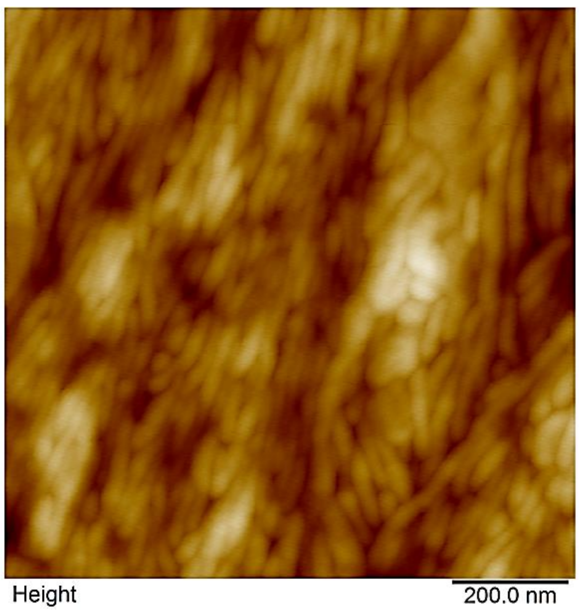
Dielectric properties of polymers with lateral resolution using an AFM approach: nanoDielectric Spectroscopy

Daniel E. Martínez-Tong, Paul Markus, Angel Alegría

danielenrique_martineztong001@ehu.eus

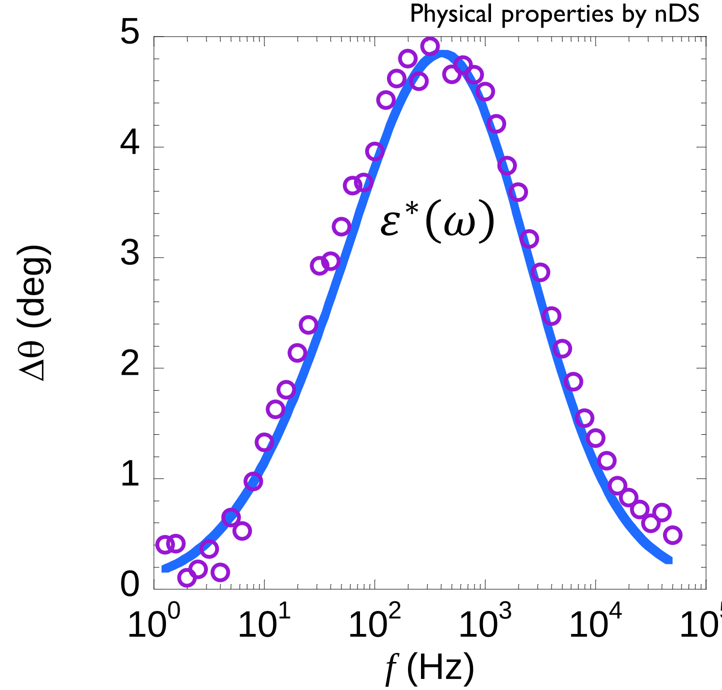
From images…

Polymer surface (AFM)



…to spectroscopy

Physical properties by nDS



Universidad del País Vasco
Euskal Herriko Unibertsitatea

Goals

1. Use **Atomic Force Microscopy** (AFM) to perform **dielectric spectroscopy** measurements at the nanoscale on semicrystalline polymer thin films.

2. Connect the nanoscale dielectric results with the **dielectric relaxation** of the material in a **quantitative way**.

3. Present recent results on AFM measurements under controlled humidity

…but why AFM?

Why Atomic Force Microscopy?

(1) Lateral resolution: We want to be able to know how different zones/areas of a sample contribute to an "overall response".

(2) Miniaturization of samples/devices: We want to perform measurements of samples with characteristics sizes/features of $\sim 10^2$ nm, small areas, low mass.

(1) Introduction to **Atomic Force Microscopy (AFM)**

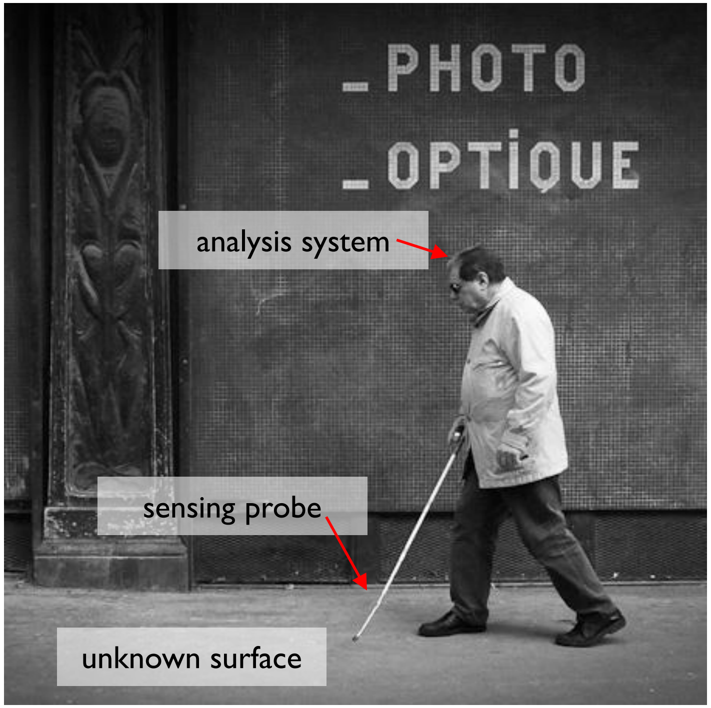
VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

Atomic Force Microscope

G. Binnig[(a)] and C. F. Quate[(b)]
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

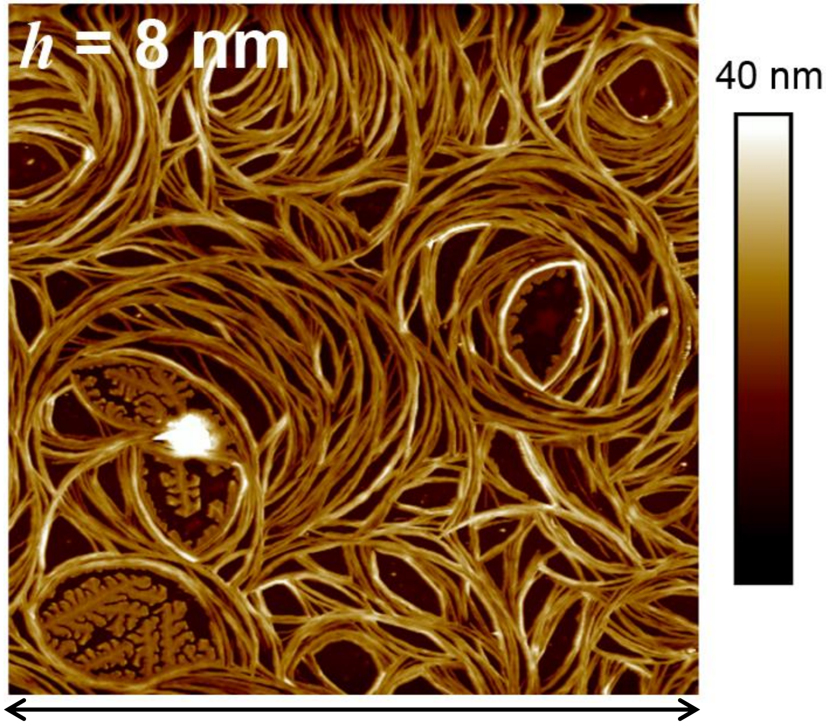
and

Ch. Gerber[(c)]
IBM San Jose Research Laboratory, San Jose, California 95193
(Received 5 December 1985)



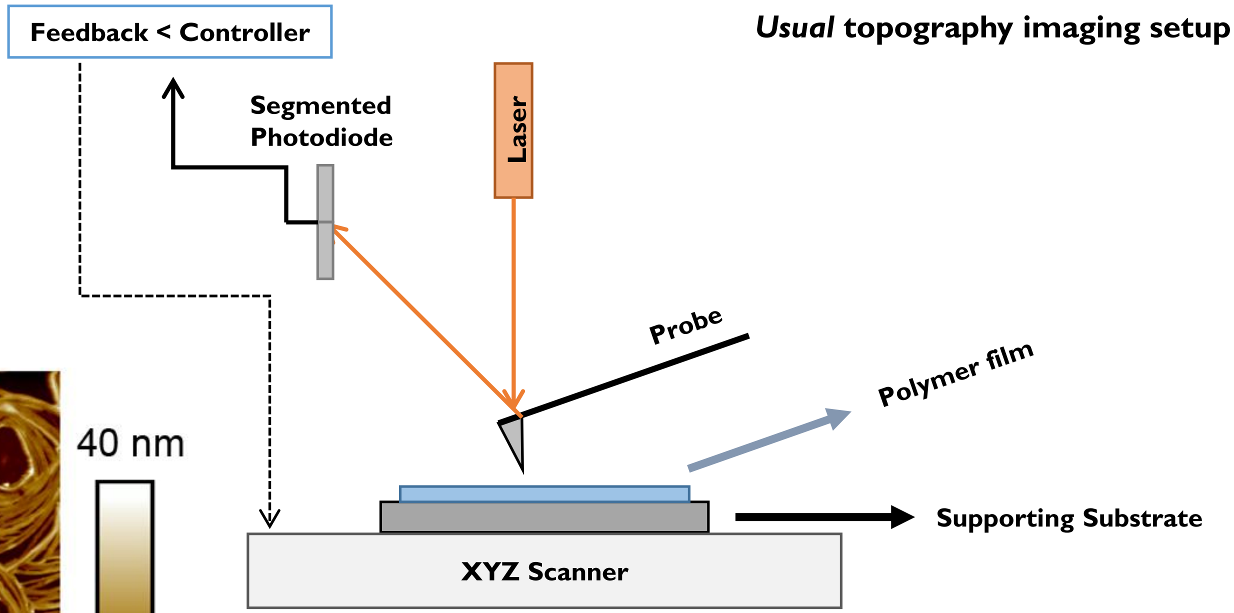
(I) Introduction to **Atomic Force Microscopy (AFM)**

AFM topography image:
PLLA semicrystalline structure



Soft Matter **11**, 6179 (2015)

Usual **topography imaging setup**



AFM Summary

(1) Probe-based microscopy technique.

(2) High lateral (< 20 nm) and vertical resolution (below 1 nm).

(3) Environment and temperature of both tip and sample can be controlled.

(5) Radiation damage: None

(6) Specimen preparation: Requires "smooth" surfaces.

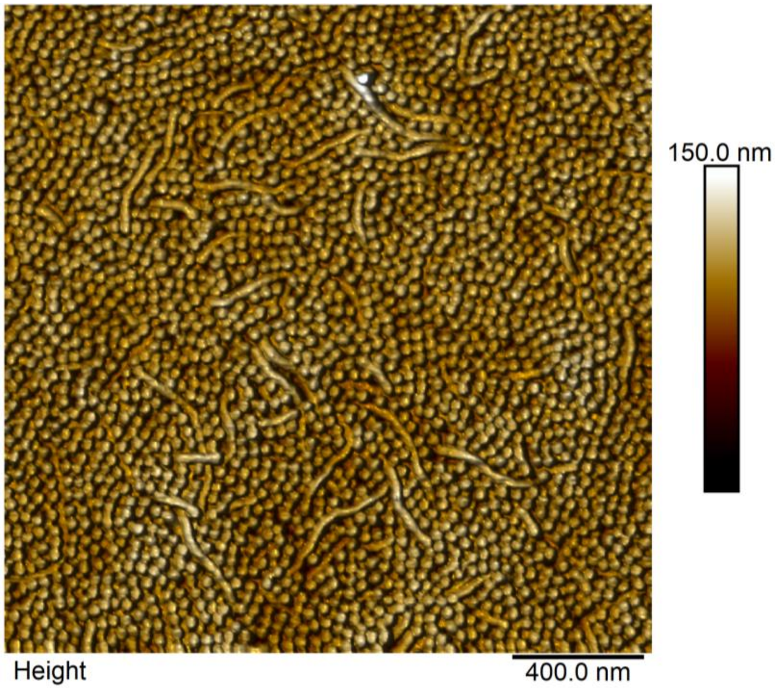
(7) Chemical analysis: Can be integrated into different systems (X-ray, Raman, IR,…)

(1) Introduction to **Atomic Force Microscopy (AFM)**

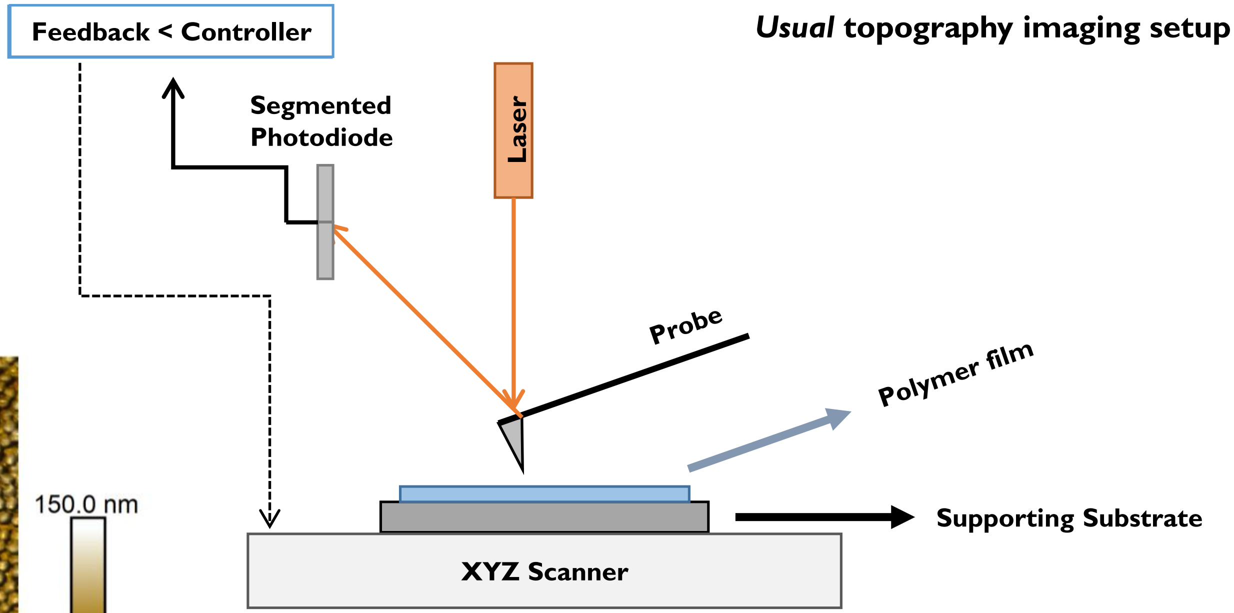
The AFM works as a Force sensing tool:

