Analytical and numerical approaches to the local contact potential difference on (001) ionic surfaces: implications for Kelvin Probe Force Microscopies

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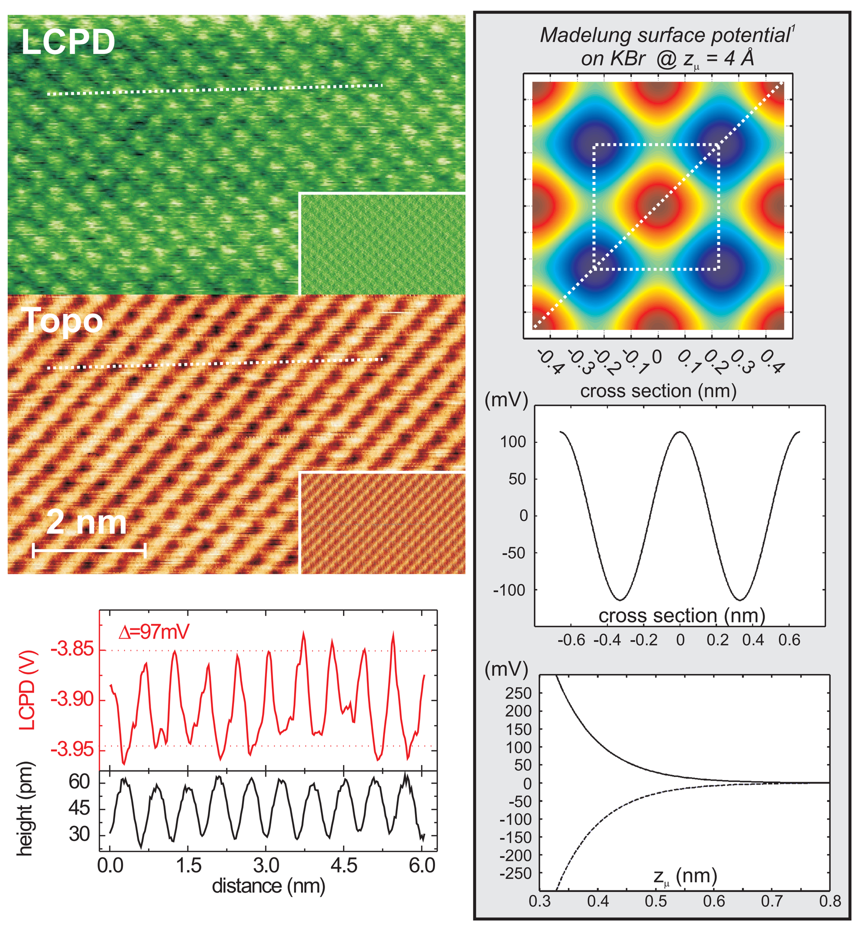
Abstract

An analytical model of the electrostatic force between a biased tip and the (001) surface of an ionic crystal is reported. The expression of the force can be split into two major contributions: the first stands for the coupling between the microscopic structure of the tip apex and the capacitor formed between the tip, the ionic crystal and the counter-electrode; the second term depicts the influence of the Madelung surface potential on the mesoscopic part of the tip, independently from its microscopic structure. The former has a short-range character with the lateral periodicity of the Madelung surface potential whereas the latter rather has a medium-range character and acts as a static component which shifts the total force. These electrostatic forces are in the range of ten pico-Newtons. Beyond the dielectric properties of the crystal, a major effect is the ionic polarization of the sample due to the influence of the tip/counter-electrode capacitor. When explicitly considering the crystal polarization, an analytical expression of the bias voltage to be applied on the tip to compensate for the "Local CPD" (LCPD), *i.e.* to cancel the electrostatic force, is derived in the AM-KPFM case.

Indeed, the analytical expression of the compensated CPD exhibits the lateral periodicity of the Madelung surface potential. However, the strong dependence of the force upon the atomic structure of the tip and upon the tip-sample distance makes questionable the possibility to quantitatively interpret KPFM measurements in the short-range regime. Nevertheless, the analytical approach remains helpful since it allows us to address in detail the influence of each contribution to the LCPD.

With this goal in mind, numerical simulations which mimic the usual KPFM bias spectroscopy curves have been performed with the nc-AFM simulator. When weighting differently the two contributions (short *vs.* medium-range), it is possible to derive a panel of trends, some of them having been experimentally observed. We have particularly focused on: i-the frequency shift of the first eigenmode of the cantilever, which is crucial while FM-KPFM experiments and ii-the evolution of the modulated amplitude of the second eigenmode of the cantilever, which is rather used while AM-KPFM experiments.

