OAK RIDGE National Laboratory

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Investigation and Manipulation of Domains on Small Length Scales in Ferroelectric Materials: Limits and Opportunities

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Outline

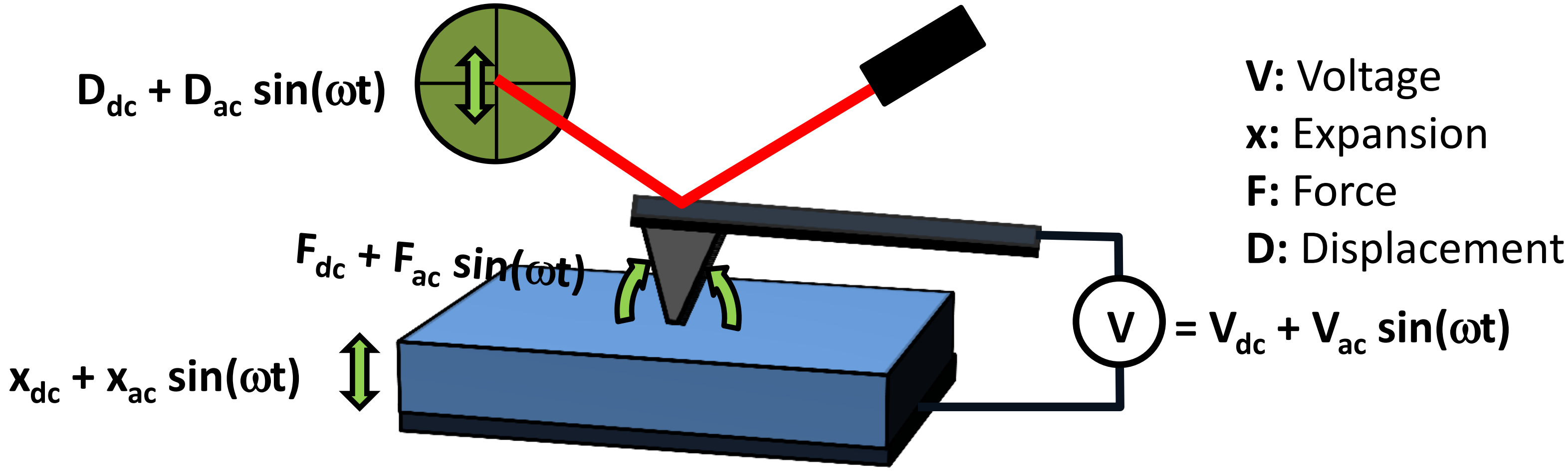
- What can we study?
  - → *Electromechanical phenomena overview*
  - → *Ferroelectrics in particular*
  - →*"New" ferroelectrics (ultra-thin, strained, ...)*
- Dominant signal contribution for ferroelectrics
  - → *d_{33} and electrostatic tip-sample interaction*
- Ionic transport in Li-ion battery cathodes
- Solid-liquid interface and EDL for ionic liquids
- Summary

What Can We Study?

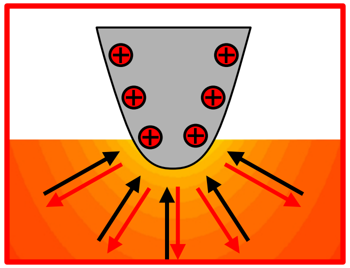
Scanning Probe Microscopy (SPM)

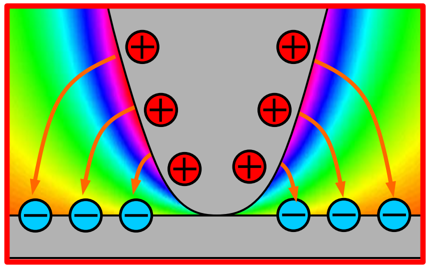
Investigate electromechanical phenomena on the nanoscale

Practical: Apply a bias → Measure change in cantilever position

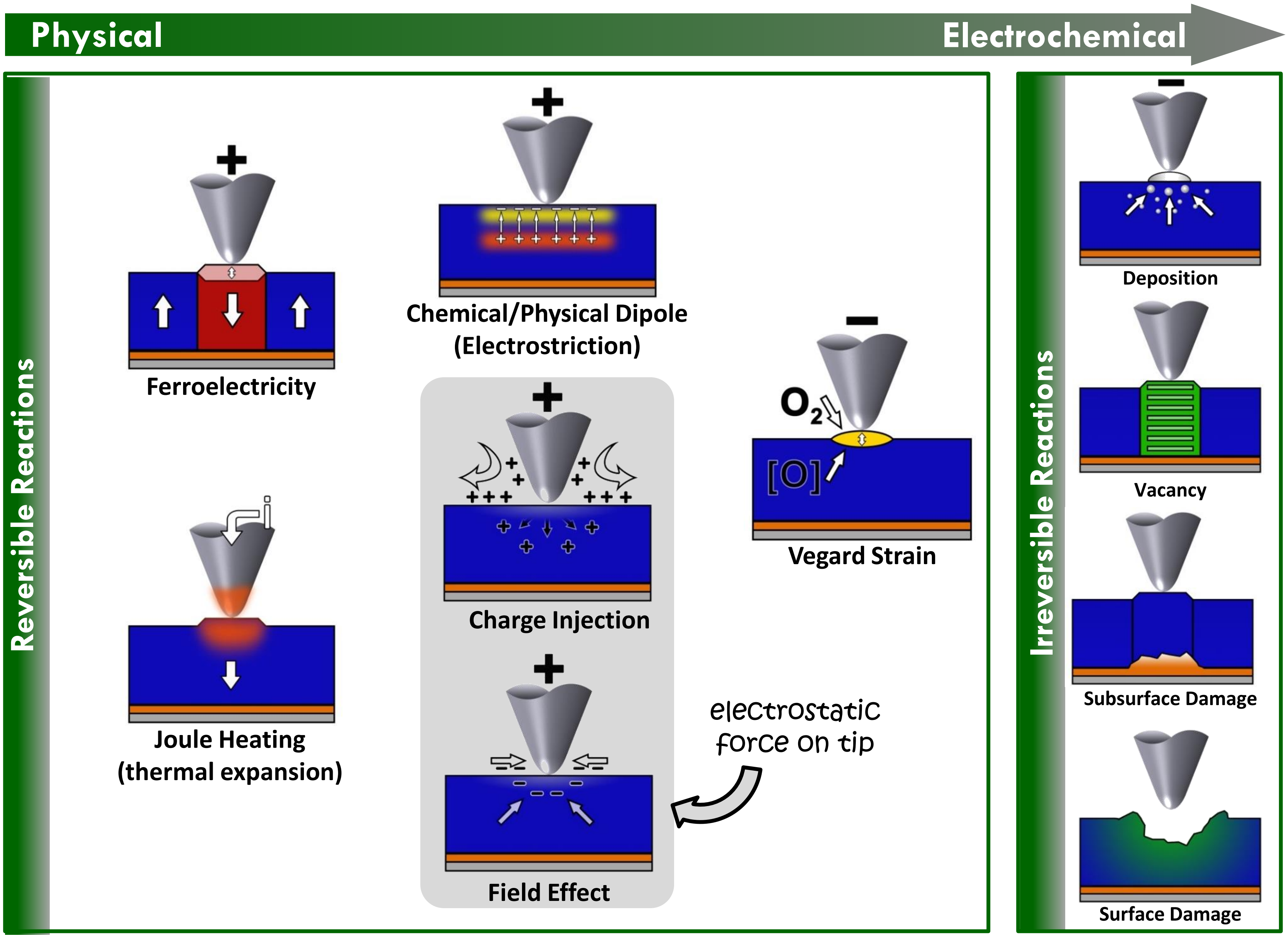


1) Sample volume expansion vs. force on tip
2) Static vs. dynamic





Electromechanical Phenomena

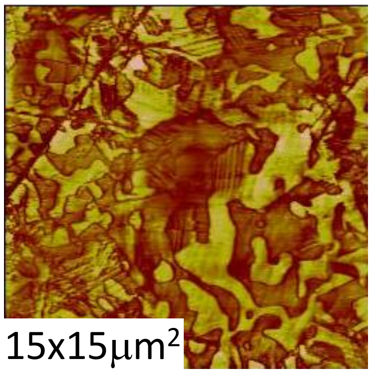


Stephen Jesse

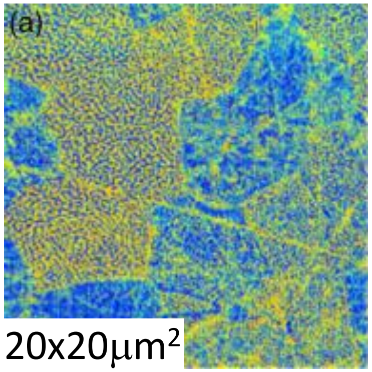
Piezoresponse Force Microscopy (PFM): Domain imaging (V_{ac}) and manipulation (V_{dc})

