interaction tip-sample}} + F_{drive}\cos\omega t$$

Hook

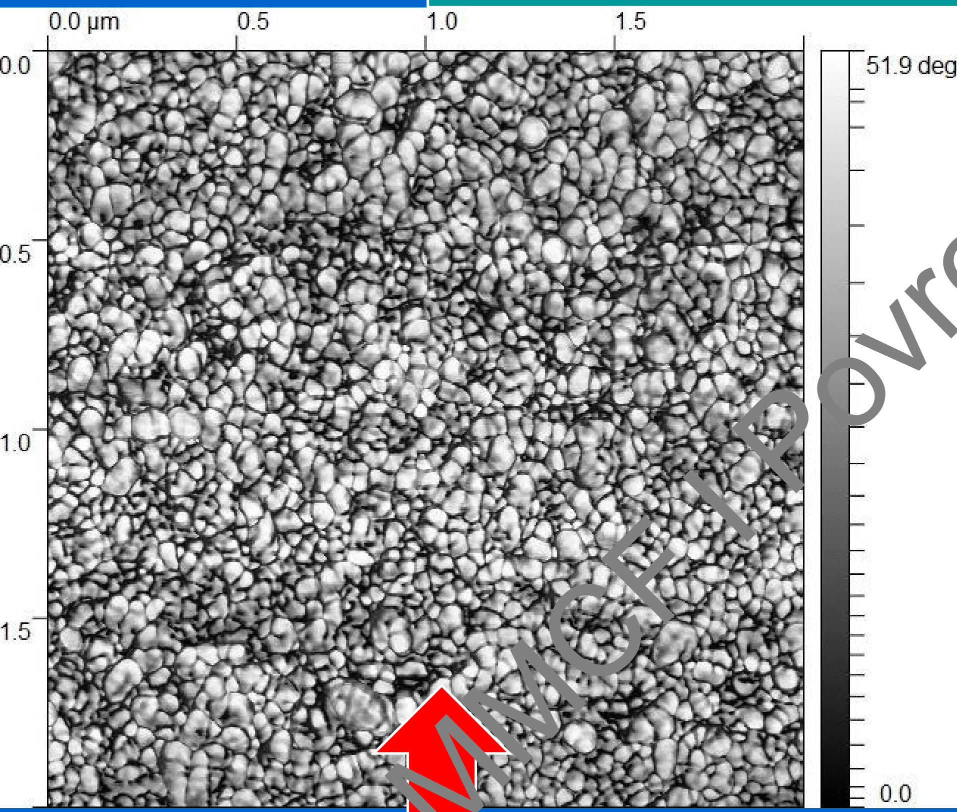
Dissipation (dumping)