The machine wants to keep a constant force, via the Feedback loop

AFM topography image:
PS-co-PDMS self assembly



***Usual* topography imaging setup**



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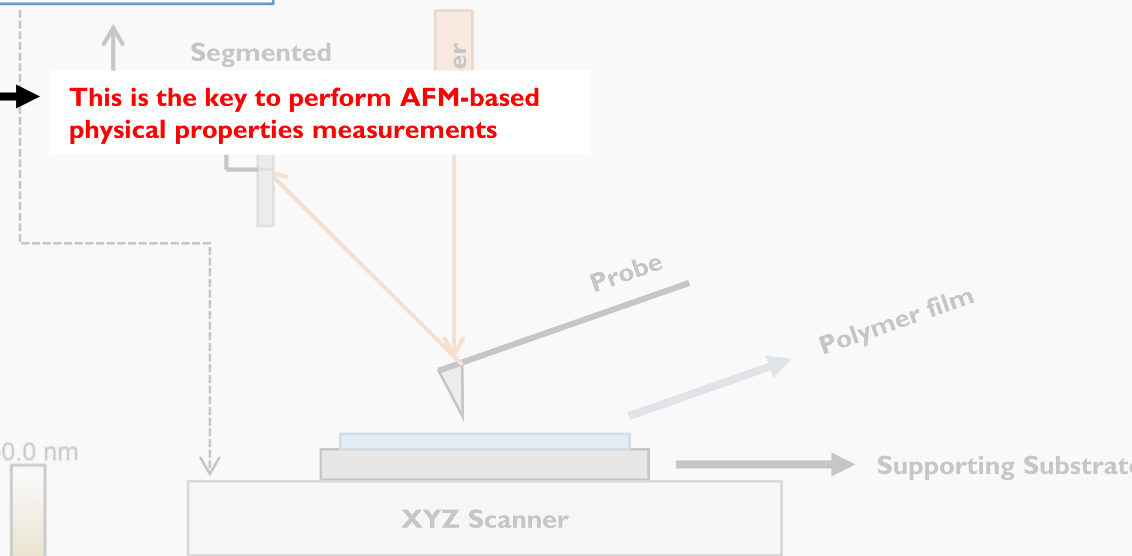
Feedback < Controller

This is the key to perform AFM-based physical properties measurements

Usual topography imaging setup



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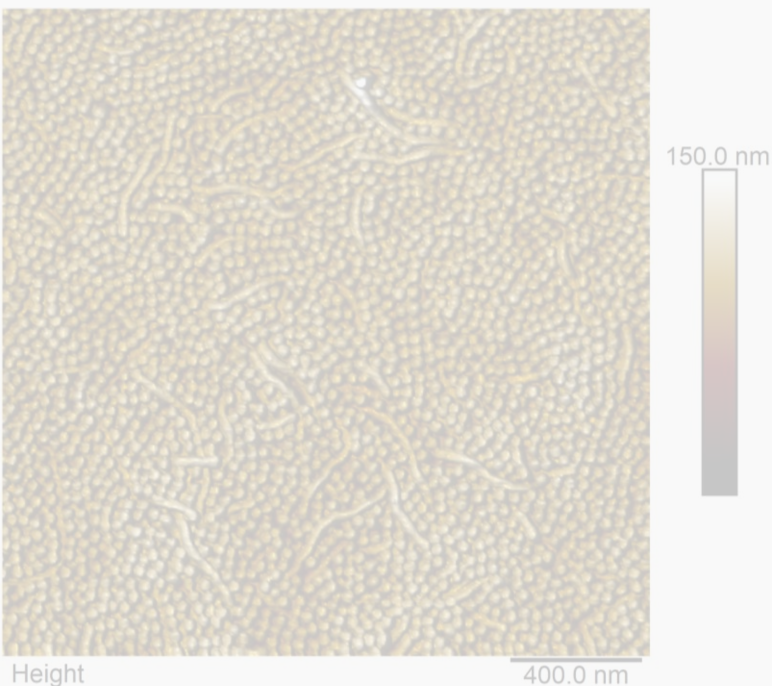

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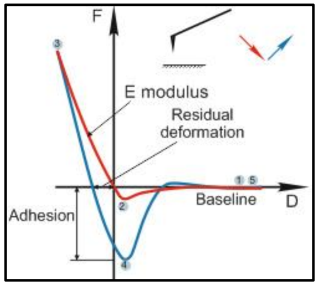
(1.1) **Surface physical properties** via AFM, on polymers

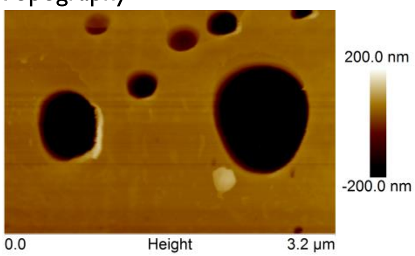
The AFM works as a Force sensing tool
The machine wants to keep a constant force, via the Feedback loop

Nanomechanical properties

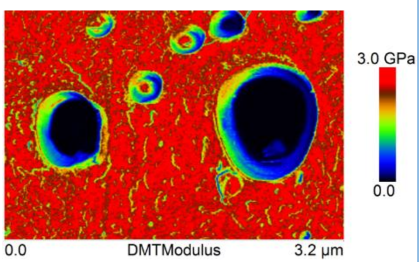
Compos. Sci. Technol. **104**, 34 (2014)



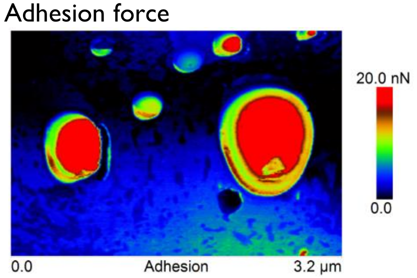
Topography



Mechanical Modulus



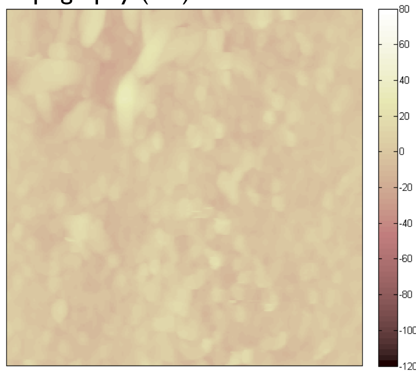
Adhesion force



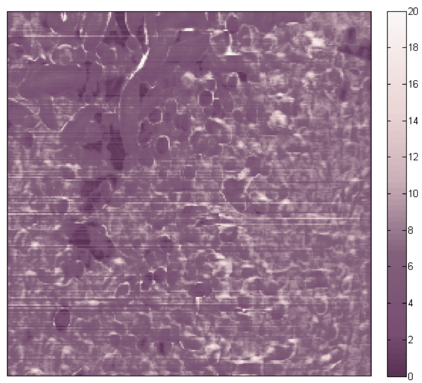
Friction force microscopy

Submitted (2018)

Topography (nm)



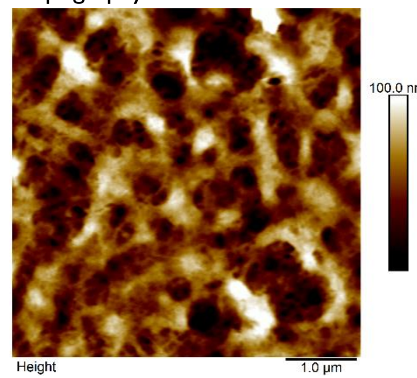
Friction force (nN)



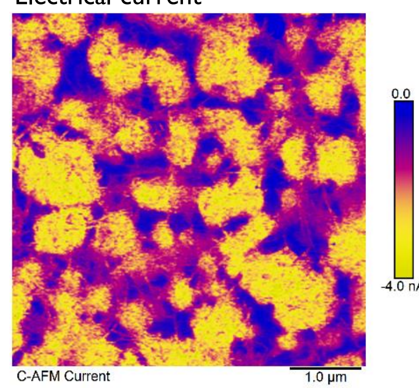
Conductive-AFM (C-AFM)

Polymer **77**, 70 (2015)

Topography

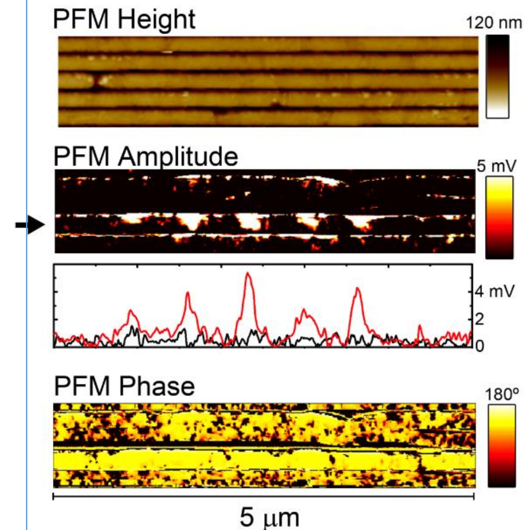


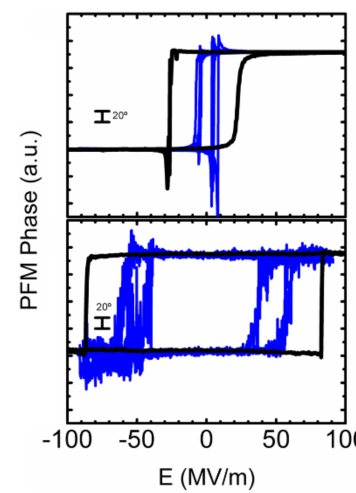
Electrical current



Ferroelectric AFM

Appl. Phys. Lett. **102**, 191601 (2013)





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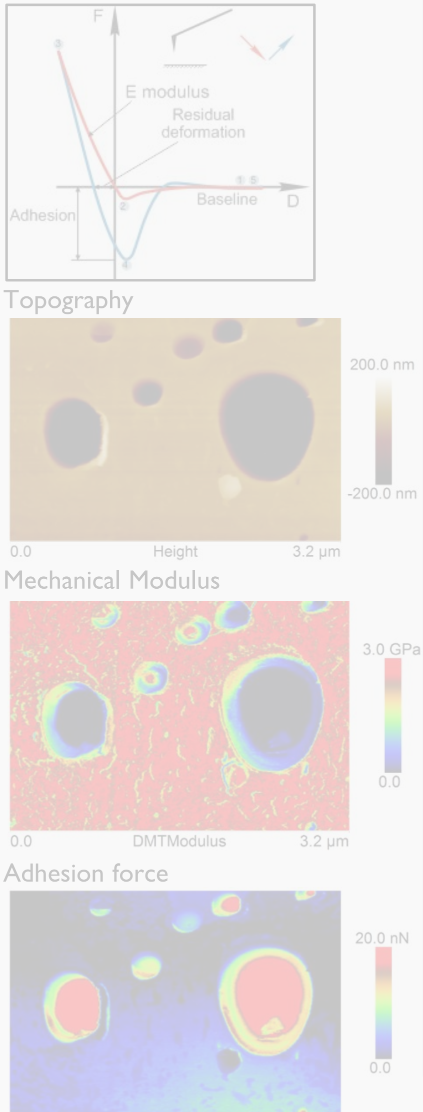

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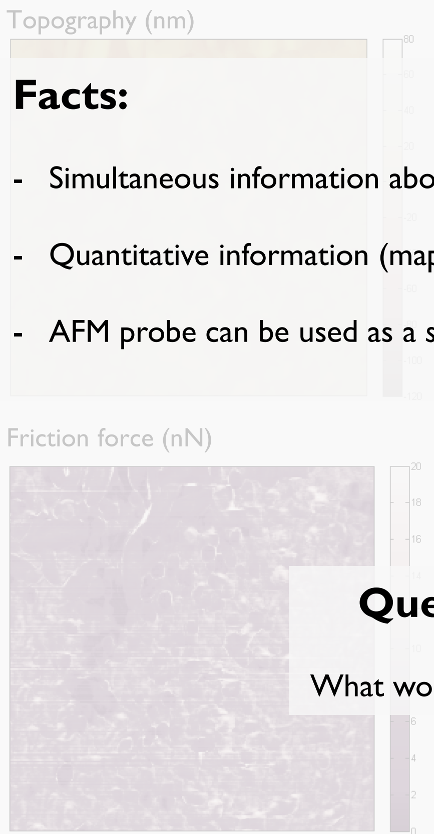

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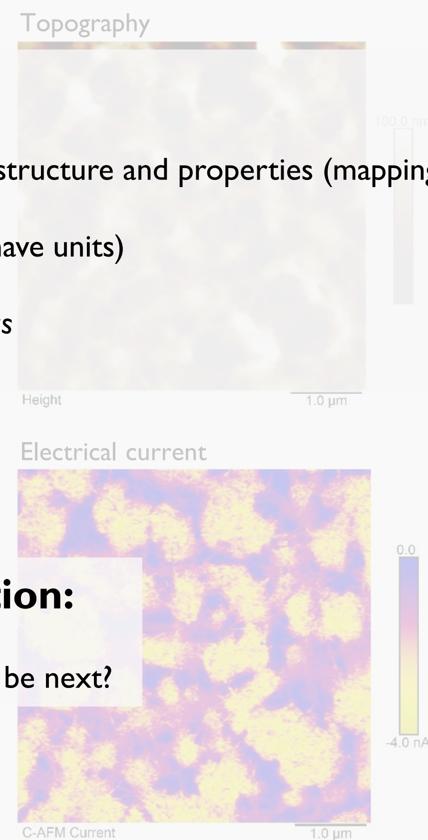

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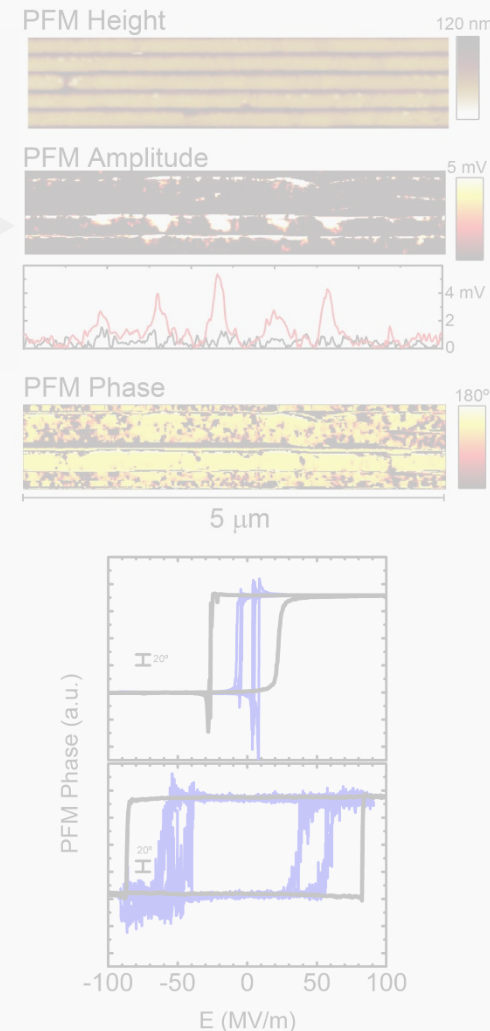


Facts:

