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Latex film and macrocrystal formation: scanning probe and microchemical results

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Outline

- The **problem**: latex film properties, macrocrystal defects arising from *particle heterogeneity*
- **Precedents**: deviations from expected latex behavior: coagulation, zonal centrifugation
- The **approach**: analytical microscopies, *e.g.* ESI-TEM, BEI/FESEM, *SPM* (SEPM, EFM, MFM)
- **Results**:
 - inter- and intra-particle heterogeneity
 - effect on latex self-arraying and film formation
 - detection of non-particulate constituents

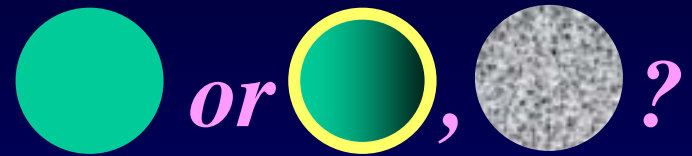
Polymers (thermoplastics, rubbers, thermosetting)

- **Formed by macromolecular covalent or entangled networks**
- **Ionic groups in ionomers or in sites formed tribochemically**
- **Usual assumption: electroneutrality, in the supramolecular scale.**

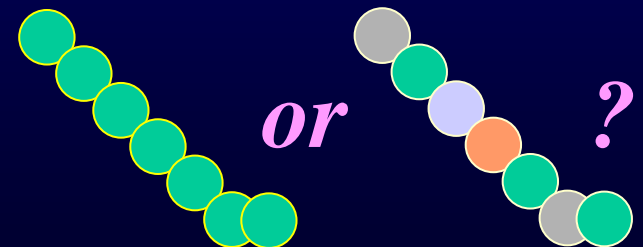
Electroneutrality, where?

- **Electrets and charge injection**
- **The Costa Ribeiro effect**
- **Thermo-stimulated currents (Mascarenhas, Leal Ferreira)**
- **Space charges, residual charges**
- **Interfacial double layers, interfacial polarization**
- *Problem:* **Insulator degradation**
- *Problem:* **Eletrostatics of the environment**

Colloidal particles



- Crystalline or amorphous
- Micro- to nanometric dimensions
- Colloidal stability is *kinetic*, dependent on electric repulsions
- Chemical composition: average and local
- Usual hypothesis: uniform chemical composition, *but few proofs for this assumption*



Working hypotheses

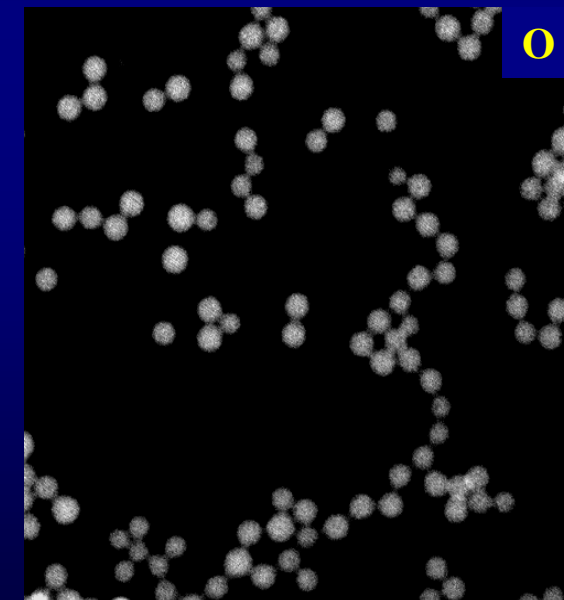
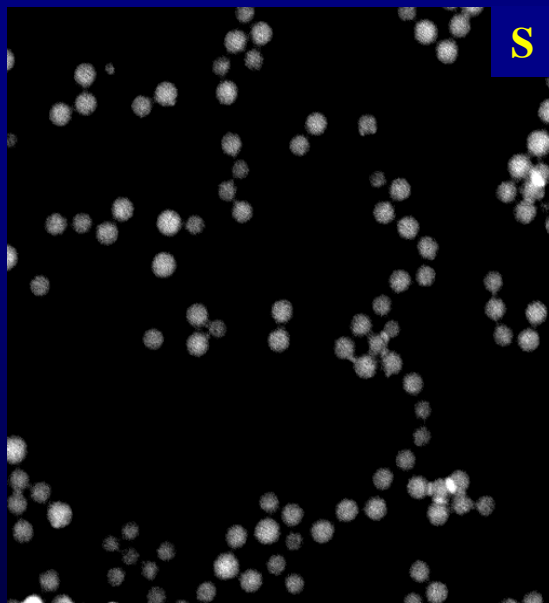
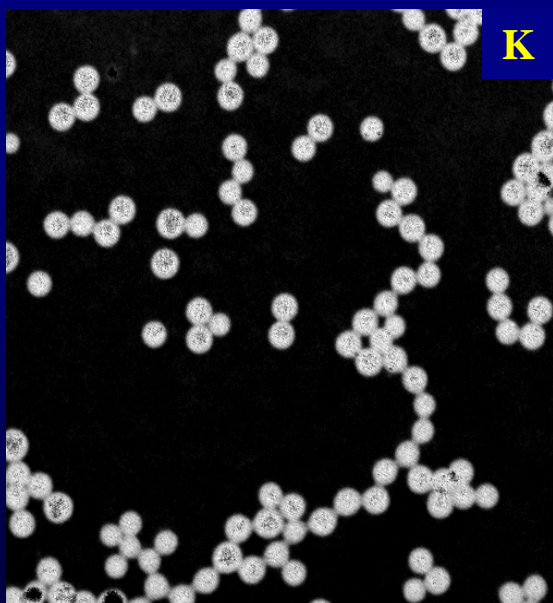
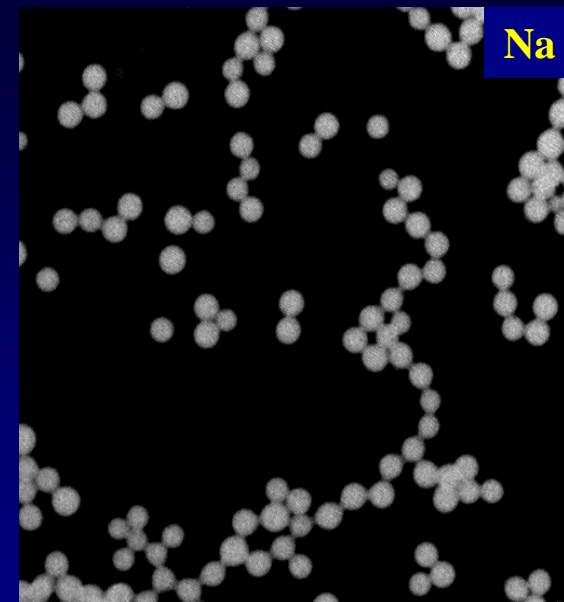
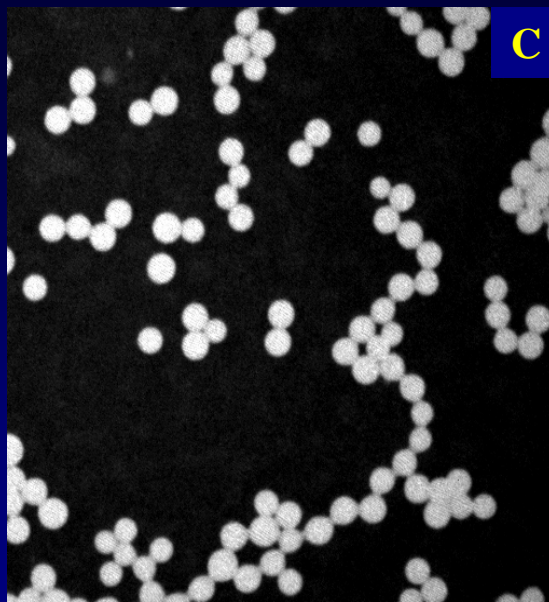
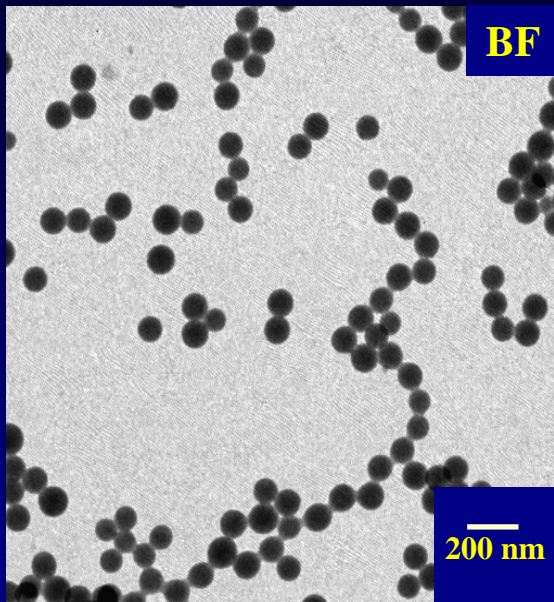
- Chemical and electrical non-uniformity, within particles and among particles
- Discrete sub-populations, or continuous variations of composition and properties

Hypotheses testing

- Microanalysis, enhanced by association to chemical separation techniques
- ESI-TEM, BEI-EDAX-SEM, scanning probe microscopies
 - (and many others)

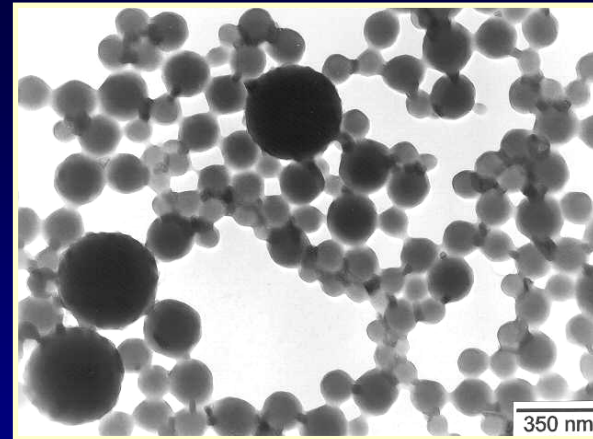
Electron spectroscopy imaging (ESI-TEM)

- **TEM with an electron energy monochromator**
- **Acquisition of EELS (electron energy-loss spectra)**
- **(Inelastic) scattered electrons carry information on the position of the scattering elements in the sample**
- **Element mapping with a high sensitivity, even for light elements (C, O, N, S, Na)**

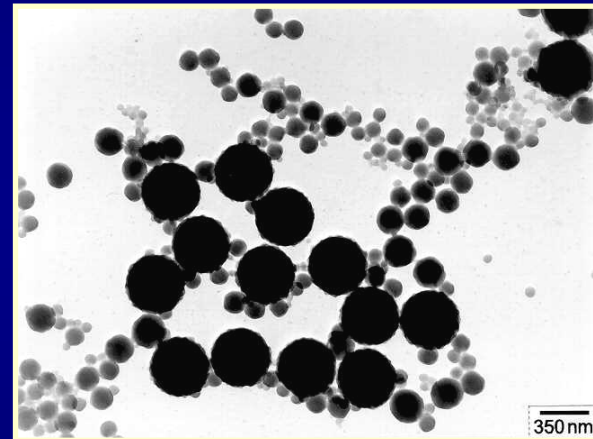


PS-M, a polystyrene latex (M. Braga, C.A.P.Leite et al., J.Phys.Chem. 2001)

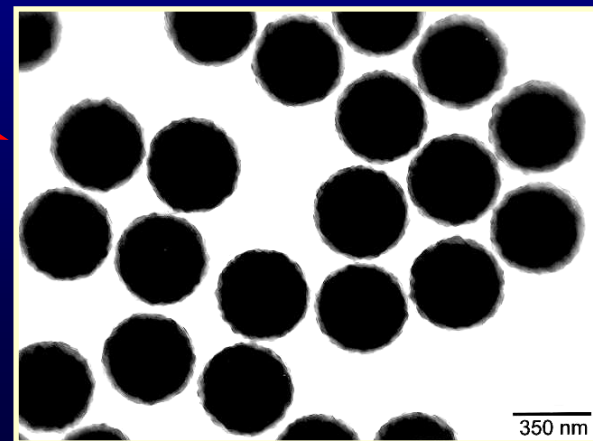
Latex fractionation by colloidal crystallization and sedimentation



