Propriedades elétricas

- **Tópico importante mas complexo**
- **Temas correlatos: eletrólitos (Físico-Química de Matéria Condensada), polieletrólitos (Físico-Química de Macromoléculas), interfaces e duplas camadas elétricas (Eletroquímica)**
- **Partículas coloidais têm múltiplas cargas, como os polieletrólitos, estando imersas em soluções eletrolíticas e sendo rodeadas por uma interface carregada, como os eletrodos.**
- **A Física básica de que dependemos aqui é a Eletrostática, aplicada a sistemas formados por muitas partículas carregadas.**

Electrostatic charging: an old but still unsolved problem

"Surprisingly, although electrostatic charging is well known, it remains among the most poorly understood areas of solid-state physics."

"Most researchers believe that insulator charging is a surface phenomenon."

Schein LB, Recent progress and continuing puzzles in electrostatics. *Science*, 316, 1572-1573 (2007).

ALSO: Bailey AG, The charging of insulator surfaces. *J. Electrostat.*, 51-52, 82-90 (2001), Castle GSP, Contact charging between insulators. *J. Electrostat..*, 40-1, 13-20 (1997)

Eletrostática de Isolantes: um problema antigo e mal resolvido

by Harper:

"A crucial question for the explanation of the production of static charge is whether the charging of insulators comes from a transfer of electrons, of ions, or of both.

Montgomery: ***always*** electrons

Loeb: ***generally*** electrons

Henry ***feels*** that the question is ***still an open one***.

I (Harper) am of the opinion...that the carriers are ***never*** electrons when the material being charged is strictly an insulator."

Adrian G. Bailey, 2001

Formação de interfaces eletricamente carregadas

Mecanismos

Diferença nas funções de trabalho das fases

Ionização de grupos superficiais

Adsorção diferencial de íons

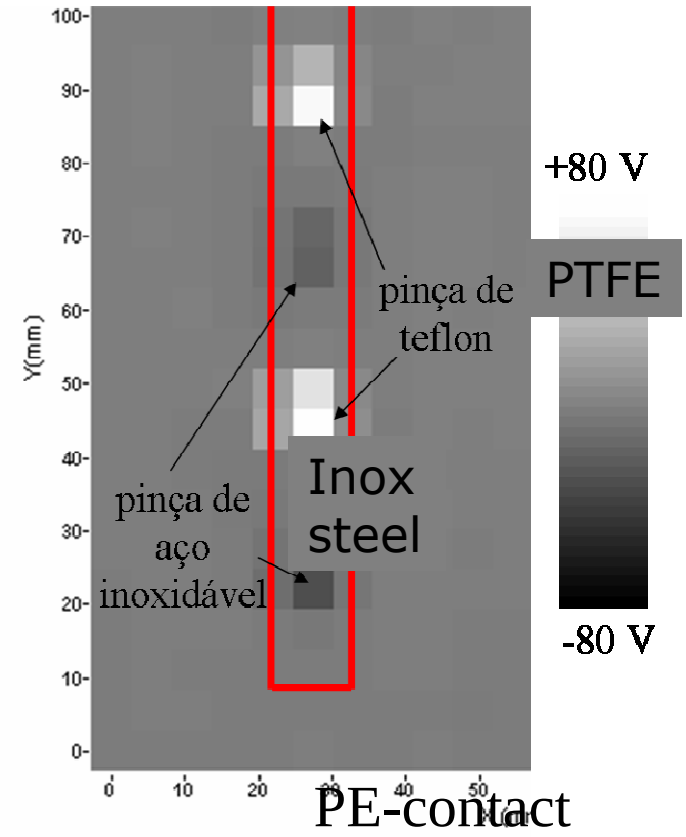
Dissolução diferencial de íons

- Many contradictory data for insulator charging exist in the literature.
- These range from lhe classic imprecise and variable versions of the "Triboelectric Series" through to carefully controlled experiments which show completely opposite results.
- Cases cited by Schein where three different studies show Teflon charging positively, negatively and not at all when contacted with gold.
    - Castle, J. Electrostatics 40-41 (1997) 13-20
    - L.B.Schein, *Electrophotography and Development Physics,* Springer, 1996

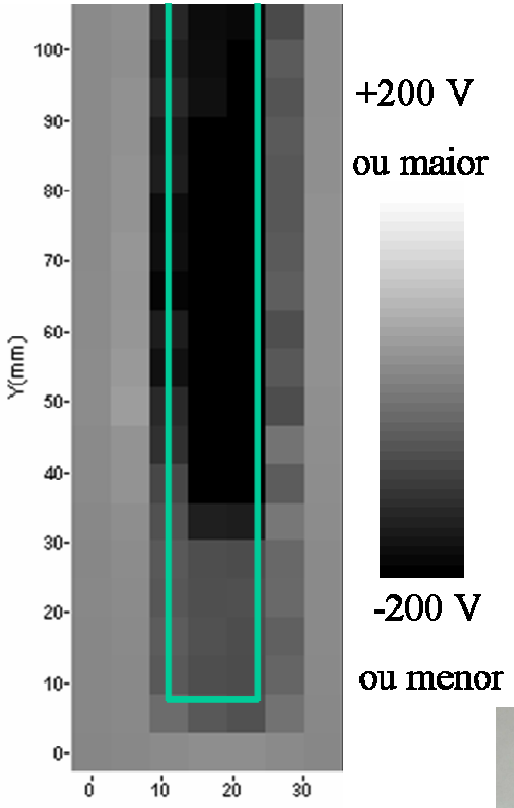
Eletricidade ao nosso redor

- **Estamos imersos em poderosos campos elétricos. Se estes fossem visíveis, então mesmo a área mais desolada da Terra mostraria um aspecto impressionante.**
- **Sentado no topo de um morro, você veria uma floresta de linhas de força brotando do chão, e esticando-se até à ionosfera.**
- **Você poderia observar estas linhas do campo varrendo o horizonte e juntando-se sob as tempestades.**

Contact and piezo-gun charging



PE-contact



PP under negative ions

Eletricidade ao nosso redor (cont.)

- **O campo elétrico que rodeia a Terra é muito mais dinâmico que os campos magnético ou de gravidade. Vivemos sobre um oceano de carga negativa que gera um campo elétrico de cerca de 100 volts por metro de elevação. Debaixo de uma tempestade, esse campo pode subir a milhares de volts por metro.**
- **As cargas que geram esse campo são fixas, portanto não geram correntes elétricas. Estas surgem quando o ar (por exemplo) é ionizado sob a ação do campo elétrico. (Shawn Carlson, Detecting the Earth`s Electricity, Scientific American 281 (Julho de 1999), 76.)**

Origem da eletricidade do ambiente

Em toda interface existe uma diferença de potencial elétrico, portanto há uma separação entre cargas positivas e negativas, de um e de outro lados da interface.

Isso é demonstrado por uma das primeiras experiências científicas de qualquer estudante, que é a *eletrização* de um pente, de cabelos, tecidos ou outros materiais, pelo atrito.

Por essa razão, as gotas da chuva descarregam sobre a Terra uma enorme quantidade de carga elétrica.

Ionização de grupos superficiais

Na superfície de um látex que contenha p.ex. carboxilas de poli(ácido acrílico): a ionização das carboxilas libera grupos H^+ no meio, e deixa grupos COO^- na superfície.

O pK de grupos superficiais difere, frequentemente, do pK do mesmo grupo em uma molécula pequena dissolvida, devido ao efeito das demais cargas na superfície.

No caso de carboxilas, o pK pode ser 7 em superfícies de carga negativa elevada, ao invés de 4,5 ou 5, como no ácido acético.

Adsorção diferencial de íons

- **A adsorção pode ser tão intensa e específica que termina por vencer a contribuição eletrostática:**
  - **íons Ba^{2+} adsorvem em hematita, mesmo em um pH tal que as partículas tenham carga positiva**
  - **partículas de óleo (hidrocarboneto) em água são negativas, porque a adsorção de íons hidroxila é mais acentuada que a adsorção de íons H^{+}.**

Dissolução diferencial de íons

Quando se dissolve iodeto de prata em água até a saturação, as partículas de iodeto de prata remanescentes apresentam carga negativa.

Há retenção de ânions iodeto, mais que de cátions prata. O K_{ps} do AgI é 10^{-16} mas as partículas só são neutras quando pAg = 5,5 (e pI = 10,5), isto é, quando há um excesso de prata sobre iodeto, em solução.

O equilíbrio de solubilidade do iodeto de prata: $(AgI)_p = Ag_{(p-m)}I_{(p-n)}^{(n-m)} + mAg^+ + nI^-$

Triboplasma

Formado nas operações de cominuição ou moagem na preparação de colóides.

Altas densidades de energia em algumas regiões provocam alterações químicas locais importantes formando um *triboplasma.*

A relaxação térmica do material leva à eliminação das espécies transientes muito reativas, mas deixa espécies ainda ativas (por exemplo, peróxidos, em matéria orgânica).

A moagem de quartzo provoca rupturas de cadeias O-Si-O; metade dessas rupturas formam radicais livres; a outra metade forma íons, que contribuem para as cargas da superfície das partículas.

A equação de Poisson-Boltzmann

- Partícula em meio líquido: positiva ou negativa, em líquido com carga oposta formando um sistema globalmente *eletroneutro*.
- Duas relações fundamentais: a equação de Poisson, da Eletrostática, e a equação de Boltzmann, da Mecânica Estatística.

Poisson (Cont.)

- A divergência do vetor deslocamento dielétrico é igual à densidade local de cargas :

$$\text{div } \boldsymbol{D} = \text{div } \varepsilon \boldsymbol{E} = \rho$$

- Como $\boldsymbol{E} = -\text{ grad } \phi$, resulta

$$(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)\ \psi = -\ \rho/(\varepsilon_0 \varepsilon_r).$$

Em uma dimensão

$(\partial^2/\partial x^2)\ \psi = -\ \rho/(\varepsilon_0 \varepsilon_r)$

Quando $\phi = k(x)$, $\rho = 0$

$\psi = a + bx$, $\rho = 0$

$\psi = a + bx^2$, $\rho = b > 0$

(excesso de cargas positivas no ponto)

$\psi = a - bx^2$, $\rho = b < 0$

(excesso de cargas negativas no ponto)

Boltzmann *Cont.*

- A equação de Boltzmann diz que a concentração de partículas em uma região do líquido é função do potencial elétrico naquele ponto, com relação ao seio do líquido:

  $n_i = n_i^o \exp(-w_i/kT)$ onde $w_i = z_i e \psi$

- ...e as cargas acumuladas afetam o gradiente de potencial no ponto.

Cont.

- Aplicando-se a equação de Boltzmann ao cálculo de potencial elétrico nas vizinhanças de uma superfície dotada de carga elétrica, obtemos a equação de Poisson-Boltzmann. Esta é uma equação diferencial não-linear, que não tem solução analítica. Isto cria enormes problemas, porque nos obriga a fazermos simplificações para tratarmos de problemas concretos.

Poisson-Boltzmann

- The equation can be written as:

$$\vec{\nabla} \cdot \left[\epsilon(\vec{r})\vec{\nabla}\Psi(\vec{r})\right] = -4\pi\rho^{f}(\vec{r}) - 4\pi\sum_{i} c_{i}^{\infty} z_{i}\lambda(\vec{r})qe^{\frac{-z_{i}q\Psi(\vec{r})}{k_{B}T}}$$

  where represents the position-dependent dielectric, represents the electrostatic potential, represents the charge density of the solute, represents the concentration of the ion *i* at a distance of infinity from the solute, z_i is the charge of the ion, *q* is the charge of a proton, k_B is the Boltzmann constant, *T* is the temperature, and is a factor for the position-dependent accessibility of position *r* to the ions in solution. If the potential is not large, the equation can be linearized to be solved more efficiently.

- Software disponível:
  - Adaptive Poisson–Boltzmann Solver
    - http://apbs.sourceforge.net/
  - Zap - A Poisson-Boltzmann electrostatics solver.
    - http://www.eyesopen.com/products/toolkits/zap.html

Preços

- **ApplicationPrice (USD $)Miscellaneous**
- AFITT65,000Brood35,000EON22,050Requires aligned structures, such as from ROCSFILTER16,540FRED55,125Omega55,125QuacPac33,075ROCS63,000Smack16,540Szybki27,565VIDA & VIVANTTBD
- **ToolkitPrice (USD $)Application software included with toolkit purchase**
- Szybki TK33,075SzybkiLexichem TK33,075Name and structure interconversion applicationsOEChem TK44,100Babel and numerous SCUT MonkeysOgham TK16,540Depiction applicationsOmega TK71,665Includes Omega applicationShape TK78,750ROCSSpicoli TKTBD Zap TK27,565

Equação PB: casos-limites

$\psi = \psi_o \exp(-\kappa x)$ (quando $\psi_o < 26$ mV)

- κ tem dimensões de (comprimento^{-1}) e é a constante de decaimento exponencial do potencial elétrico. Por isso, $1/\kappa$ é chamado de "espessura da dupla camada".
- A magnitude de κ é dada por:

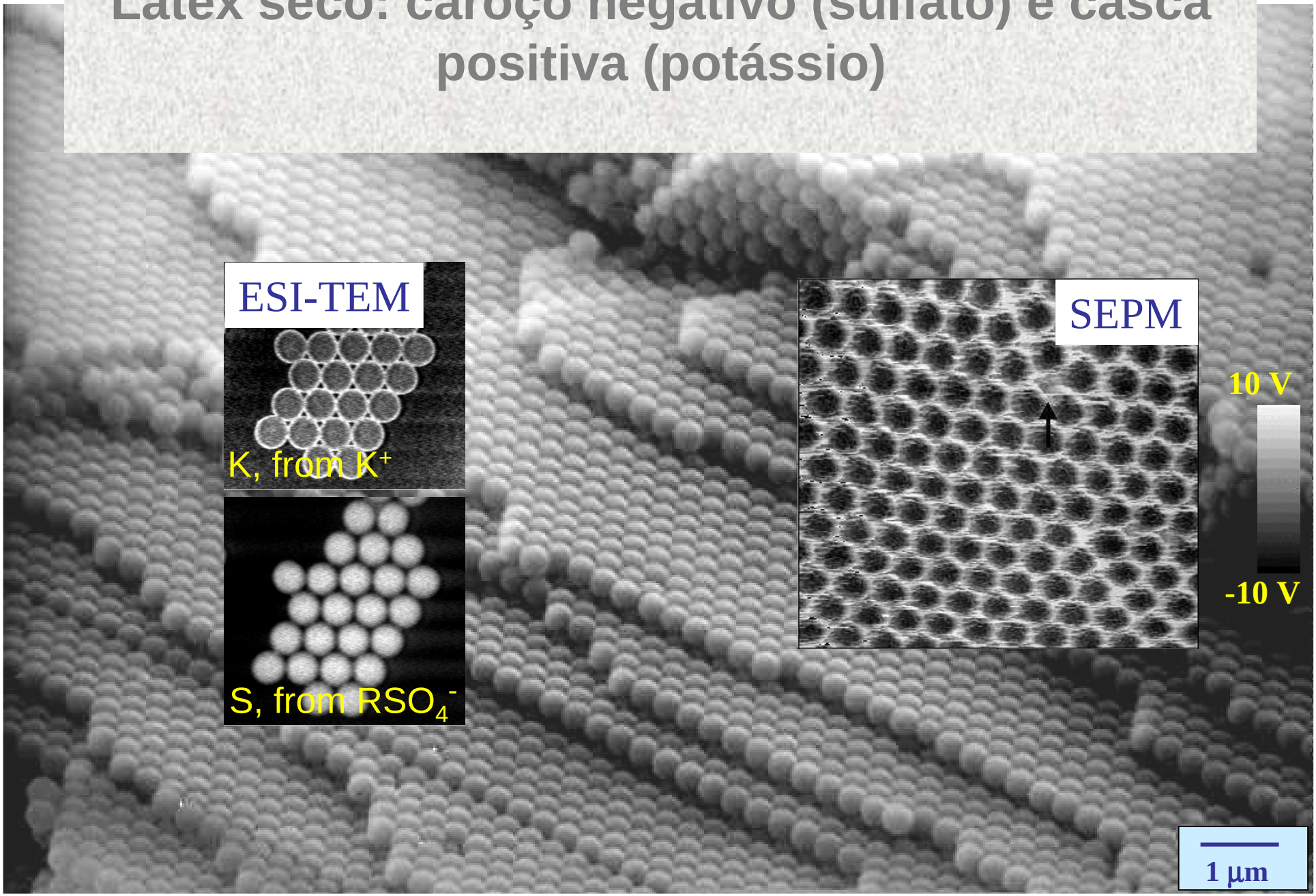
$$\kappa = (e^2 \Sigma n_i^o z_i^2)/\varepsilon kT)^{1/2}$$

Dupla camada elétrica em interface látex-água
camada de Stern
camada de Gouy-Chapman

A dupla camada elétrica

- Um modelo para a distribuição de cargas em uma partícula.
- Partículas secas de um látex aniônico: íons sulfato estão no interior da partícula, contra-ions de sódio ou potássio estão na superfície.
  - Por outro lado, partículas de látex em água migram em direção a um eletrodo positivo, isto é, elas apresentam uma carga global negativa.

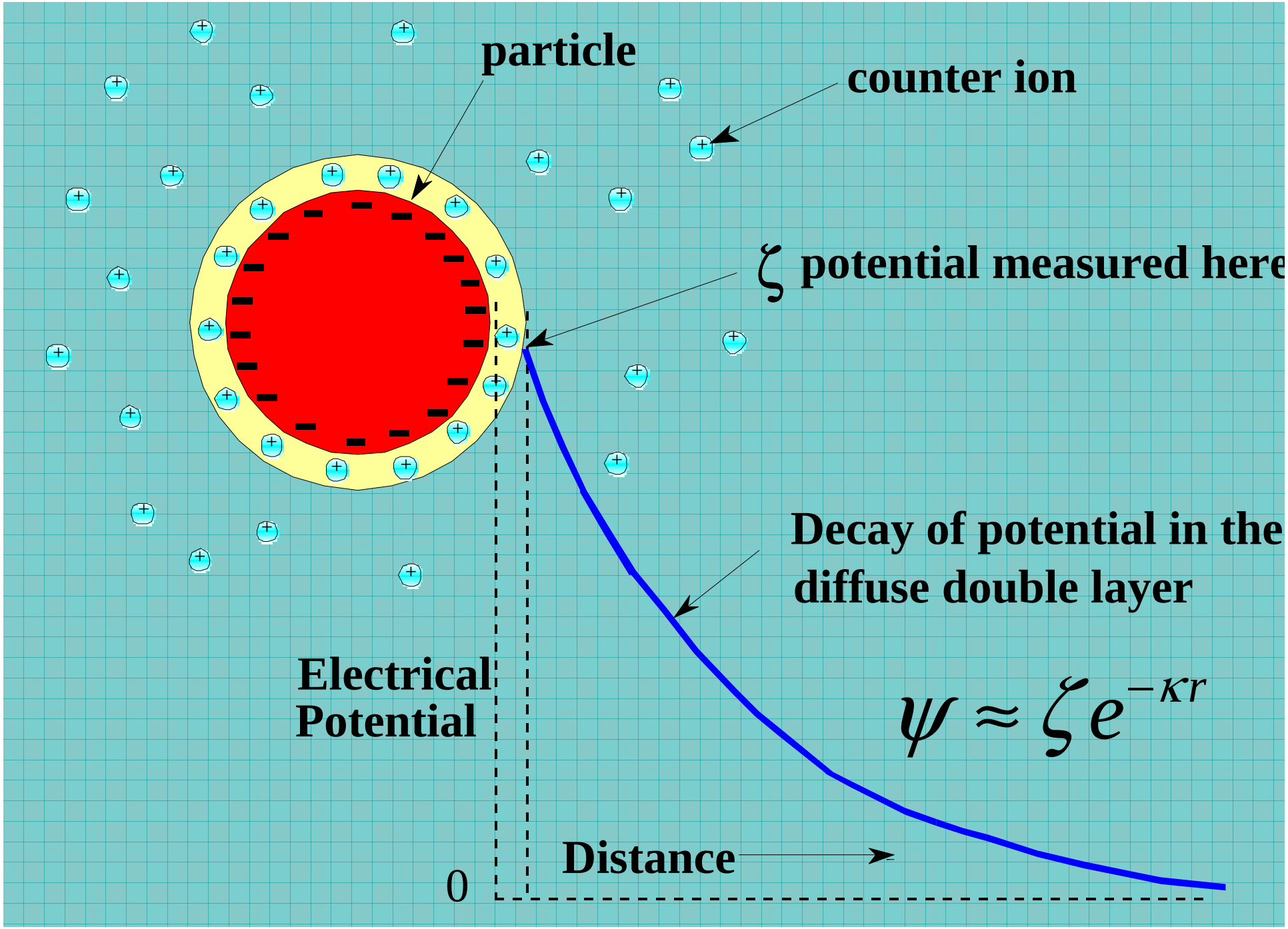
Látex seco: caroço negativo (sulfato) e casca positiva (potássio)



Dupla camada elétrica

Na superfície do látex (e de outras partículas coloidais):

- **uma parte dos contra-ions se encontra fortemente ligada à superfície;**
- **há moléculas de água imobilizadas junto à superfície, orientadas segundo seus dipolos;**
- **moléculas de outros solutos, iônicos ou não, podem estar também fortemente adsorvidas, seja devido a interações dipolares, seja devido a ligações covalentes ou coordenativas;**
- **à medida em que nos afastamos da superfície, encontramos água e íons mais livres. O excesso de concentração de íons potássio, no caso do látex, diminui à medida em que nos afastamos da superfície, até atingir a concentração média no líquido.**
- **A concentração de ânions, como cloreto, é muito pequena junto à superfície, aumentando gradativamente até atingir a concentração média.**


particle
counter ion
ζ potential measured here
Decay of potential in the diffuse double layer
Electrical Potential
$\psi \approx \zeta e^{-\kappa r}$
Distance
0

Espessura da dupla camada (caso-limite)

- A espessura da dupla camada κ^{-1} é dada por:

$$\kappa^{-1} \approx \frac{10}{\sqrt{c}} nm$$

onde c é a concentração de eletrólito em mM

Portanto κ^{-1} = 10 nm em sal 1mM e 1nm em sal 100mM.

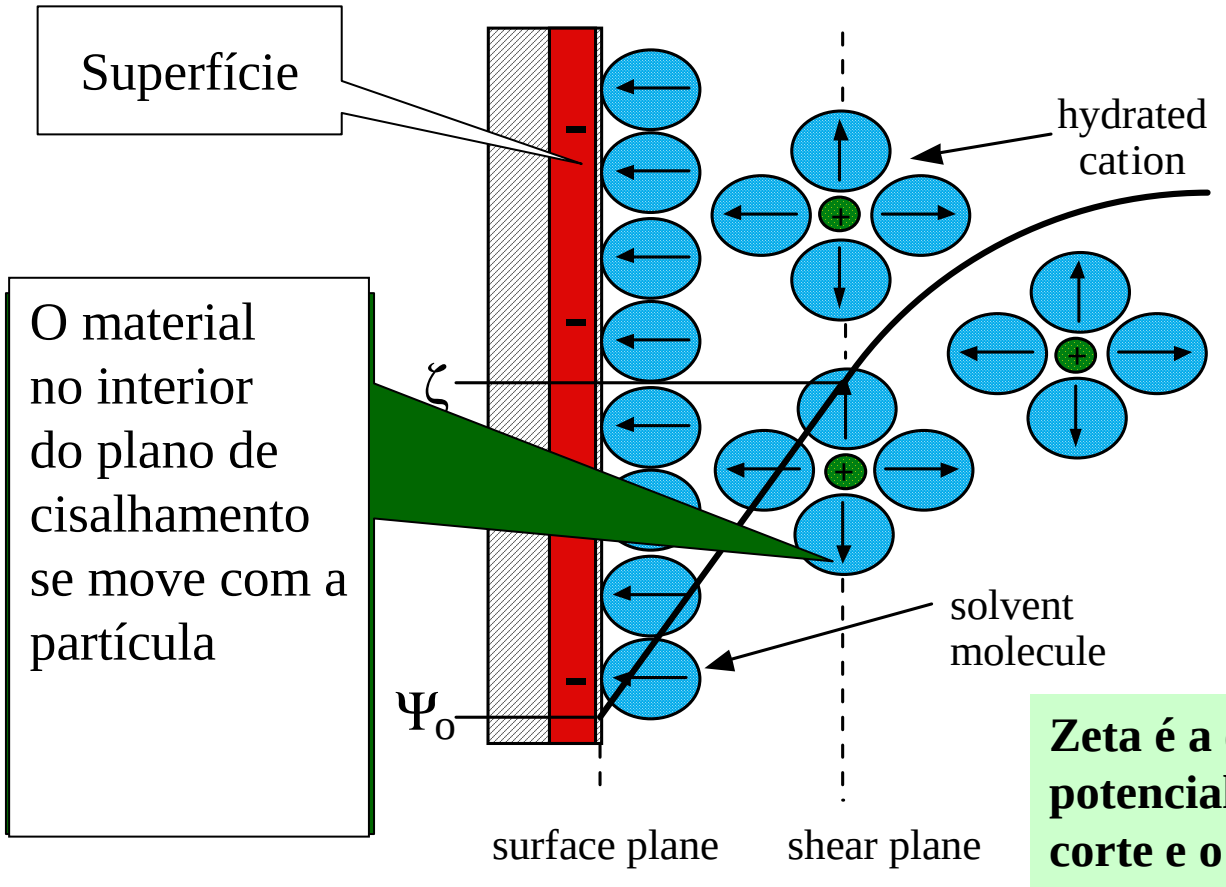
Superfície de cisalhamento

- Entre as partes fixa e difusa da dupla camada elétrica há uma região de separação
- Uma superfície de cisalhamento entre a partícula e o restante do líquido.
- Tudo que está entre o interior da partícula e esta superfície move-se com a mesma velocidade que a partícula
- Tudo que estiver além da superfície de cisalhamento move-se independentemente da partícula, exceto por estar sujeito ao campo elétrico gerado por esta.

Potencial zeta

- Potencial elétrico na superfície de cisalhamento determina a *mobilidade* das partículas (sua velocidade em um campo elétrico), obtida de medidas *eletroforéticas*.
- **$u_E = (2\varepsilon\zeta/3\eta)\ f(\kappa a)$ é uma expressão geral, devida a Henry;**
- **$u_E = \varepsilon\zeta/\eta$ é a equação de Smoluchowski, válida quando κa é muito grande (força iônica significativa e partículas muito grandes); $u_E = 2\varepsilon\zeta/3\eta$ é a equação de Hückel, válida quando κa é muito pequeno, isto é, pequena força iônica e partículas muito pequenas.**

O potencial zeta ζ

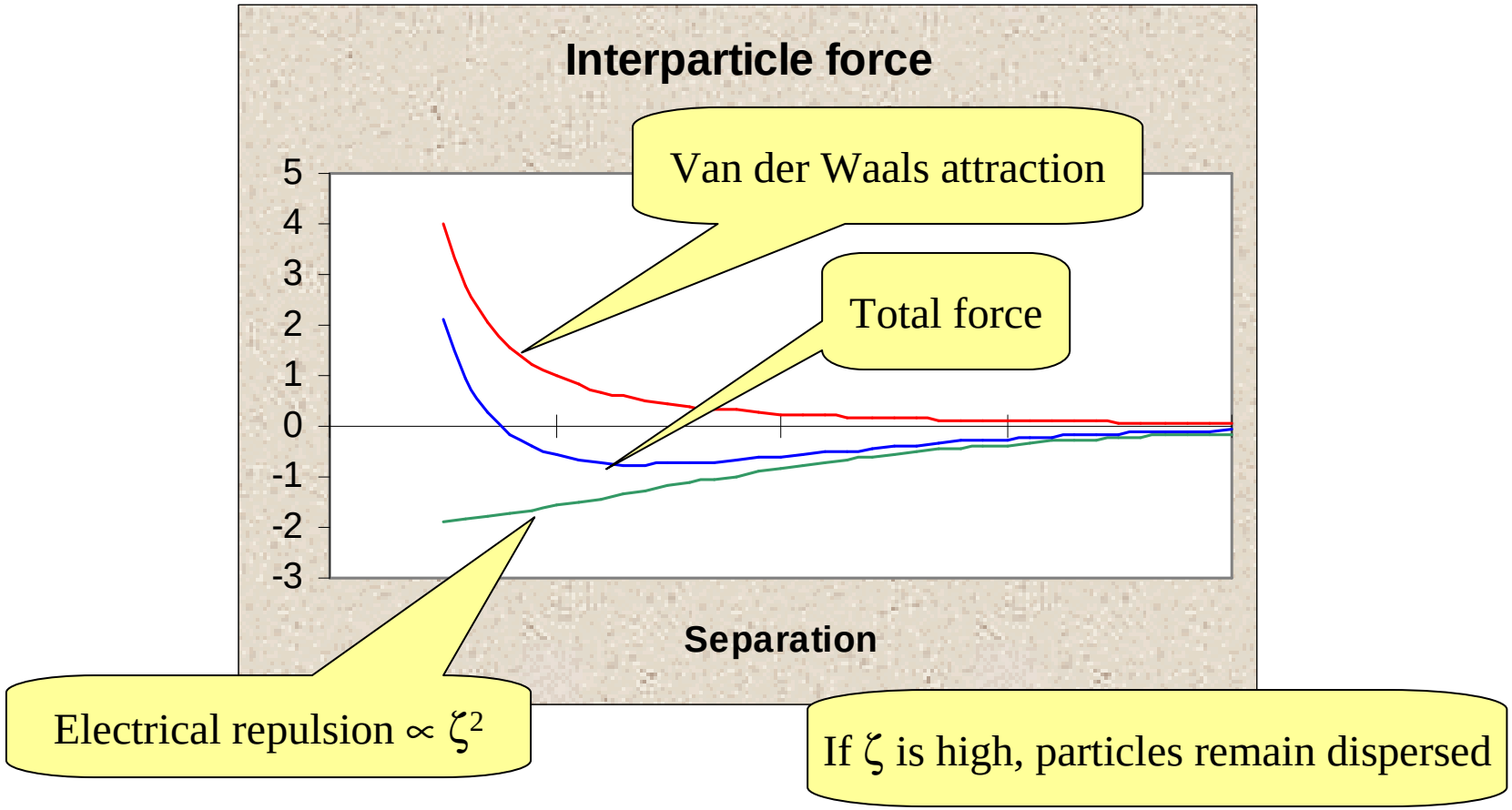


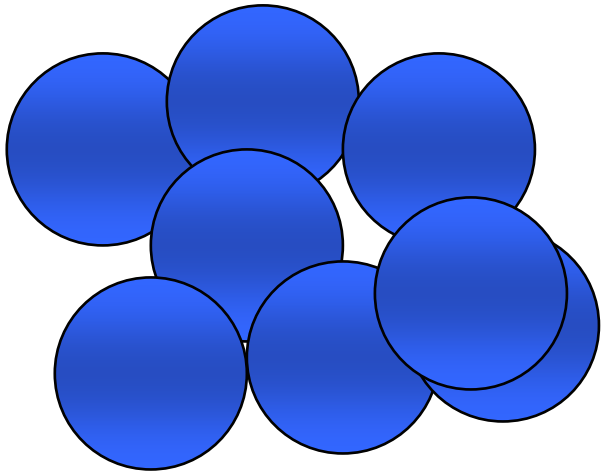
Zeta é a diferença de potencial entre o plano de corte e o seio do eletrólito.