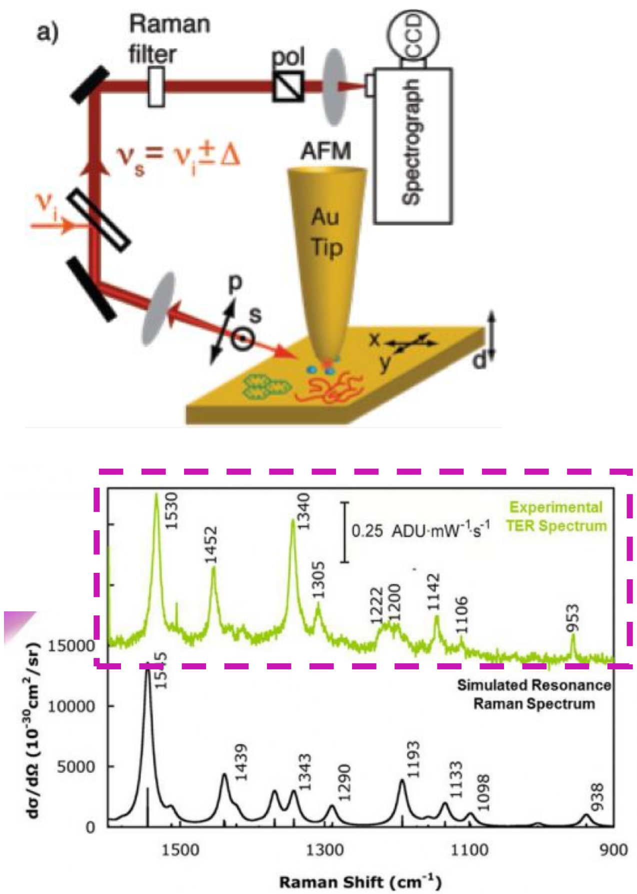
- Simultaneous information about structure and properties (mapping)
- Quantitative information (maps have units)
- AFM probe can be used as a *stylus*

Question:

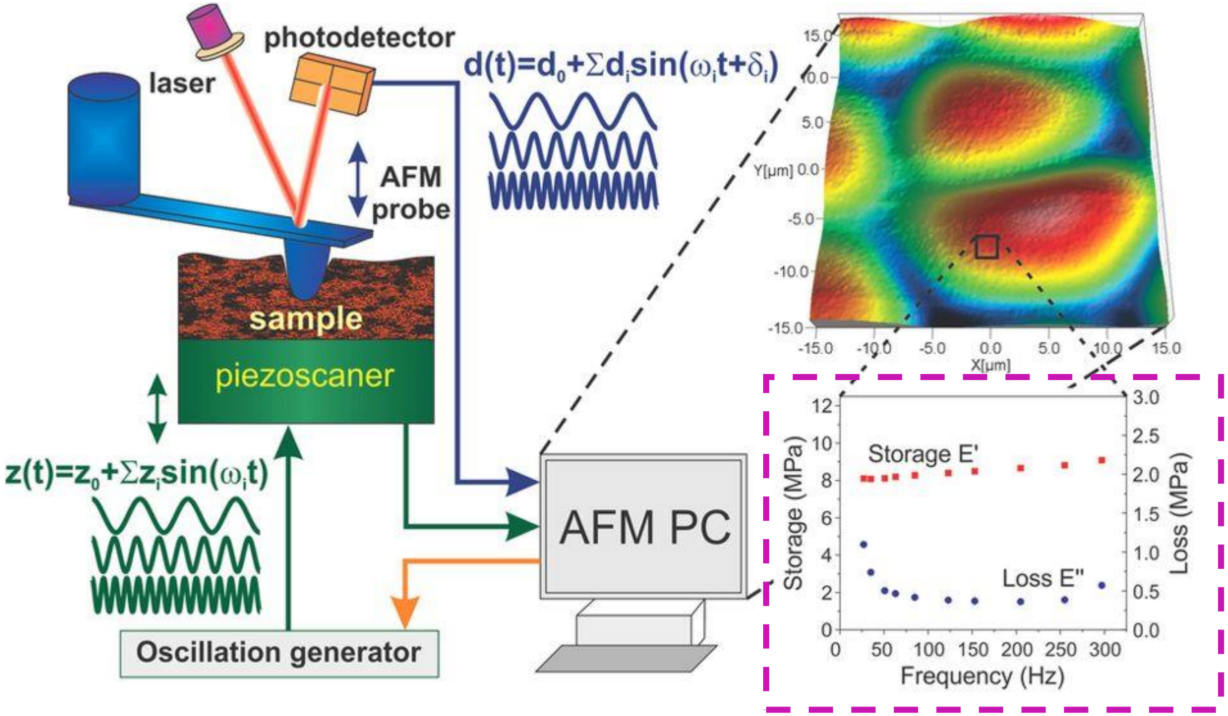
What would be next?

(1.2) **Spectroscopy-based** AFM

Tip-enhanced Raman Spectroscopy



Nanomechanical Spectroscopy



(1.2) **Spectroscopy-based** AFM

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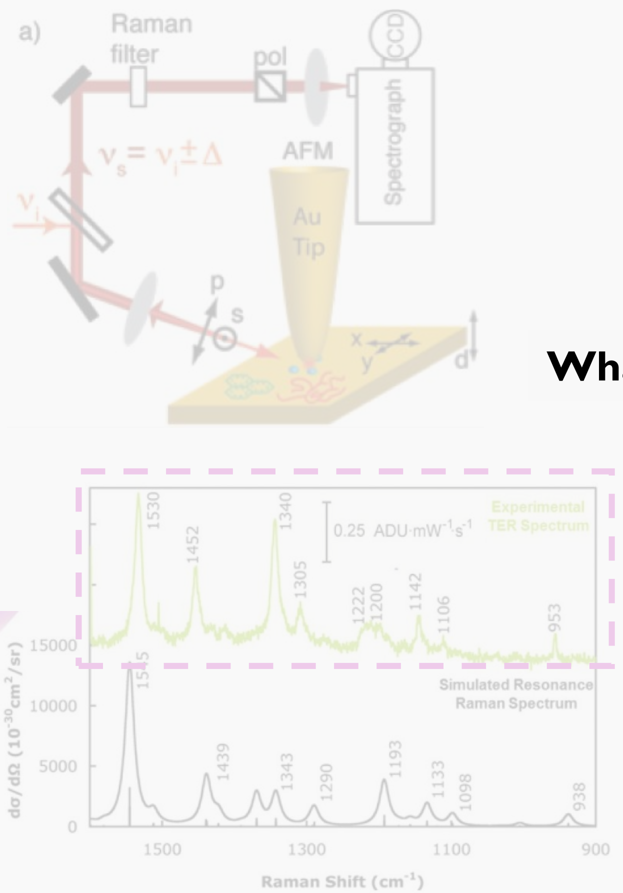
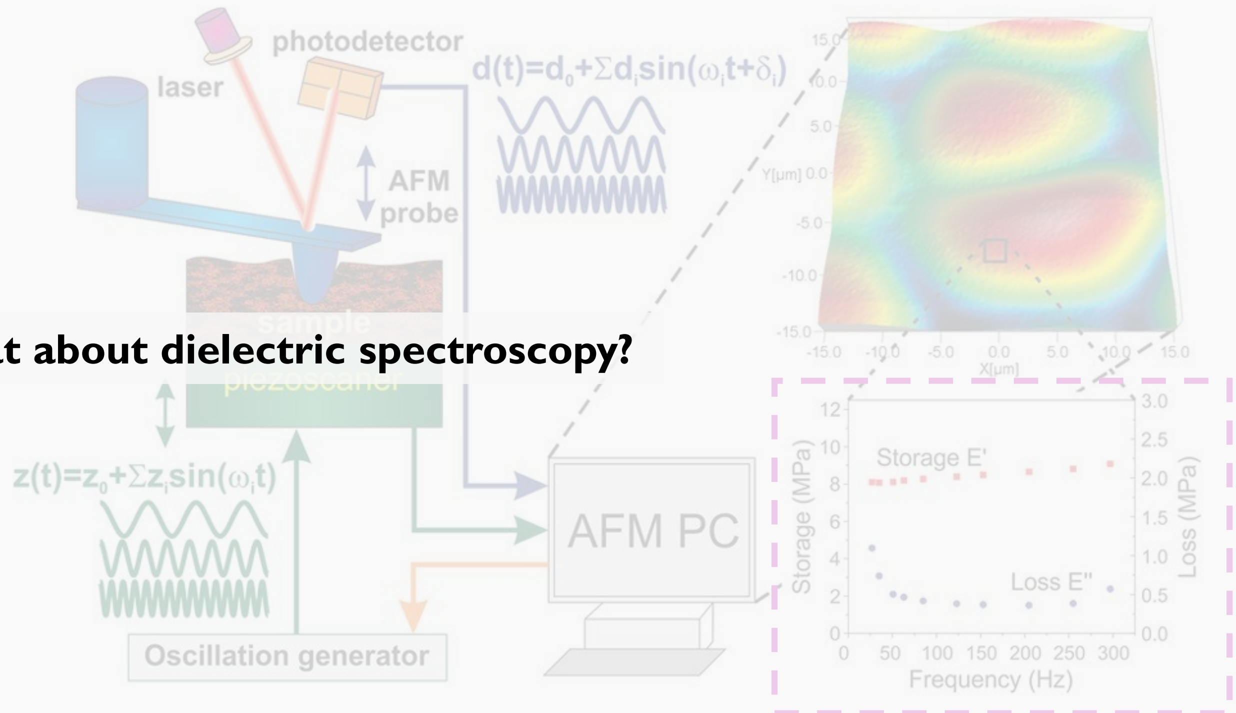


Nanomechanical Spectroscopy

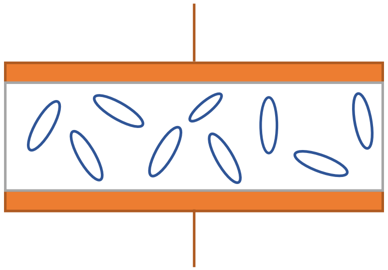


What about dielectric spectroscopy?

(2) **Dielectric relaxation spectroscopy**

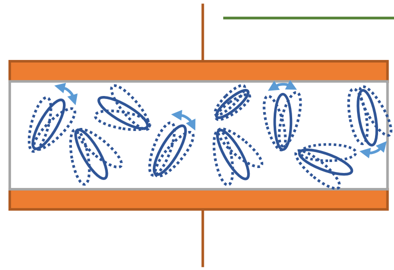
Orientation of molecular electric dipoles due to the application of an electric field.

$\vec{E}(\omega) = 0$



$\vec{E}(\omega) \neq 0$

Frequency sweep



Impedance analyzer

$Z^*(\omega)$, $C^*(\omega)$, $M^*(\omega)$,…

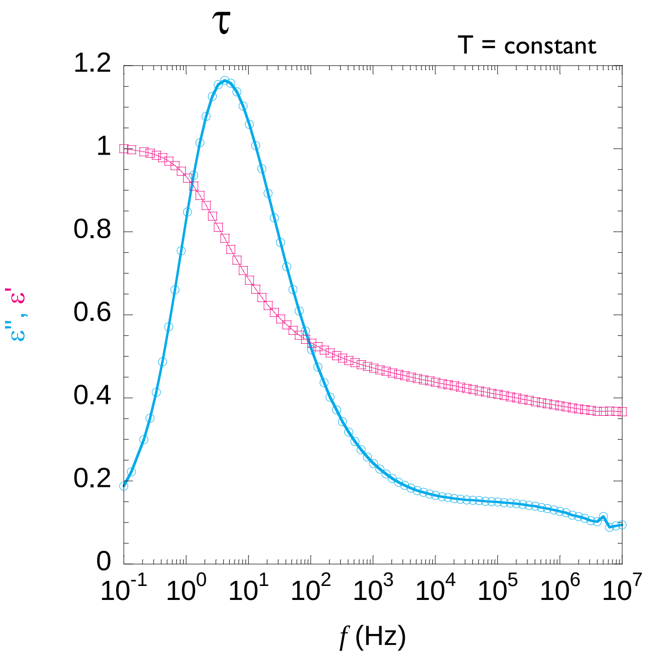
$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$

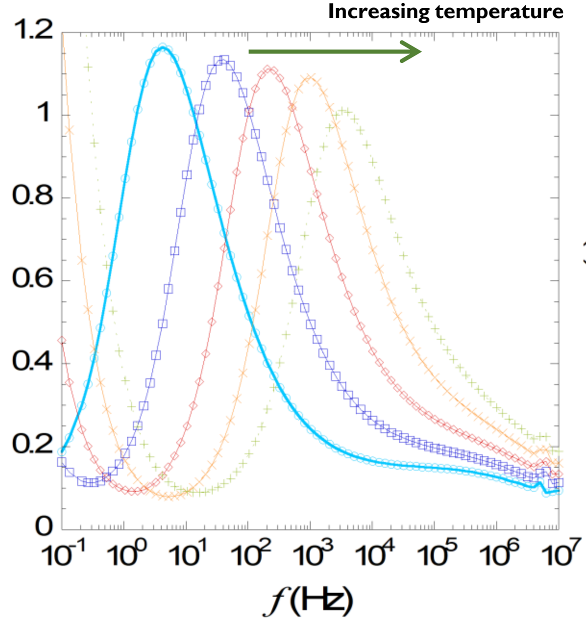
$\tan\delta = \varepsilon''(\omega) / \varepsilon'(\omega)$

<u>Average</u> response is measured:

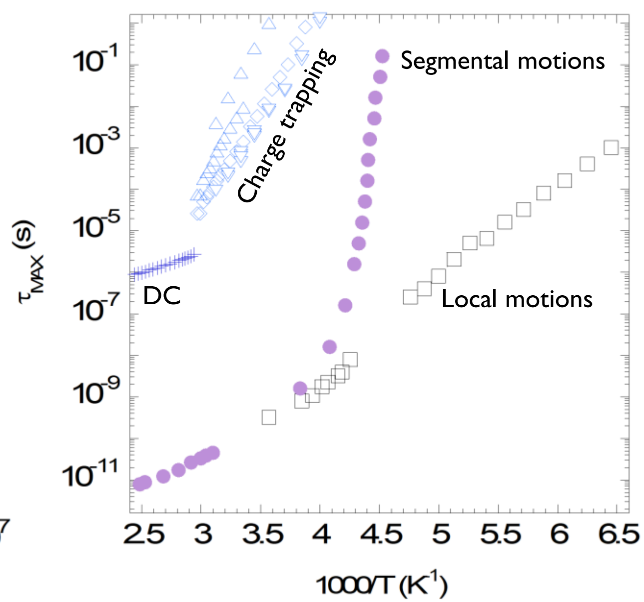
<u>P1. There is not spatial resolution</u>

In the complex dielectric permitivitty representation, one gets…





Relaxation plot



Dielectric properties of polymers with lateral resolution using an AFM approach: nanoDielectric Spectroscopy

