Microchemistry and Macroionics of Colloids and Polymers

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Outline

- The **problem**: latex, polymer film properties, macrocrystal defects and ***particle heterogeneity***
- **Precedents**: polymer film deffects and failure; deviations from expected latex behavior
- **Hypothesis**: chemical heterogeneity
- The **approach**: analytical microscopies
- **Results:**
  - ***chemical domains and local charge excess (macroionics)***
  - ***detection of non-particulate constituents***

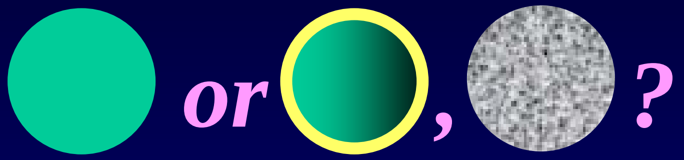
Polymers (thermoplastics, rubbers, thermosetting)

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

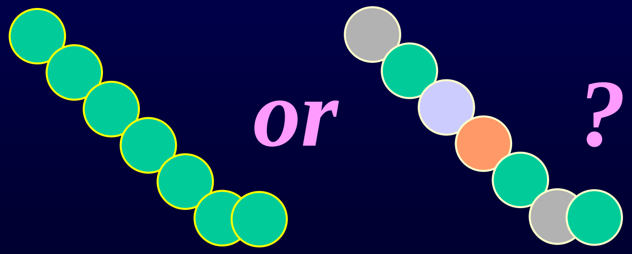
Electroneutrality, where?

- **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**

Coloidal particles

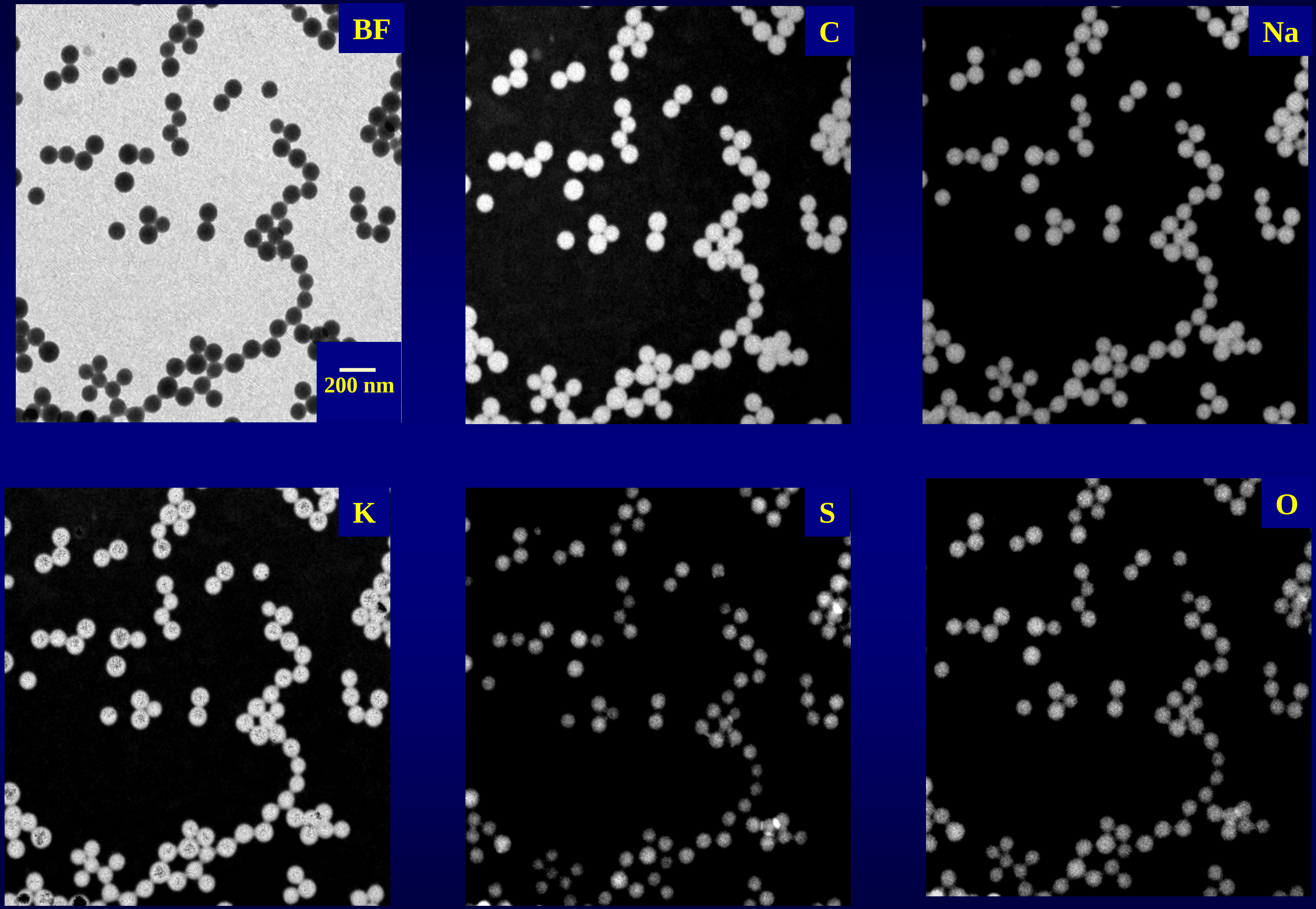


- Crystalline or amorphous
- Micro- to nanometric dimensions
- Colloidal stability is *kinetic*, dependent on electric repulsions
- Chemical composition: average and local
- **Usual hypothesis: uniform chemical composition, *but few proofs for this assumption***



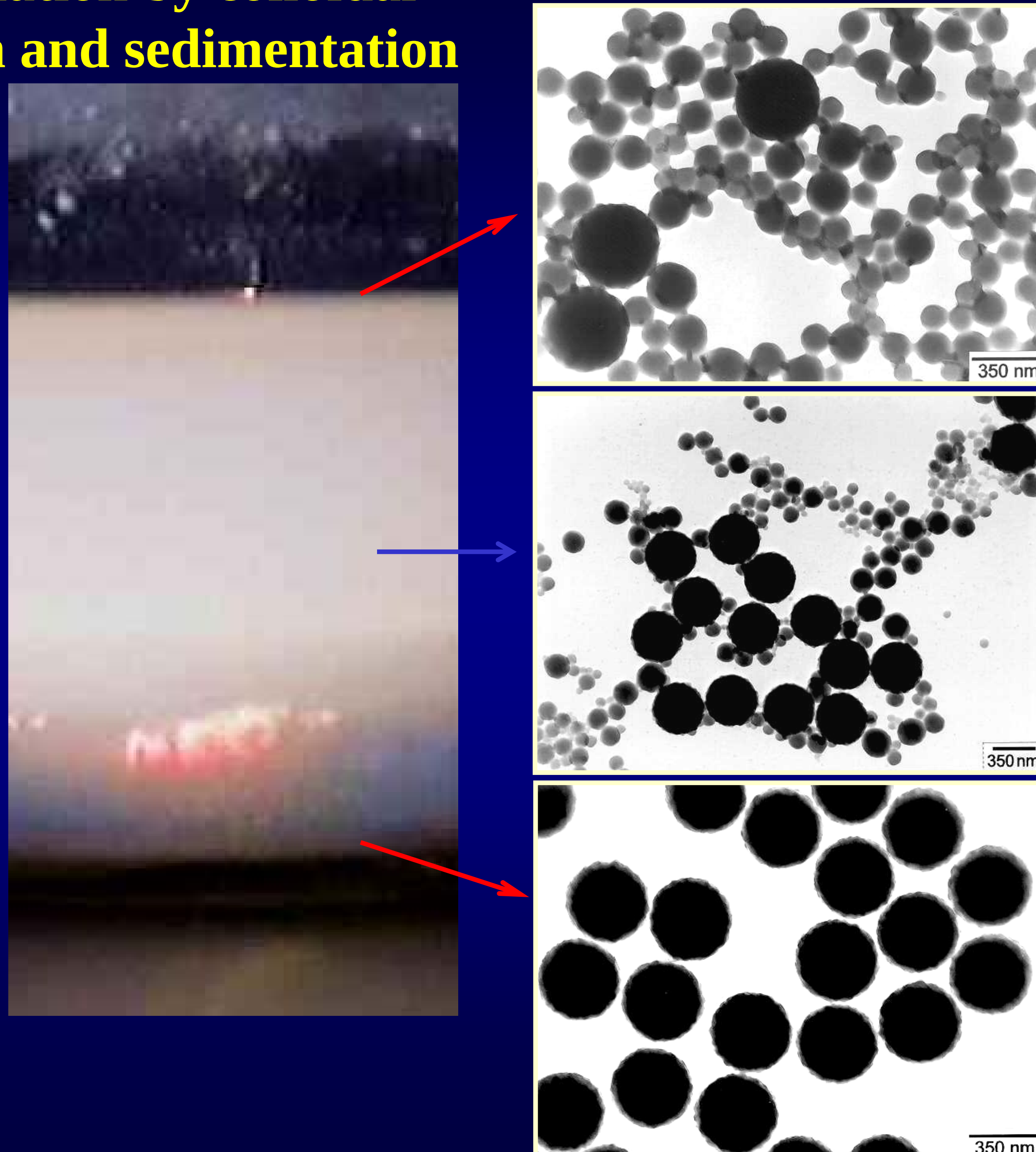
Electron spectroscopy imaging (ESI-TEM)

- **TEM with an electron energy monochromator**
- **Acquisition of EELS (electron energy-loss spectra), a *single molecule* analytical procedure**
- **(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