A importância do potencial ζ

- Potencial zeta afeta as interações entre as partículas.
- Isto afeta:
  - reologia
  - filtração/remoção de água
  - shelf life
  - estabilidade coloidal
  - e zeta é um parâmetro que informa sobre a química da superfície (por exemplo, o tipo de revistimento da superfície)

Força entre partículas depende de ζ

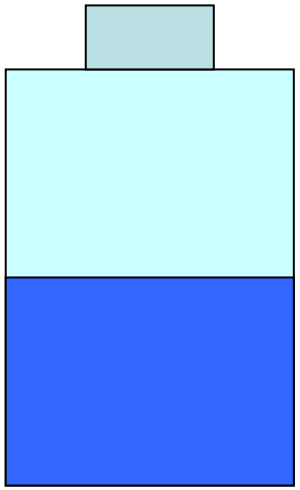




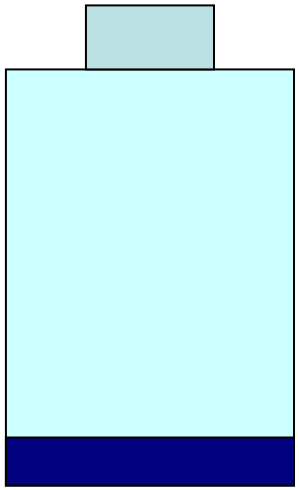
Se ζ **é muito pequeno** (< 25mV), partículas rígidas agregam formando redes abertas e floculam...

Isto afeta:

- Propriedades de armazenagem

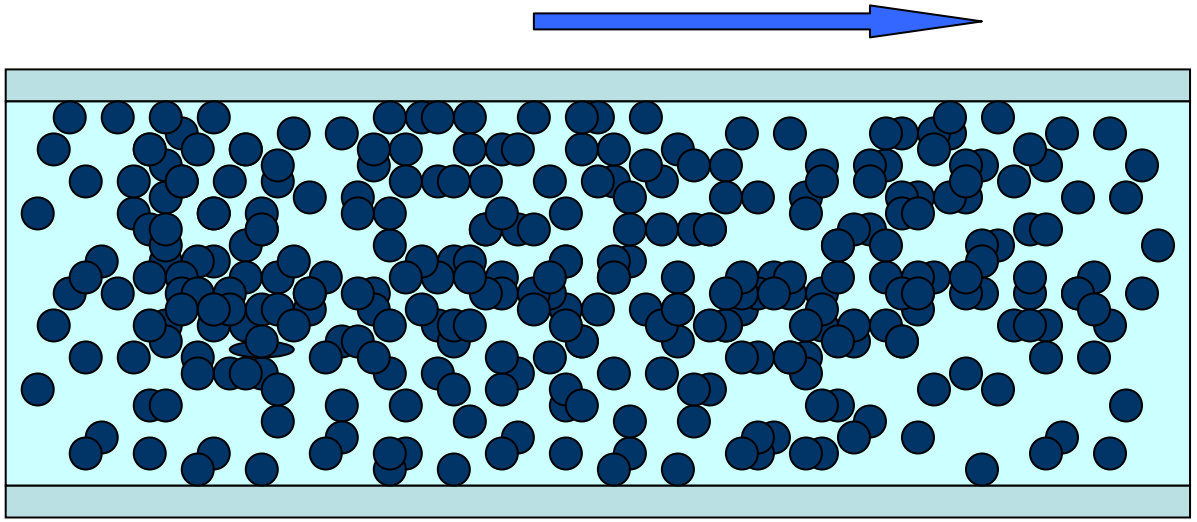


Estrutura de flocos abertos
Facilmente redispersa



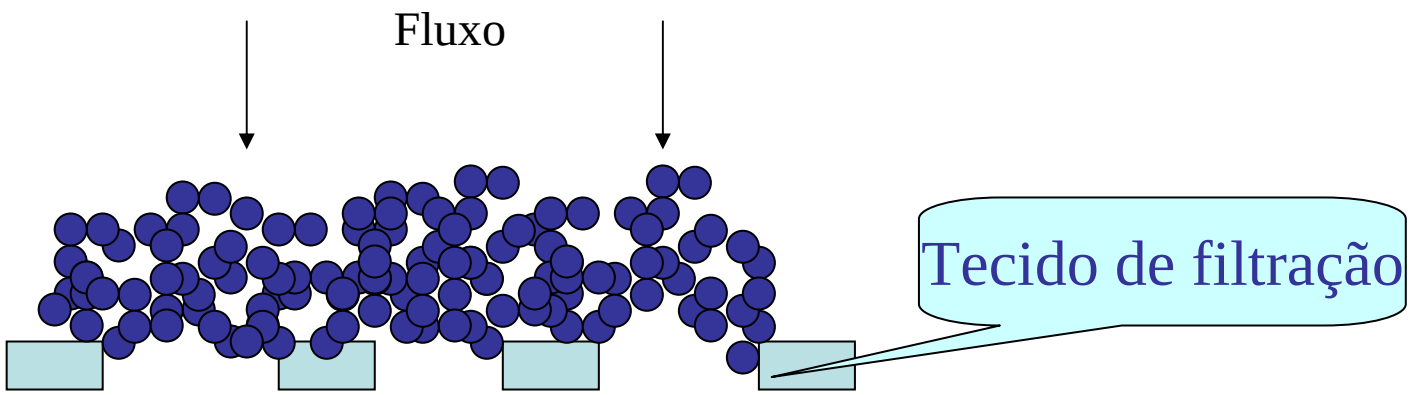
Estrutura densa
Difícil de redispersar

- **Reologia:**

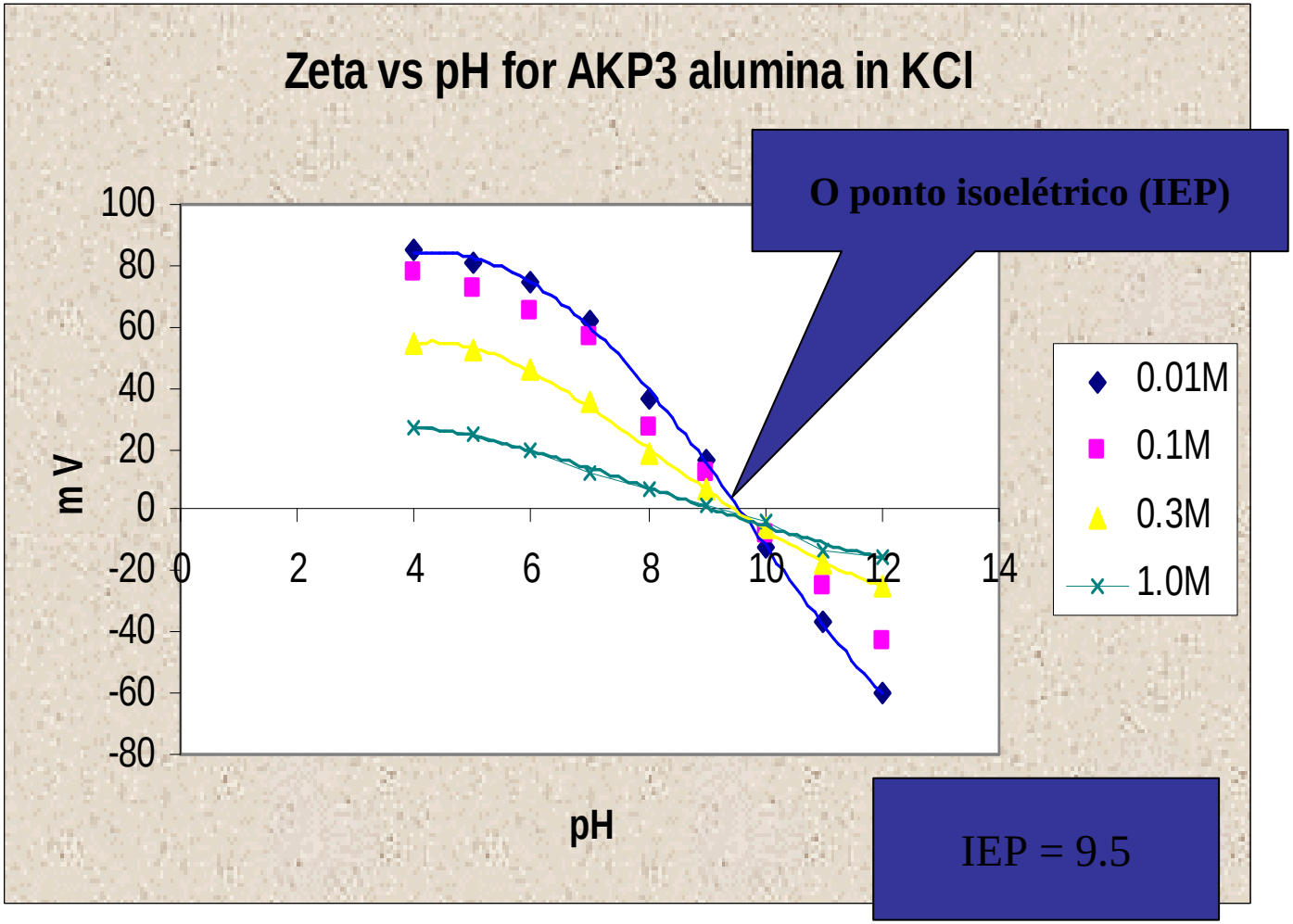


- Partículas formam redes elásticas

- A porosidade e resistência dos flocos afeta a velocidade de filtração e de remoção de água



Controlando o potencial zeta



- Zeta depende de pH, eletrólito, concentração, tensoativo, polieletrólito…

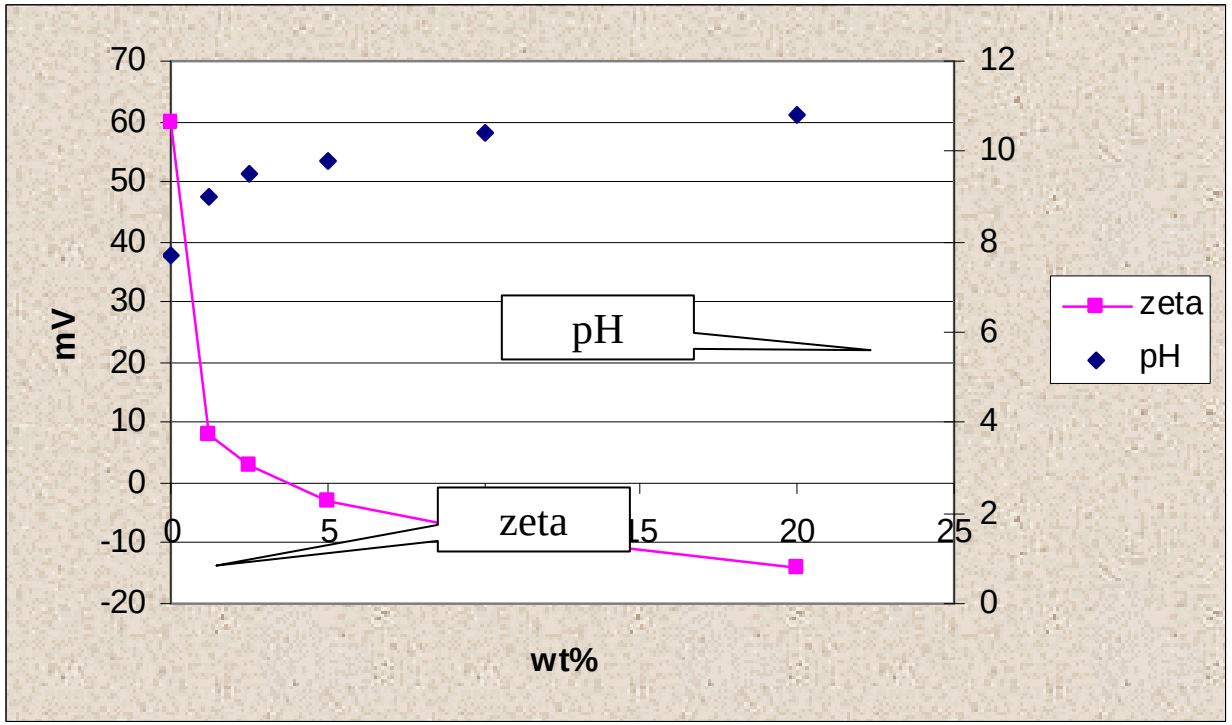
O problema da diluição

- Muitos equipamentos requerem dispersões diluídas

- Muitas amostras têm de ser drasticamente diluídas, o que pode alterar o potencial zeta.

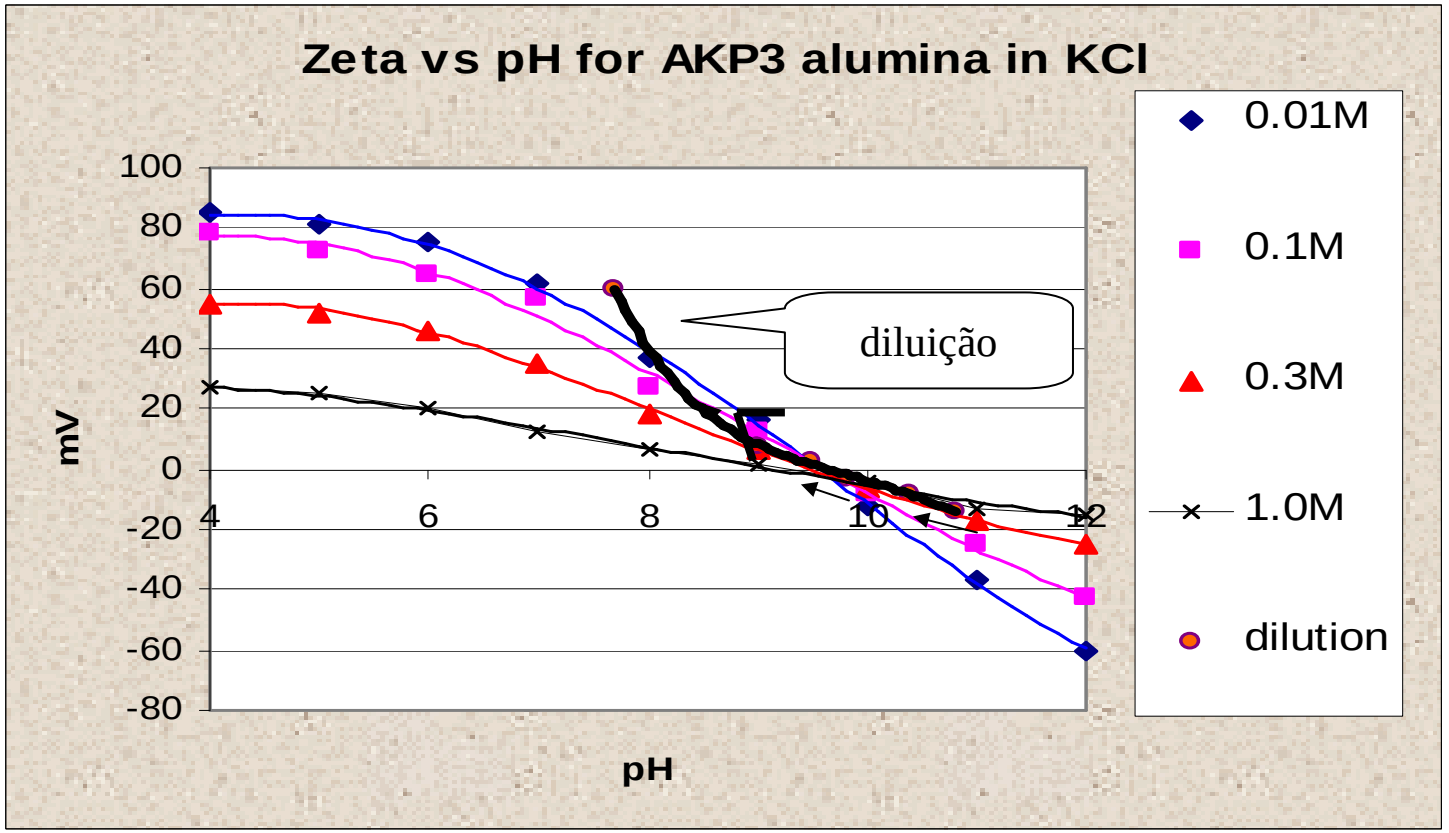
O problema da diluição

- Exemplo: alumina diluída com DDI



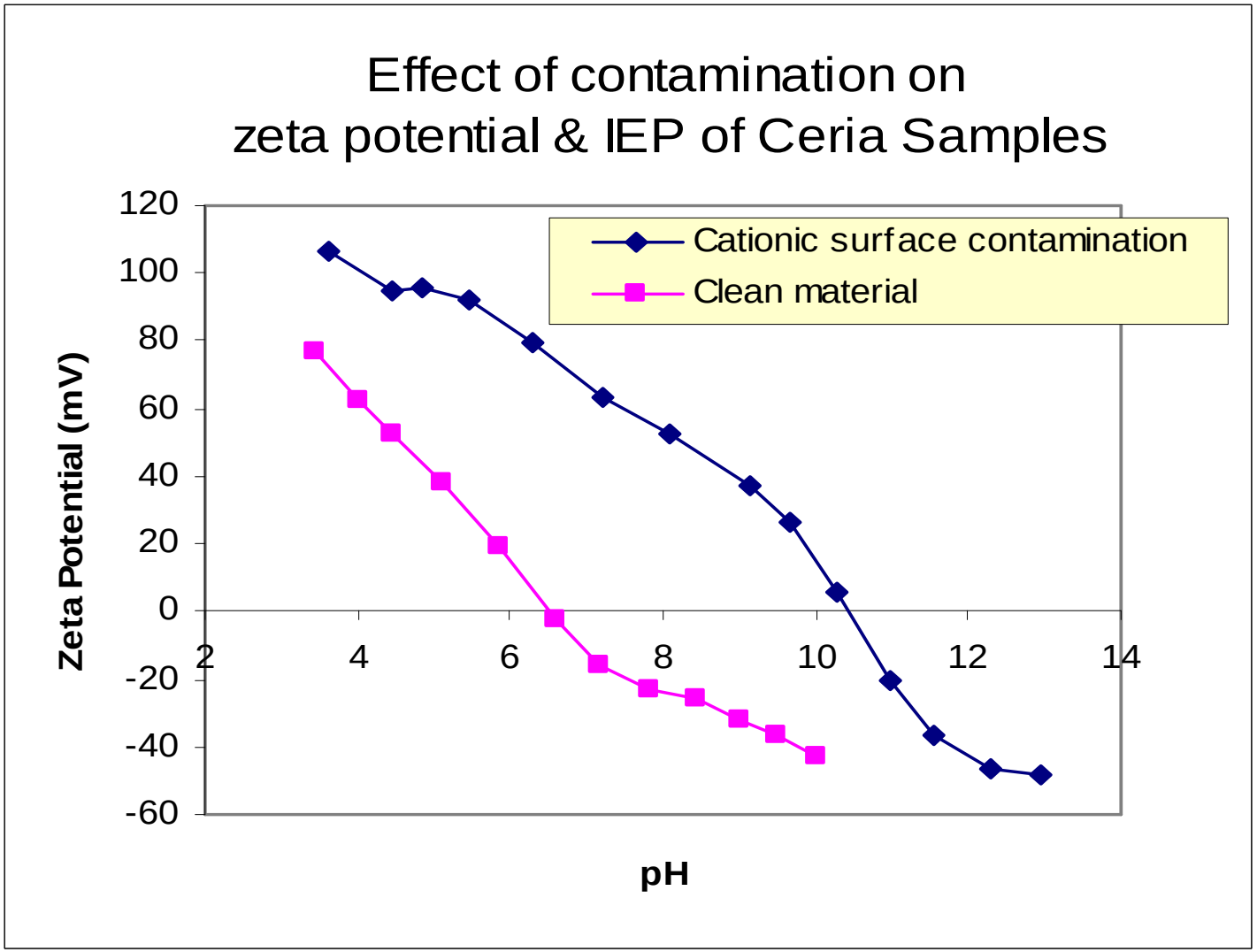
Zeta muda de -15 até +60 mV.

Por que zeta mudou?



- Porque o pH e a força iônica mudaram.

- Amostras muito diluídas são facilmente contaminadas com tensoativos



Determinação de potencial zeta

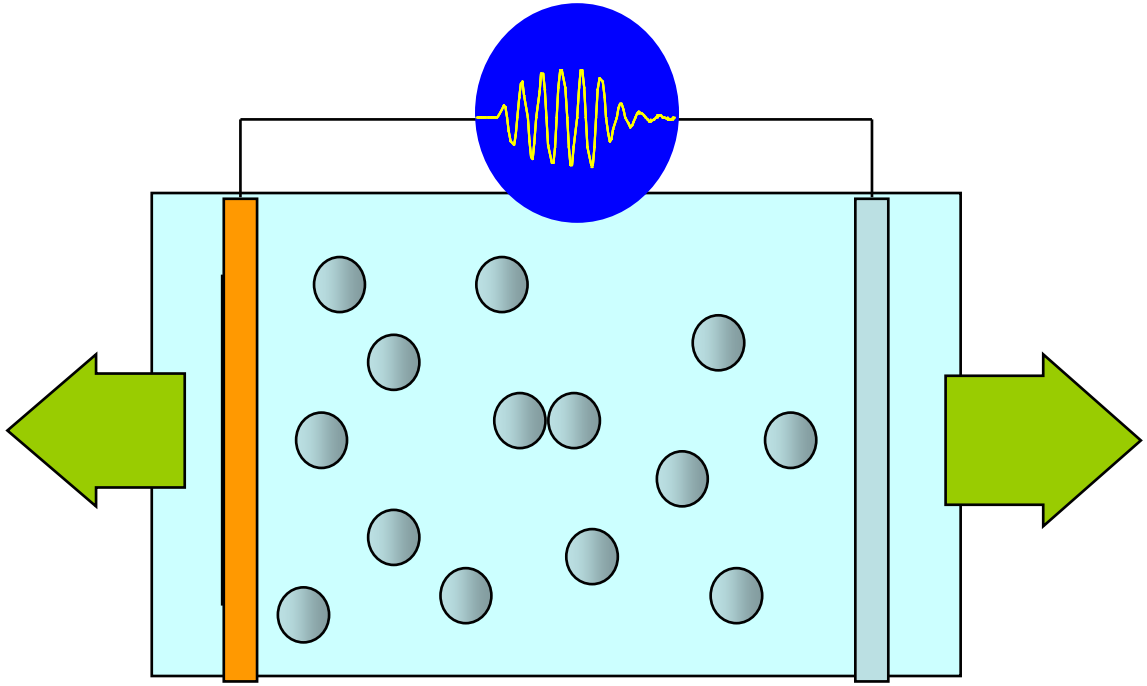
- Microeletroforese
  - Determinação de velocidade de migração das partículas no campo elétrico
    - Observação visual (ou vídeo)
    - Efeito Doppler
  - Cálculo da mobilidade
    - $u=v/E$
    - κa é muito grande: $u= \varepsilon\xi/\eta$ (limite de Smoluchowski)
    - $\kappa a<<1$: $u= 2\varepsilon\xi/3\eta$ (limite de Hückel)
    - Em geral: $u= 2\varepsilon\xi/3\eta\ f(\kappa a, \xi)$ (Henry)
      - Wiersema, Loeb, Overbeek, JCIS 1966
    - http://web.med.unsw.edu.au/phbsoft/mobility_listings.htm

Medindo sem diluição

- Técnicas que determinam zeta e tamanho de partículas
  - Eletroacústica
  - Atenuação de ultrassom

O Efeito Eletroacústico

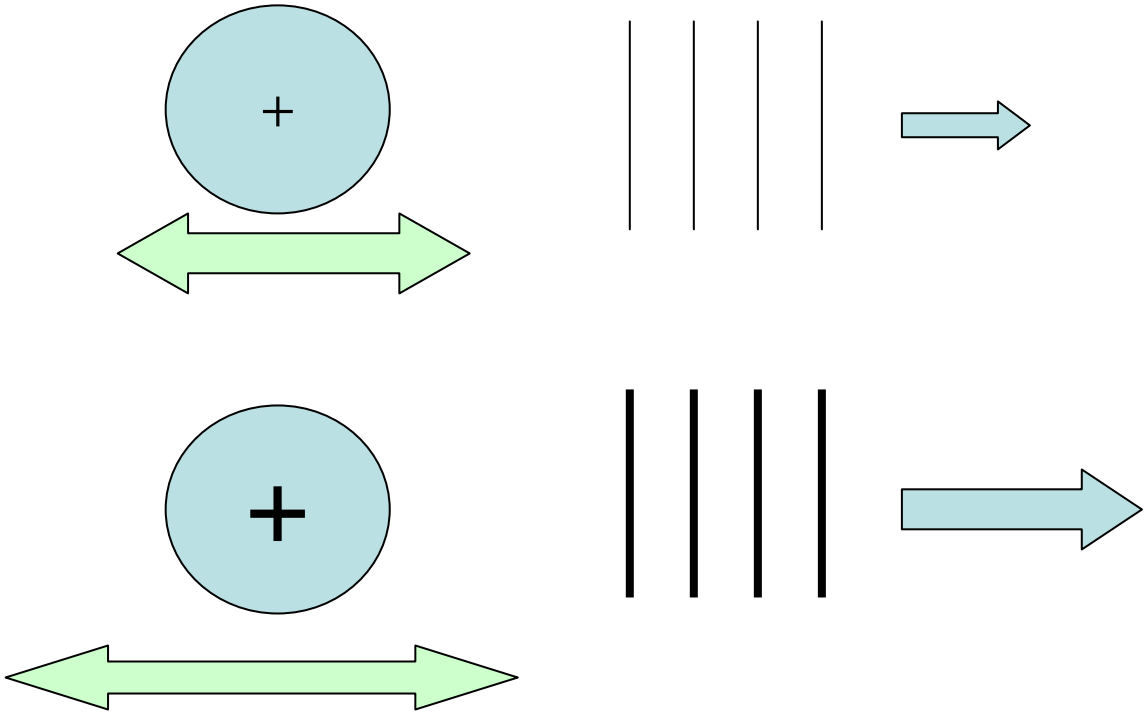
Aplica-se AC à amostra e gera-se uma onda acústica



O som se propaga além da dispersão

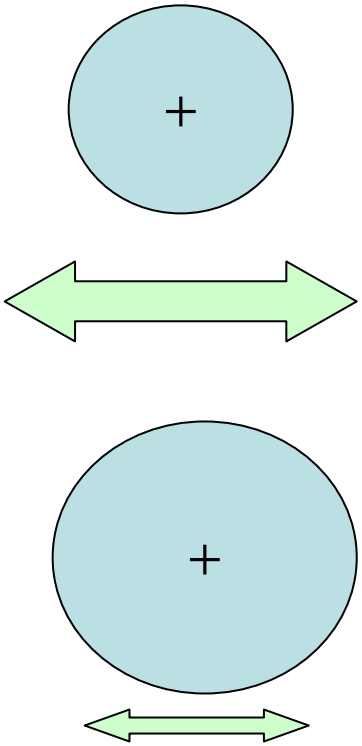
Ultrassom é medido, fornece zeta e diâmetro

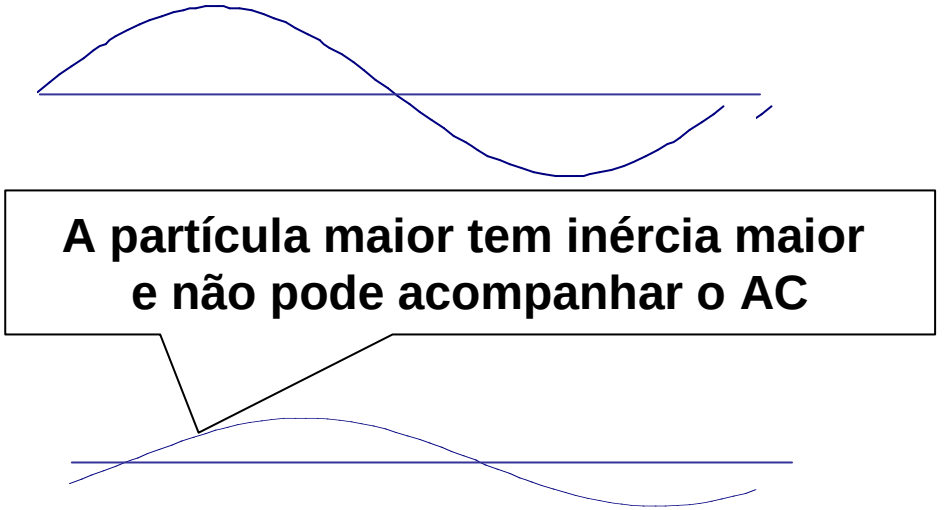
Qual é a conexão entre zeta e som?



Quanto maior for ζ, mais rápido é o movimento das partículas e mais intenso é o som

Por que ESA depende do tamanho?

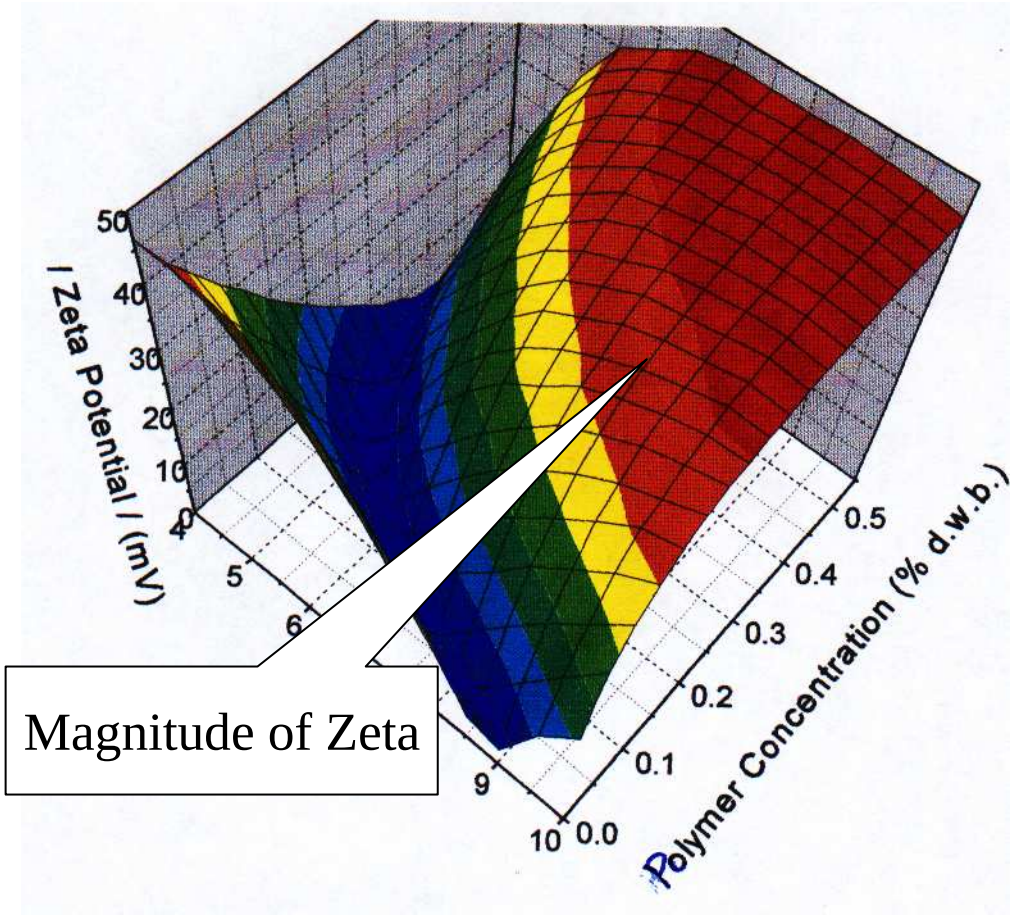




A defasagem em ESA depende do tamanho da partícula

Também há metodos baseados na *atenuação* do som pela dispersão.

