Contact potential difference on the atomic-scale probed by Kelvin Probe Force Microscopy: an imaging scenario

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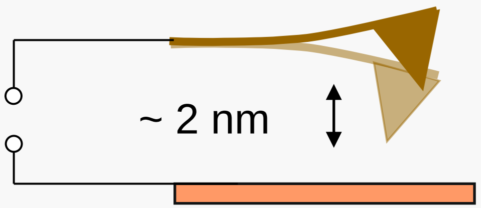
Kelvin Probe Force Microscopy: concept

Goal : deriving the Contact Potential Difference of a sample w.r.t. the AFM tip

Bias voltage applied between the tip and the surface :

$$V_b = V_{DC} + V_{AC} \sin(2\pi f_{mod} t)$$



Noncontact-AFM:

Cantilever vibrates in its fundamental eigenmode (f_0)

Attractive electrostatic force: $$F_{el} = \frac{1}{2}\frac{\partial C}{\partial z}V^2$$ with $$V = V_b - V_{CPD} = V_b - \Delta\Phi / e$$

$\Delta\Phi$ = Work functions difference between tip and sample (= CPD)

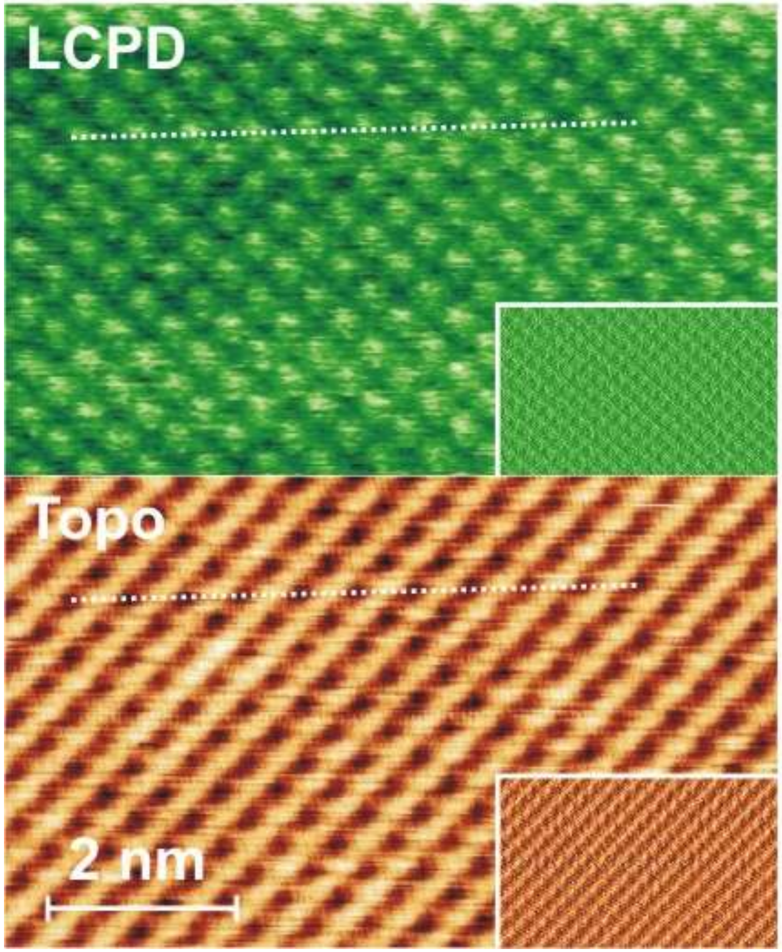
⇨ Induced vibrations of the cantilever at f_{mod} and $2f_{mod}$

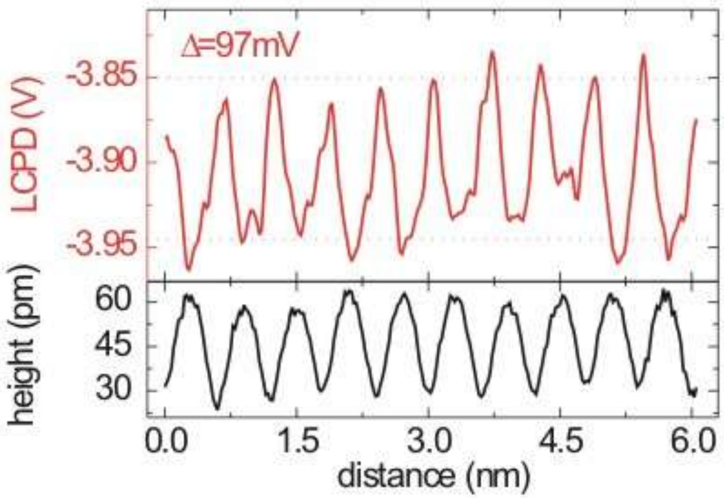
⇨ Detection and cancellation of the f_{mod} component (Δf in FM-KPFM, $A^{(1)}$ in AM-KPFM) by applying a proper DC bias voltage which matches the CPD

⇨ **V^2 DEPENDENCE OF THE FORCE REQUIRED, OTHERWISE NO KPFM CONTRAST**

Atomic-scale KPFM contrast on ionic surfaces

AM-KPFM (UHV) on bulk KBr(001)[1]





- ❑ Atomic-scale contrast of the CPD (Local CPD, LCPD):
  - ✓ **Madelung surface potential** of the crystal?
  - ✓Compliant with the magnitude of the measured signal?
  - ✓ Instrumentation (controllers)?
- ❑ Atomic-scale KPFM contrast as well reported on SC samples (earlier results), but neither understood in details