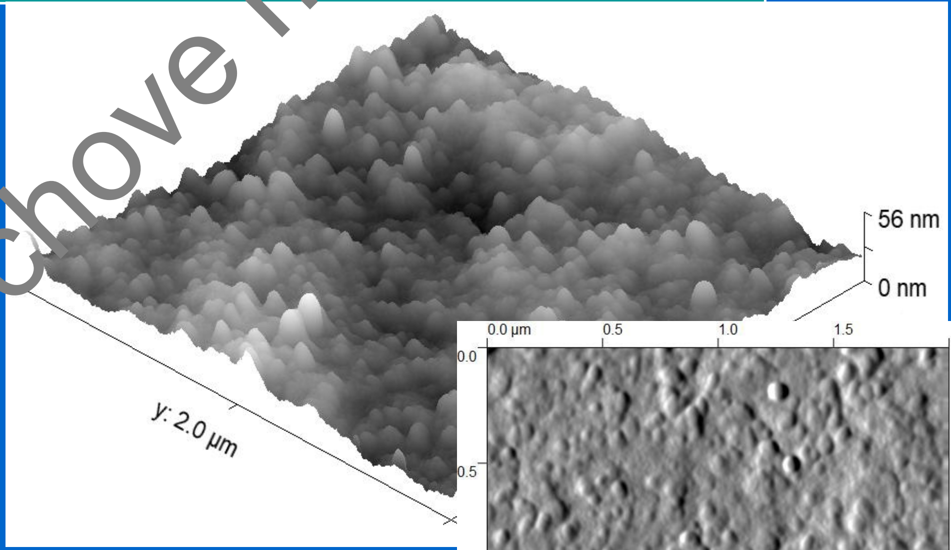
Interaction tip-sample

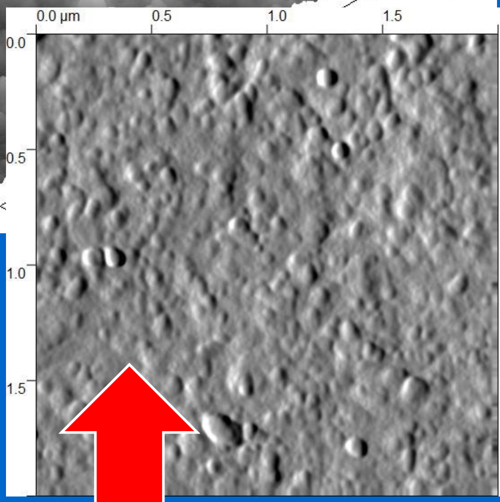
$$\omega_0 = \sqrt{k/m}$$

Semicontact mode (tapping) phase imaging

Enhances edges of (nano)structure boundaries.
Less affected by height fluctuation