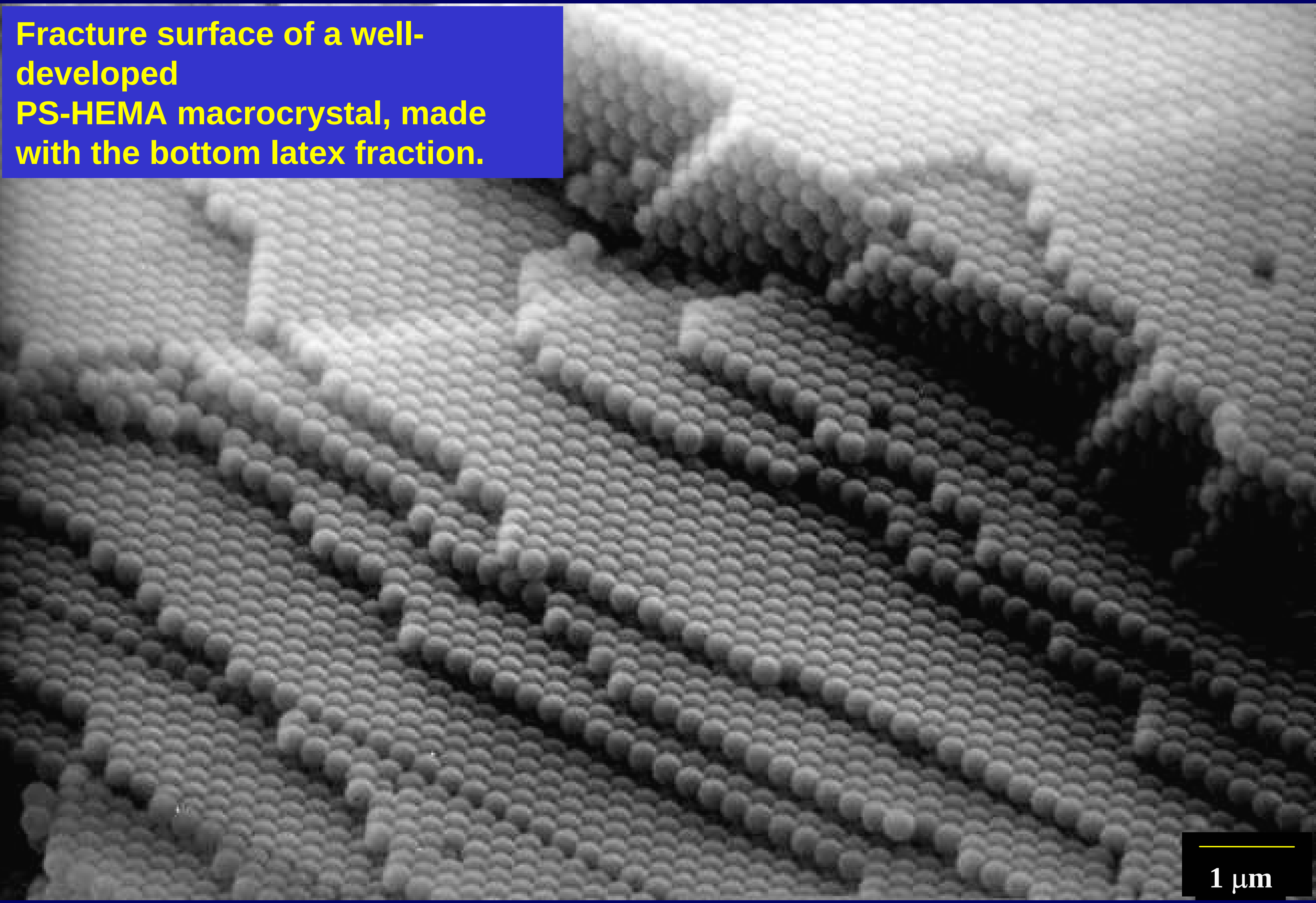


D = 159 nm
ζ = -36 mV

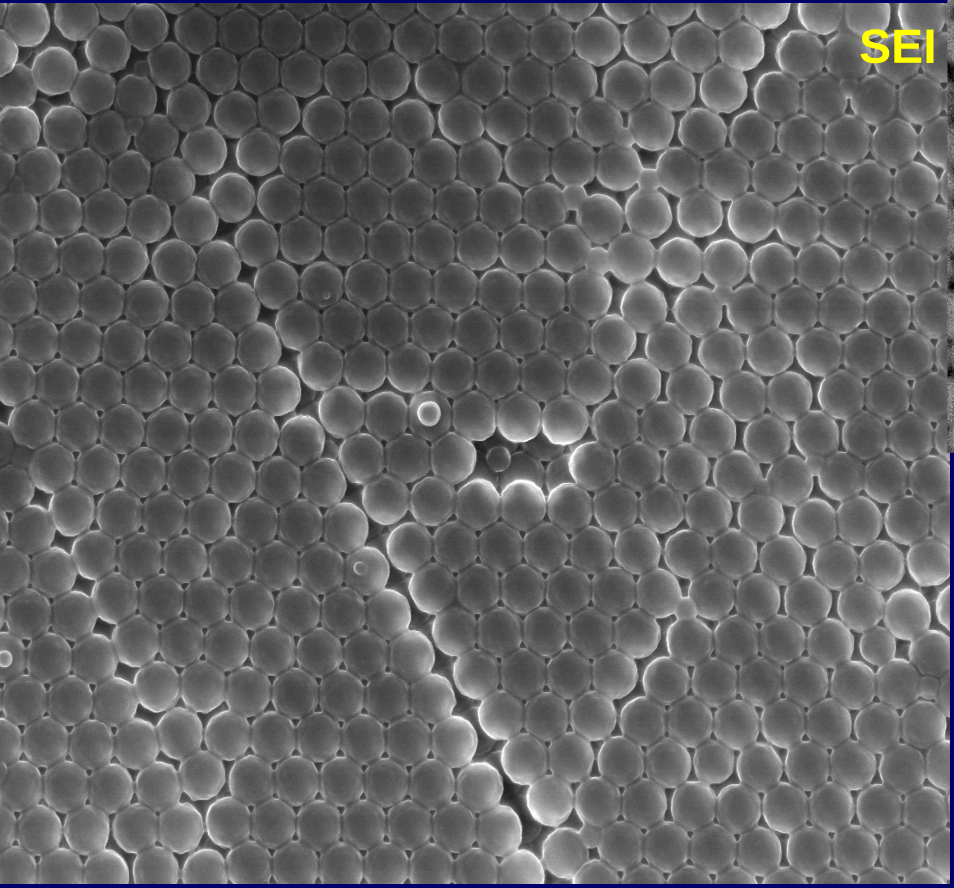
D = 189 nm
ζ = -42 mV

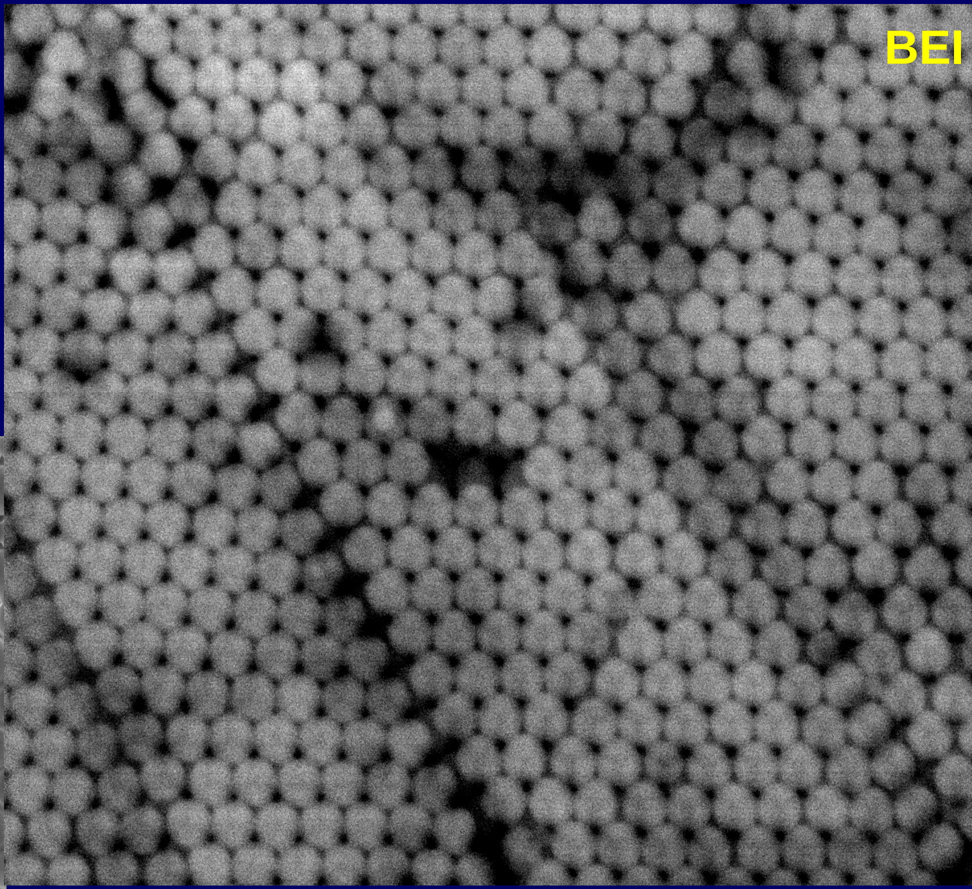
D = 414 nm
ζ = -54 mV

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

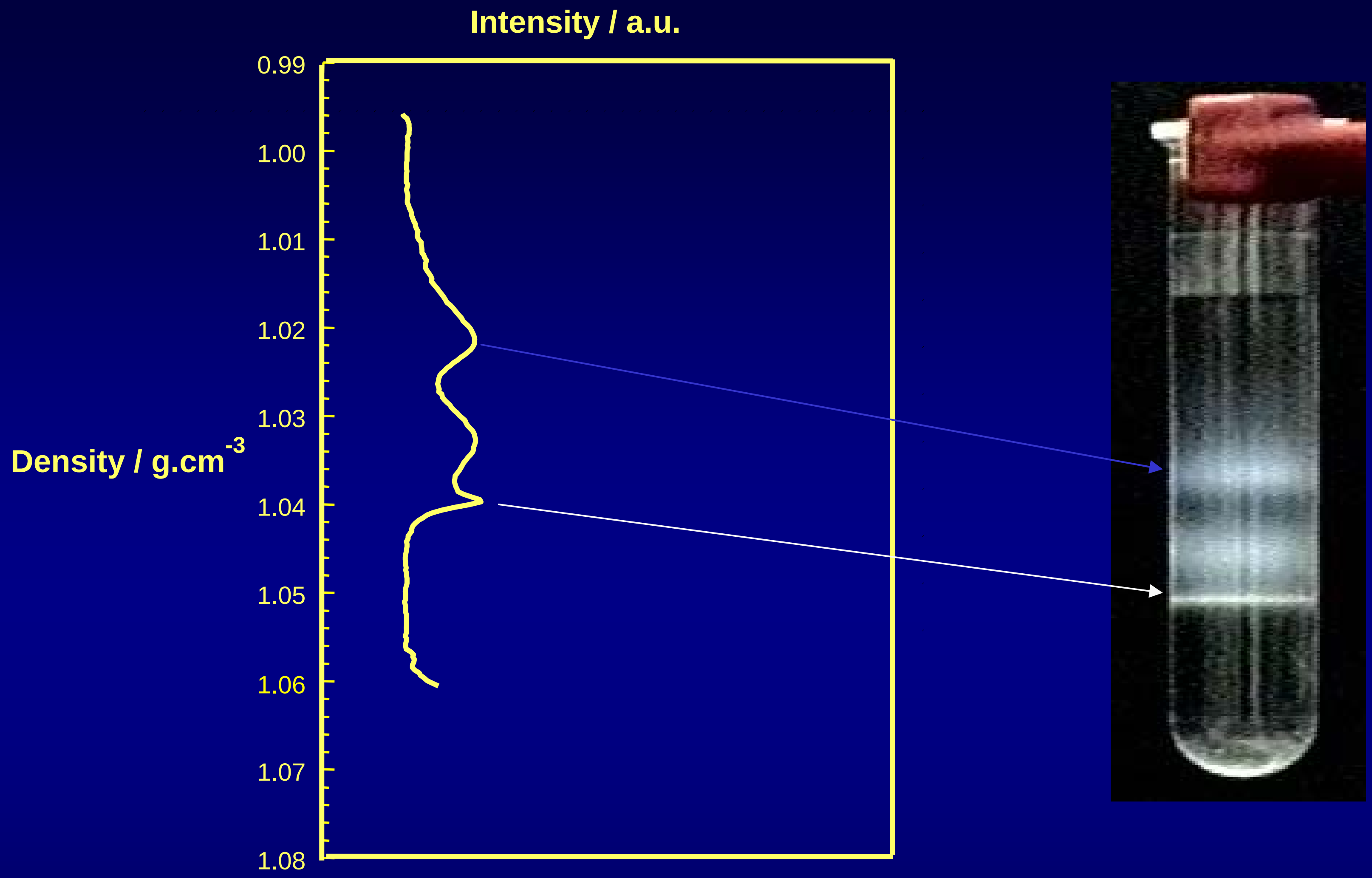


BEI and SEI images of PS-HEMA latex do not match each other. *Chemical domain geometry* is different from particle geometry.



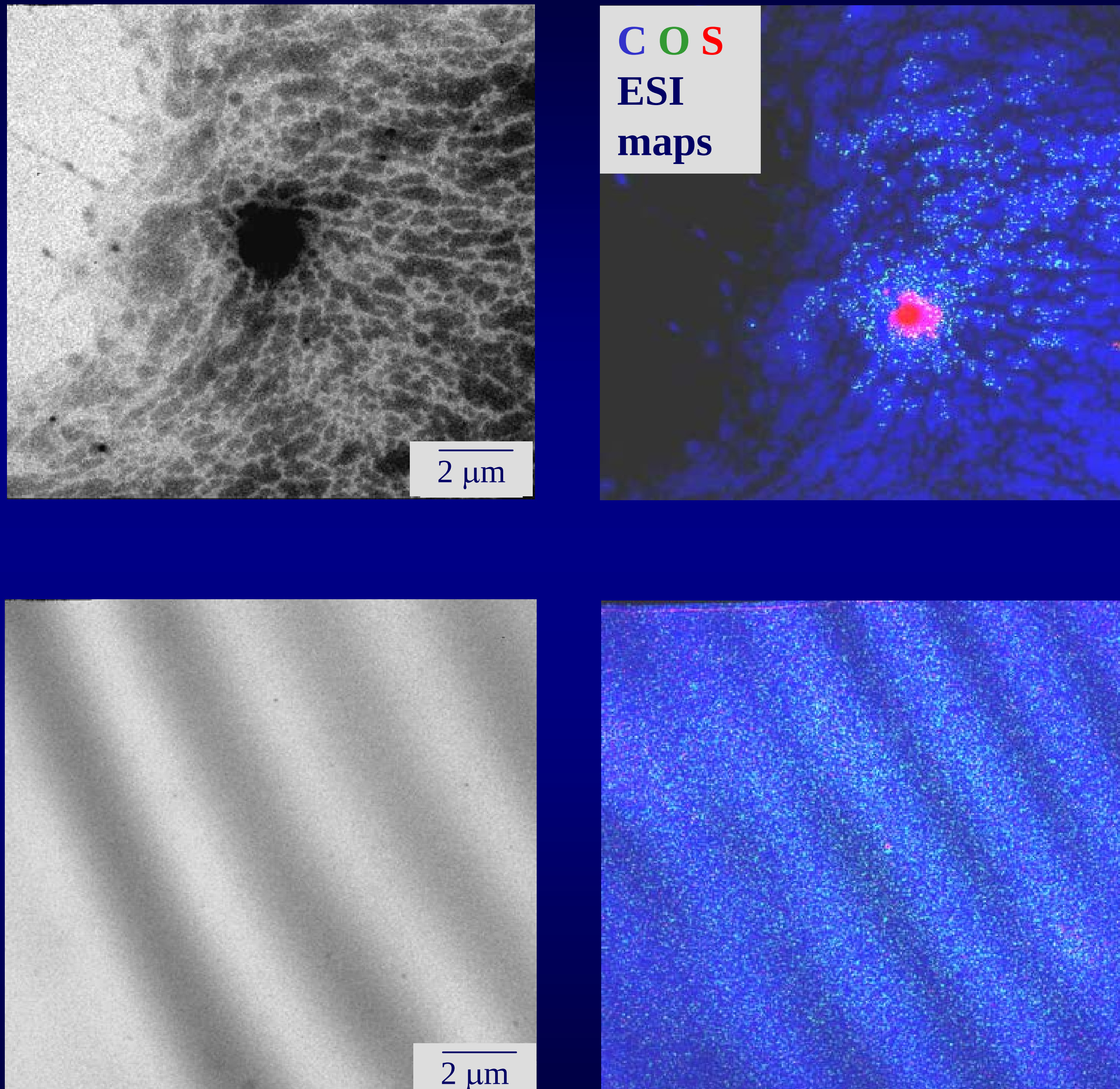


Particles clustered around line and point defects are darker than well-organized particles.
Their average atomic numbers are lower: richer in styrene, poorer in acrylic.