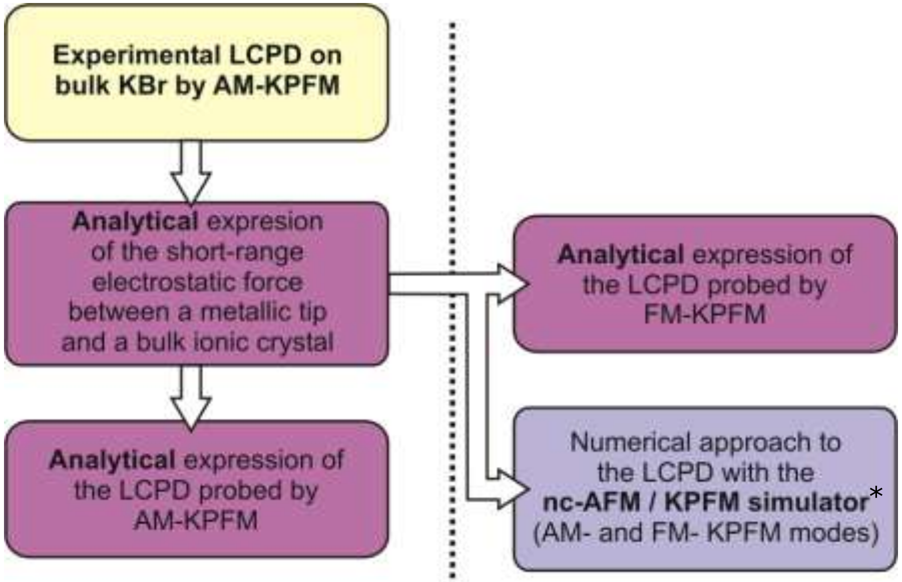
[1] F. Bocquet *et al.*, Phys. Rev. B **78**, 035410 (2008)

- **Short-Range and bias-dependent Electrostatic forces (SRE forces) play a key role in the occurrence of the atomic-scale contrast in KPFM images.**

- **What are the underlying processes?**

- **How do they influence the experimental measurement of the LCPD in terms of magnitude and lateral resolution?**

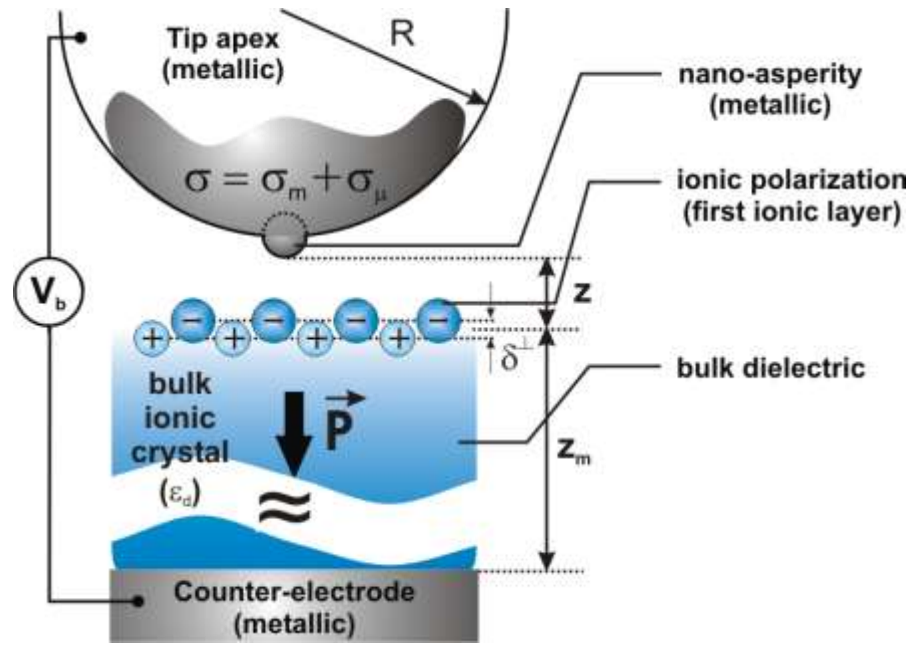
Our approach to the LCPD on KBr so far



F. Bocquet *et al.*, Phys. Rev. B **78**, 035410 (2008)

L. Nony *et al.*, Nanotechnology **20**, 264014 (2009)

Geometry of the problem:



Major findings:

❑ SRE forces, i.e. bias dependent forces with a short-range nature, do occur between the AFM tip and the surface when they are