Experimental context

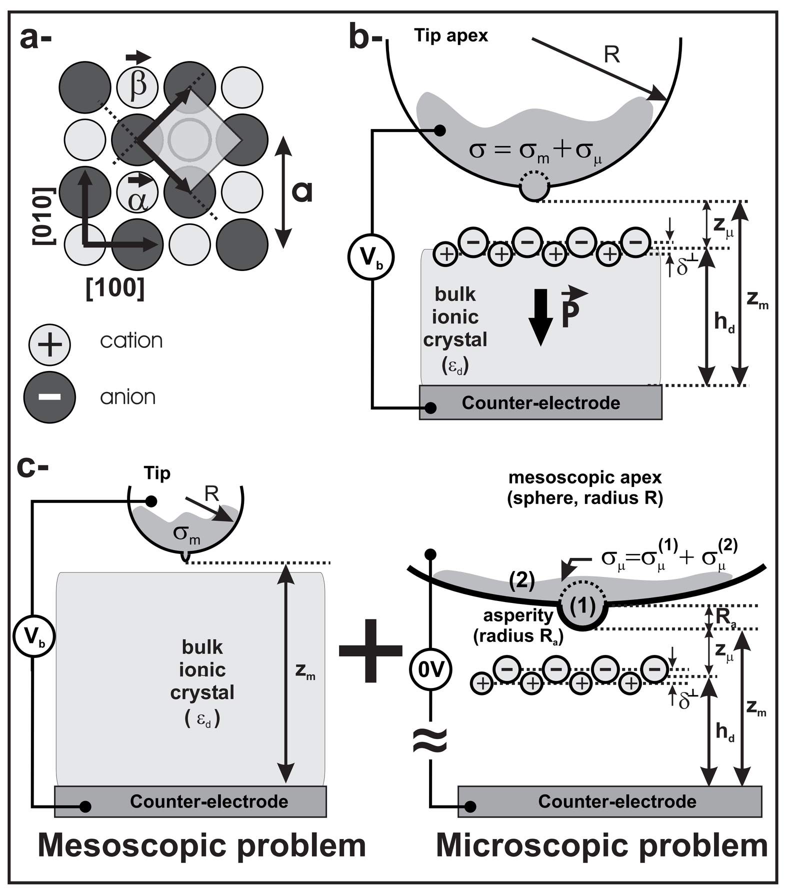


☑ **Contact Potential Difference atomic contrast on bulk KBr(001) by AM-KPFM (UHV)**

❓ Connection with the **Madelung surface potential**?
❓ Quantitative measurements?
❓ Instrumental artifacts?

☑ Analytical and numerical investigations
☑ Concept of **Local Contact Potential Difference**[2] **(LCPD)**

Electrostatic model[3]



☑ Tip apex: microscopic structure (nano-asperity, area 1, radius R_a) + mesoscopic half-sphere (area 2, radius R): **METALLIC**
☑ Surface charge density has 2 origins:
☞ **capacitive (mesoscopic) contribution: σ_m, connected with V_b**
☞ **Madelung surface potential-mediated (microsc.) contribution: σ_μ**
☑ Explicit description of the ionic polarization of the sample
☑ Classical approach

$$F_{es} = \int_{\text{tip}} \frac{(\sigma_m + \sigma_\mu)^2}{2\epsilon_0} \hat{n}.\hat{u}_z dS = F_m + F_{m\mu} + F_\mu$$

$$F_{es} = F_{m\mu}^{(1)} + F_{\mu}^{(2)}$$

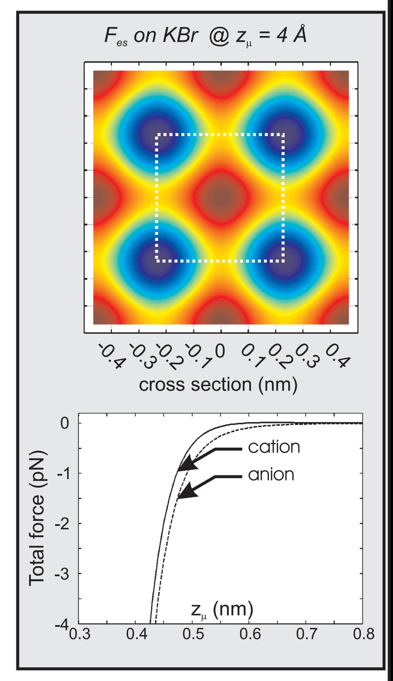
short-range electrostatic force

force due to the capacitive coupling on the nanoasperity : V_b

force due to the image charges of the ions within the mesoscopic part of the tip influenced by the Madelung surf. pot. : V_b^2