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**



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**

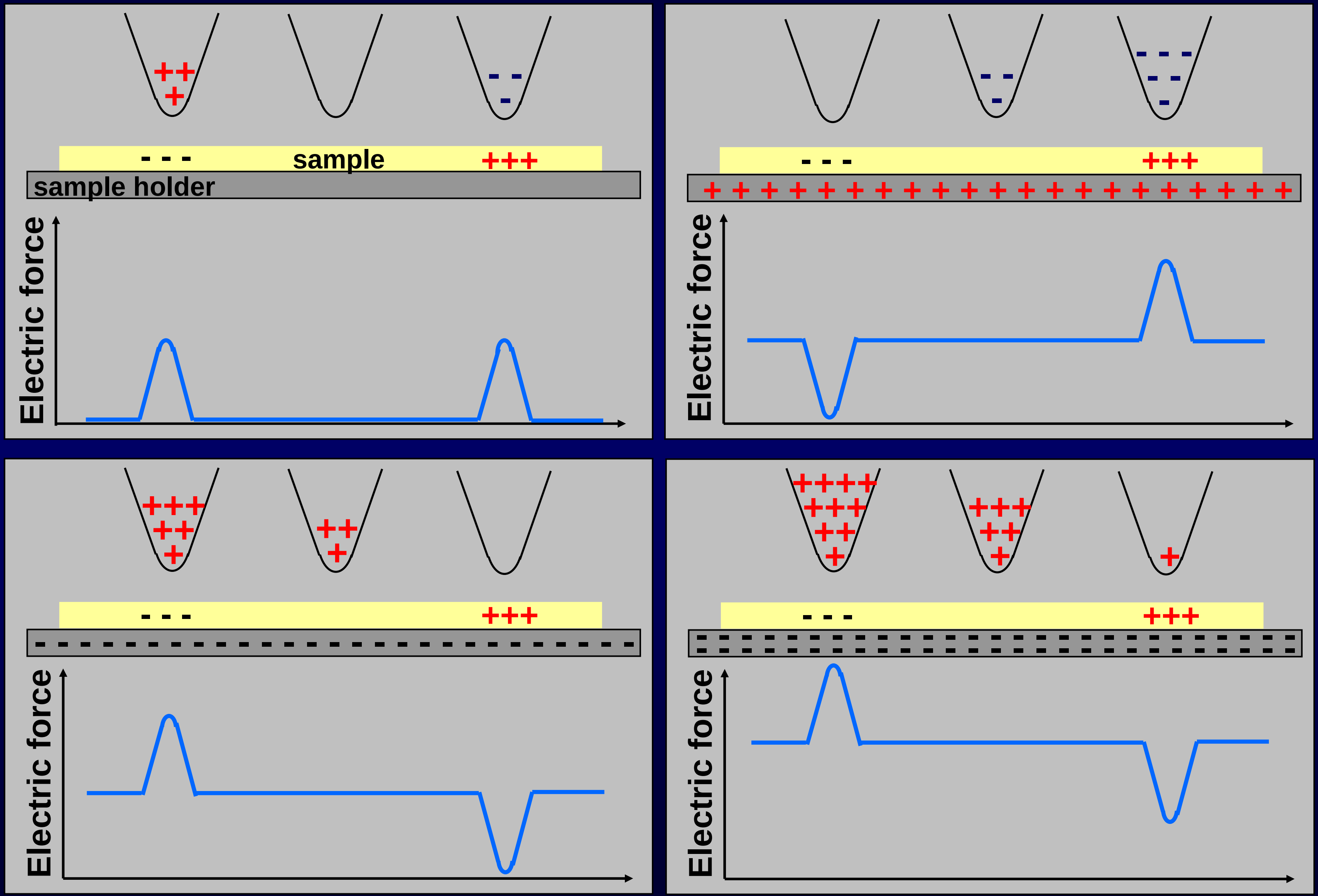
Many other imaging modes:

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

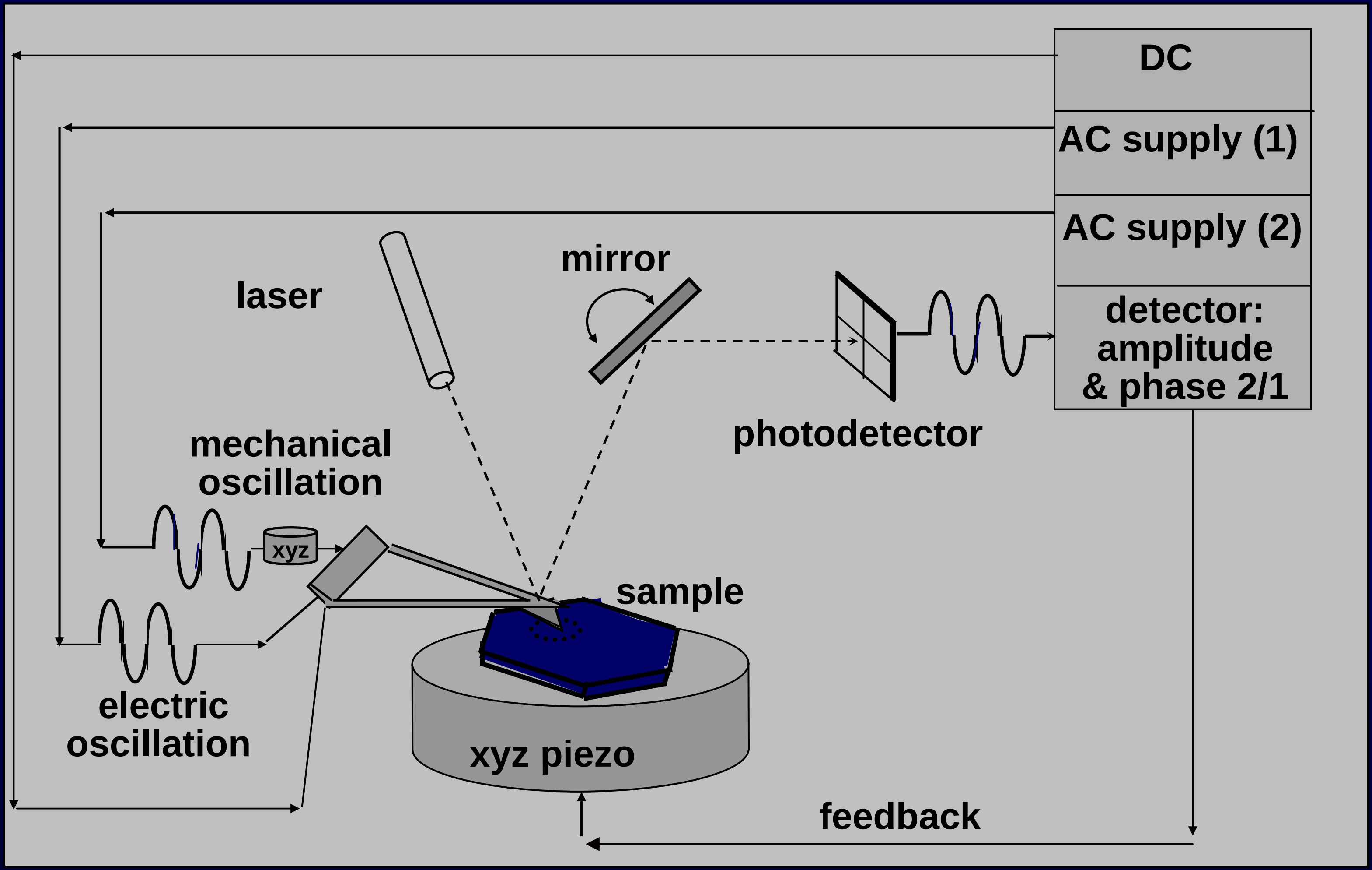
Scanning electric probe microscopies: SEPM, EFM

- 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

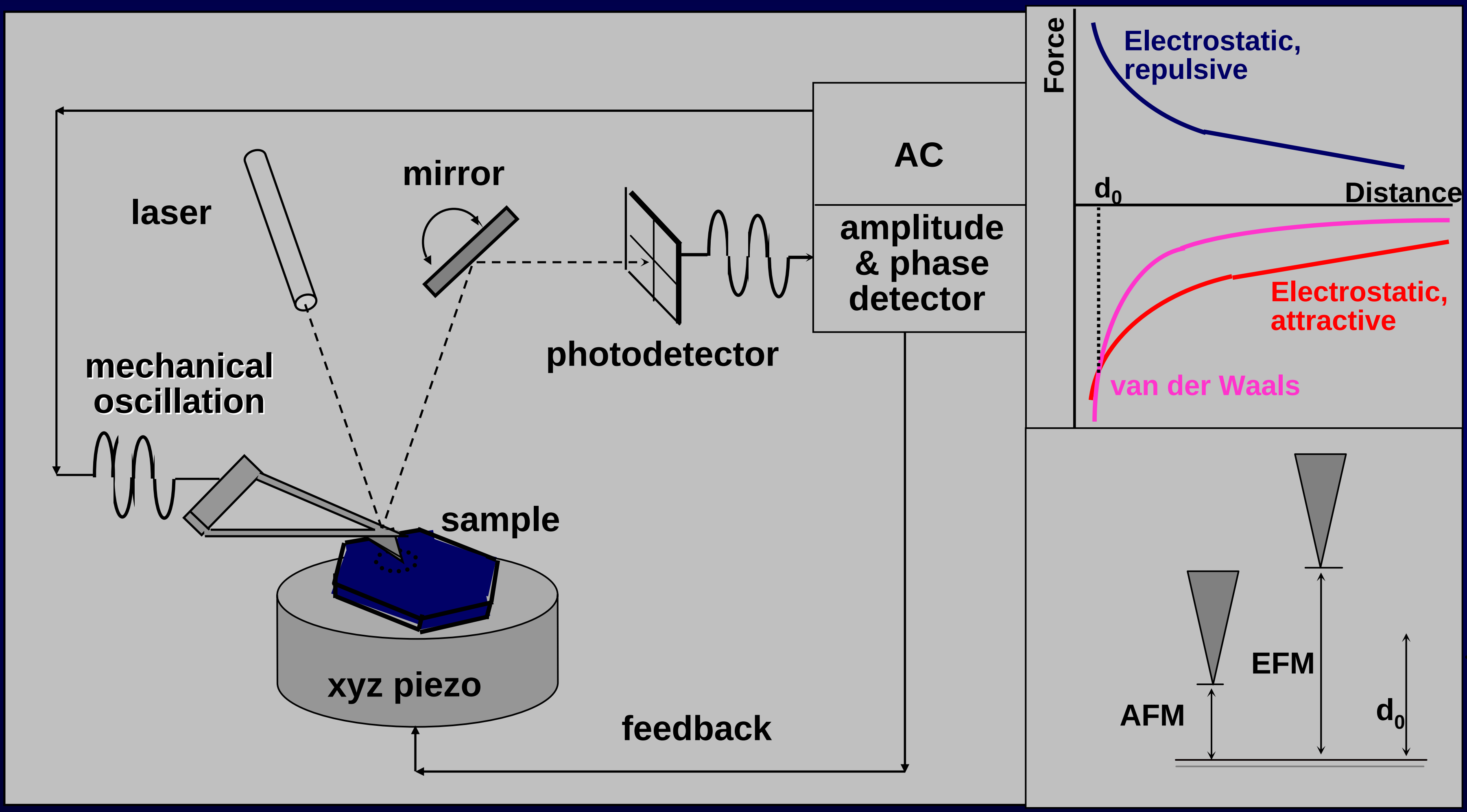
Induction of electric charges on the tip



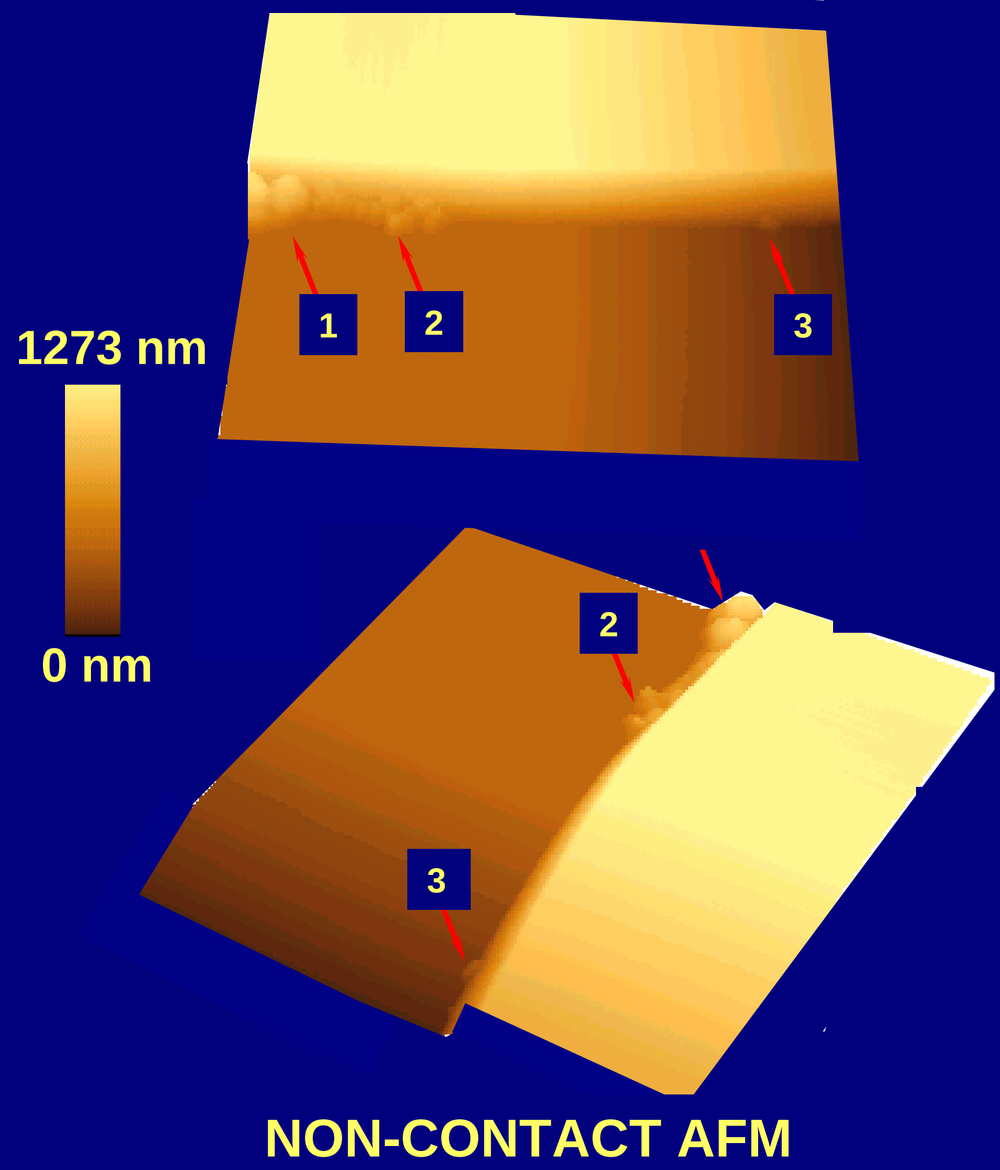
SEPM: scanning electric potential microscopy

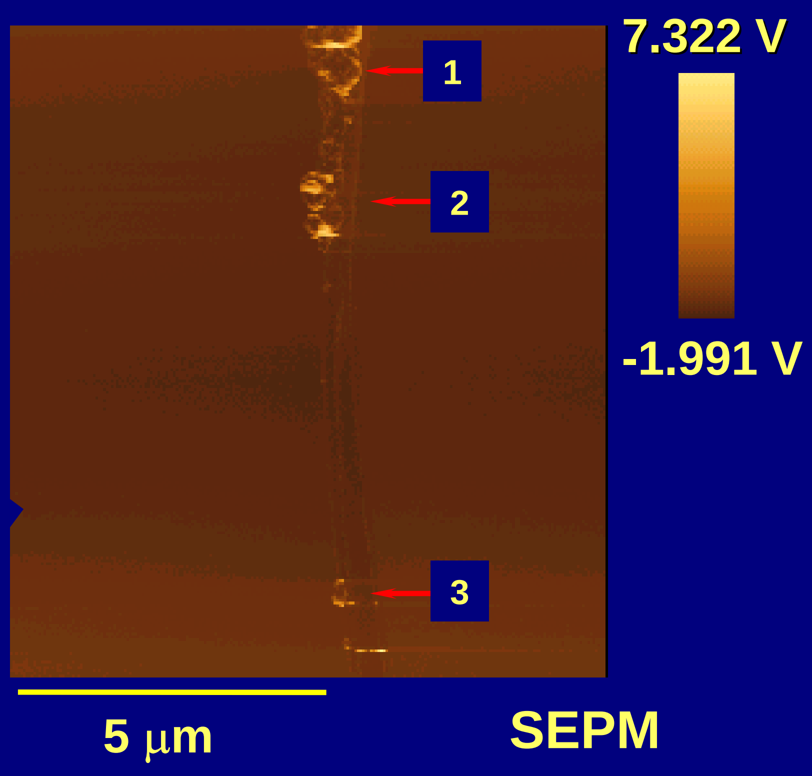


EFM: electric force microscopy



TiO_2 particles on a mica step: separation of van der Waals and electrostatic interactions: positive shells on negative cores.

