BDS2016 Tutorials:

Local Dielectric Spectroscopy

by Scanning Probes

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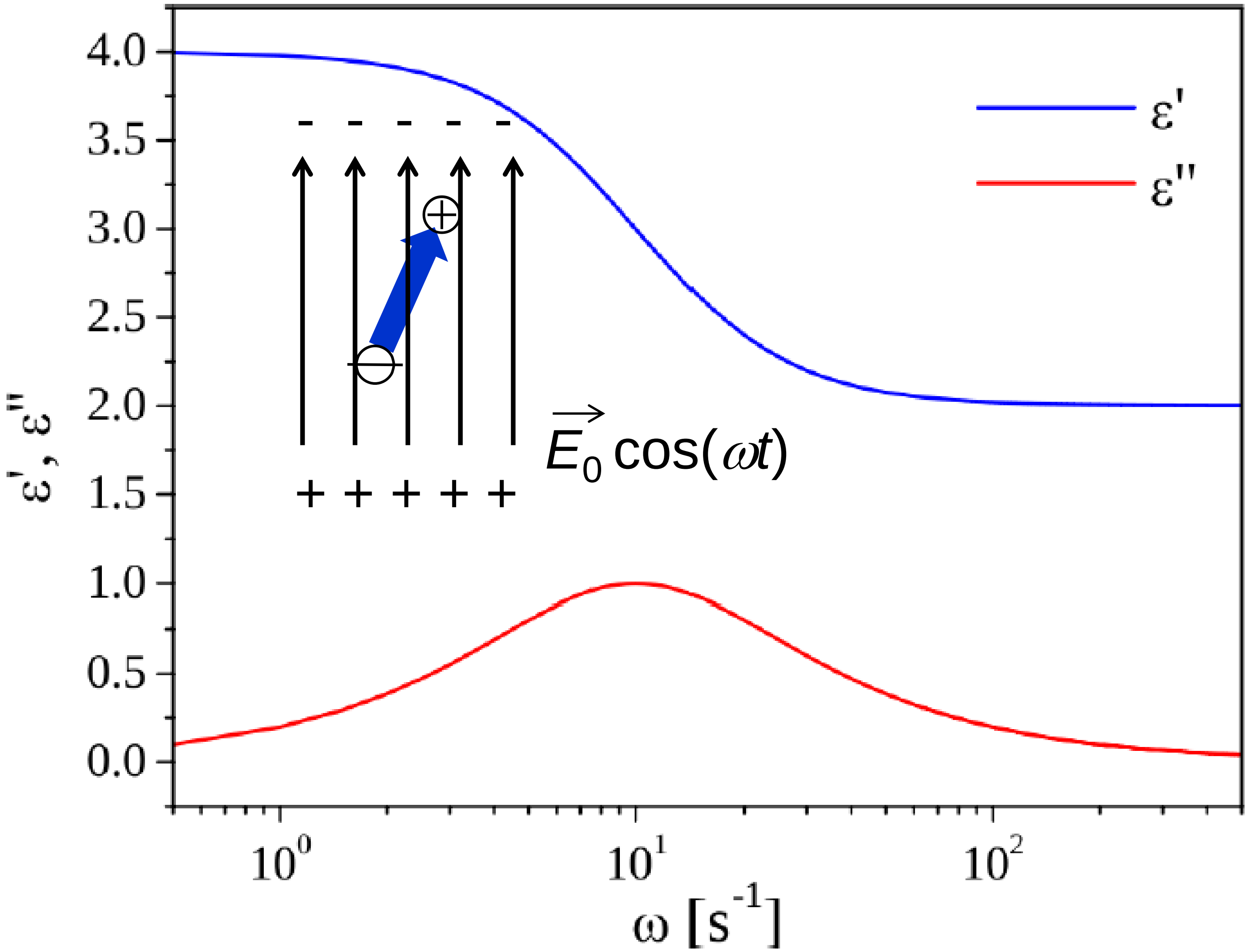
OUTLINE

- Broadband Dielectric Spectroscopy (BDS): Information on relaxation dynamics through electric polarization.

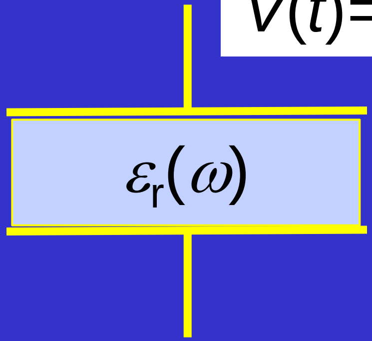
- Local Dielectric Spectroscopy (LDS, or nanoDS): the same kind of information, on a nanometer-size volume of material.

- How Local Dielectric Spectroscopy can be realized by resorting to scanning probe techniques like the Atomic Force Microscope.

ORIENTATIONAL DIELECTRIC RESPONSE



BROADBAND DIELECTRIC SPECTROSCOPY



$V(t)=V_0\cos(\omega t)$ $\quad$ $I(t)=I_0\cos(\omega t - \delta)$

$$\hat{Z}(\omega)=\frac{\hat{V}(\omega)}{\hat{I}(\omega)}$$

$$\hat{Z}_0(\omega)=\frac{1}{i\omega C_0} \qquad C_0=\frac{\varepsilon_0 A}{D}$$

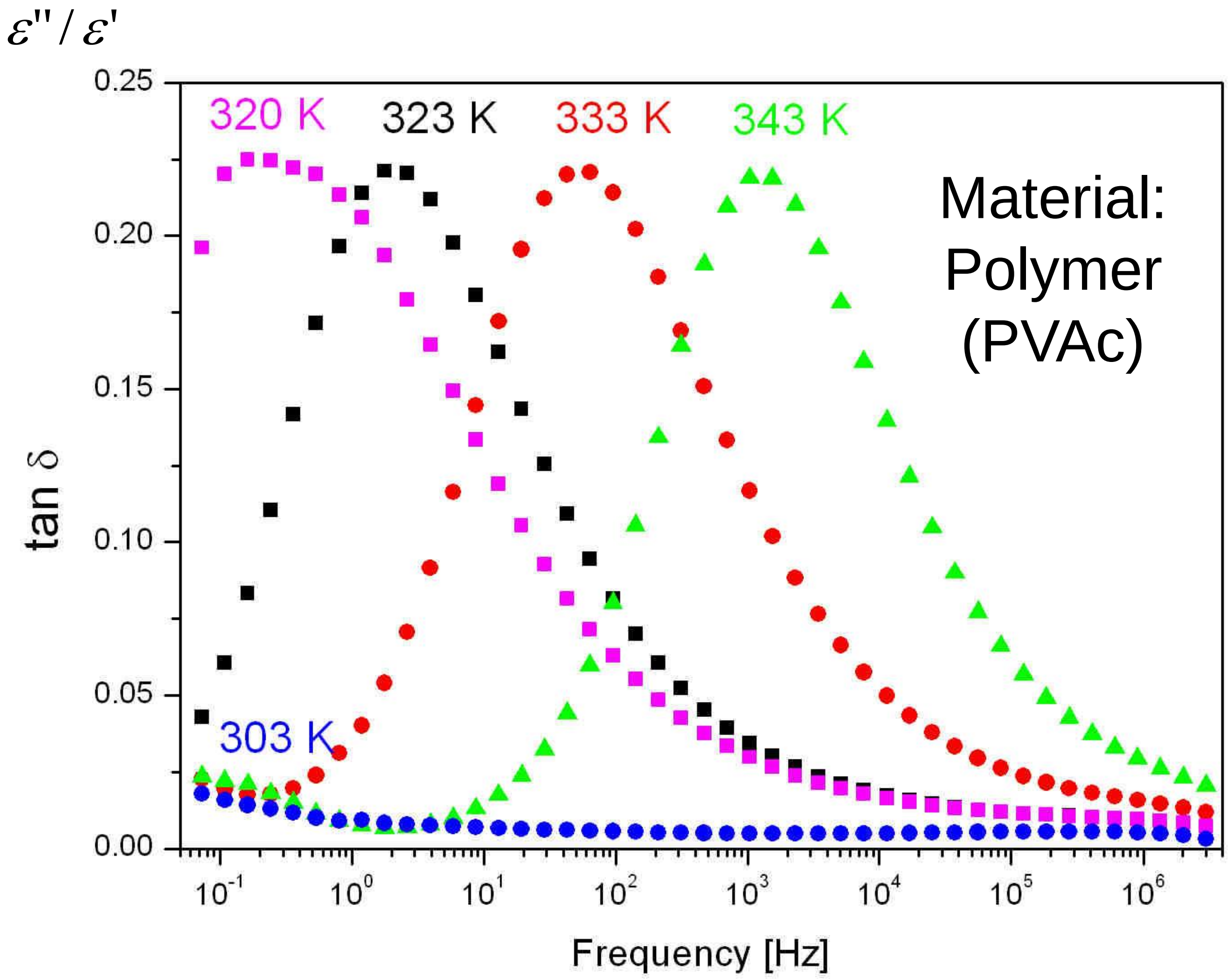
Void parallel plate capacitor

$$\hat{Z}(\omega)=\frac{1}{i\omega\hat{C}(\omega)} \qquad \hat{C}(\omega)=\frac{1}{i\omega\hat{Z}(\omega)}=\hat{\varepsilon}_r(\omega)C_0$$