❑ Not or

❑ The q … **s at the surface**

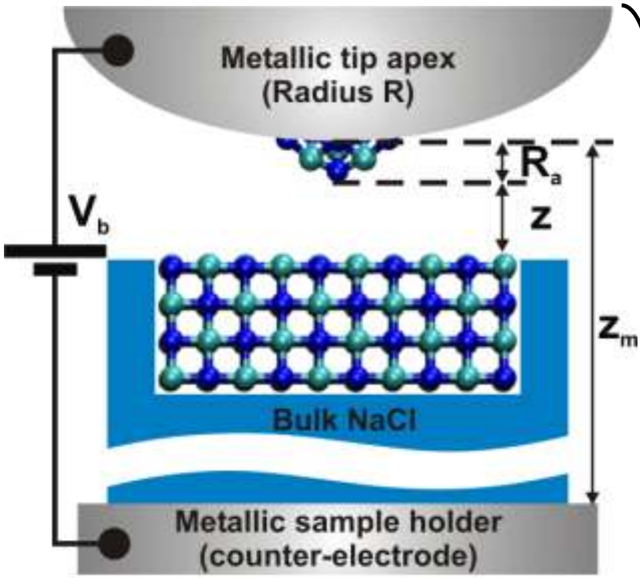
❑ The L … **crystal BUT not**

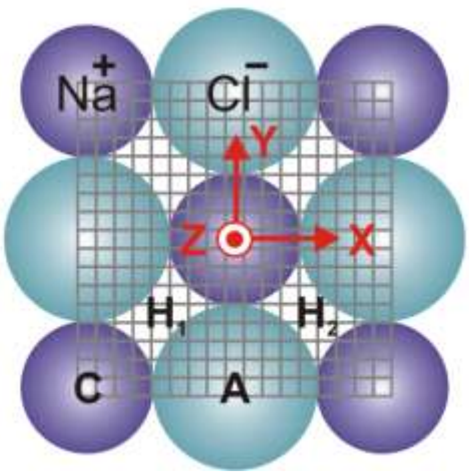
Combination between analytical SRE force and the simulator: usefull to understand the physics of the process. However, owing to the unrealitic geometry of the tip, large LCPD values are predicted (+/- 5 V between ionic and cationic sites) → not fully consistent with the experimental results (ranging from 0.1V up to +/- 2 V maximum)

BETTER DESCRIPTION OF THE TIP REQUIRED!

*L.Nony *et al.* Phys. Rev. B **74**, 235439 (2006)

Improving the model: fully numerical approach





L.Nony *et al.*, accepted in Phys. Rev. Lett.

- **Atomistic simulations (SciFi):**
  - ✓ ions treated atomistically in a core-shell model
  - ✓ **Ionic relaxation and electronic polarization and ionic polarization are taken into account**
  - ✓ force convergence criterion : 1 meV / Å / ion

- **Tip:**
  - ✓ metallic tip apex : 5nm radius
  - ✓ tip **cluster**: 4x4x4 described atomistically; oriented along the [111] direction w.r.t. the surface, Na-terminated
  - ✓ protrudes with an height R_a = 3Å from the metallic apex: **carries a charge of +1 compensated by applying -0.91V to the tip**

- **Sample:**
  - ✓ NaCl **slab**: 10x10x4 described atomistically
  - ✓ bulk NaCl: 5mm thick, described as a continuous medium

- **Mesh of the unit cell:**
  - ✓ X x Y x Z x V = 17 x 17 x (8nm-0.3nm)/0.005nm x (2.3V - -3.4V)/0.01 V ~ 255 Msamples to handle
  - ✓ **four particular sites investigated: cationic (C), anionic (A) and inequivalent hollow (H_1, H_2) sites**

(X, Y, Z, Bias) 4D force field + VdW + long-range capacitive force (~ V_b^2) → **nc-AFM / KPFM simulator (FM-KPFM mode)** → **Topographical & CPD images** / **Spectroscopic curves**

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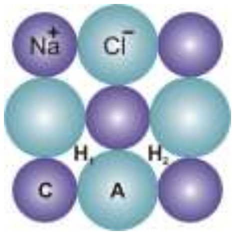
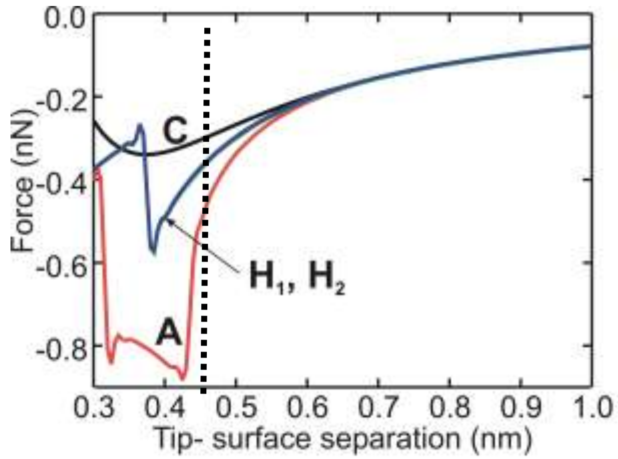
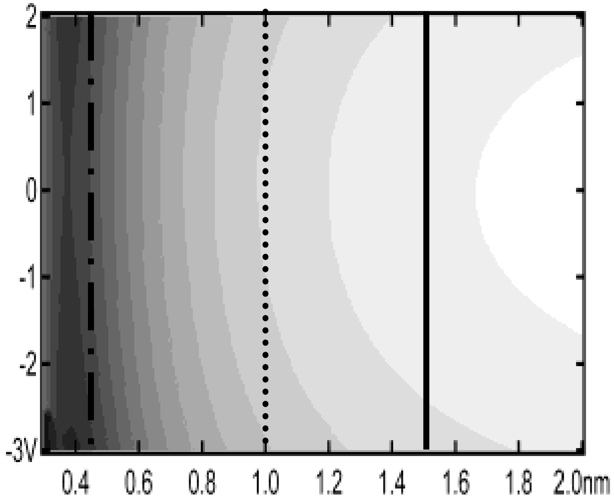
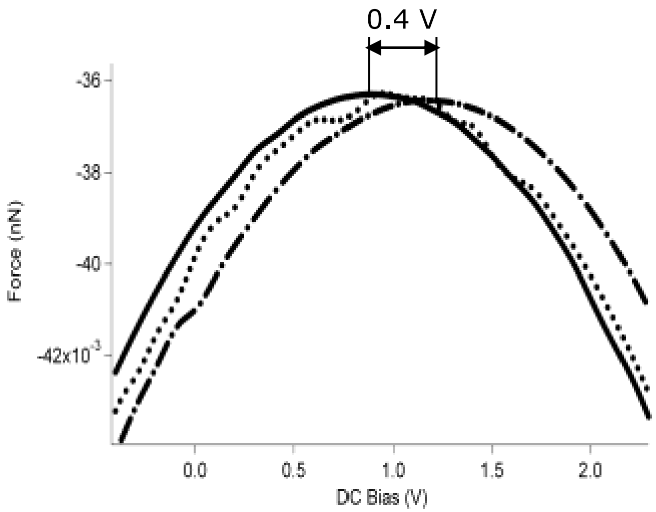
Force field: evidence for SRE forces