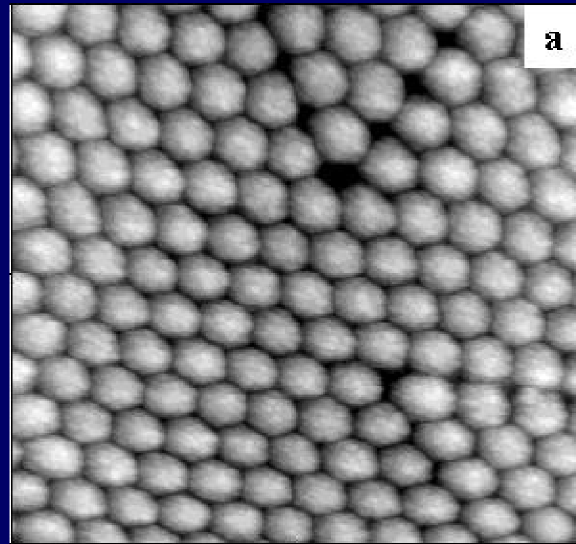




AFM, non-contact image

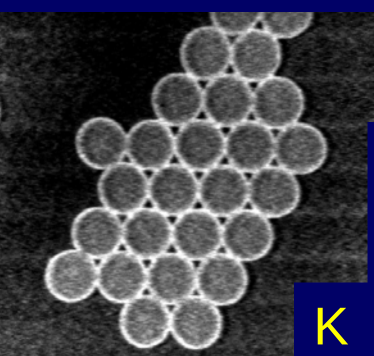
232 nm

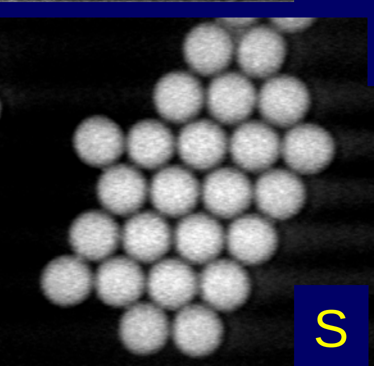
0 nm



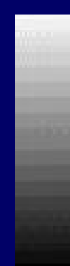
Poly (styrene-co-hydroxyethyl metacrylate), a macrocrystal-forming latex

Scanning electric potential image



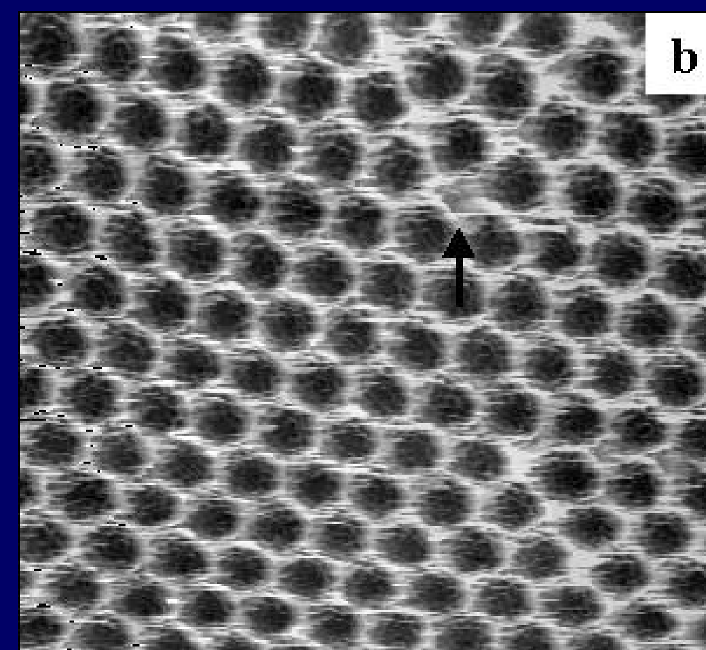


A positive mesh with negative particle cores



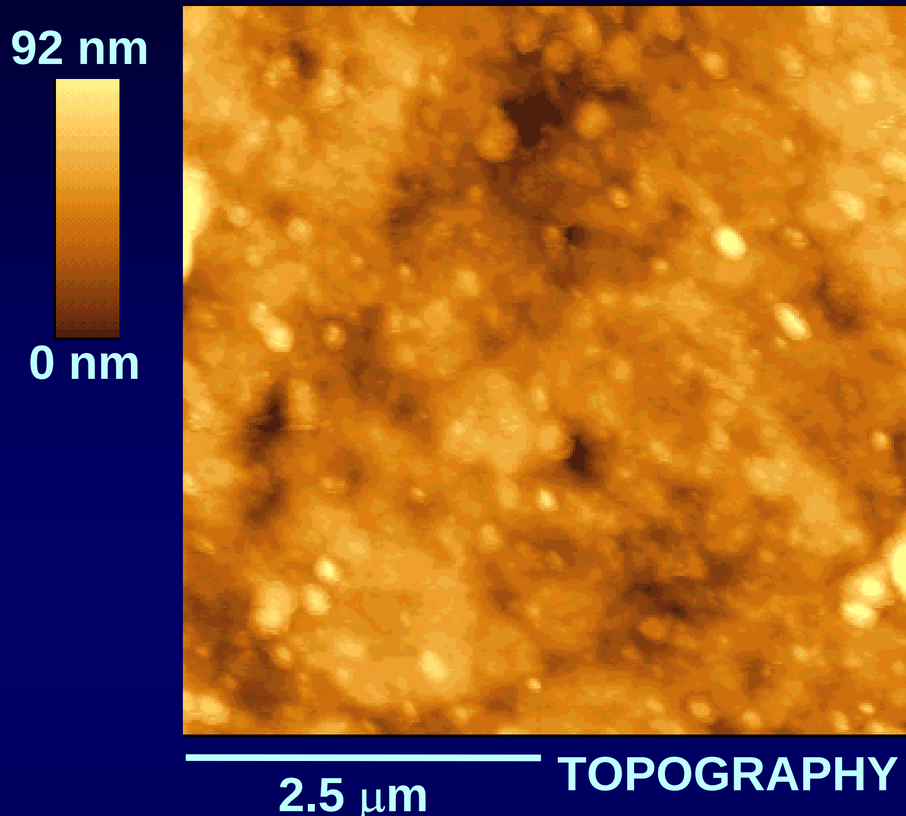
9.736 V

-9.651 V

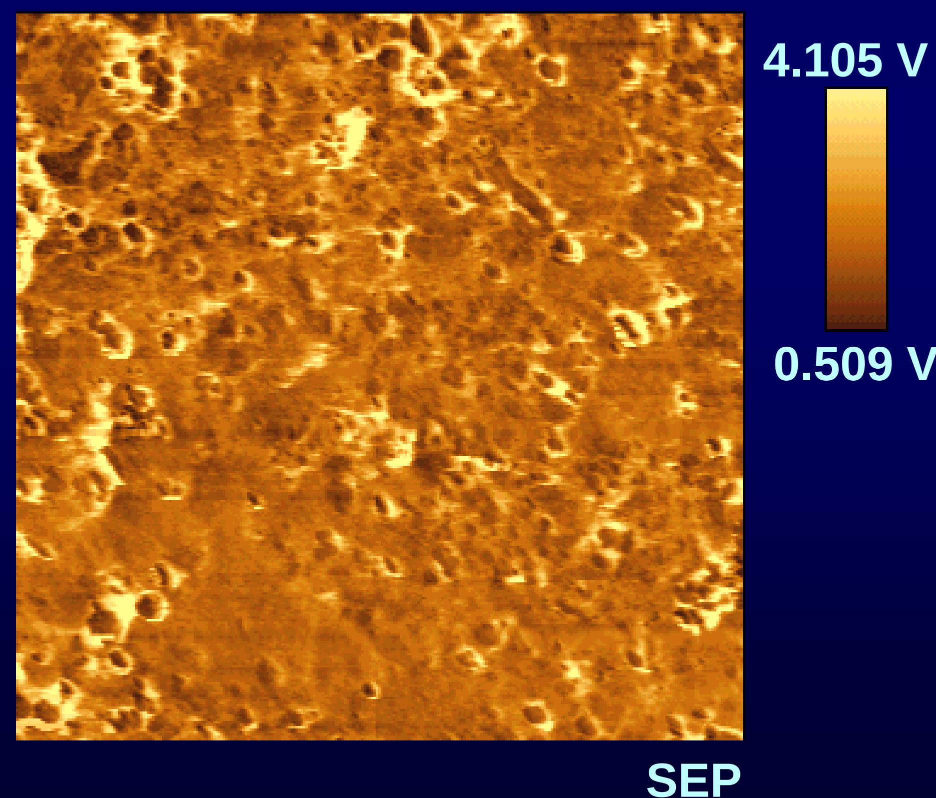


0 µm 5.27

POLYPROPYLENE FILM
(thickness = 0.175 mm)



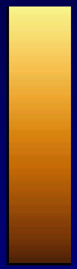
- Background: is very rough (topography), but flat in SEP picture.



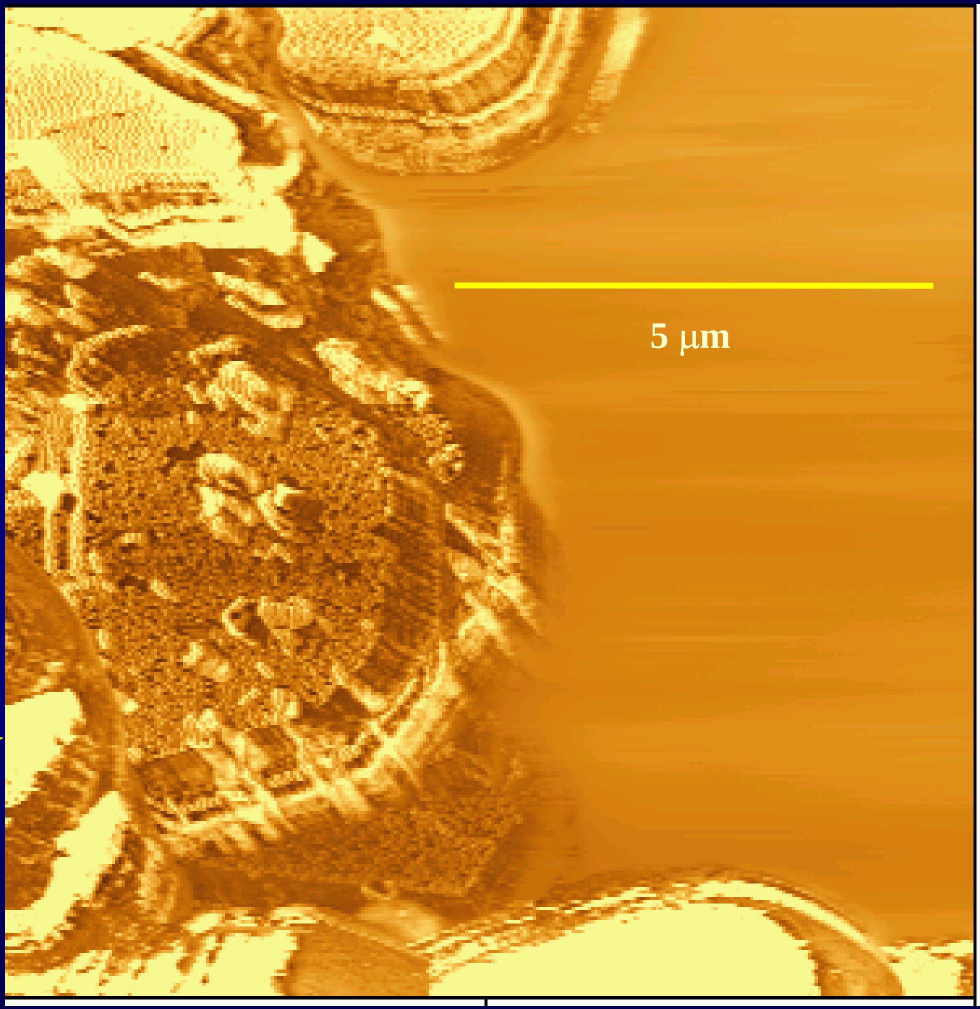
- Elevations appear as sites requiring a more negative bias and surrounded by a positive halo.