$D = 159 \text{ nm}$
 $\zeta = -36 \text{ mV}$

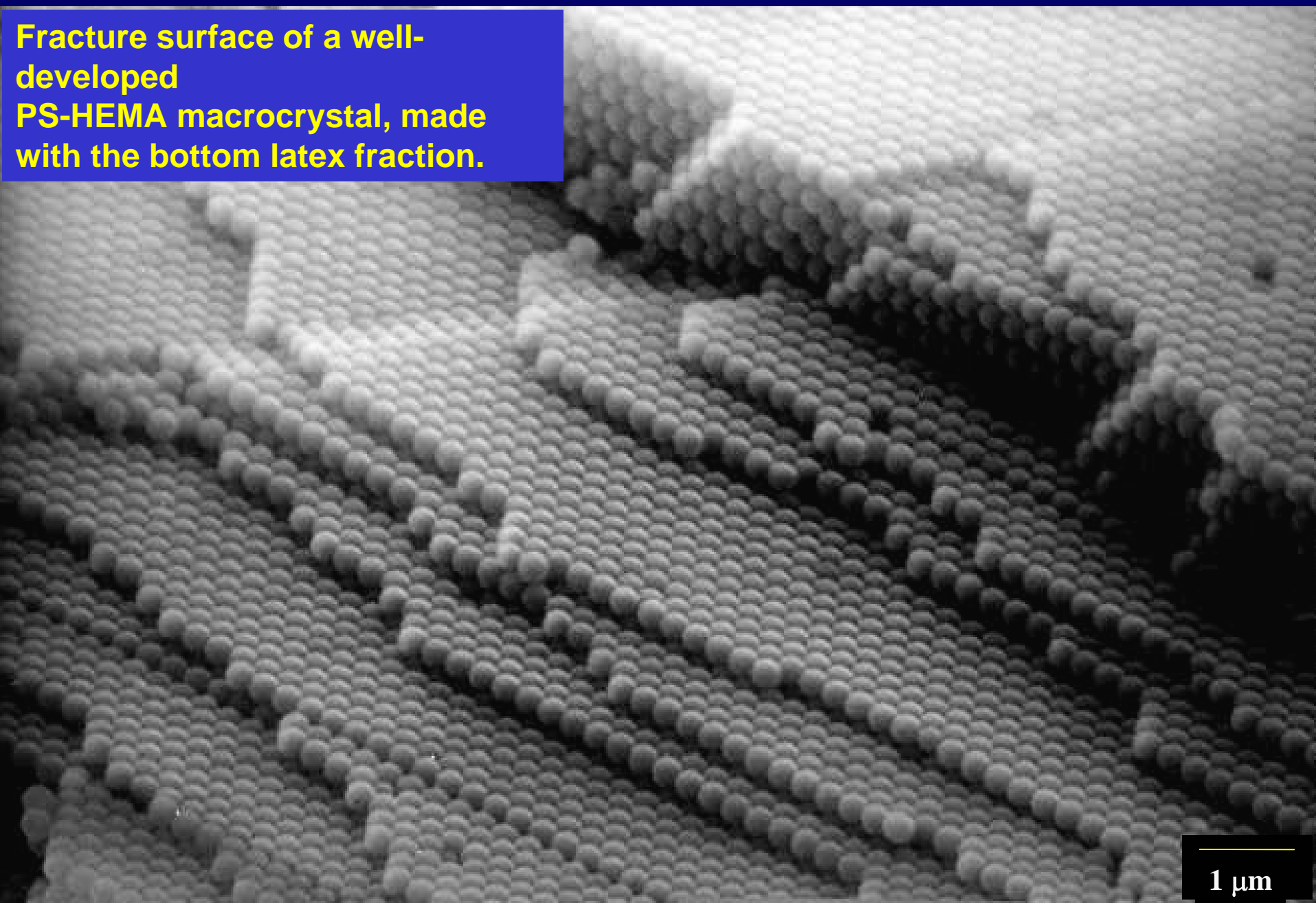


$D = 189 \text{ nm}$
 $\zeta = -42 \text{ mV}$



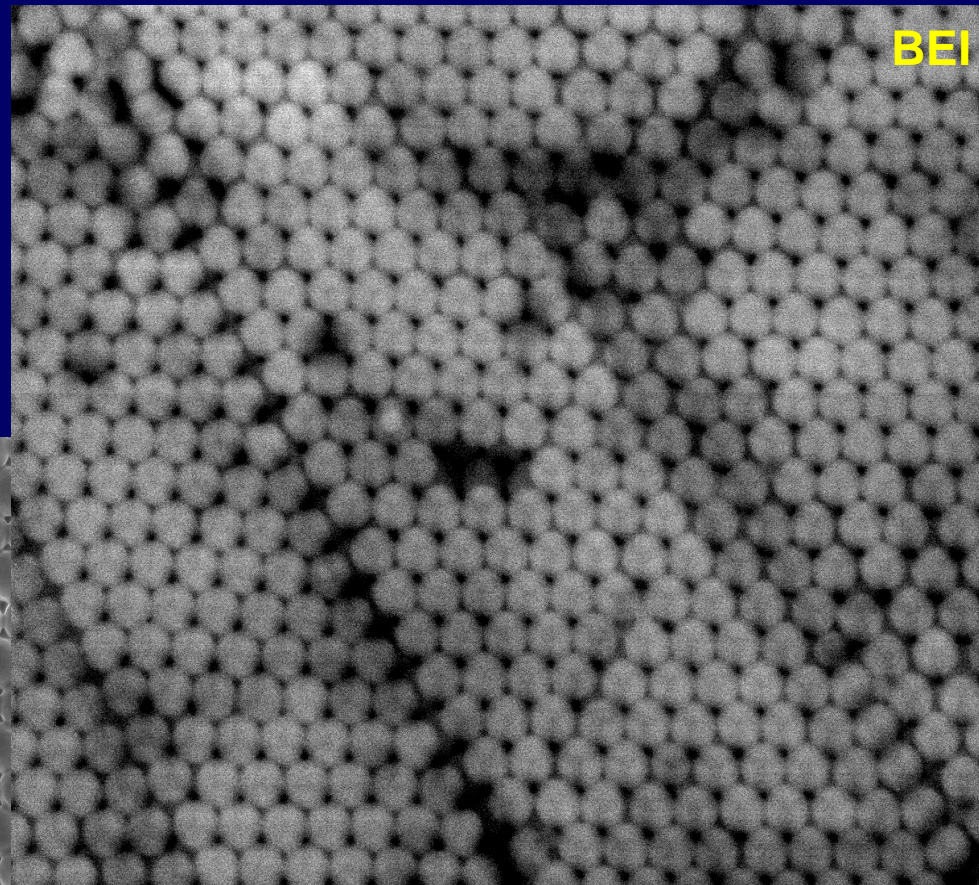
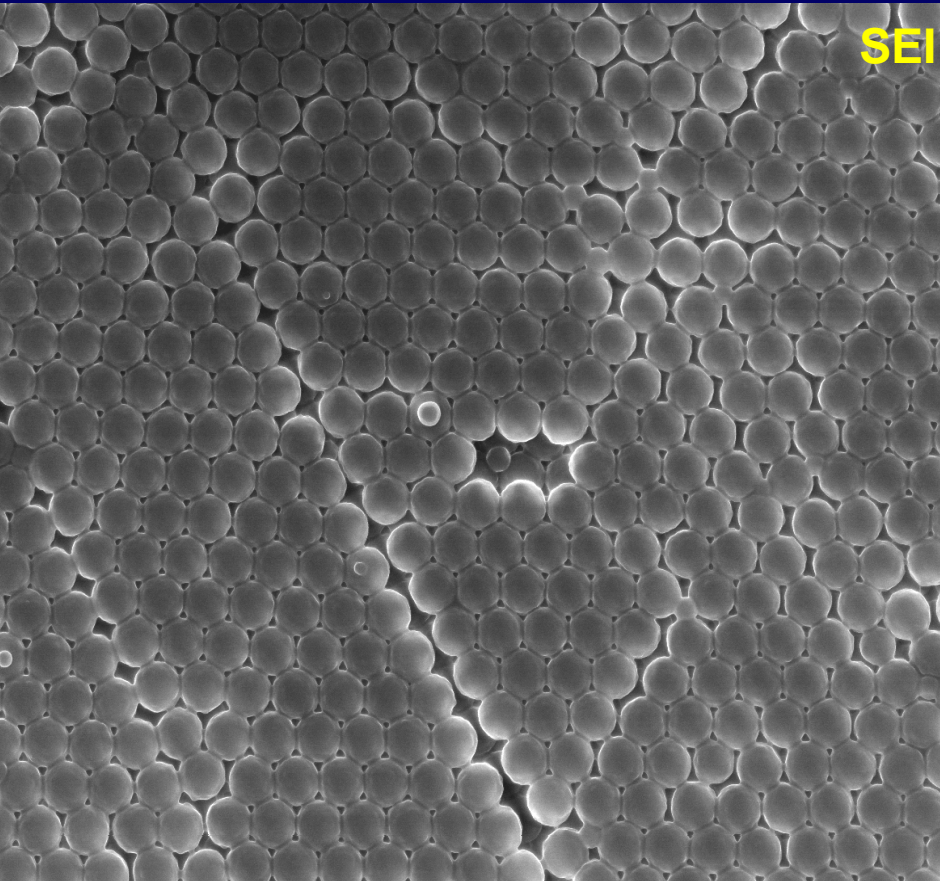
$D = 414 \text{ nm}$
 $\zeta = -54 \text{ mV}$

Fracture surface of a well-developed PS-HEMA macrocrystal, made with the bottom latex fraction.