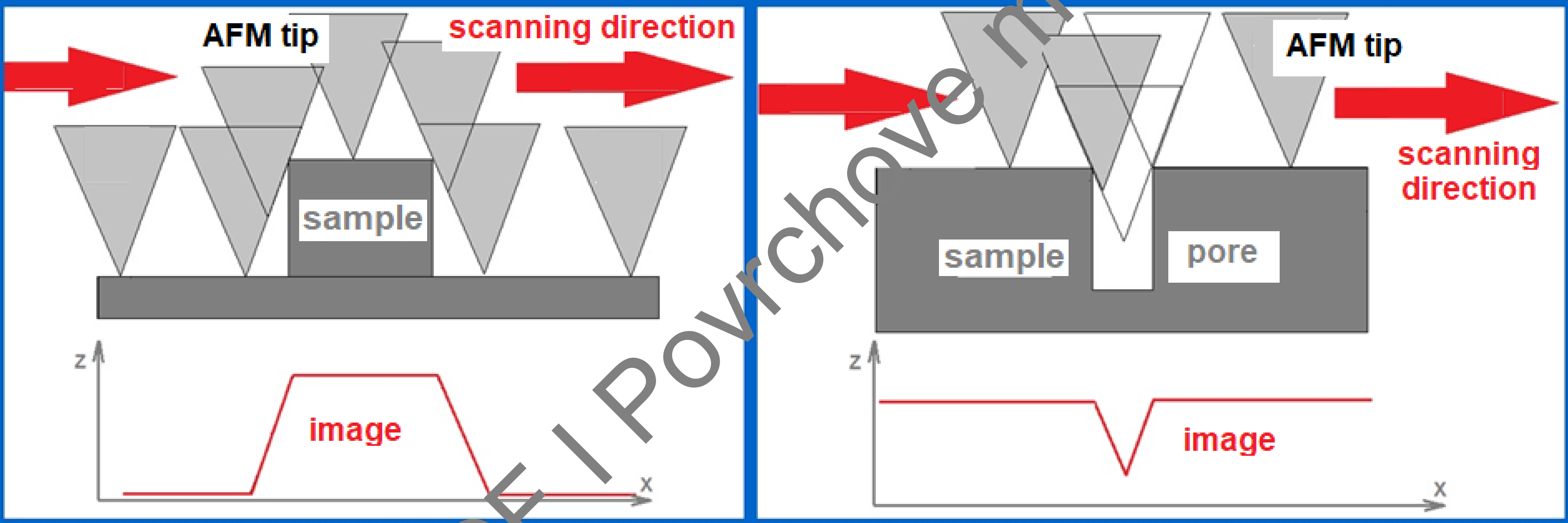




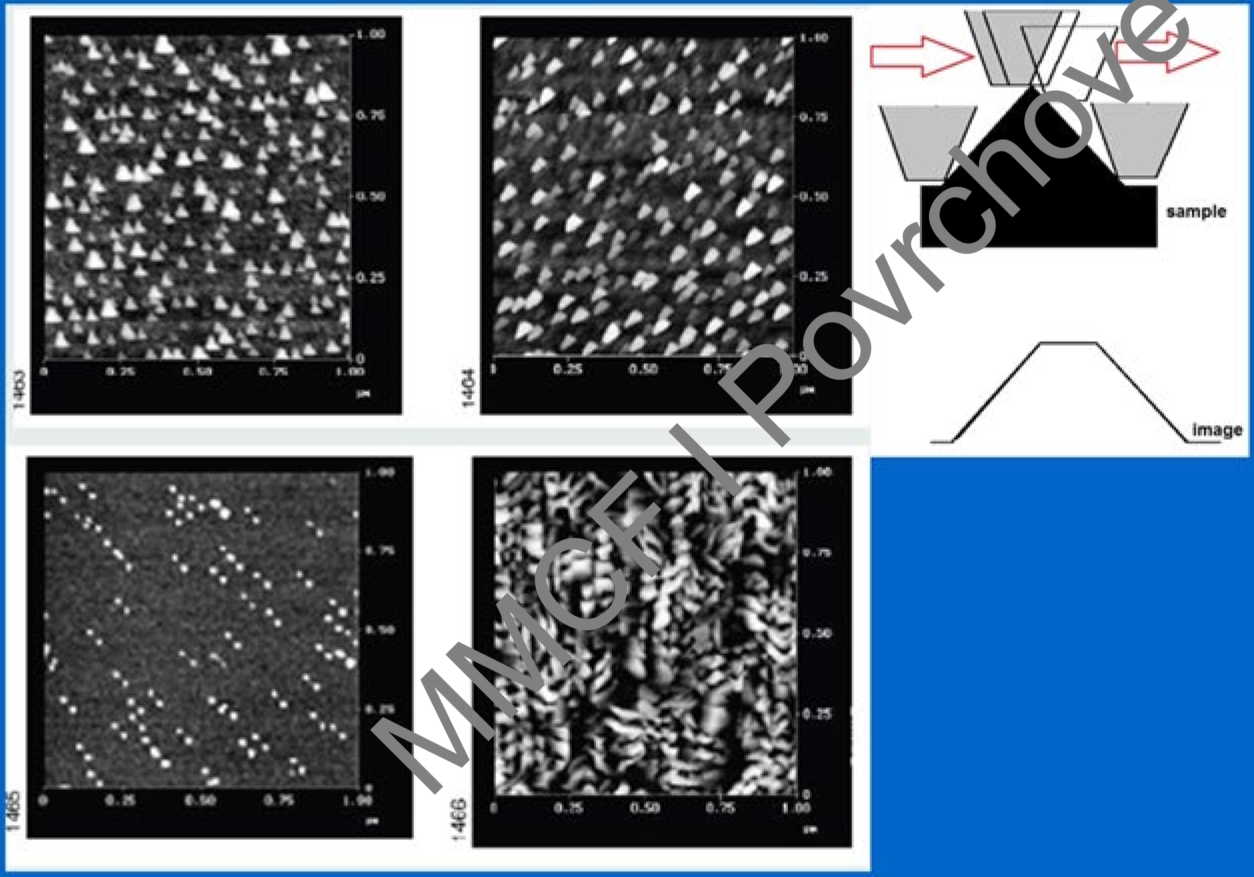
Nanograins ZrO_2 imaged by AFM tapping phase mode (top-view)