$$F_{es}(V_b) = B \times V_b \exp\left\{-\frac{2\pi}{a'} z_\mu\right\} \times [\cos(\tilde{x}_0) + \cos(\tilde{y}_0)] + (A V_b^2 + C) \times \exp\left\{-\frac{4\pi}{a'} z_\mu\right\}$$

with $V_b = V_{dc} + V_{ac} \sin(2\pi f_K t)$



AM-KPFM

Bias modulation : $f_K = 6.24\ f_0$ (2nd res.)
Goal : $A_K(V_{dc}) = 0$

Analytic expression for A_K:

Differential equation for the 2nd eigenm. (z_1) : triggered by F_{es}

☑ Dynamics of the fundamental eigenm. not influenced by z_1
☑ A_K << lattice constant
☑ z_1 dynamics only governed by f_K terms: $z_1(t) = A_K \sin(2\pi f_K t + \varphi_K)$

$A_K(V_{dc}, z_\mu)$

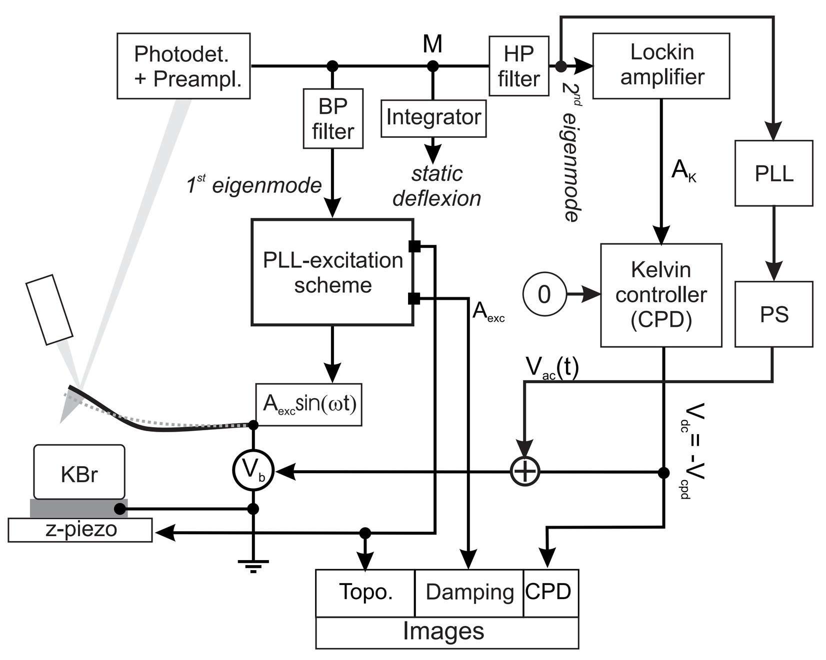
Condition on V_{dc} to get $A_K(V_{dc}, z_\mu) = 0$:

Equ. 1

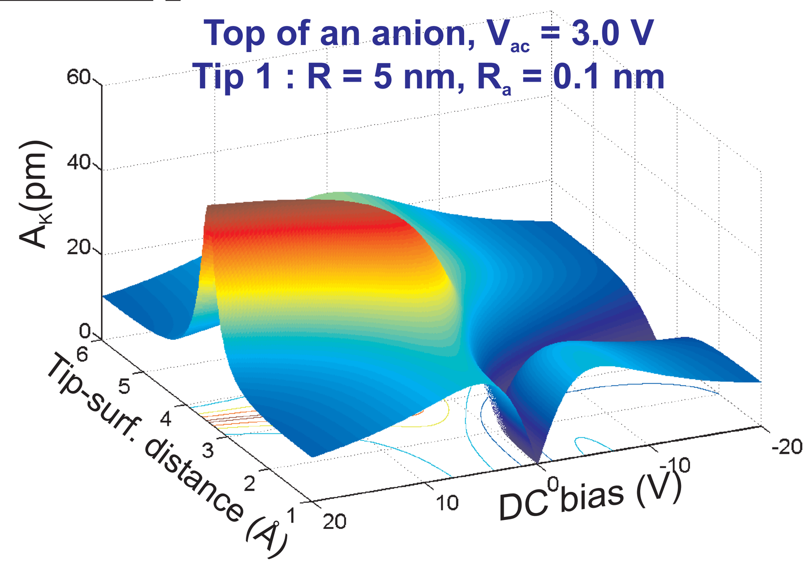
$$V_{dc}^{(c)} = -\frac{\tilde{\epsilon}_d \epsilon_0 a'^2}{4\pi \chi_d'^2} \frac{a_0}{b_0} \frac{K_{m\mu}^{(1)}}{K_{\mu}^{(2)}} e^{\frac{2\pi}{a'}(D+R_a-A_0)} (\cos(\tilde{x}_0) + \cos(\tilde{y}_0))$$