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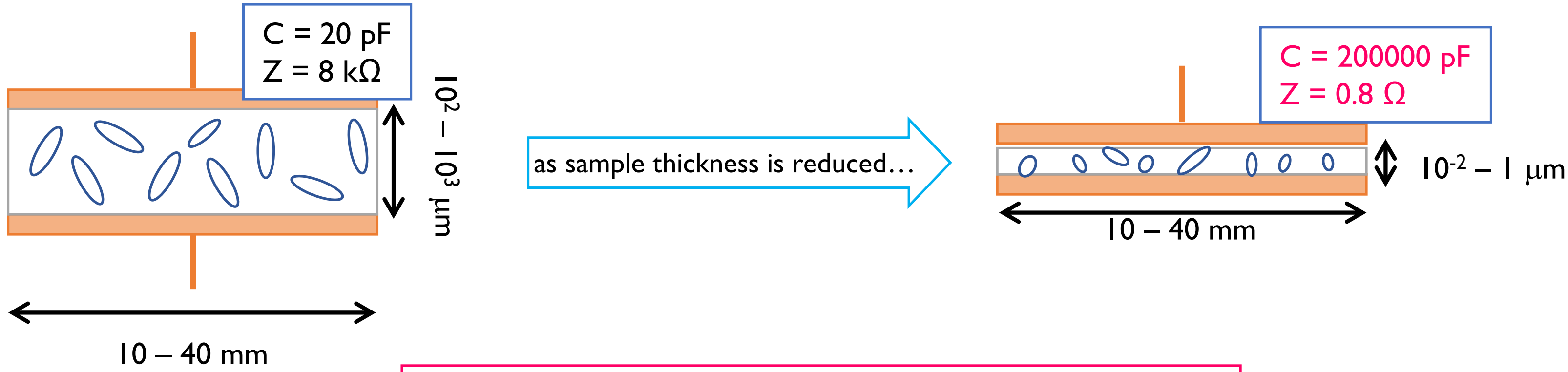
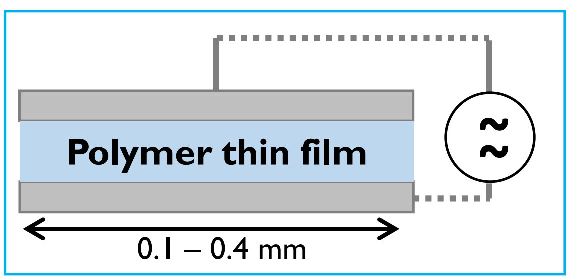


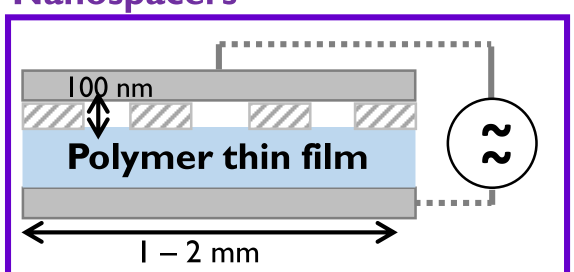
P2. Sample size/geometry imposes a constraint
Alternatives must be seeked

Capping between conducting layers



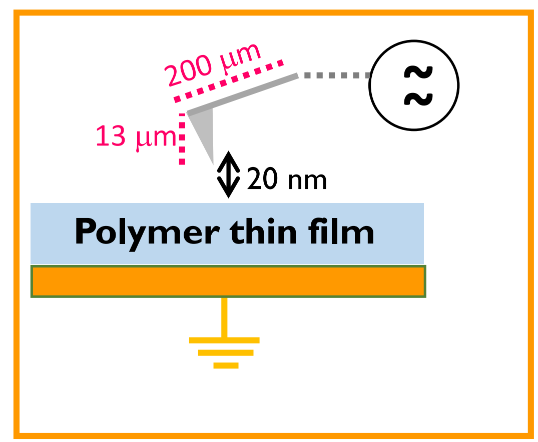
Napolitano et al. Eur. Phys. J. E (2013)
Martínez-Tong et al. Macromolecules (2014)

Nanospacers



Neubauer et al. Macromolecules (2016)
Tress et al. Science (2013)

AFM-based methods

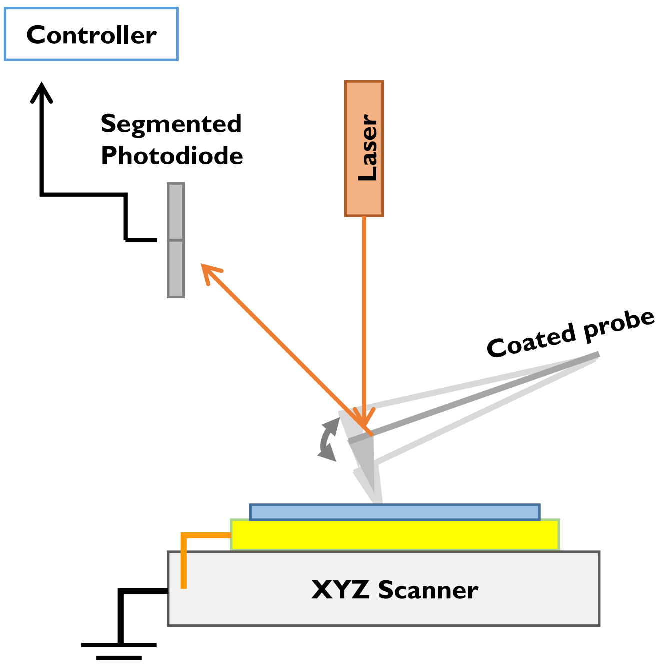


Miccio et al. Ultramicroscopy (2014)
Martínez-Tong et al. Soft Matter (2017)

(3) nanoDielectric Spectroscopy (nDS) = AFM + Electrical Force Analysis

nDS is based on the Electric Force Microscopy (EFM) technique. Here a double-pass approach is performed: each line is scanned twice, in such a way one can obtain simultaneously the surface topography and a signal arising from the electric probe/sample interactions.

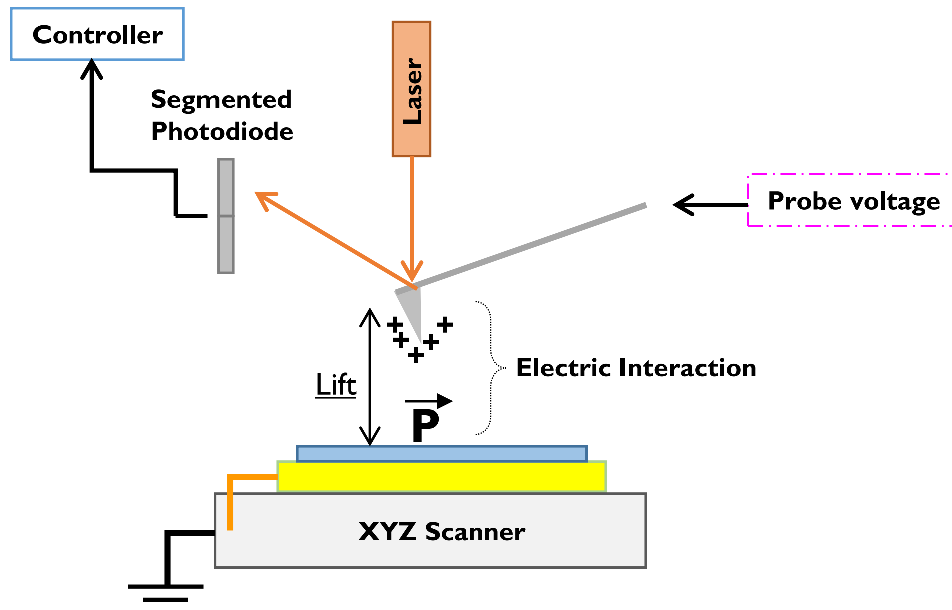
First scan: Topography characterization (tapping)



A mechanical excitation is applied to the probe.

The surface scanning is performed as the probe is being **vibrated close to its resonant frequency.**

Second scan: Electric interaction (EFM/nDS)



With the probe lifted from the polymer surface, a sinusoidal electric excitation is applied.

Electric probe-surface interactions lead to **cantilever oscillations**.

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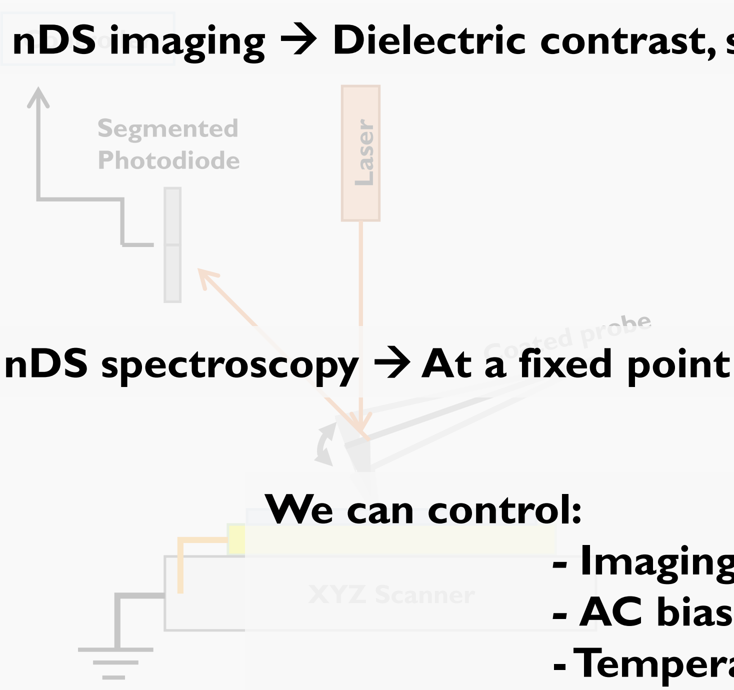
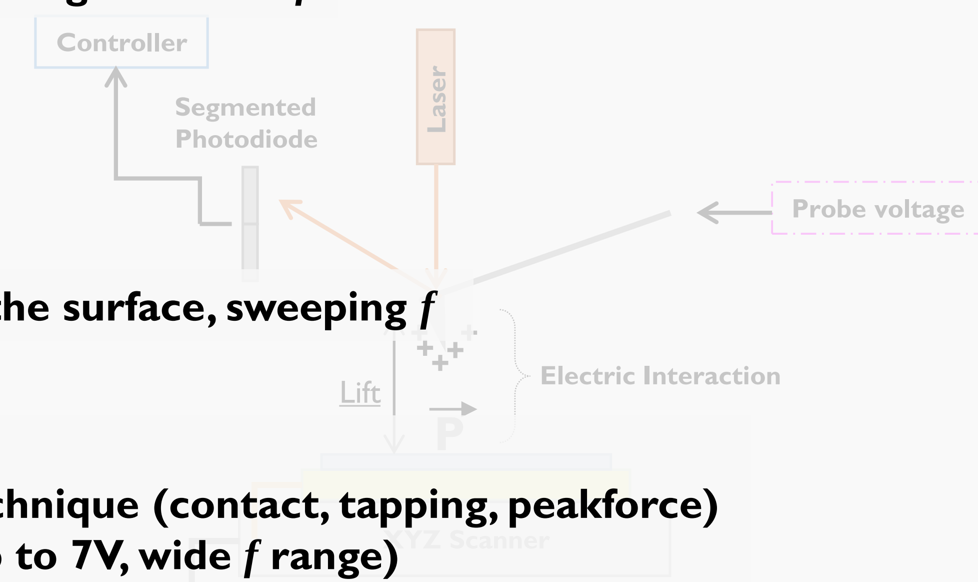
Under this generally idea, and applying an AC probe voltage… interaction (EFM/nDS)

nDS imaging → Dielectric contrast, scanning at a fixed *f*





nDS spectroscopy → At a fixed point of the surface, sweeping *f*

We can control:

- **Imaging technique (contact, tapping, peakforce)**
- **AC bias (up to 7V, wide *f* range)**
- **Temperature (-20 °C → 200 °C)**
- **Environment / RH**

A mechanical excitation is applied to the probe.

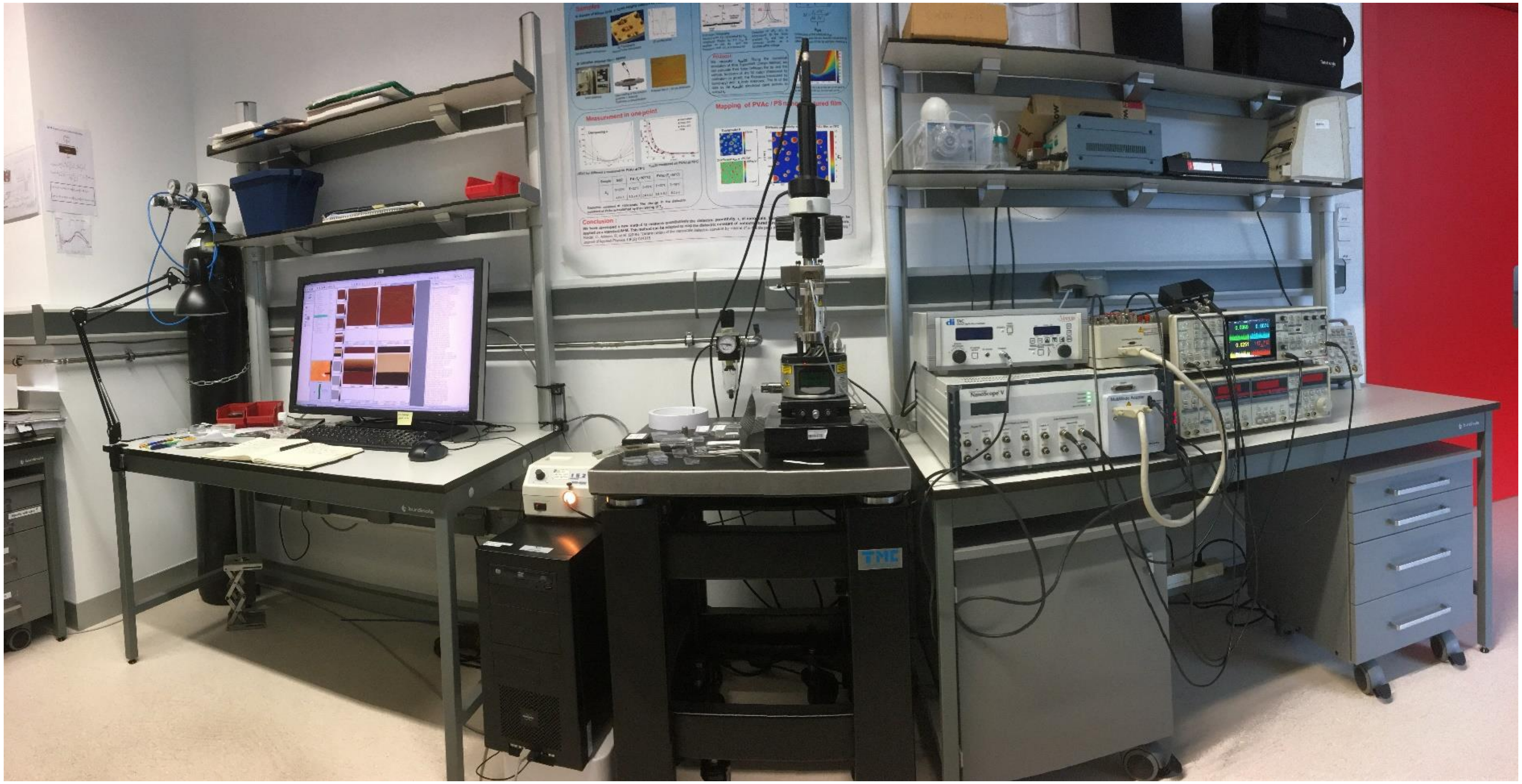
The surface scanning is performed as the probe is being **vibrated close to its resonant frequency.**

With the probe lifted from the polymer surface, a sinusoidal electric excitation is applied.