Filled by dielectric

$$\hat{\varepsilon}_r(\omega)=\frac{\hat{C}(\omega)}{C_0}=\frac{\hat{Z}_0(\omega)}{\hat{Z}(\omega)}=\varepsilon'(\omega)-i\varepsilon''(\omega)$$

DIELECTRIC RELAXATION SPECTRUM



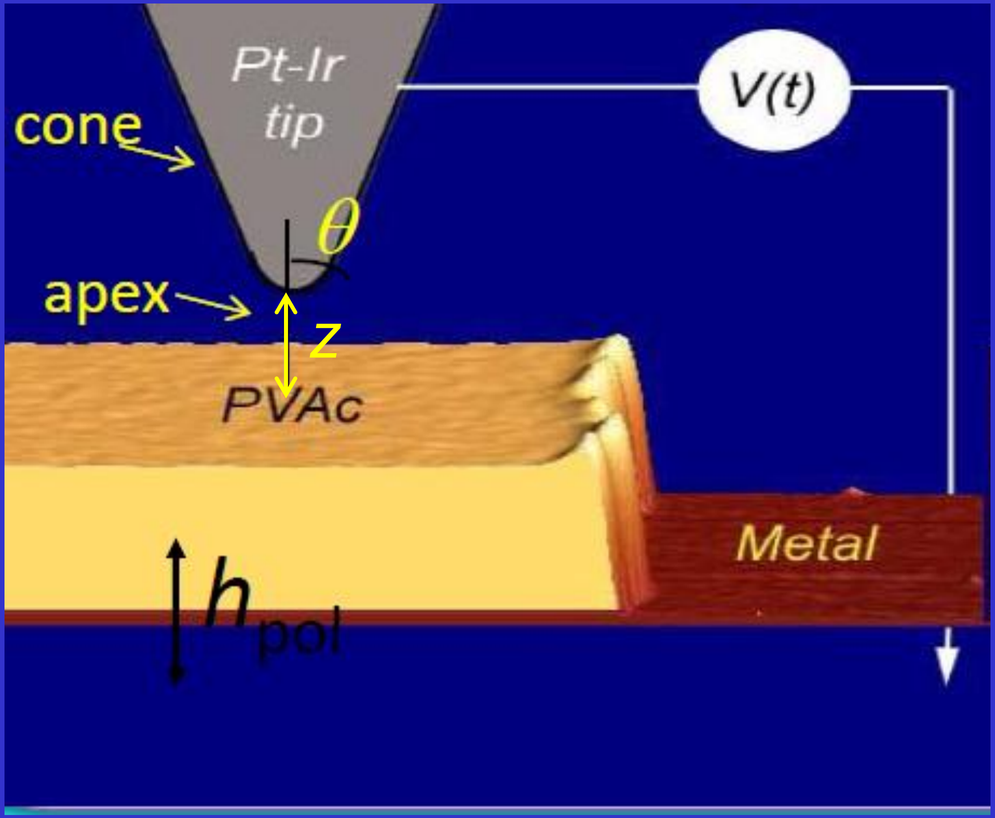
Material:
Polymer
(PVAc)

MOTIVATION FOR LOCAL MEASUREMENTS

- BDS provides the average behavior of a macroscopic sample volume.

- Behavior of nanometer-size volume:
    - *Single macromolecules*
    - *Heterogeneity*
    - *Interface*

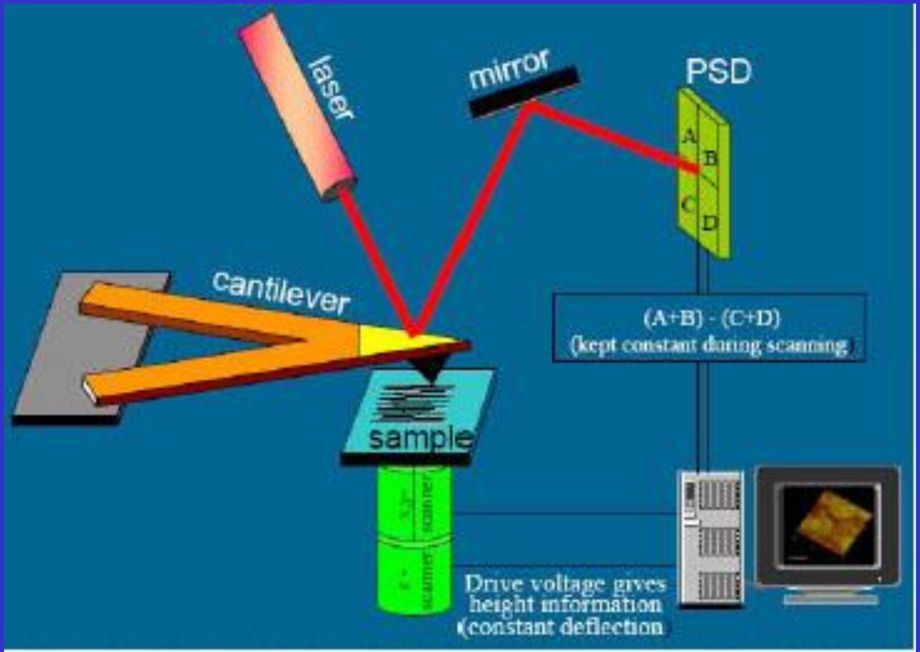
DIELECTRIC PROPERTIES ON A LOCAL SCALE



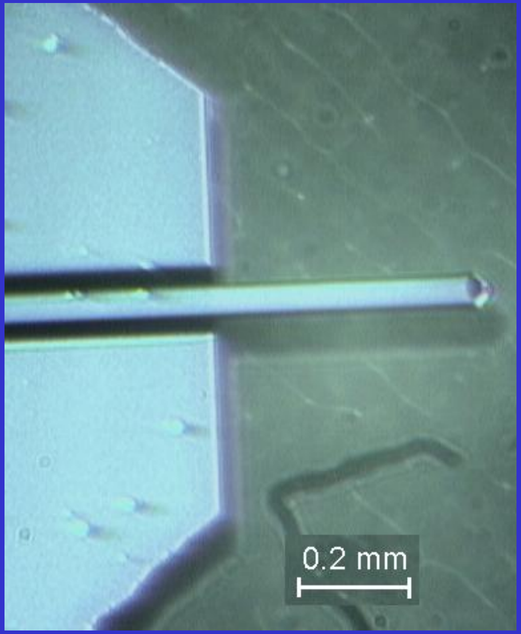
- A conductive tip acts as a nanometer-size electrode.
- Applying electric potential to the tip, a localized electric field is generated.
- A current is produced, like in BDS.
- Current measurement noise prevents sensitivity to capacitance < 1 aF.

ATOMIC FORCE MICROSCOPE (AFM)

Also a *force* is produced, that depends on polarization *charge*, that can be measured accurately if the tip is the one of an ATOMIC FORCE MICROSCOPE.