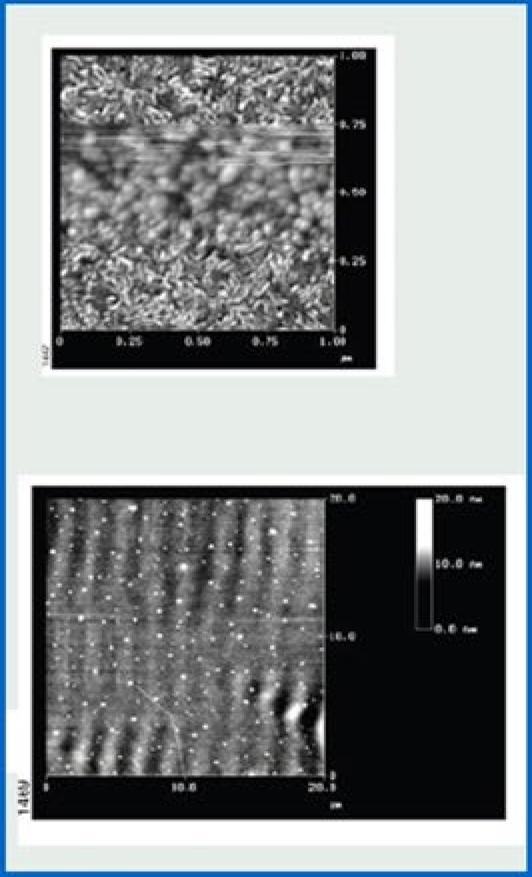
Identical location imaged by 3D topography and amplitude mode (top-view)