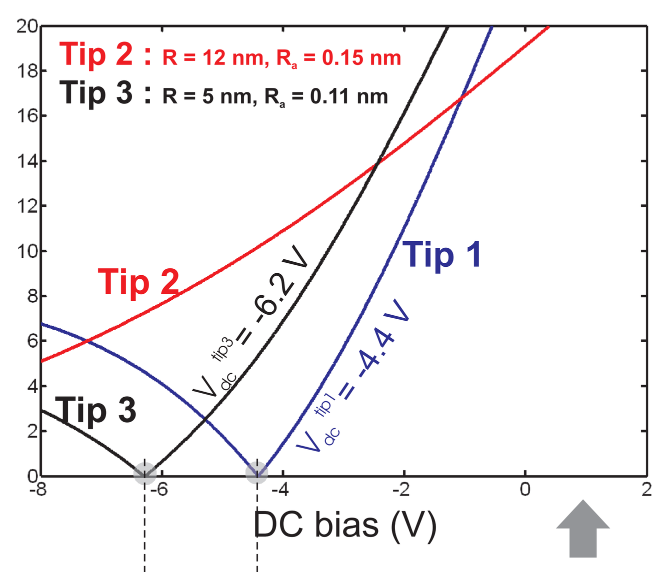
Tip geometry parameters
0 order Fourier coefficients of the exponential terms in F_{es}
Tip-surface distance dependence
Madelung potential spatial modulation

Numerical implementation[5]:

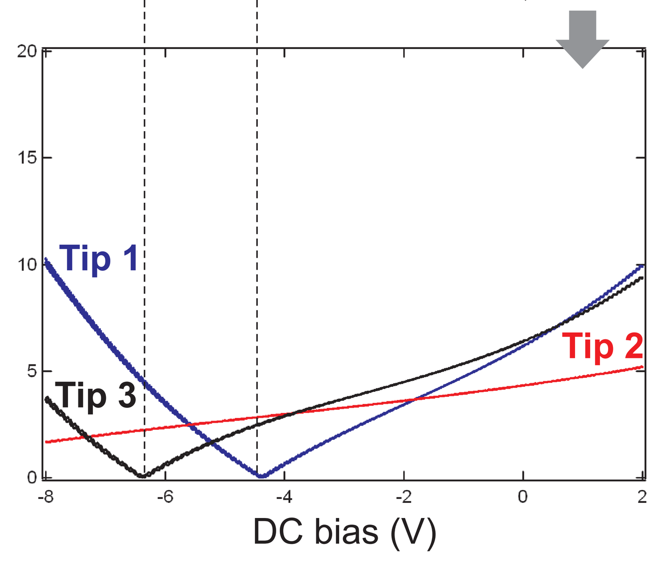


Results[6]:





Spectroscopy (z_μ = 3.0 Å)



FM-KPFM

Bias modulation : f_K ~ 2.5kHz
Goal : $\Delta f(V_{dc})$ = minimum

Analytic expression for Δf_{es}:

F. Giessibl's formula[4]:

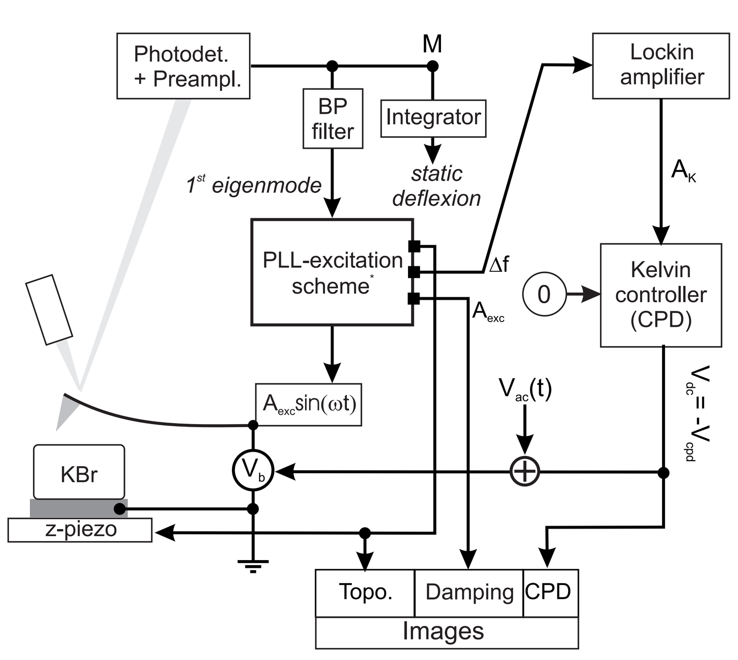
$$\Delta f_{es} = -\frac{f_0}{k_0 A_0} \int_0^{1/f_0} F_{es}(V_b) \cos(2\pi f_0 t) dt$$

$\Delta f_{es}(V_{dc}, z_\mu)$

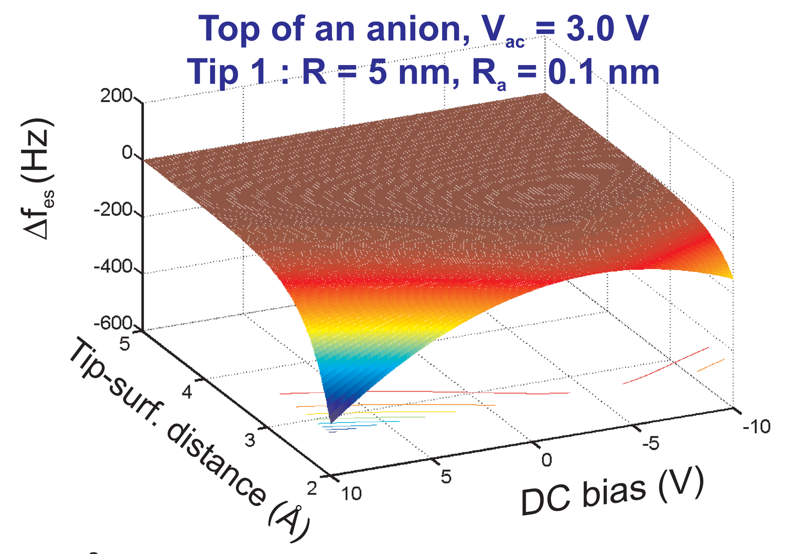
Condition on V_{dc} to minimize Δf :

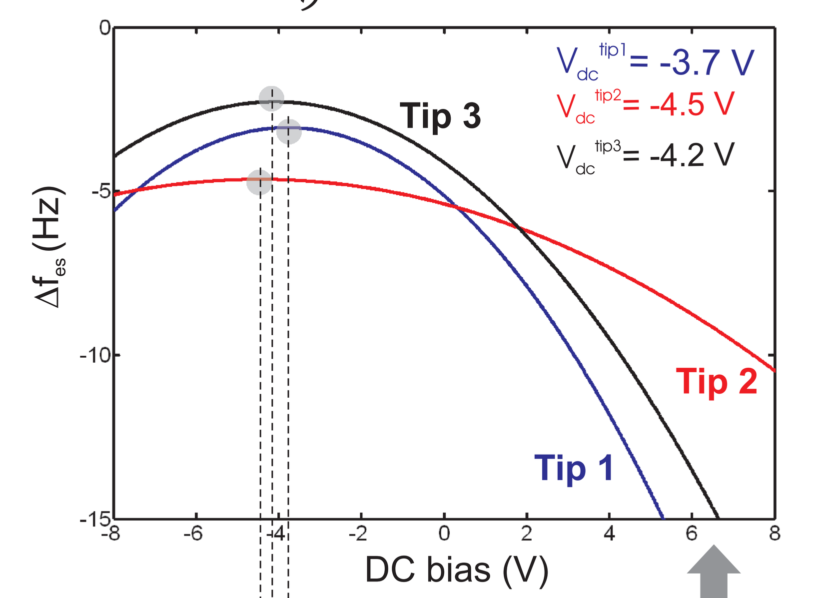
Derivable, but not tractable!
Exhibits :
☑ Madelung surface potential spatial modulation
☑ Tip-surface dependence
☑ Tip geometry dependence
☑ Experimental parameters dependence