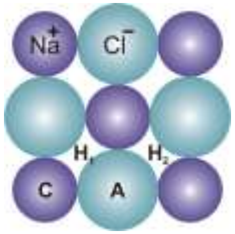


Evidence for SRE forces (top of a cation)

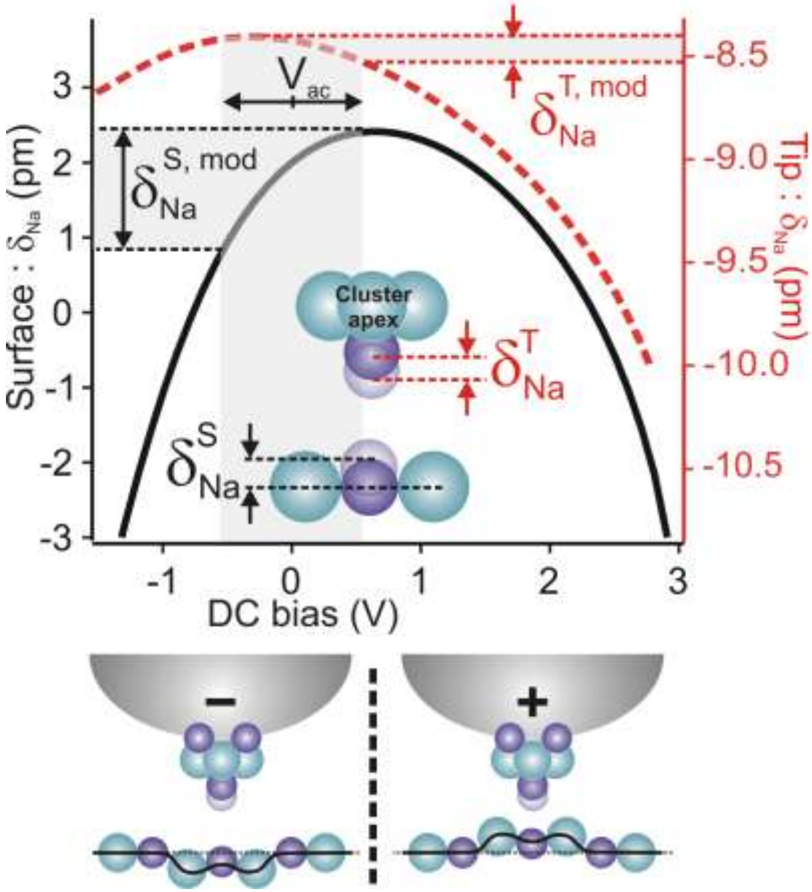




Ionic displacements at the tip-surface interface

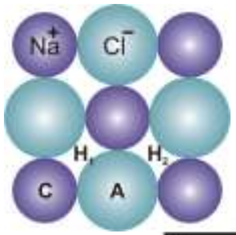


Cores displacements of the closest ions at the interface:



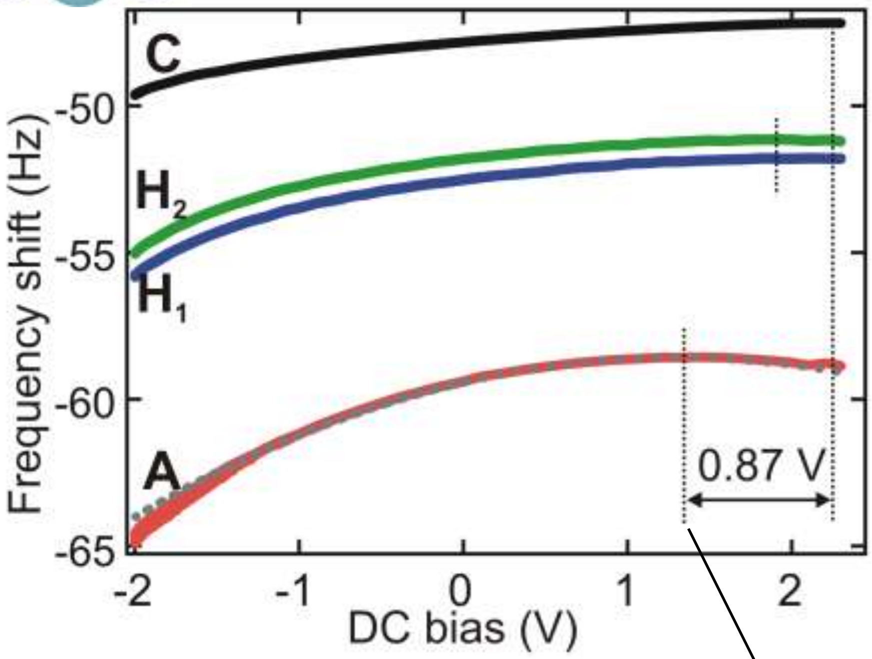
- ❑ AC Modulation of the applied bias triggers ionic displacements at the tip-surface interface
- ❑ Self-consistent influence between chemical and SRE forces
- ❑ Deviation from the usual capacitive (parabolic-like) force