Imaging of OP and IP domains in ceramics and thin films

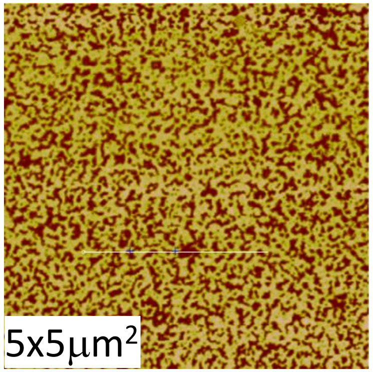
Ceramic PZT



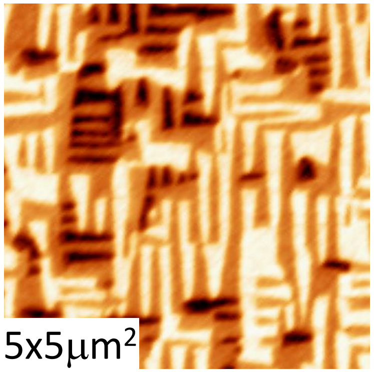
Ceramic PLZT



PZT thin film

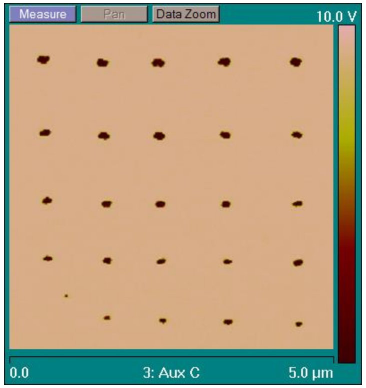


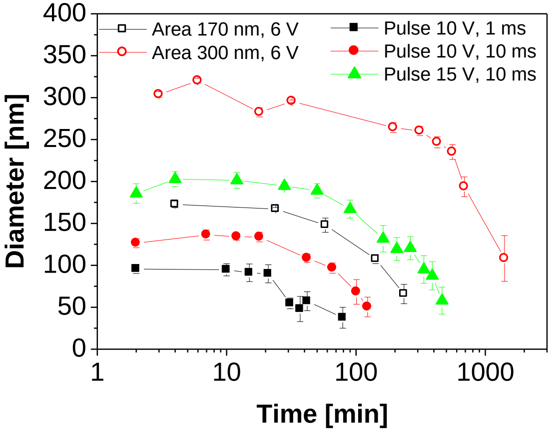
BFO thin film

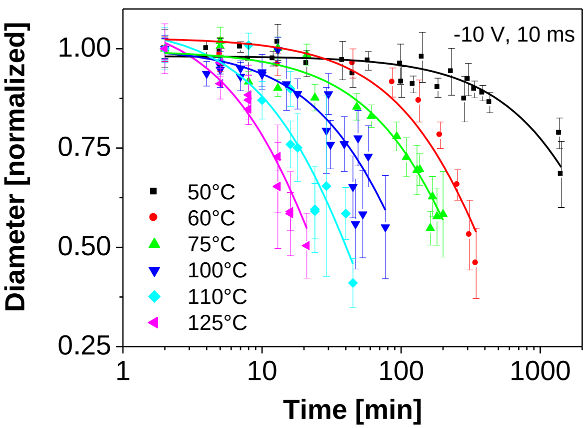


Stability of nanodomains

PZT thin film



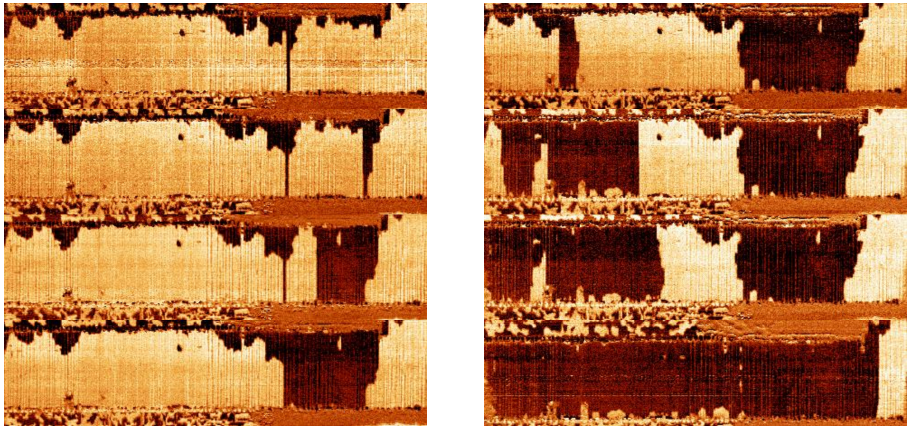




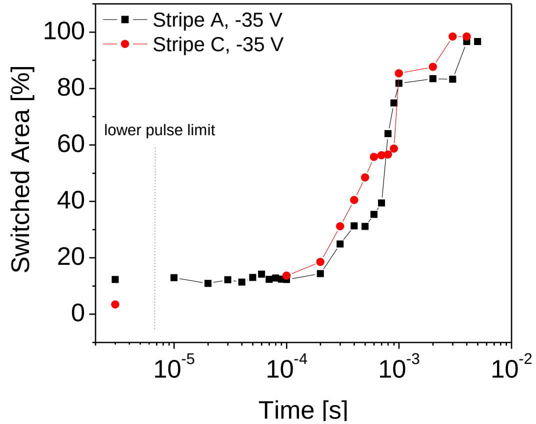
Ferroelectrics

In-plane capacitor switching

BFO thin film



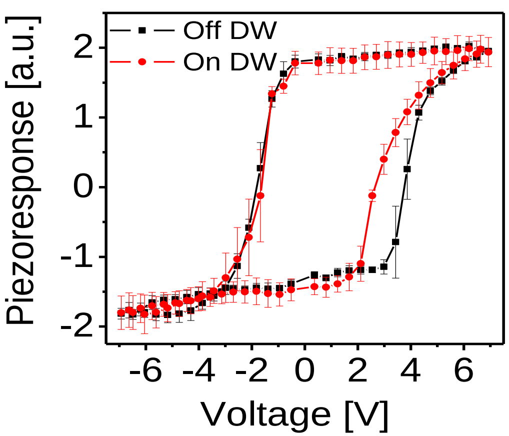
Increasing time



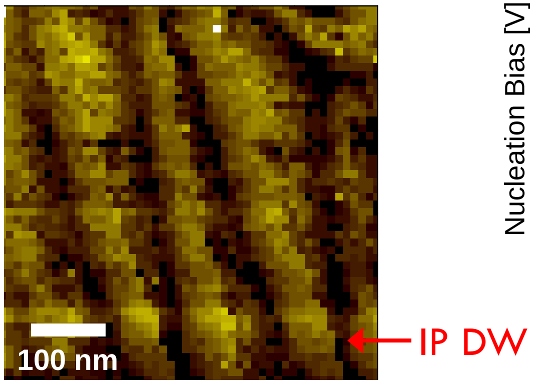
Balke et al., Adv. Func. Mater. 20, 3466 (2010)

Map of switching parameters

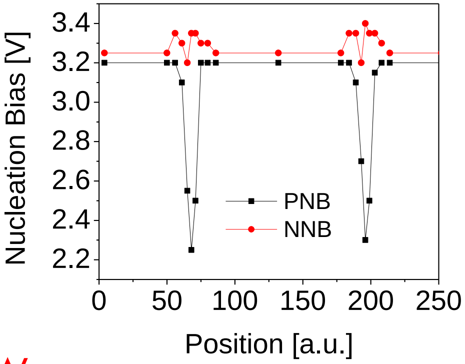
BFO thin film

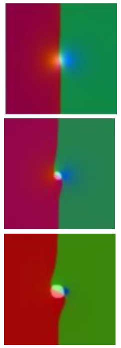


Map of positive nucleation voltage



Simulation of nucleation voltages



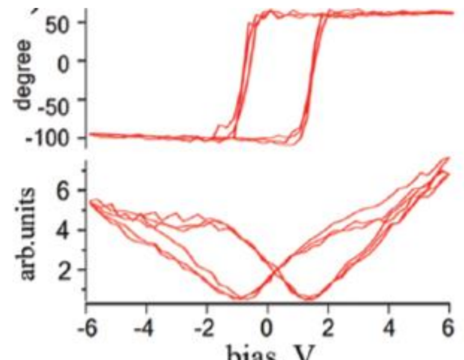


Balke et al., Nat. Nanotechnol. 4, 868 (2009)

Pushing the limits … is everything ferroelectric?

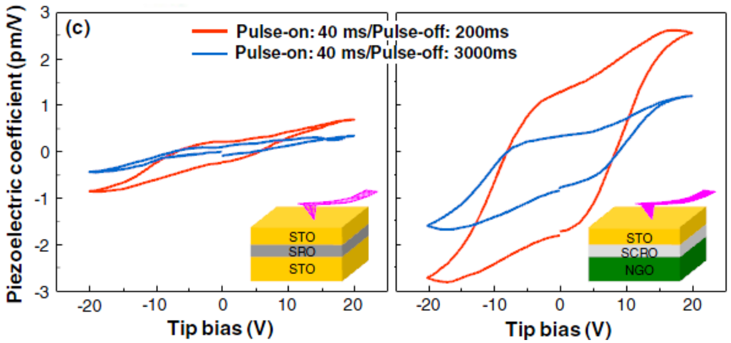
"New" ferroelectrics

Ultra-thin BTO



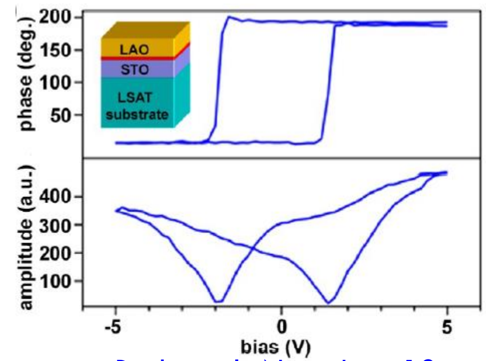
Gruverman et al., Nano Lett. 9, 3539 (2009)

Strained and strain-free STO



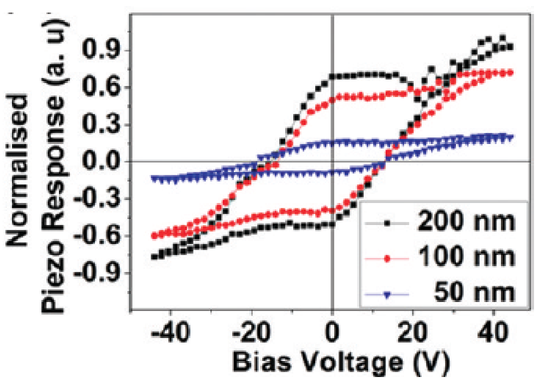
Jang et al., PRL 104, 197601 (2010)

LAO/STO



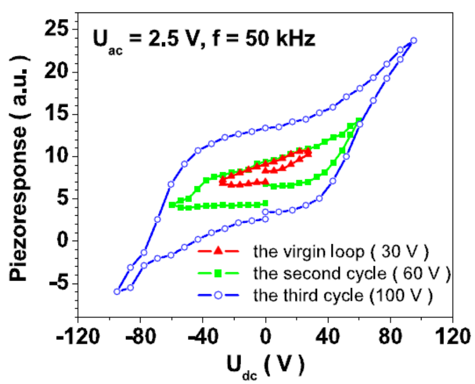
Bark et al., Nano Lett. 12, 1765 (2012)

Sb_2S_3



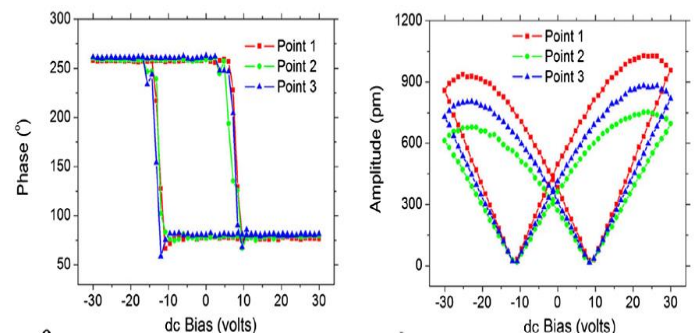
Varghese et al., Nano Lett. 12, 868 (2012).

ZnO



Bidkin et al., Nanotechnol. 21, 235703 (2010)

Aortic walls



Liu et al., PRL 108, 078103 (2012).