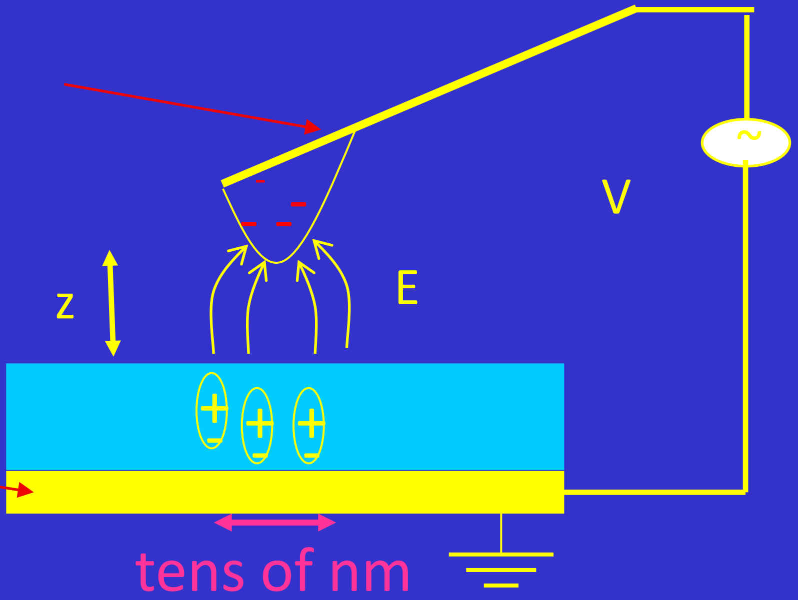
Microscope setup



Cantilever force sensor

Capacitance > 8 10^{-22} F. Y. Martin et al, Appl. Phys. Lett. 52, 1103 (1988).

ELECTROSTATIC FORCE MICROSCOPE



conductive
probe

conductive
substrate

Y. Martin et al, Appl. Phys. Lett. 52, 1103 (1988).

SOURCES OF ELECTRIC FORCE

- Coulomb force: $$F_C \approx \frac{q_S q_T(q_S, \Delta V)}{4\pi\varepsilon_0 z^2}$$ (Static charges)

- Capacitive force: $$F \approx \frac{1}{2}\frac{dC}{dZ}\Delta V^2$$ (Induced charges)

$$\Delta V = \Phi_{surf} + V_a = (\Phi_{surf} + V_{dc}) + V_{ac}\cos(\omega_m t)$$

(v_{dc})

- ω_m modulation frequency

- Φ_{surf} surface potential difference, V_a external applied potential

DIELECTRIC PROPERTIES BY FORCE MEAS.

$$U_{el}(t) = \frac{1}{2} C(z, \varepsilon) V^2(t)$$

$$F_{el,z}(t) = \frac{dU_{el}(t)}{dz}$$

$$V_a(t) = V_{dc} + V_0 \cos(\omega t) \quad \Rightarrow$$

$$F_{dc} = \frac{1}{2} \frac{\partial C(z, \varepsilon_s)}{\partial z} v_{dc}^2 + \frac{1}{4} \frac{\partial C(z, \varepsilon(\omega))}{\partial z} V_0^2$$

$$F_{\omega}(t) = \frac{\partial C(z, \varepsilon(\omega))}{\partial z} v_{dc} V_0 \cos(\omega t)$$

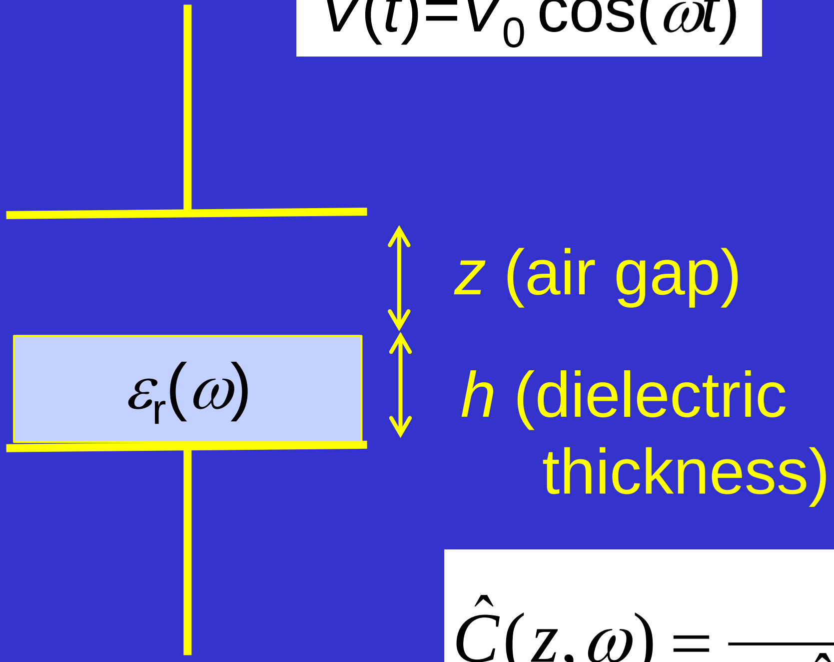
$$F_{2\omega}(t) = \frac{1}{4} \frac{\partial C(z, \varepsilon(\omega))}{\partial z} V_0^2 \cos(2\omega t)$$

“Local dielectric spectroscopy” (LDS)

P.S. Crider et al., Appl. Phys. Lett. 91, 013102 (2007).

CAPACITANCE MEAS. BY FORCE MICROSCOPY

$V(t)=V_0\cos(\omega t)$



Series capacitor

$$\hat{Z}(z,\omega)=\frac{1}{i\omega C_0(z)}+\frac{1}{i\omega\hat{C}_1(\omega)}$$

$$C_0(z)=\frac{\varepsilon_0 A}{z}$$

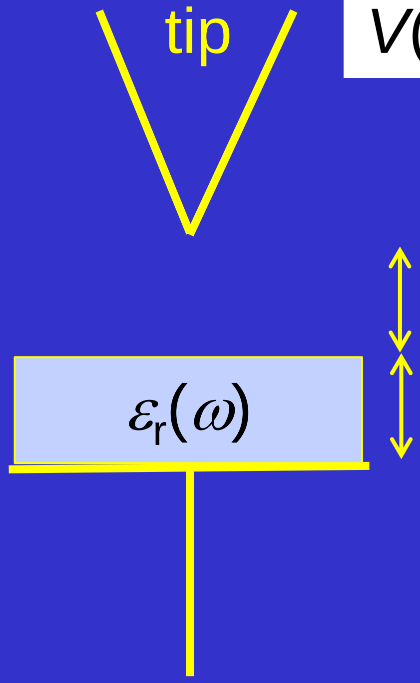
$$\hat{C}_1(\omega)=\frac{\varepsilon_0\hat{\varepsilon}_r(\omega)A}{h}$$

$$\hat{C}(z,\omega)=\frac{1}{i\omega\hat{Z}(z,\omega)}$$

Capacitance is no longer a linear function of ε_r !

Simple modeling for this geometry is needed to carry out ε_r

CAPACITANCE MEAS. BY FORCE MICROSCOPY



tip

$V(t)=V_0 \cos(\omega t)$

z (air gap)