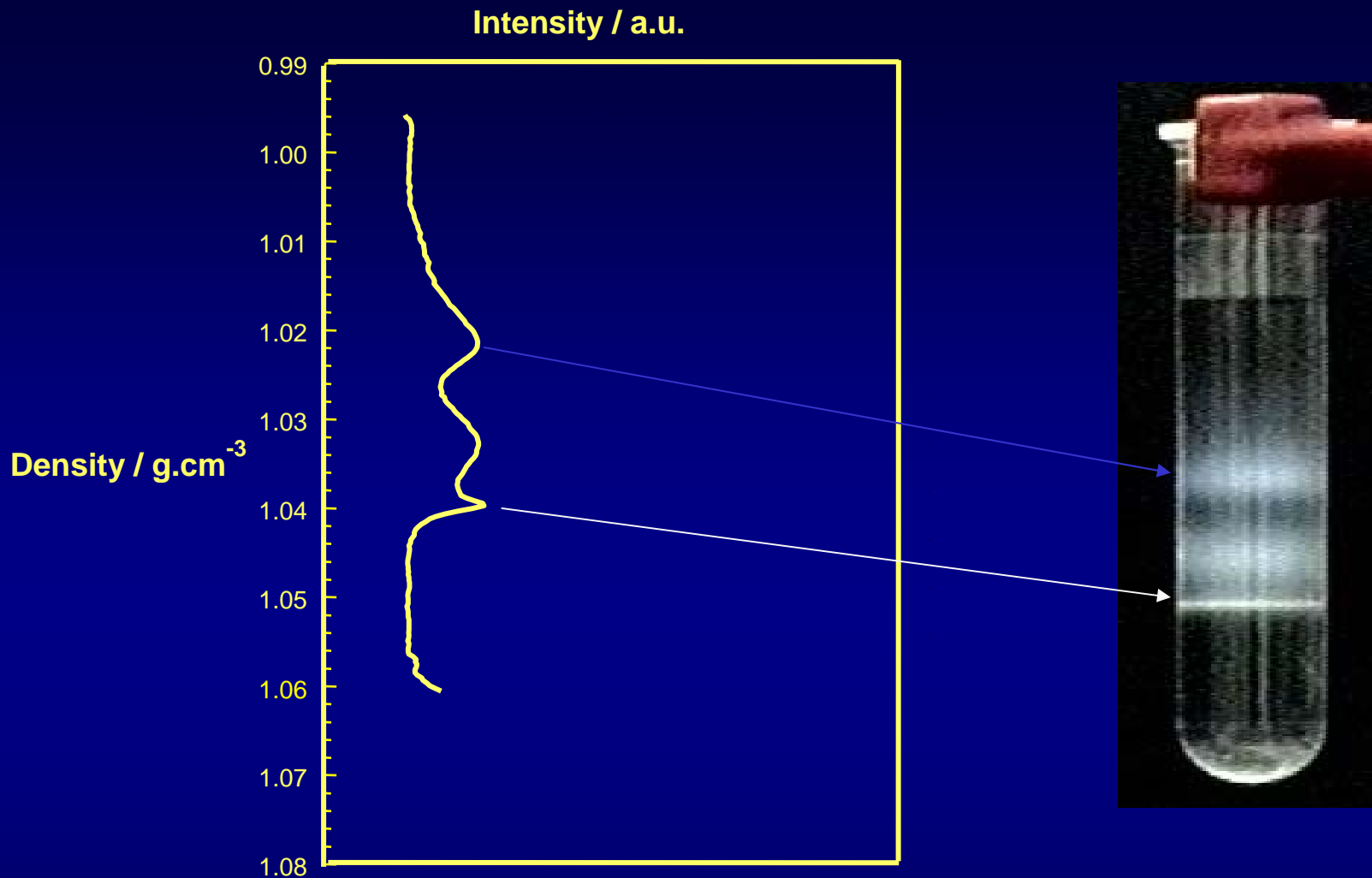


1 μm

BEI and SEI images of PS-HEMA latex do not match each other.
Chemical domain geometry is different from particle geometry.

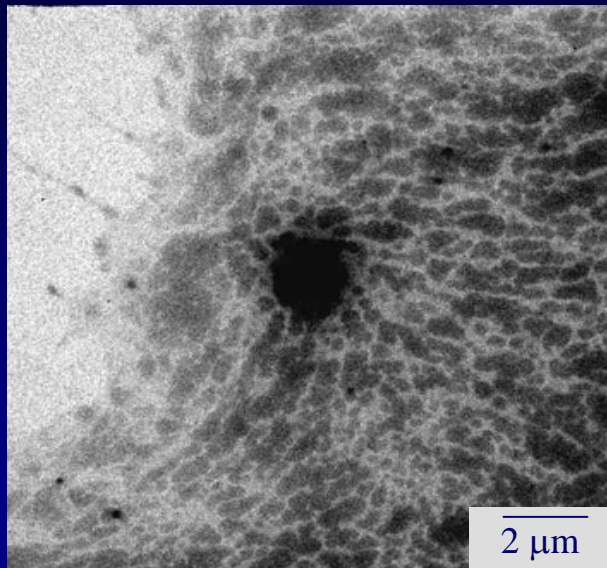


Particles clustered around line and point defects are darker than well-organized particles.
Their average atomic numbers are lower: richer in styrene, poorer in acrylic.

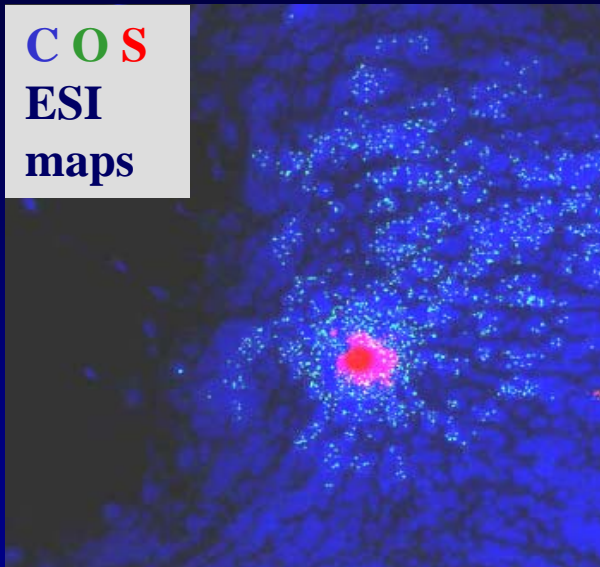


Profile of a PS* zone after 20 min centrifugation in a sucrose gradient (19,000 rpm).

*** : PS-M, exposed to chloroform vapor for 24 h**

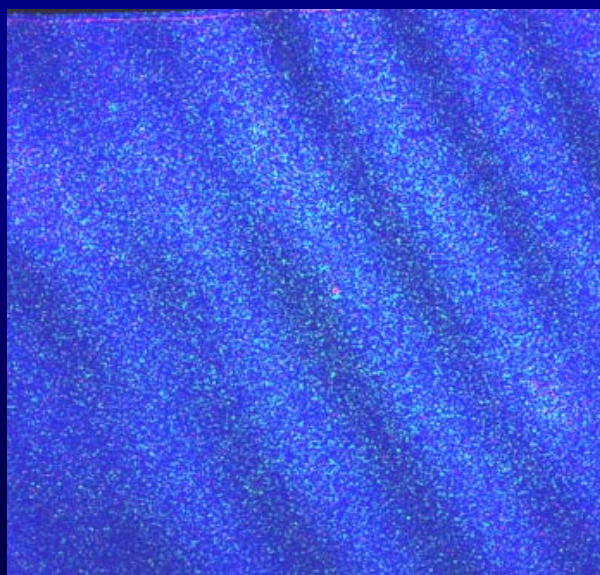
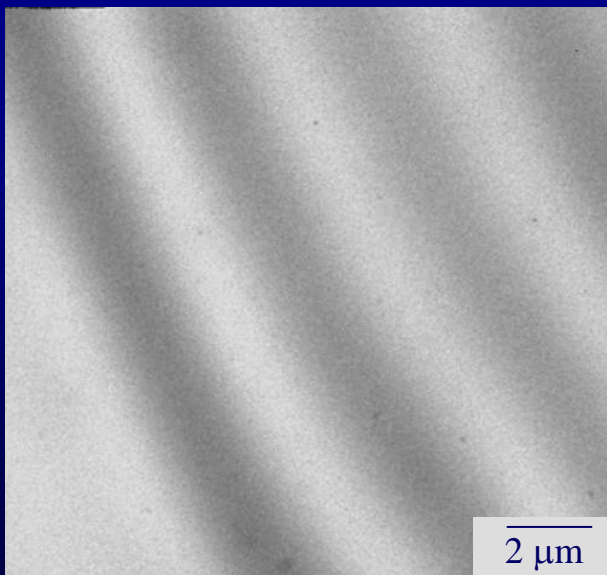


C O S
ESI
maps



Upper
fraction

**Poly(S-BA),
fractionated by
zonal
centrifugation**



Lower (denser)
fraction

Chemical information from scanning probe microscopies

AFM images (contact, non-contact, tapping, phase contrast, lateral force) yield morphological and (indirect) chemical information, based on:

- **friction**
- **viscoelasticity**
- **changes in the Hamaker constant**

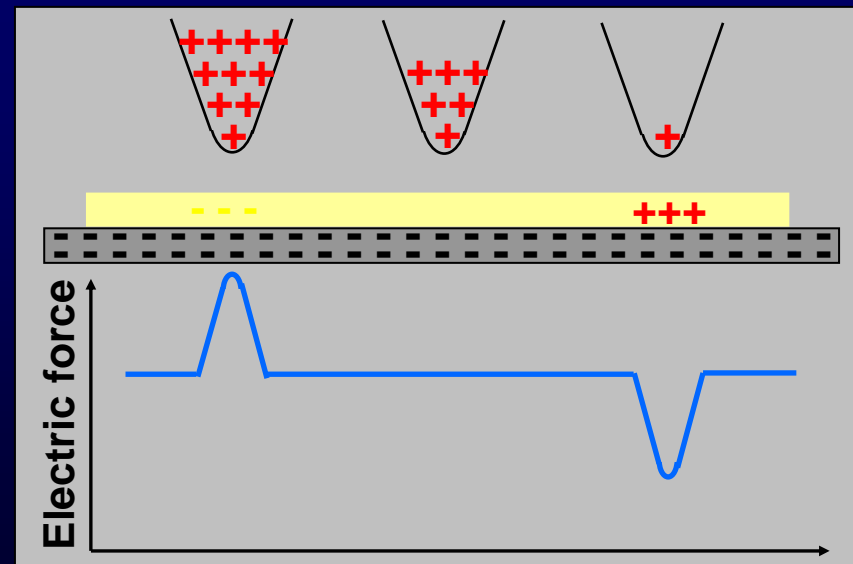
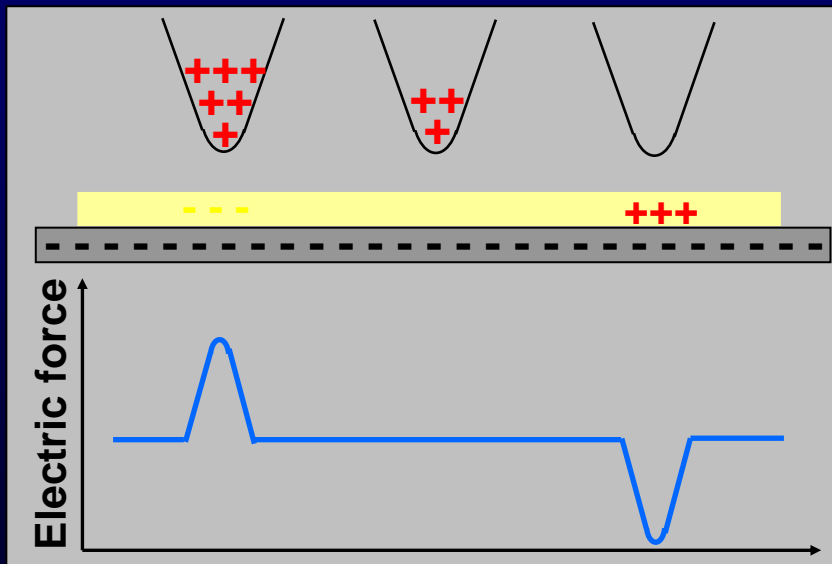
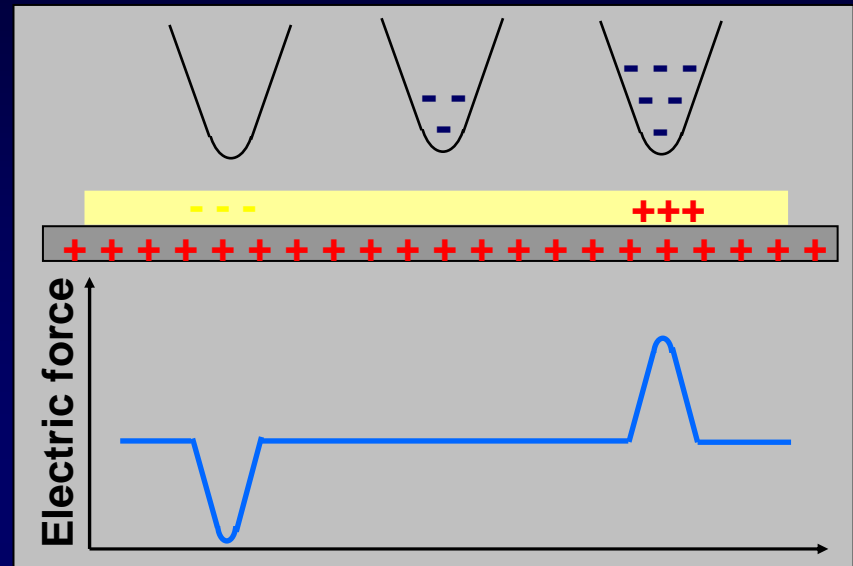
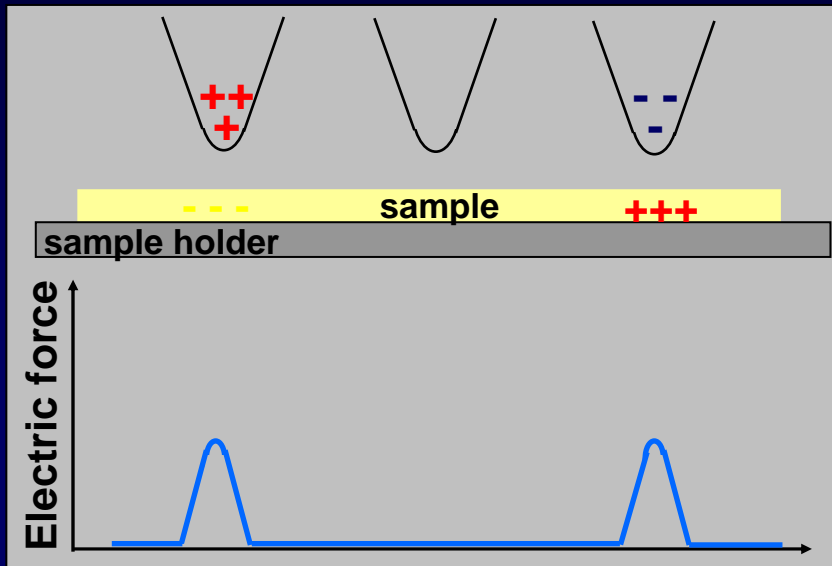
Many other imaging modes:

- **electric potential**
- **electric force**
- **magnetic force**
- **thermal conductivity**
- **specific probes, coated with interacting layers**
- *more, new types...*

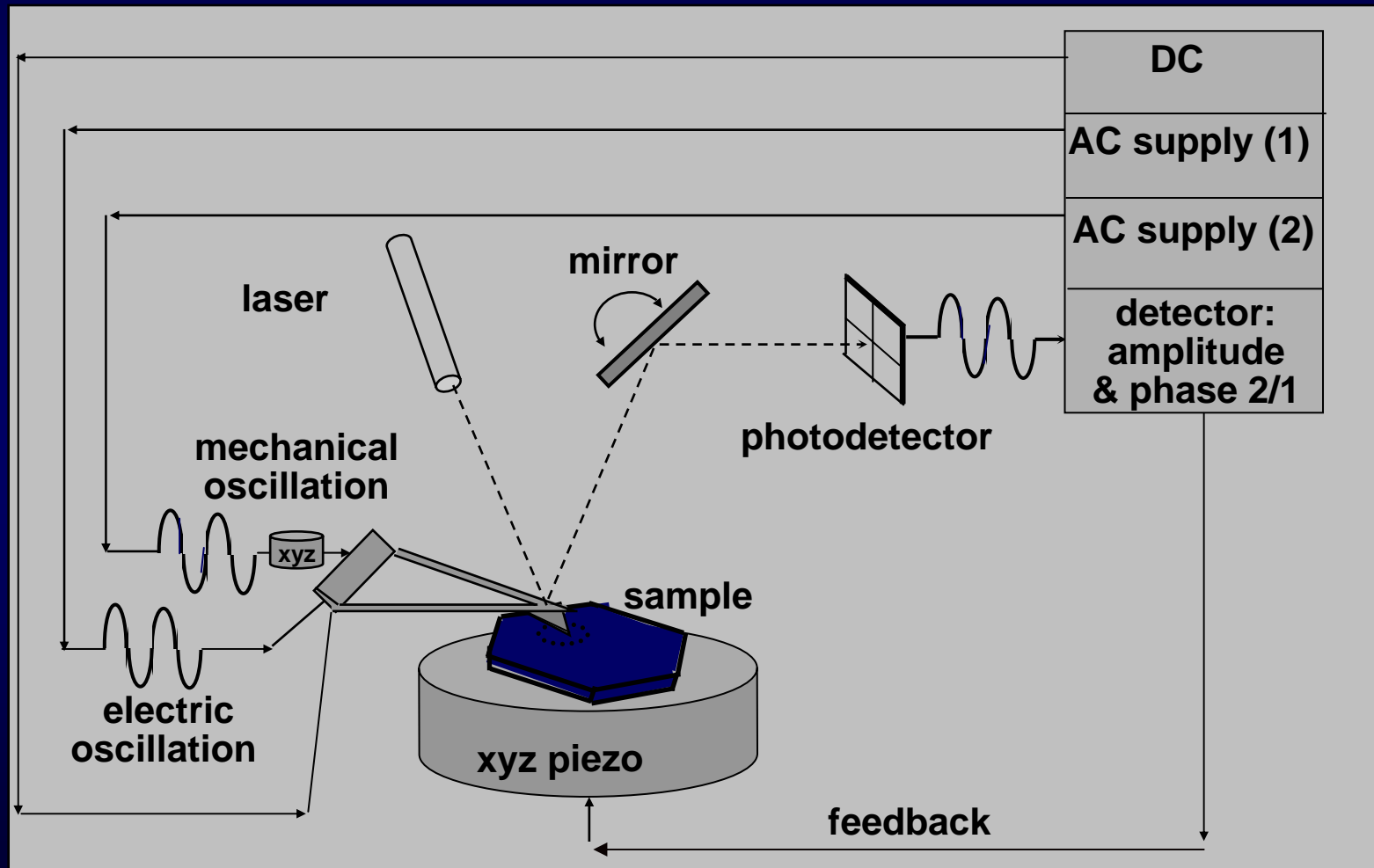
Scanning electric probe microscopies: SEPM, EFM

- **Image contrast depends on the electrostatic interaction between the probe and the sample**
- **Identification of domains with different electric charge excess**
- **Image acquisition simultaneous to non-contact AFM imaging: same field**

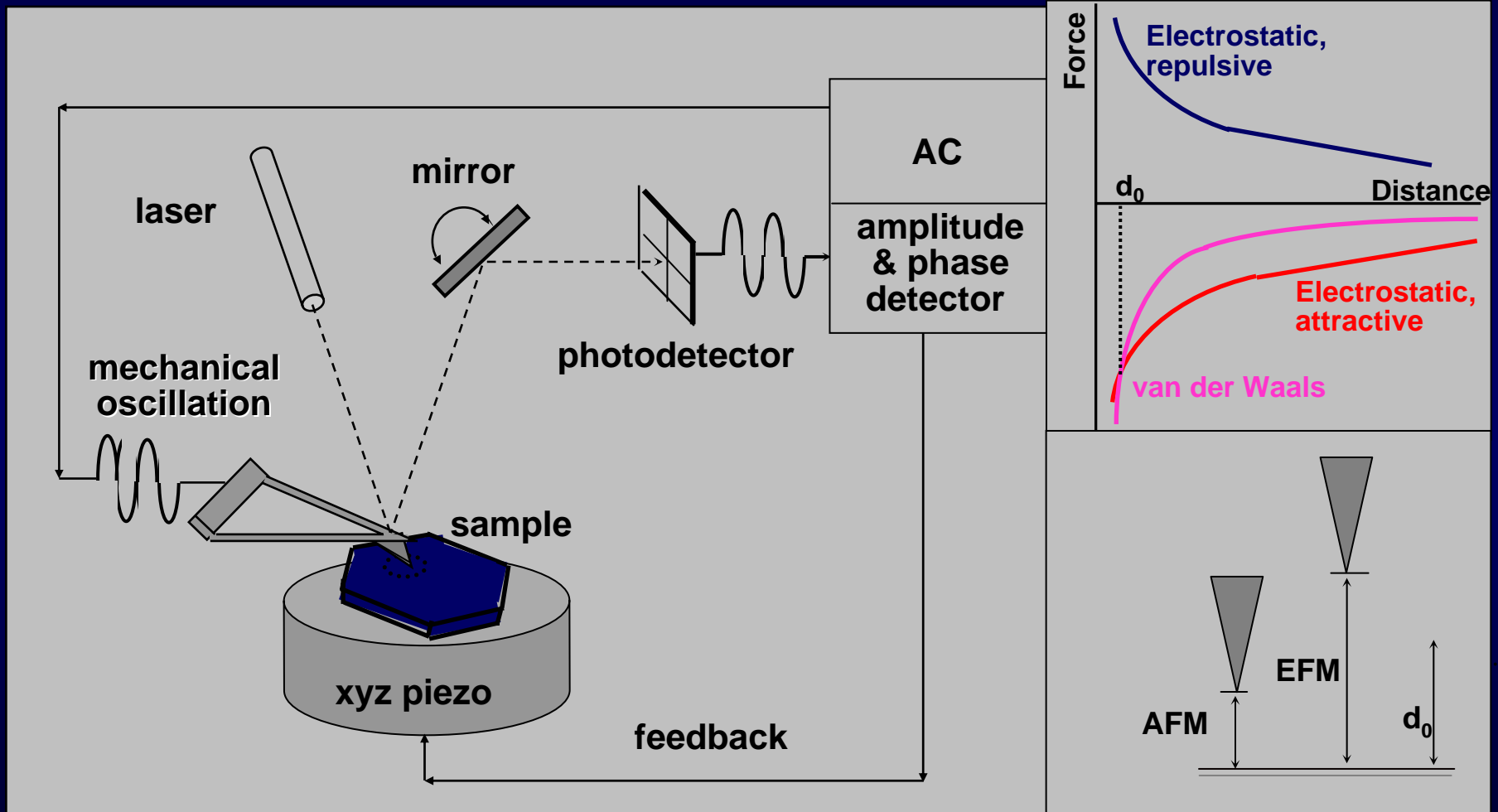
Induction of electric charges on the tip



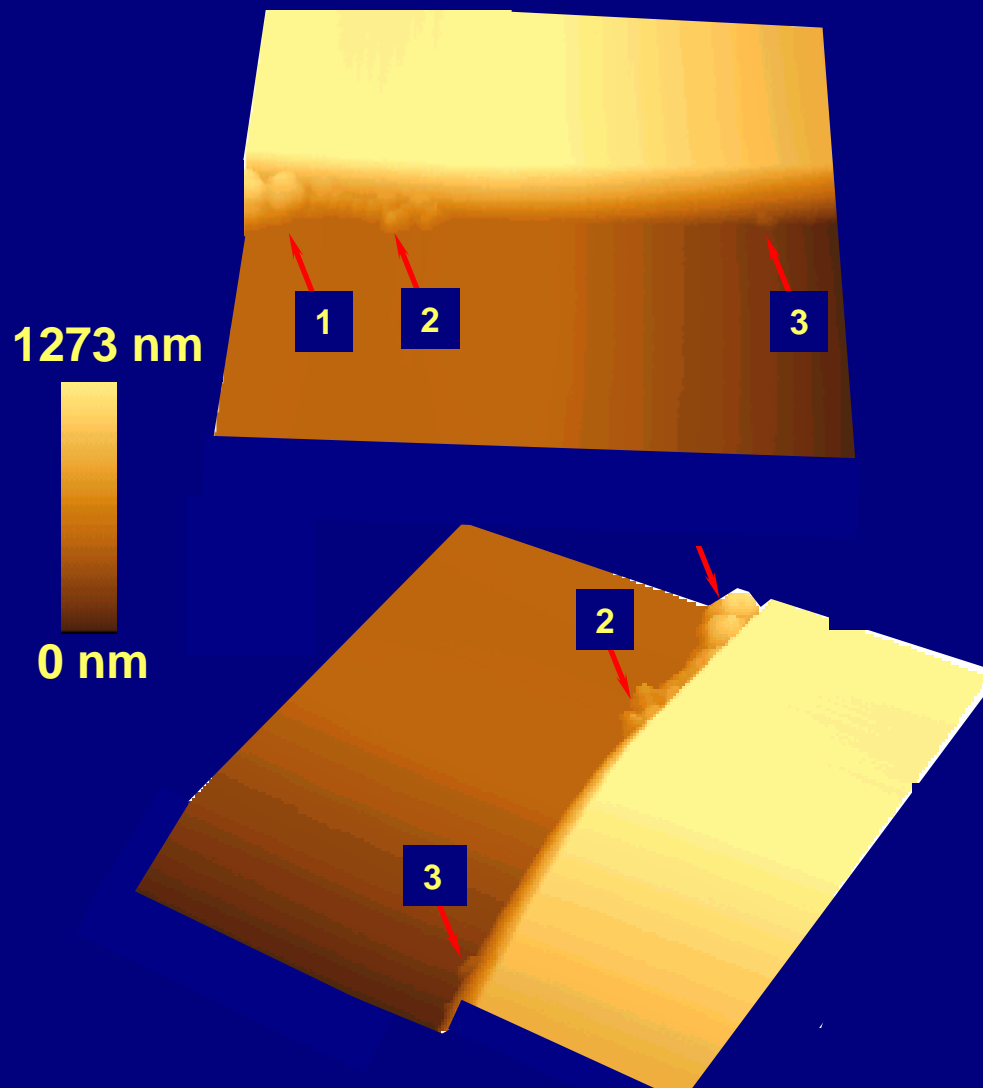
SEPM: scanning electric potential microscopy