Connection with the LCPD by means of the nc-AFM/KPFM (FM-KPFM) simulator



Simulated spectroscopic curves (Δf vs. V_{DC}):

z = 0.45 nm



-LCPD @ z=0.45nm site A

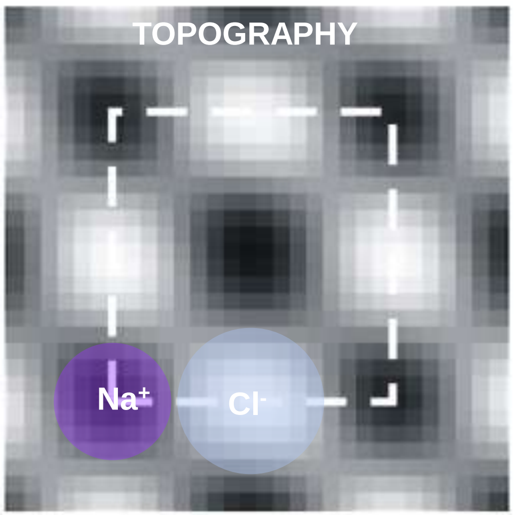
- ❑ No parabolic dependence (consistent with the force)
- ❑ LCPD is site-dependent (atomic-scale contrast possible)
- ❑ Resonance effect: experimentally observed and theoretically predicted

Numerical topographical and KPFM images

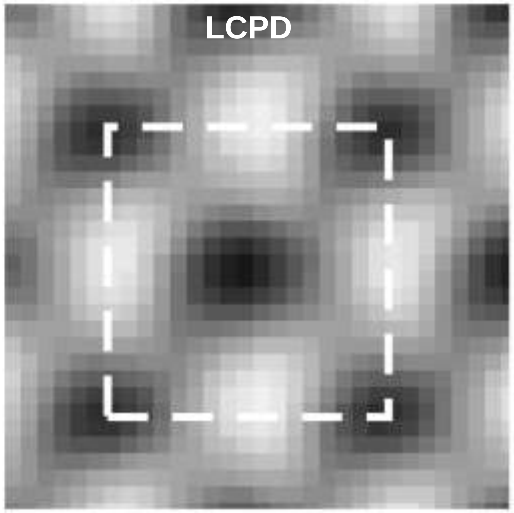
Simulated scans:

- ❑ nc-AFM (main) parameters: A_0 = 8 nm p-p ; Q = 35000 ; f_0 = 150 kHz
- ❑ FM-KPFM pamareters: V_{AC} = 0.5 V; f_{mod} = 1 kHz
- ❑ scan speed : 1.5 s/line

Distance controller engaged: Δf = - 47.22 Hz (z_{start} ~ 0.45 nm)

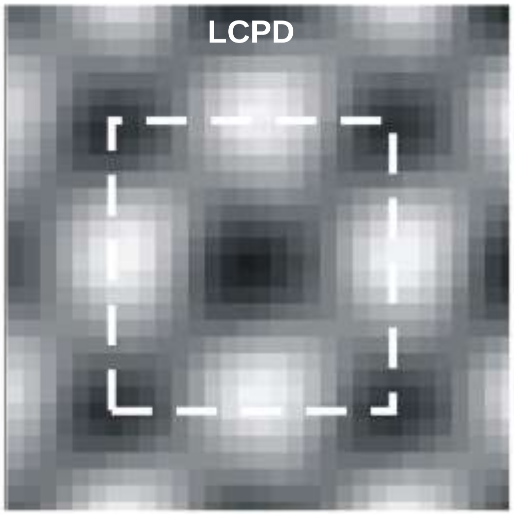


Contrast range: 38 pm



Contrast range: 0.56 V

Constant height: z = 0.45 nm



Contrast range: 0.86 V
→ consistent with the spectro. curves

- ❑ Simultaneous atomic-scale topographical and KPFM contrast
- ❑ Magnitudes of the contrasts **now consistent with the experimental observations** (30pm, 0.1V)
- ❑ The z-regulation prevents from measuring the “correct” LCPD value (spectro. curves)

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Take-home message

- Fully numerical approach to the atomic-scale KPFM contrast: combination of atomistic simulations with the nc-AFM / KPFM simulator

- SRE are site-dependent, which makes the achievement of the atomic-scale KPFM contrast possible

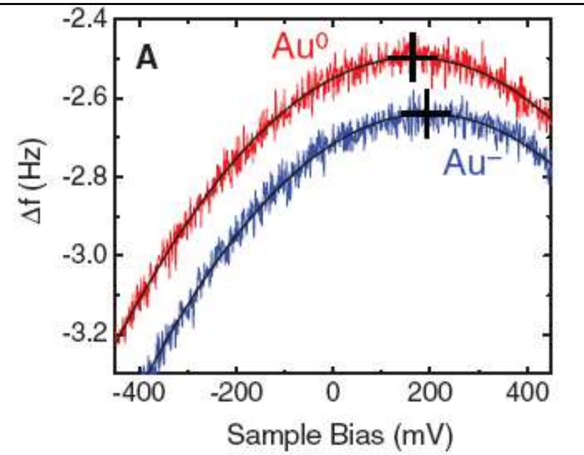
- The atomic-scale KPFM contrast relies on the ionic displacements at the tip-surface interface that are triggered by the AC modulation of the applied bias (in the range of ~ 1 to 2 pm only!!!)

- The LCPD contrast has the lateral periodicity of the Madelung surface potential but does not match it owing to self-consistent influence of chemical and SRE forces

Measuring the Charge State of an Adatom with Noncontact Atomic Force Microscopy

Leo Gross,[1*] Fabian Mohn,[1] Peter Liljeroth,[1,2] Jascha Repp,[1,3] Franz J. Giessibl,[3] Gerhard Meyer[1]