Electric probe-surface interactions lead to **cantilever oscillations**.

(3) **nanoDielectric Spectroscopy**

nDS is based on **Amplitude Modulation EFM:** the conducting probe oscillates when an electrical interaction with the polymer surface takes place

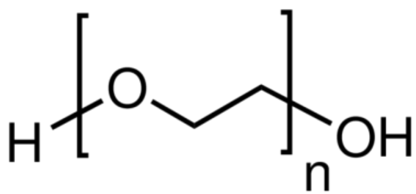


In our setup: Bruker Multimode 8 AFM + Nanoscope V controller. + SR830 Stanford Research LIA. Probes: PFTUNA by Bruker

Application to

Ionic transport in poly(ethylene oxide) (PEO) thin films

(4) Poly(ethylene oxide) (PEO) in thin film geometry

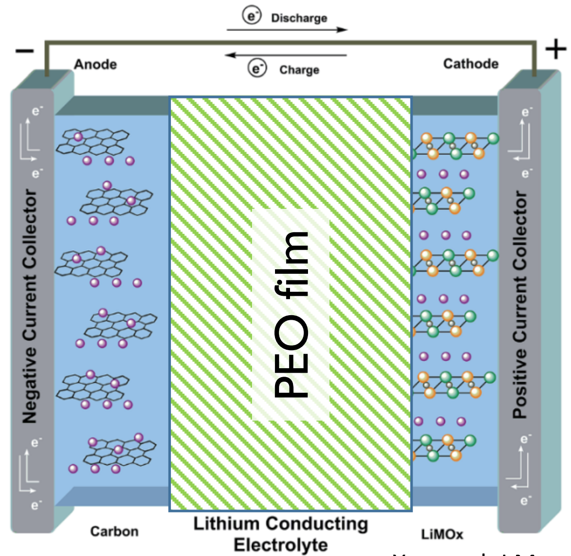


currently considered candidate as a:

Solid polymer electrolyte

✓ Good ionic conduction when doped with Li salts.

✓ Applications might require thin film geometries



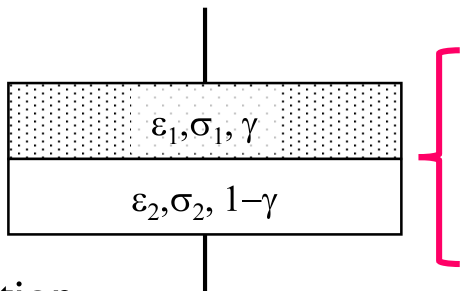
Xue et al, J Mater Chem A, 2015

Problems to be addressed:

1. Film preparation conditions:

PEO **crystallization** during preparation is strongly controlled by the solvent used. Toolan et al. Macromolecules 2016

2. The role of semicrystalline-polymer nanostructures on charge transport:



$\varepsilon^*_{MWS}(\omega)$

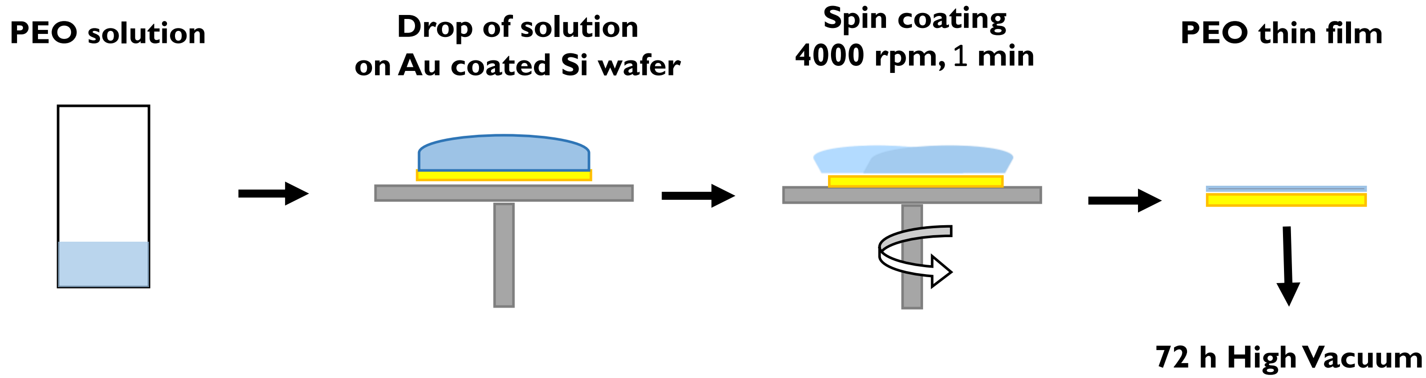
Maxwell-Wagner-Sillars (MWS) polarization

Blocking of charge carriers at inner dielectric boundaries, such as at the ones between crystalline and amorphous areas. This leads to an additional contribution to the polarization.

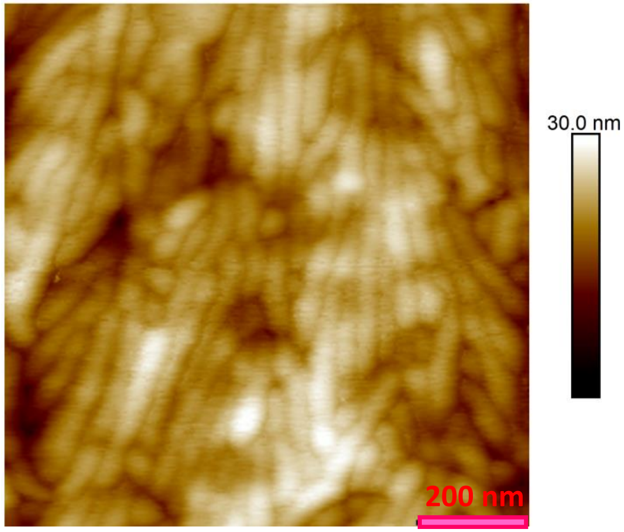
Full details: D. E. Martinez-Tong, L. A. Miccio and A. Alegria. Soft Matter 13 (2017) 5597-5603

(4) nDS experiments on PEO thin films: Sample preparation

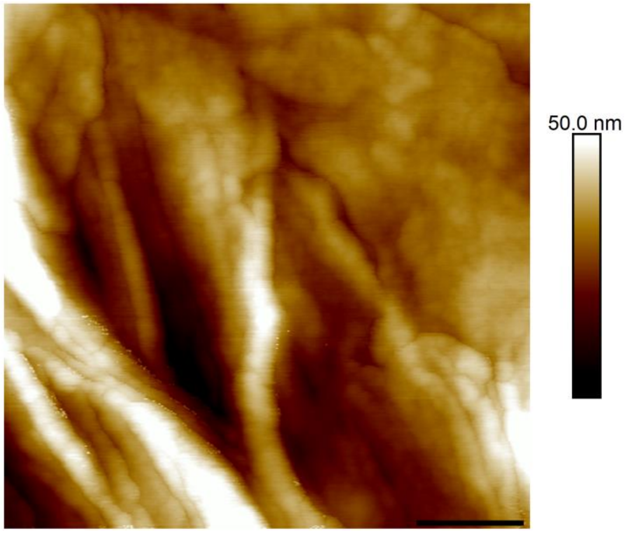
- Mw = 94000 g/mol
- T_m = 60 °C,
  T_c = 50 °C,
  T_g = - 60 °C



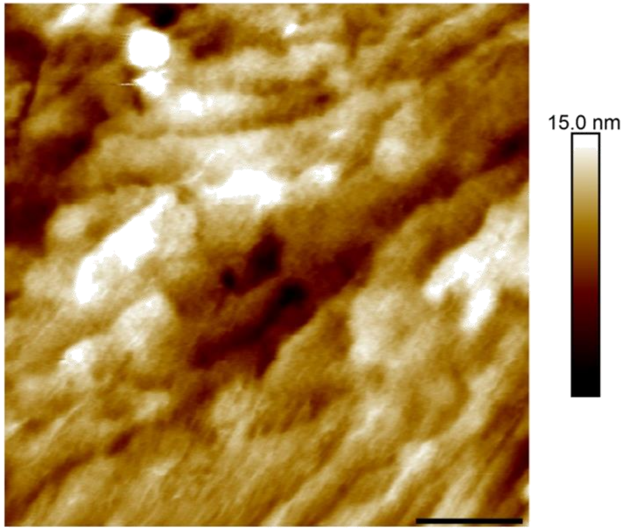
AFM topography



Acetonitrile



Chloroform



Melt

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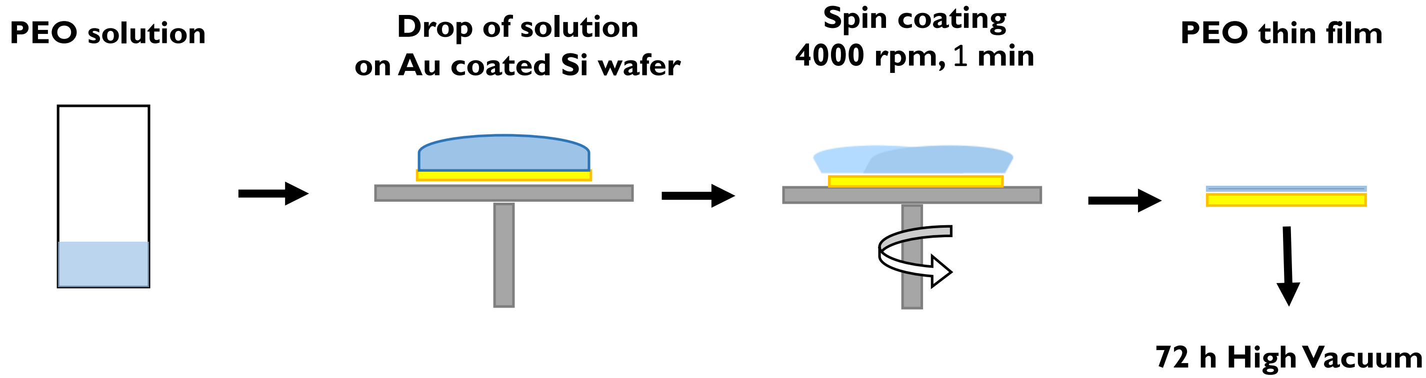
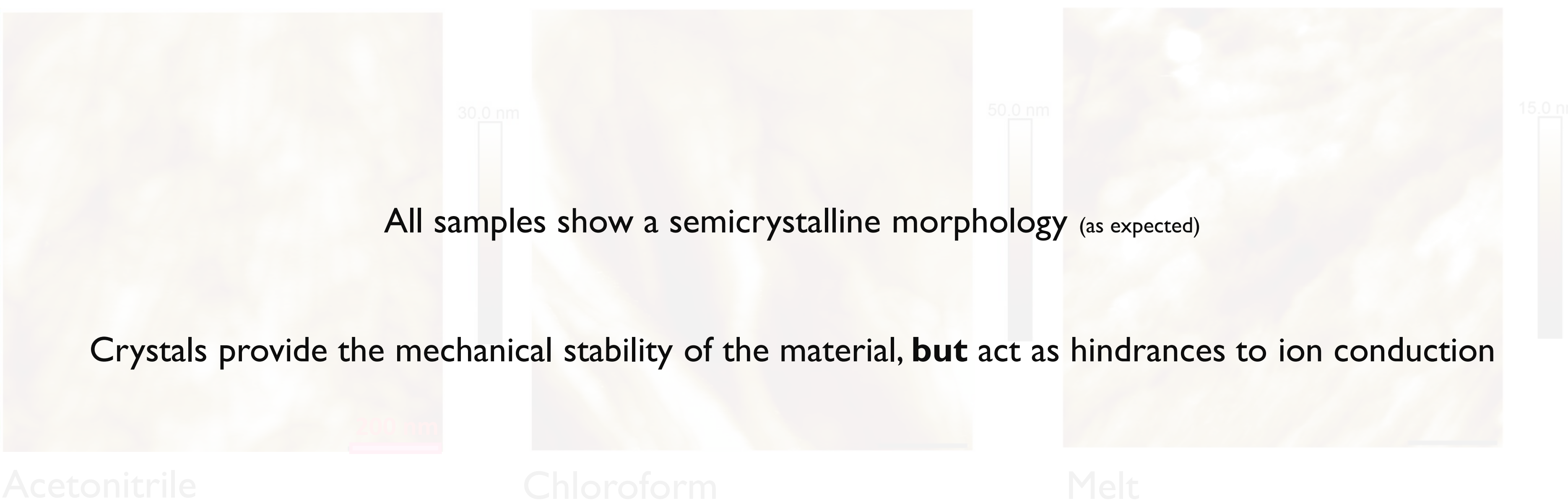


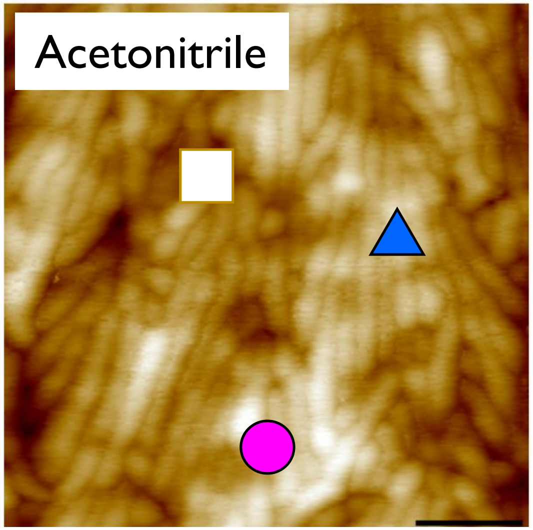
AFM topography

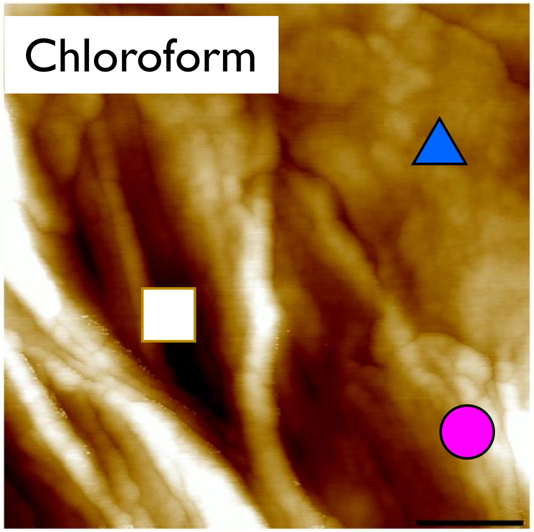


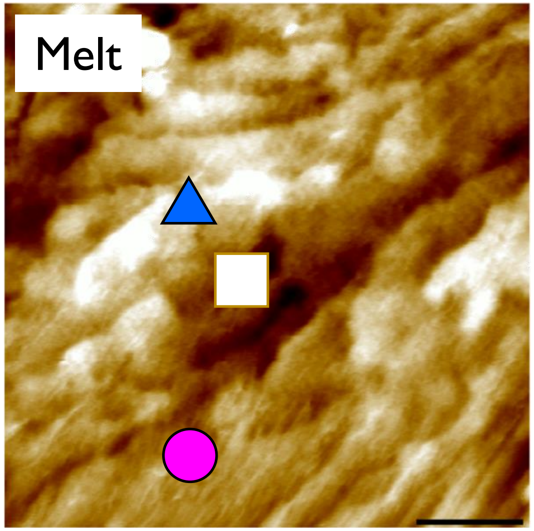
All samples show a semicrystalline morphology (as expected)