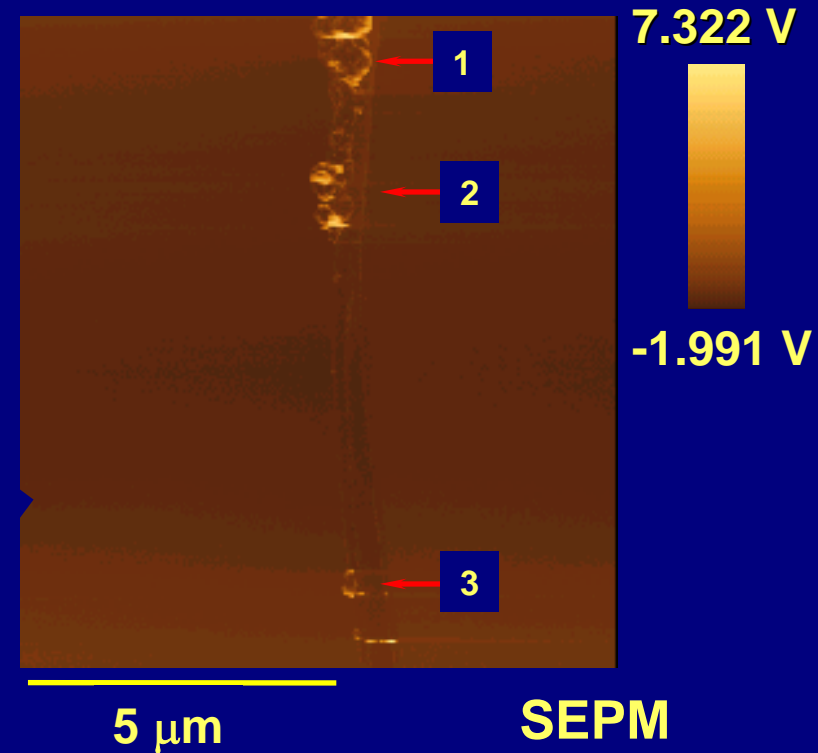
EFM: electric force microscopy



**TiO₂ particles on a mica step: separation of van der Waals and electrostatic interactions:
positive shells on negative cores.**

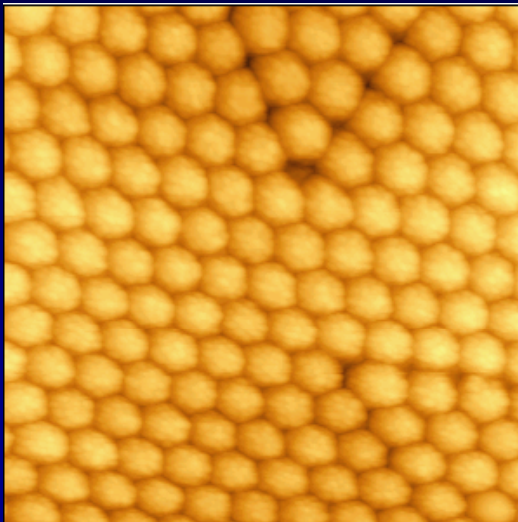


NON-CONTACT AFM



AFM, non-
contact image

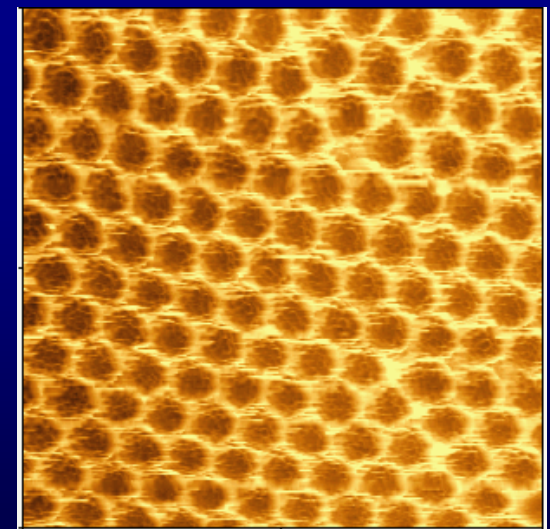
5.27 μm
349 nm
2.63 μm
0.00 nm
0 μm



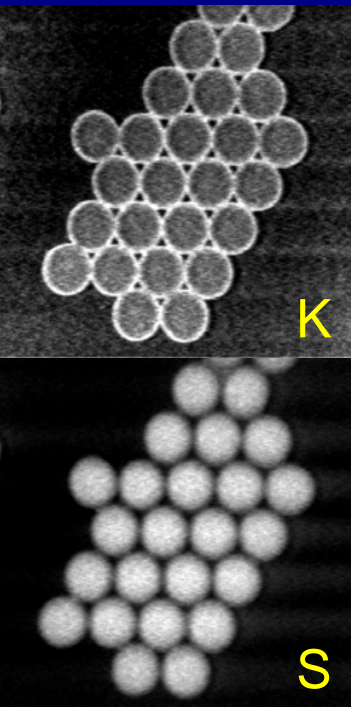
*Poly (styrene-co-hydroxyethyl
metacrylate), a macrocrystal-
forming latex*

Scanning electric potential
image

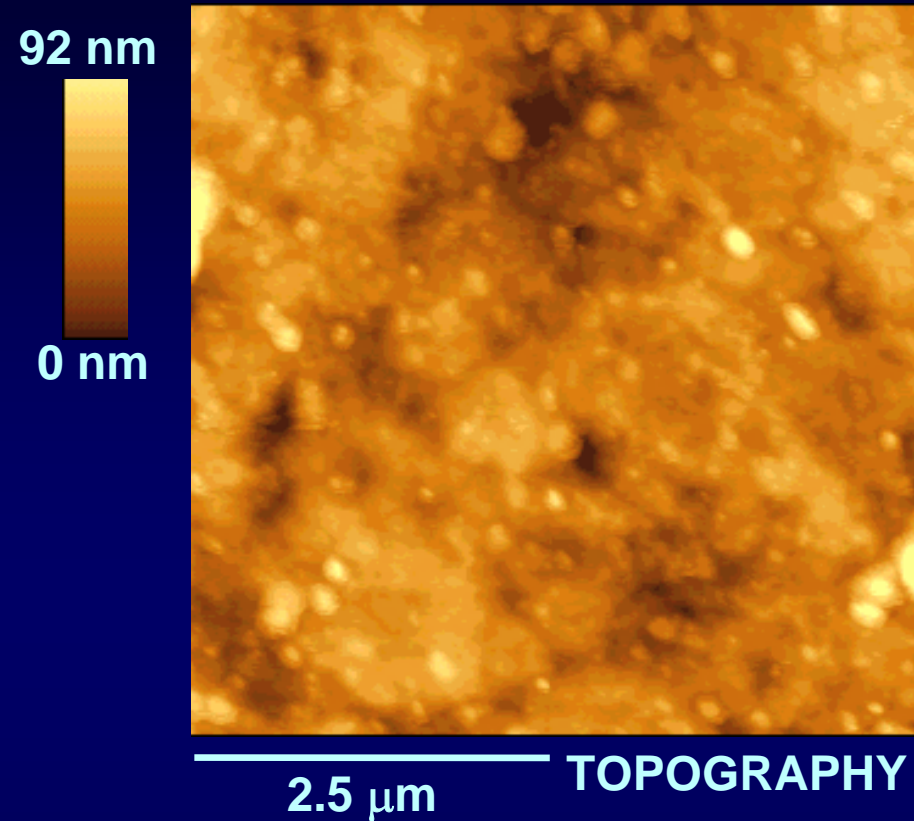
10.00 V
-10.00 V



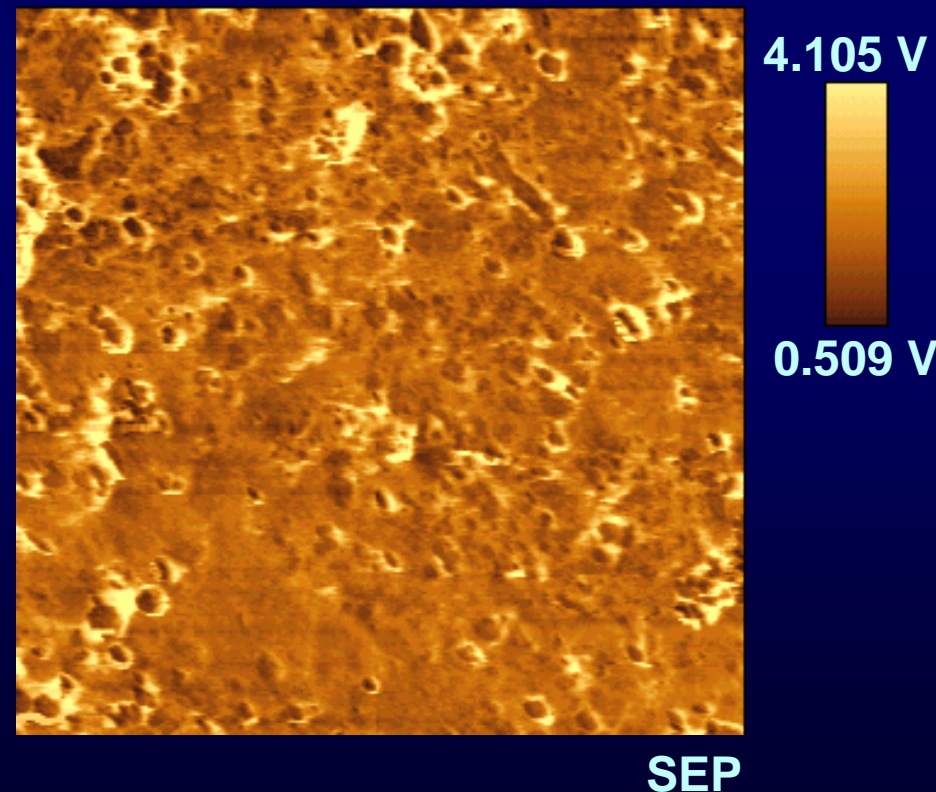
*A positive mesh
with negative
particle
cores*



POLYPROPYLENE FILM (thickness = 0.175 mm)

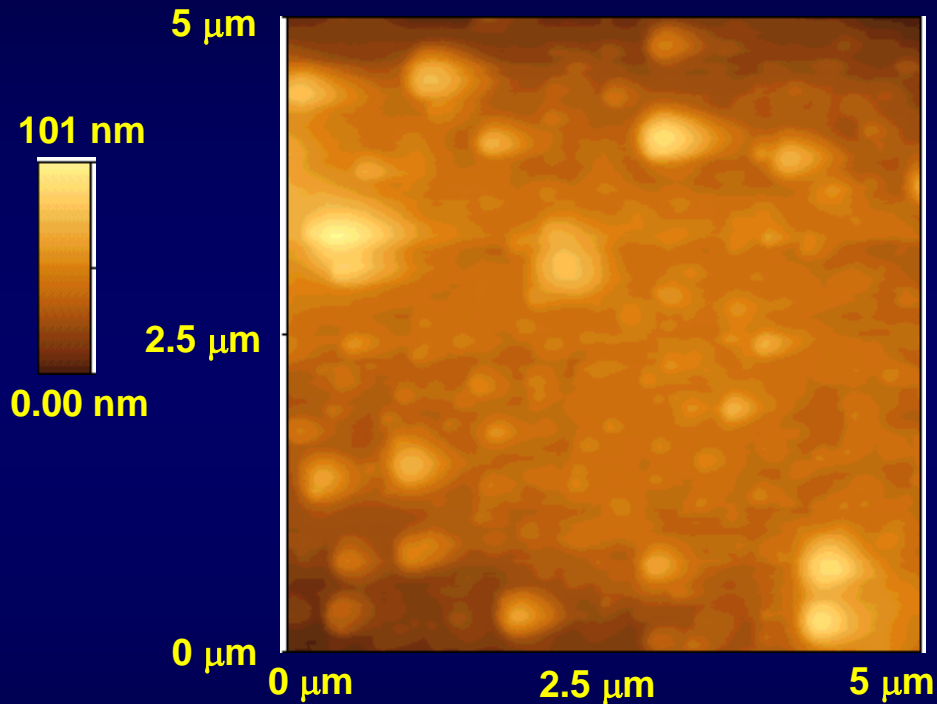


- Background: is very rough (topography), but flat in SEP picture.