Dominant Signal Contribution for Ferroelectrics

d_{eff}: effective piezoelectric constant
k: stiffness
C': Capacitance gradient

$$V = V_{dc} + V_{ac}\sin(\omega t)$$

Piezoelectricity

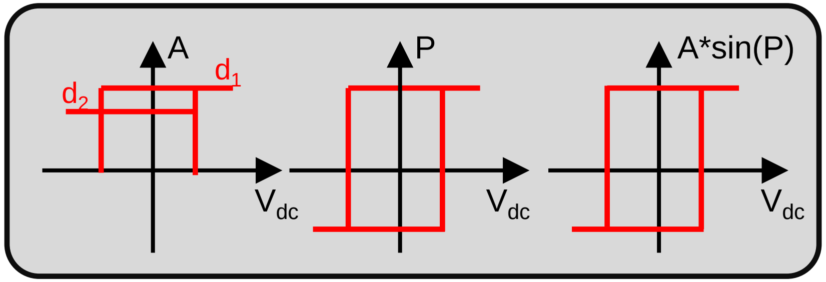
$$x = d_{eff} V$$

$$x = d_{eff}[V_{dc} + V_{ac}\sin(\omega t)]$$

$$x_\omega = d_{eff} V_{ac}\sin(\omega t)$$

$$x_\omega = d_{eff}(V_{dc}) V_{ac}\sin(\omega t)$$

⇒ sample dependent



Electrostatics

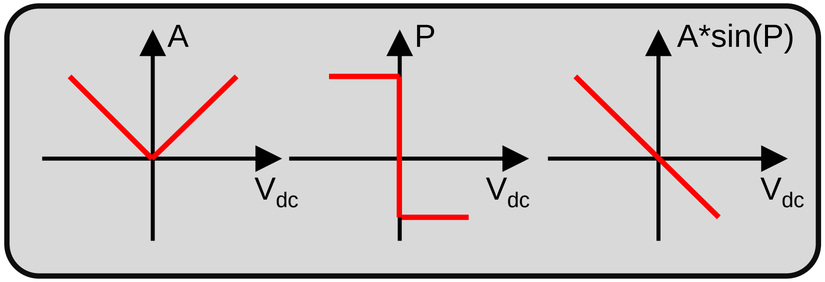
$$x = \frac{1}{2} k^{-1} C' V^2$$

$$x = \frac{1}{2} k^{-1} C' [V_{dc} + V_{ac}\sin(\omega t)]^2$$

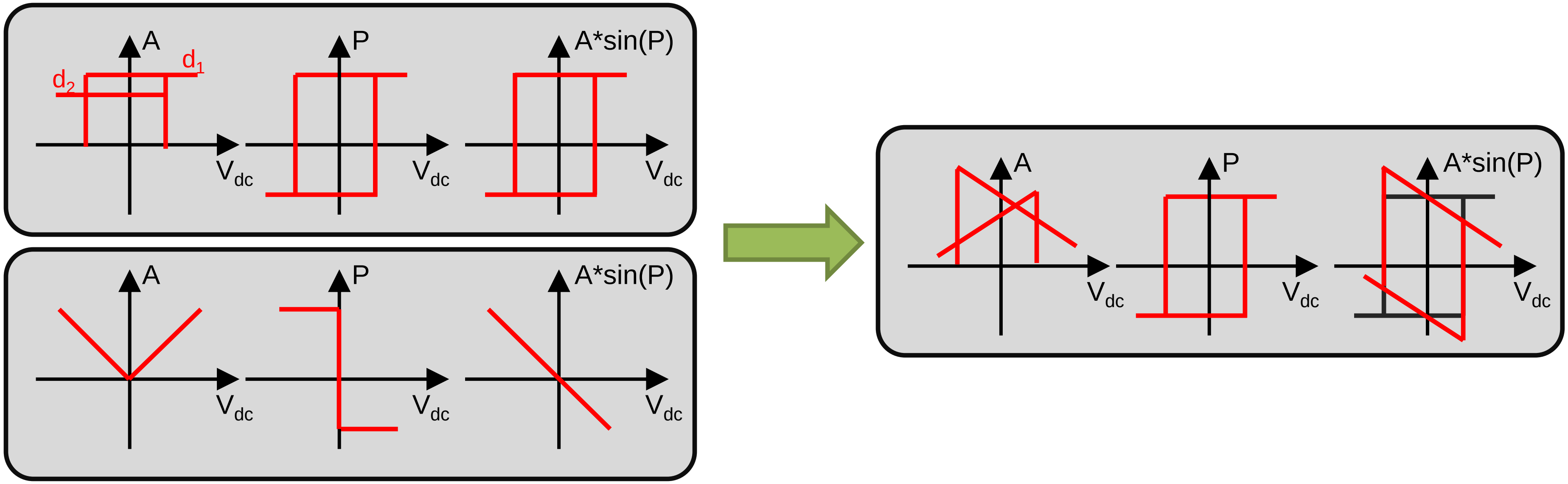
$$x_\omega = k^{-1} C' V_{dc} V_{ac}\sin(\omega t)$$

⇒ tip and sample dependent

$$x_{2\omega} = \frac{1}{4} k^{-1} C' V_{ac}^2 \cos(2\omega t)$$



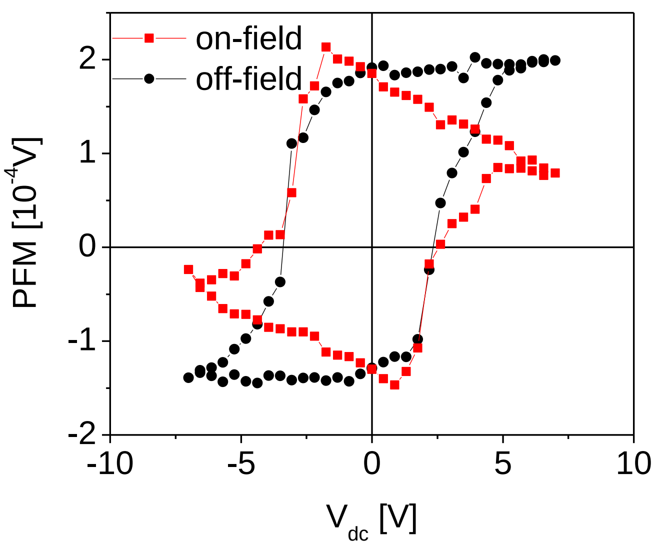
Ideal Ferroelectrics

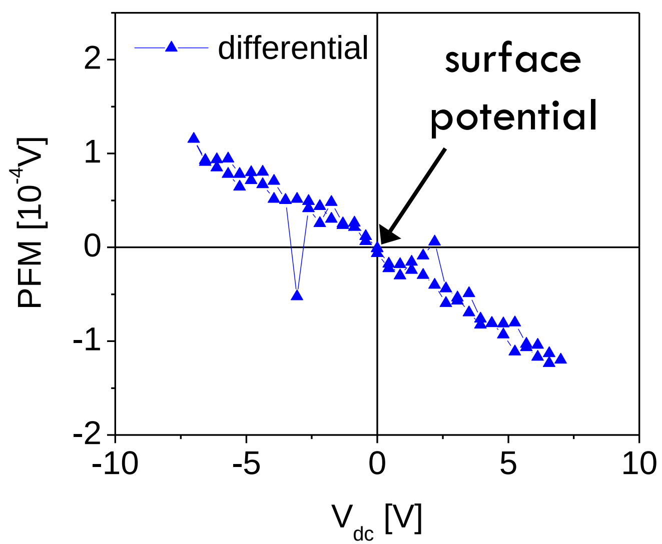


<u>PZT thin film</u>

On-field: $V_{dc}+V_{ac}$
- *Piezoresponse*
- *Electrostatics*

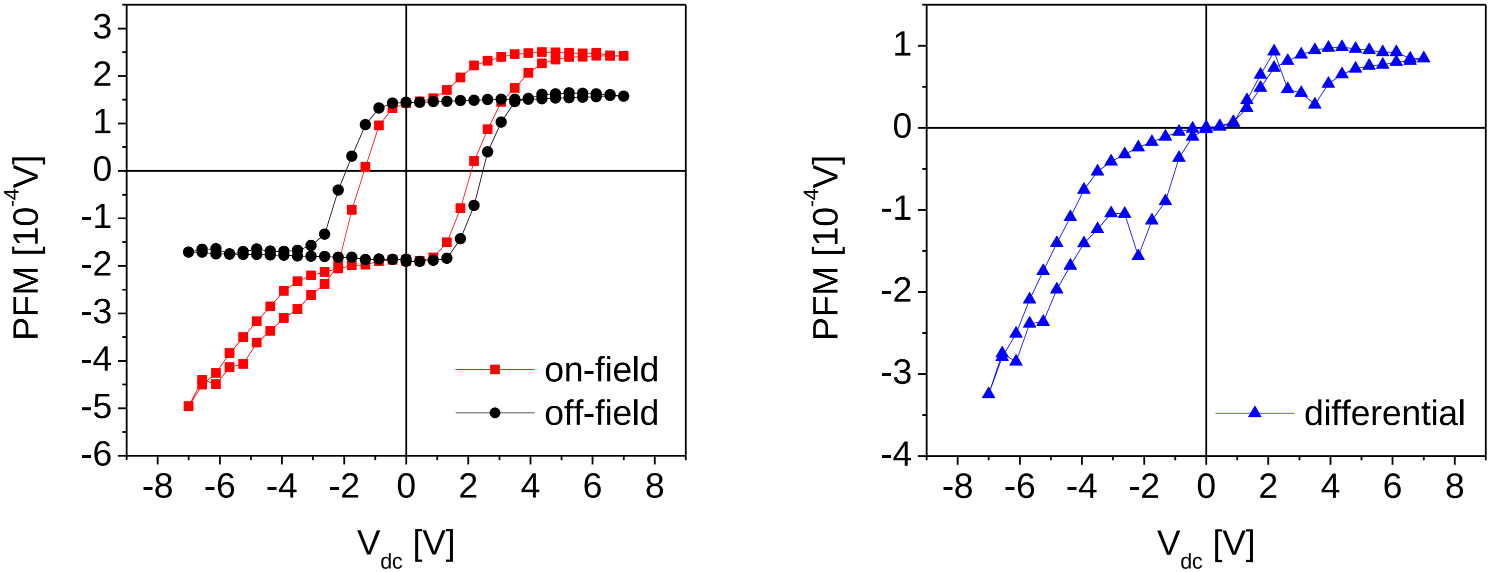
Off-field: V_{ac} only
- *Piezoresponse*





Real Ferroelectrics

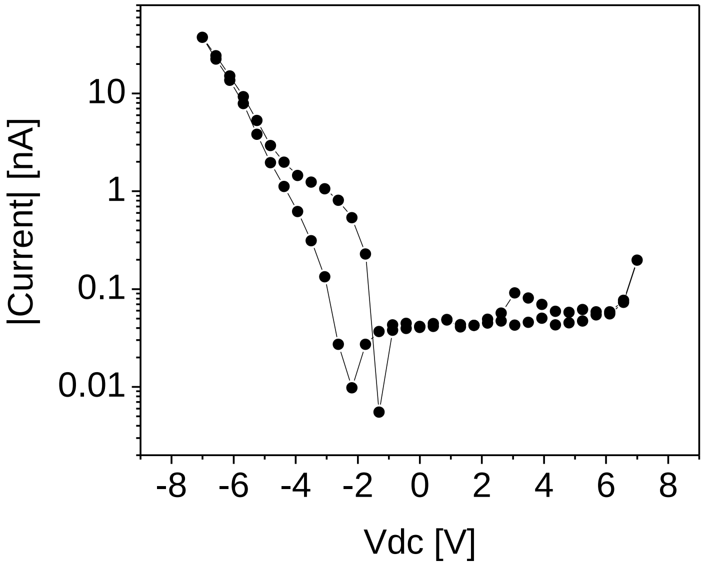
BFO thin film

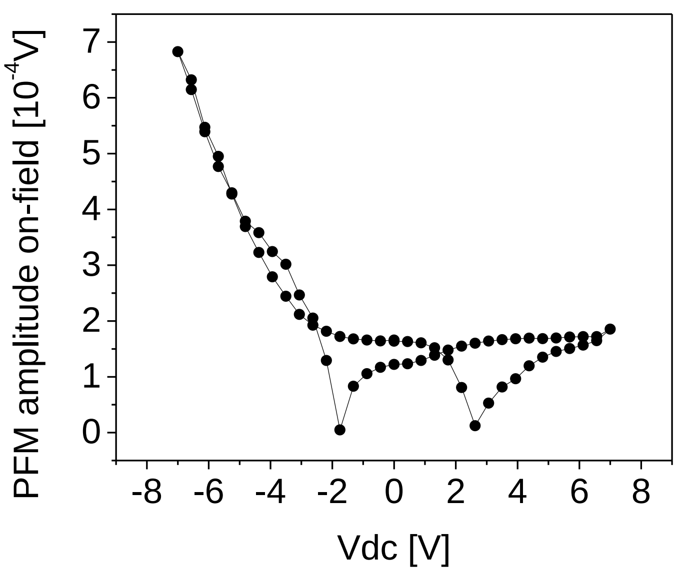


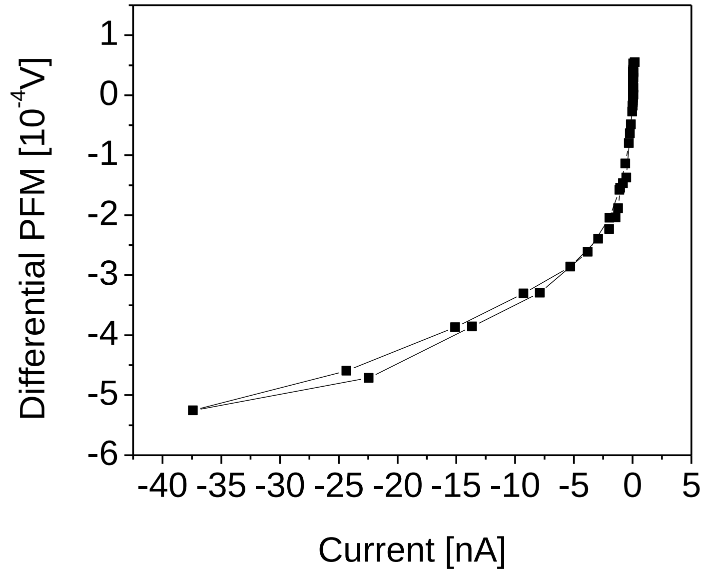
- Loop shape deviates strongly from the ideal case
- BFO thin films have often problems with leakage (high current flow)