Numerical implementation[5]:

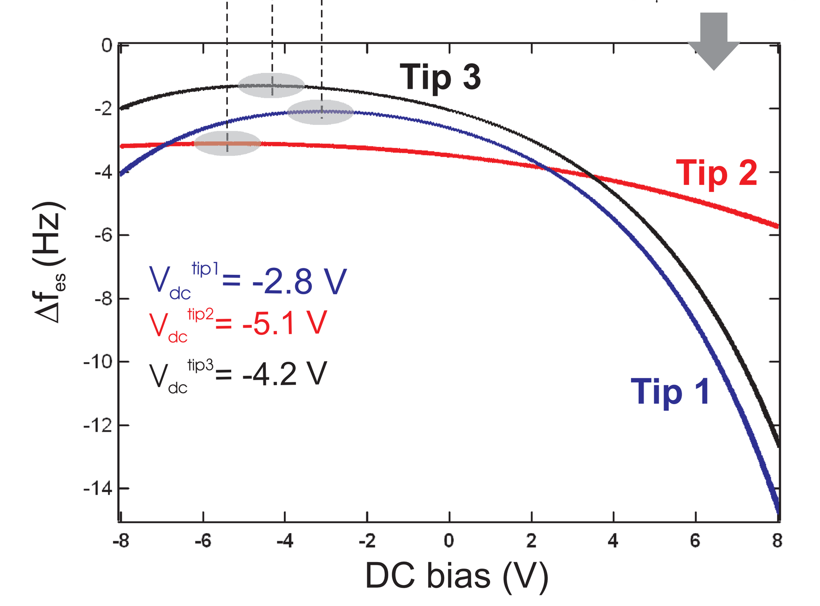


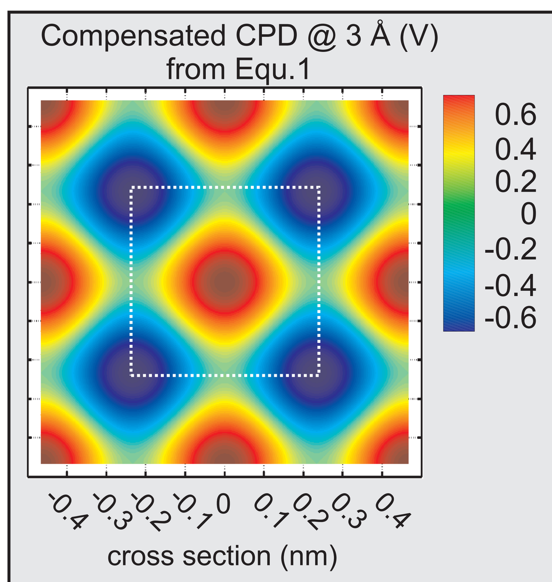
Results[6]:





Spectroscopy (z_μ = 3.0 Å)





Summary

☑ **Local CPD correlated to the lateral periodicity of the Madelung surface potential**
☑ **BUT the experimental contrast can't directly be fitted with the Madelung surface potential:**
☞ **strong tip-geometry dependence**
☞ **experimental parameters dependence (A_0, V_{ac})**
☑ AM- and FM-KPFM do not provide similar LCPD contrast under similar conditions
☑ Some (not necessarily blunt!!!) tips do not produce LCPD within the range of standard dc voltages (+/- 5 V)

Outlooks

☑ Inverse problem (measurements → Madelung potential) feasible, but really meaningful?
☑ Influence of other forces on the measured LCPD : chemical short-range, Van der Waals?

References & Notes :
1 - R.E. Watson *et al.*, Phys. Rev. B **24**, 1791 (1981)
2 - The concept of "Local Work Function" has already been introduced by K. Wandelt (Appl. Surf. Sci. **111**, 1 1997) on metals
3 - F. Bocquet *et al.*, Phys. Rev. B **78**, 035410 (2008)
4 - F. Giessibl, Phys. RevB **56**, 16010 (1997)
5 - L. Nony *et al.*, Phys. Rev. B **74**, 235439 (2006)
6 - The generic parameters for analytic and numeric approaches are similar : A_0 = 4 nm, f_0 = 150 kHz, no Van der Waals interaction, no chemical short-range interaction. The numerical settings for the PLL and the amplitude controller are optima (cf. ref.[5]), which ensures that the phase and A_0 are always properly adjusted.

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