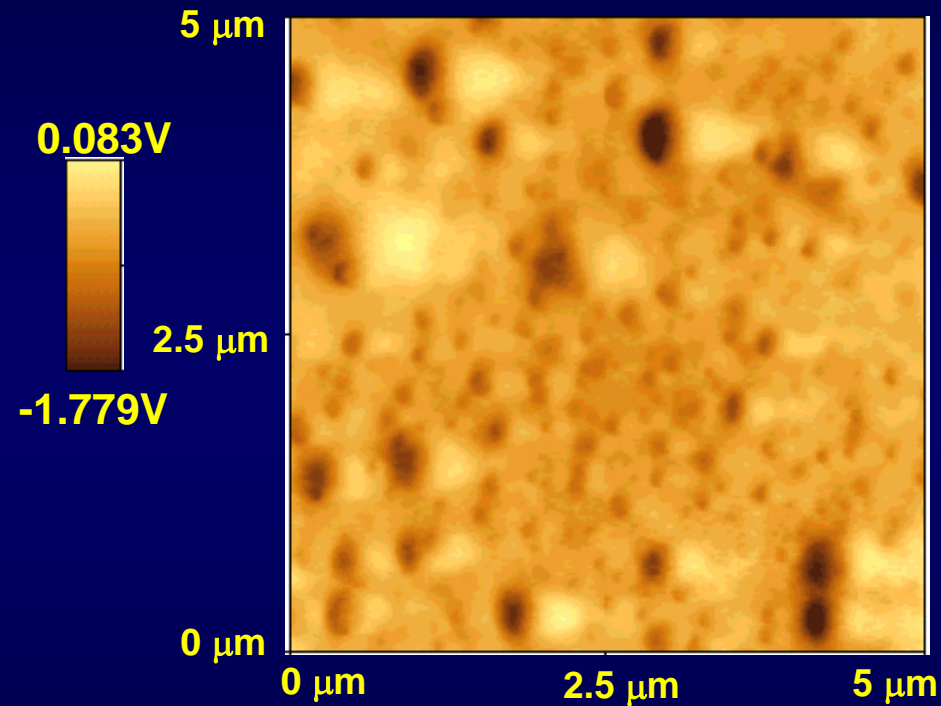


- Elevations appear as sites requiring a more negative bias and surrounded by a positive halo.

The printing surface of a desk-jet film



TOPOGRAPHY



SEPM

Elevations are bipolar: consistent with polyelectrolyte spreading on the PET surface

Non-contact AFM



Alumina (from 0.1% aq. SDS)

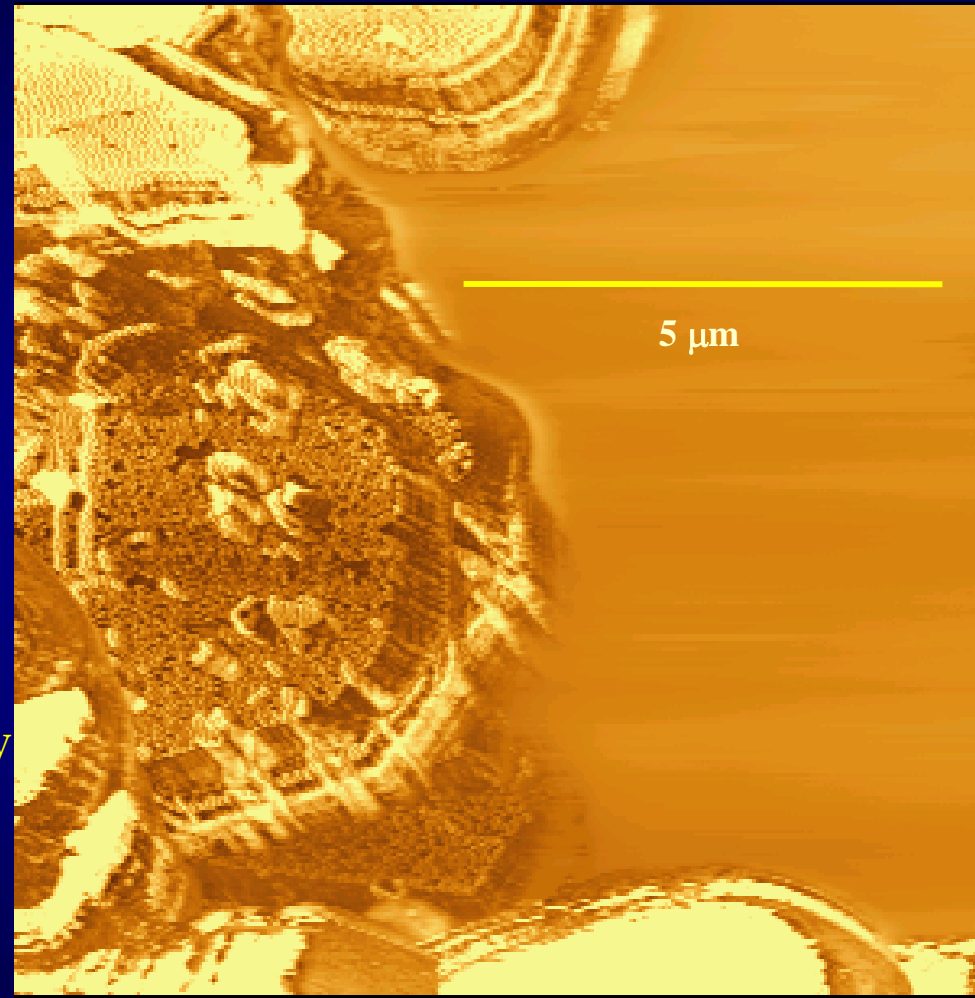
3874 nm

0.00 nm

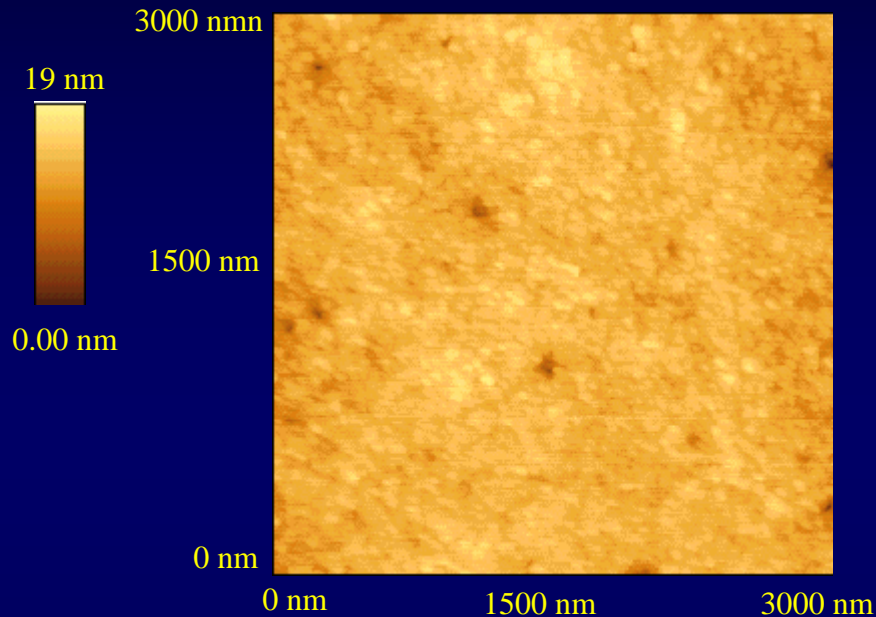
10.000 V

-2.171 V

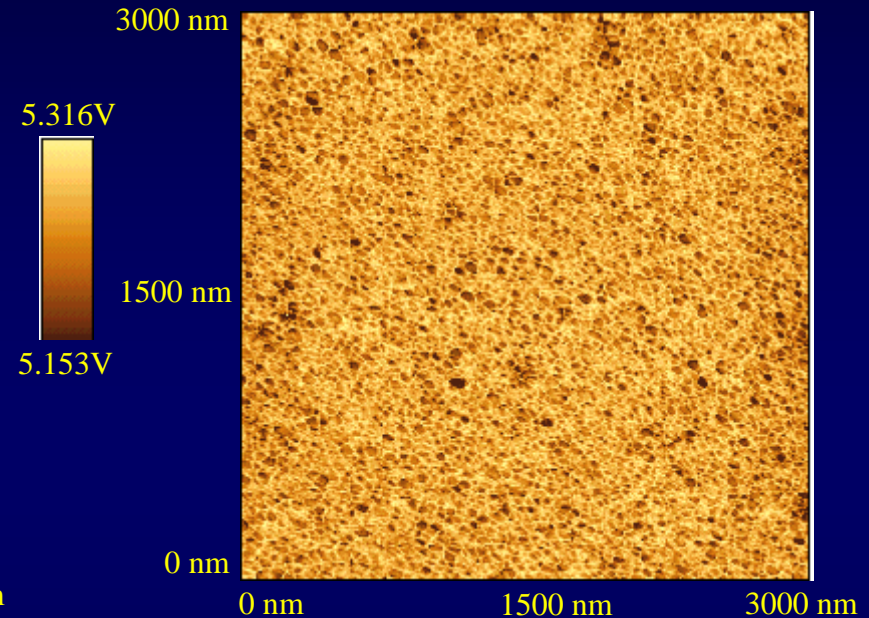
SEPM, *scanning electric potential microscopy*



Film of SiO₂ nanoparticles ($\varnothing = 36.5 \pm 1.0$ nm)