Real Ferroelectrics

BFO thin film







Joule heating

$$x = \beta R I^2$$

$$x = \beta R [I_{dc} + I_{ac} \sin(\omega t)]^2$$

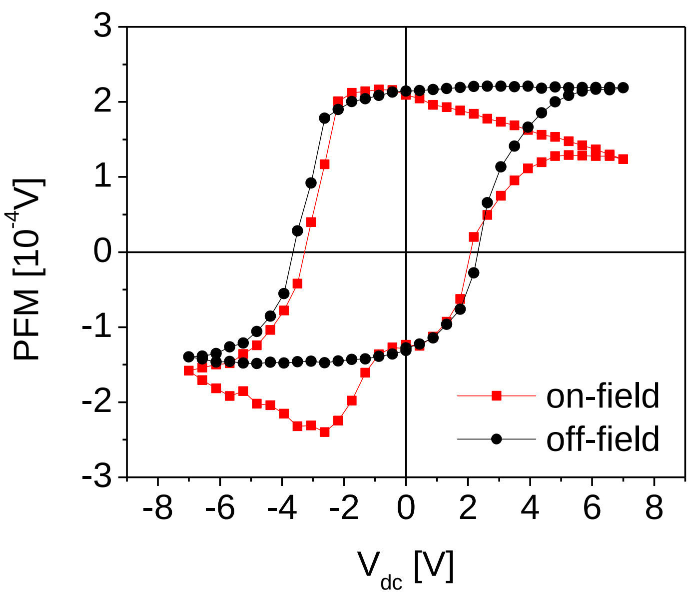
$$x_{\omega} = 2 \beta R I_{dc} I_{ac} \sin(\omega t)$$

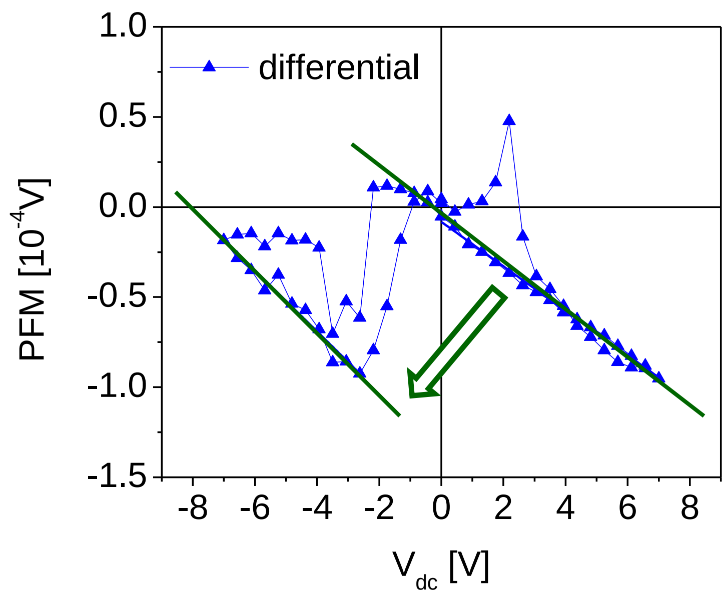
$$x_{2\omega} = -\frac{1}{2} \beta R I_{ac}^2 \sin(\omega t)$$

β: Joule heat transduction coefficient

Real Ferroelectrics

PZT thin film



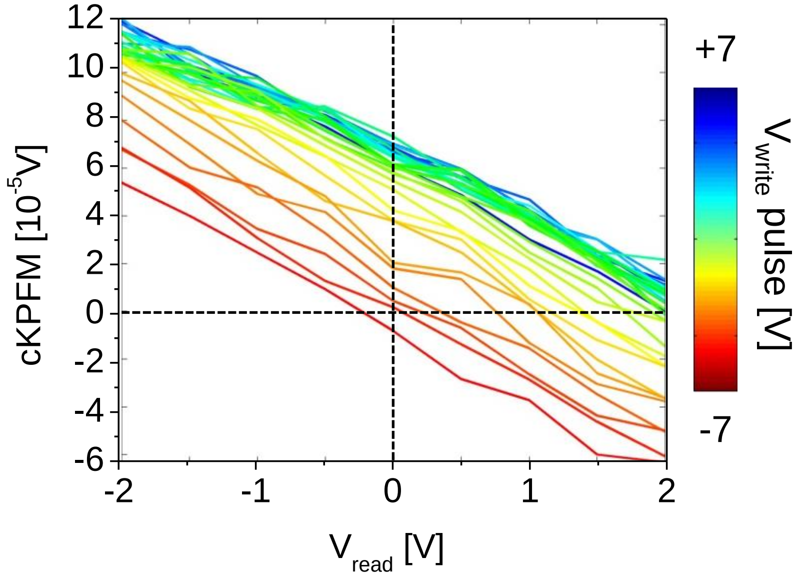


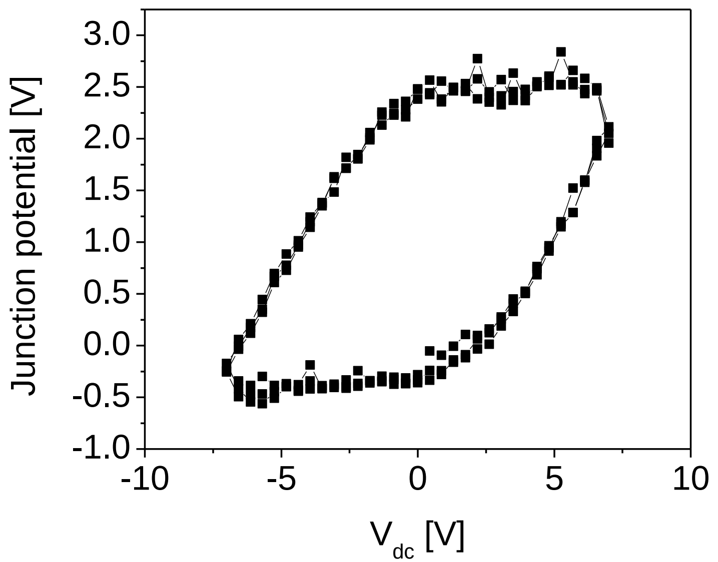
- Loop is shifted down for negative voltages
- Shift in differential loop towards more negative surface potential

How to measure the effect of change in surface potential?

Contact Kelvin Probe Force Microscopy (cKPFM): Change of electrostatic tip-sample interactions after V_{dc} voltage pulses

Example: amorphous HfO_2 thin film on Si



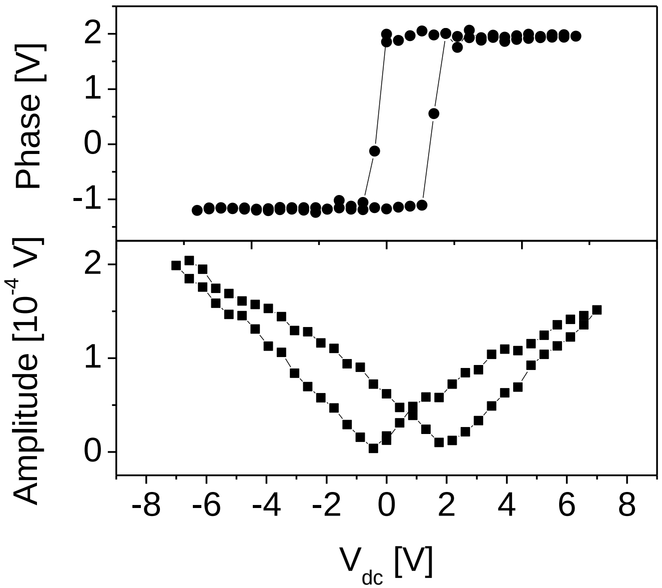


- Hysteretic change in surface potential due to dynamic charge trapping and de-trapping.
- Change in surface potential through charge injection from the tip.

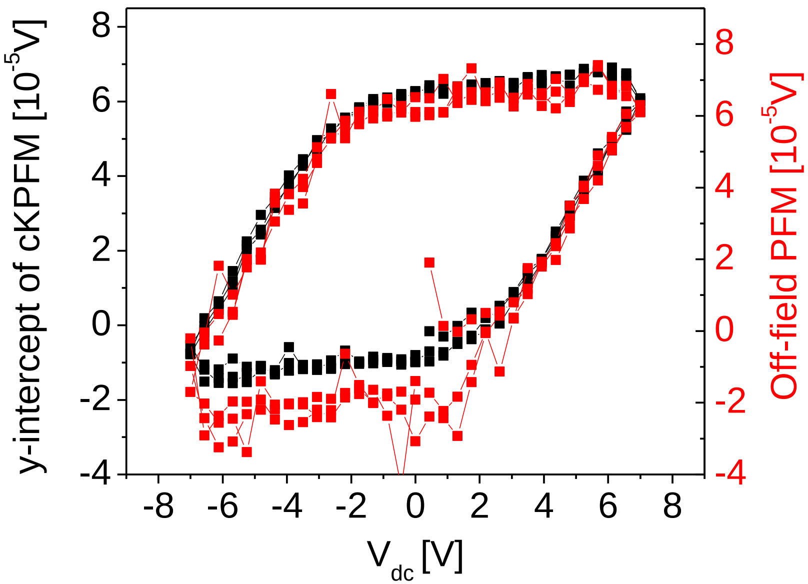
cKPFM

Hysteretic surface charge change + electrostatics = PFM loop!

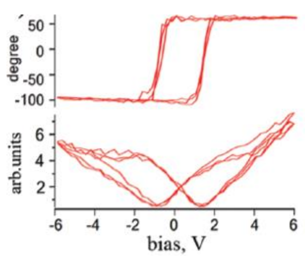
On-field loop

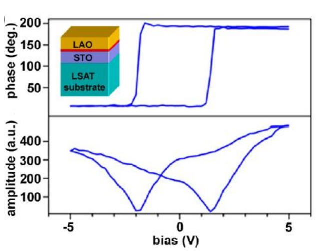


Off-field loop



Reminiscent of many PFM loops published on non-traditional ferroelectrics!