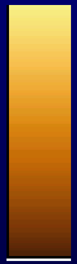
A. Galembeck et al., Polymer 2001

Non-contact AFM

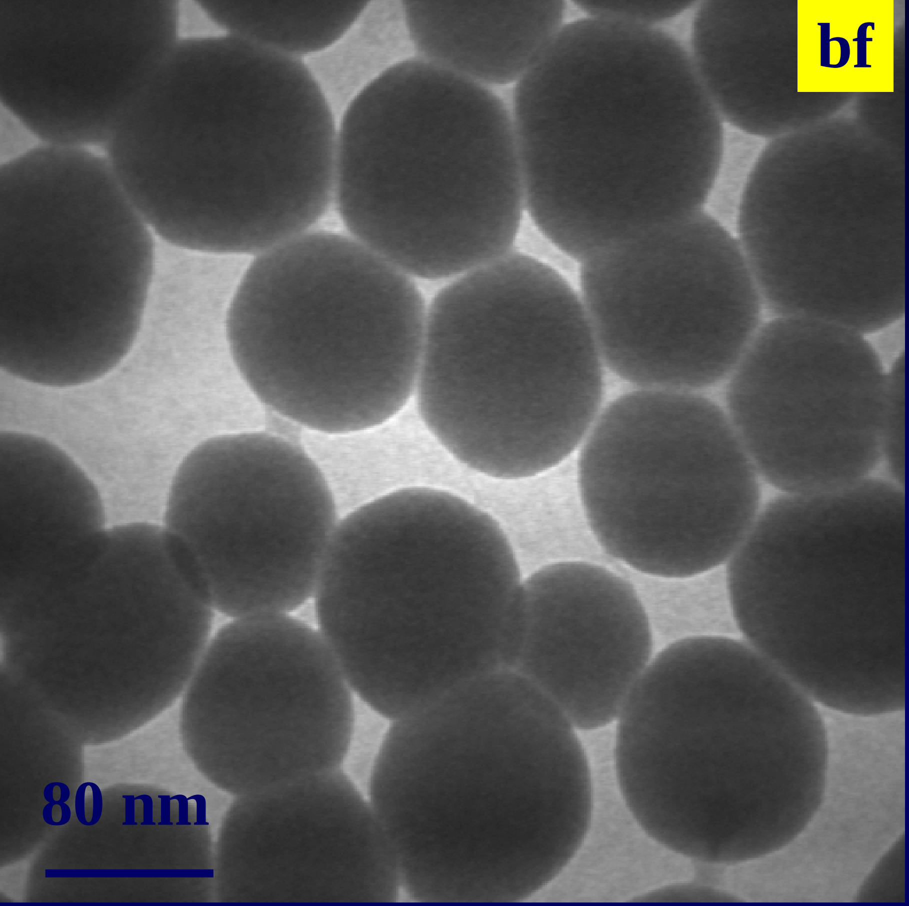


SEPM, *scanning electric potential microscopy*

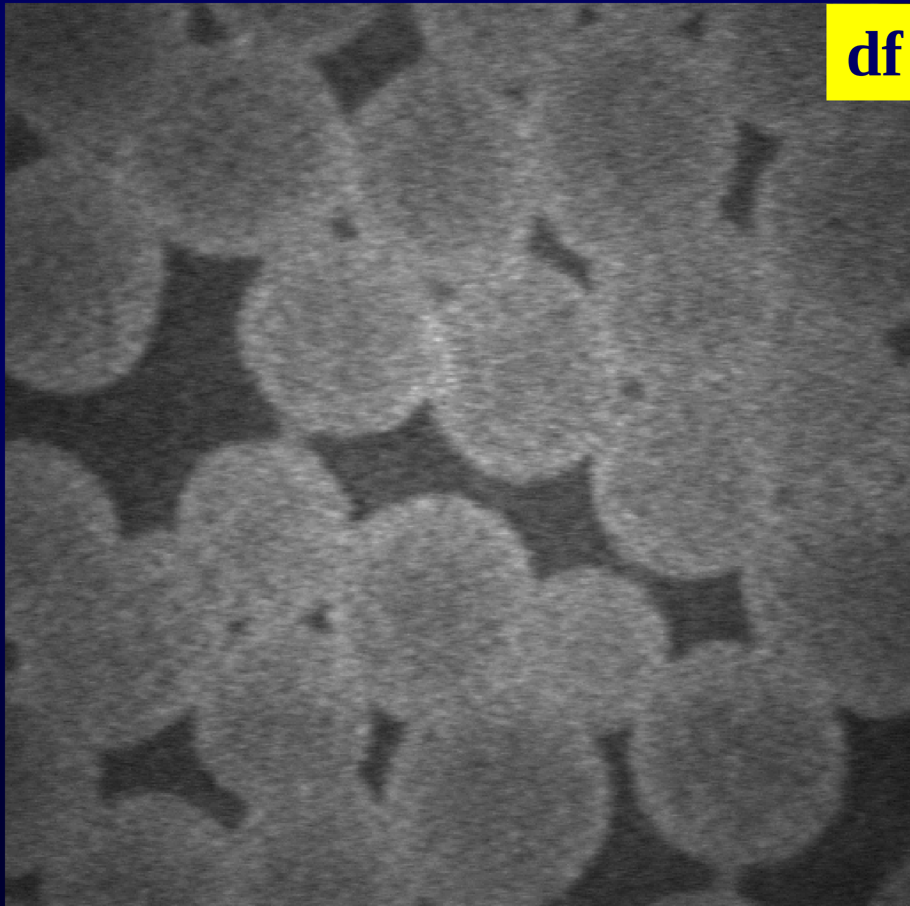




Alumina (from 0.1% aq. SDS)

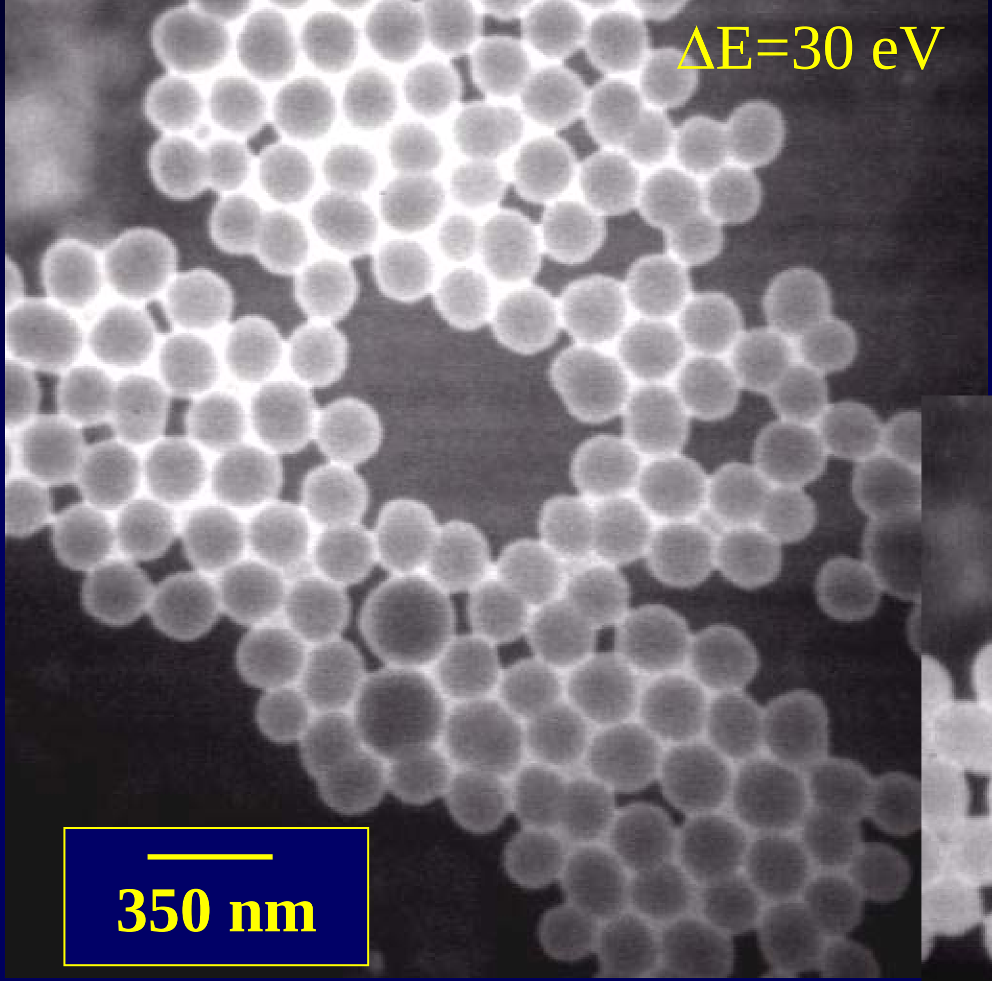


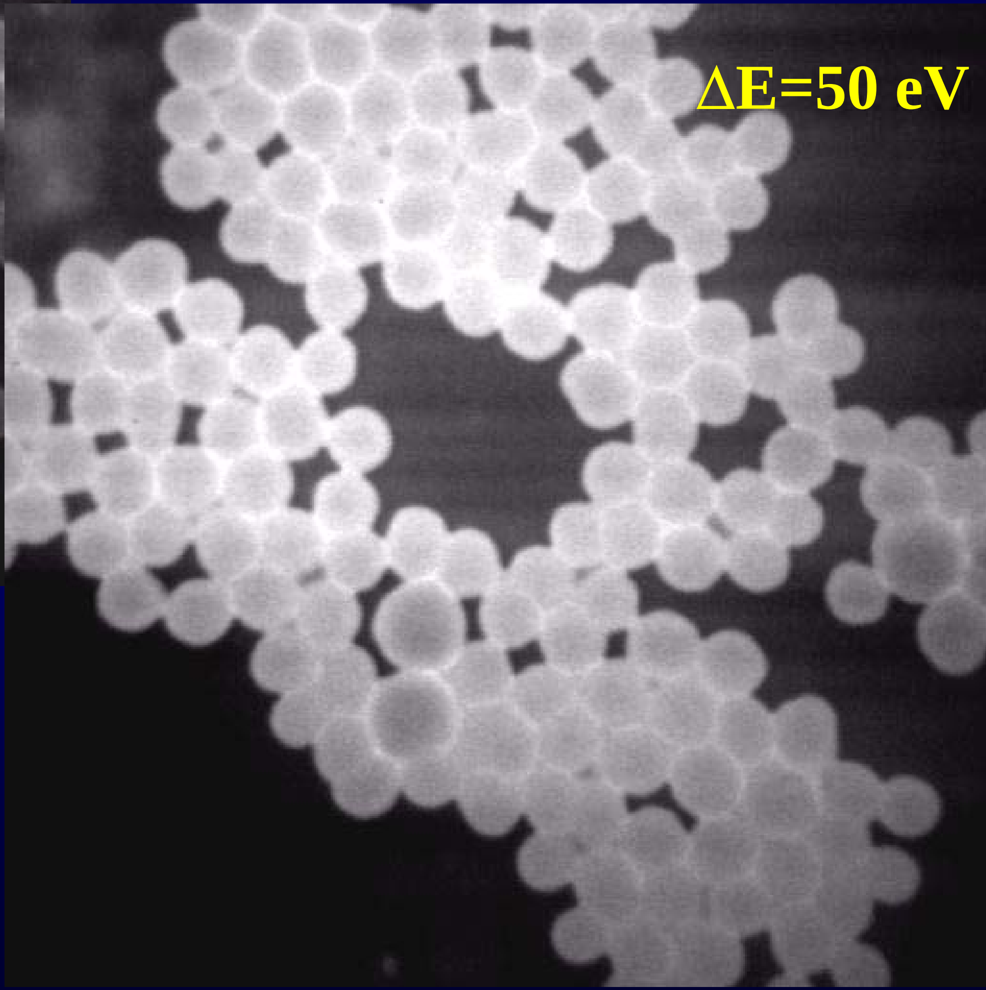
Bright- and dark-field images
ϕ = 141 nm



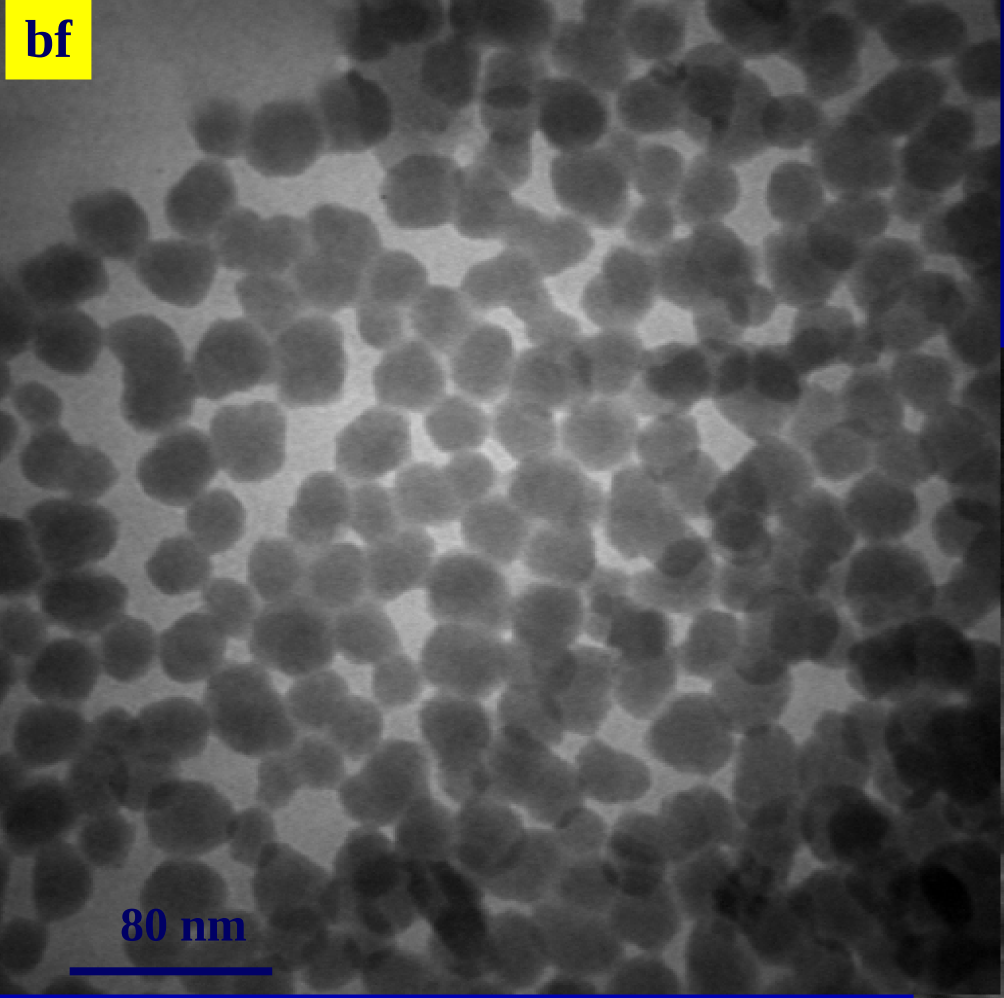
At this position of the aperture, the particle bulk scatters less than the surface material.