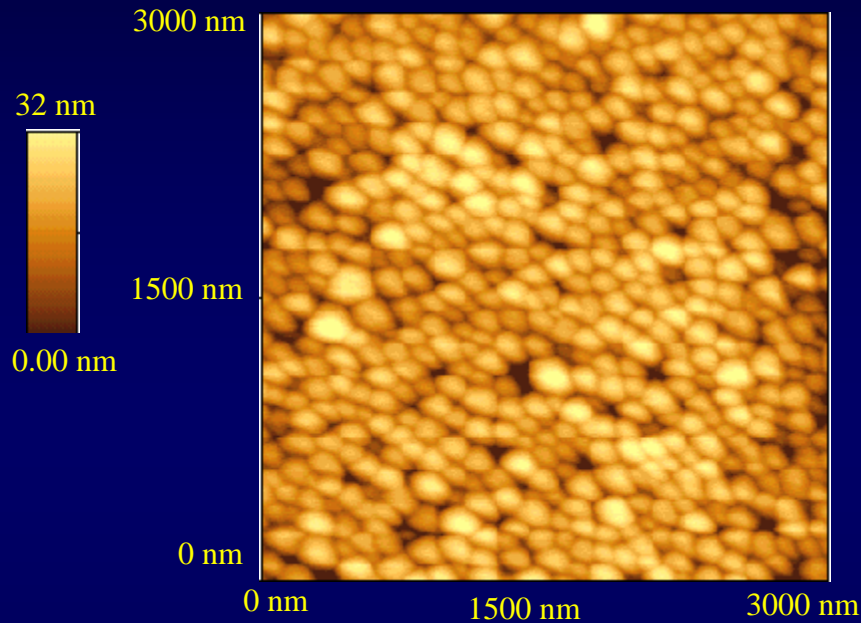
TOPOGRAPHY



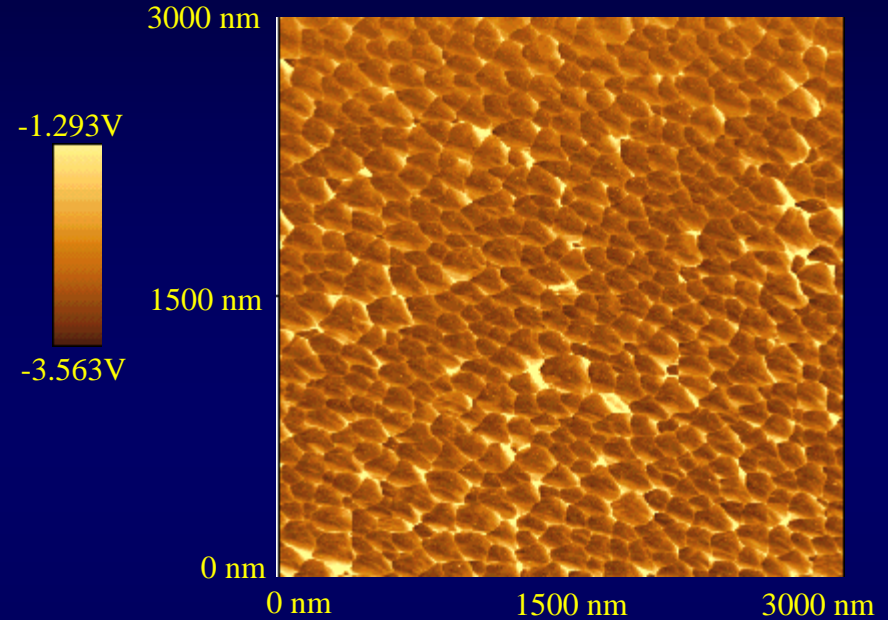
SEPM

- ✓ Topography: it is not possible to identify the original particles.
- ✓ EF: shows a large contrast between neighboring domains, in the same size range as the particle diameters.

Film of SiO₂ nanoparticles ($\varnothing = 141.5 \pm 2.5$ nm)



TOPOGRAPHY



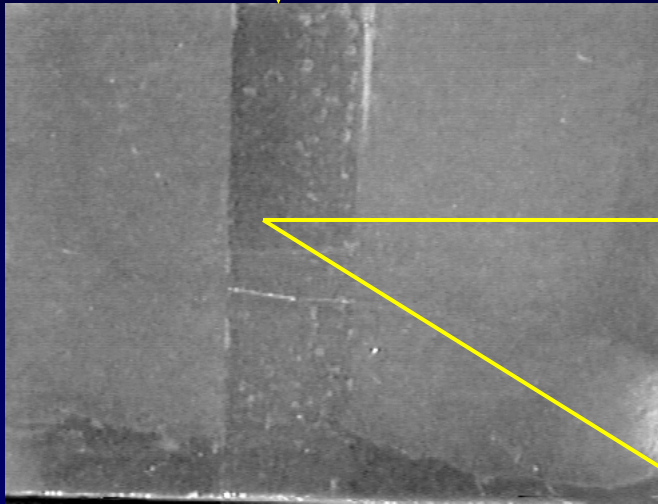
SEPM

- ✓ The particles are distorted anisotropically, during the film formation (checked by rotating the sample)
- ✓ The particle borders are visible, thus excluding the prevalence of particle coalescence or inter-particle diffusion.

Modification of natural rubber latex by polyphosphates

- **NaPP effect on film spreading and adhesion to glass and thermoplastics**
 - **Film morphology**
- **Electric potential mapping**
 - **Modulus mapping**
- **Film microchemistry**
 - **A tentative model**

adhesive tape-coated area



Film with adesive tape

Tape peel testing

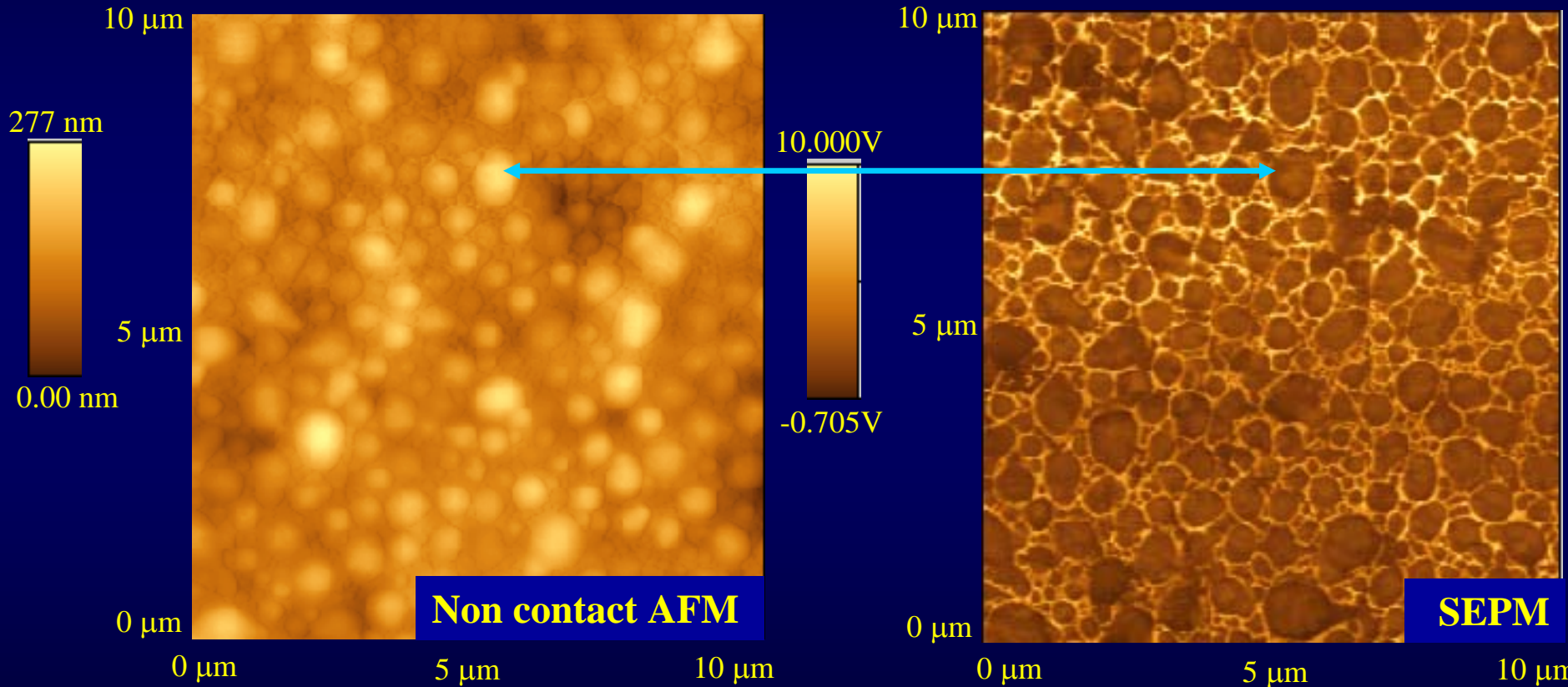


**pristine
latex film
after first peel:
rubber is
peeled-off.**



**polyphosphate-
modified
latex
film
after third
tape peel:
rubber is not
damaged.**

Natural rubber film topography (non-contact AFM) and scanning electric potential (SEPM) images

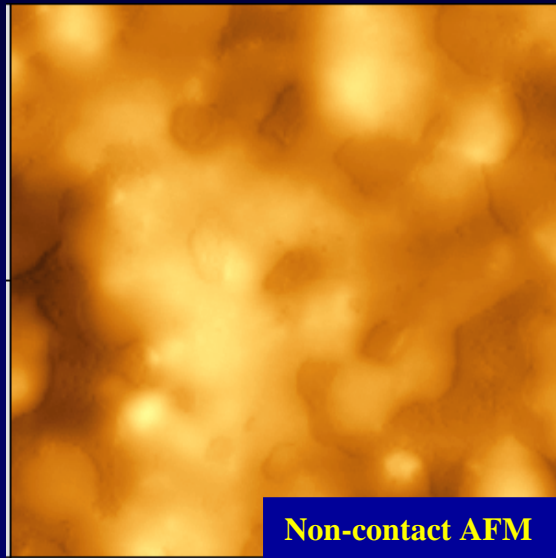


**Individual particles are observed as elevations.
Negative cores dispersed in a positive matrix.**

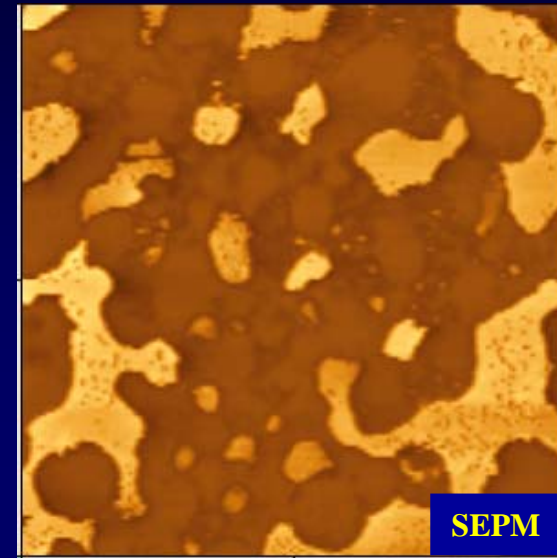
Natural rubber + sodium polyphosphate film