12 JUNE 2009 VOL 324 SCIENCE



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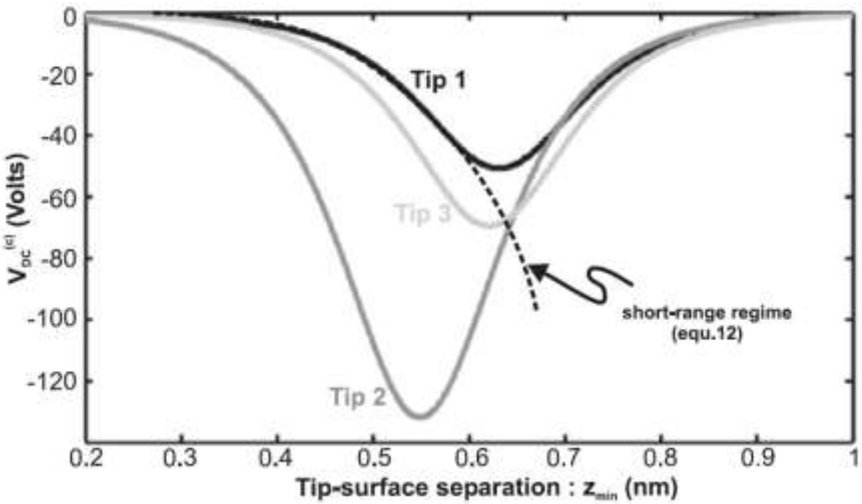
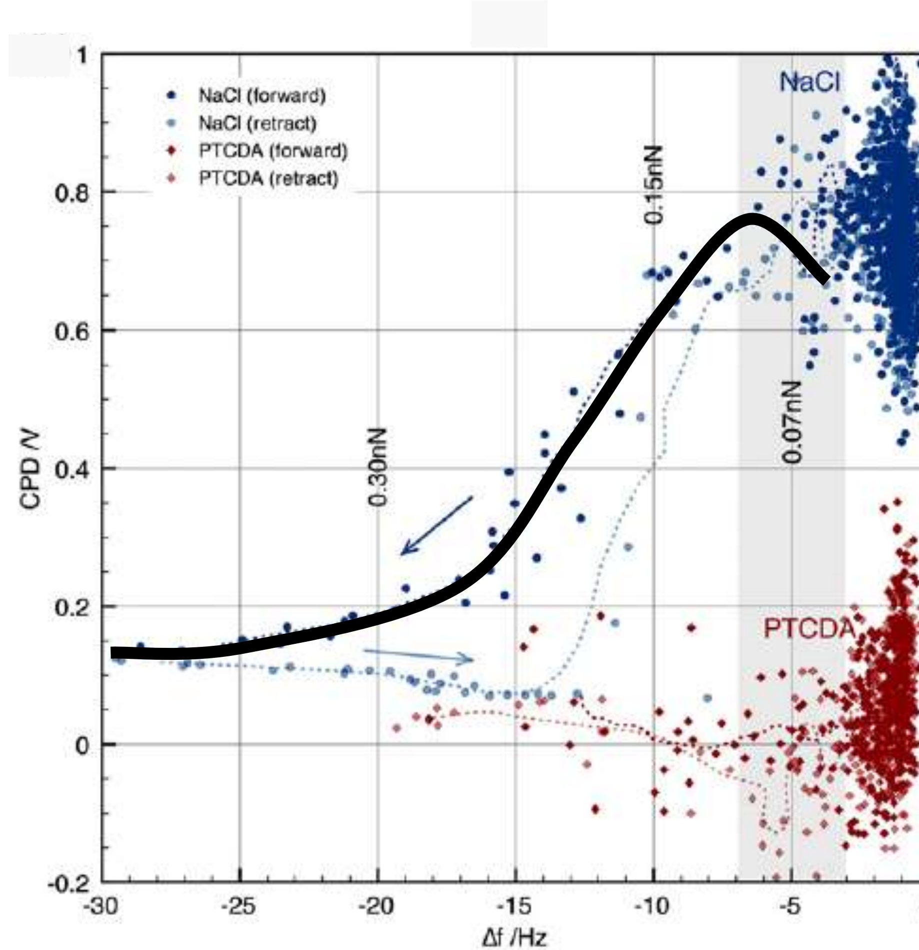
Resonance effect of the LCPD



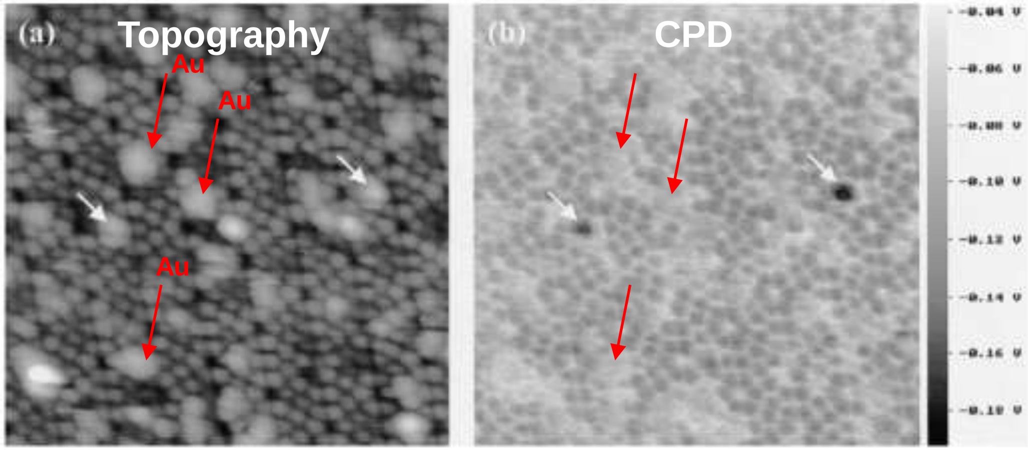
L. Nony et al., Nanotechnology **20**, 264014 (2009)