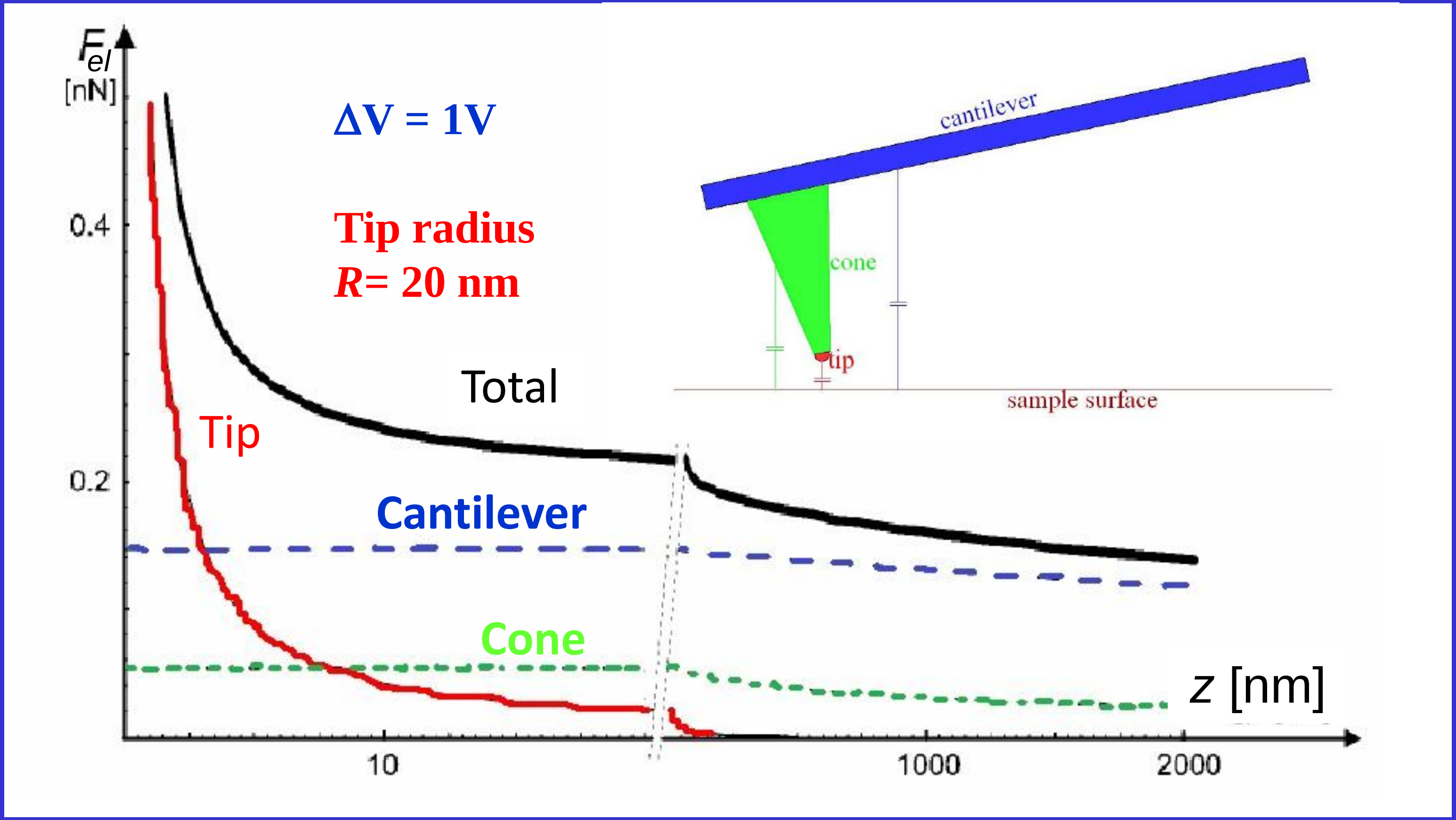
$\varepsilon_r(\omega)$

h (dielectric thickness)

Series capacitor + tip (not plane) ⇨ Capacitance is no longer a linear function of ε_r !

Modeling for this geometry is needed to carry out ε_r

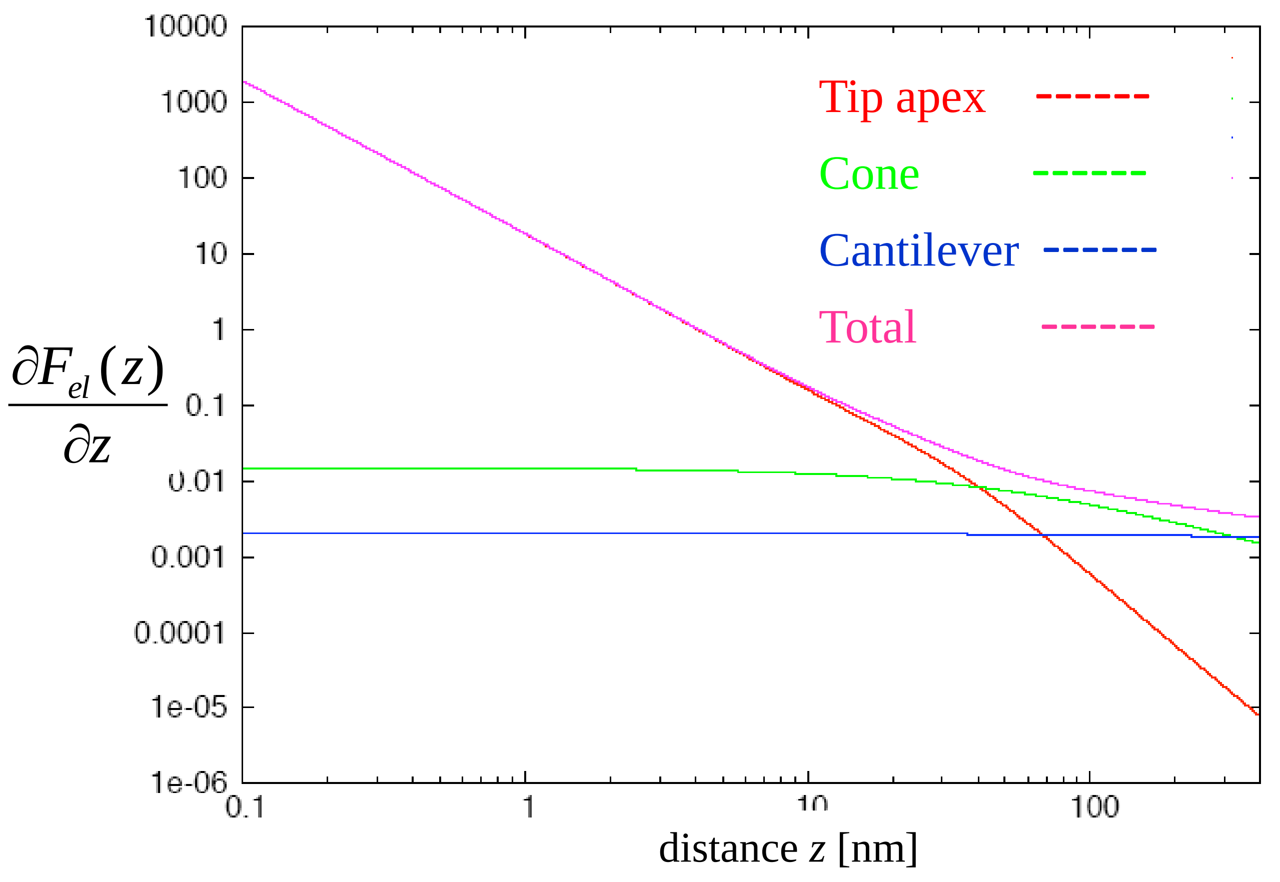
TIP/SAMPLE MODELING



Apex contribution to total force is dominant at small distance only (few nm)

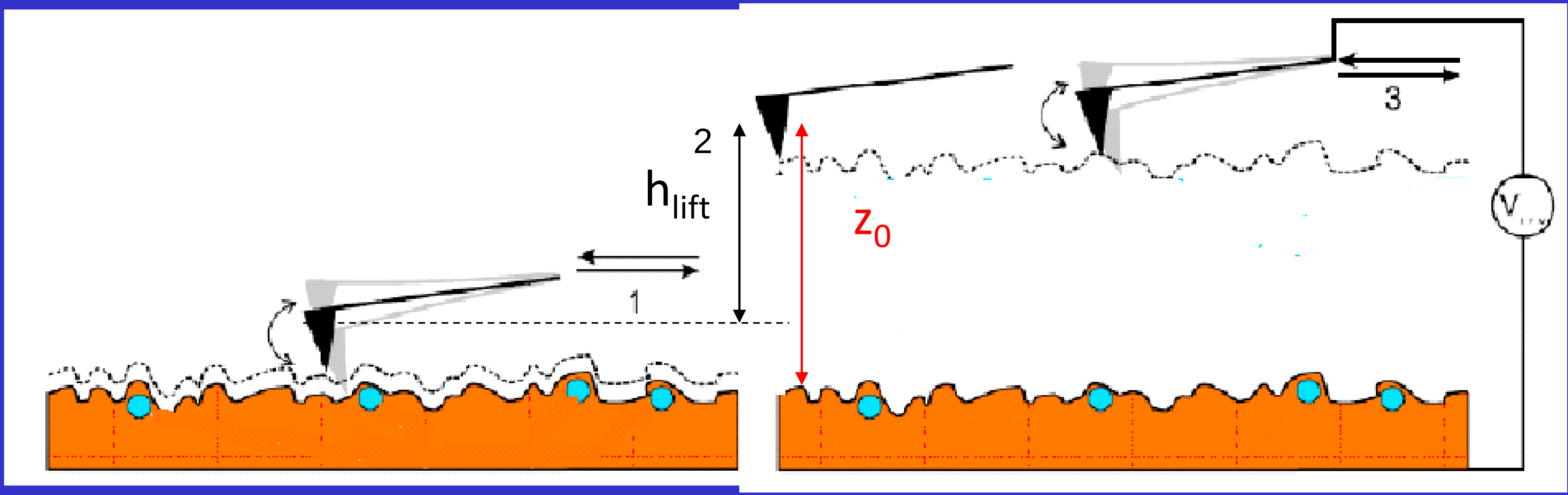
J. Colchero, A. Gil, A.M. Barò, *Phys. Rev. B* **64**, 245403 (2001)

SPATIAL RESOLUTION: FORCE vs. GRADIENT



- Force gradient allows to increase resolution.
- AFM is capable to measure *z*-gradient.