Controle de aditivos



- Adição de PAA à alumina, em função do pH
- Titulação automática

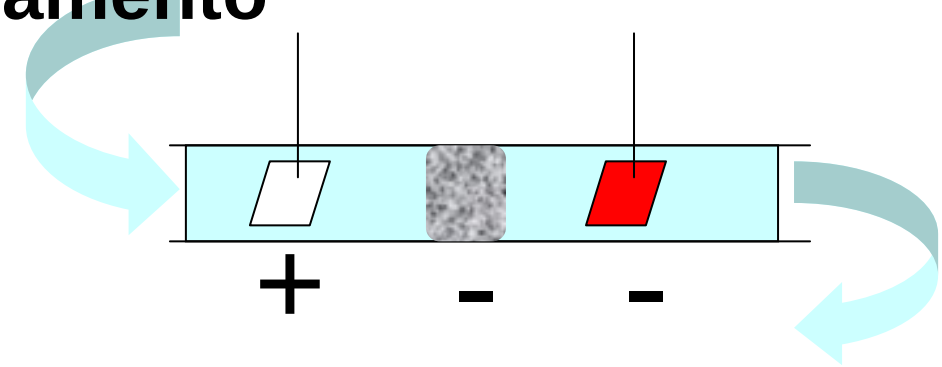
Eletroforese em gel

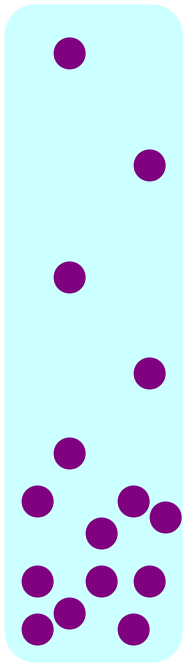
- Técnica muito usada na análise de proteínas e fragmentos de DNA.
- Várias versões
  - A velocidade de migração de proteínas desnaturadas na presença de SDS é função da sua massa molar.
  - http://br.youtube.com/watch?v=5eMsgidAY5E

Outros fenômenos eletrocinéticos (além da eletroforese)

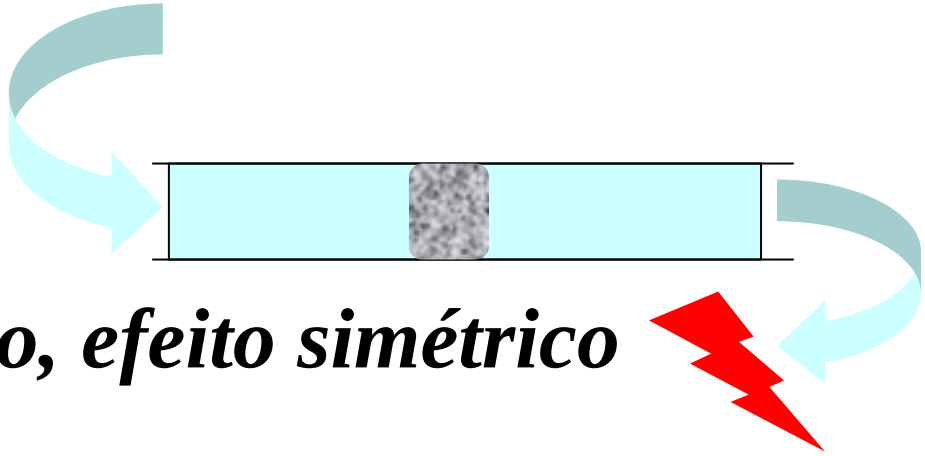
- Eletro-osmose
- Eletrodecantação
- Potencial de sedimentação
- Potencial de escoamento
- Potencial de junção (?)
- Triboeletricidade (?)
- Dieletroforese

***eletro-osmose*: escoamento de líquido causado por uma diferença de potencial elétrico**





***potencial de sedimentação*: as partículas sedimentam gerando excesso de carga no fundo do tubo e diferença de potencial entre topo e fundo**



potencial de escoamento, efeito simétrico à eletro-osmose

Dieletroforese

- **Dielectrophoresis** (or DEP) is a phenomenon in which a force is exerted on a dielectric particle when it is subjected to a non-uniform electric field. This force does not require the particle to be charged. All particles exhibit dielectrophoretic activity in the presence of electric fields. However, the strength of the force depends strongly on the medium and particles' electrical properties, on the particles' shape and size, as well as on the frequency of the electric field. Consequently, fields of a particular frequency can manipulate particles with great selectivity. This has allowed, for example, the separation of cells or the orientation and manipulation of nanoparticles and nanowires.

- H. A. Pohl, "The Motion and Precipitation of Suspensoids in Divergent Electric Fields", J. Appl. Phys. 22(7), 869–871 (1951).
- Pohl, H. A., 1958, "Some effects of nonuniform fields on dielectrics", J. Appl. Phys., 29(8), 1182 - 1188.
- Pohl, H. A., 1978. Dielectrophoresis the behavior of neutral matter in nonuniform electric fields. Cambridge University Press. Cambridge.

Características da dieletroforese

Pohl wrote in his book defining dielectrophoresis as the translational motion of neutral matter caused by polarization effects in a nonuniform electric field. The phenomenological bases are catalogued below:

- The dielectrophoresis force can be seen only when particles are in the nonuniform electric fields.
- Since the dielectrophoresis force does not depend on the polarity of the electric field, thus the phenomenon can be observed either with AC or DC excitation.
- Particles are attracted to regions of stronger electric field when their permittivity exceeds that of the suspension medium.
- When permittivity of medium is greater than that of particles, this results in motion of particles to lesser electric field.
- DEP is most readily observed for particles with diameters ranging from approximately 1 to 1000 μm. Above 1000 μm gravity, and below 1 μm Brownian motion, overwhelm the DEP forces.
    - http://en.wikipedia.org/wiki/Dielectrophoresis

Separação

- Dielectrophoresis Field-Flow Fractionation, introduced by Davis and Giddings[7], is a family of chromatographic-like separation methods. In DEP-FFF, DEP forces are combined with drag flow to fractionate a sample of different types of particles[6][8][9][10].
- Particles are injected into a carrier flow that passes through the separation chamber, with an external separating force (a DEP force) being applied perpendicular to the flow.
- By means of different factors, such as diffusion and steric, hydrodynamic, dielectric and other effects, or a combination thereof, particles (<1 μm in diameter) with different dielectric or diffusive properties attain different positions away from the chamber wall, which, in turn, exhibit different characteristic concentration profile. Particles that move further away from the wall reach higher positions in the parabolic velocity profile of the liquid flowing through the chamber and will be eluted from the chamber at a faster rate.

- Davis, J.M. and J.C. Giddings, 1986. "Feasibility study of dielectrical field-flow fractionation". Sepa. *Sci. and Tech.* 21, 969-989.
- Giddings, J.C., 1993. "Field-Flow Fractionation: Analysis of macromolecular, colloidal, and particulate materials". *Science*. 260, 1456-1465.

Reconfiguração de nanoagulhas entre eletrodos

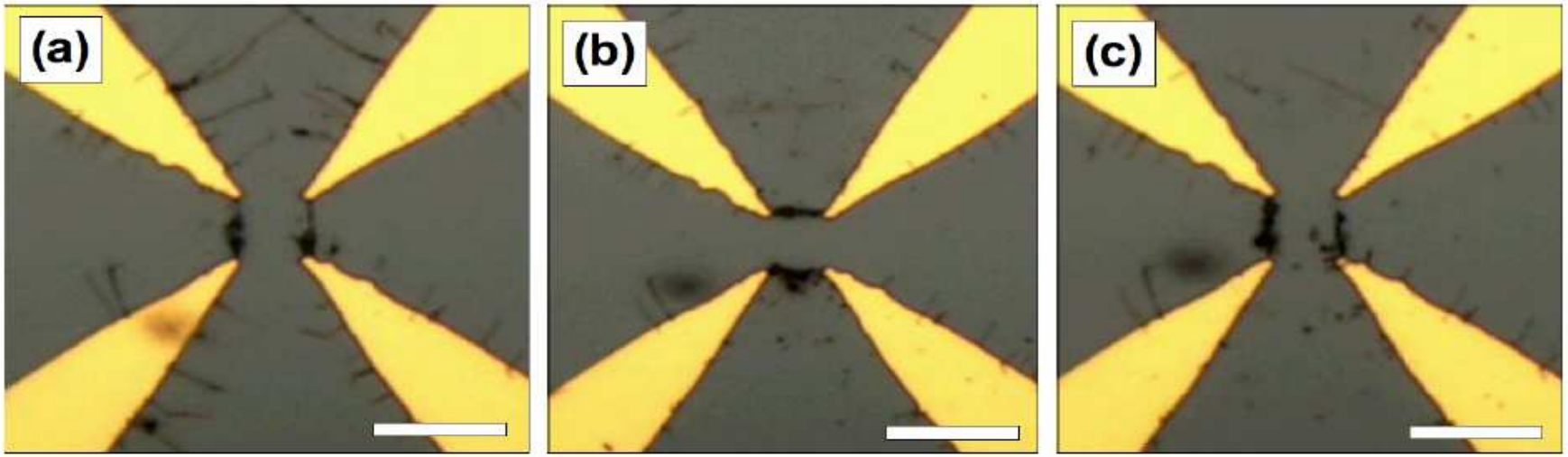


Figure 4. Microscope images of four-electrode parallel reconfiguration of nanowires. Each pair of diagonally opposite electrodes is held at a constant relative phase of 180°, while the relative phase between the upper-left and upper-right electrodes is modulated from (a) 0° to (b) 180° to (c) 0°. The scale bars are 20 μm. Supporting movie S3 of this process is available at stacks.iop.org/Nano/17/4986 (2.4 MB MPEG).

Alex D. Wissner-Gross et al. in Nanotechnology 2006
http://alexwg.org/Nanotechnology2006.pdf

Lab talk
Apr 16, 2008

Large-scale fabrication approach of CMOS compatible high-performance nanotube transistors

Due to their nanometer dimensions and superior electrical properties, carbon nanotube field effect transistors (CNT-FETs) could one day replace the traditional silicon metal oxide semiconductor field effect transistor.

For large-scale fabrication of CNT-FETs to become possible, CNTs need to be placed at selected positions of the circuit with high yield and each CNT-FET needs to be addressed individually with its own local gate. The assembly also needs to be carried out in an environment that does not damage other components in the circuit.

Saiful Khondaker and Paul Stokes

Dielectrophoretic (DEP) assembly of CNTs is promising as it offers a quick and convenient method to assemble CNTs from solution. http://nanotechweb.org/cws/article/lab/33811/1/figure

Carga e descarga de dielétricos: um novo modelo.

Fernando Galembeck

Instituto de Química
Universidade Estadual de Campinas
Instituto do Milênio de Materiais Complexos

The problem: electroneutrality and charges in dielectrics

- Polymers, glasses and other insulators are usually considered as electroneutral, at a supramolecular scale...
- ...*but they become electrostatically charged* under various conditions.
- *Thus, which are the species bearing charges in charged polymers and where (microscopically) are they?*

Electrostatic charging: an old but still unsolved problem

"Surprisingly, although electrostatic charging is well known, it remains among the most poorly understood areas of solid-state physics."

"Most researchers believe that insulator charging is a surface phenomenon."

Schein LB, Recent progress and continuing puzzles in electrostatics. *Science*, 316, 1572-1573 (2007).

ALSO: Bailey AG, The charging of insulator surfaces. *J. Electrostat.*, 51-52, 82-90 (2001), Castle GSP, Contact charging between insulators. *J. Electrostat..*, 40-1, 13-20 (1997)

…still unsolved problem

"Through the years many "models" or correlations have been suggested for insulator charging.

…correlations with dielectric constant,

…the basic and acidic nature of the materials,

…polymer "work function,"

…surface chemistry determined by measuring the residence time of probe molecules using inverse gas chromatography.

However, no reasonable explanation of the effective electric field has yet emerged."

Schein LB, Recent progress and continuing puzzles in electrostatics. *Science*, 316, 1572-1573 (2007).

Electrostatic charging: an old but still unsolved problem

by Harper:

"A crucial question for the explanation of the production of static charge is whether the charging of insulators comes from a transfer of electrons, of ions, or of both.

Montgomery: ***always*** electrons

Loeb: ***generally*** electrons

Henry ***feels*** that the question is ***still an open one***.

I (Harper) am of the opinion...that the carriers are ***never*** electrons when the material being charged is strictly an insulator."

Adrian G. Bailey, 2001

Frequent answer

- Charged carriers in insulators are
  - trapped electrons and holes
- ...but in polymers they should be anions and cations
  - since polymers are molecular species
- Which anions and cations in polyethylene, polypropylene...?

Contact Charging Between Insulators

- Contact charging between insulators was one of the earliest manifestations of electrical science.
- Yet reproducible experiments remain a challenge.
- A generally agreed upon theory of insulator-insulator charging remains elusive.
    - *G.S.P. Castle, J. Electrostatics 1997*

Triboelectrification

The amount of the generated charge depends on many factors such as:

a) the nature and work function of the materials;

J Electrostatics 51-52 (2001) 374-380 (AG Bailey)

b) the nature of contacts, the particle size and shape;

Pharm. Pharmacol. Commun. 4 (1998) 111–115 (G. Rowley et al)

c) the surface roughness;

Phys. Chem. Mech. Surf. 3 (1985), 2817–2821 (Vladykina et al)

d) contamination;

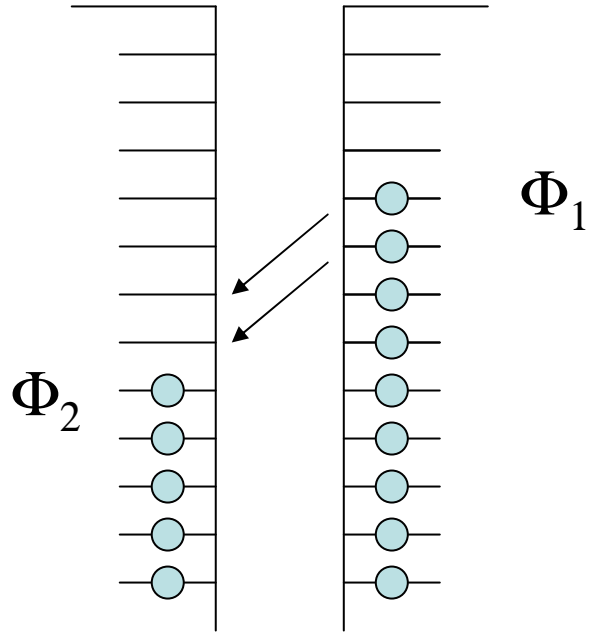
Pharm. Pharmacol. Commun. 5 (1999) 429–433 (G Rowley et al)

e) ambient conditions.

J. Electrostatics 22 (1989) 213–227 (T Nguyen et al)

Widely-quoted theory

- Surface state theory
  - low and high density limits



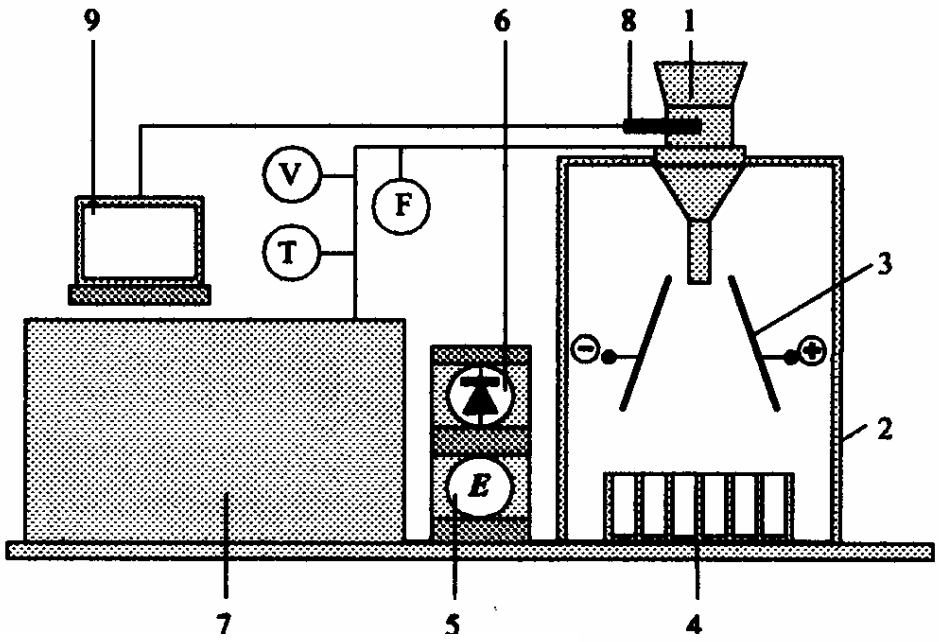
The resulting surface charge density is

$$\sigma_L = -eN(\Phi_1 - \Phi_2)$$

N= density of surface states (unit energy.unit area)$^{-1}$

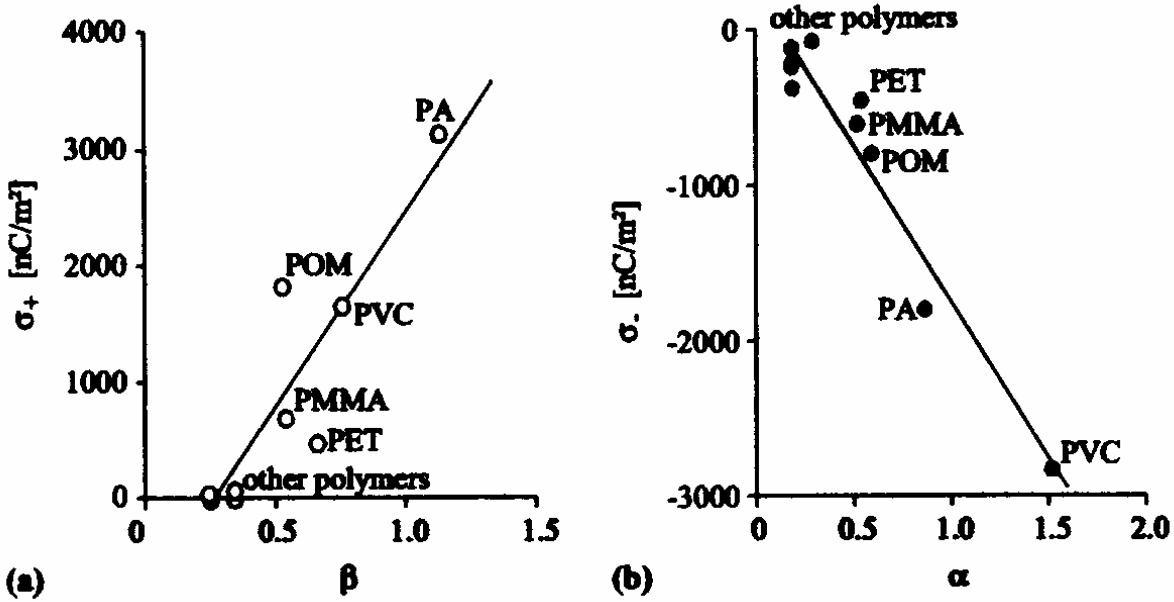
Φ= surface work function

Neglect of contributions from the bulk



Correlation between charge density and electron-pair transfer (Lewis acid-base properties)

But: negative and positive charges on the same polymer (equivalent to 0,1ppm)



Many important topics

- Maxwell-Wagner effect
- Costa Ribeiro (thermodielectric) effect
- Charge separation by electrosmosis or junction/sedimentation/streaming potentials
- Electrets
- Interfacial polarization, thermally stimulated currents
- Tribochemical effects
- ***...but: again, which are the relevant species in each case, and how are they distributed?***

Consequences

- **Safety problems**
  - **Dust explosions**
  - **Fires**
  - **Pharmaceuticals**
- **Important technologies**
  - **Polymer recycling**
  - **Electrospinning**
  - **Solid paint**
  - **Electrocopying**

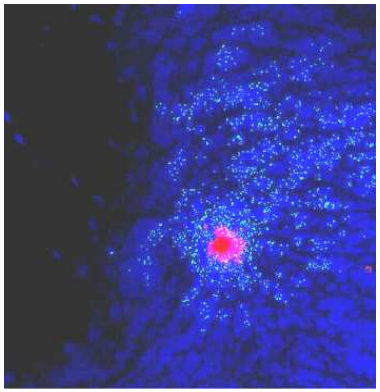
- **For nanotechnology:**

  Electrostatic force is even larger than the inertial force, for micromachine parts made of insulators.

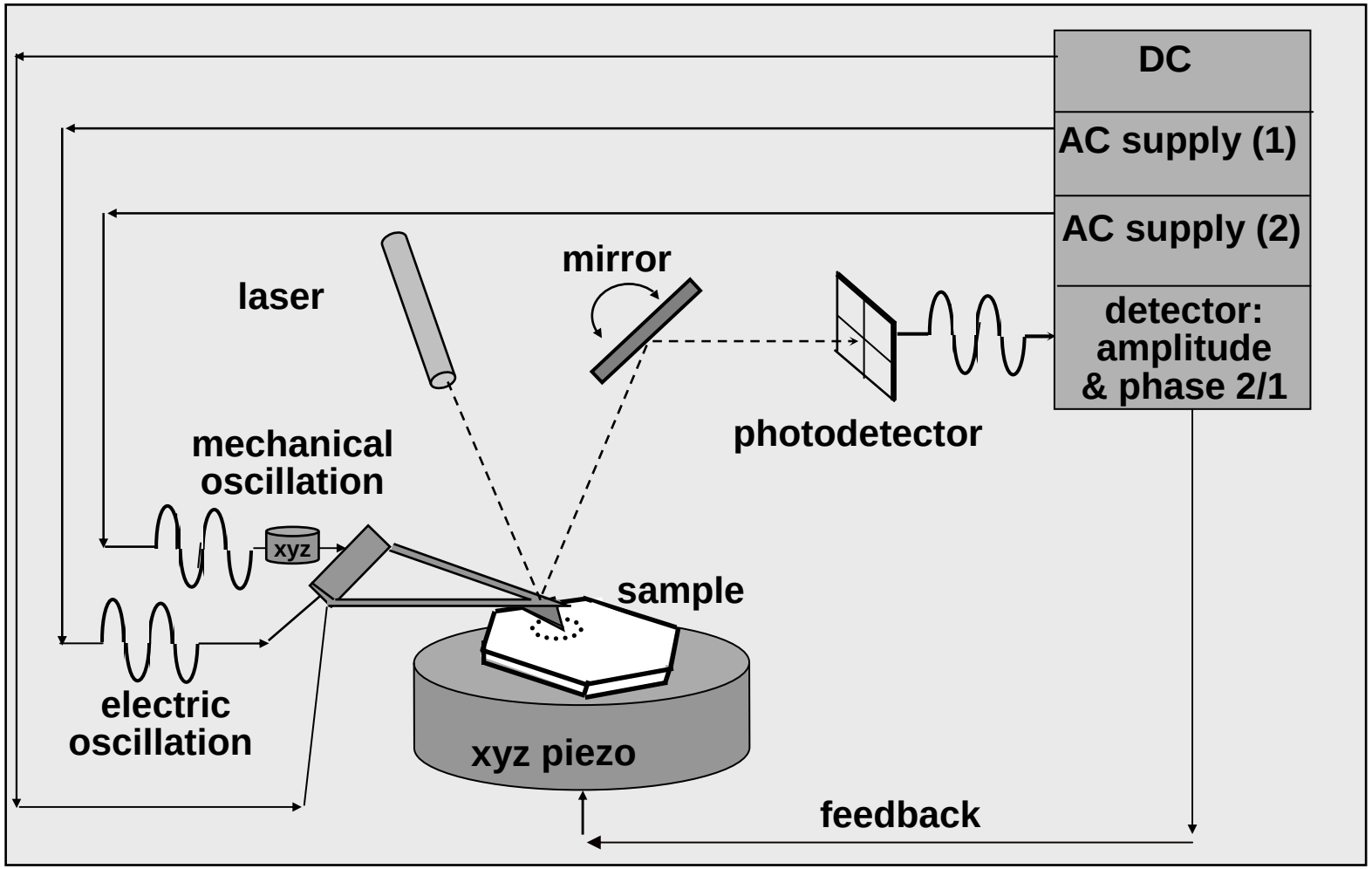
  - *The electrification of the insulator is not well understood, especially at the micro-scale. Fujisawa and Enomoto, AIST*
- **For space research:**
  - *Space suit generates 20 kV*

Microscopic approaches: micro(nano)chemical tools

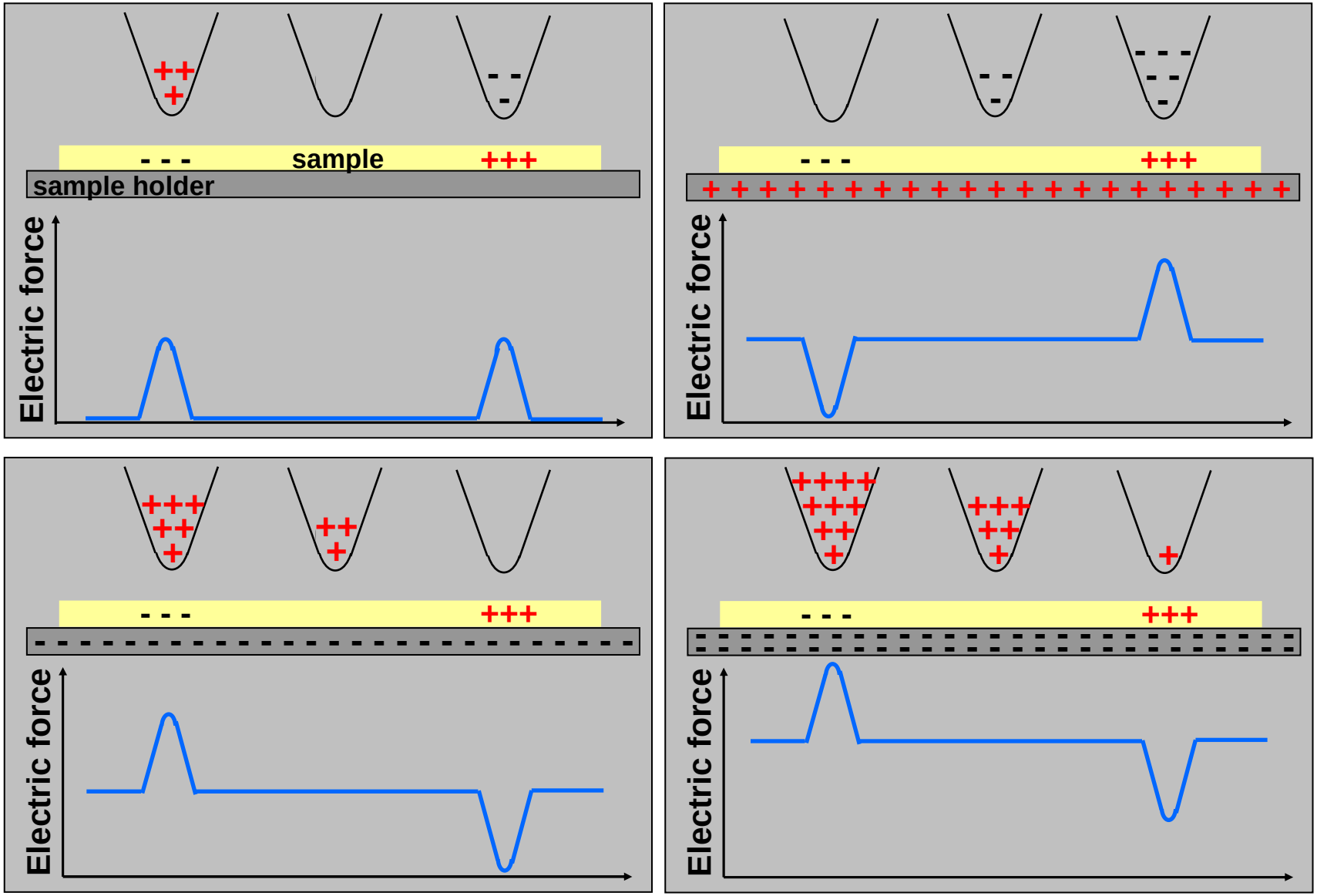
- **SEPM**
  - **based on the Kelvin method for electric potential measurements**
  - **electric potential mapping concurrent to atomic force imaging**
- **ESI-TEM**
  - **electron energy loss spectra from selected areas**
  - **elemental maps**
  - **high sensitivity to light elements (S, C, O)**



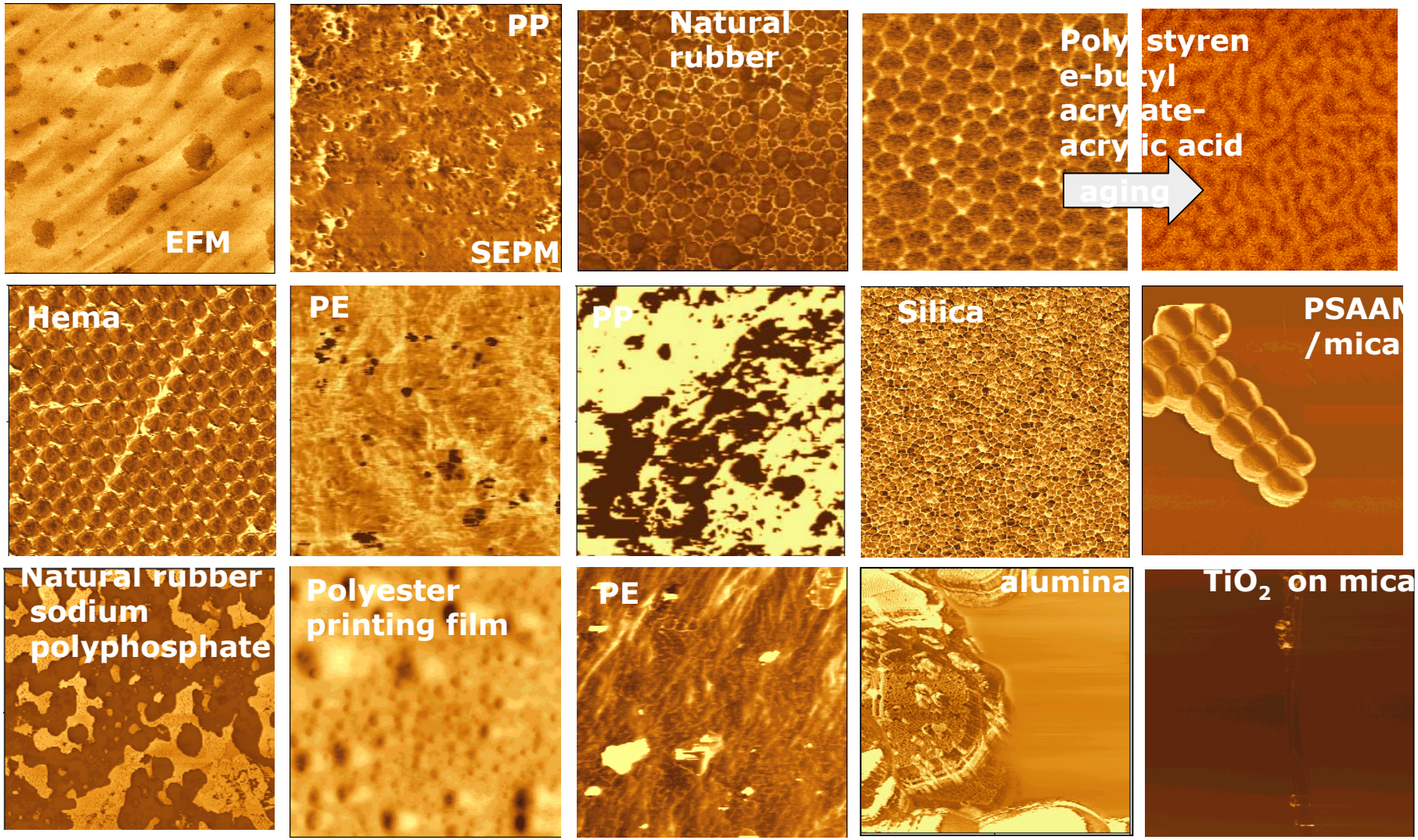
SEPM: scanning electric potential microscope
Kelvin method with force detection