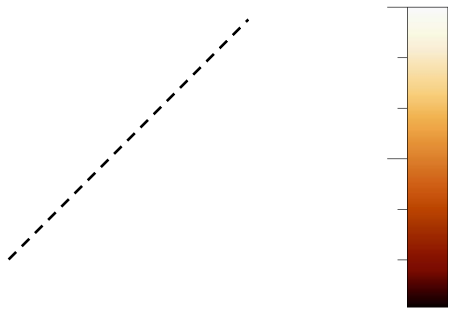




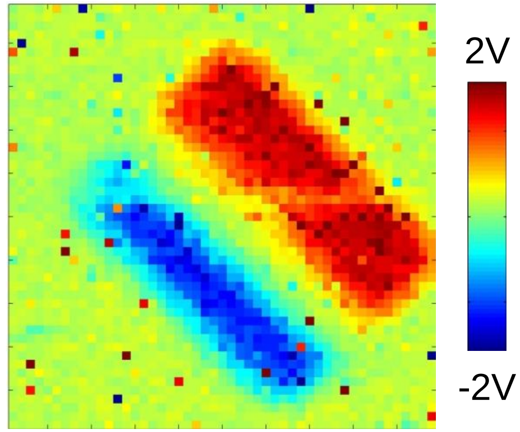
Hysteresis is mainly determined through the change in surface potential.

cKPFM

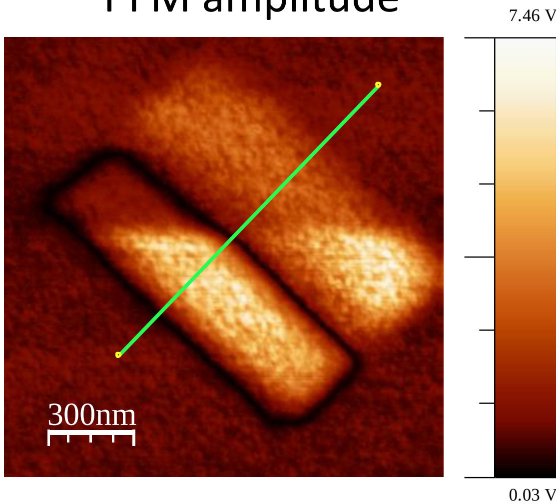
Surface potential via KPFM



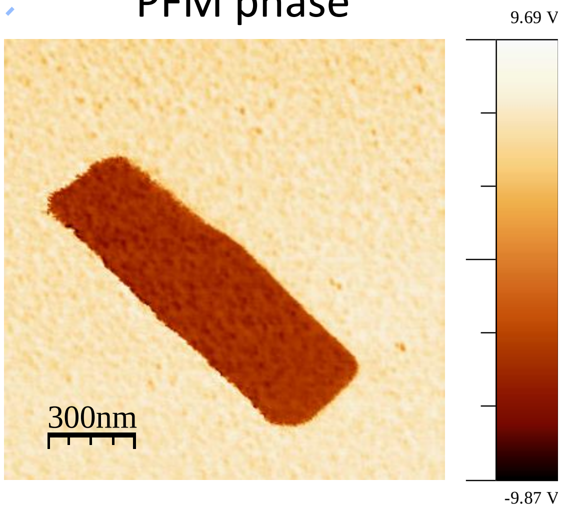
Surface potential via cKPFM

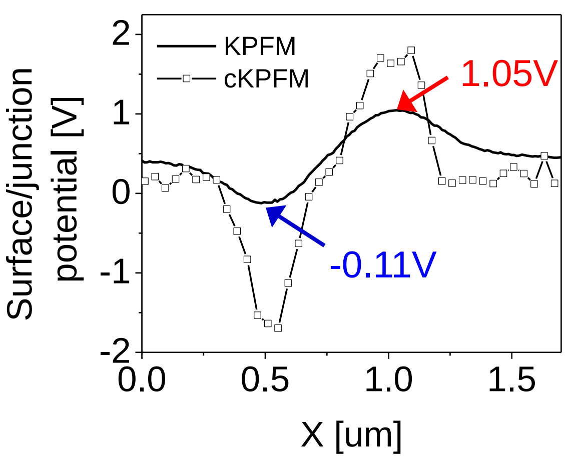


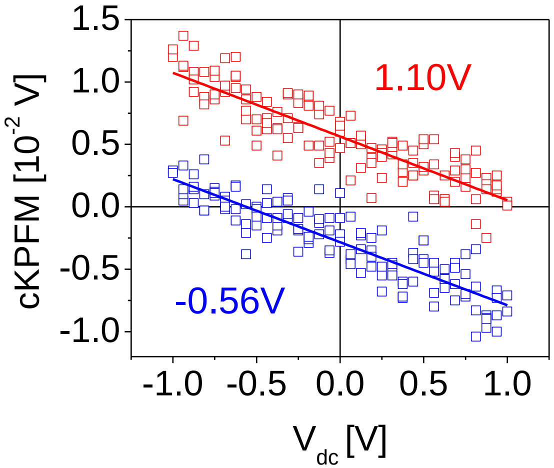
PFM amplitude



PFM phase







Summary 1

Ferroelectrics

• PFM can be used to image and manipulate domains.

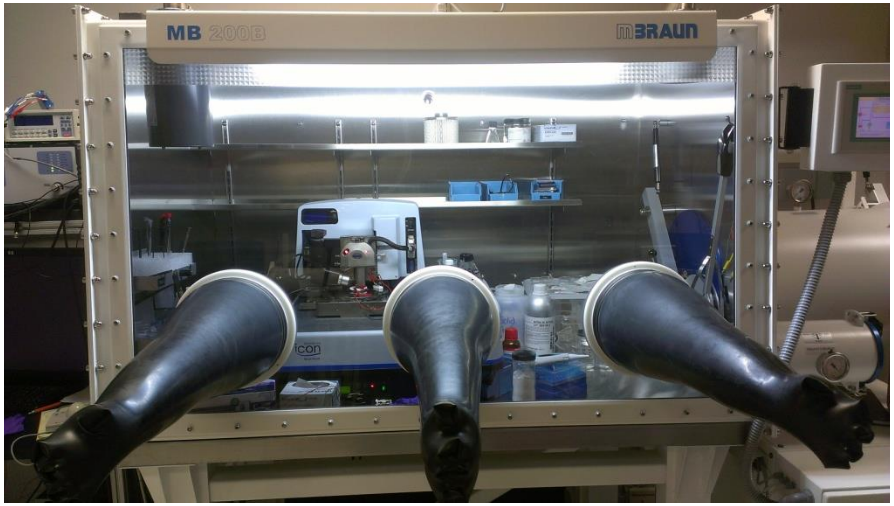
• Piezoelectricity is not the only signal origin during PFM.

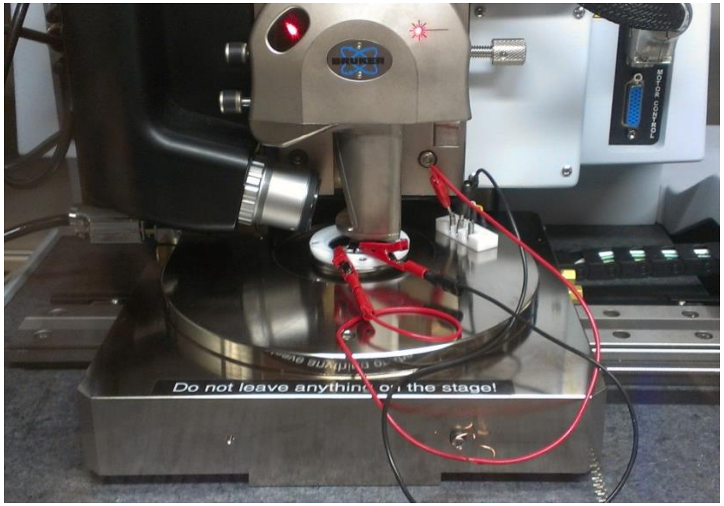
• PFM on non-traditional ferroelectrics and ferroelectrics with weak polarization needs to be carefully studies to avoid misinterpretation of data.

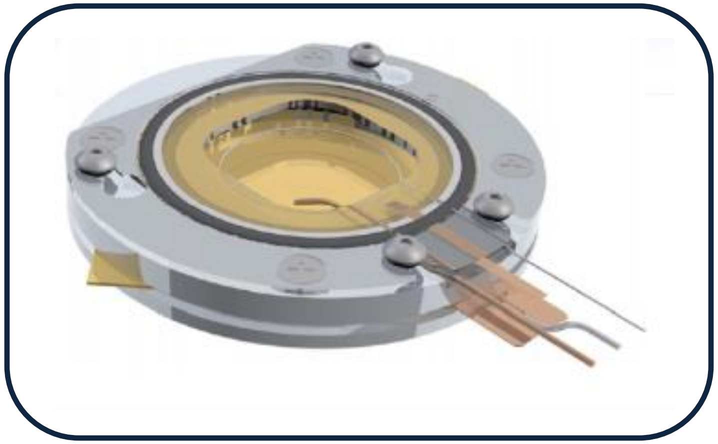
• contact KPFM can help to study tip-induced changes in surface potentials and differentiate it from piezoelectric response.

Ionic Transport in $LiCoO_2$

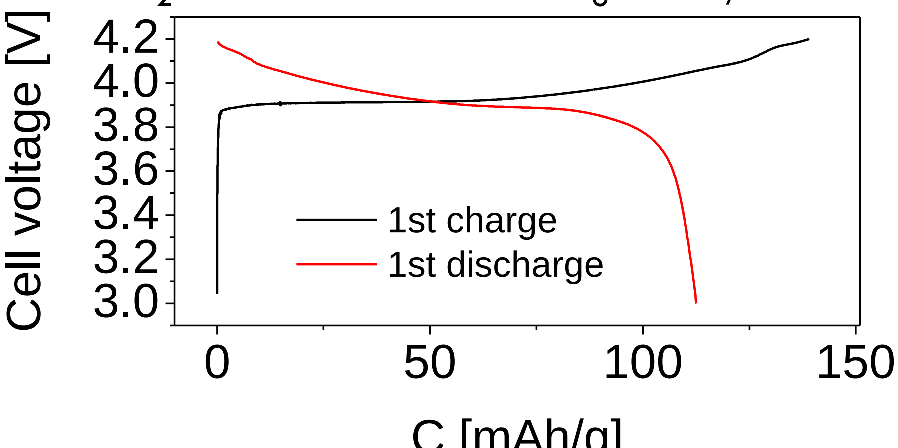
rf-sputtered thin films on Au/Al_2O_3







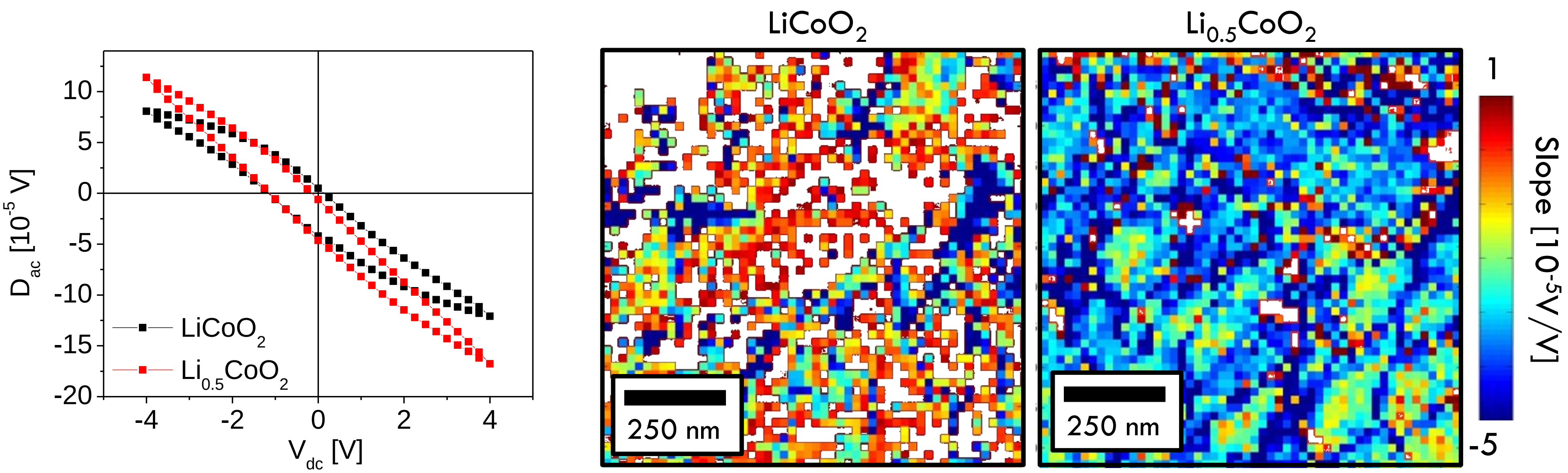
$LiCoO_2$ vs. Li metal in 1MLiPF$_6$ in DC/DMC