S. Burke et al., Nanotechnology **20**, 264012 (2009)

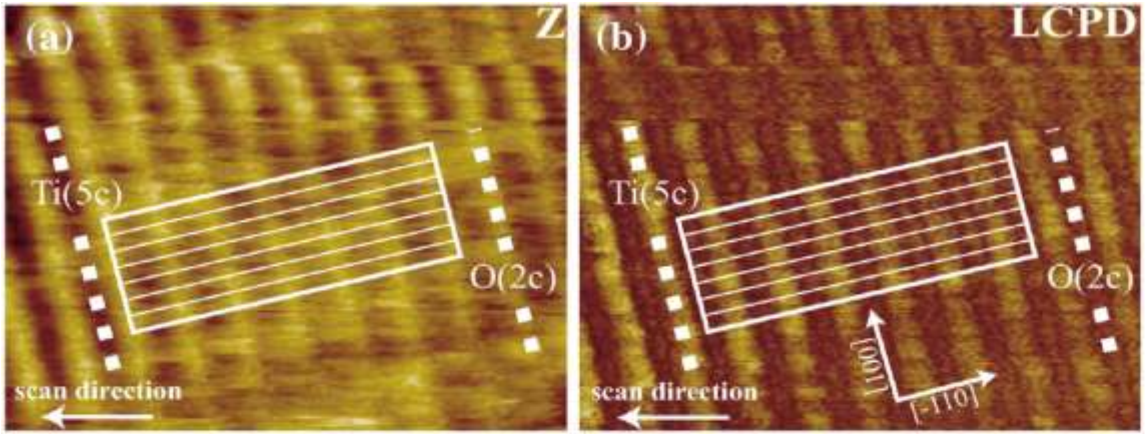
High-resolution KPFM: what is being measured?

- S. Kitamura *et al.*, Appl. Surf. Sci. **157**, 222 (2000) : **Au/Si(111) 7x7**



*"The potential difference of atomic structures...**does not seem to reflect the work function** as we initially expected. It is therefore considered that the atomic potential difference reflects the local electron density on the surface."*

- G.H. Enevoldsen *et al.*, Phys. Rev. Lett. **100**, 236104 (2008) : **TiO_2(110)**



*"... **the absolute values of the LCPD are determined to a very large degree by the tip sharpness** and the conductive nature of the tip (metallic, ionic), and a quantitative comparison between atomic-scale LCPD measurements and surface potentials derived by theory should take this finding into account."*

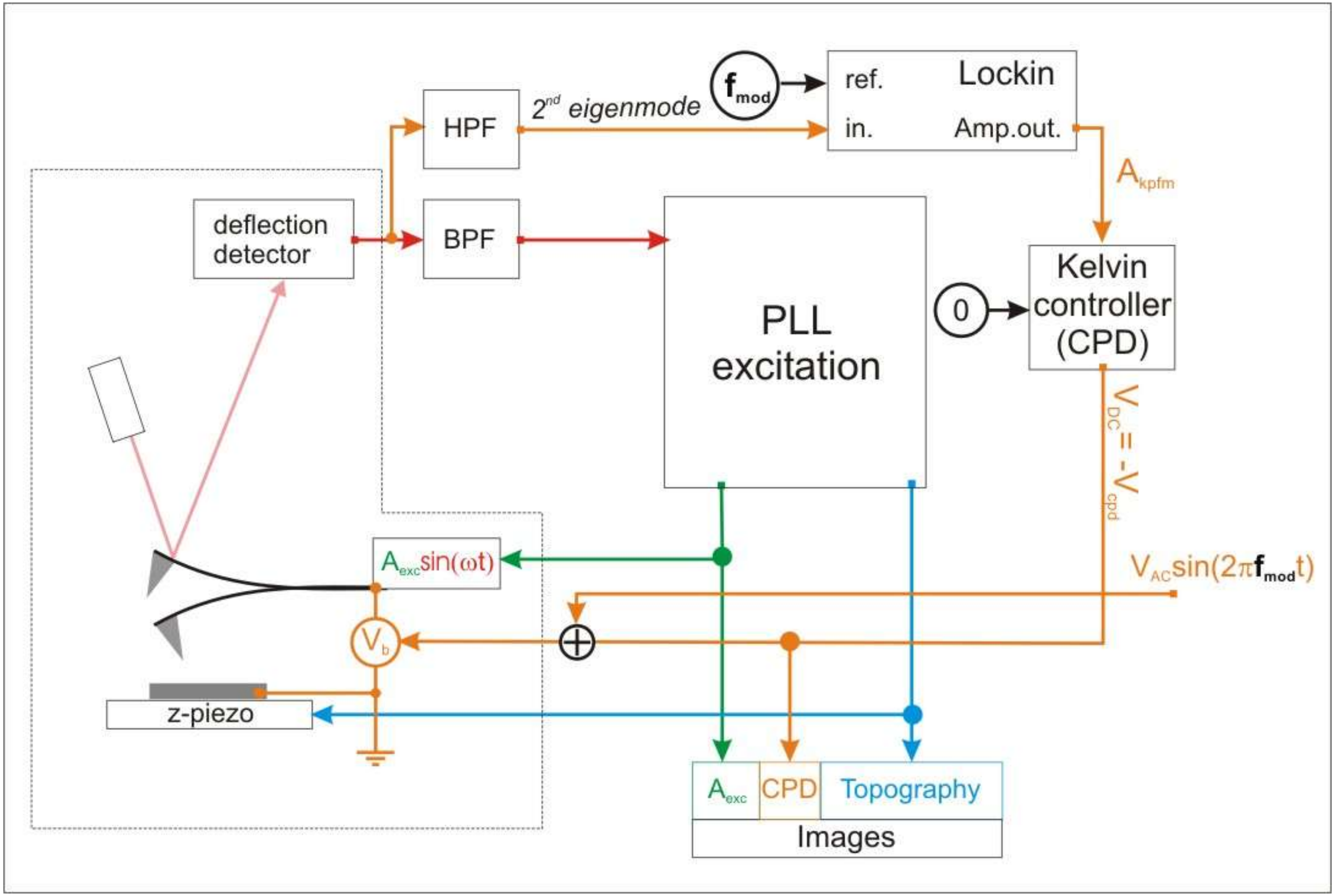
Features of the nc-AFM simulator[1]