Induction of electric charges on the tip modifies the tip-sample interaction

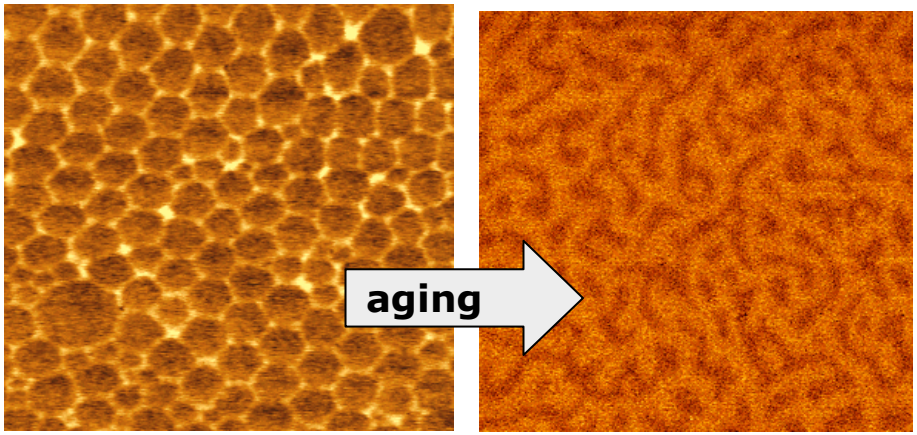


Complex potential distribution patterns and large electric potential gradients in every insulator examined

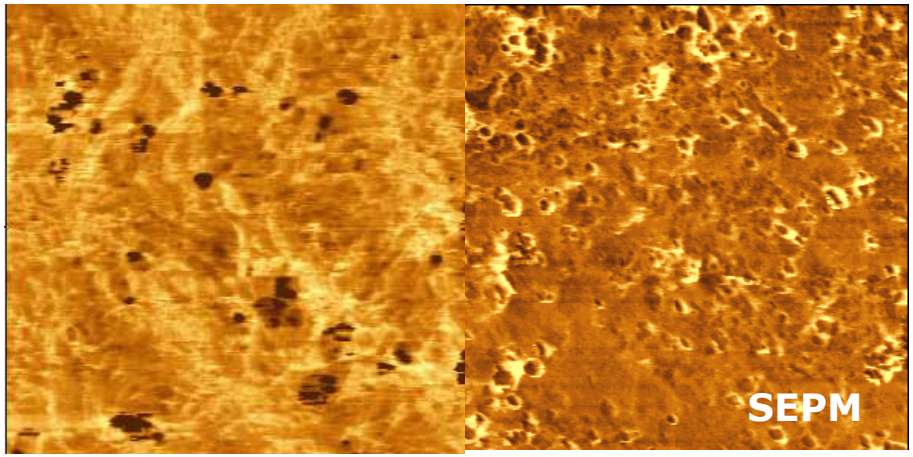


Complex potential distribution patterns and large electric potential gradients in every insulator examined

Poly(styrene-butyl acrylate-acrylic acid)



Polyethylene

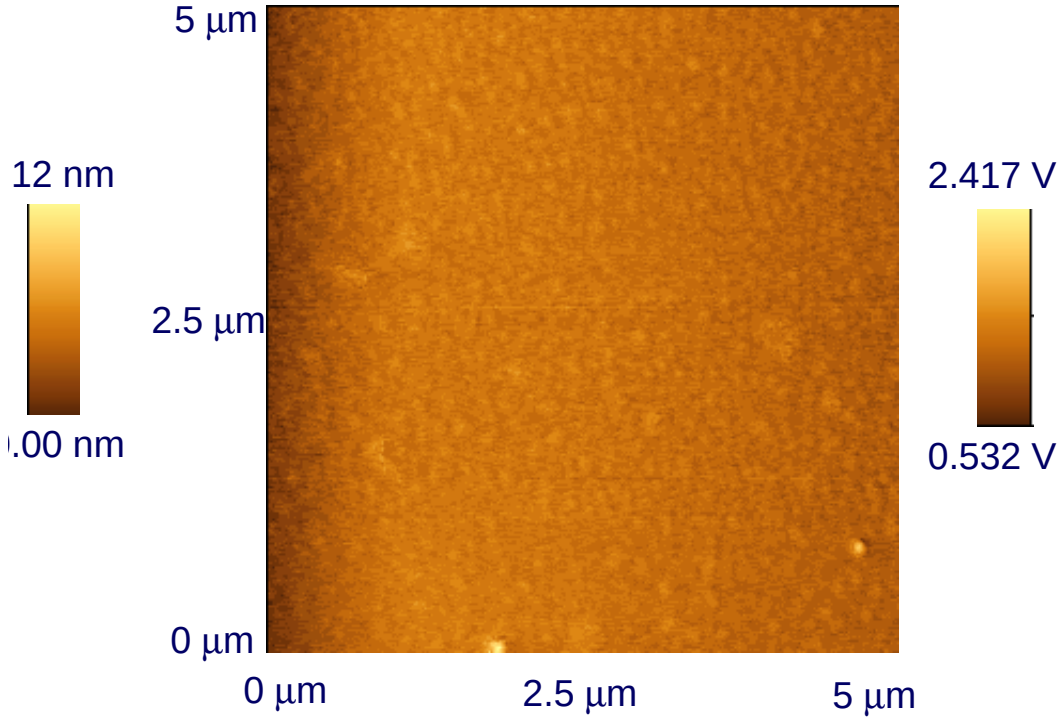


Polypropylene

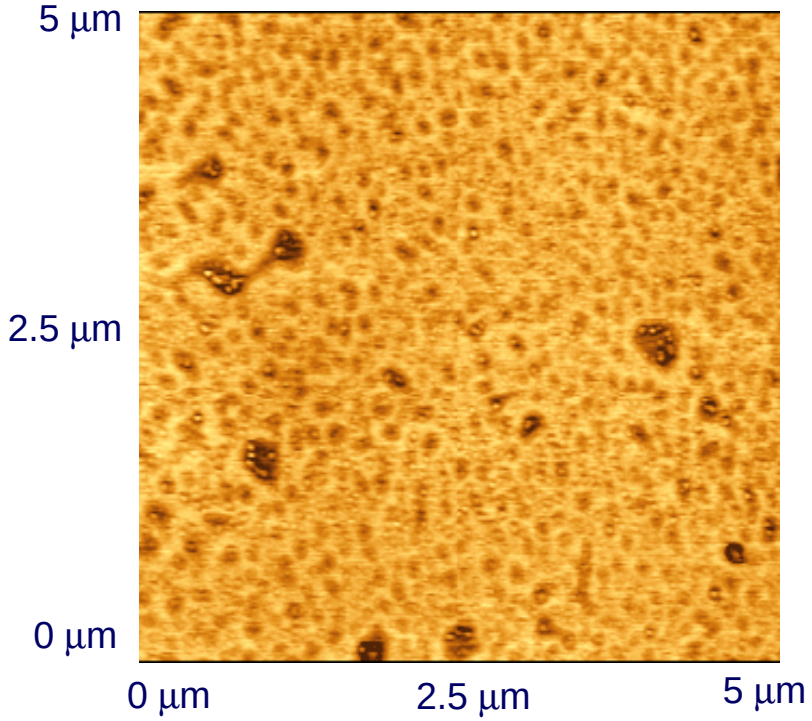
Natural rubber latex film

Av thickness 250 nm

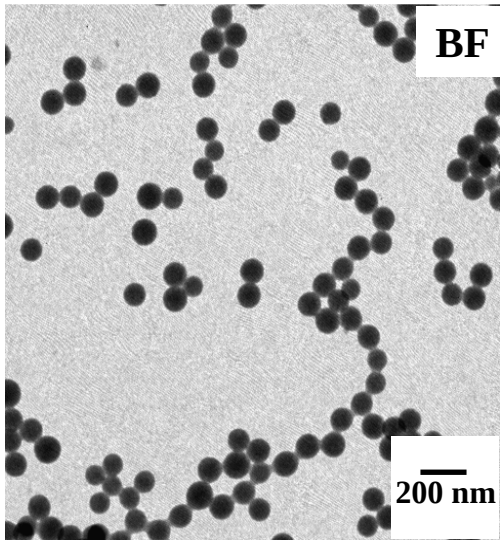
RRIM 60 clone from *H. brasiliensis.* Centrifuged latex (1000 RPM at 5^{o}C for 2 h, without stabilizer.

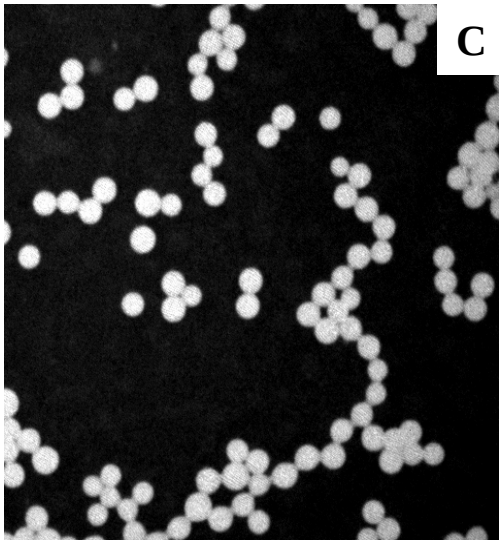


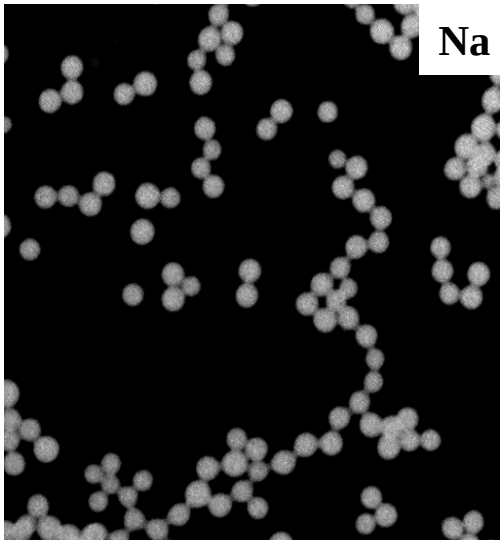
TOPOGRAPHY



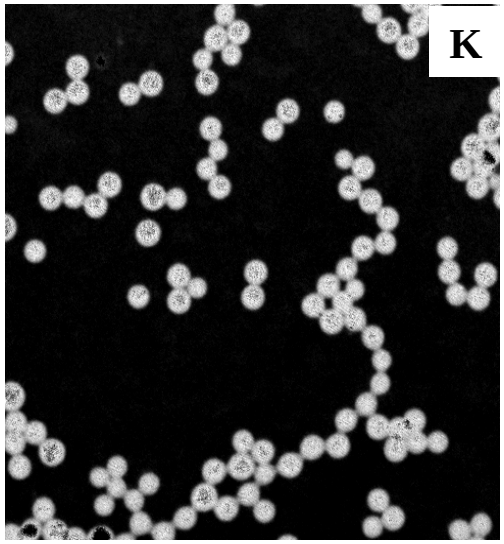
SEPM

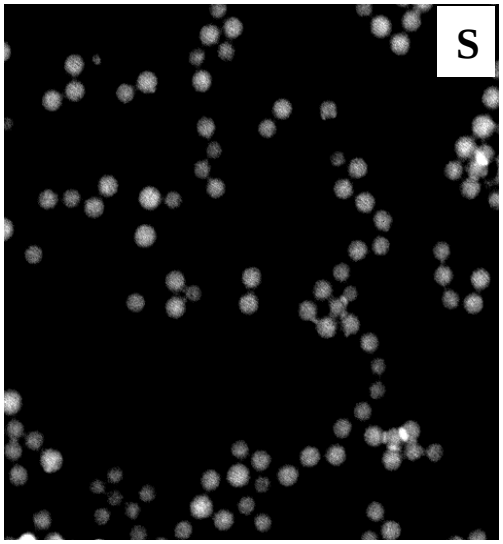


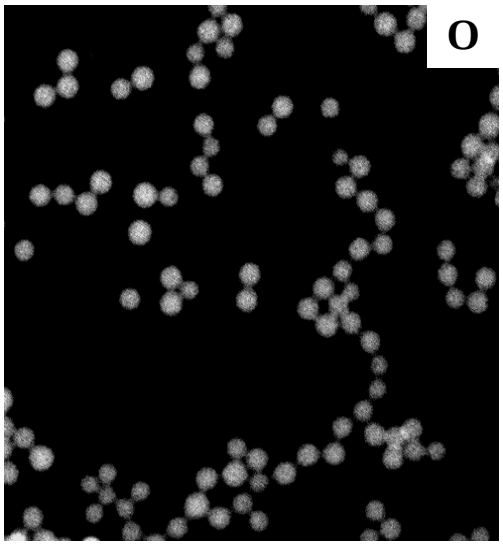




PS-M latex: persulfate initiator, surfactant stabilizers



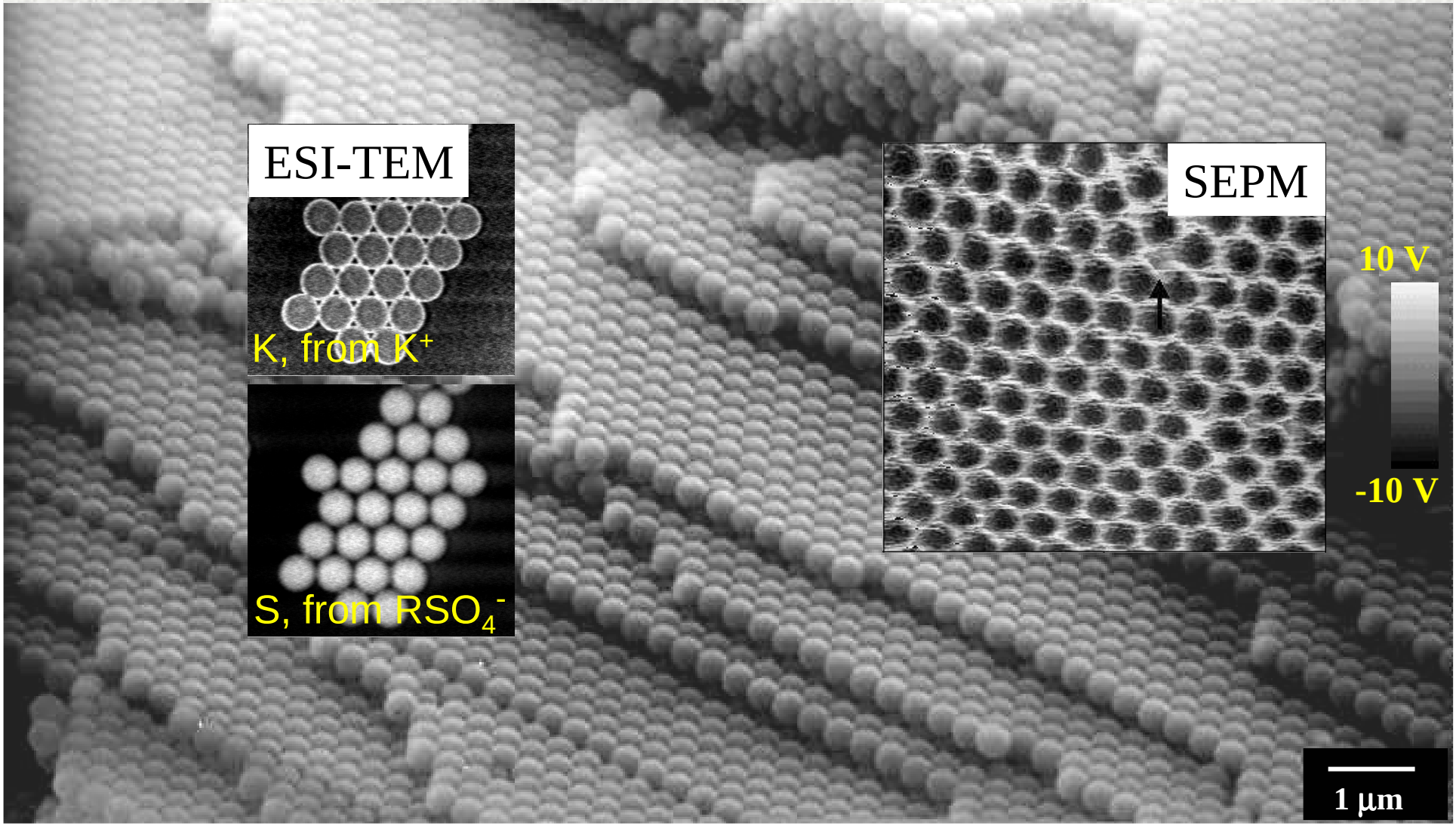




S (negative charge) distribution less homogeneous than Na (or K, positive charges) distribution: excess local charges.

(Braga et al., J. Phys. Chem. B 2001)

Charge patterns of polystyrene and other “neutral” polymers: PS-HEMA macrocrystal is actually a positive mesh with negative particle cores



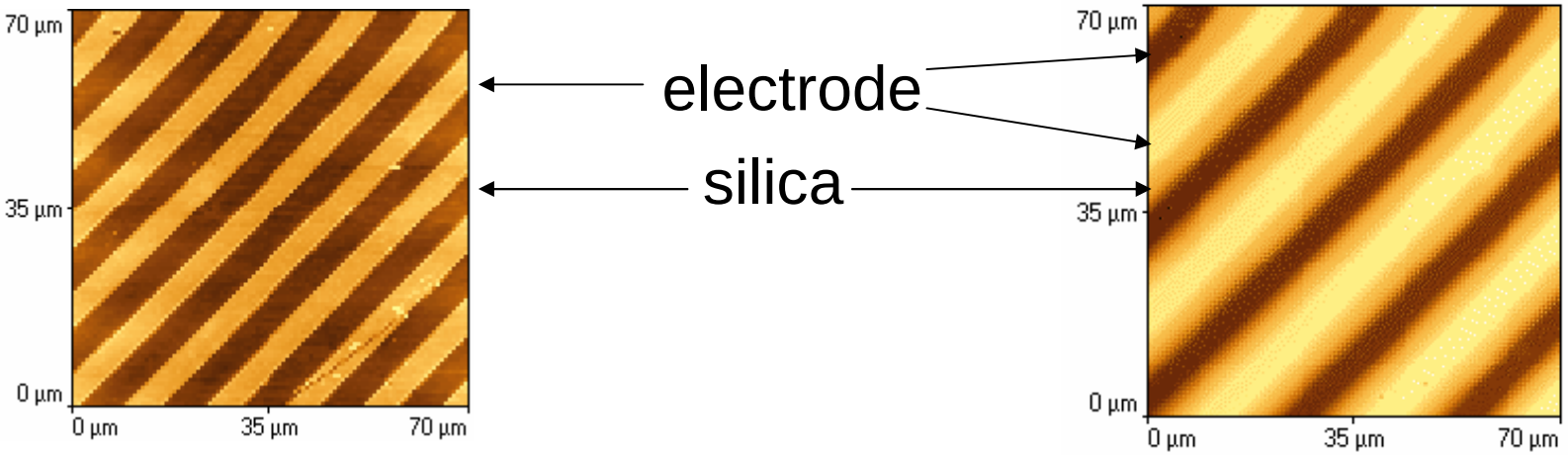
Charge carriers

- In latexes and latex films: ions bound to the polymer chains (from polymerization initiators) and counter-ions.
- Identified by the combination of SEPM and analytical electron microscopy (ESI-TEM).
- In cellulose, polyethylene, polypropylene, polystyrene...?

Problem: SEPM calibration

Calibration sample:
electrodes evaporated on Ti, over silica film on silicon wafer

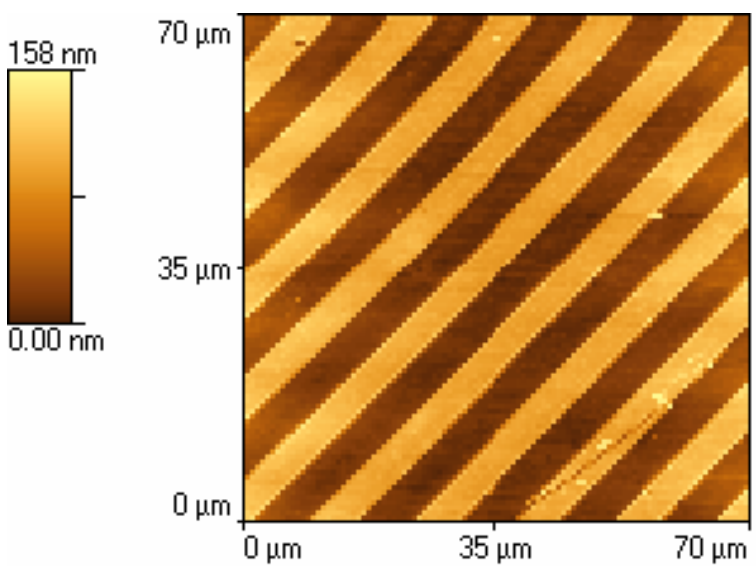
- Electrodes are polarized using an external power supply

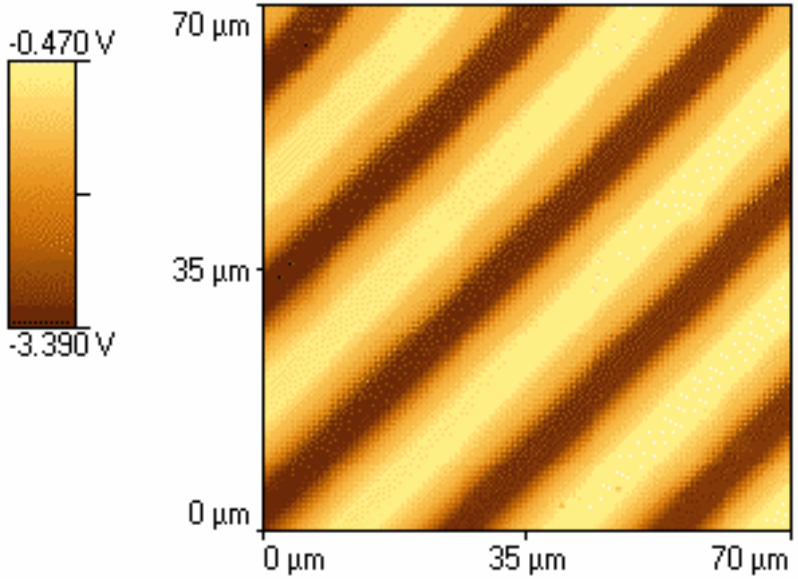


AFM SEPM

R. F. Gouveia, C. A. R. Costa, and F. Galembeck Electrostatic Patterning of a Silica Surface: A New Model for Charge Build-Up on a Dielectric Solid, J. Phys. Chem. B 2005, 109, 4631-4637

Quantitative disagreement



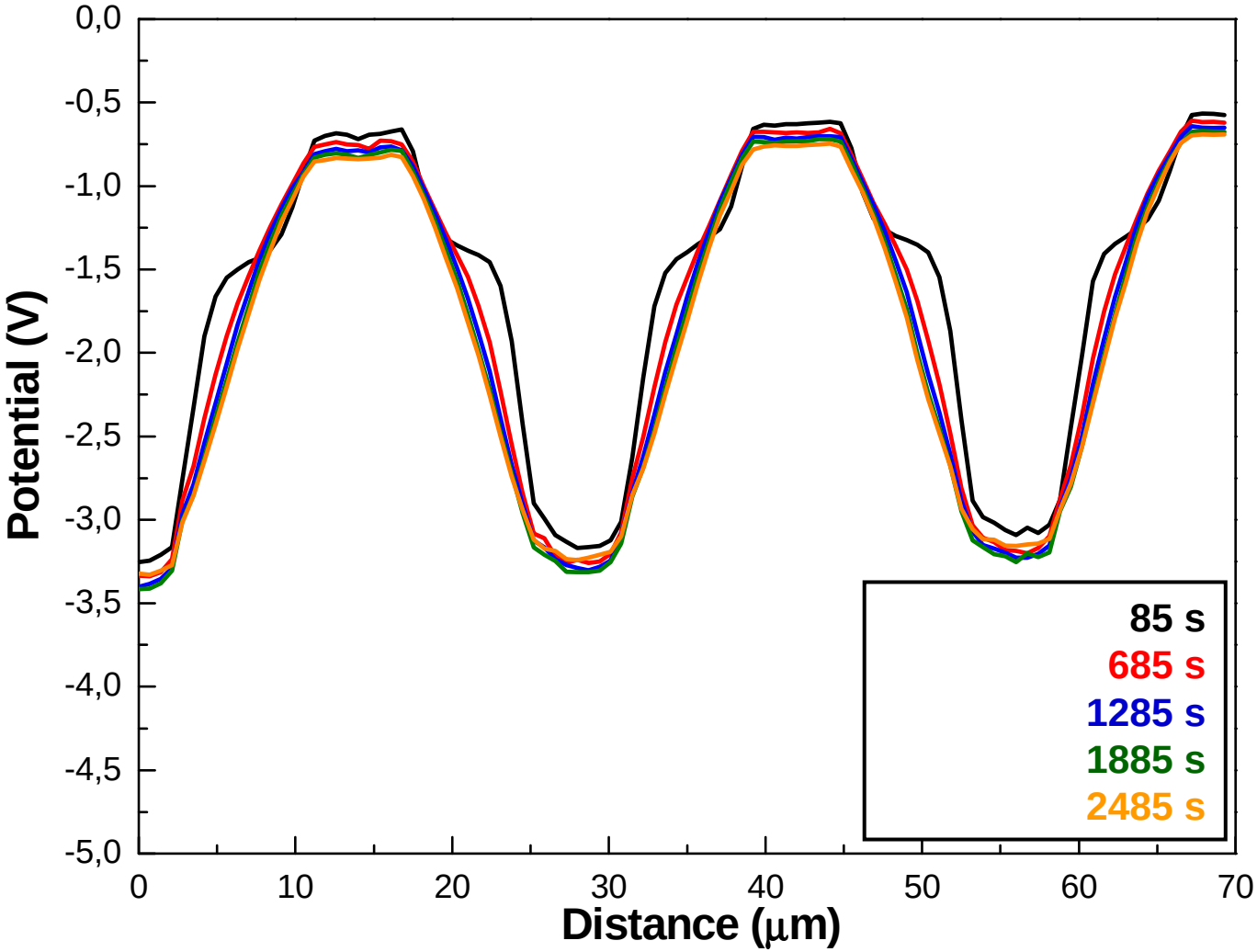


AFM

SEPM: -5V and 0 V (grounded)

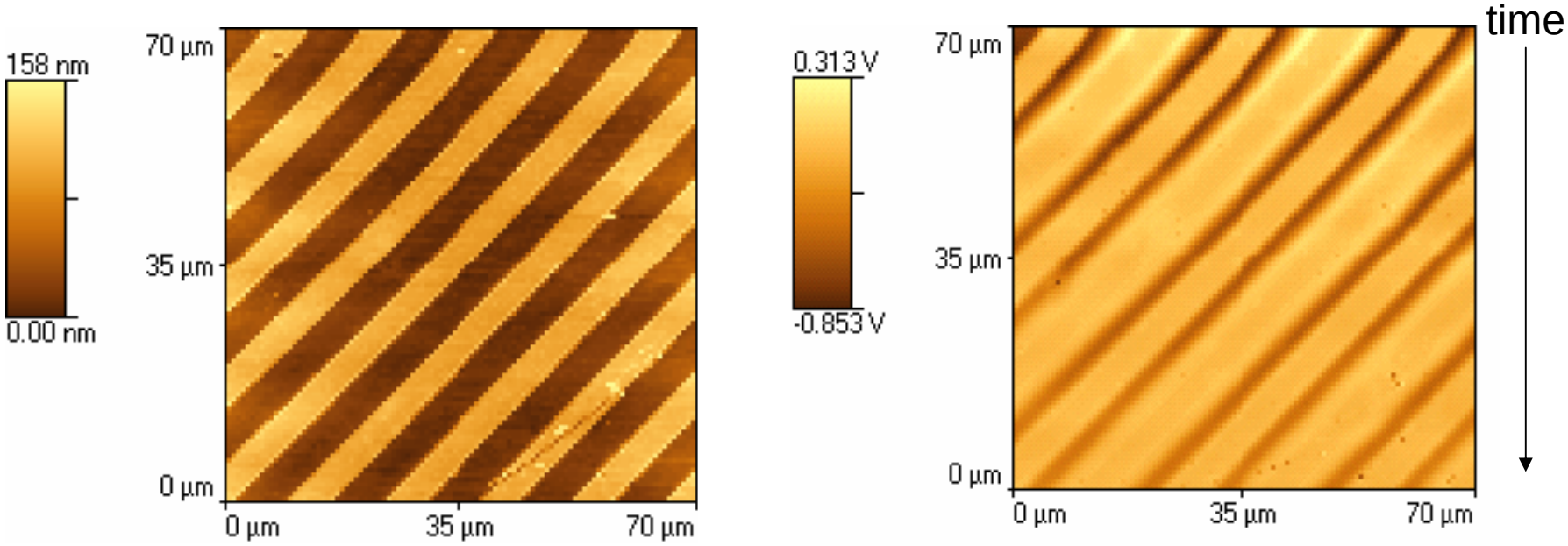
Scanning started immediately after electrode polarization.
Five consecutive scans, 10 minutes apart.

Time-dependence



Line-scans from the five consecutive SEPM images acquired under electrode bias.
The scanned lines are 10 microns below the top of each image.