IMAGES ACQUIRED USING INELASTICALLY-SCATTERED ELECTRONS (plasmon region)



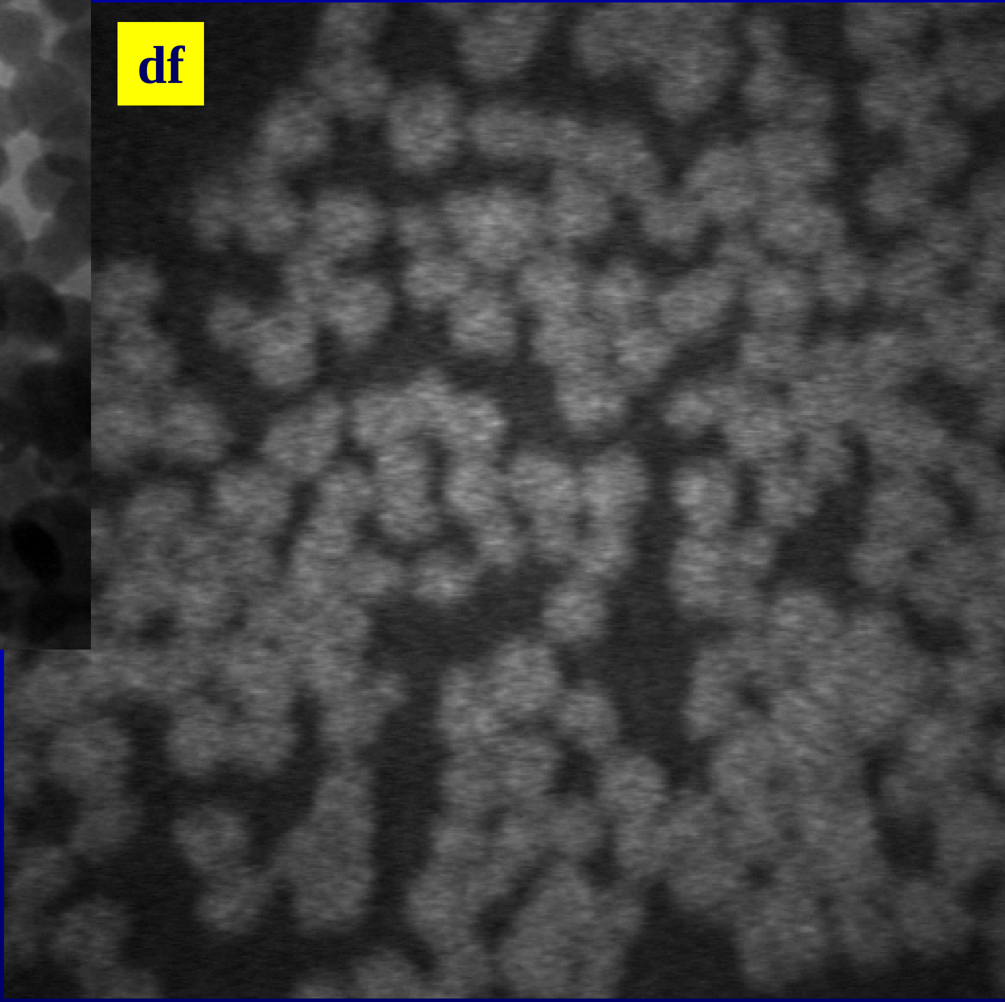


Scattering ability from particles core and shell is different
Also, non-particulate material



Differentiated domains throughout the particles.

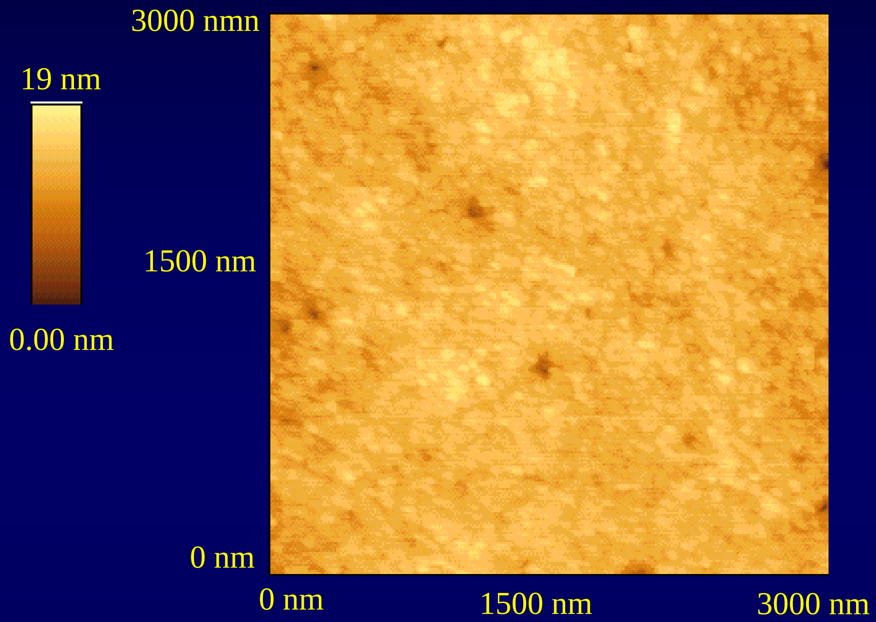
No core-and-shell structure.



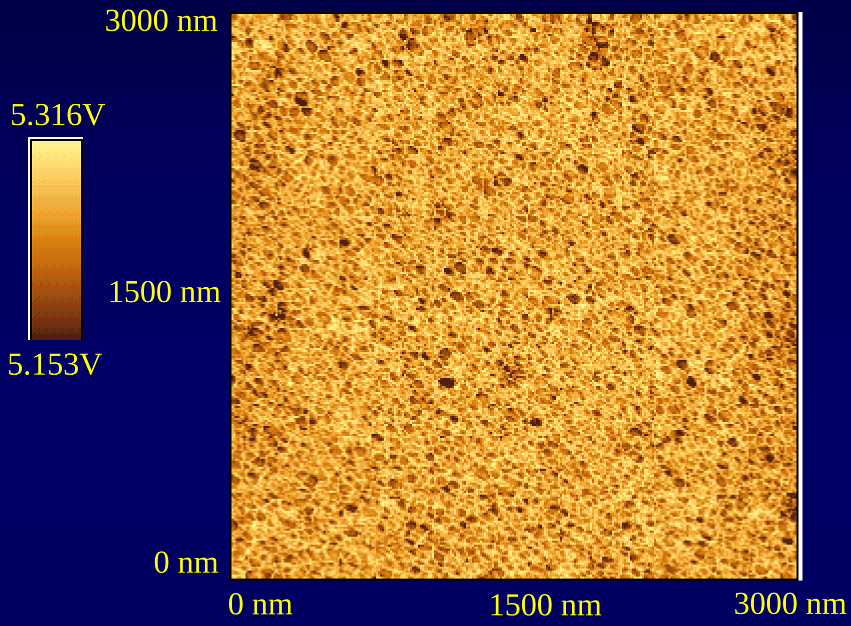
Bright- and dark-field images

ϕ = 36.5 nm

Film of SiO_2 nanoparticles ($\varnothing$ = 36.5 $\pm$ 1.0 nm)



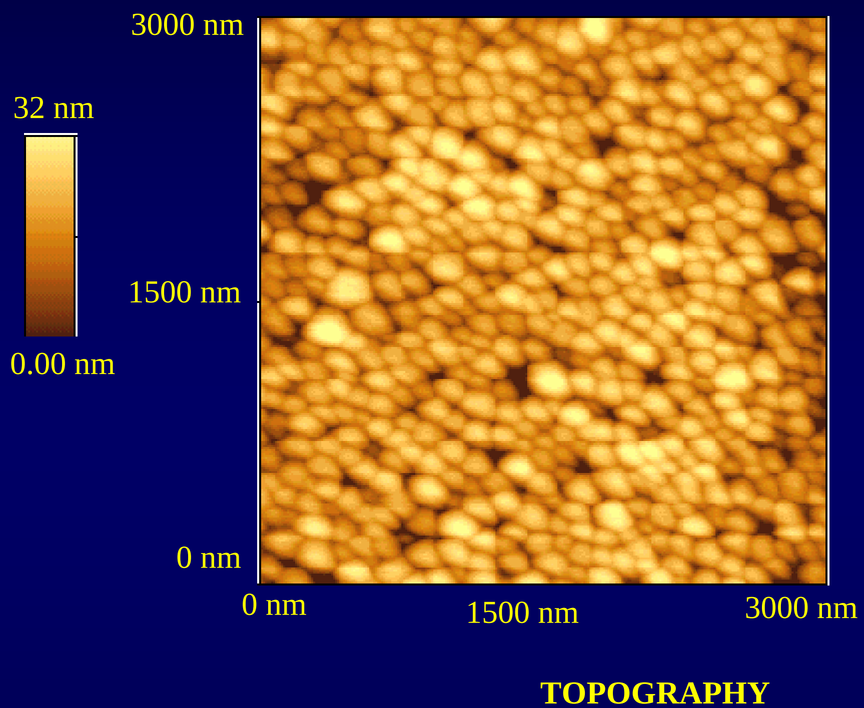
TOPOGRAPHY

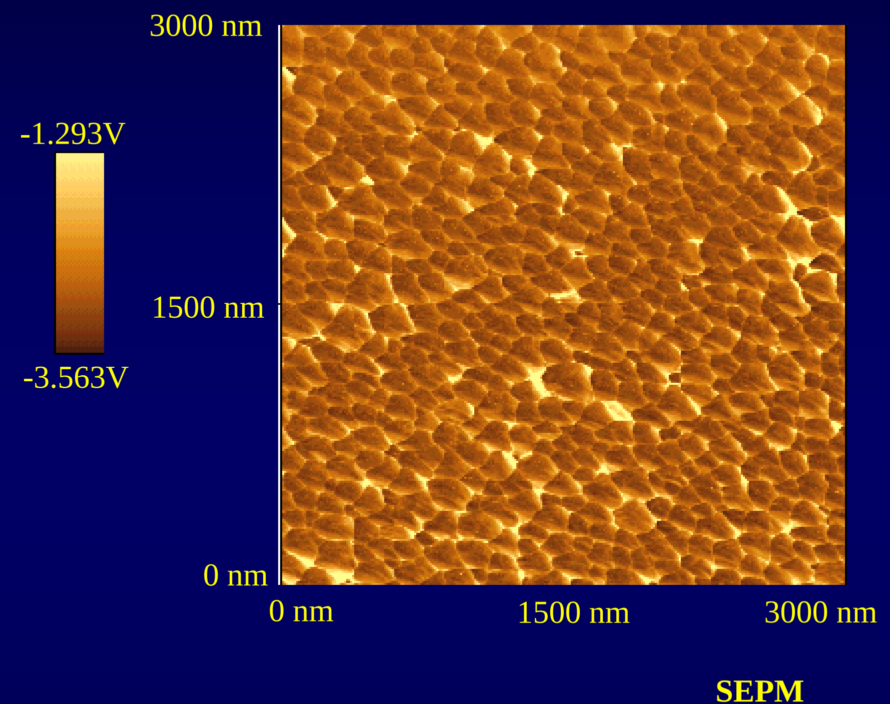


SEPM

- ✓ **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.**

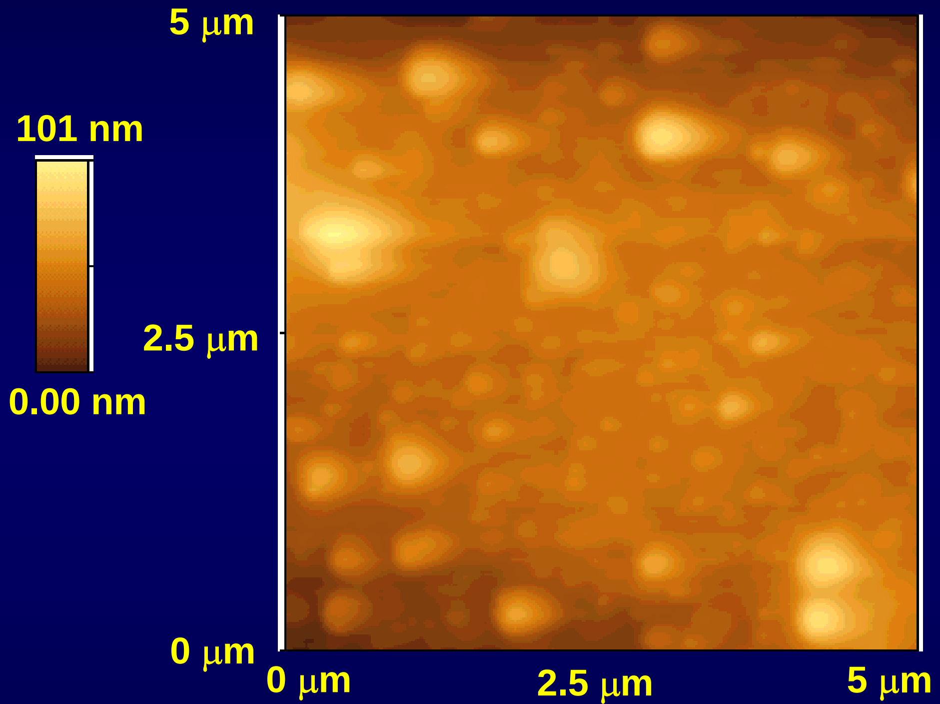
Film of SiO_2 nanoparticles ($\varnothing$ = 141.5 ± 2.5 nm)



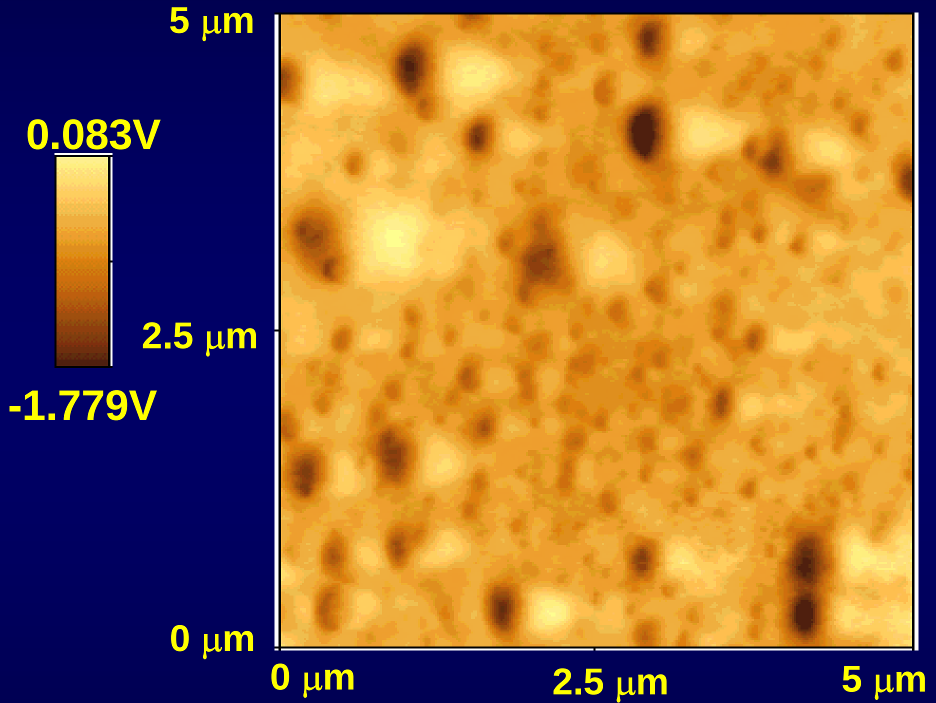


- ✓ The particles are distorted anisotropically, during the film formation (checked by rotating the sample)
- ✓ The particle borders are visible, thus excluding the prevalence of particle coalescence or inter-particle diffusion.