AFM OPERATION: TAPPING and LIFT MODE



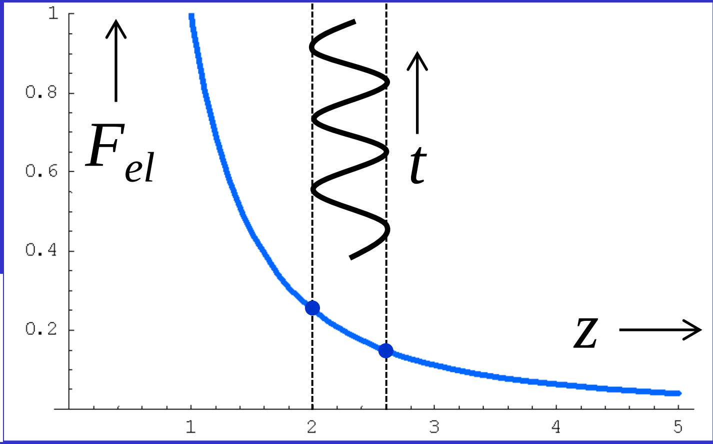
Topography is detected (1) by a dynamic AFM mode named *TAPPING MODE* *(cantilever oscillates at its resonant frequency)*

V_a is applied only during Lift scan (3) (to avoid charge transfer to sample)

FORCE and GRADIENT DETECTION

- Cantilever: forced harmonic oscillator (F_d) in a force field (F_{el})

$$m\ddot{z} + \gamma\dot{z} + kz = F_d \cos(\omega_d t) + F_{el}(V, z, \varepsilon)$$



$$F_{el}(V, z, \varepsilon) \cong F_{el}(V, z_0, \varepsilon) + \frac{\partial F_{el}(V, z, \varepsilon)}{\partial z}(z - z_0) + \ldots$$

$$m\ddot{z} + \gamma\dot{z} + \boxed{\left(m\omega_0^2 - \frac{\partial F_{el}(V, z, \varepsilon)}{\partial z}\right)} z = F_d \cos(\omega_d t) + \boxed{\left(F_{el}(V, z_0, \varepsilon) - \frac{\partial F_{el}(V, z, \varepsilon)}{\partial z} z_0\right)}$$

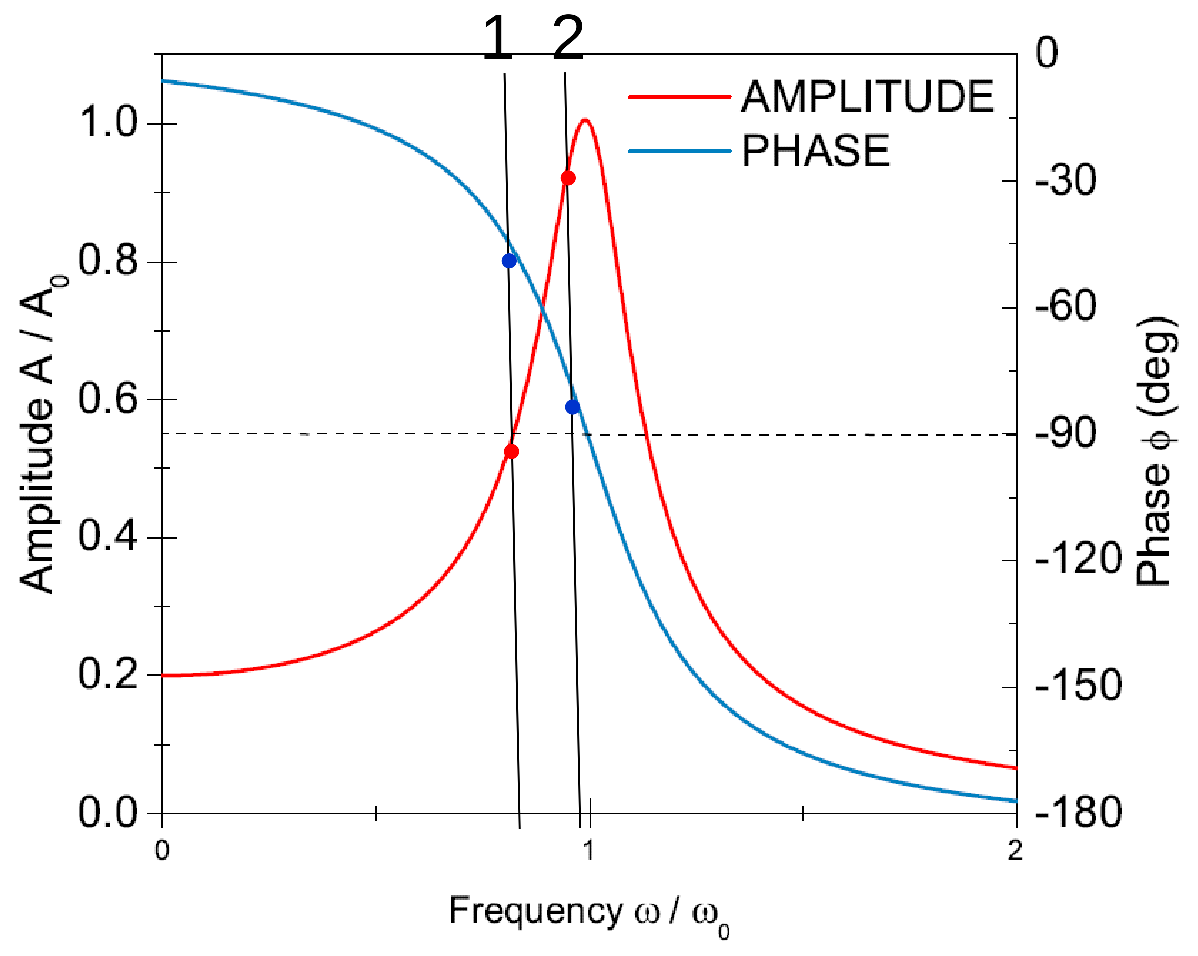
Resonant frequency shift →

$$\Delta\omega_{res} \approx -\frac{\omega_{res}}{2k}\frac{dF_{el}}{dz}$$

Static deflection ξ

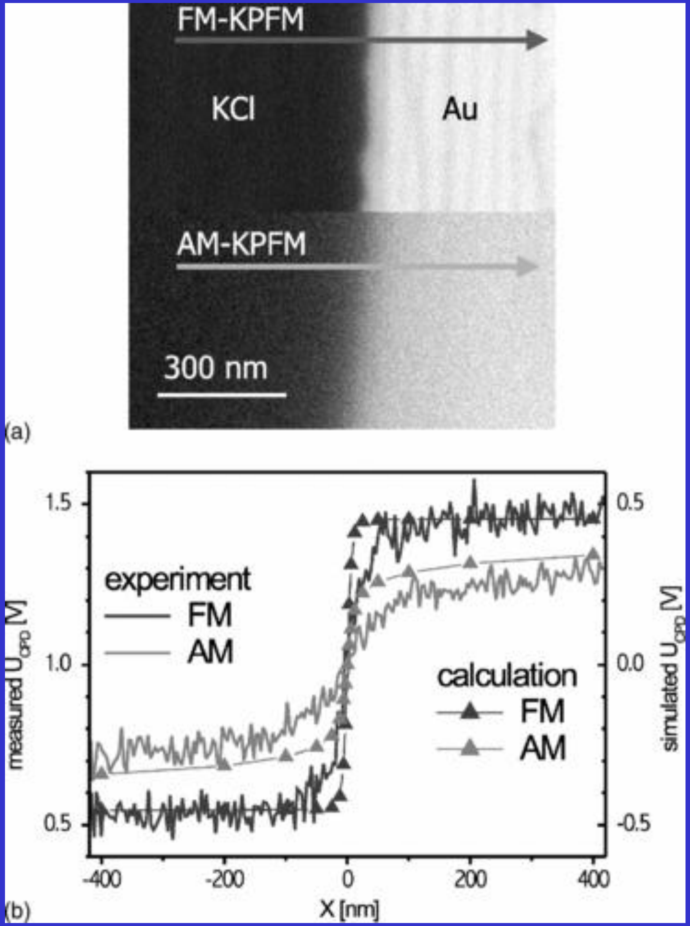
- ξ sensitive mainly to F_{el}

THE FREQUENCY SHIFT



- FM: “Chase” resonance frequency by a “self-oscillator.”