Grounded electrodes

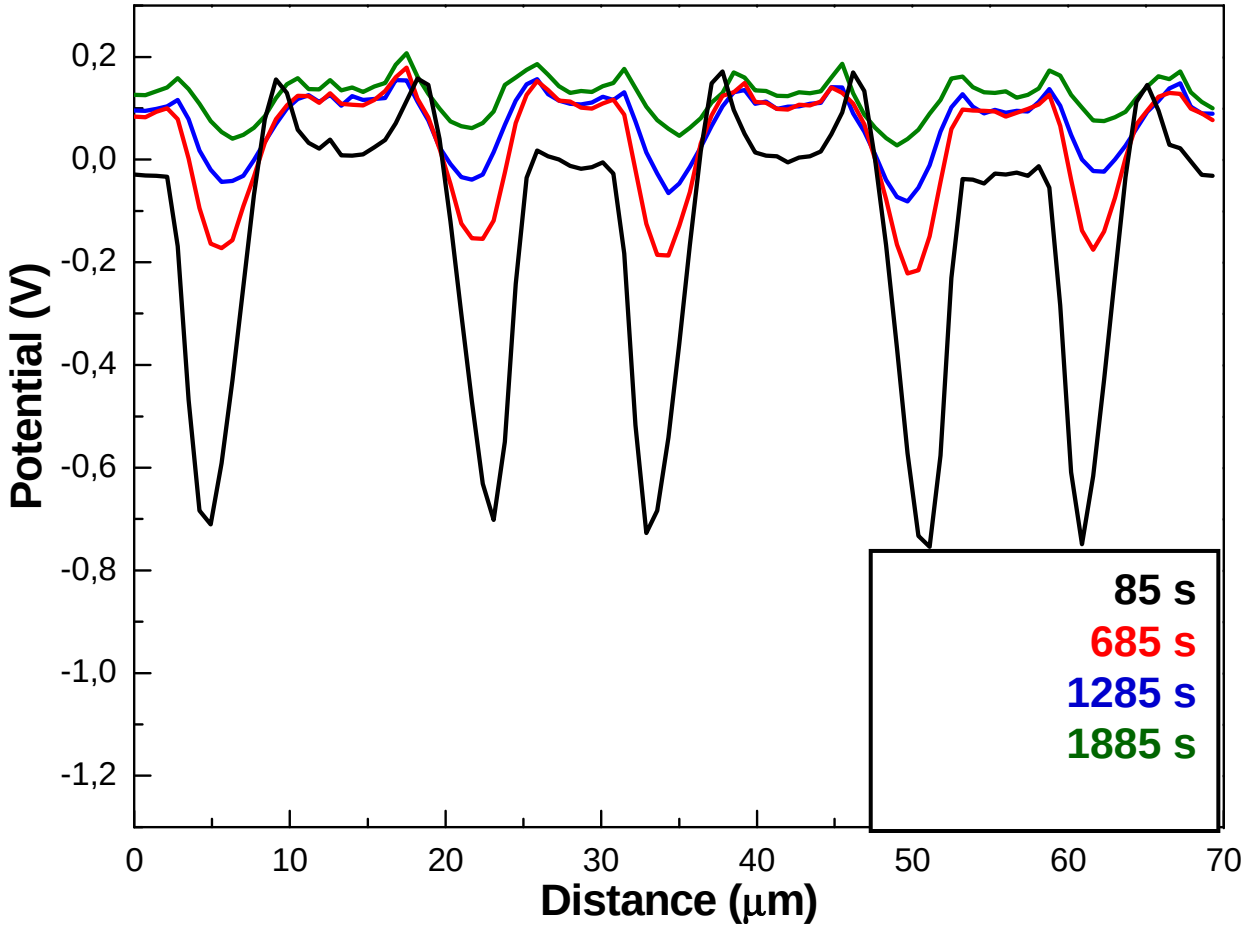


AFM

SEPM (grounded electrodes)

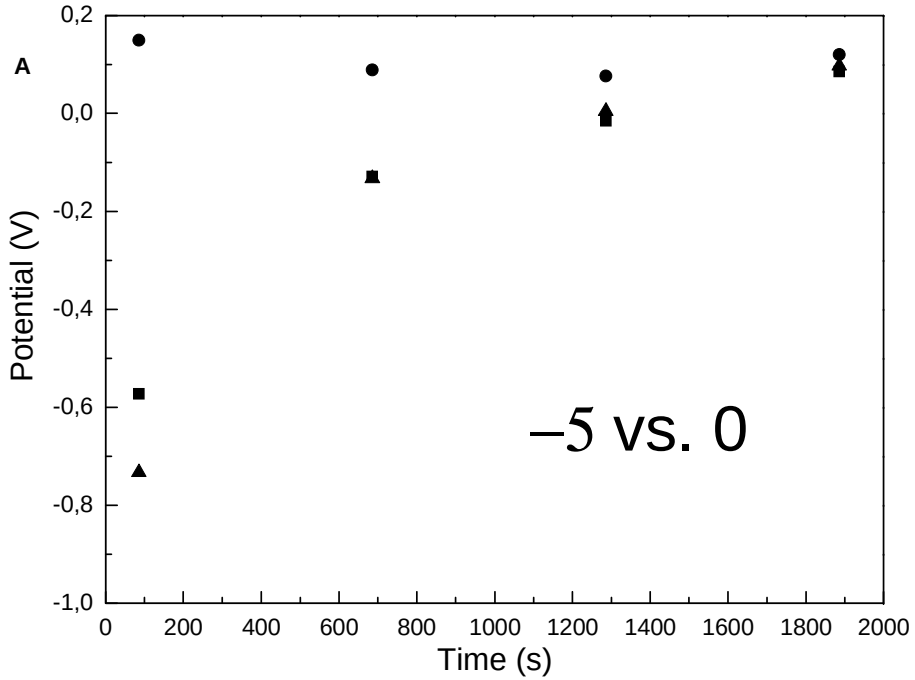
Scanning started immediately after electrode grounding.
Five consecutive scans, 10 minutes apart.

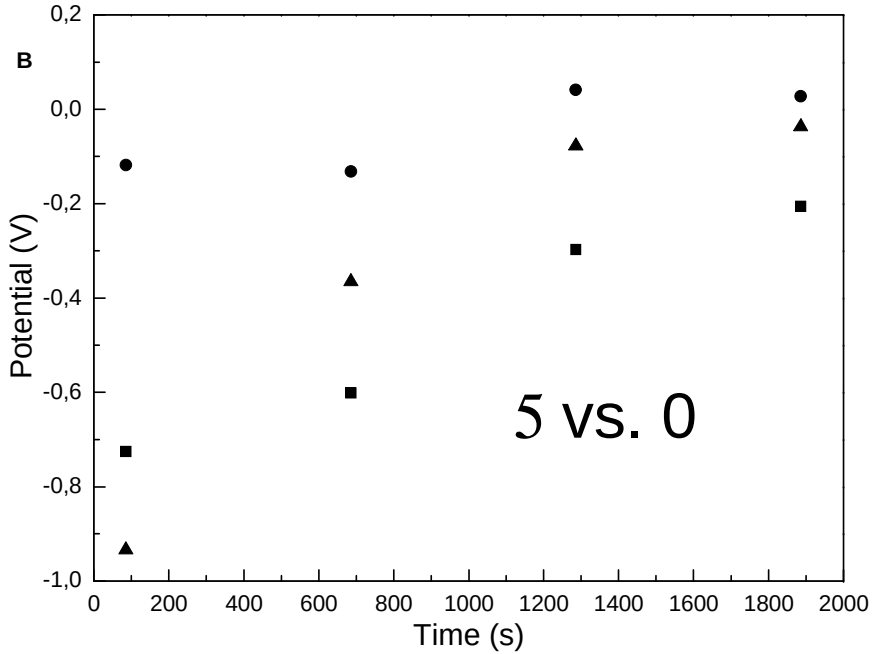
Slow dissipation



Line-scans from the four consecutive SEPM images acquired after grounding all electrodes.
The scanned lines are 10 microns below the top of each image.

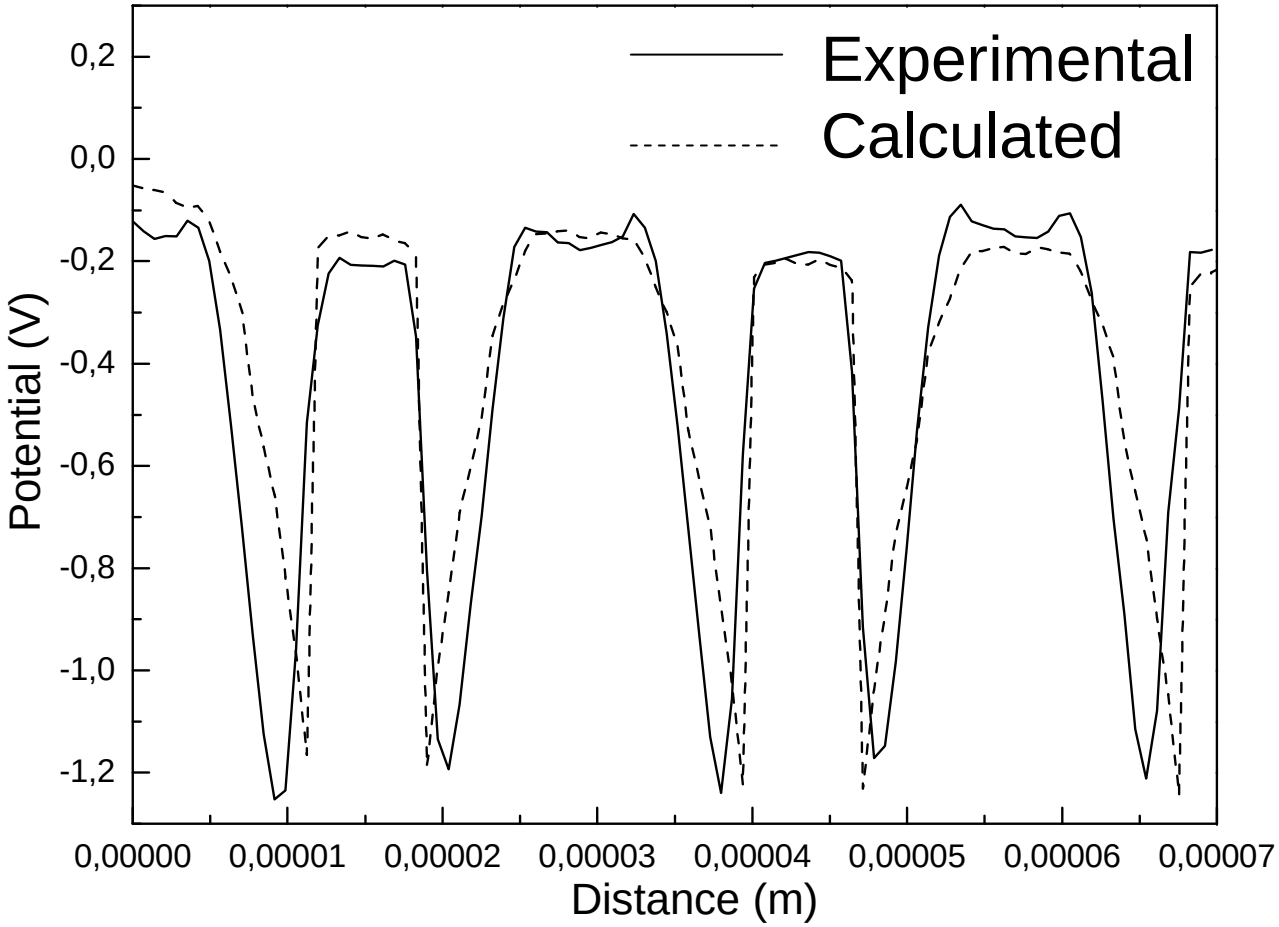
Relaxation





Circles: points adjacent to positive electrode.
Triangles: points adjacent to negative electrode.
Squares: points in the central area of the insulator stripes.

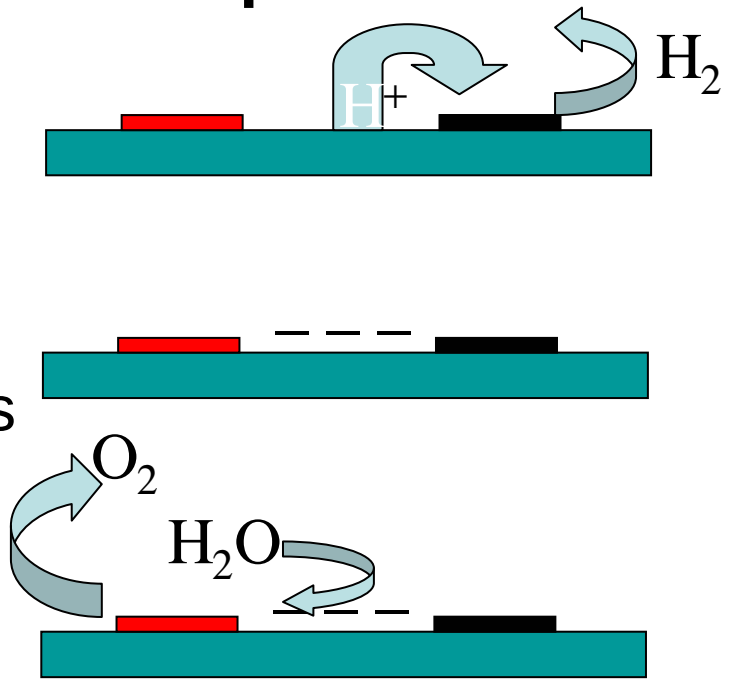
Potential simulation



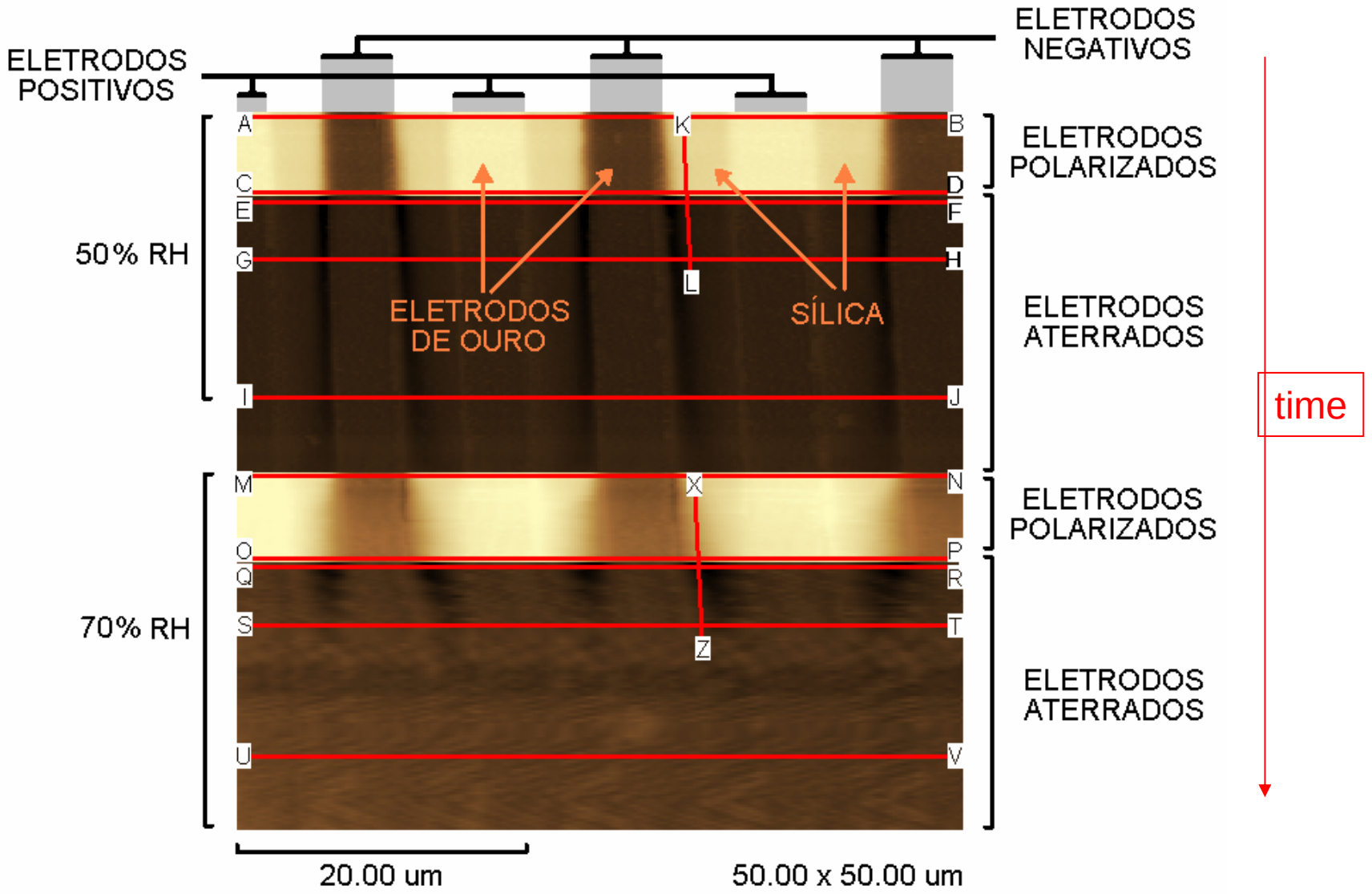
Typical surface charge concentration: <1 ppm:
A great challenge for any surface analytical method.

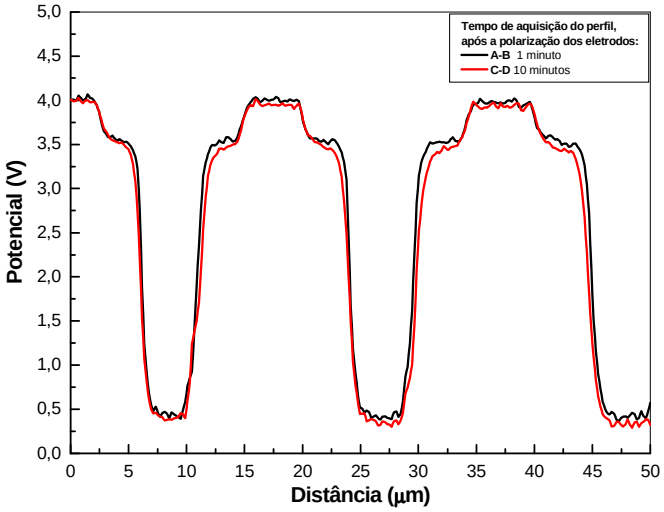
Model for charge build-up on silica

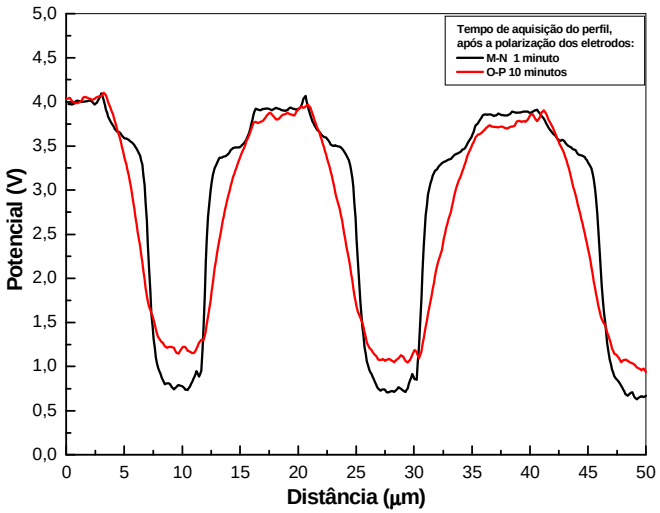
- Surface silanol groups: Si-O-H
- H^+ discharge on polarized electrodes
- Immobile Si-O^- groups persist, producing domains with excess negative charges
- Grounded electrodes: vapor adsorption followed by discharge of OH^-
- Verification: charge and discharge rates depend strongly on relative humidity



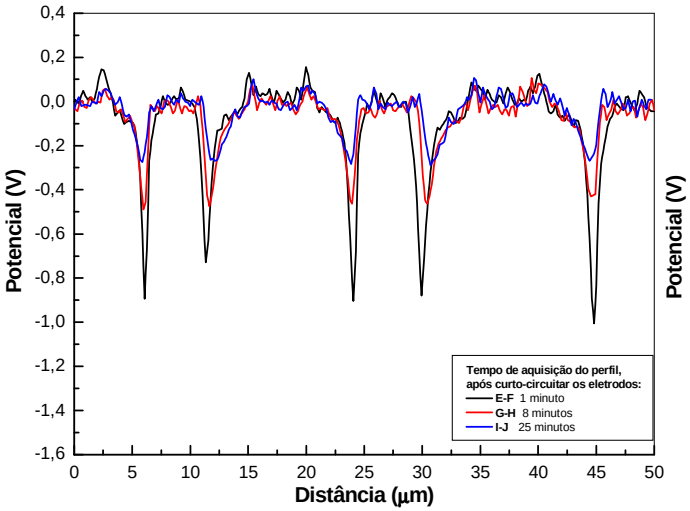
Variable RH effect

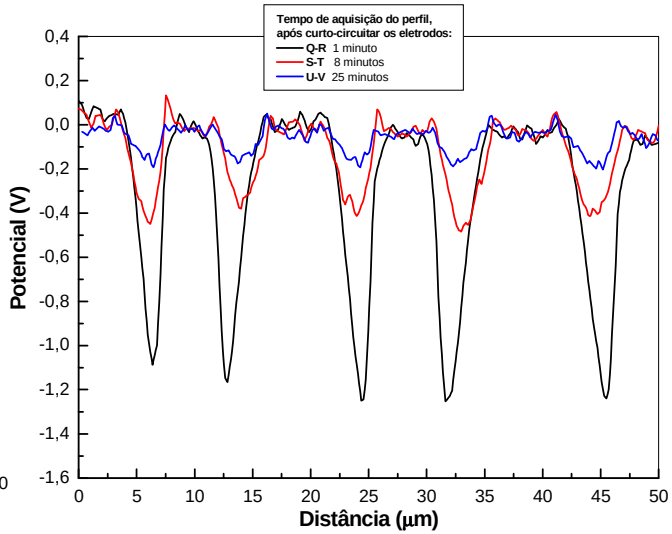


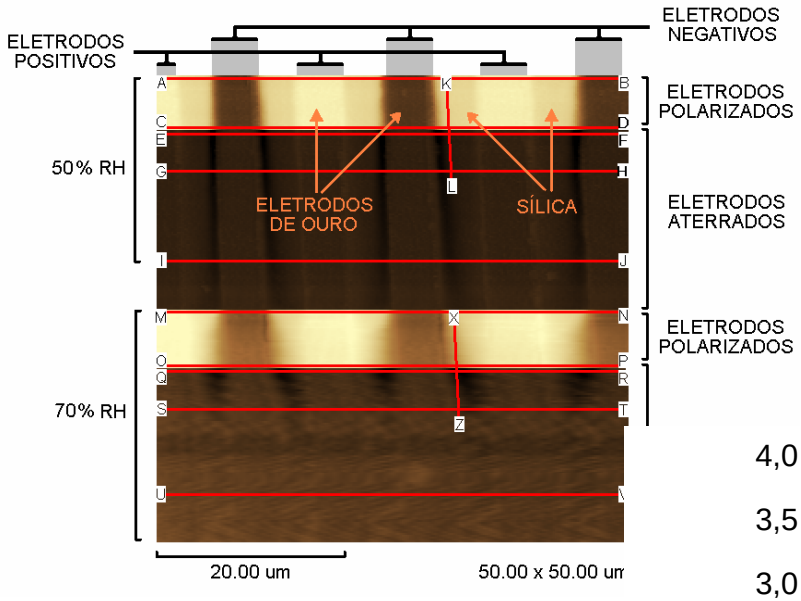




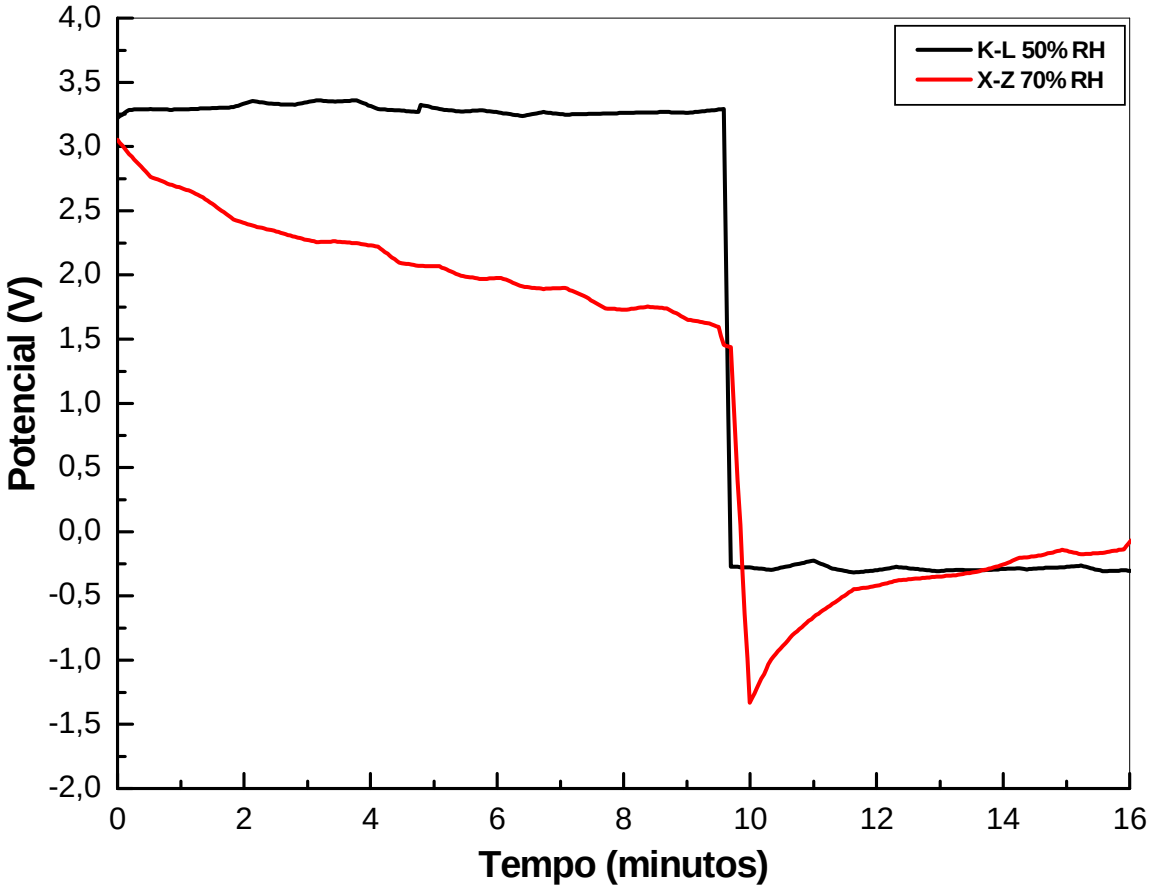
Faster change under high RH





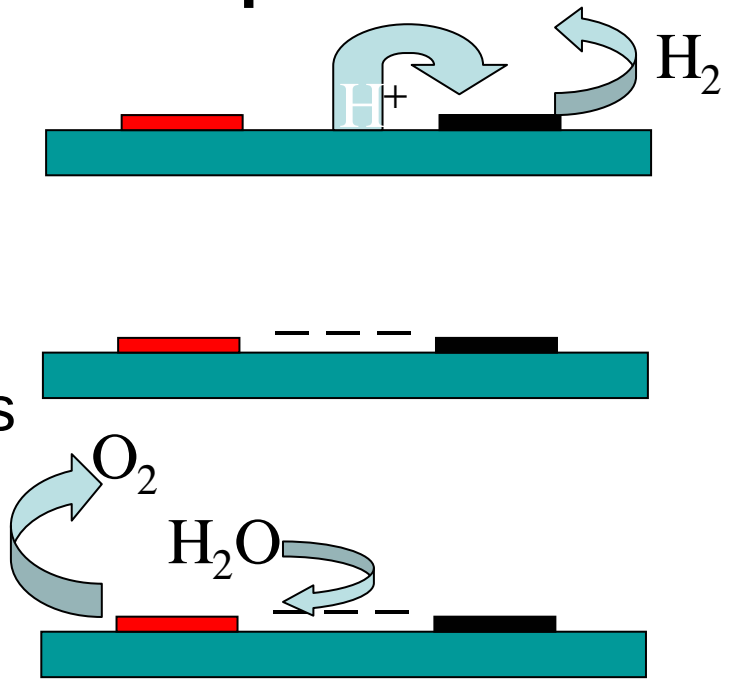


Charge build-up and dissipation are both faster under high RH



Model for charge build-up on silica

- Surface silanol groups: Si-O-H
- H^+ discharge on polarized electrodes
- Immobile Si-O^- groups persist, producing domains with excess negative charges
- Grounded electrodes: vapor adsorption followed by discharge of OH^-
- Verification: charge and discharge rates depend strongly on relative humidity

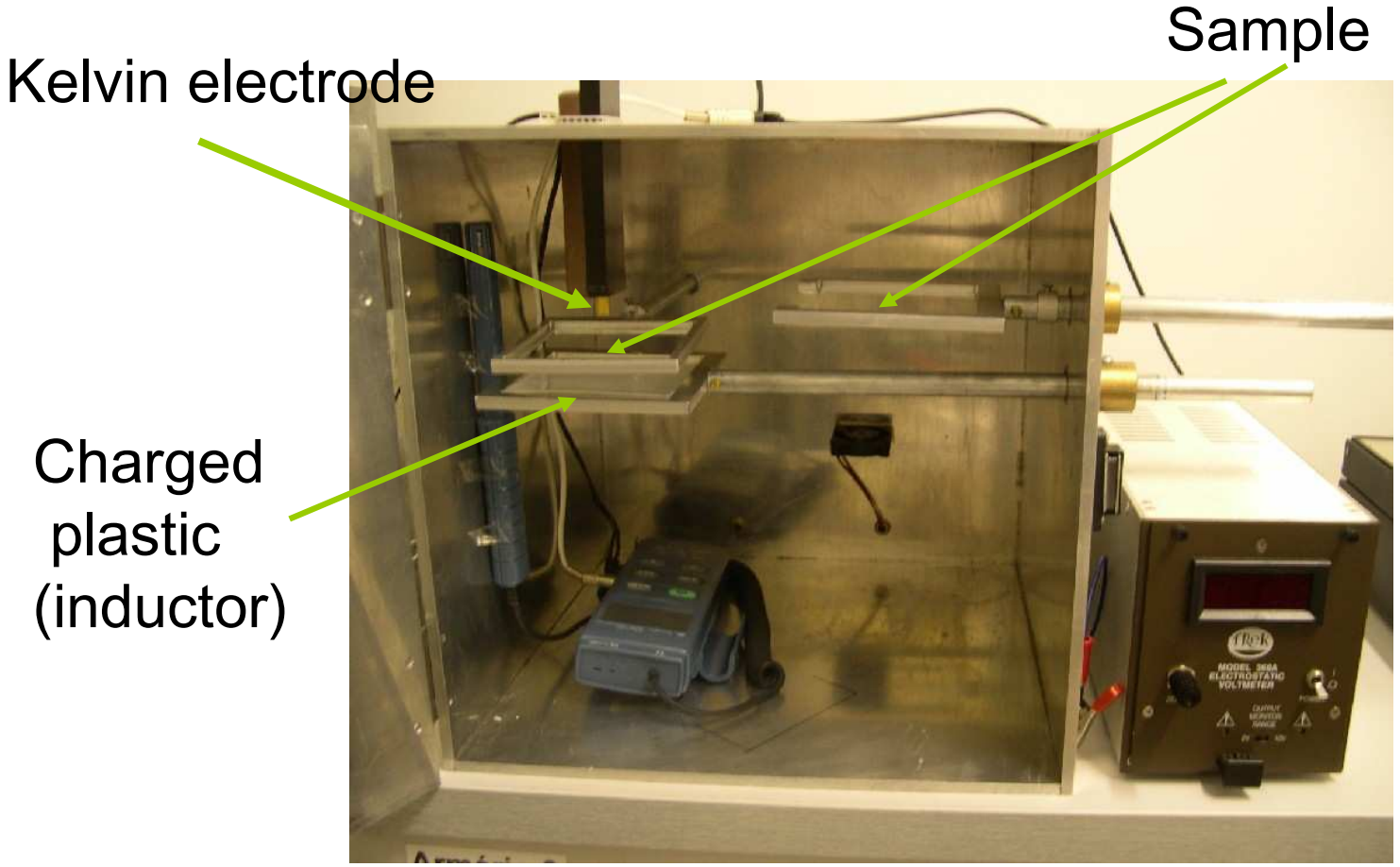


Charge induction in insulators

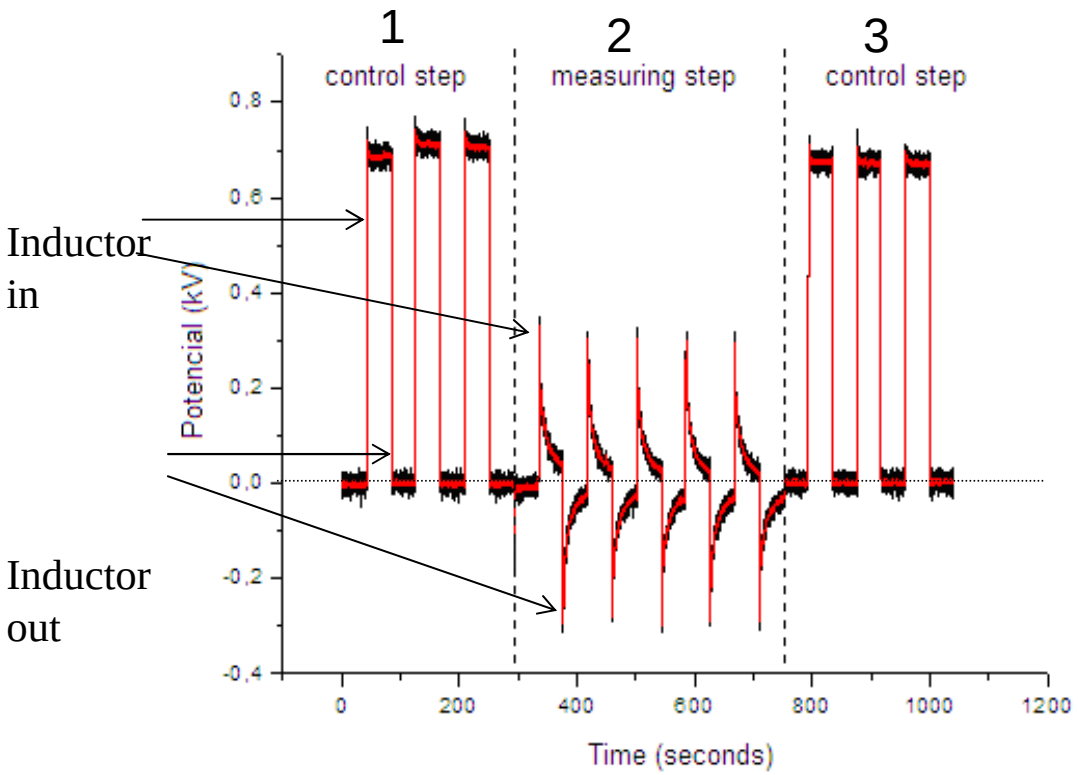
- In metals: electrons are displaced under an electric field and may be driven to/from the ground.