Sergiy Kalnaus, Nancy Dudney

Ionic Transport in $LiCoO_2$

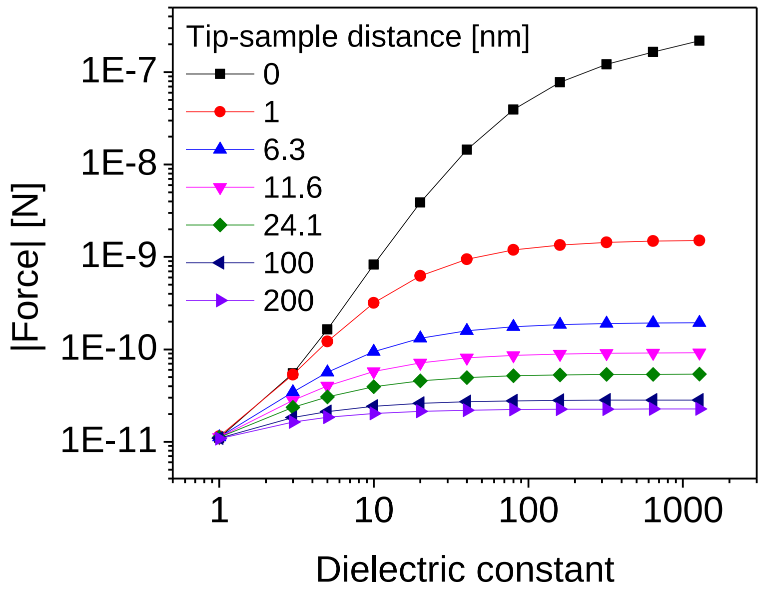
Comparison of LCO in different charging states (ex-situ)

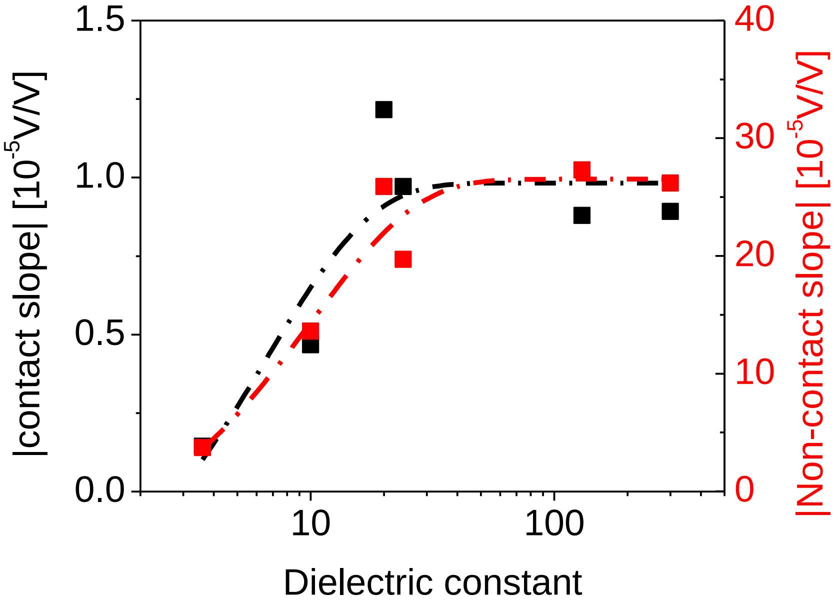


- higher Li-ion mobility when Li-ions are removed from LCO
- Higher slope at the grain boundaries for $Li_{0.5}CoO_2$

Purely electrostatic case: $x_\omega = k^{-1} C' V_{dc} V_{ac} \sin(\omega t)$

Slope is proportional to ε in non-contact and contact



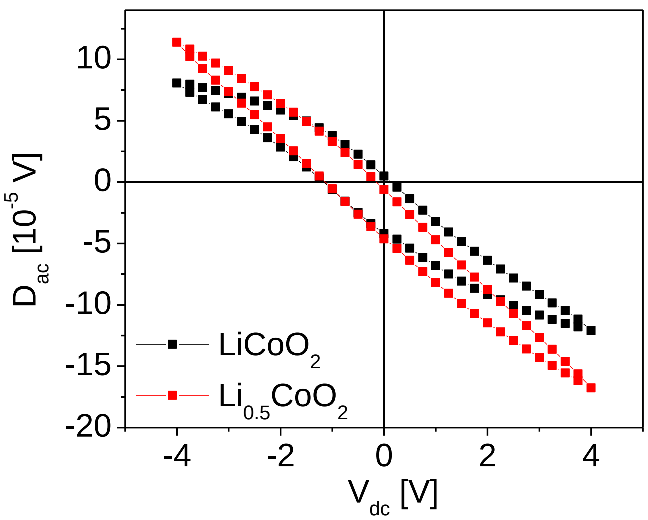


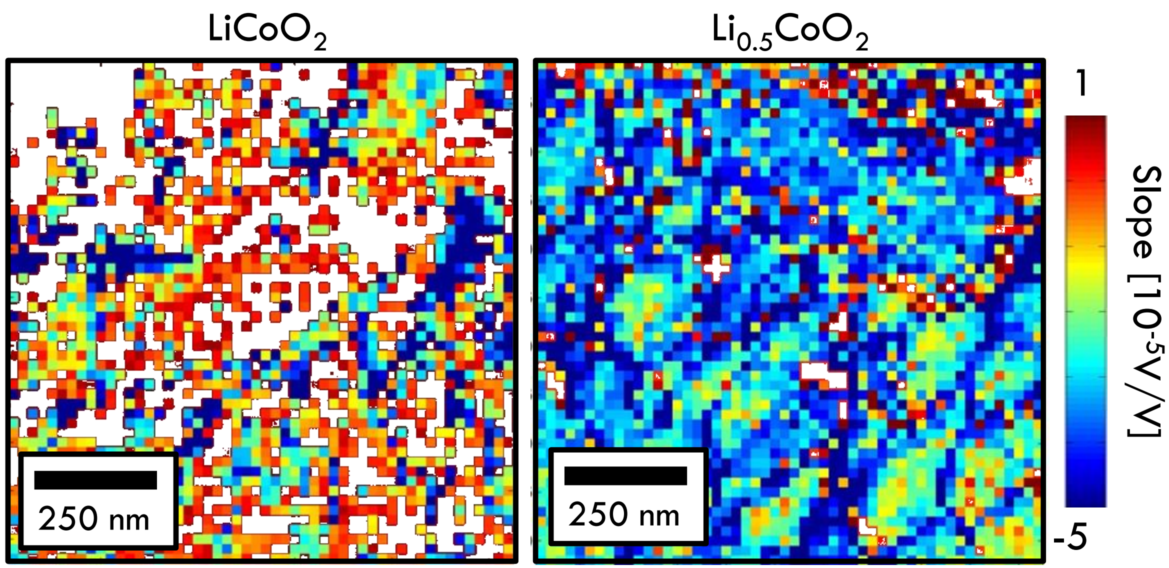
- Ceramics/substrates with known dielectric constant
- Non-contact and contact can be treated equivalent
- Slope is proportional to ε if ε <20

Alexander Tselev

Ionic Transport in $LiCoO_2$

Comparison of LCO in different charging states (ex-situ)



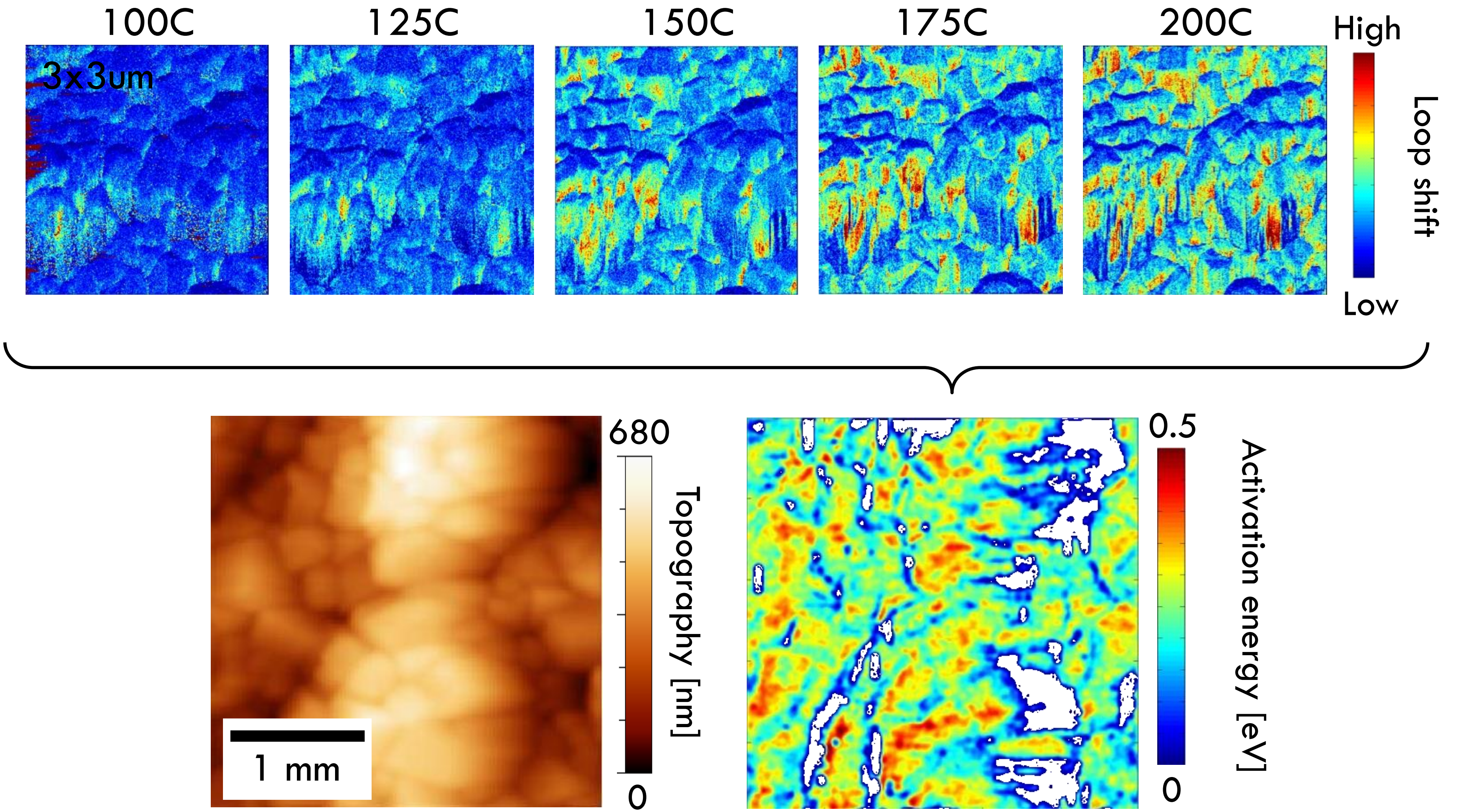


- higher Li-ion mobility when Li-ions are removed from LCO
- Higher ε at the grain boundaries for $Li_{0.5}CoO_2$