Crystals provide the mechanical stability of the material, **but** act as hindrances to ion conduction

AFM topography & nDS Spectra



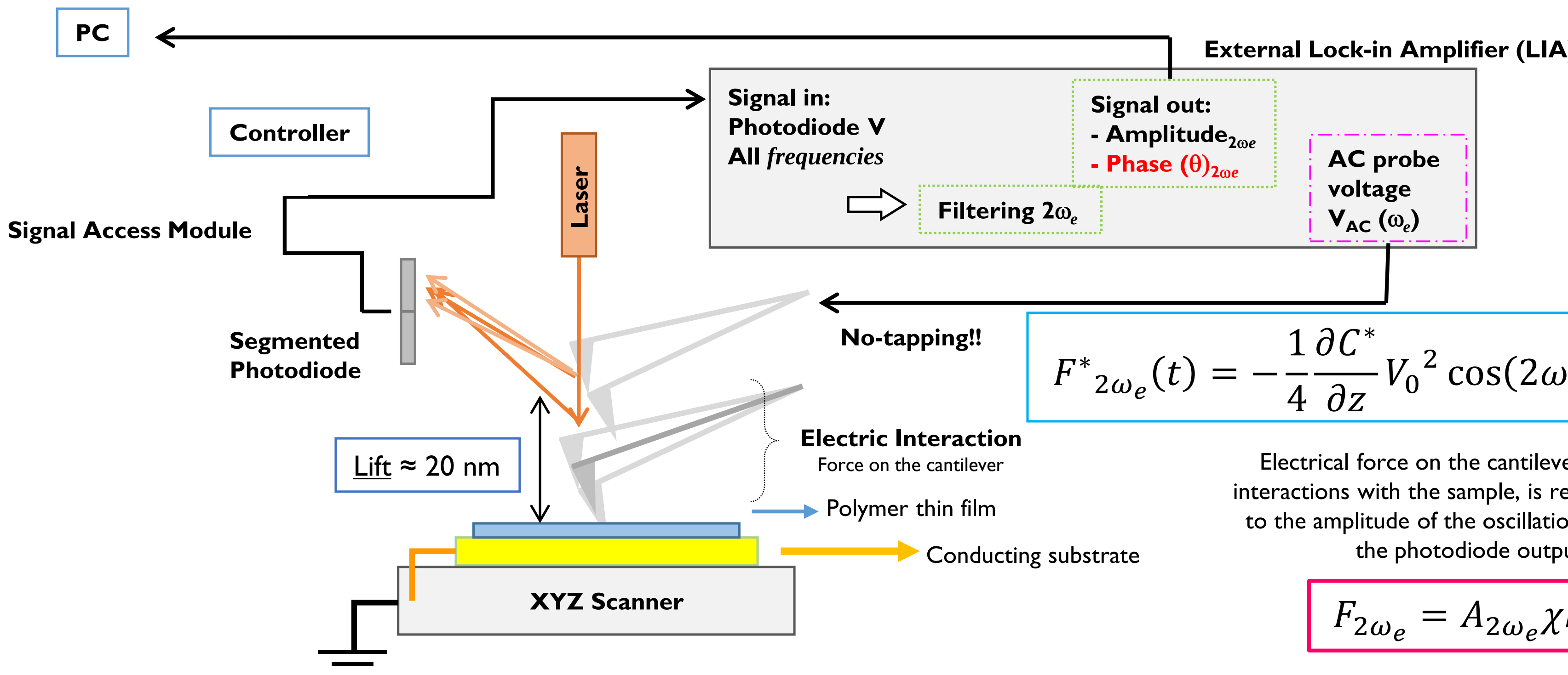




How do we make spectroscopy on these points?

nanoDielectric Spectroscopy details

nDS is based on **Amplitude Modulation EFM:** the conducting probe oscillates when an electrical interaction with the polymer surface takes place



$$F^*{}_{2\omega_e}(t) = -\frac{1}{4}\frac{\partial C^*}{\partial z} V_0{}^2 \cos(2\omega_e t)$$

Electrical force on the cantilever, by interactions with the sample, is related to the amplitude of the oscillations of the photodiode output by:

$$F_{2\omega_e} = A_{2\omega_e} \chi k_c$$

Miccio et al. Journal of Applied Physics, 2014.

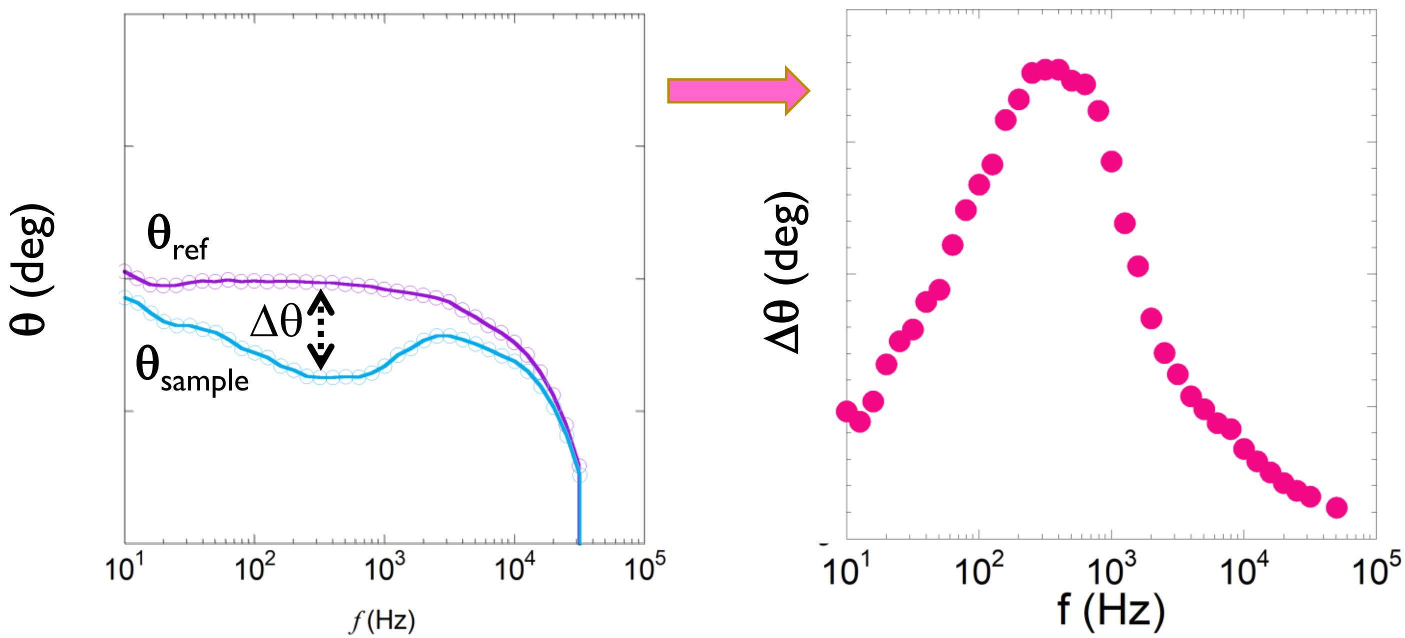
The Lock-in phase (θ) is the important parameter for analysis

nanoDielectric Spectroscopy details

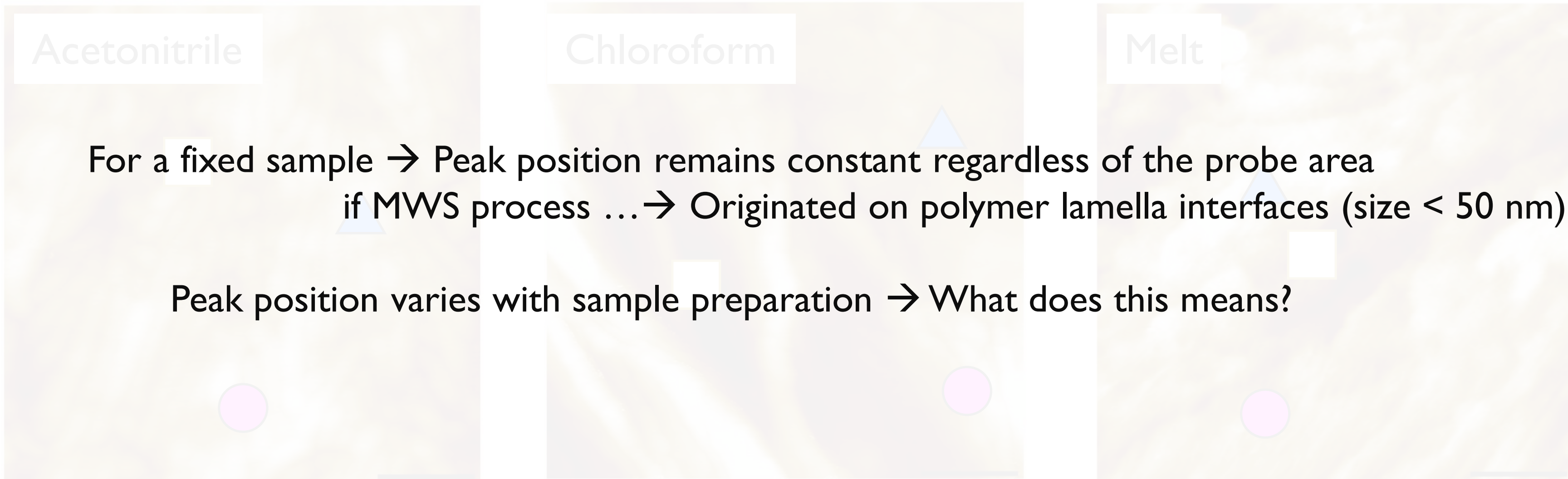
In order to study the dielectric properties of the sample, we probe a **phase shift:**

$$\Delta\theta(\omega) = \theta_{ref}(\omega) - \theta_{sample}(\omega)$$

where θ_{ref} is the phase measured on a "dissipation-free sample" (lossless material) and θ_{sample} is the phase measured on the polymer sample.



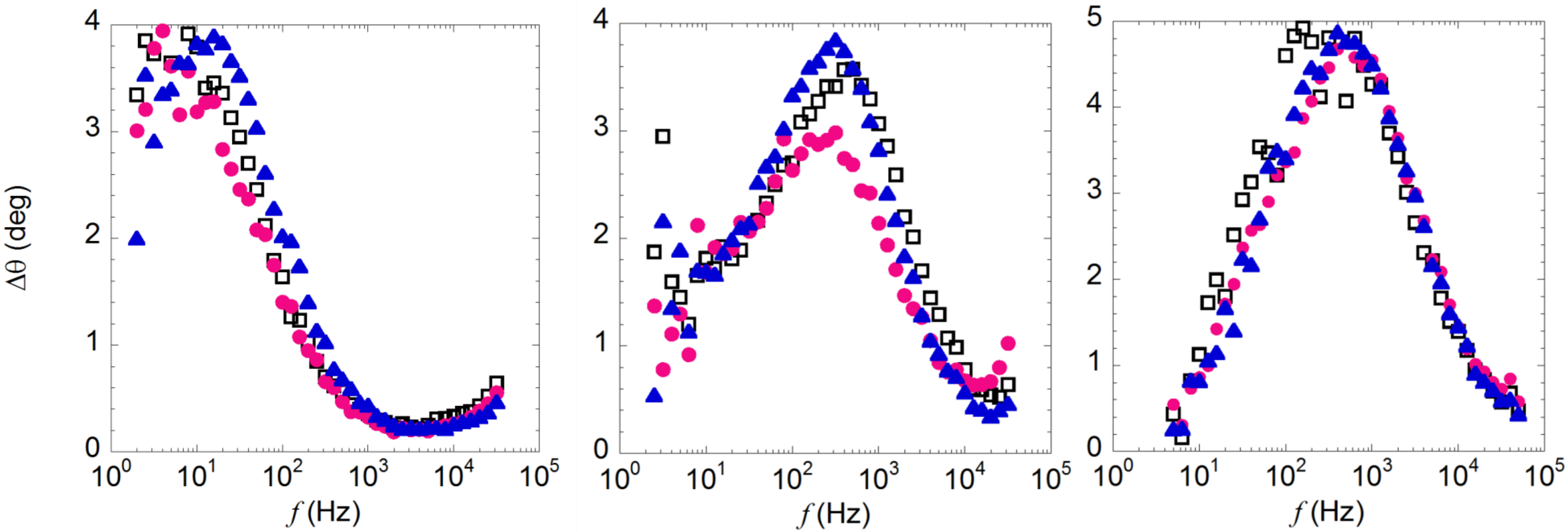
AFM topography & nDS Spectra



For a fixed sample → Peak position remains constant regardless of the probe area

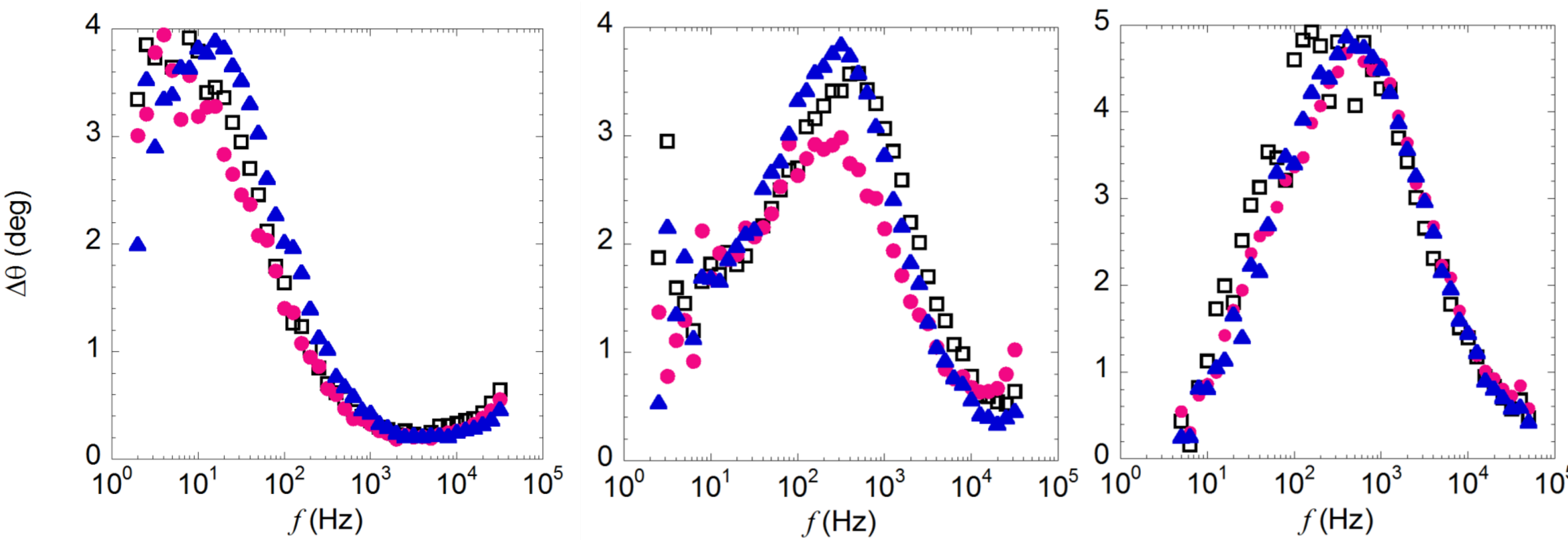
if MWS process …→ Originated on polymer lamella interfaces (size < 50 nm)

Peak position varies with sample preparation → What does this means?