- In insulators: how do excess charges build up in the presence of a field?

New approach: charge induction experiments

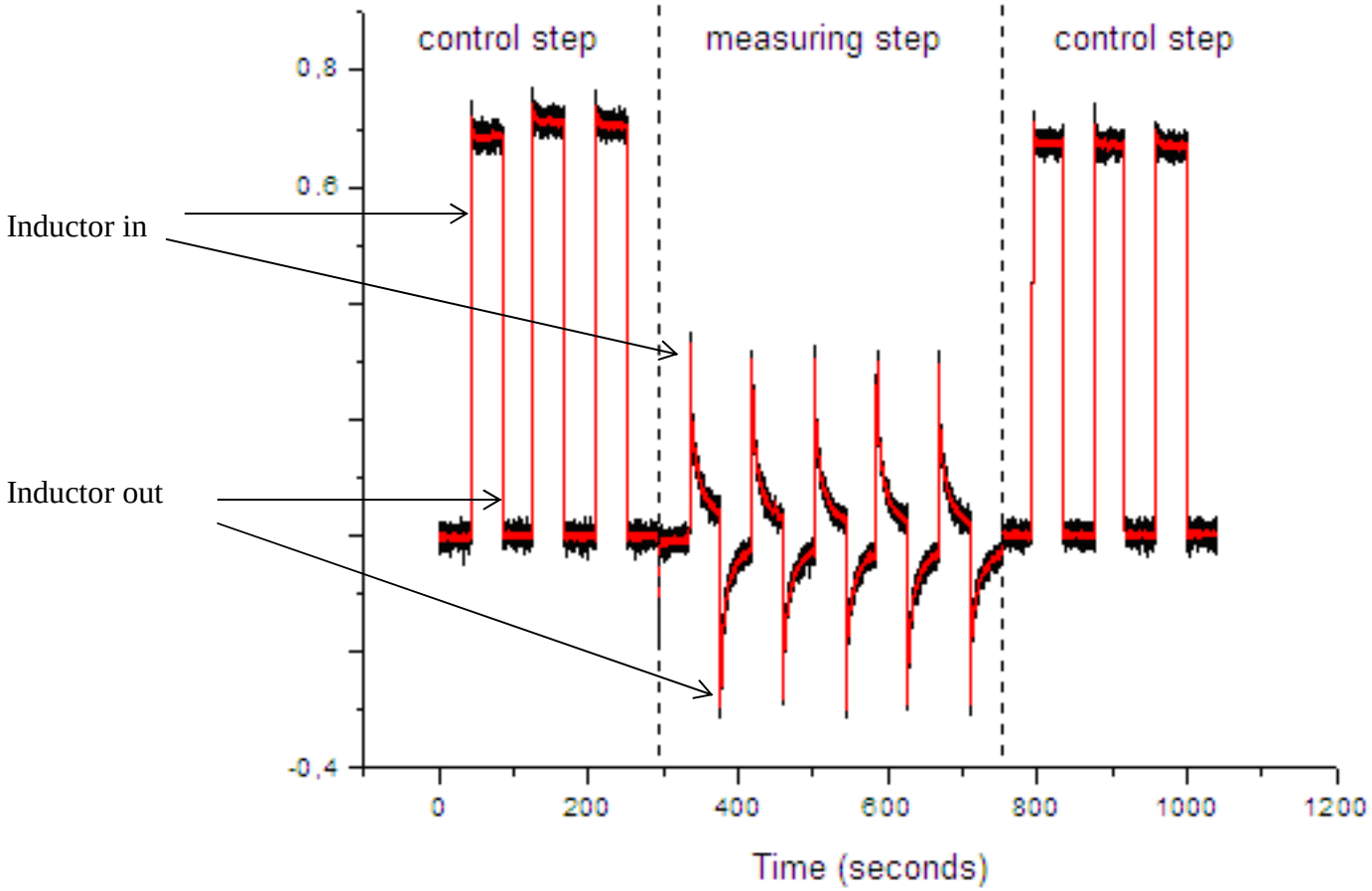


L.C.Soares et al., JBCS, *in press*



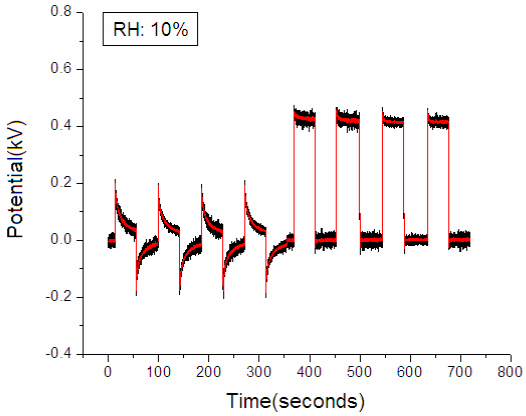
1) Charged inductor is moved in and out below the electrode.
2) Sample is introduced, charged inductor is moved in and out.
3) Sample is withdrawn, charged inductor in and out.

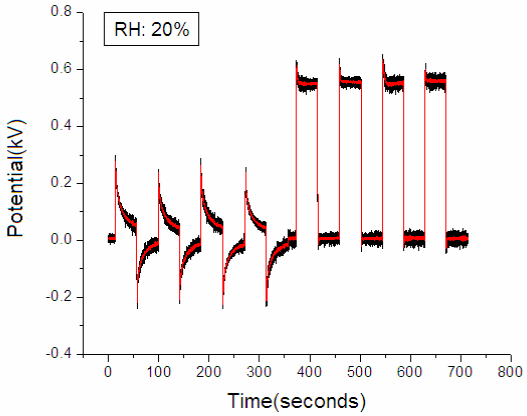
Charges opposite to inductor potential accumulate on glass

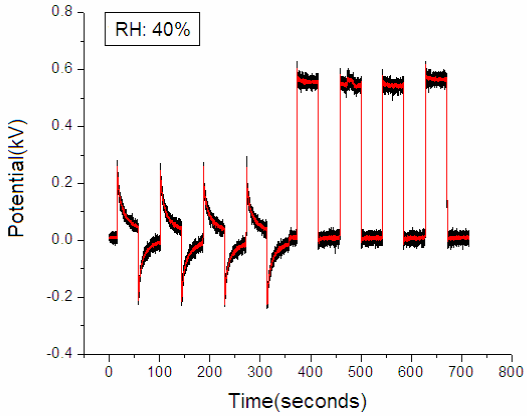


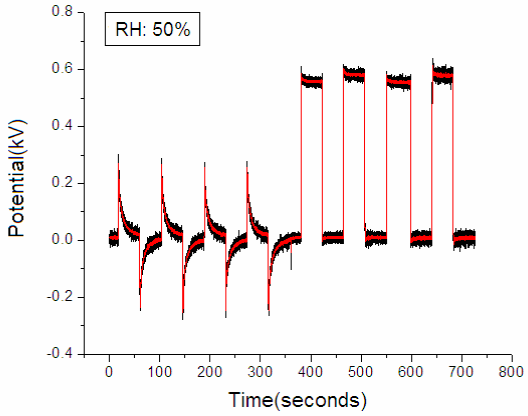
Kinetics of charge build-up and dissipation

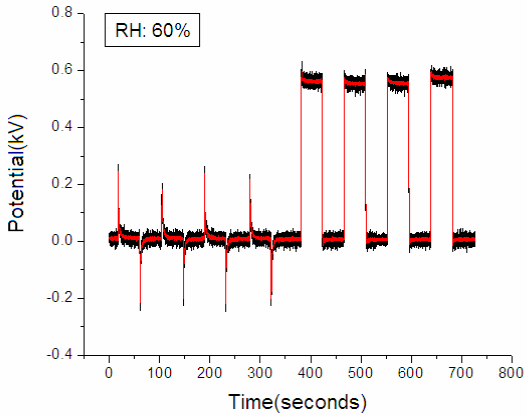
RH (%)	A=Maximum potential following insertion of inductor (V)	B=Minimum potential following inductor withdrawal (V)	C= Inductor potential (V)	A/C	B/C	Decay constant (k) after inductor insertion (s^{-1})	Decay constant (k) after inductor withdrawal (s^{-1})
70	-19 ± 2	24 ± 2	-280	-0.068	0.086	2.43	-------
60	-121 ± 11	138 ± 6	-443	-0.273	0.312	**0.841**	**1.01**
50	-213 ± 16	251 ± 9	-532	-0.400	0.472	**0.244**	**0.260**
40	-267 ± 2	268 ± 2	-552	-0.484	0.486	**0.136**	**0.142**
30	-261 ± 21	280 ± 1	-580	-0.450	0.483	**0.125**	**0.128**
20	-273 ± 6	282 ± 5	-594	-0.460	0.475	**0.122**	**0.124**
10	-284 ± 4	288 ± 4	-610	-0.466	0.472	**0.113**	**0.105**

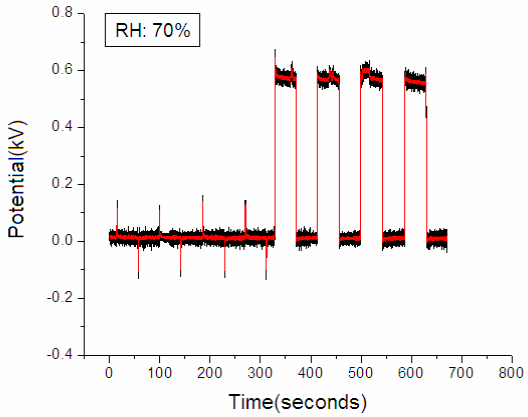




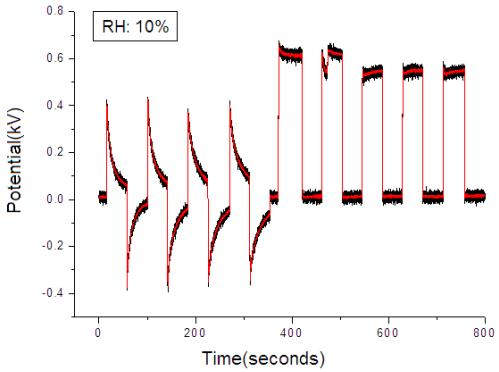


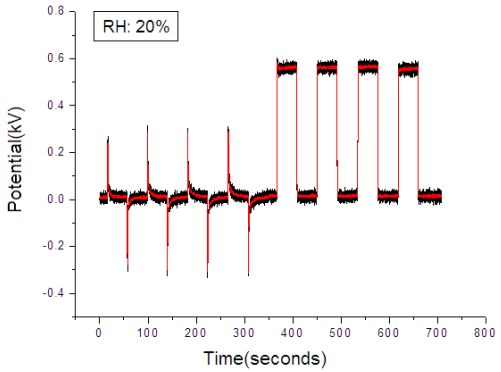


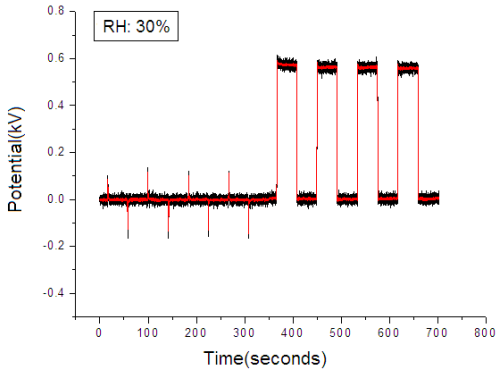


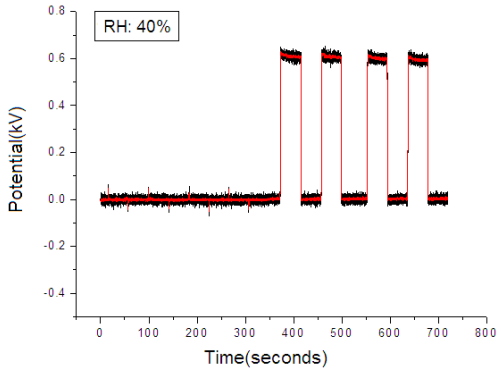


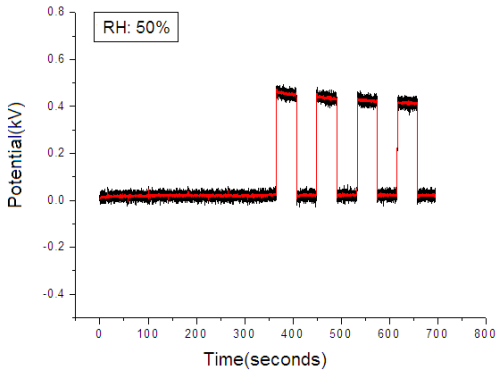
Faster shielding by glass at high relative humidity

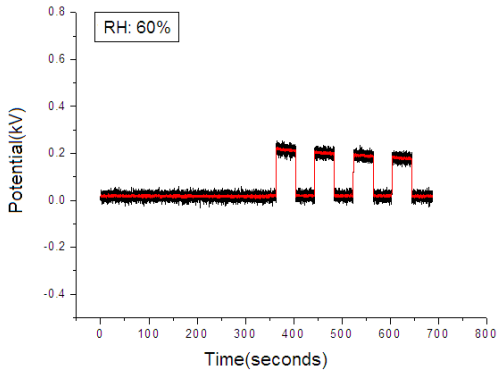




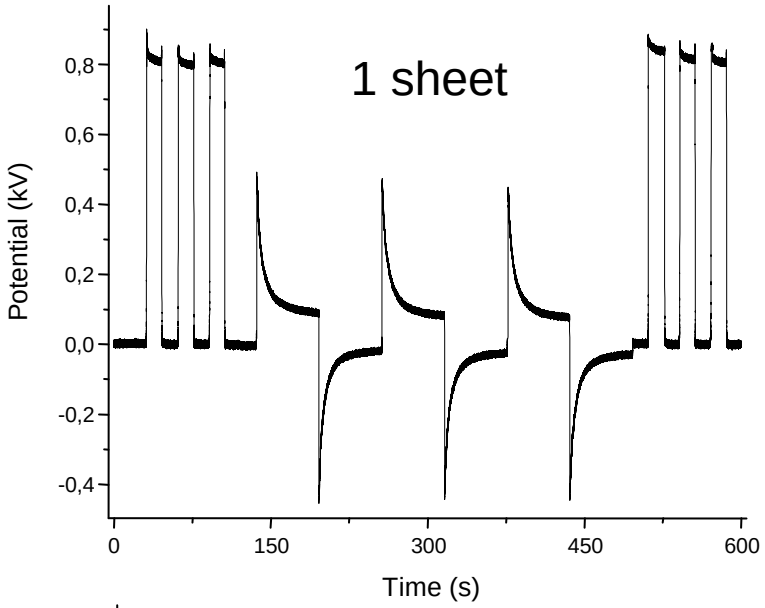


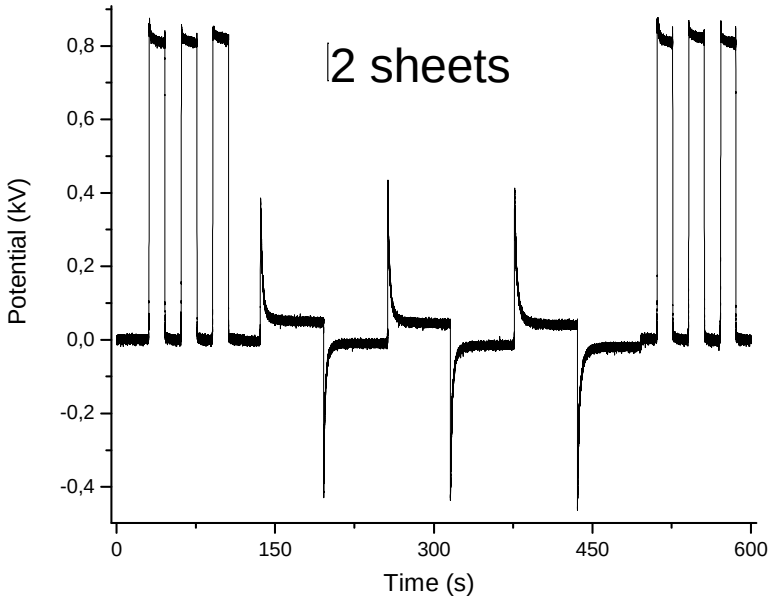


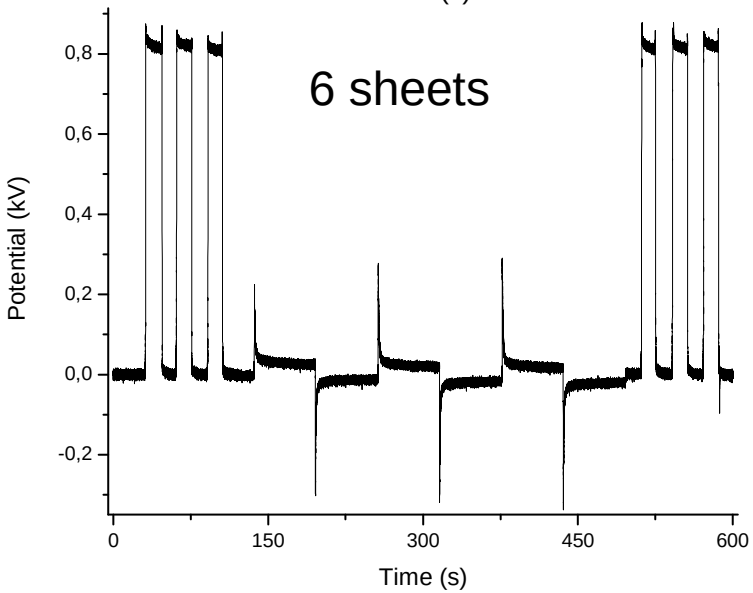


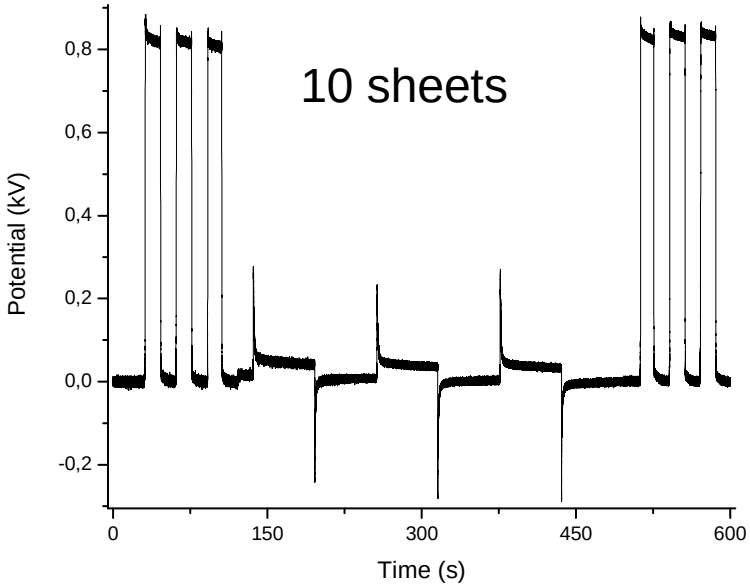


RH effect on cellulose film (filter paper)





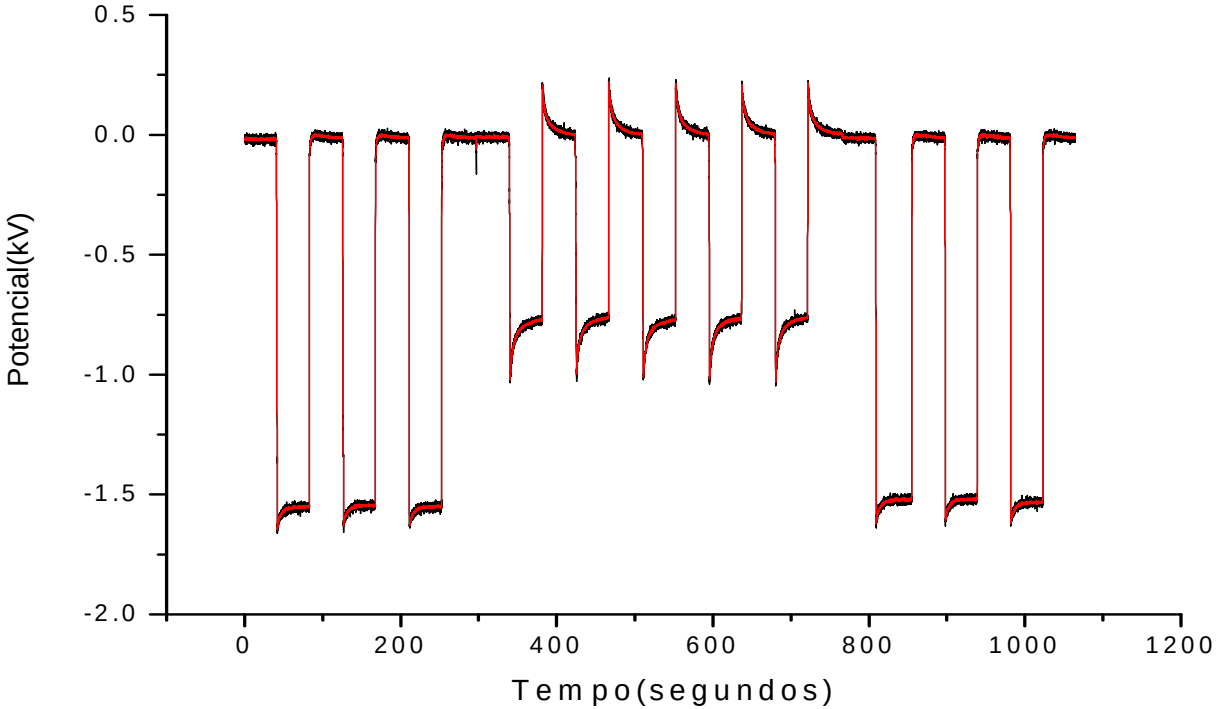


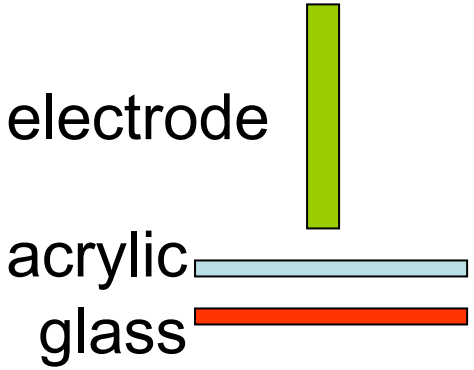


DEPENDENCE ON THE NUMBER OF SHEETS – 10% RH

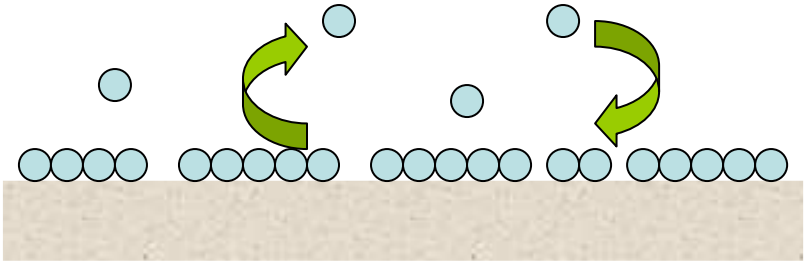
Changing the geometry

again, sample accumulates charges opposite to inductor





Model

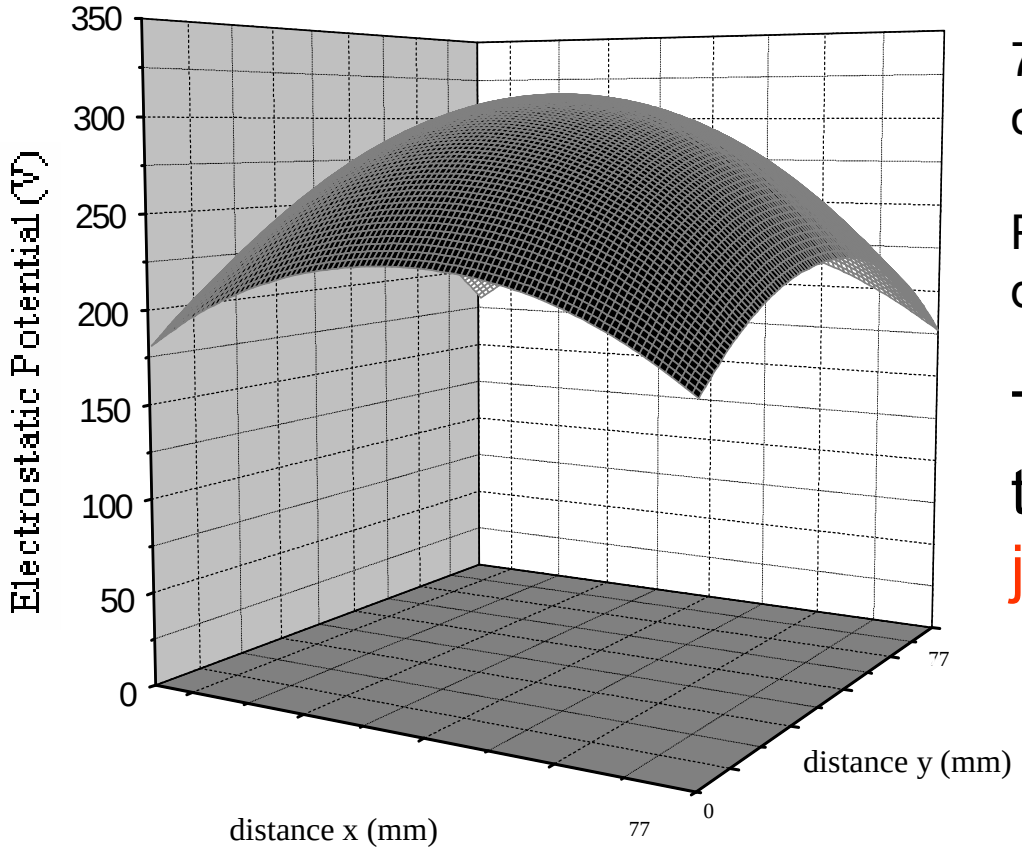


- Adsorbed water acquires excess positive or negative charge under V
  - $\mu_i = \mu_i^\circ + RT\,(\ln x) + zFV$
  - excess $[H^+]$ under negative V (or $[OH^-]$ under V>0)
- To reach equilibrium under V, charges are transferred to and from the sample
- Charge transfer is done by water vapor adsorption-desorption events
- Potential stability depends on the rate of adsorption-desorption events

Conclusion

- Both charging and discharging are faster at high RH.
- Charging and discharging rates are equal under constant RH (water adsorption equilibrium).
- Electrostatic charge acquisition and stability depends on water adsorption-desorption rates.
- Atmosphere exchanges electric charges with insulators.

Calculated potentials



7.7 x 7.7 cm^2 flat surface at a concentration of 1 charge/μm^2.

Potentials calculated at 1 cm distance from the surface.

The occupied fraction of the surface area is just 10^{-6} –10^{-7}.