EXAMPLE OF SPATIAL RESOLUTION IMPROVEMENT



AM (Amplitude Modulation):
Force mode (ξ)

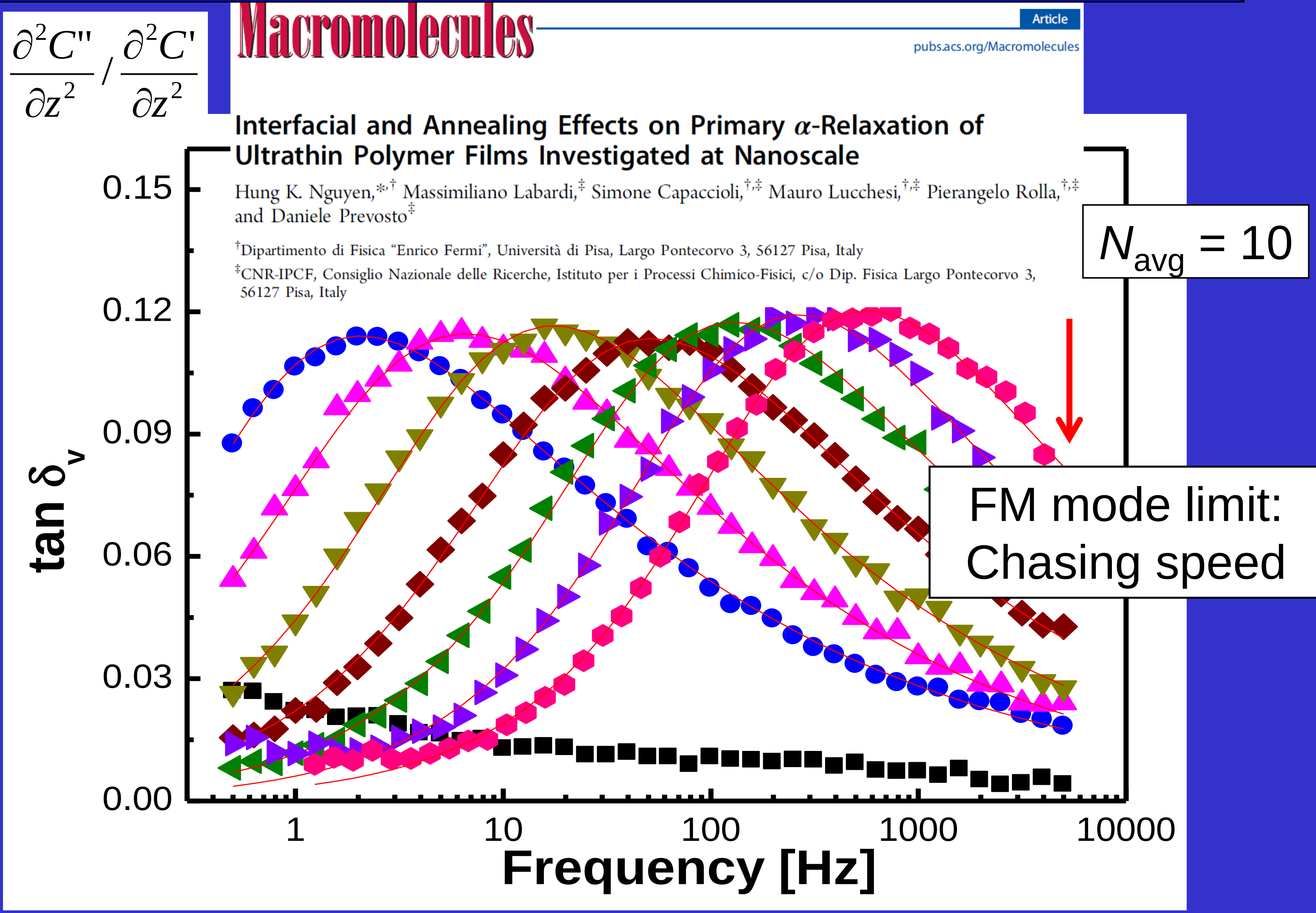
FM (Frequency Modulation):
“Chasing” mode (force gradient)

Improvement of spatial resolution with FM mode.

U. Zerweck, Ch. Loppacher, T. Otto, S. Grafstrom, L.M. Eng, *Phys. Rev. B* **71**, 125424 (2005)

LDS – FREQUENCY MODULATION

$$\frac{\partial^2 C''}{\partial z^2} / \frac{\partial^2 C'}{\partial z^2}$$



Macromolecules Article

pubs.acs.org/Macromolecules

Interfacial and Annealing Effects on Primary α-Relaxation of Ultrathin Polymer Films Investigated at Nanoscale

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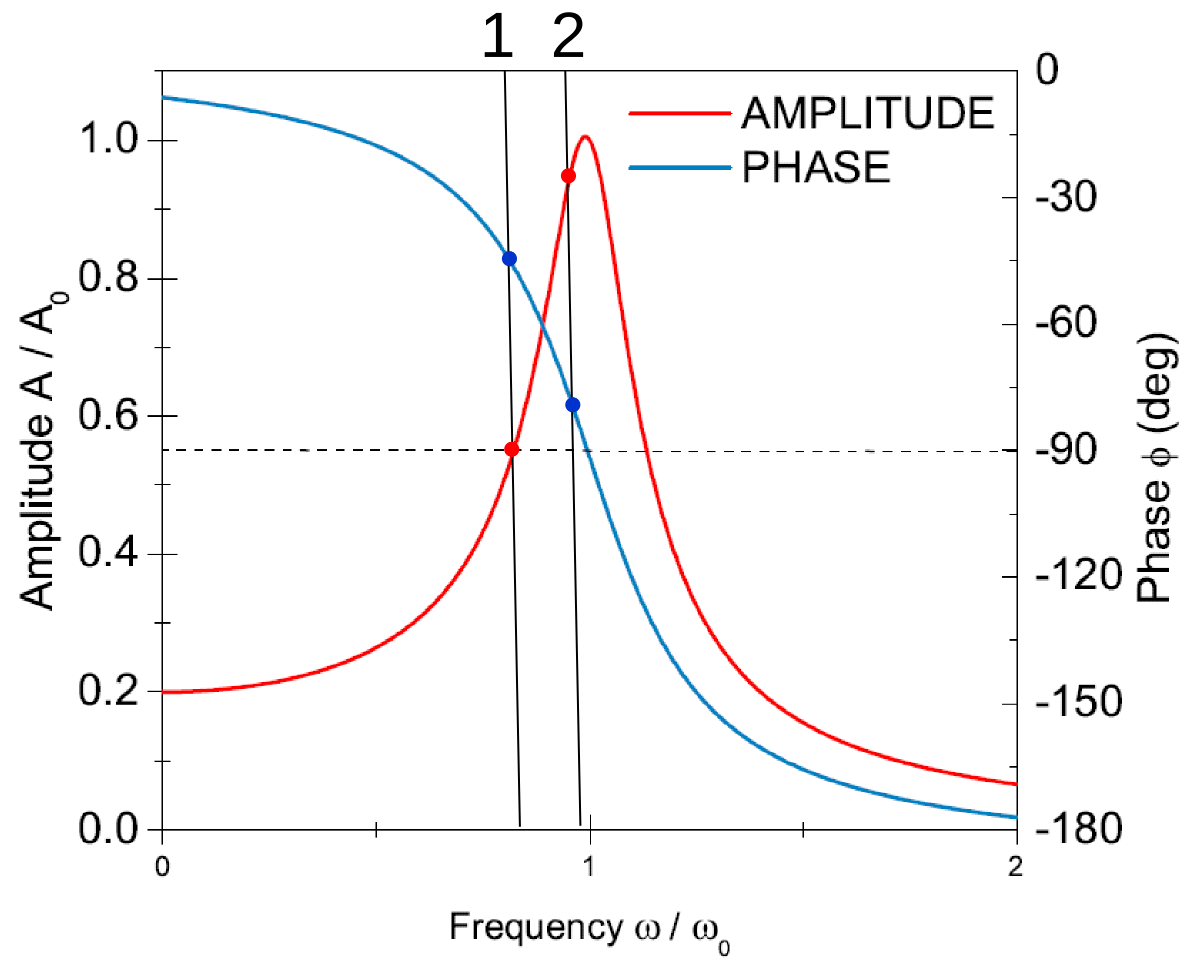
N_{avg} = 10