How can we extract data from these peaks ?

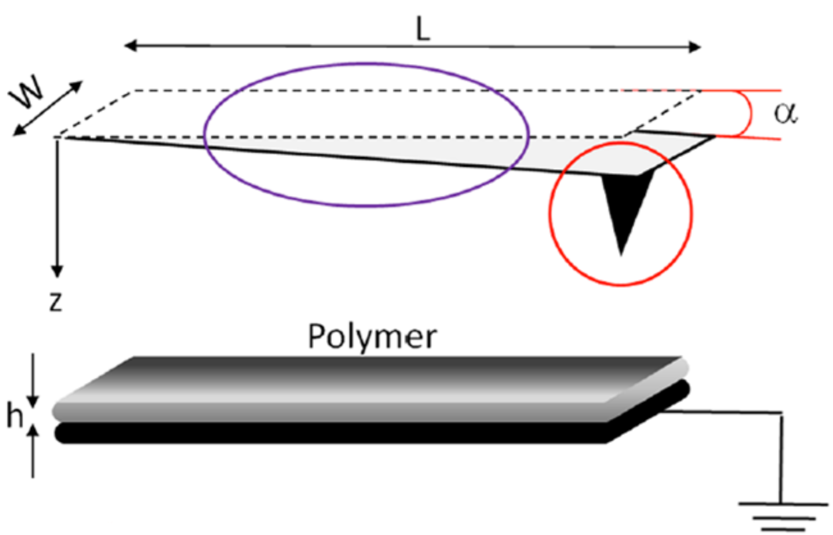
<u>and make it quantitative and useful,</u> <u>while still learning from it</u>

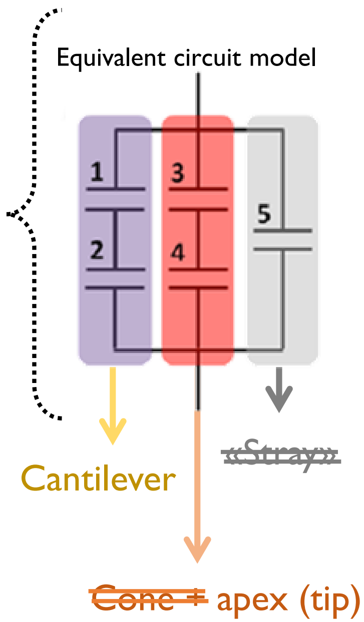


Obtaining the dielectric relaxation properties by nDS data modeling

Miccio et al. Journal of Applied Physics, 2014.

Please recall that this is a "capacitor"





in general…

$$F^*{}_{2\omega_e}(\omega) = func\left(\frac{\partial C^*}{\partial z}\right)$$

$$F^*{}_{2\omega_e}(\omega) \propto \frac{\partial C^*{}_{CANT}}{\partial z} + \frac{\partial C^*{}_{TIP}}{\partial z}$$

Cantilever contribution

$$F^*_{2\omega_e\_CANT}(\omega) \propto \frac{\varepsilon_0 W}{T}\left[\left(1+\frac{h}{T\varepsilon^*{}_{AV}}\right)^{-1} - \frac{T}{L\sin\alpha}\ln\left(1+\frac{L\sin\alpha}{T}\left(1+\frac{h}{T\varepsilon^*{}_{AV}}\right)^{-1}\right)\right]$$

Apex (tip) contribution

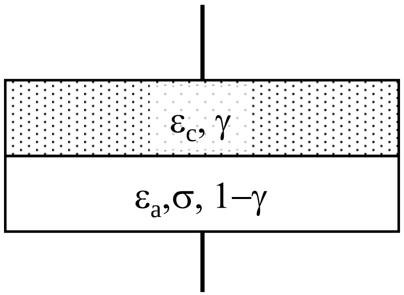
$$F^*_{2\omega\_TIP}(\omega) \propto 2\pi\varepsilon_0 \frac{R^2(1-\sin\theta_0)}{z^2+zR(1-\sin\theta_0)}\left(1+\frac{h}{z\varepsilon^*{}_{LOC}}\right)^{-1}\left(1+\frac{h}{[z+R(1-\sin\theta_0)]\varepsilon^*{}_{LOC}}\right)^{-1}$$

Gomila Model

Choosing a dielectric function

$$\varepsilon^*(\omega) = \varepsilon^*_{LOC}(\omega) = \varepsilon^*_{AV}(\omega)$$

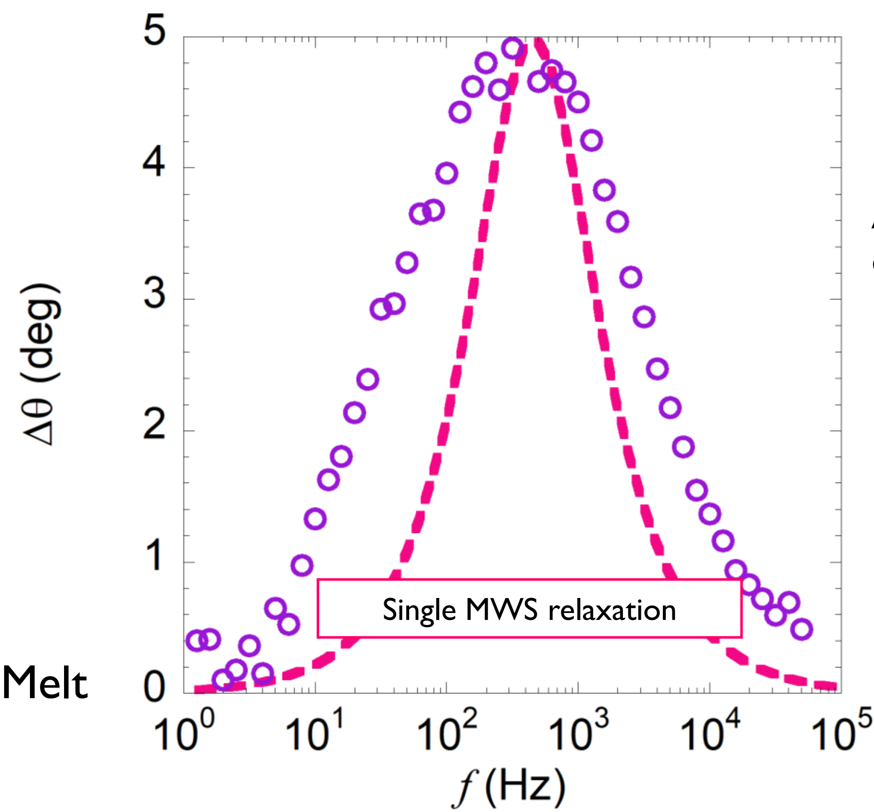
Maxwell-Wagner-Sillars (MWS) model



$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{MWS}}{1 + i\omega/\omega_{MWS}}$$

$$\begin{cases} \Delta\varepsilon_{\mathrm{MWS}} = \dfrac{\varepsilon_c}{\varphi}\left[1 - \dfrac{\varepsilon_a}{\dfrac{\varepsilon_c}{\varphi}(1-\varphi) + \varepsilon_a}\right] \\ \omega_{\mathrm{MWS}} = \dfrac{\sigma\varphi}{\varepsilon_0[\varepsilon_c(1-\varphi) + \varepsilon_a\varphi]} \end{cases}$$

PEO Melt



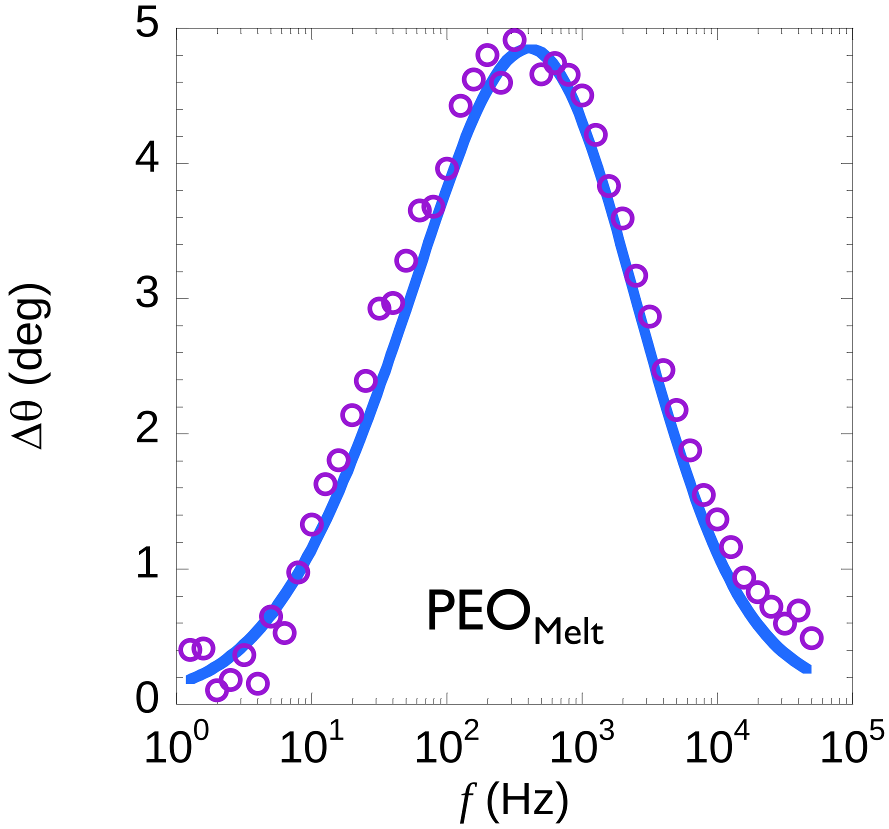
A single MWS relaxation does not account for the data distribution width; however…

$$\varepsilon^*(\omega) = \int_0^\infty \varepsilon^*_{\mathrm{MWS}}(\omega)\, g(\log_{10}\sigma)\mathrm{d}(\log_{10}\sigma)$$

Choosing a dielectric function

MWS functions distribution

$$\varepsilon^*(\omega) = \int_0^\infty \varepsilon^*{}_{\mathrm{MWS}}(\omega)\, g(\log_{10}\sigma)\mathrm{d}(\log_{10}\sigma)$$



<u>Gaussian distribution of MWS relaxations</u>

<u>Best possible parameters:</u>

ε_c = 2.5
ε_a = 3.0

φ = 0.18 ⟶ Crystallinity

σ = 10^{-7} to 10^{-11} S/cm
σ_{peak} = 1.7×10^{-9} S/cm ⟶ Conductivity

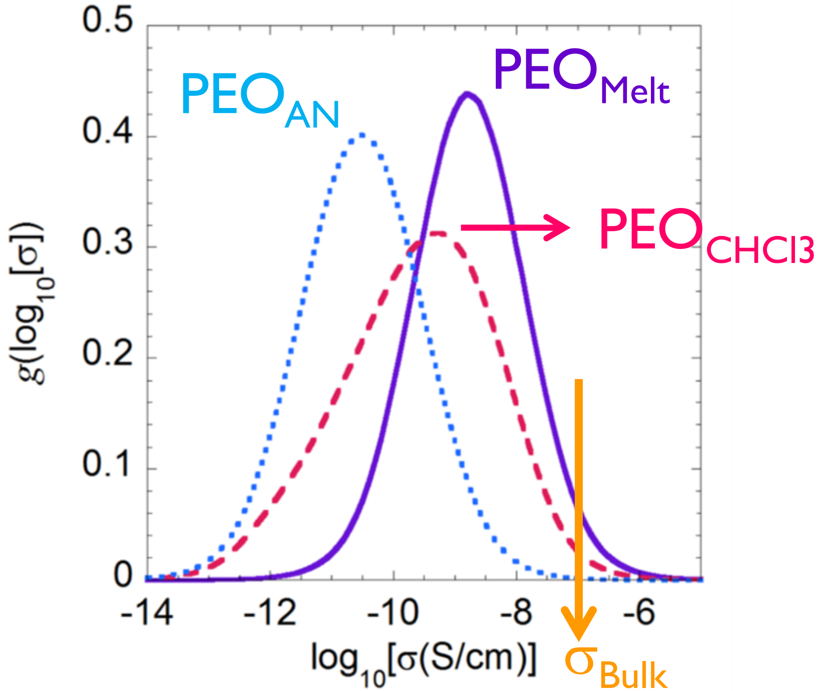
$$\omega_{\mathrm{MWS}} = \frac{\sigma\varphi}{\varepsilon_0[\varepsilon_c(1-\varphi)+\varepsilon_a\varphi]}$$

PEO_{AN} films (highly polar solvent) present an amorphous phase with relatively low conductivity (~10^{-11} S/cm): **efficient molecular packing**.

PEO_{Melt} films show an increase in the average conductivity (~10^{-9} S/cm): **poorer molecular packing**.

PEO_{CHCl3} films (low-polar solvent) present an intermediate situation (~10^{-10} S/cm), but **higher heterogeneity**.