Conclusions

- Chemical and electric map pictures are now available for some materials.
- Silica can be electrostatically patterned, with reproducible results.
  - *Excess negative charges in silica are surface silicate ions.*
- Induction in glass and paper: water vapor exchange with the atmosphere.
  - *Charging and discharging are both faster under high RH. Charge carriers are water cluster ions.*

Current targets

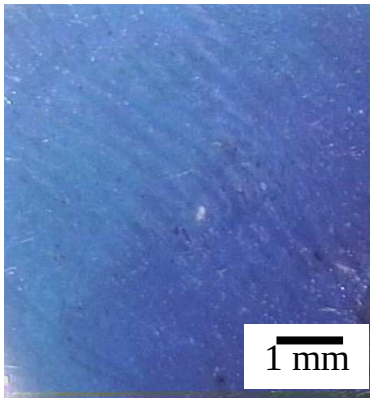
- New procedures for charge patterning of dielectrics
  - Nanoelectrolithography
- Improving materials properties
- Better predictability of materials interactions and compatibility
- Back to a dream from Tesla: can we use atmospheric electricity?

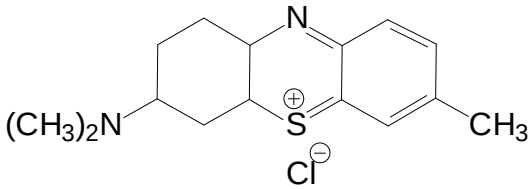
Applying these results...

- **Hydrophobic polymer modification by water-soluble agents, *e.g.* polystyrene dyeing (JPhysChem 2003, patent).**

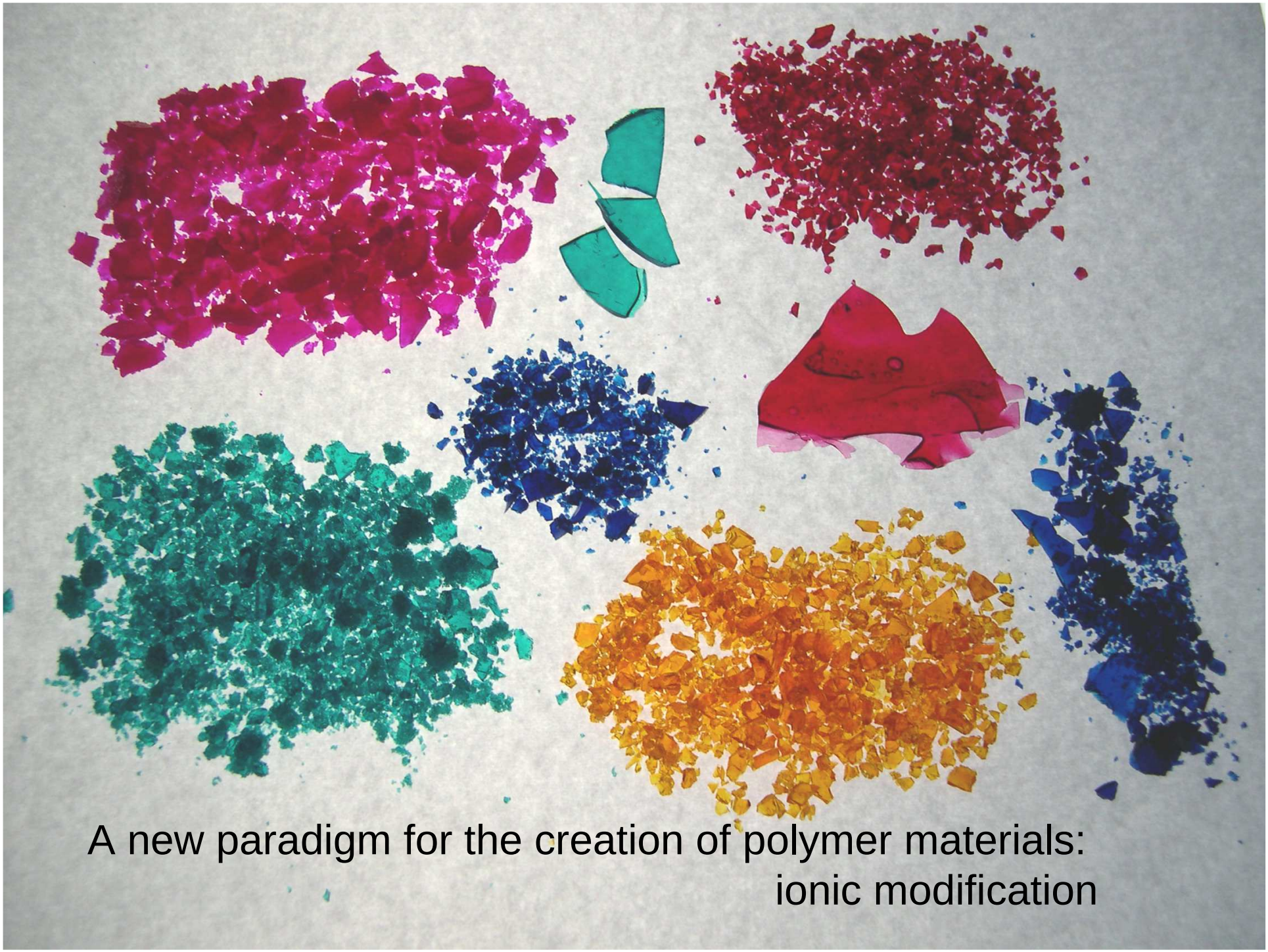
polystyrene + methylene blue

pellets + $CHCl_3$ tinted latex + $CHCl_3$





- **Other targets: thermoplastic rubbers, special adhesives.**


A new paradigm for the creation of polymer materials:
ionic modification

Polymer-clay nanocomposites: adhesion mediated by electrostatic interactions

F.Bragança, M.Rippel, L. Valadares, H. Schumacher, C. Leite and F.Galembeck

Universidade Estadual de Campinas, Campinas SP, Brazil

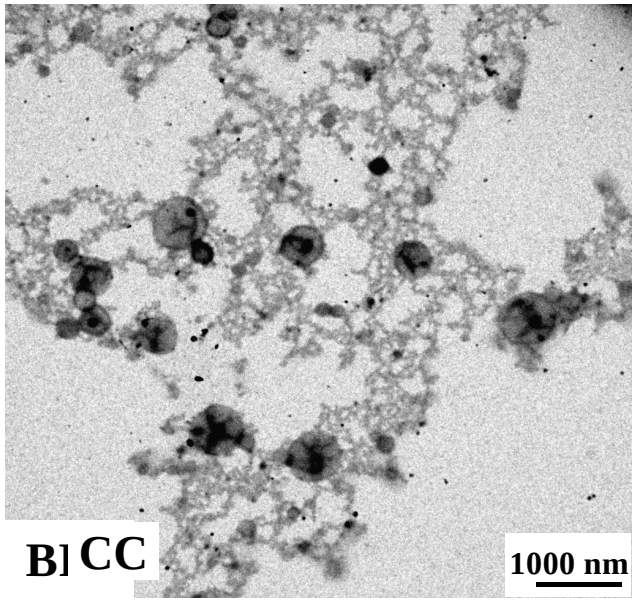
Synopsis

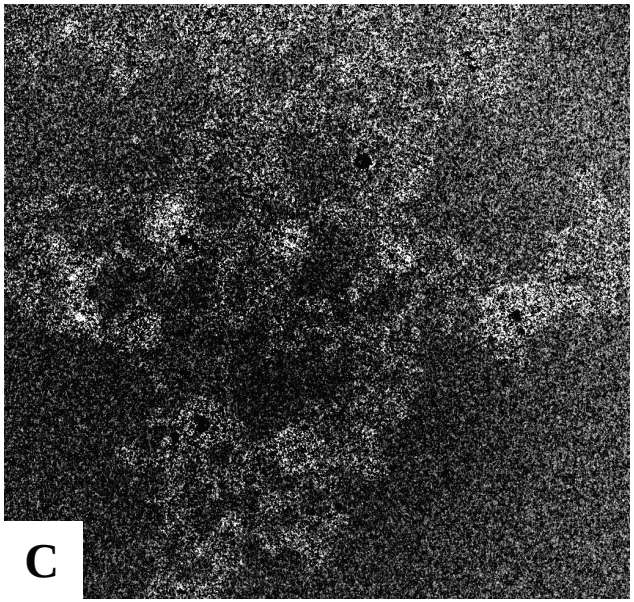
- Polymer-clay nanocomposites
- Natural rubber’s secret: a nanocomposite
- Polymer latex + clay aqueous dispersion
- Properties
- Electrostatic adhesion
- Ionic modulation of properties

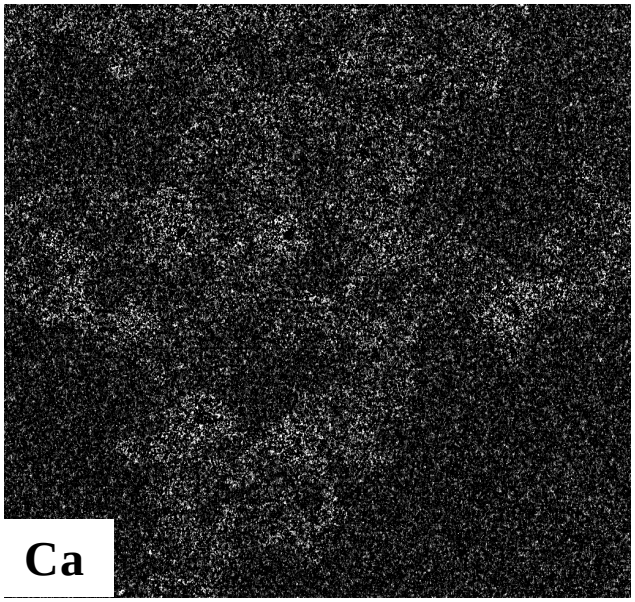
Natural rubber: open questions

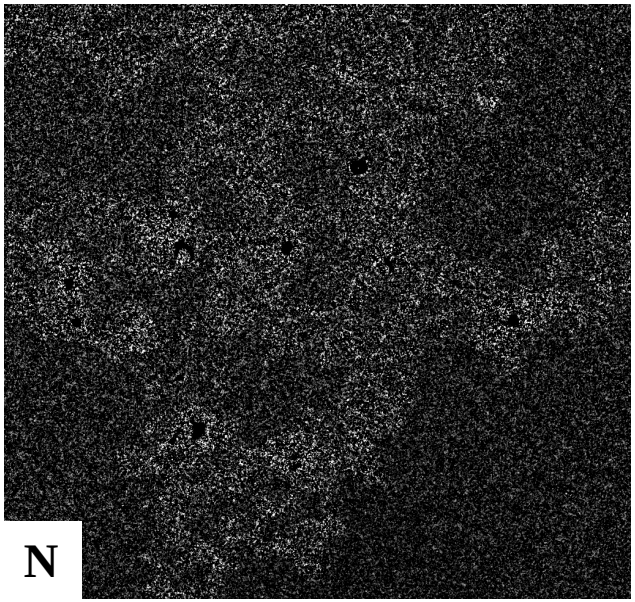
- Why natural rubber is superior to poly(cis-isoprene), in many aspects?
- Many researchers believe that proteins found in natural rubber account for its properties, but deproteinized rubber properties are similar to those of NR.
- Latex contains many elements, beyond C and H. What is their role?
- What is the nature of NR gel?

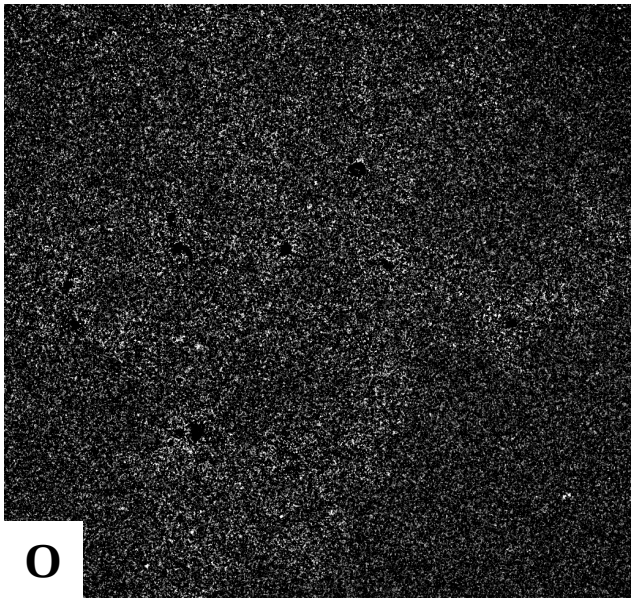
Elemental distribution (ESI-TEM)

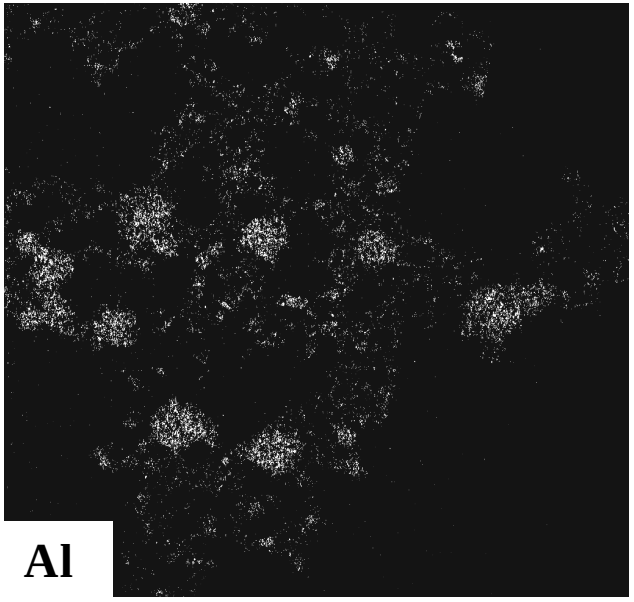




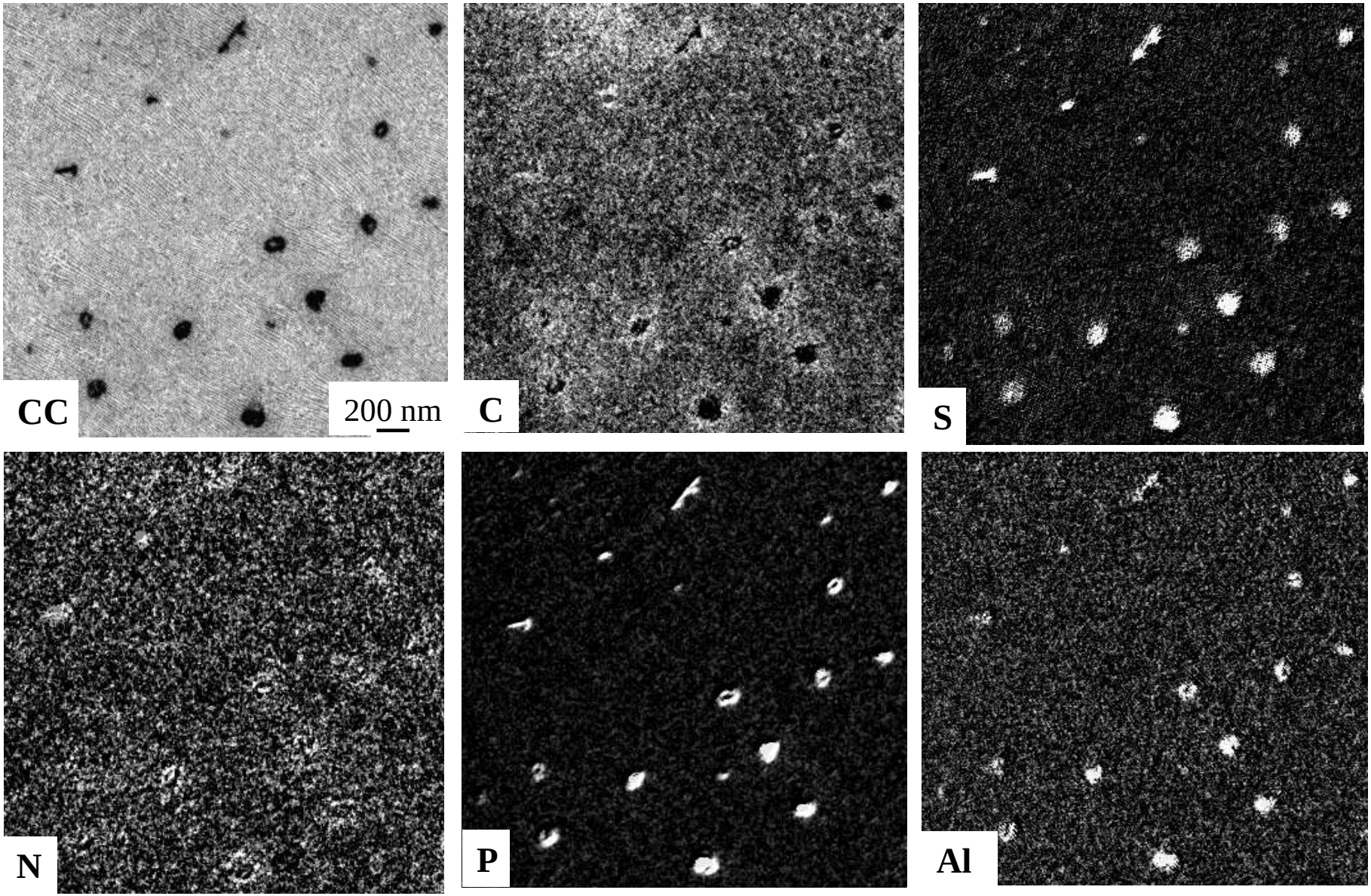




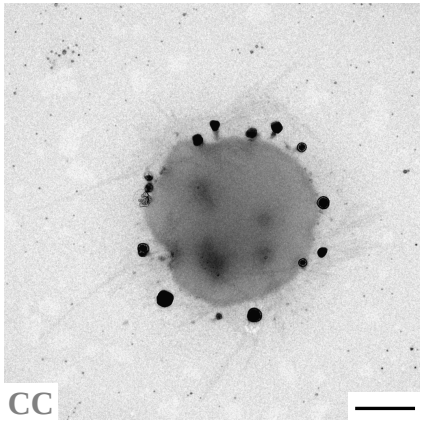


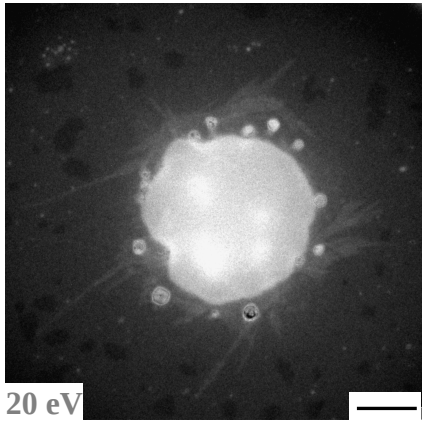


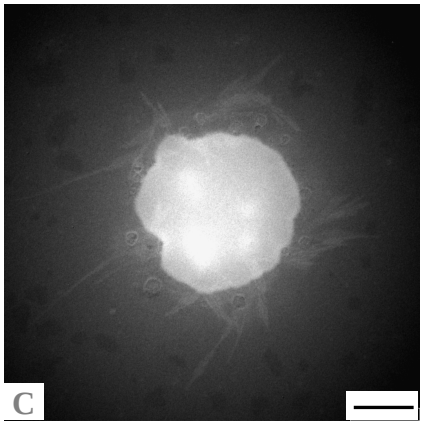
Elemental distribution

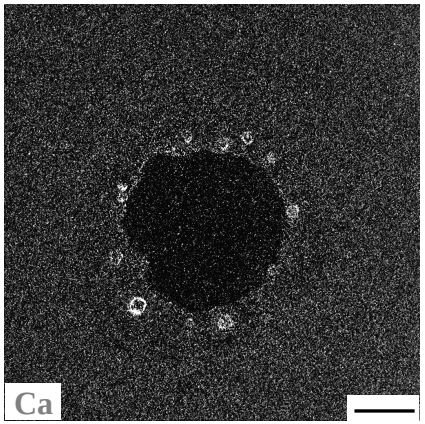


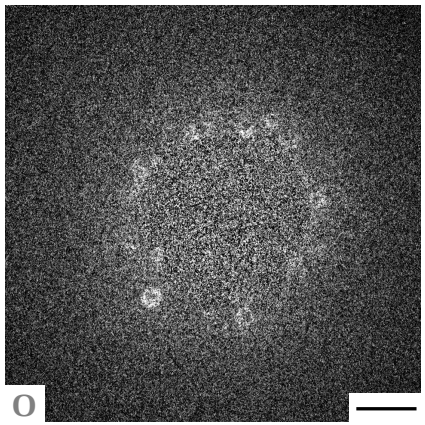
Aged latex particle

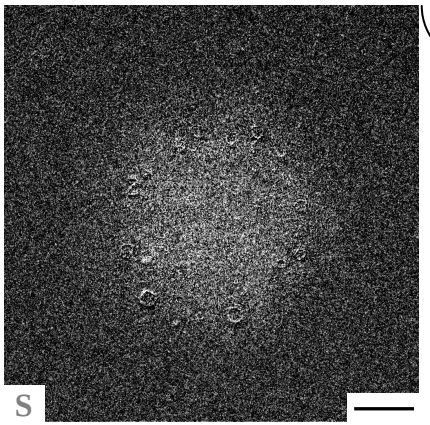




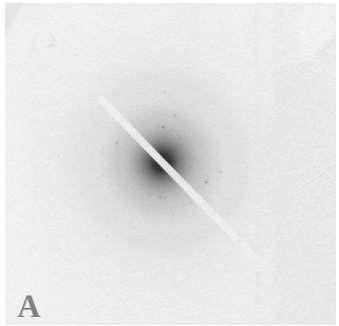


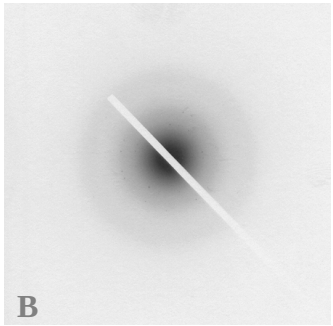


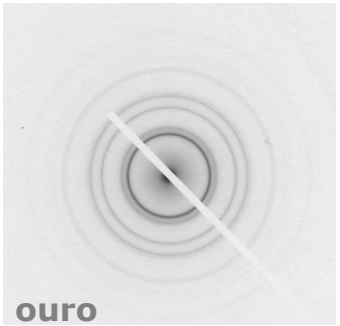




Slow formation of crystallites







Electron diffraction patterns

$2CaSO_4.H_2O$, $2CaSO_4.4H_2O$ ou $2NaSO_4.CaSO_4$

Nature’s secret

Natural rubber is a natural nanocomposite.

Thus, its mechanical properties are not matched by any synthetic rubber.

Polymer-layered silicate nanocomposites

Improved properties:

- Mechanical: modulus, strength
- Lower gas permeability
- Uniform films
- Greater thermal resistance
- Increased fire resistance

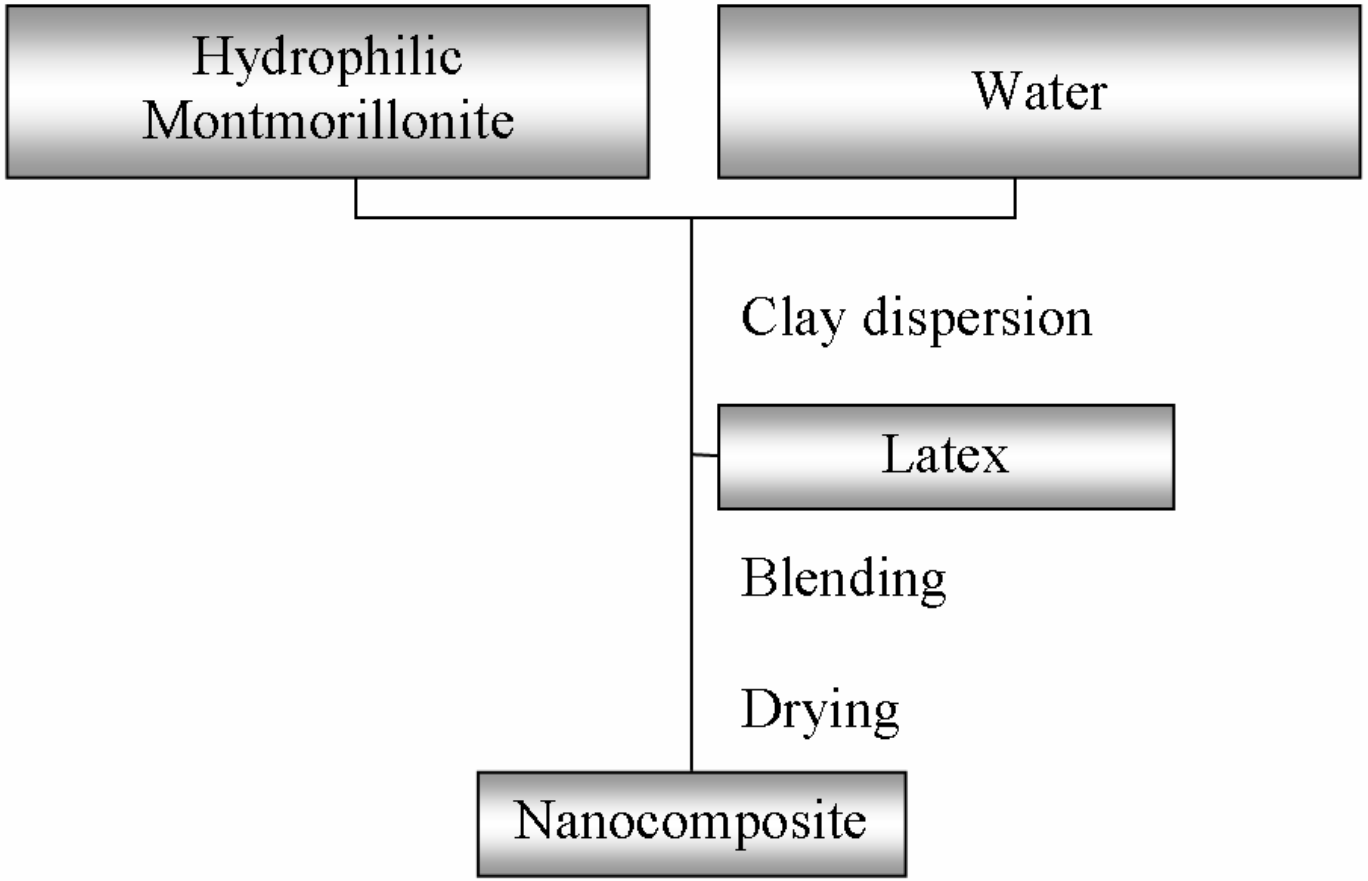
Singh, S.; Ray, S.S. *J. Nanosci. Nanotech.* **2007**, 7, 2596-2615.
Vasa, P.; Ayyub, P.; Singh, B.P. *Appl. Phys. Letters,* **2005**, 87, Art. No. 063104
Siengchin, S.; Karger-Kocsis, J.; Thomann, R. *J. Appl Polym. Sci.* **2007**, 105, 2963-2972.
Vyazovkin, S.; Dranca, I.; Fan, X.W.; *et al. J. Phys. Chem. B,* **2004**, 108, 11672-11679.

Preparation methods

- Intercalation of polymer in solution
- *In situ* intercalative polymerization
- Melt intercalation

Ramanathan, T.; Stankovich, S.; Dikin, D.A.; *et al*. *J. Polym. Sci. Part B-Polym. Phys*. **2007**, 45, 2097.
Ray, S.; Galgali, G.; Lele, A.; Sivaram, S. *J. Polym. Sci. Part A-Polym Chem.* **2005**, 43, 304.
Murugan, A.V.; Quintin, M.; Delville, M.H.; *et al*. *J. Mater. Res.* **2006**, 21, 112.
Shah, R.K.; Paul, D.R.; *Polymer*, **2004**, 45, 2991.

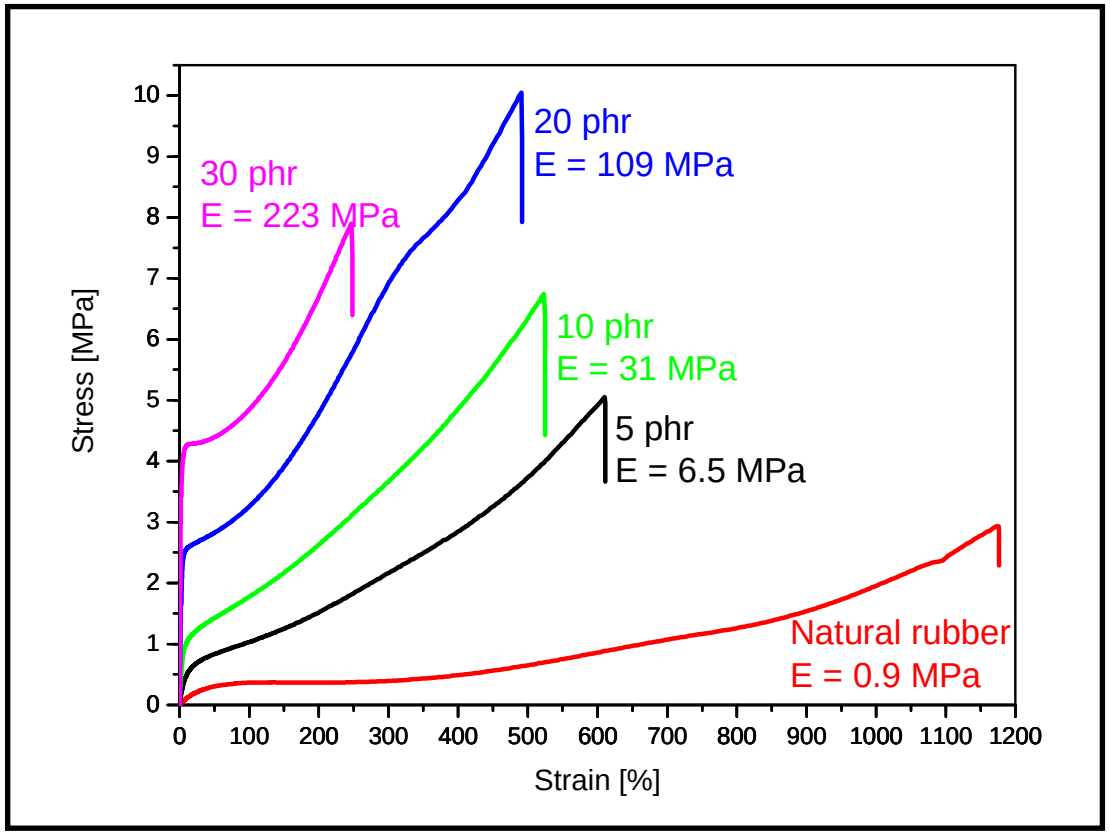
Preparation of nanocomposites in aqueous media using latex



Varghese, S., Karger-Kocsis, J., *Polymer*, **2003**, 44, 4921.
Wu, Y.P., Wang, Y.Q., Zhang H.F. *et al. J. Compos. Sci. Tech.* **2005**, 65, 1195
Valadares, L. F., Leite, C. A. P., Galembeck, F., *Polymer*, **2006**, 47, 672.
Valadares, L. F., Murakami, M. M., Rippel, M. M., Galembeck, F., PI0301193-3, **INPI**, 2003.