FM mode limit: Chasing speed

PHASE MODULATION (PM)



Constant frequency: phase is proportional to frequency shift

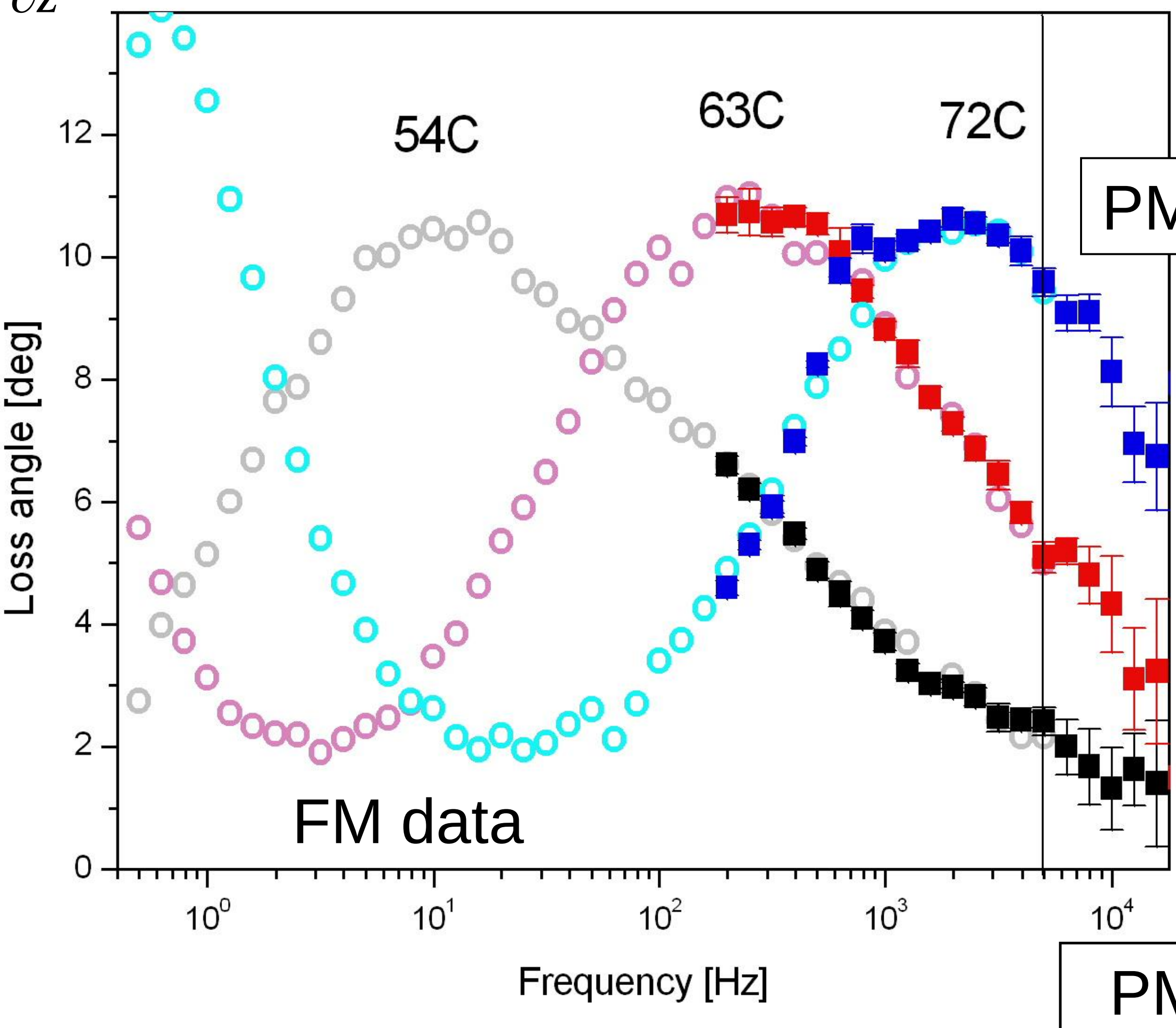
BANDWIDTH EXTENSION WITH PHASE MOD.

$$\frac{\partial^2 C''}{\partial z^2} / \frac{\partial^2 C'}{\partial z^2}$$

Material: PVAc

$N_{avg} = 4$

PM data



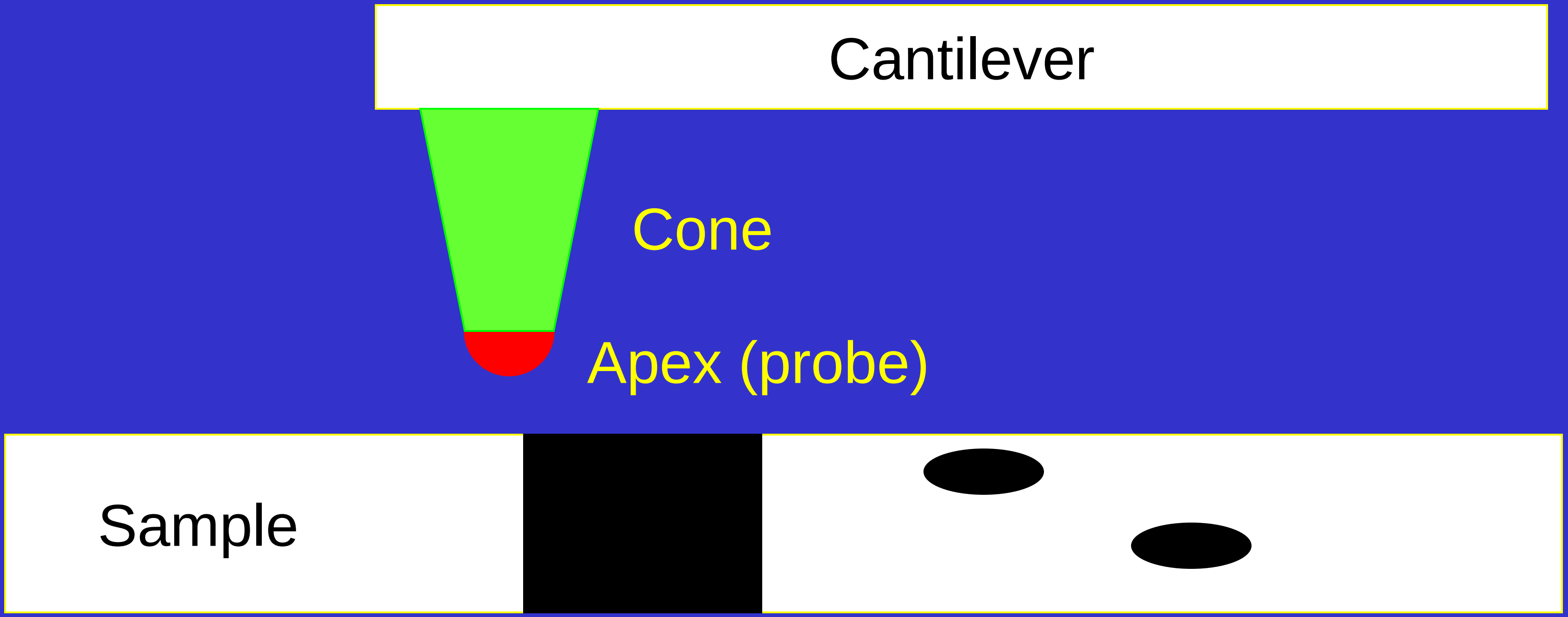
PM mode limit:
LIA time const

LDS BANDWIDTH EXTENSION

- Frequency bandwidth of LDS can be extended up to MHz range and more.