non-contact AFM and scanning electric potential (SEPM) images

156 nm
0.00 nm



4.494V
-8.536V

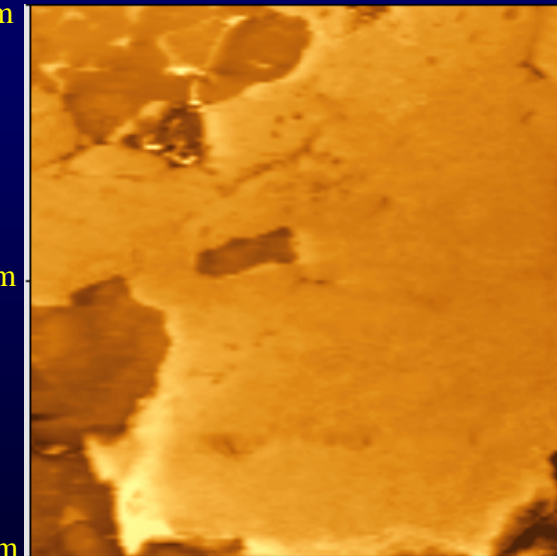


**PP-NR
film
surface**

2299 nm
0.00 nm

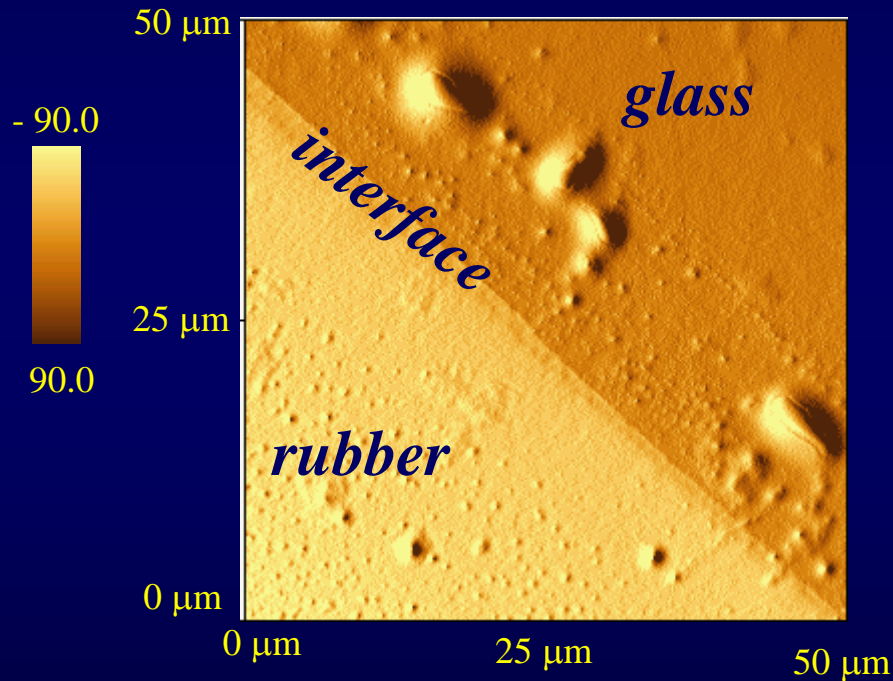


10.054V
-4.026V
5 μm
2.5 μm
0 μm

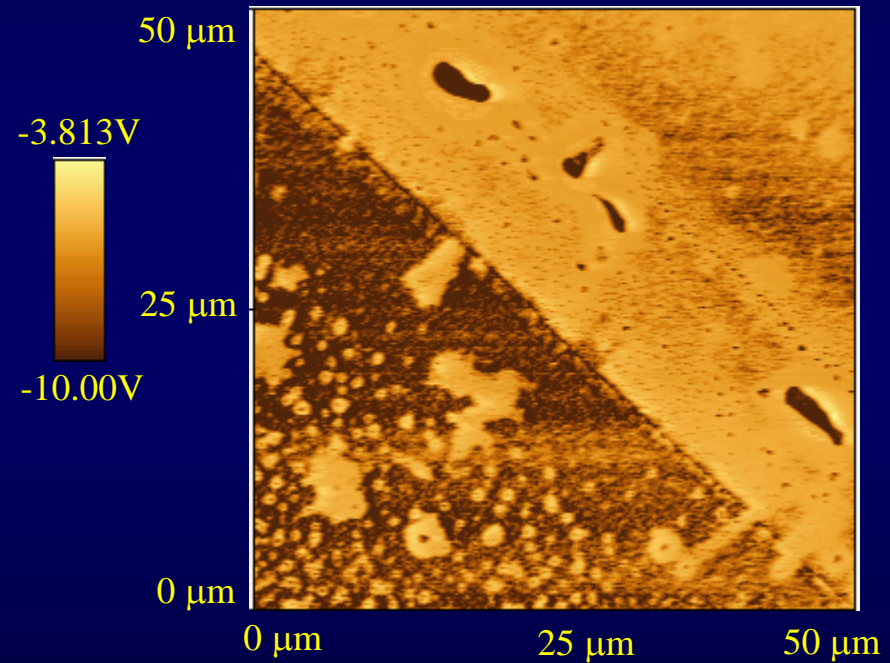


**PP-NR
film
surface in
contact
with the
glass**

Natural rubber + sodium polyphosphate fracture (non-contact AFM) and scanning electric potential (SEPM) images



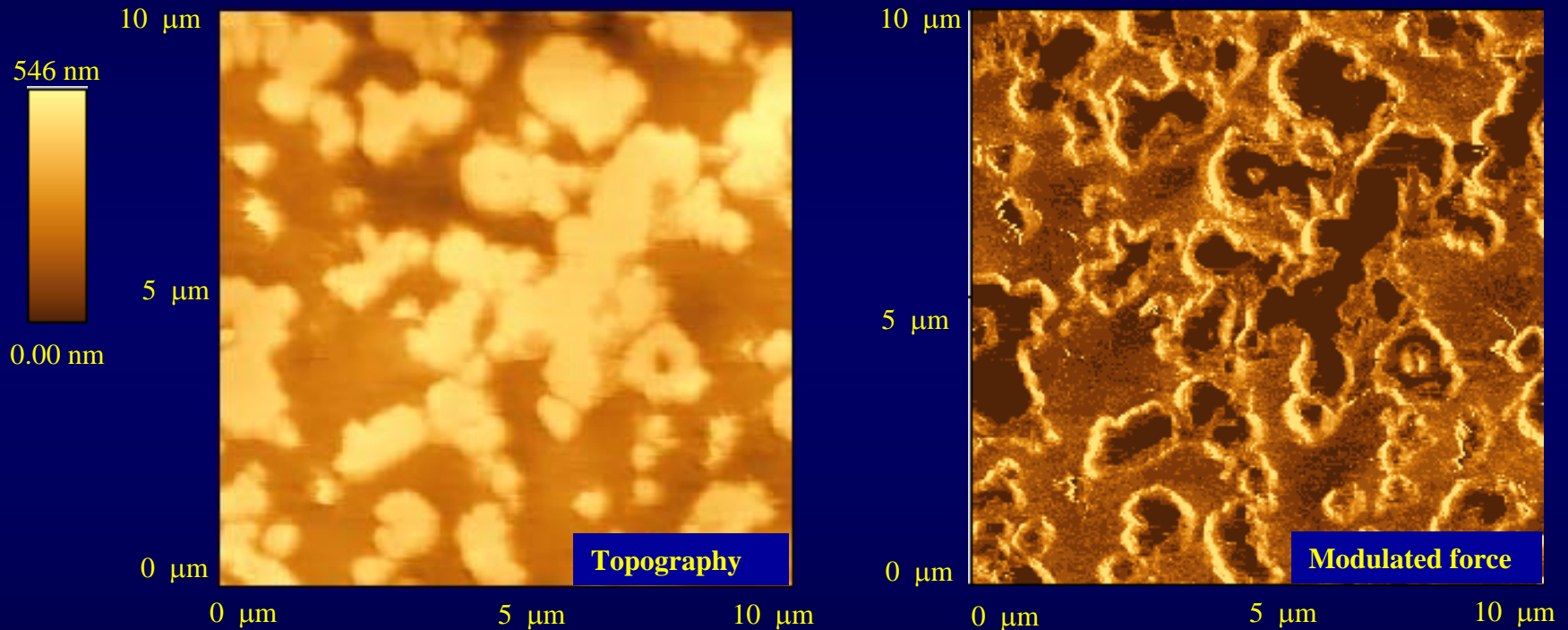
Non-contact AFM



SEPM

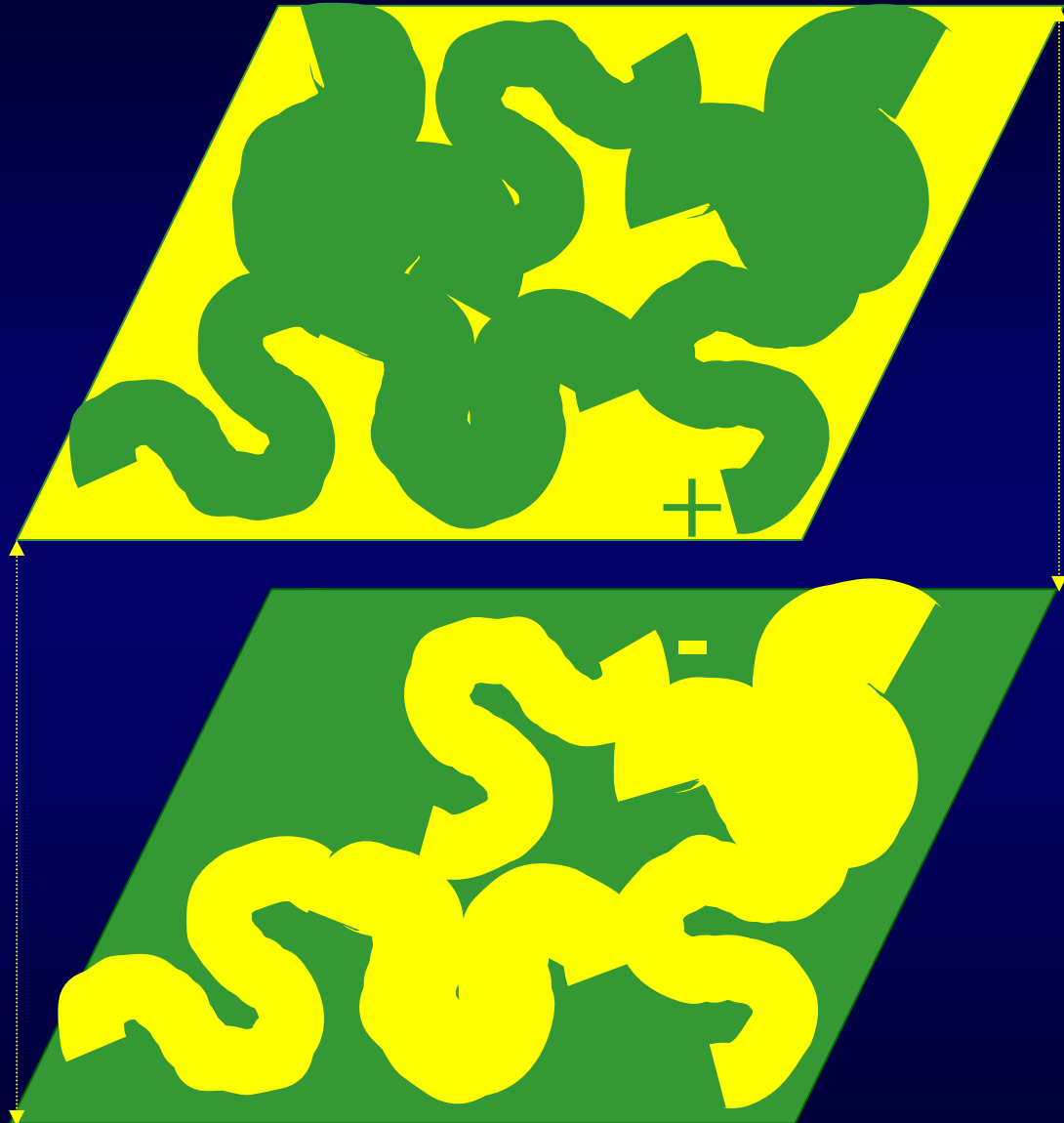
A layered structure at the glass-rubber interface

Modulated force image of PP-NR film: dark is low-modulus, bright is high-modulus



**Dark domains of soft rubber,
interpenetrated with harder rubber domains.
Interfaces have the highest modulus.**

**A model for
adhesion
improvement on
glass and acrylic:
the PP-rubber
film has charged
domains, which
bind to the
replicating
surface.**



Conclusions

- Sodium polyphosphate improves latex spreading, dry and wet adhesion of NR on glass and acrylic.
- Triphosphate-NR films contain birefringent domains, no adhesion improvement.
- *PP-NR film morphology and electric charge distribution pattern is different from NR.*
- *Films contain domains of different moduli.*
- Mutual exclusion of C and P, Na, N, O – rich domains.

Current problems

- Effects of particle constituent distribution (inter- and intraparticle).
- *Applications of the di(multi)polar character of particles: adhesion, mechanical properties*
- Nature and control of the sites with finite charge densities, in polymers and oxides
- *Charge pattern effect on (hetero)coagulation, film formation and superplastic behavior*
- Adsorbate patterning in surfaces
- *New techniques, for new problems*

Acknowledgements

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- **Serrana de Mineração S.A.**