The printing surface of a desk-jet film



TOPOGRAPHY



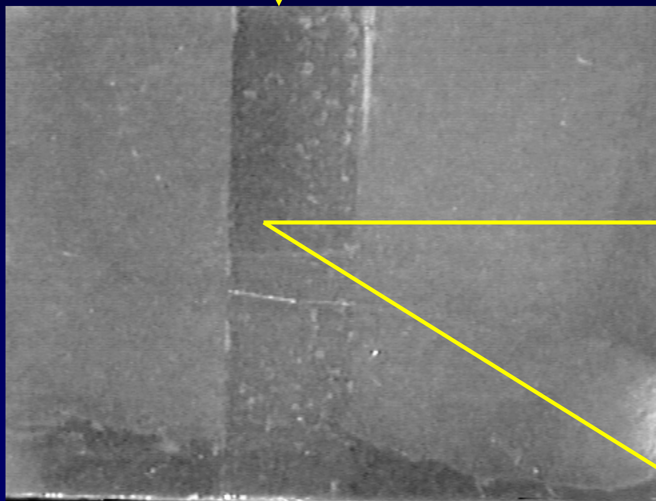
SEPM

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

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



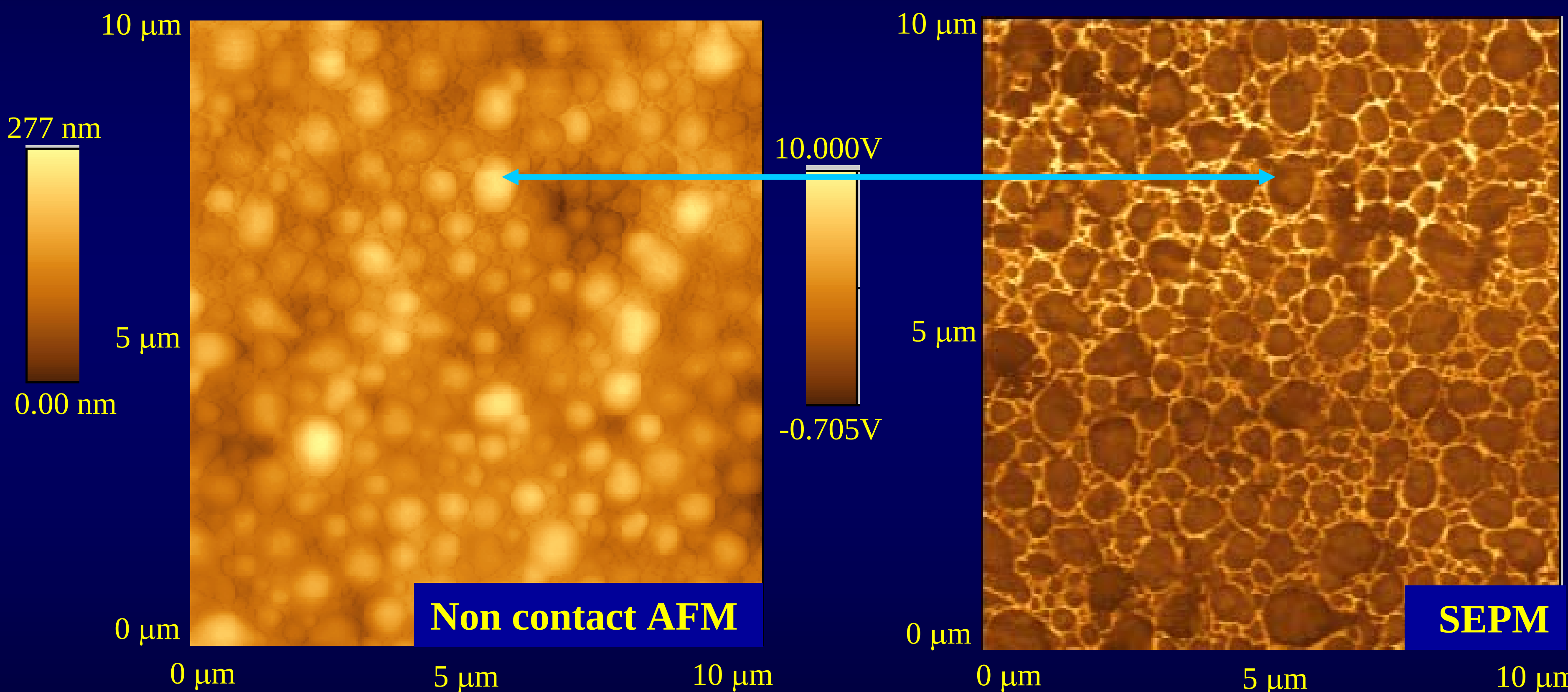
Film with adesive tape

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.

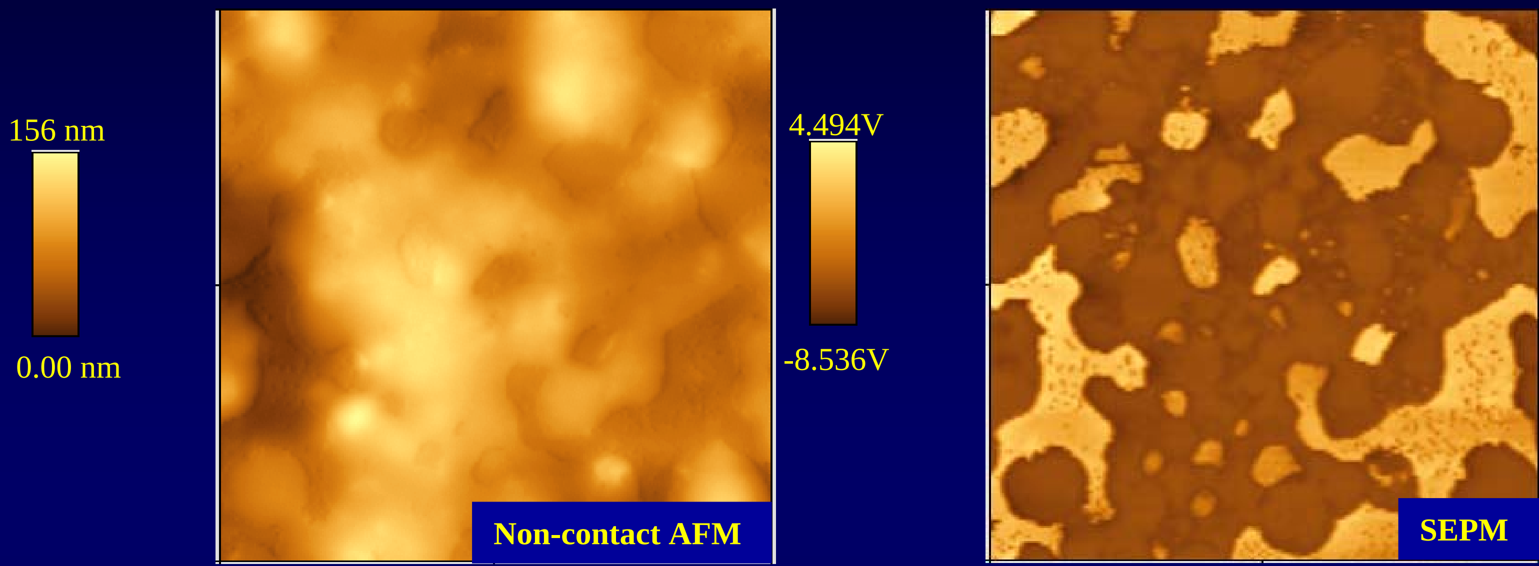
Natural rubber film topography (non-contact AFM) and scanning electric potential (SEPM) images



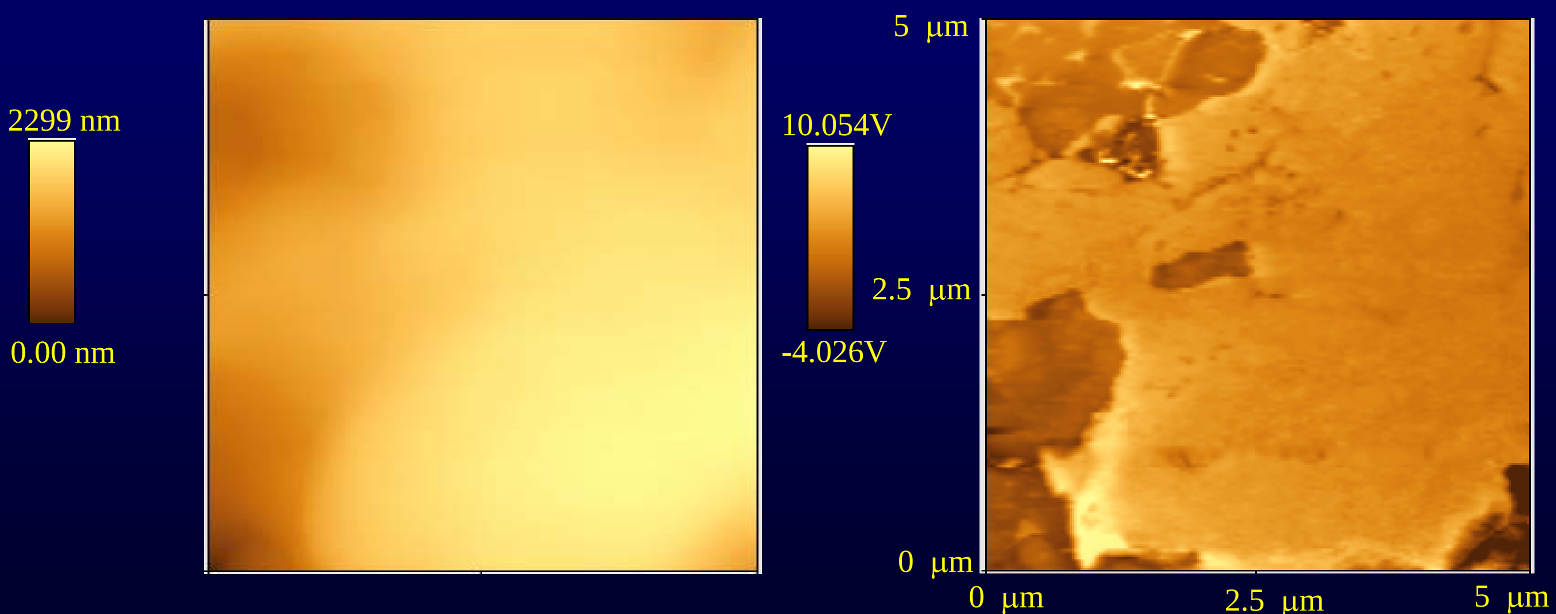
Individual particles are observed as elevations.
Negative cores dispersed in a positive matrix.