Conductivity distribution



Now…

<u>What's the next step in this Project?</u>

nDS experiements under controlled humidity

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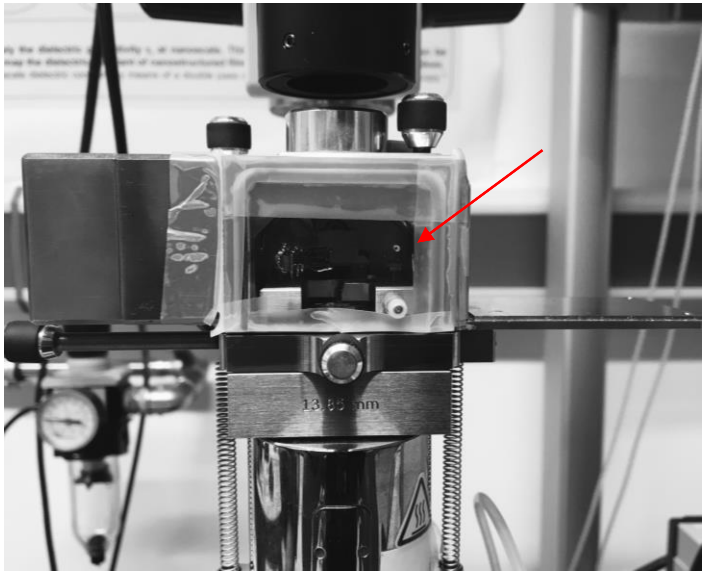


RH conditions:

- 13 - 70 RH%
- PID controlled

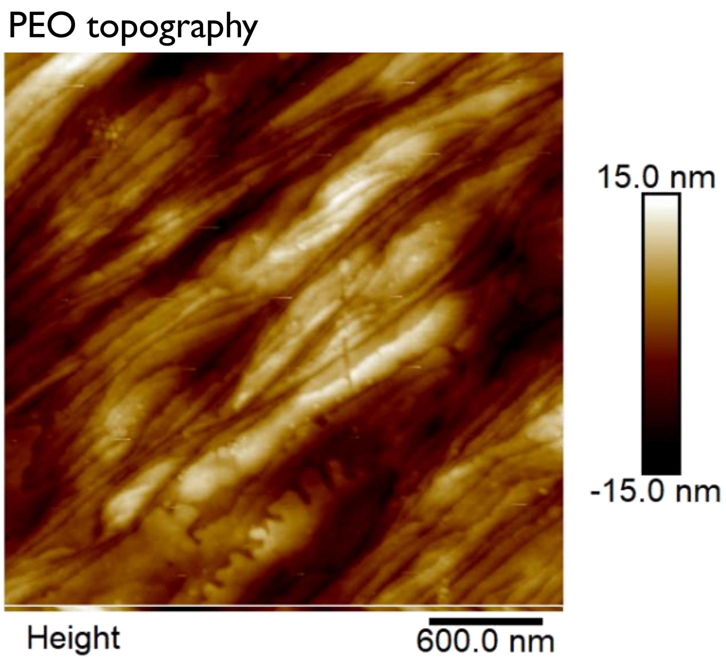
Sample:

- PEO thin films (35 kDa)
- Heated to 100 °C for 15 min
  @ 100 sccm N2 Flow
  => Equilibrated over night (13 %RH)
- 10-15 min equilibration, after RH-Change

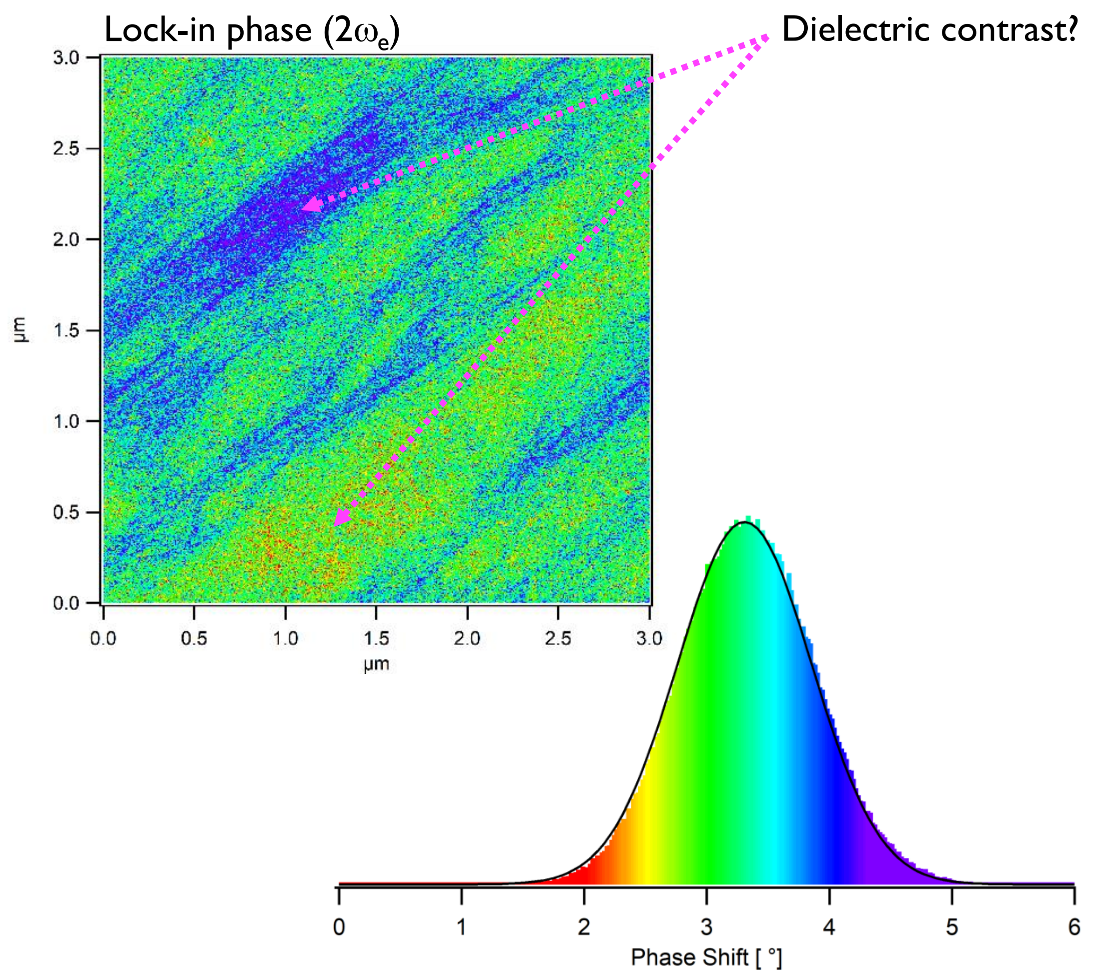
nDS experiements under controlled humidity

nDS imaging (1 kHz, 13% RH)

First scan: Topography characterization (tapping)



Second scan: Electric interaction (EFM/nDS)

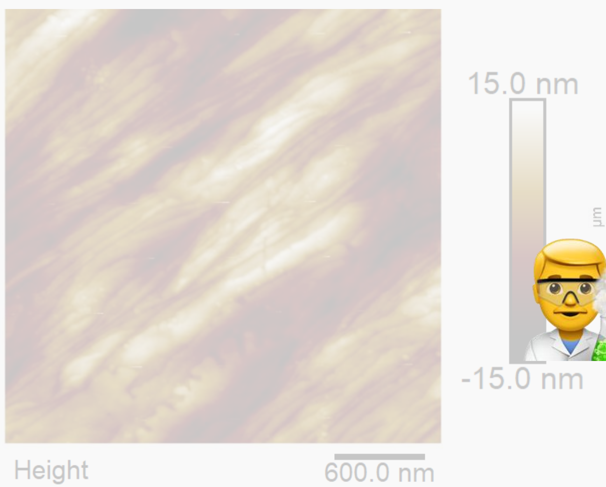


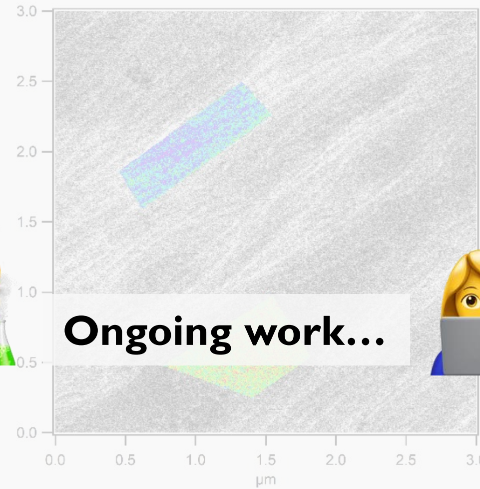
nDS experiements under controlled humidity

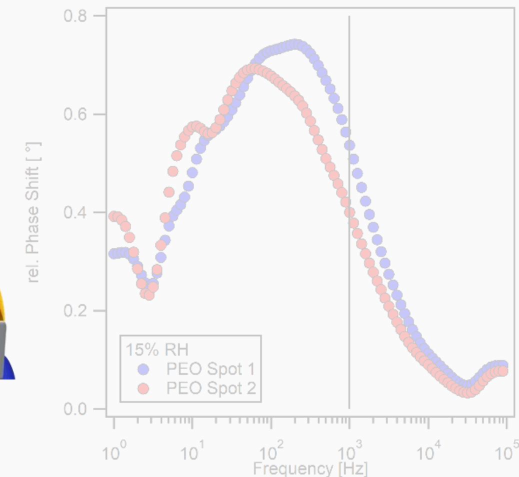
nDS spectroscopy (variable RH)

Ongoing work…

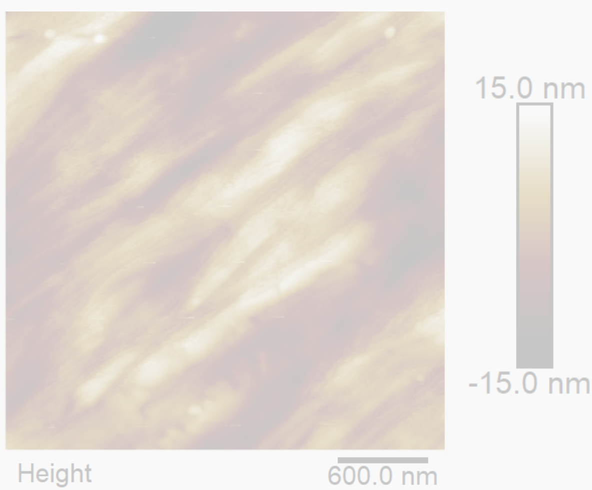
13 %RH

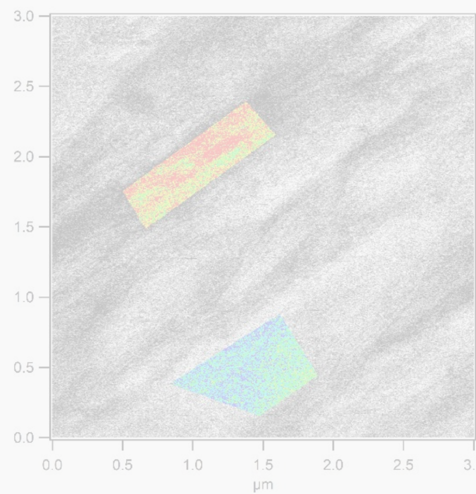


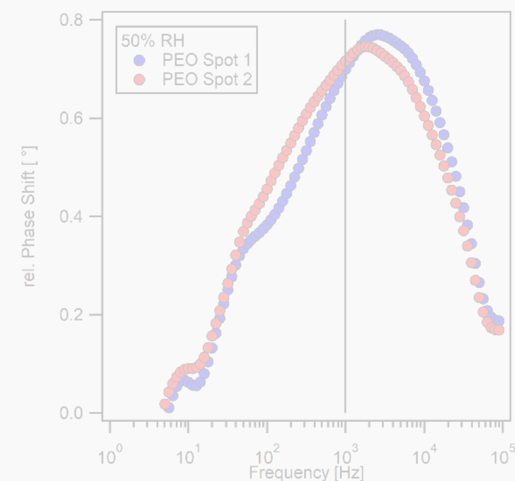




50 %RH







Take home messages

- AFM provides structural information, property mapping, and the possibility to perform spectroscopy measurements with lateral resolution. We can control and play with variables as temperature and humidity.

- nanoDielectric Spectroscopy (nDS) measurements, provide surface topography, dielectric contrast maps & dielectric spectra on polymer films. For example, on PEO thin films allowed the study of interfacial polarization processes. → Provided magnitudes of physical interest, as conductivity distributions.

Acknowledgments

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Angel Alegria

CFM

eman ta zabal zazu

Universidad del País Vasco

Euskal Herriko Unibertsitatea

DIPC

Dielectric properties of polymers with lateral resolution using an AFM approach: nanoDielectric Spectroscopy

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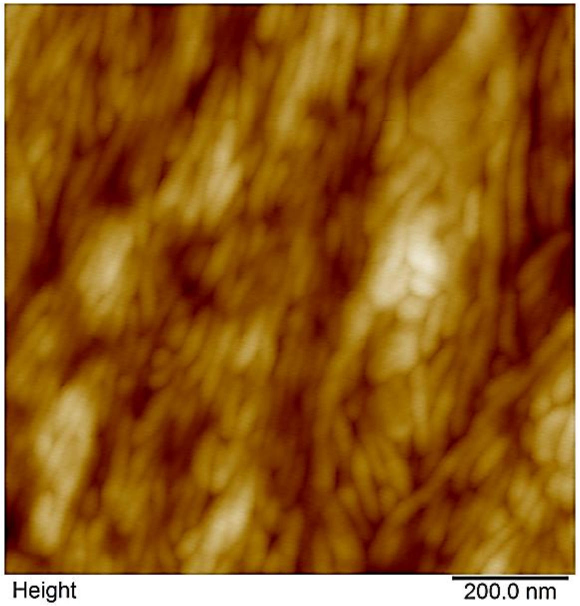
Thank you!

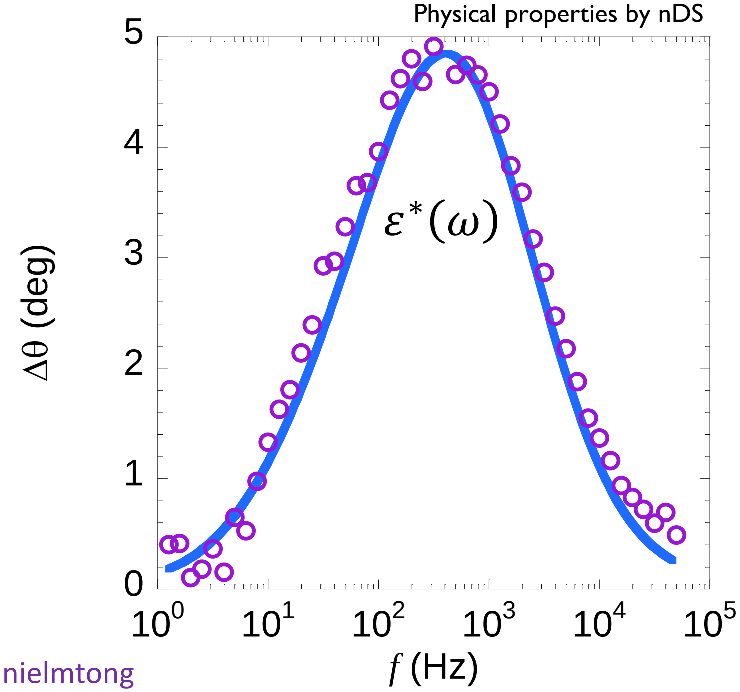
From images…

Polymer surface (AFM)



…to spectroscopy

Physical properties by nDS



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