- **Numerical implementation of a real nc-AFM electronic setup[2]** (mix of analog/digital devices)
- **The Phase-Locked Loop (PLL) detects Δf AND provides the phase-shifted excitation to the cantilever**
- Initially developed to address the issue of *apparent dissipation*

- **Main results :**
  - **No unwanted phase-shift if the PLL center frequency is continuously updated : *i.e.* no apparent dissipation**
  - **No apparent dissip. while : $2x\tau_{PLL} \sim 0.7$ ms $< \tau_{APIC} \sim 2$ ms $< \tau_{DPIC}$**
  - **Apparent dissipation can conditionally be generated, but can't exceed 15% of the intrinsic dissipation of the free cantilever : likely not experimentally relevant in UHV at room temp.**

[1]L. Nony *et al.*, Phys. Rev. B **74**, 235439 (2006), [2]Ch. Loppacher *et al.*, Appl. Phys. A **66**, 215 (1998)

Numerical implementation of the AM-KPFM mode within the nc-AFM simulator

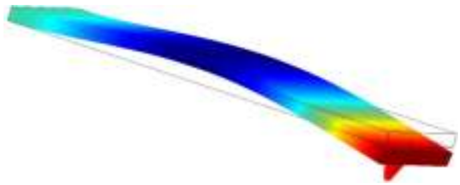


Numerical description of the coupling between the eigenmodes in AM-KPFM

First eigenmode :

f_0 ~ 150 kHz
k_0 ~ 30 N/m
Q_0 ~ 30000 (Δf_{HWHM}= 2.5 Hz)
Actuated mechanically

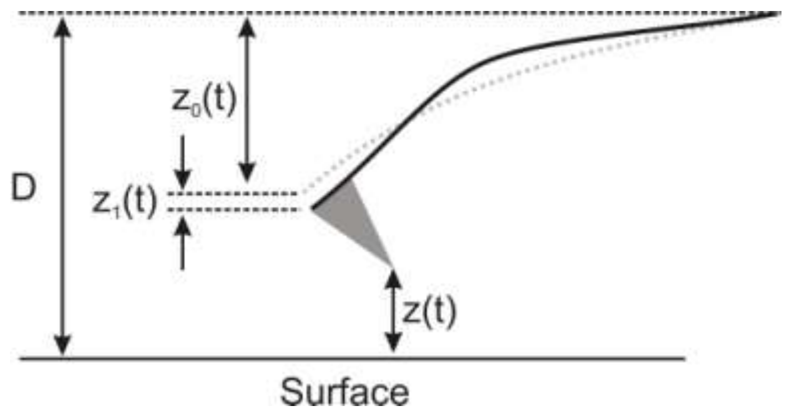
Second eigenmode :



$f_1 = 6.3f_0$ ~ 945 kHz
k_1 ~ $36k_0$ ~ 1100 N/m
Q_1 ~ 8000 (Δf_{HWHM}= 60 Hz)
Actuated electrostatically

Coupling occurs due to the **interaction force**
Instantaneous tip-surface distance :

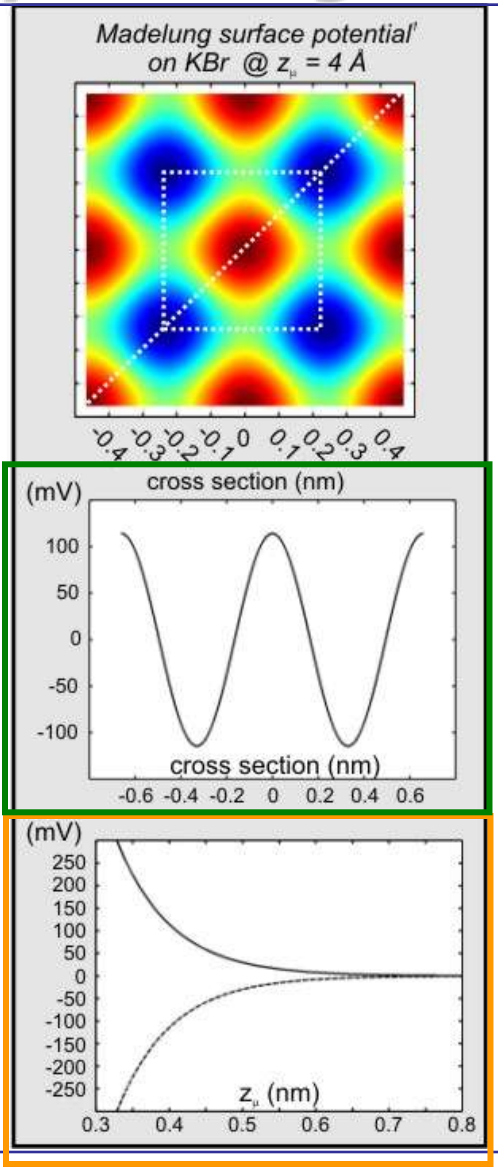
$$z(t) = D - z_0(t) - z_1(t)$$



How is the Madelung potential derived? Why is one single topmost ionic layer enough?

Madelung surface potential[1]:

$$V_s(x,y,z_\mu) = -\frac{q}{\pi\epsilon_0 a'}\cosh[\tilde{\delta}^{\perp}(V_b)]\tilde{\chi}(x,y)e^{-(2\pi/a')z_\mu}$$



[1] R.Watson *et al.*, Phys. Rev. B **24**, 1791 (1981)