Suggesting that the Li-ion removal happens different in grains and grain boundaries

Ionic Transport in $LiCoO_2$

Temperature dependent measurement of y-intercept at $0V_{dc}$



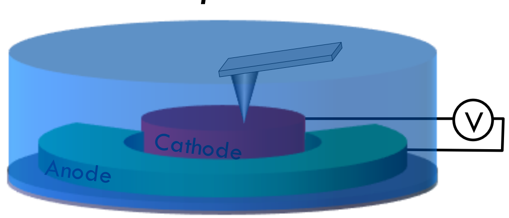
Balke et al., Nano Lett. 12, 3399 (2012)

Ionic Transport in $LiCoO_2$

Ultimate dream:

Correlation of nano- and macroscale properties through in-situ experiments

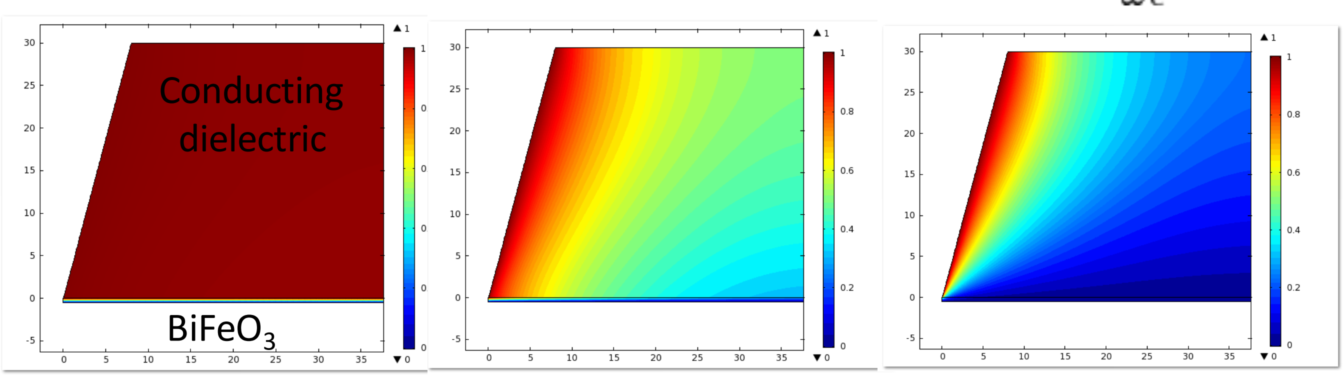
Liquid



Liquid environment challenging for SPM → different talk

Electric potential

$$\tan\delta = \frac{\omega\epsilon'' + \sigma}{\omega\epsilon'}.$$

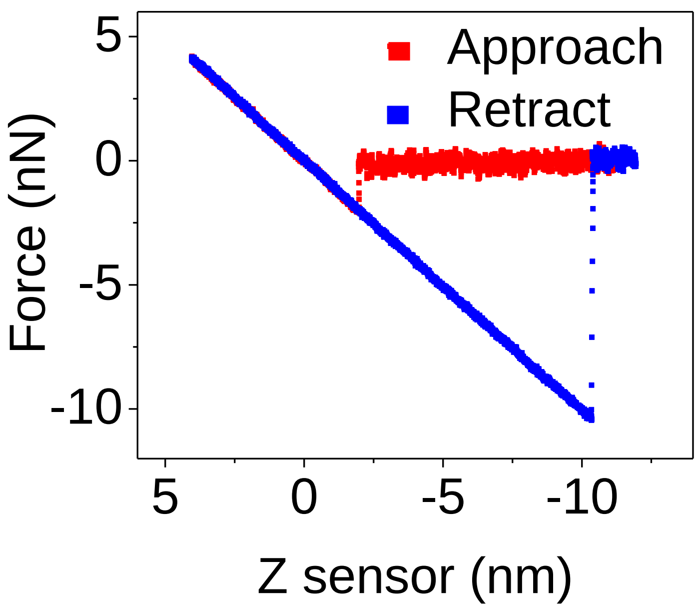


tan δ >>100 | tan δ ~100 | tan δ <1

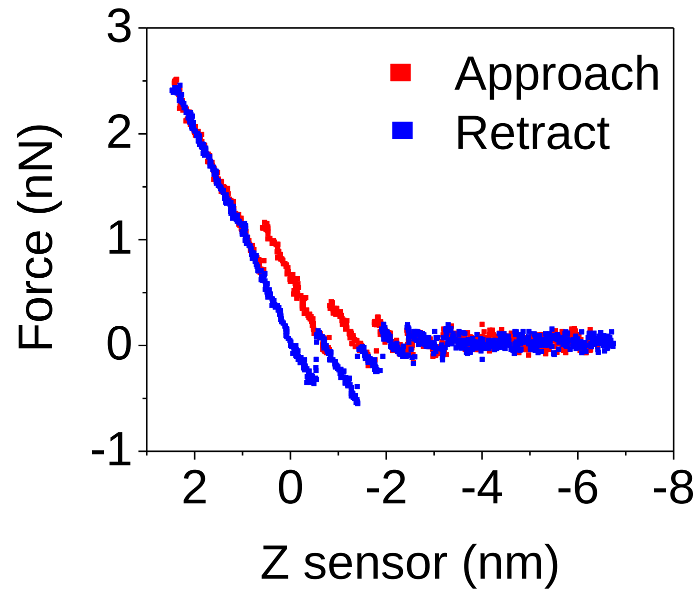
Alexander Tselev

AFM force spectroscopy to study the electric double layer formed by room temperature ionic liquids on HOPG