Natural rubber nanocomposites mechanical properties

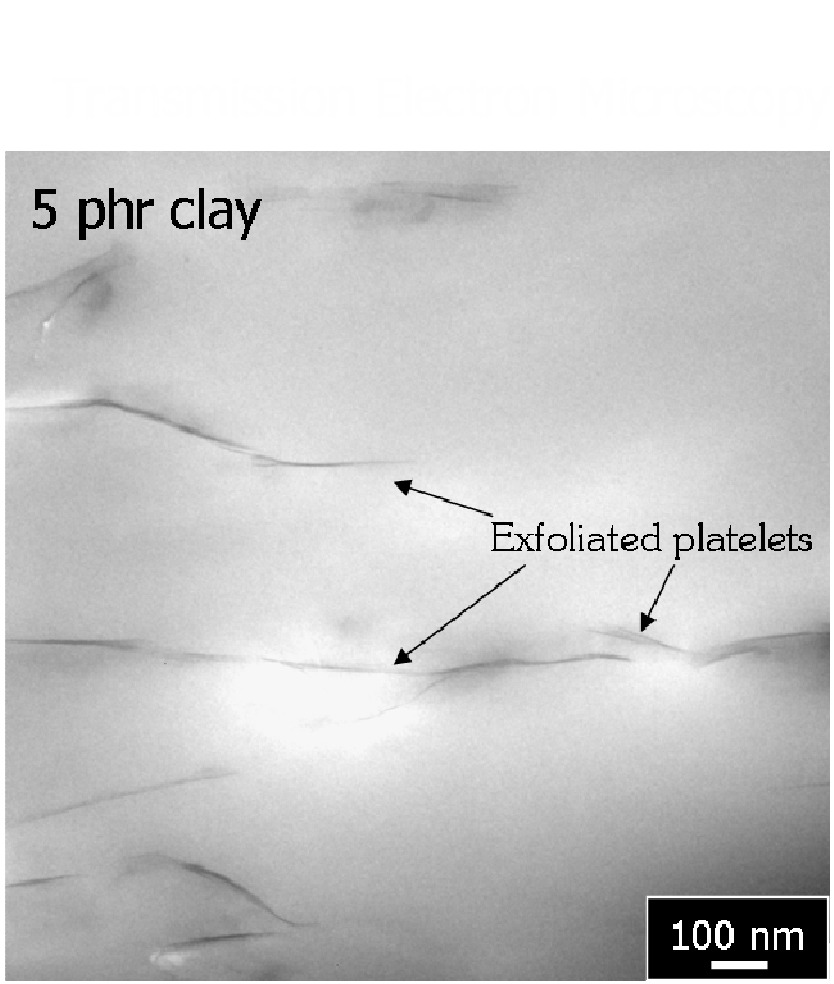
Mechanical testing of natural rubber-montmorillonite nanocomposites

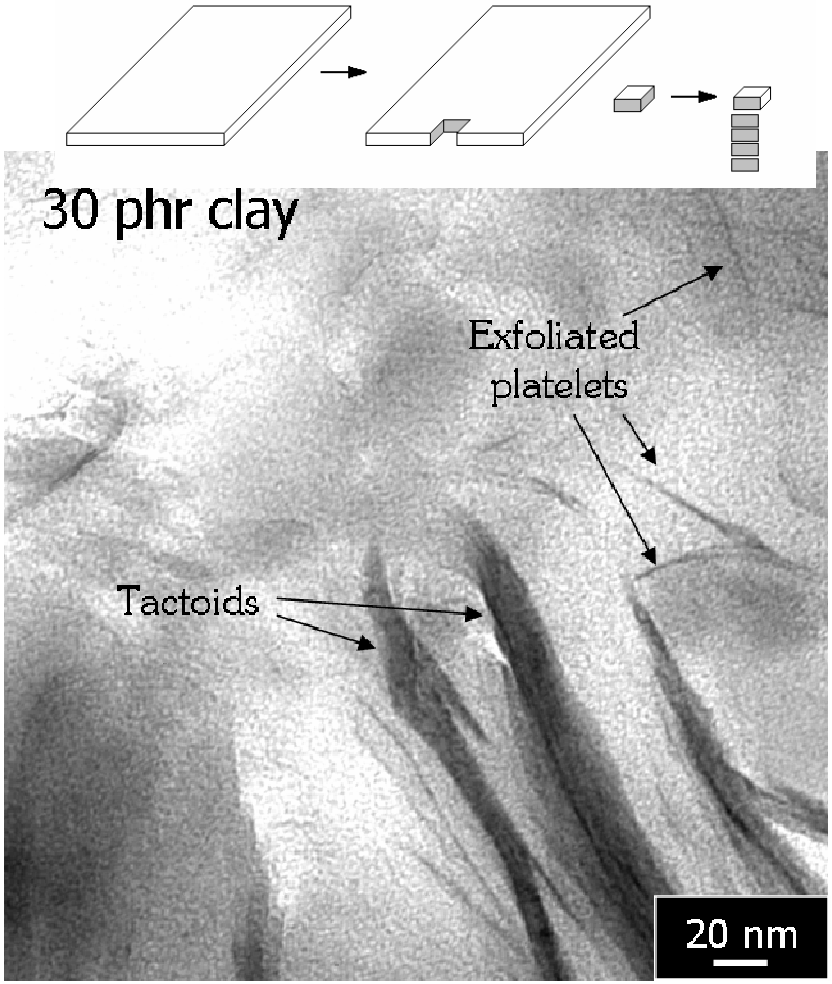


- Modulus: 250 times higher
- Stress under breaking: 2.5 times higher

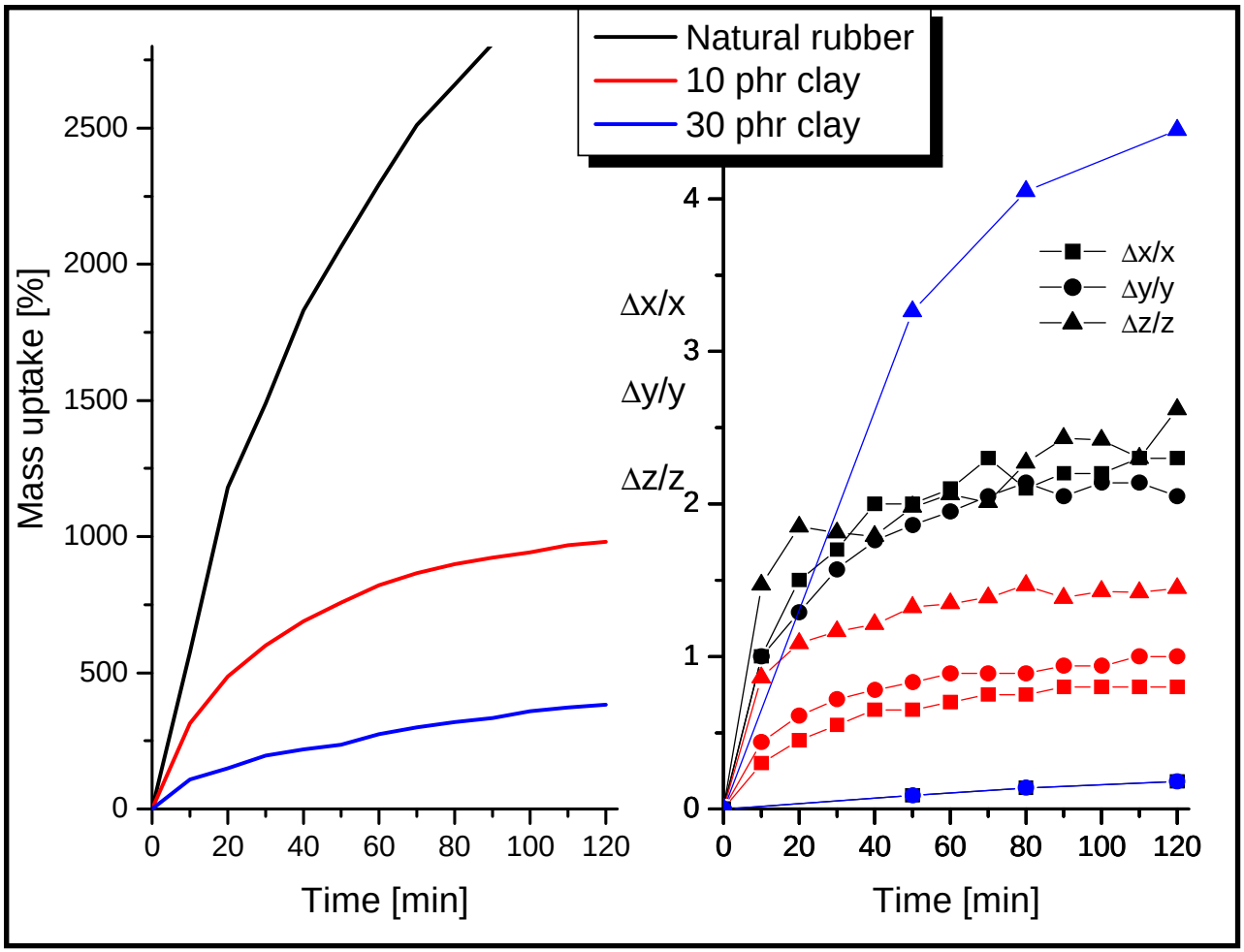
Valadares, L. F., Leite, C. A. P., Galembeck, F., **Polymer**, 2006, 47, 672.

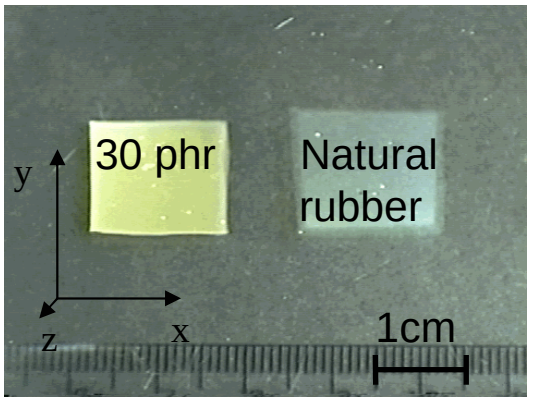
Clay within rubber





Lower xylene swelling Anisotropy



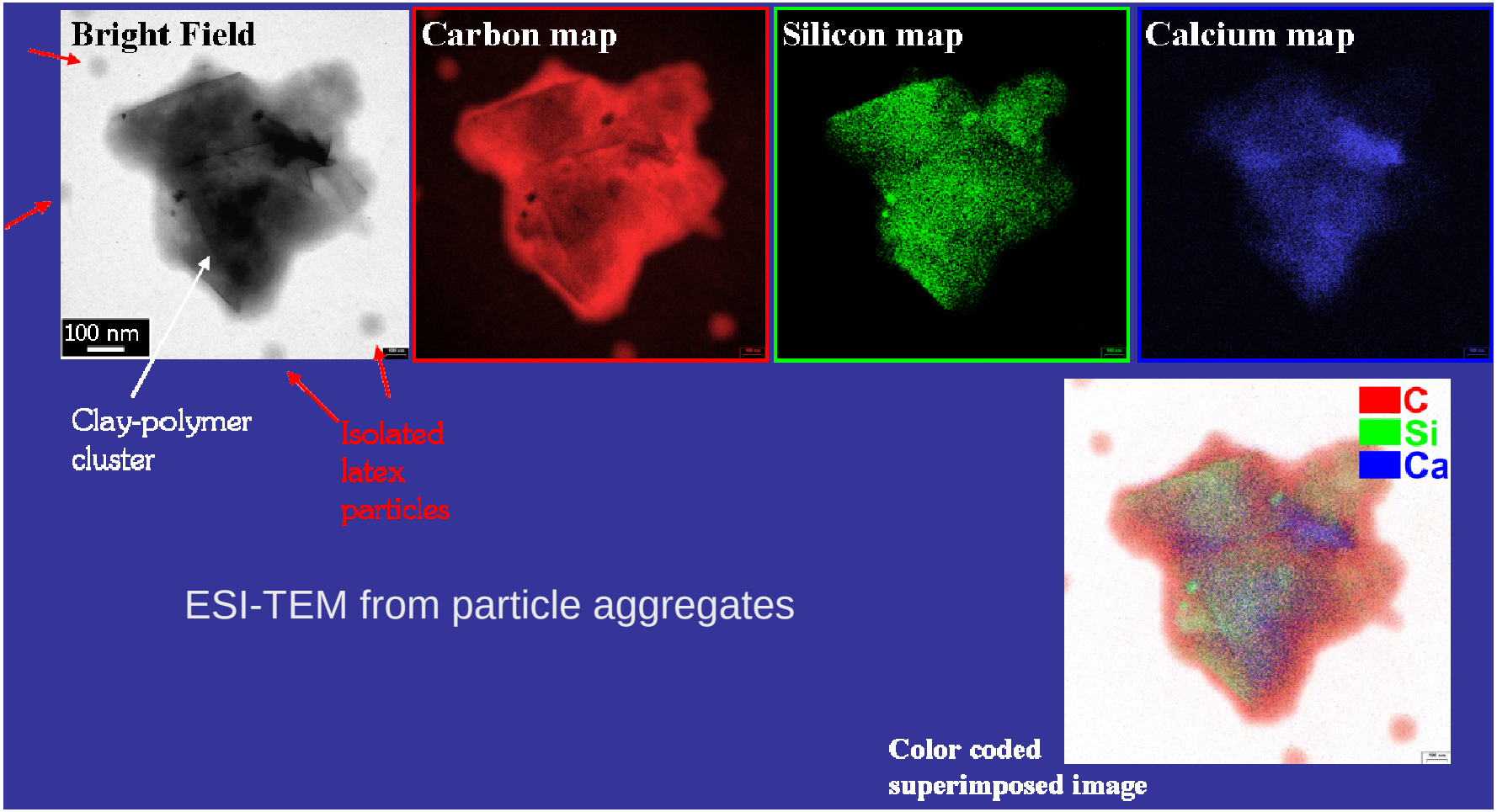


(phr = per hundred rubber)

Formation and stability: hypotheses

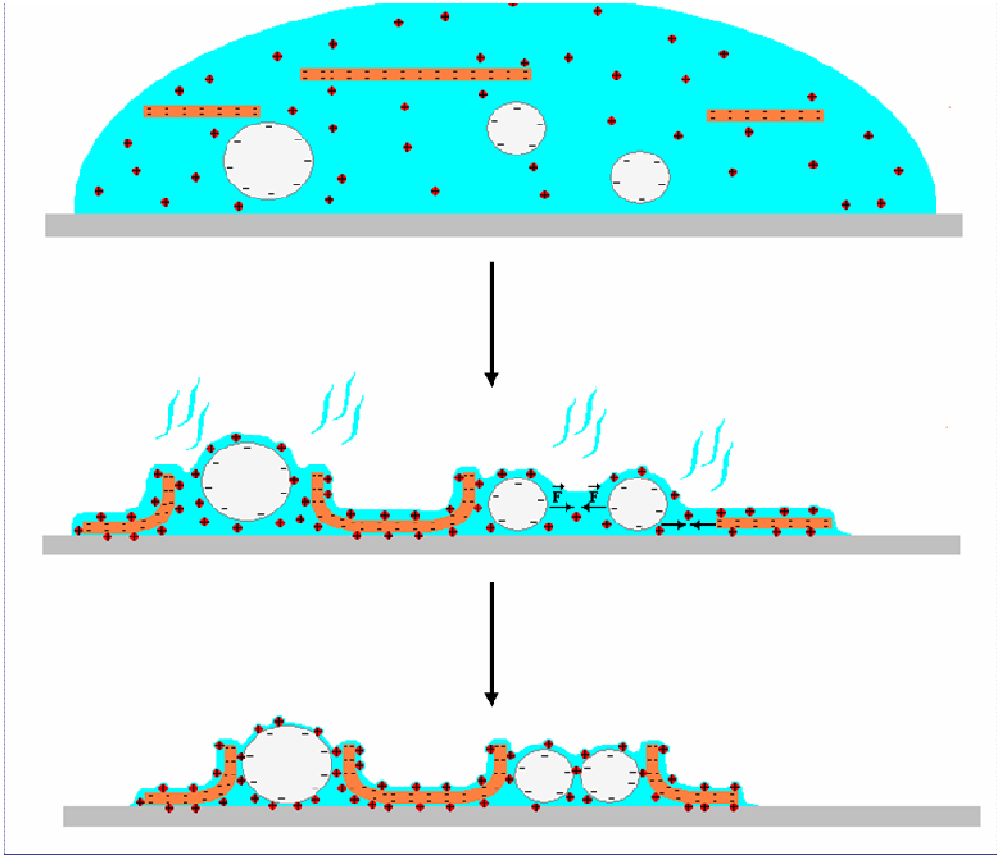
- Capillary adhesion during drying
  - Accounts for intimate particle mixing
  - Inespecific
- Electrostatic adhesion in the dry monolith
  - Accounts for the stability of the composite
  - Independent on the nature of particle bulk
- Both are controlled by interfacial properties

Styrene-acrylic latex and Ca^{2+}-montmorillonite

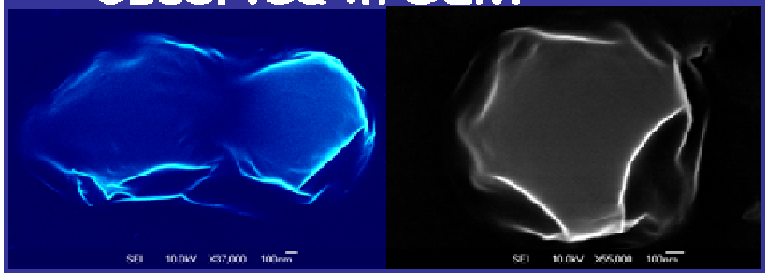


ESI-TEM from particle aggregates

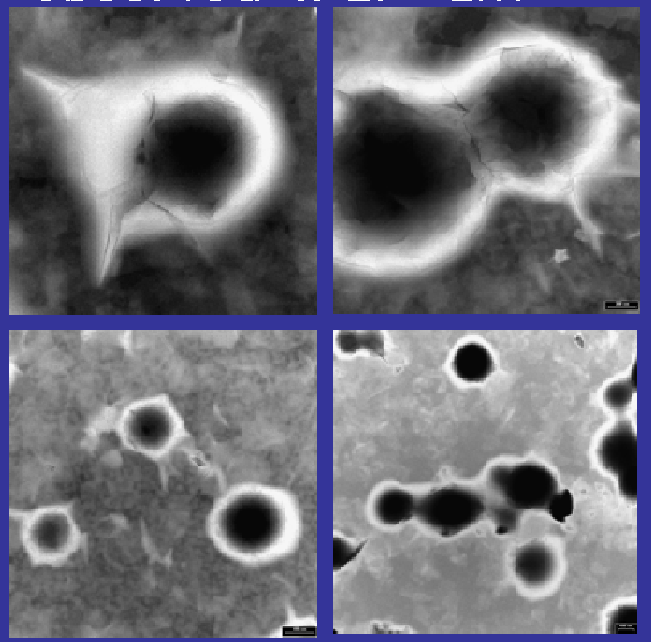
Hypothesis for clay-rubber aggregate formation



Clay-rubber aggregates observed in SEM

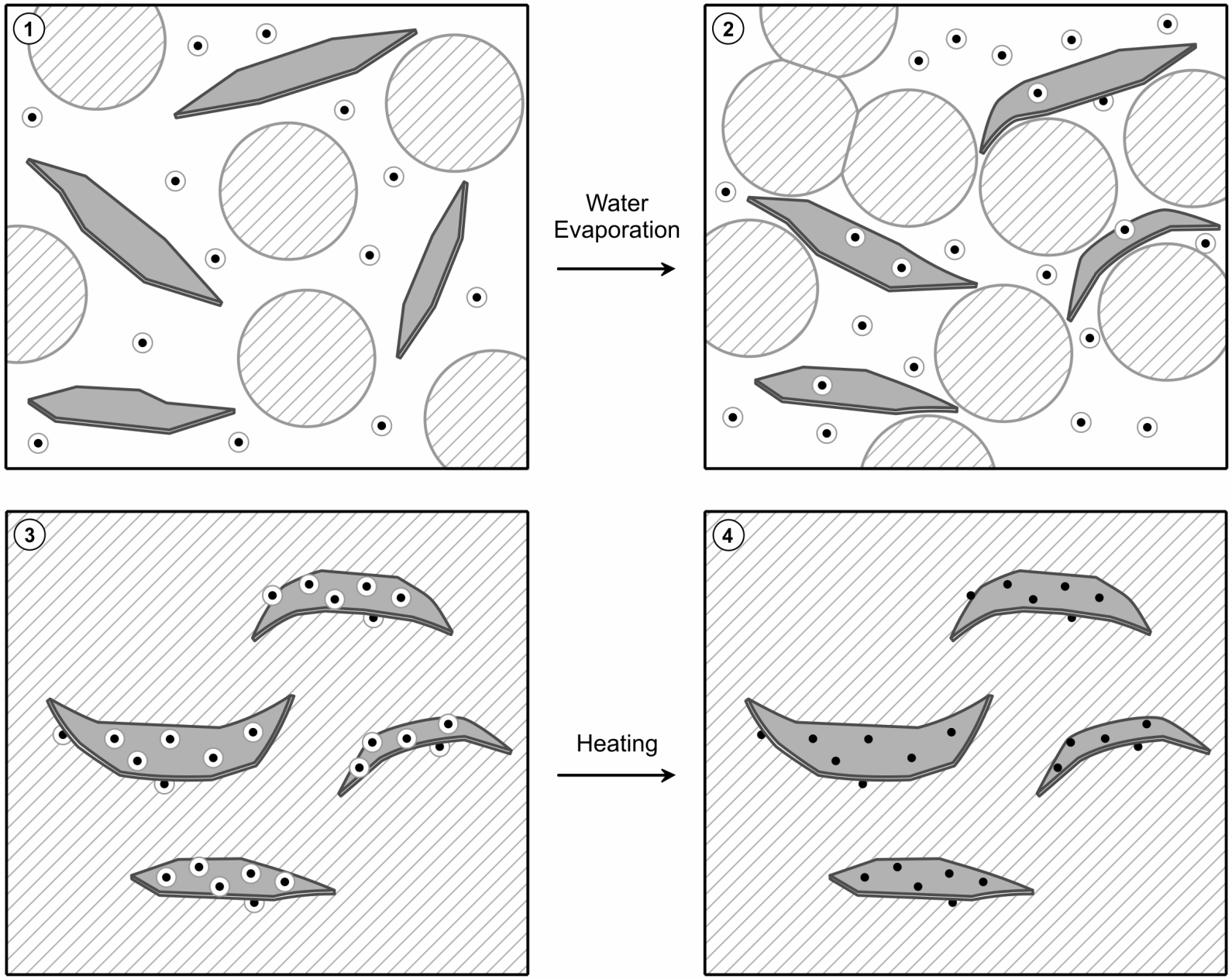


Clay-rubber aggregates observed in EFTEM



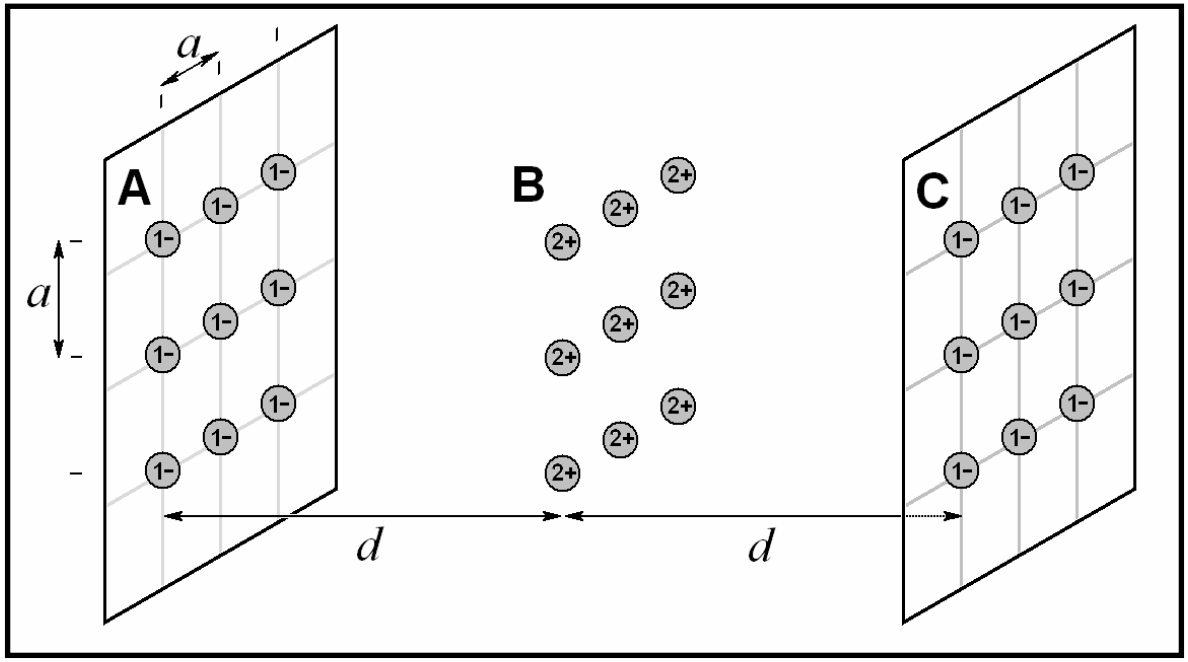
Polymer-clay
Nanocomposites
Formation

Model:



Electrostatic adhesion energy

Model: charge sandwich with zero or negative overall charge



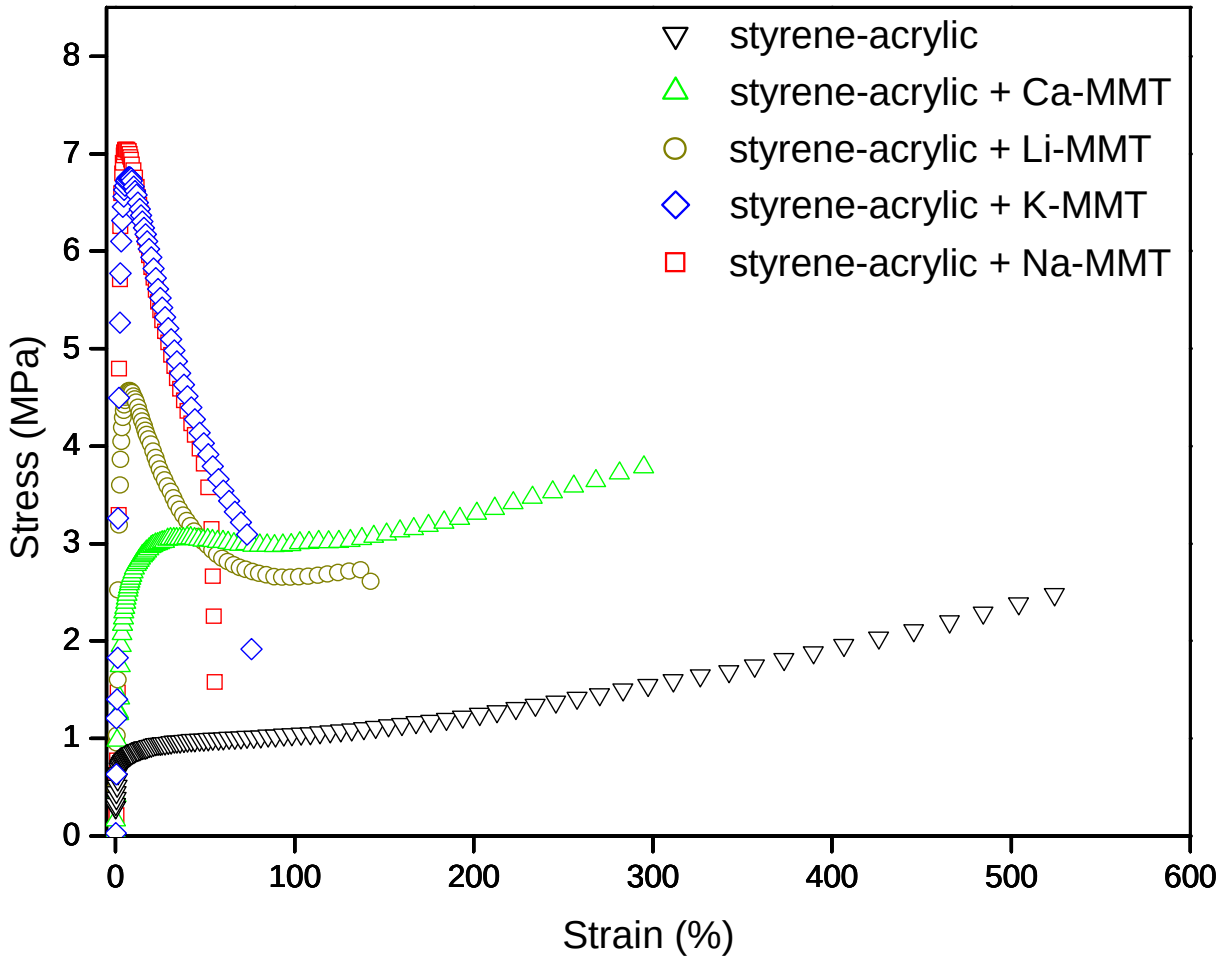
$$E_T = \frac{1}{4\pi\varepsilon\varepsilon_0}\left(\sum_{i,j,k,l=1}^{n} \frac{q_{(A,(i,j))}q_{(B,(k,l))}}{r_{(A,B,(i,j),(k,l))}} + \sum_{i,j,k,l=1}^{n} \frac{q_{(B,(i,j))}q_{(C,(k,l))}}{r_{(B,C,(i,j),(k,l))}} + \sum_{i,j,k,l=1}^{n} \frac{q_{(A,(i,j))}q_{(C,(k,l))}}{r_{(A,C,(i,j),(k,l))}} + \sum_{\substack{i,j,k,l=1 \\ (i,j)\neq(k,l)}}^{n} \frac{q_{(B,(i,j))}q_{(B,(k,l))}}{r_{(B,B,(i,j),(k,l))}} \right)$$

$$\overline{E} = \frac{6.02\times10^{23} E_T}{\text{number of charges}} : \text{electrostatic energy /mol of ions}$$

New hypothesis

- Clay counter-ions acting as ionic bridges affect mechanical and morphological properties of the nanocomposite.
- Changing nanocomposite properties due to changes in the counter-ions.

Mechanical properties



Stress-strain curves depend largely on the counterion

Braganca, F.D.; Valadares, L.F.; Leite, C.A.D.; Galembeck, F. *Chem. Mater.* **2007**, 19, 3334.

Model vs. measurement

	Work for 1% deformation (J)	Difference between nanocomposite and rubber (J)	Mols of ions in the test sample	Elastic energy per mol of ions (J/mol)
Rubber	$0.386 .10^{-3}$			
Rubber - $Li^{+}MMT$	$2.17.10^{-3}$	$1.79.10^{-3}$	$2.43.10^{-5}$	73.6
Rubber - $Na^{+}MMT$	0,00497	0,00459	4,914E-05	93.3
Rubber - $K^{+}MMT$	0,00466	0,00428	2,999E-05	143

From the model:
151 J/mol, for monovalent cations and 50.5% replacement of positive charges by voids

Positive counterions play an important role on the properties of polymer-clay nanocomposites.

Polymer-clay interfacial adhesion is mediated by ionic bridges between the two immiscible negative phases.

Conclusion: the initial hypotheses were verified

- Capillary adhesion during drying
- Electrostatic adhesion in the dry monolith
- Depends on the intervening ionic species

A styrene-acrylic resin cast on polyethylene: poor film, poor adhesion

The same but with clay: good film, good adhesion to PE