AFM artefacts

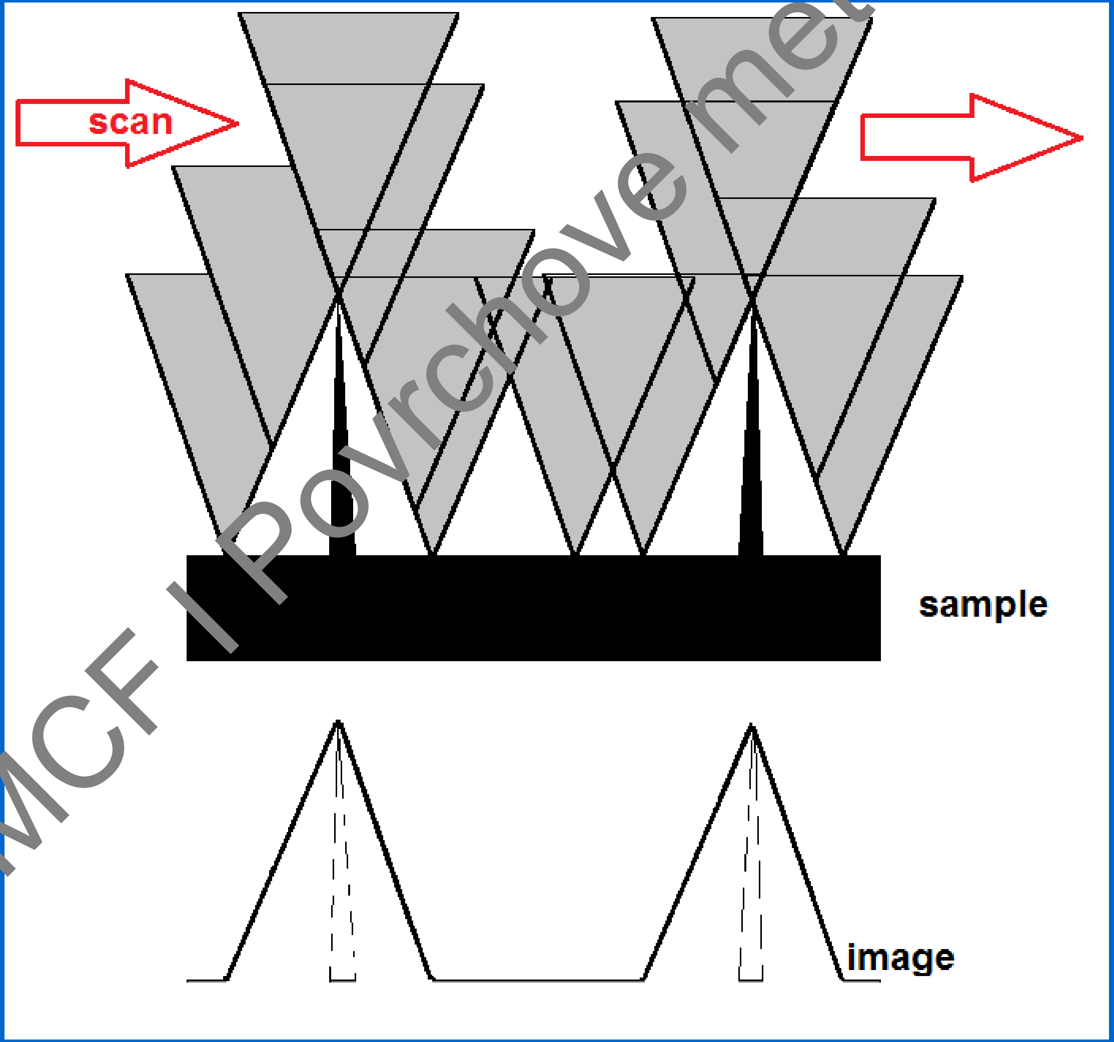


AFM artefacts

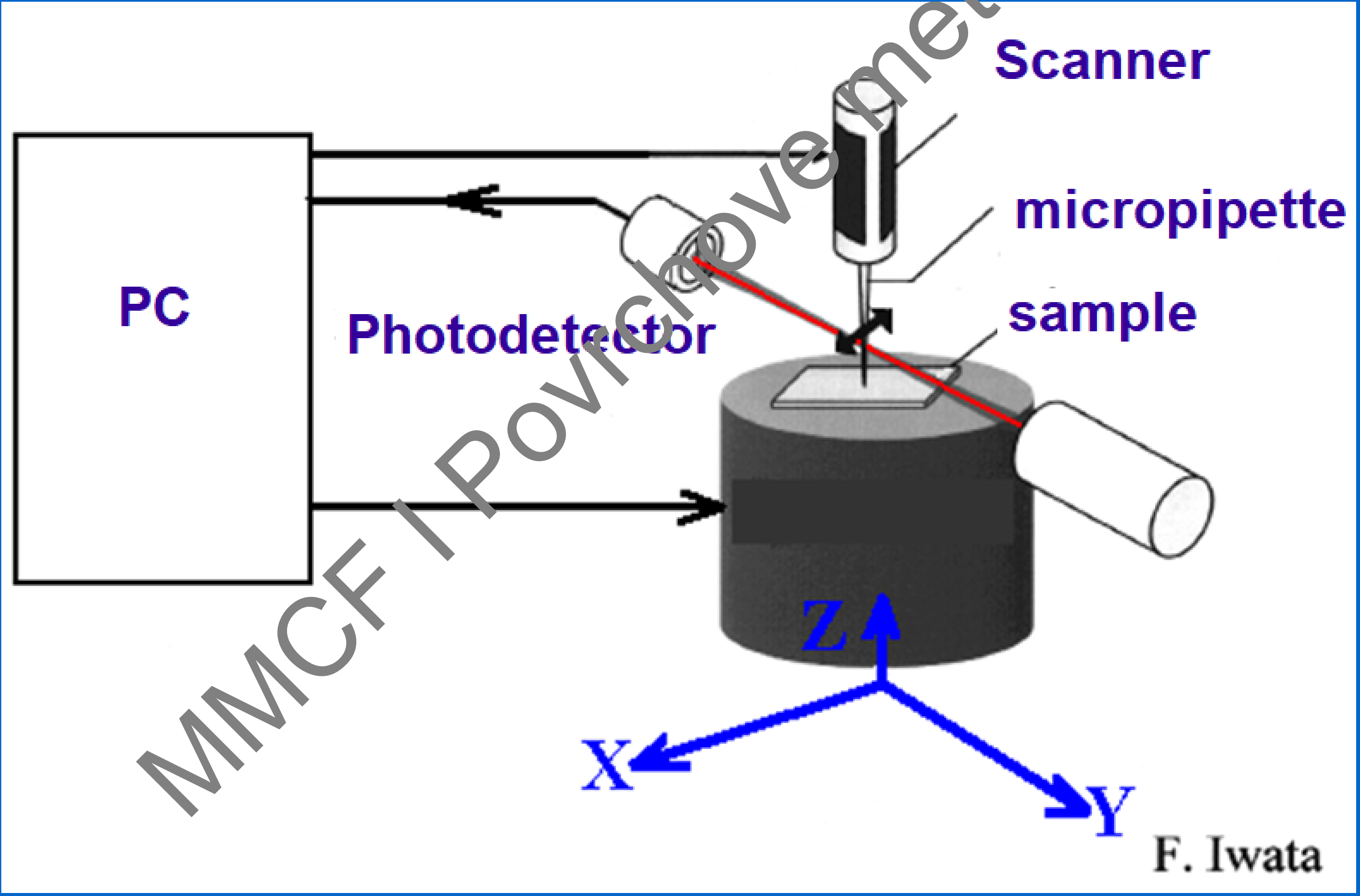




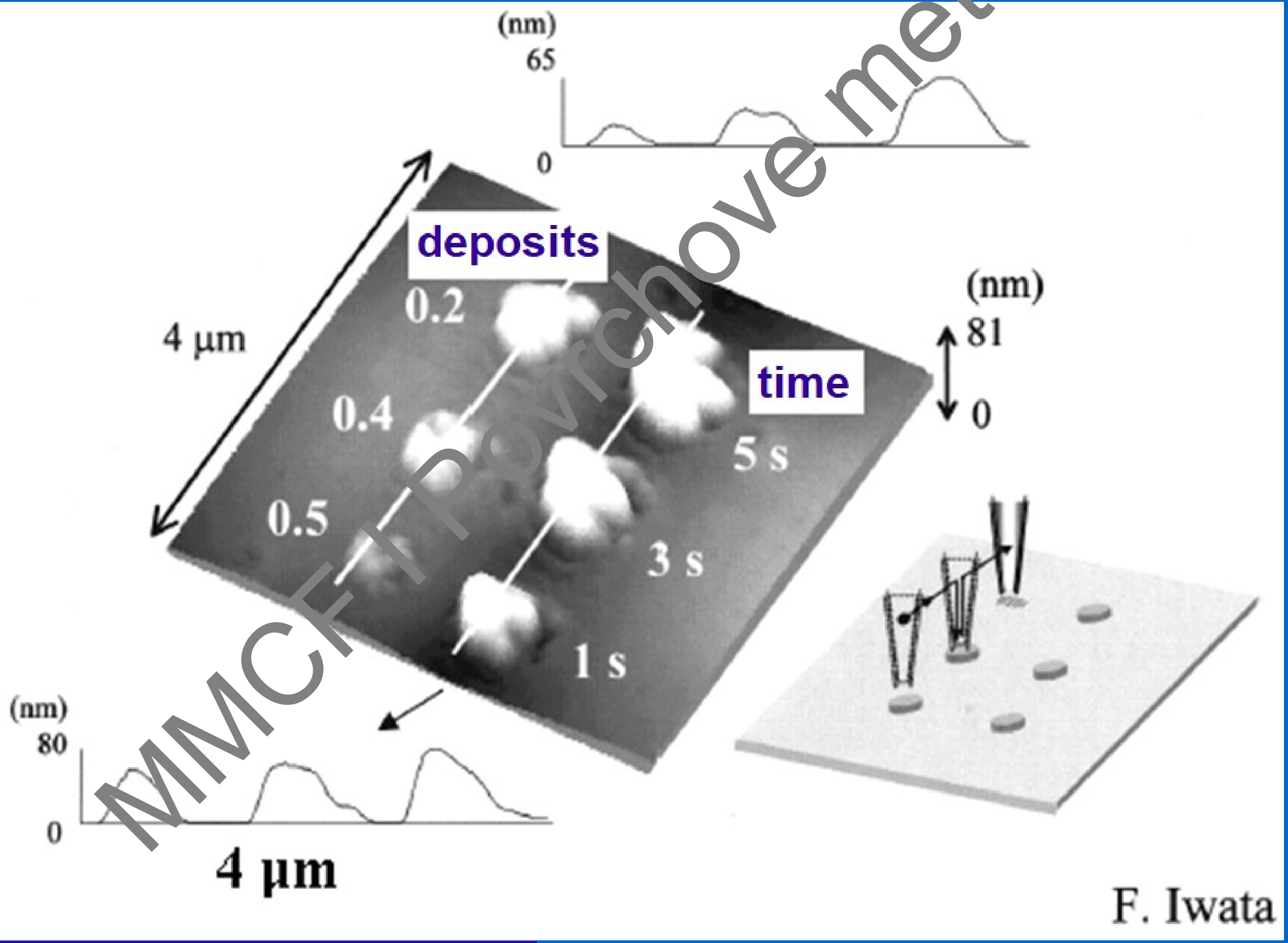
AFM artefacts: Self-image of AFM tip



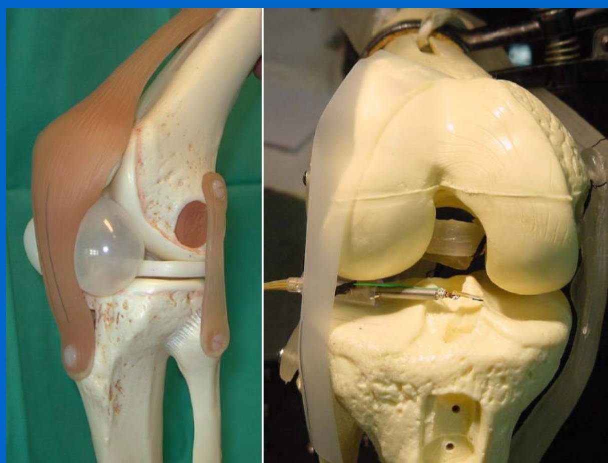