Natural rubber + sodium polyphosphate film

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

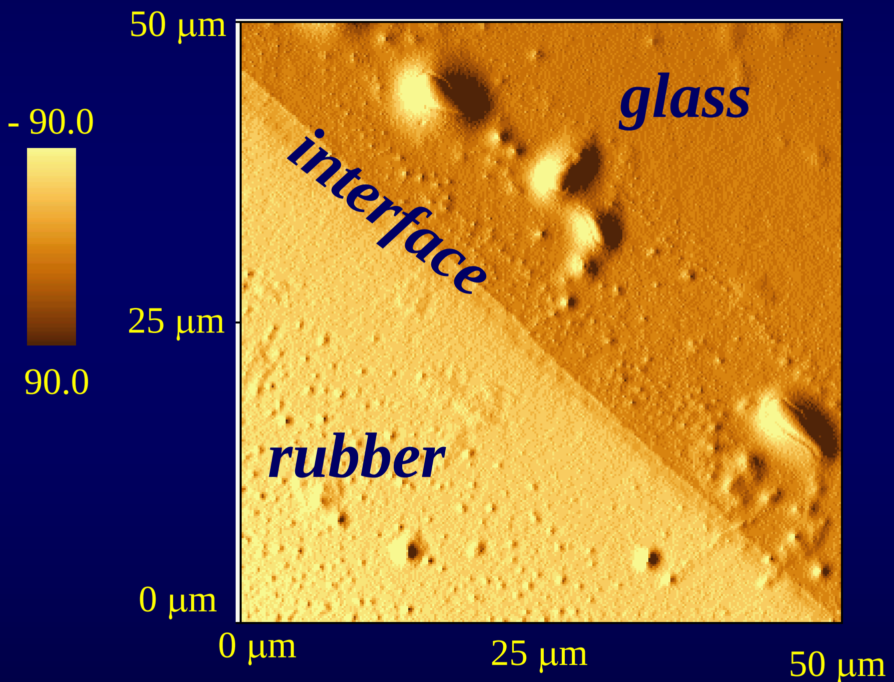


PP-NR film surface

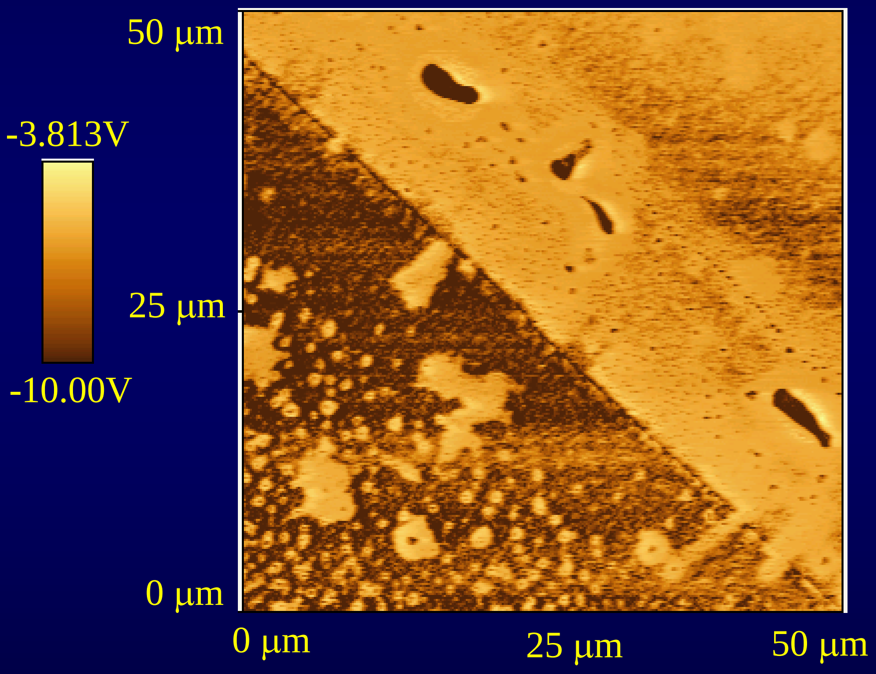


PP-NR film surface in contact with the glass

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



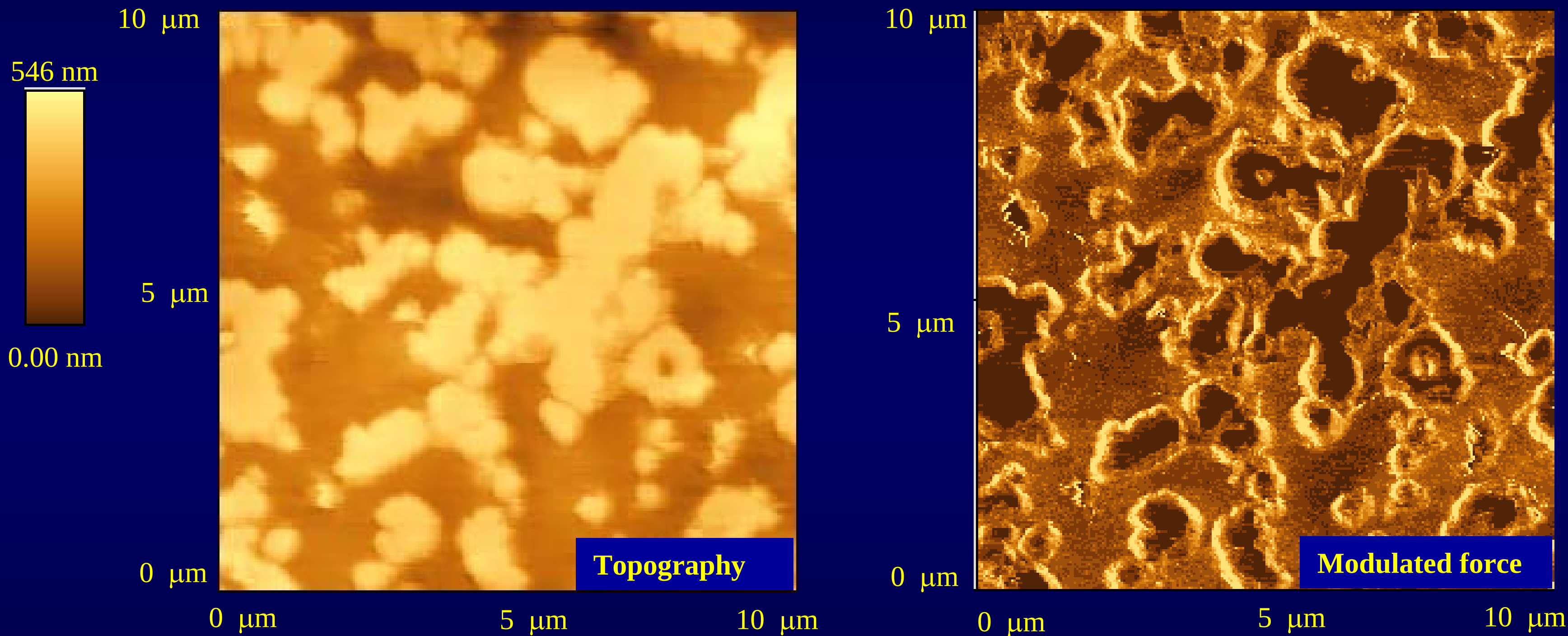
Non-contact AFM



SEPM

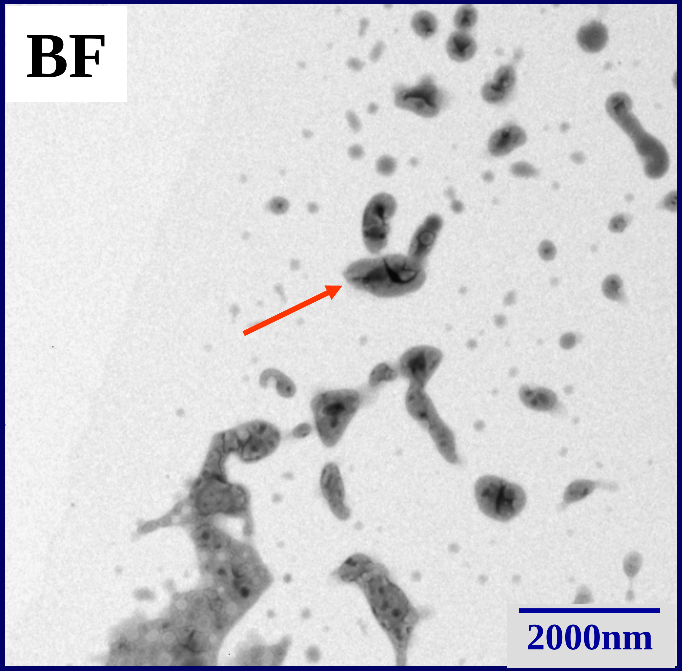
A layered structure at the glass-rubber interface

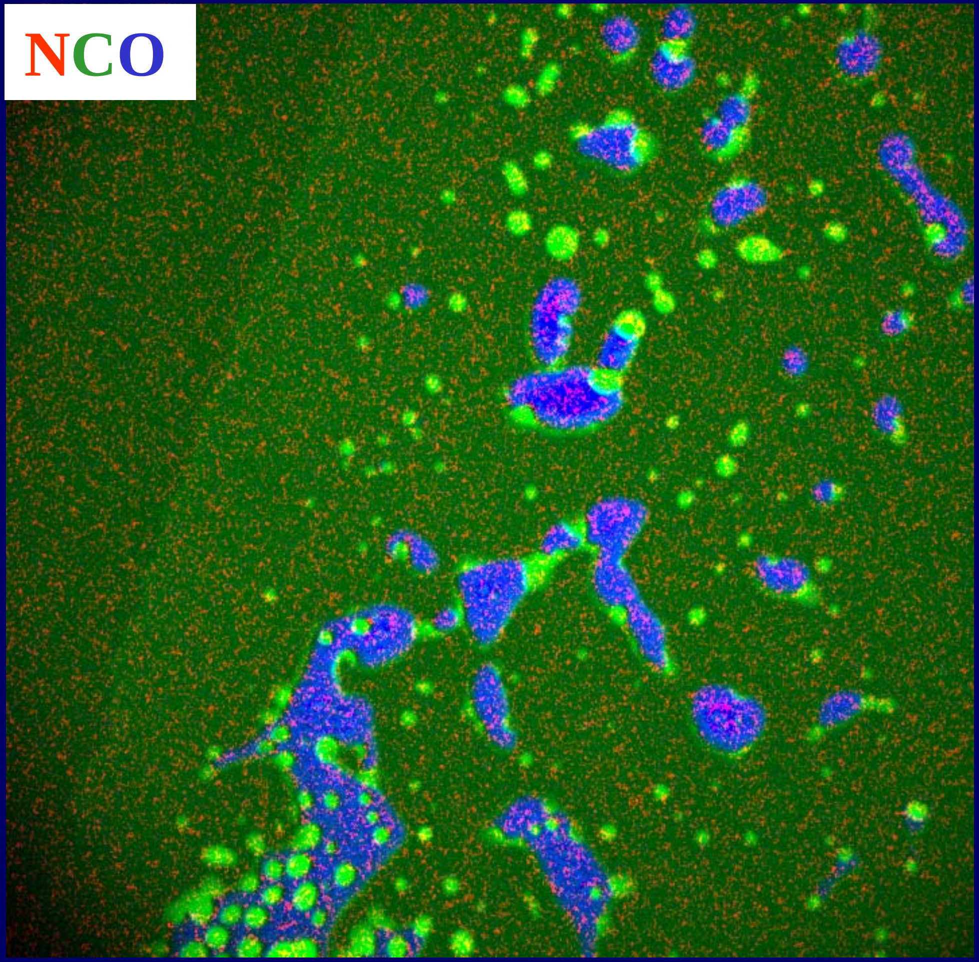
Modulated force image of PP-NR film: dark is low-modulus, bright is high-modulus

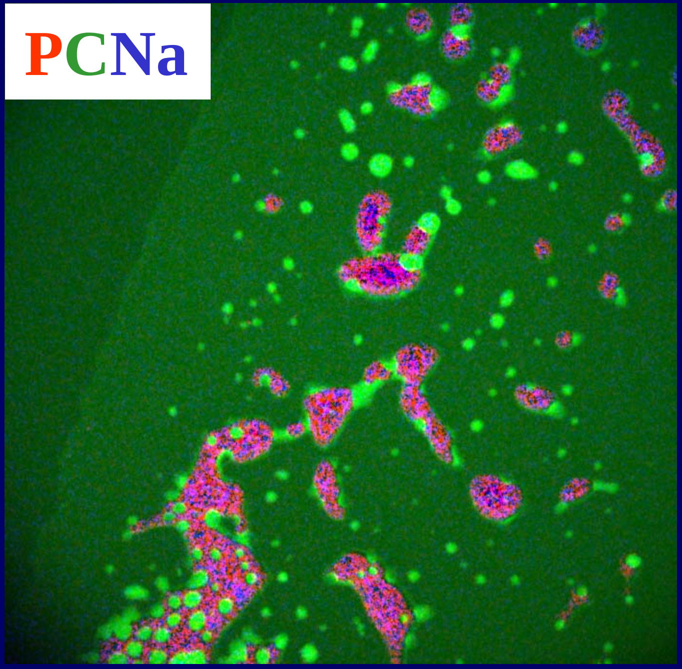


Dark domains of soft rubber, interpenetrated with harder rubber domains. Interfaces have the highest modulus.

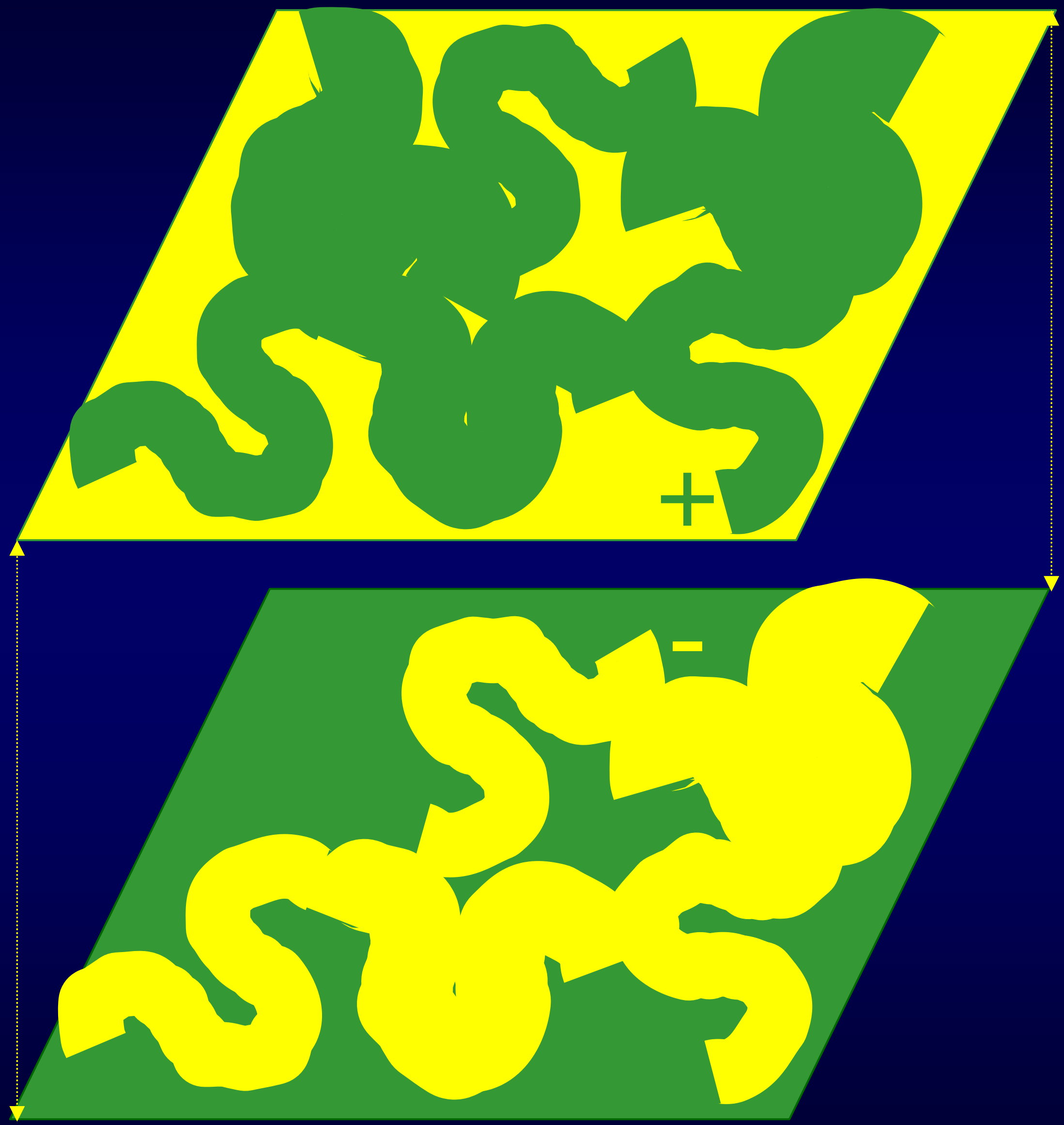
ESI-TEM elemental maps of a polyphosphate-modified latex sub-monolayer







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 birrefringent domains, no adhesion improvement.**
- ***PP-NR film morphology and electric charge distribution pattern are different from NR.***
- ***Films contain domains of different moduli.***
- **Mutual exclusion of *compatible* C and P, Na, N, O – rich domains.**

Current problems

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

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