SEE TALK O-71 on Thursday 15th by M. Labardi et al.

APPLICATION OF LDS TO INTERFACE STUDY

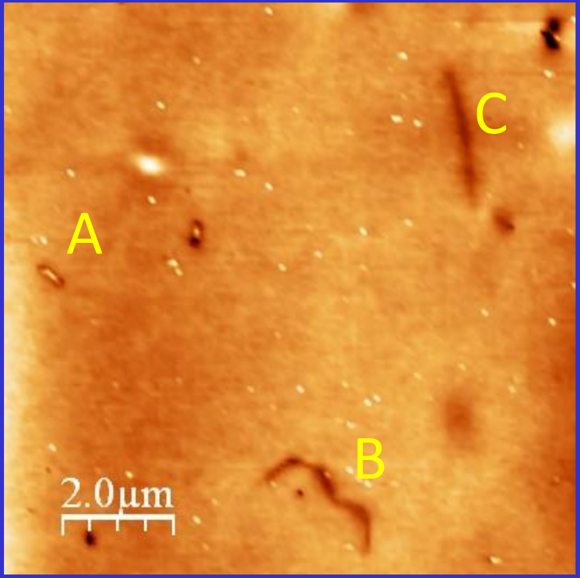


Interface region is probed :

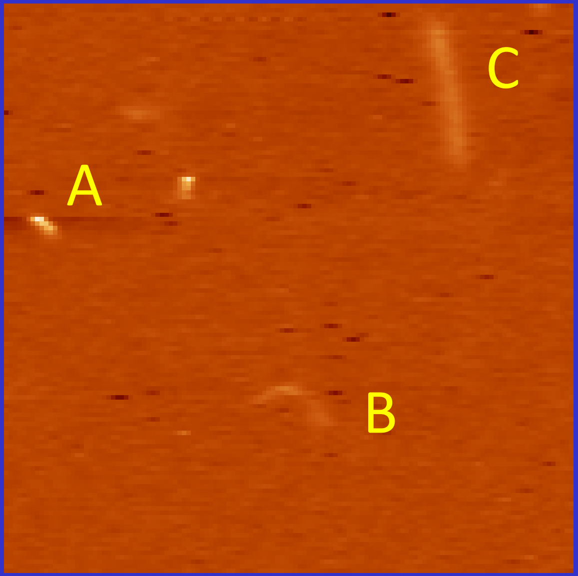
- “in section,” (phase separations emerging to free surface), or
- “in depth” (nanostructures near to free surface).

$Mo_6S_2I_8$ NANOWIRES IN PVP FILM

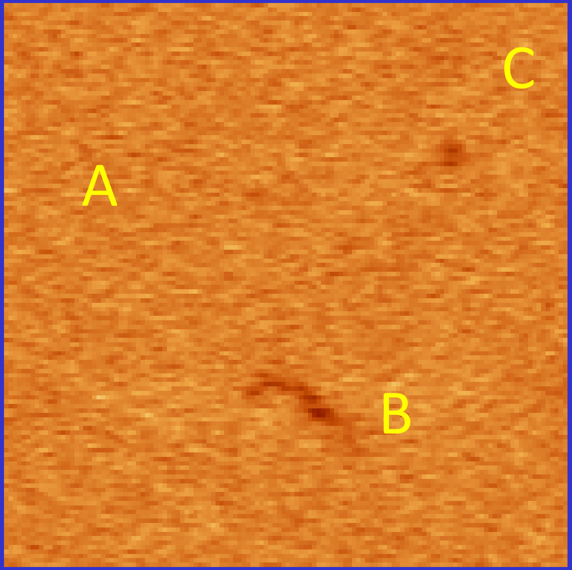
- Polymer: poly (vinyl pyrrolidone), $T_g \approx 145$ C.



Topography



Electric, amplitude

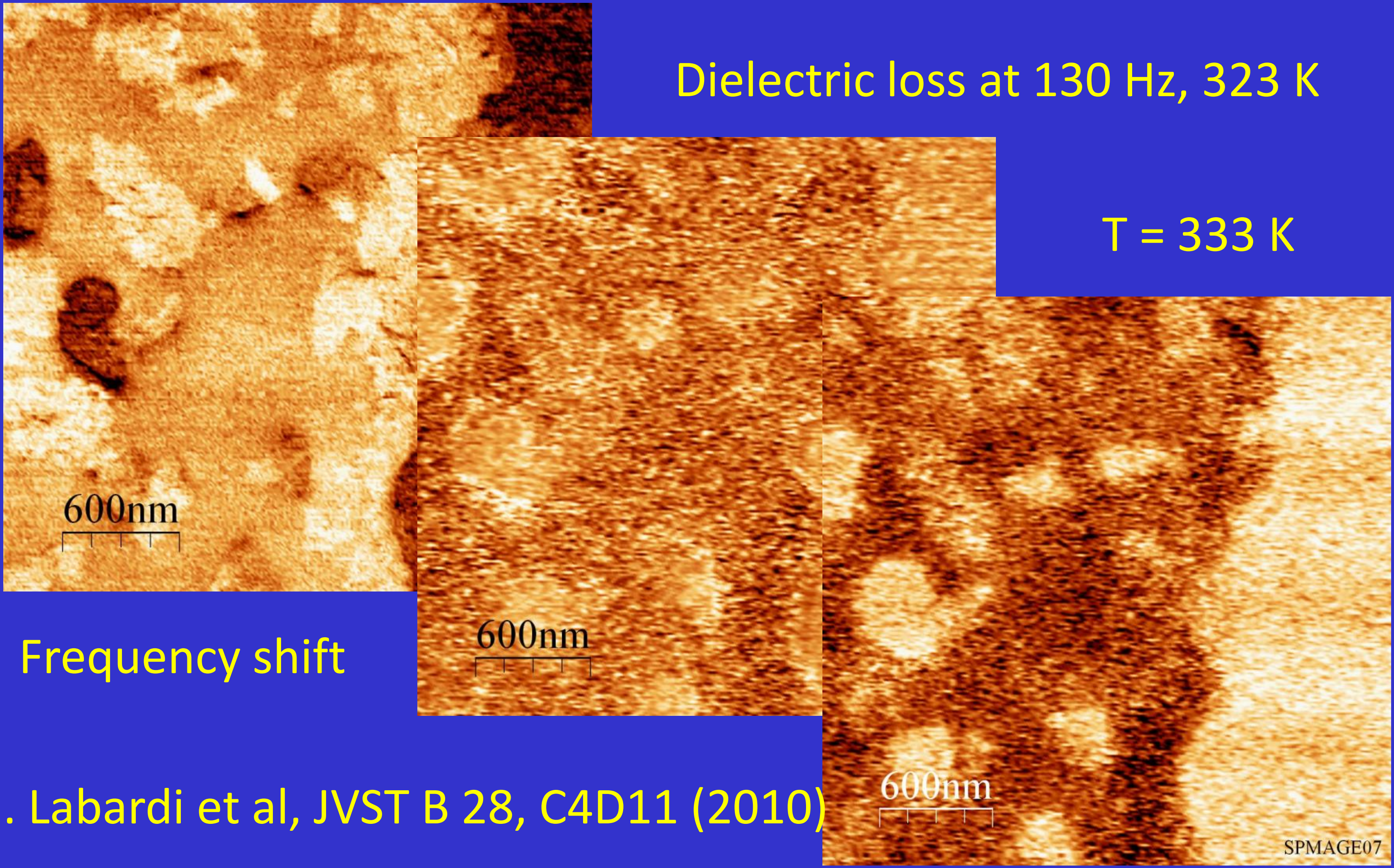


Electric, phase

- $T = 171.6$ C
- $f = 226$ Hz

M. Labardi et al, J. Non-Cryst. Solids 379, 224 (2013)

MMT CLAY IN PVAc FILM



Dielectric loss at 130 Hz, 323 K

T = 333 K

Frequency shift

M. Labardi et al, JVST B 28, C4D11 (2010)

CONCLUSIONS

- Scanning Force Microscopy gives access to electrical properties on a nanometer scale.
- Local Dielectric Spectroscopy can be operated on frequency and temperature regimes comparable to the ones of BDS, allowing comparison of average properties with local ones, even of single macromolecules.
- Interfaces in nanocomposite materials can be studied by this technique, when they are placed near to the free surface of the sample.