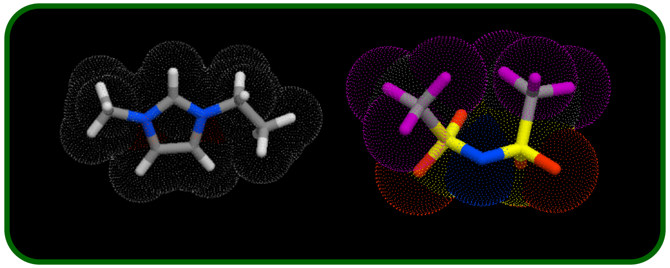
In air



In RTIL

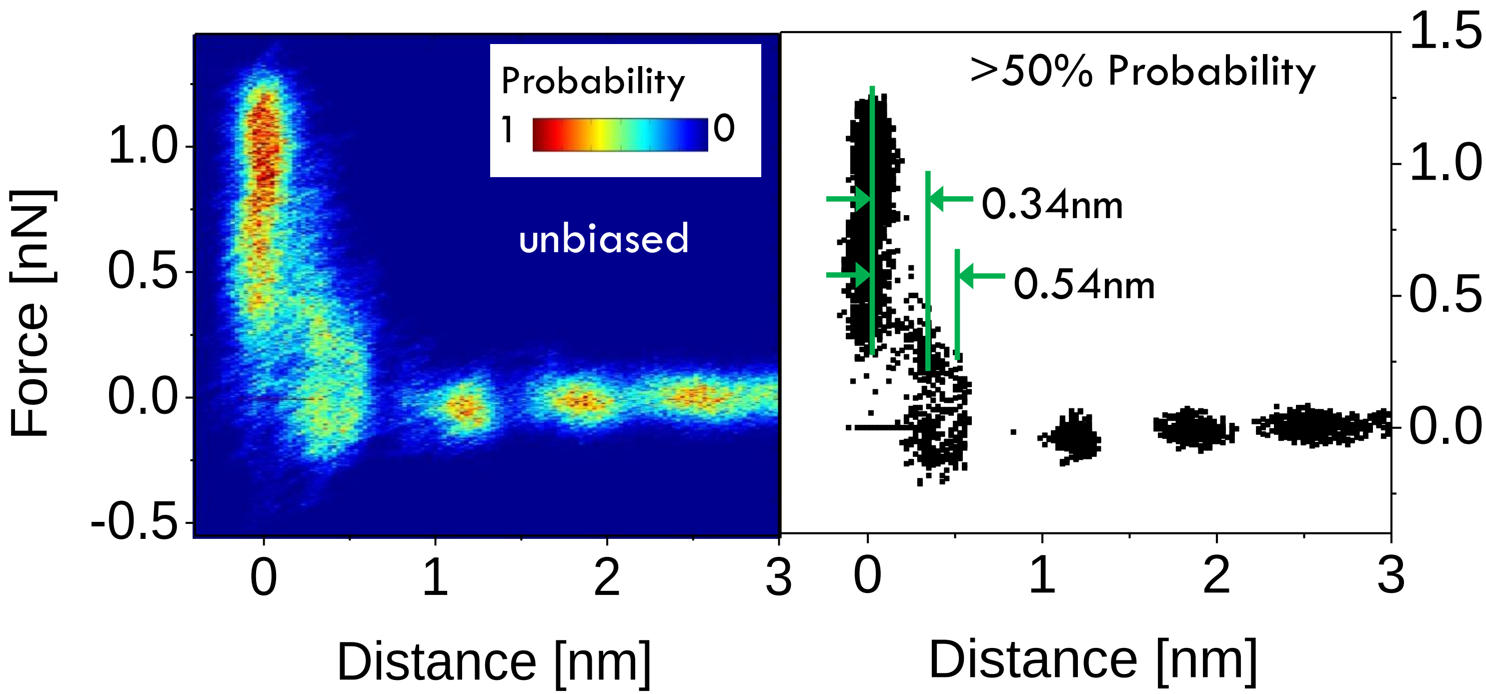


$[Emim]^+[Tf_2N]^-$



Solid-Liquid Interfaces

Force spectroscopy on model surfaces (HOPG) in Emim-Tf_2N

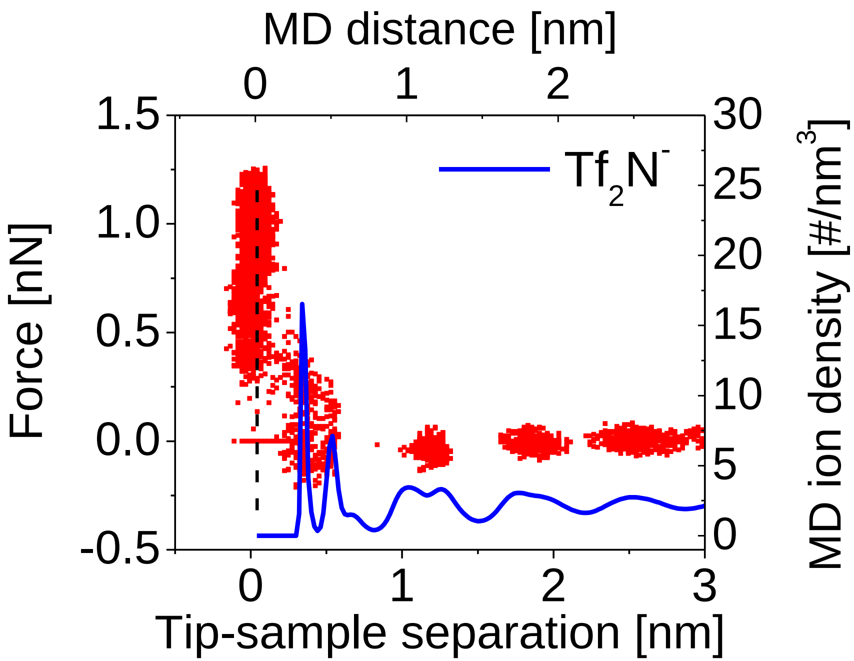


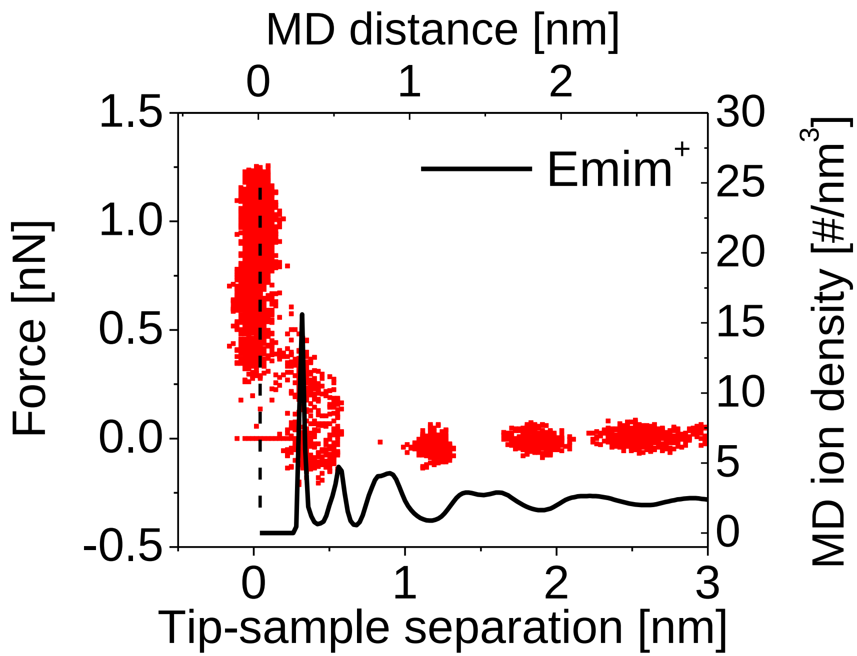
Statistical approach to identify ion positions.

Black et al., Nano Lett. 13, 5954 (2013).

Solid-Liquid Interfaces

Comparison of F-d with MD:

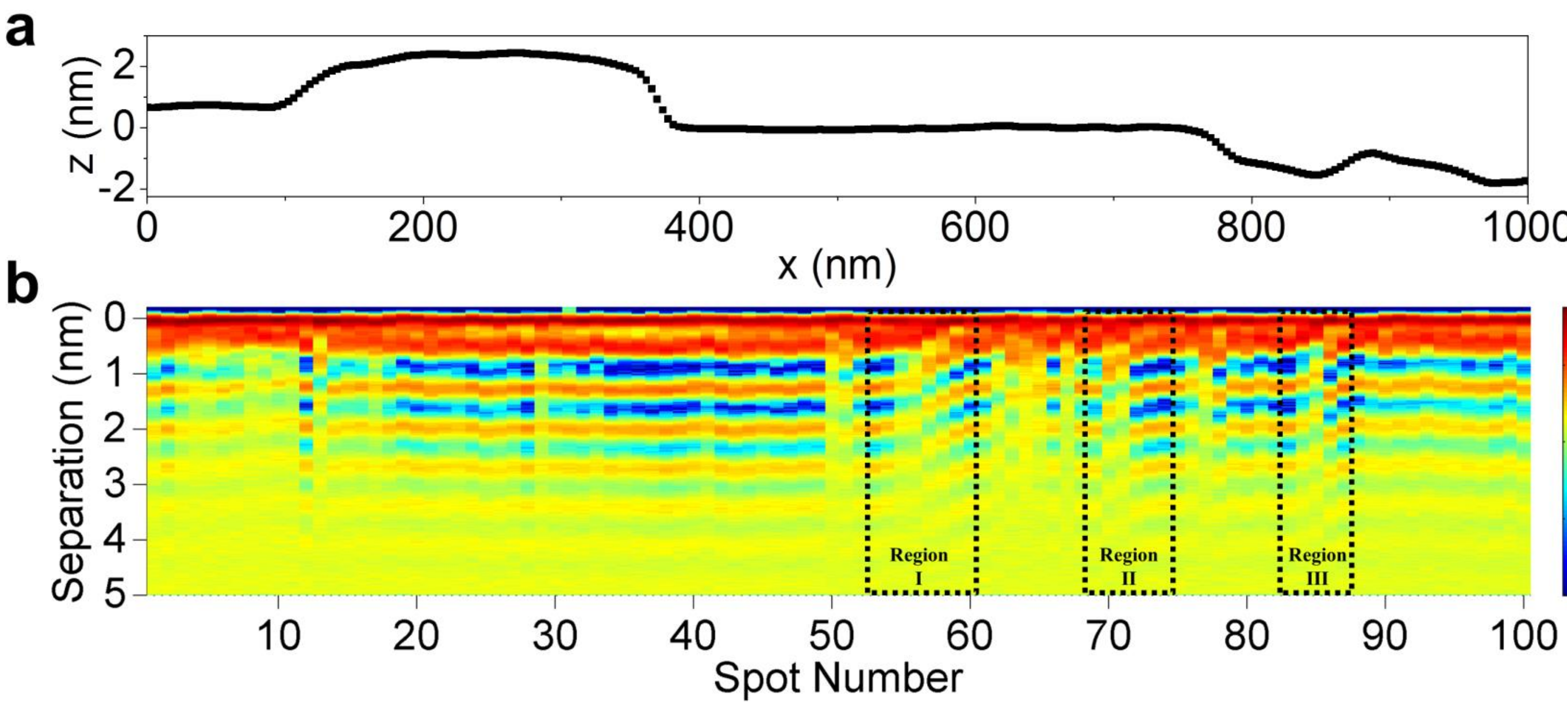




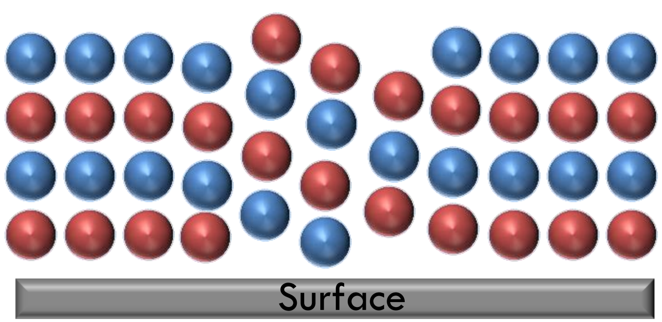
The measured ion positions coincide with anion positions.

Black et al., Nano Lett. 13, 5954 (2013).

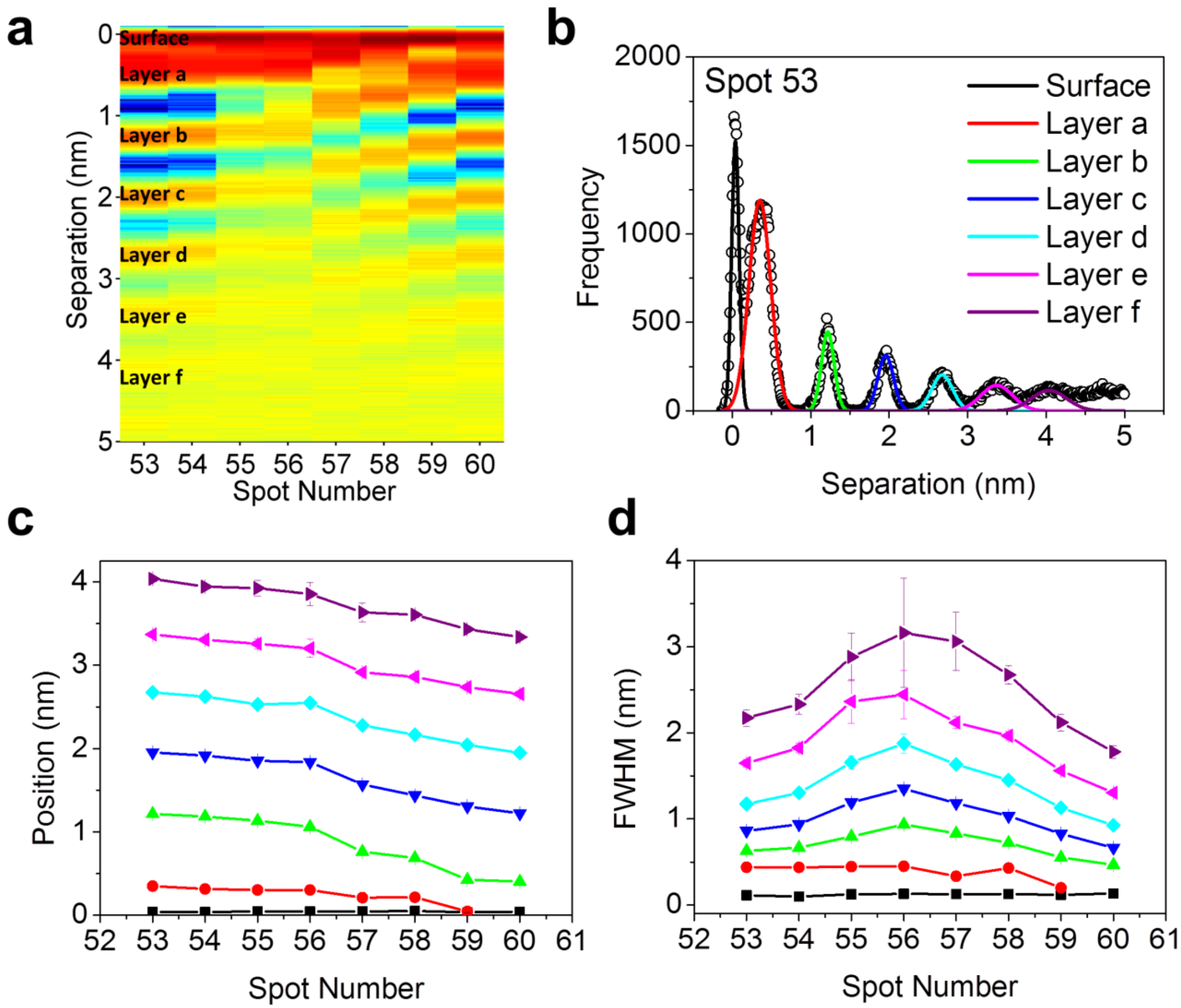
Solid-Liquid Interfaces



Edge dislocations observed in the ionic layering in regions with no step edges.



Solid-Liquid Interfaces



Width of ion layer as measure for disorder.

Disorder is increased when ions are not in their equilibrium position.

Summary 2

Energy storage systems

- SPM can be used to study energy storage systems.
- Changes in dielectric properties can help looking at ionic transport.
- Force spectroscopy can “see” ion layering in the EDL for ionic liquids.
- Ionic liquids behave as liquid crystals and show ordering defects.
- Functionality of extended defects in future studies.

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