Special: Dual function of micropipette: AFM scanning tip and micro-dispenser

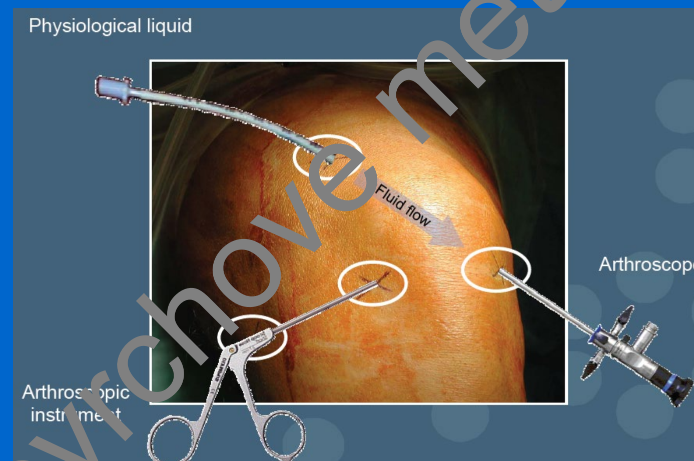


Nano-lithographic AFM with scanning micropipette

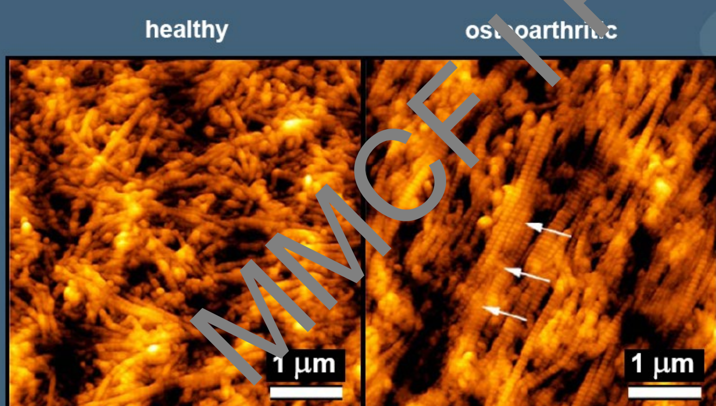


Special: AFM *in vivo* - Scanning Force Endoscope

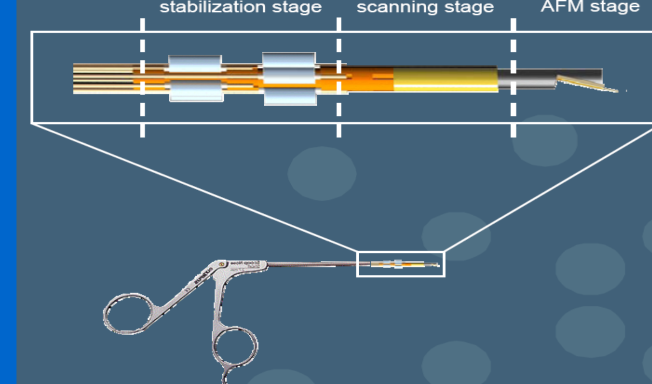




Diagnosing cartilage diseases at an early stage



M. Stolz *et al.*, Biophys. J. 2004; 86 3269-3283



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